COSIA WATER EPA

2018 Water Research Report

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INTRODUCTION

This report summarizes progress for projects related to improving the use and management of water by the Mining Group of Canada's Oil Sands Innovation Alliance (COSIA) Water Environmental Priority Area (EPA). Projects included cover the period from 2012 to 2018.

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

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

*In 2017, Canadian Natural Resources Limited purchased Shell Canada Energy's Albian Sands operation.

All COSIA Water EPA projects previously supported by Shell Canada Energy were transferred to Canadian Natural Resources Limited.

This report is funded by:

- Canadian Natural Resources Limited
- Imperial Oil Resources Limited
- Suncor Energy Inc.
- Syncrude Canada Ltd.
- Teck Resources Limited

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Front cover image courtesy of Cenovus Energy Inc.

BEST PRACTICES

Standardize Measurement and Quantification Techniques

COSIA Project Number: WE0027

COSIA GAP/Opportunity Area: Best Practices

Industry Champion: Canadian Natural Resources Limited

Industry Collaborators: Imperial Oil Resources Limited, Suncor Energy Inc., Syncrude Canada Ltd., Teck Resources Limited

Status: Year 4 of 5

PROJECT SUMMARY

The Mining Best Practices Group was formed in 2016 and is attended by a set of representatives from the COSIA mining group. The group brings together oil sands operators to share information on their water practices and technologies and to accelerate the dissemination of this knowledge and information. Specifically, the group provides a forum for companies to identify operating issues; share lessons learned; determine common problem areas; develop best practices for each problem area; and create documents capturing the data, observations and learnings for each topic.

PROGRESS AND ACHIEVEMENTS

In 2016, the group focused on discussions and studies concerning naphthenic acids (NAs), comparisons between oil sands sites, and in situ measurement techniques for oil sands water streams. NAs is a term that has been used historically to describe the complex mixture of dissolved organic compounds in process-affected water as a result of direct contact with oil sands ore in the extraction process. Currently, all water that is in contact with oil sands or used in an oil sands processing facility (water that is commonly referred to as oil sands process-affected water [OSPW]), must remain on the oil sands leased site and cannot be released to the environment as there are currently no government water release criteria available. Although no release criteria exist, oil sands industry members believe that at least some of the remaining NAs will need to be removed from the OSPW prior to being released. OSPW is currently being studied and researched within COSIA in various Environmental Priority Area (EPA) studies and Joint Industry Projects (JIPs) to understand its constituents, toxicity and treatment technologies.

Work on understanding and measuring NAs continued in 2017. Additionally, the mining best practices group looked at various types of on site water management. As almost all water sources are within the oil sands sites, there are many opportunities for the operators to share water management learnings and best practices - beginning with a review of each operator's water flow sheets.

A successful workshop on these learnings and best practices was held in 2017. In 2018, additional workshops were held on best practices in basal water management (groundwater at the base of the McMurray formation that must be removed in advance of mining) and on tailings water chemistry. As well, an Environmental Data Standardization workshop took place to look at how each operator manages their water-related data to find out ways to make it easier for operators to efficiently store, retrieve, and share regional data. It is expected that workshops will also be held in 2019 to continue sharing information on best practices.

LESSONS LEARNED

As there are many different techniques to measure and quantify the dissolved organic compounds in OSPW, the work conducted in 2016 and 2017 by the mining best practices group focused on generating an industry-wide best practice to standardize measurement and quantification techniques. Over the past few years, industry and academic papers were published on this subject based on various EPA studies and JIPs. It is expected that the mining best practices group will release an industry paper on laboratory test techniques for quantifying NAs in late 2019.

From the initial review of each operator's on site water flow sheet, it was found that there were many differences in how each operator dealt with water and that each operator had a unique set of challenges. This led to a more detailed set of workshops, including an oil sands site water balance workshop in late 2017 which reviewed how each operator kept track of water volumes entering their site, and water volumes and water chemistry in the various on site storage facilities. This may seem to be a simple task, however some water sources (such as water/snow run off, some ground water flows) and water losses (such as pond evaporation, and water absorption/adhesion with the oil sands tailings) cannot be accurately measured and had to be modelled and estimated. The operators presented the various methods and modelling techniques that they used to estimate these gains and losses. These techniques and models have evolved over the decades with increasing accuracy, which allows for tighter control of on site water inventories and reduced fresh water intake to the site.

A basal water aquifer is a pressurized water aquifer that is present at each of the oil sands mines. As the aquifers are pressurized, de-pressurization is required near the open pits mining area to prevent the mines from flooding. Usually a series of wells around the mining area pump the basal water into a storage facility on site. From the operator presentations, it was found that the chemistry of this water varies from operator to operator. Some experienced little operational effects of this de-pressurization water. Others had to segregate this water from the overall on site water inventory. Research is being completed on COSIA-based JIP projects to find solutions to treat and dispose of this water.

In fall 2018, a workshop was held on best practices of tailings water chemistry. As the majority of all water currently remains on site, this water is recycled over and over through the oil sands plant and process units. As such, chemistry of this water is crucial for maximizing recycle rates and reduction of on site water inventories, thus reducing fresh water intake. In this workshop, oil sands mine operators presented topics on current chemistries, how chemistries have changed over time, modelling software to predict chemistry, and future considerations to take into account.

PRESENTATIONS AND PUBLICATIONS

As the Mining Best Practices Group consists of internal COSIA members only, no external presentations have been produced.

RESEARCH TEAM AND COLLABORATORS

The Mining Best Practices Group consists of COSIA members only and has not enlisted external research bodies.

Overburden Dewatering Effectiveness Study

COSIA Project Number: WJ0099

COSIA GAP/Opportunity Area: Water Mining

Research Provider: Imperial Oil Resources Limited and Golder Associates Ltd.

Industry Champion: Imperial Oil Resources Limited

Status: Year 3 of 4

PROJECT SUMMARY

Oil sands mining operations remove glacial material (called overburden) and any overlying peat material prior to advancing an ore mining face. The overburden materials may be used as either trafficable or construction material. However, the moisture content of the overburden is typically too high for these purposes and often requires the overburden to be dewatered. Normally, Imperial's Kearl Mine site performs the dewatering using a network of ditches. Collected water is then released to the environment after passing through sedimentation ponds and achieving the required release criteria.

Experience at Kearl Mine demonstrates that dewatering operations can be effective for coarser overburden material (e.g., sand, silt) but is often not effective for finer overburden material (e.g., till, clay). However, the complex relationship between the reduction of moisture content and heterogeneous soil types by gravity-driven dewatering (ditches) has not been well defined.

Given that the main objective of dewatering operations is to reduce the moisture content of the overburden materials, it is important to know the feasible range of moisture content reduction in various soil types and how far in advance it is necessary to initiate dewatering operations. The technological objectives of this project were to determine:

1. the ability to reduce overburden moisture content using ditches;
2. the impact of finer overburden material on the effectiveness of reducing moisture content; and
3. guidance to the design of dewatering measures, such as spacing between dewatering ditches.

PROGRESS AND ACHIEVEMENTS

Imperial's field data collection program to evaluate the efficiency of the overburden dewatering system was undertaken between 2014 and 2018. The main results include:

- The percentage of soil samples classified as "non-trafficable" and "slop", according to Kearl Mine's criteria, decreased from 63% in December 2014 to 25% in January 2016. The average soil moisture content by weight reduced by 7% absolute from December 2014 to January 2016. These reductions are likely due to the dewatering effects of the drainage ditches and the relatively dry weather conditions in 2015.

- The average moisture content by weight increased by 2% absolute from January 2016 to January 2017. This small increase is likely due to spatial variability and wetter weather conditions in 2016 than 2015. The dewatering system might have little effect in reducing the soil moisture content during this monitoring period because the soils may have already been in unsaturated conditions, as indicated by the January 2016 samples.
- The percentage of the soil samples meeting the construction material criteria increased from 43% in January 2016 to 44% in January 2017, likely due to coarser soil samples in 2017 than 2016. The percentage of samples characterized as "non-trafficable" or "slop" increased from 25% in January 2016 to 32% in January 2017. This further indicates that the dewatering system might have little effect in reducing the soil moisture content during this monitoring period.
- The soils at elevations above the ditch inverts along the January 2016 transect (i.e., TP4 to TP11) and the January 2017 transect (i.e., Pit 12 to Pit 19) may be in unsaturated conditions. The data does not show higher moisture content in the middle of the transects than those samples close to the ditches, which places into question the effectiveness of the ditches.
- In Area 1 (2018 mine advance), the dewatering system influenced a reduction in the soil moisture content during the one-year period from December 2014 to January 2016. However, the dewatering system may have little effect in further reduction of the soil moisture content during the subsequent year (i.e., January 2016 to January 2017). The changes in the moisture content in this subsequent year appear to be influenced mainly by weather conditions.

LESSONS LEARNED

This project's main learnings to date are:

- The design of dewatering measures should account for the geological and the hydrogeological setting of the area to be dewatered. Dewatering ditches may not be effective if the soil has a high fines content.
- To study the effectiveness of overburden dewatering measures, monitoring the response of the groundwater table in the area to be dewatered is required.

The main recommendations for further work include:

- Collection of groundwater level information for the 2019 mine advance.
- Beyond the 2019 mine advance, groundwater levels in the future mine pit areas should be evaluated to identify the area with high groundwater tables and saturated overburden materials. This would allow a more definitive quantification of the dewatering effectiveness of various ditch spacing and depth in different soil types.

PRESENTATIONS AND PUBLICATIONS

No public presentations or publications.

RESEARCH TEAM AND COLLABORATORS

Name	Institution or Company	Degree or Job Title	Degree Start Date (Students Only)	Degree Completion Date (Students Only)
Moniz Mukto	Imperial Oil Resources Limited	PhD, PEng		
Vlad Rojanschi	Golder Associates Ltd.	Dr.Ing., PEng		
Dejiang Long	Golder Associates Ltd.	PhD, PEng		
Richard Kopp	Imperial Oil Resources Limited	PEng		

Mining Best Practices Report for Alternate Water Sourcing and Salinity Management

COSIA Project Number: WJ0061

COSIA GAP/Opportunity Area: Best Practices

Industry Champion: Canadian Natural Resources Limited

Industry Collaborators: Suncor Energy Inc., Syncrude Canada Ltd., Imperial Oil Resources Limited

Status: Completed

PROJECT SUMMARY

As there are currently no provincial or federal government criteria to allow for the release of water that has been in contact with oil sands or was used to process oil sands (commonly referred to oil sands process-affected water [OSPW]), the majority of that water typically accumulates in on site storage facilities. This leads to challenges with on site water chemistry and requires significant planning to ensure proper storage facilities are available. This COSIA Water Joint Industry Project (JIP) focused on best practices and current (2014 onwards) oil sands operator projects to reuse OSPW to reduce the site's fresh water requirements.

PROGRESS AND ACHIEVEMENTS

Water from the Athabasca River is brought to oil sands mine sites and is mainly used as make-up water and feed water for utility systems. As river water requires less pre-treatment to remove ions, salts and particulate matter (suspended solids) than other sources of on site water, it is preliminarily used to supply feed water to the boilers, which provide steam for various site processes. Typically, the majority of the steam is condensed and reused, but the remainder of the steam is evaporated by direct evaporation of the steam or by normal environmental evaporation that takes place in the on site water storage facilities. With evaporation occurring, salt ions remaining from the river water remain in the on site water storage facilities and accumulate over time. The increasing salt ions can lead to many different problems such as high metal corrosion rates, additional chemical reactions, difficulties with oil sand extraction processing (salt adversely affects bitumen removal from sand), and reclamation. In 2014, Shell Canada (formally the operator of Albian Sands, now owned and operated by Canadian Natural) was pursuing a reduction in the amount of river water that was brought to the Albian Sands site. As other (alternative) water sources would be required for boiler water, Shell Canada had to look at new technologies to clean on site water sources to a level of river water quality or better and look at technologies to remove the salts already in the on site water sources. Prior to launching a full technology assessment and development research project, COSIA mining oil sands members agreed to share their current practices, projects and research into water management that reduces river water usage and salts in OSPW. Golder and Associates was contracted to conduct interviews with all COSIA members and compile a report on the results.

LESSONS LEARNED

The main learning identified in the Golder and Associates report is that each operator faces unique challenges in reducing river water importation, water recycling and salt management. These unique challenges allow for a diverse set of technologies, practices and processes to be trialed and used within the industry, and also allow for comparisons. The report enabled Albian Sands to concentrate their research on specific technologies that would fit their site's salt management and river water reduction targets. The report also generated various topic discussions for the best practices groups, ideas for future COSIA Joint Industry Projects (JIPs), and other future areas of study.

Golder and Associates found that the most common method to reduce river water importation was to continue to recycle water and use the on site water for many different applications. Sources that require the cleanest (lowest salts and particulate matter) type of water, such as boilers, would typically use river water or ground water. Blowdown water from the boilers and cooling towers (water rejected to reduce salt and particulate concentrations) would then be sent into a central water facility to be mixed in with other water streams and used in the oil sands processing facility where higher salt and particulate concentrations could be tolerated.

In some cases, oil sands mine operators looked outside of their own oil sands operation for additional water reuses. In a few cases, the high salt and particulate streams could be used as processing water for in situ oil sands applications, thus offsetting the need for the in situ facility to import water. In those cases, pipelines were run from the oil sands mining facilities to the oil sands in situ facilities.

Oil sands mine operators with upgraders located on their oil sands site had additional options to use and reuse water as the majority of the upgrader water streams had less salts and solid particles than the oil sands processing ones. One of the operators was testing treatment of the water with coke from the upgrader, while another operator has a license to return water back to the river as it is not considered to be process-affected water. The permit to return water outlines the return criteria and includes batch testing of the water prior to being returned to ensure property purity.

PRESENTATIONS AND PUBLICATIONS

As the Mining Best Practices Group consists of internal COSIA members only, no external presentations have been produced.

RESEARCH TEAM AND COLLABORATORS

This was an internal COSIA study conducted by Golder and Associates.

MINE
WATER RETURN

Salt Load Model

COSIA Project Number: WE0010

COSIA GAP/Opportunity Area: Water Return

Research Provider: Golder Associates Ltd.

Industry Champion: Teck Resources Limited

Industry Collaborators: Canadian Natural Resources Limited, Imperial Oil Resources Limited, Suncor Energy Inc., Syncrude Canada Ltd.

Status: Completed

PROJECT SUMMARY

Management of salts by oil sands operations is a regional issue that has been evaluated by Canada's Oil Sands Innovation Alliance (COSIA). To assist with the development of a regional salt management strategy, external consultants were hired to develop a set of integrated salt loading models based on hypothetical scenarios that included a process water model and two receiving water models (GoldSim model and the Lake Athabasca hydrodynamic model). The integrated model domain comprises the Athabasca River, Lake Athabasca, and the seven companies representing existing and planned Athabasca oil sands mines.

The study area includes the Athabasca River and its tributaries between Fort McMurray and Embarras, including the oil sands mines located along this reach of the Athabasca River, plus Lake Athabasca. The length of the Athabasca River in the oil sands region was divided into five reaches within the GoldSim Athabasca River model, consistent with other Environmental Impact Assessments. Water quality was modelled in each reach, including input from oil sands operations where applicable. Assumed start and end dates for operations, as well as hypothetical dates for active and passive water releases were modelled based on information provided by participating operators.

The process water model was developed for each operation to predict the mass of each major ion and total dissolved solids (TDS), as well as the volume of the process water accumulated by each operator. The GoldSim model was developed to predict the water quality in pit lakes for each operator, and the cumulative changes in water quality in the Athabasca River. The Lake Athabasca hydrodynamic model was developed to predict circulation patterns, and spatially and temporally varying salt concentrations. The outputs of the process model were used as inputs for the receiving models. The process water and GoldSim model included major ions and TDS, whereas the Lake Athabasca model included TDS and temperature, which are important hydrodynamic variables. Two model scenarios were developed to predict Athabasca River water quality under different release conditions: 1) release of treated waters through pit lakes at mine closure (the Status Quo Scenario), and 2) release of treated waters during mining operations (the Active Release Scenario).

PROGRESS AND ACHIEVEMENTS

Process Model

The final mass of each parameter (i.e., element, TDS) accumulated during operations in the free water and tailings pore water, and the final volume of free water, as predicted by the process water model were calculated for each operator. Additionally, a time-series of masses for chlorides and TDS for both the Status Quo and Active Release Scenarios was determined. These data were input into the GoldSim model.

GoldSim Model

Predicted Athabasca River chloride and predicted TDS concentrations at Reach 5 (upstream of the confluence of the Firebag River to Embarras) from the GoldSim model were based on time series from baseline, stochastic flow condition, status quo scenario, active release scenario, and low flow (7Q10) conditions. Baseline conditions in the Athabasca River were represented in the GoldSim model by upstream flows, tributaries, present-day licensed releases and process-affected seepages.

Lake Athabasca (Hydrodynamic) Model

Mean horizontal water velocities in Lake Athabasca were extracted from the five-year calibration found in Shell (2013). The highest average velocities were at the inflow from Fond du Lac, where the lake narrows. A recirculation pattern was established in the middle of the lake, with very small velocities between the middle of the lake and the Fond du Lac and Athabasca River inflows. Inflow from the Athabasca River did not exhibit a recirculation pattern, and flow within that area exited the lake at the outflow to the Riviere des Roches.

The relationship among TDS concentrations under the Baseline, Status Quo, and Active Release scenarios in Lake Athabasca followed the same pattern predicted by the GoldSim model. Concentrations near the outlet are predicted to be similar to those near the mouth. The Baseline scenario had the lowest TDS concentrations of all the scenarios in the simulation. The concentration of TDS was initially higher under the Active Release Scenario compared to the Status Quo Scenario. The difference in TDS concentration between the Active Release and Status Quo scenarios began to decrease around the year 2033. In 2055, the TDS concentrations in Lake Athabasca near the mouth of the Athabasca River were equal under the Active Release and Status Quo scenarios, and the TDS concentrations under the Active Release Scenario remained below Status Quo concentrations for the rest of the simulation. Overall, the maximum difference in TDS concentrations in Lake Athabasca was predicted to be within 10 mg/L near the mouth of the Athabasca and less than 1 mg/L in the middle of the lake.

Under all scenarios (including Baseline), the highest concentrations of TDS were located within approximately 20 km of the mouth of the Athabasca River. Outside of this zone, TDS concentrations remained below 50 mg/L, with slightly lower concentrations near the inflow of the Fond du Lac River.

LESSONS LEARNED

Some limitations resulted from assumptions to this complex system, and those assumptions could affect model results; for example:

- Long term closure conditions will be driven by the release of pore water from the tailings, which was only evaluated prescriptively in this study. Further study of these mechanisms on a regional basis would improve confidence in long-term predictions. Changes in project site conditions will result in changes to water quality predictions.
- Only limited data regarding the chemistry of Lake Athabasca were available, especially on the Saskatchewan side of the lake. Most of the locations with aquatic chemistry data did not have measurements for every month. Flow rates for some of the identified boundaries were not available and had to be estimated from ratios and regression equations from stations that appeared to behave similarly.

It is unlikely that the key findings would be affected by these limitations, or that the key findings would change if these limitations were not present.

LITERATURE CITED

Shell. 2013. *Pierre River Mine Environmental Impact Assessment. Round 2 SIRs.* Submitted to Canadian Environmental Assessment Agency. October 2013.

PRESENTATIONS AND PUBLICATIONS

No public presentations or publications.

RESEARCH TEAM AND COLLABORATORS

Name	Institution or Company	Degree or Job Title	Degree Start Date (Students Only)	Degree Completion Date (Students Only)
Jerry Vandenberg	Golder Associates Ltd.	Associate, Senior Environmental Chemist		
Brian Gaas	Golder Associates Ltd.	Water Quality Specialist		
Hammad Mir	Golder Associates Ltd.	Senior Water Quality Modeller		
Paul Beddoes	Golder Associates Ltd.	Environmental Scientist		
Nicolas Lauzon	Golder Associates Ltd.	Associate, Water Resource Engineer		

River Ecosystem Health Assessment Using Pilot Facility

COSIA Project Number: WE0013

COSIA GAP/Opportunity Area: River Ecosystem Health Assessment Using Pilot Facility

Research Provider: Alberta Innovates - Technology Futures (Now InnoTech Alberta)

Industry Champion: Total E&P Canada Ltd.

Industry Collaborators: Canadian Natural Resources Limited, Imperial Oil Resources Limited, Suncor Energy Inc., Syncrude Canada Ltd., Teck Resources Limited

Status: Completed

PROJECT SUMMARY

Treated oil sands mine water is expected to eventually reach rivers within the Athabasca oil sands region during operation or after mine closure. An artificial stream facility will support the oil sands industry to identify, monitor, and mitigate the potential effects of mine water; lotic (flowing water) mesocosms are a proven experimental tool for evaluating aquatic ecotoxicology in natural river ecosystems. Currently, mesocosms (referred to in this report as artificial stream facilities) are included in the recommendations for alternative fish and benthic invertebrate field surveys (Environment Canada, 2012). The overall objective of the feasibility study is to identify the best conceptual design for an artificial stream facility for the oil sands that will answer priority questions relating to the potential effects of treated mine waters on the Athabasca River and its tributaries. The following priority questions were identified:

- Are there any acute and chronic toxicity effects of treated operational and reclaimed mine water on aquatic biota residing within the Athabasca River and its tributaries?
- Are there any long-term effects of treated oil sands operational and reclaimed mine water on aquatic community structure, health, and functionality of river ecosystems typical of the Athabasca River and its tributaries?

A literature review identified three main types of artificial stream facilities commonly used in environmental effects testing of industrial water and for regulatory purposes:

Mobile Facilities: Small-scale linear or circular mesocosms can be readily moved, stored, and transported to various locations. Although mobile facilities are incorporated into the Canadian Environmental Monitoring Regulations, the small mesocosm size limits habitat diversity and biodiversity. These facilities are suited for short-term ecotoxicity studies.

Modular Facilities: Semi-permanent linear mesocosms of larger size, containing multiple separate components that can be independently added or removed to alter channel scale and functionality, thereby permitting customizable channel design. These facilities are suited for longer-term ecotoxicity studies since they are large enough to accommodate habitat diversity and biodiversity.

Permanent Facilities: Fixed in-ground mesocosms, even larger than modular facilities, that are not designed to be transported and intended to function unchanged for long periods of time. However, some channel dimensions, such as width, can be modified to a customizable channel design. These facilities are also suited to longer-term ecotoxicity studies since they are large enough to accommodate habitat diversity and biodiversity.

PROGRESS AND ACHIEVEMENTS

The project was completed in February 2015.

LESSONS LEARNED

The following table lists the pros and cons of the three types of artificial stream facilities:

	Mobile: Indoor and Outdoor	Modular: Indoor and Outdoor	Permanent	
Pros	• Short-term exposure durations allow quick data collection and interpretation • Can be outdoors or indoors • Ability to have high replication • History with Canadian environmental effects monitoring • Permits in situ access of source and test waters • Facility easily relocated • Can be used alongside experiments in modular or permanent facilities to investigate ecological mechanisms of change	• Increased ambient conditions (e.g., temperature and light) • Increased channel versatility and flexibility • Space for biota (e.g., fish) and frequent sampling and monitoring • Outdoor use permits aerial colonization • Biological diversity • Allows more representative environments (e.g., pools and riffles) • Potential to overwinter • Facility could be relocated • Can extend operational period • Can be used to study direct and indirect effects, cumulative effects	• Outdoor: • Includes ambient conditions (e.g., temperature and light) • Allows aerial colonization • Space for larger biota (e.g., fish) and frequent sampling and monitoring • Allows more representative environments (e.g., pools and riffles) • Highest biological diversity • Greatest potential for overwintering • Can extend operational period • Can be used to study direct and indirect effects, cumulative effects and natural attenuation	• Indoor: • Control of operational and climatic variables • Space for larger biota (e.g., fish) and frequent sampling and monitoring • Ease of year-round testing • Allows more representative environments (e.g., pools and riffles) • Biological diversity • Can be used to study direct and indirect effects, cumulative effects and natural attenuation
Cons	• Small scale limits habitat diversity and biodiversity • Limits interactions between higher trophic levels (e.g., need for separate studies for fish and benthic invertebrates) • Limited exposure duration • Limited for study of indirect effects, cumulative effects and natural attenuation	• Requires significant temperature and light controls, especially in winter • High construction cost • Long experimental periods require higher operational costs	• Fixed facility location • Requires significant temperature and light controls, especially in winter • High construction cost • Long experimental periods require higher operational costs	• Fixed facility location • Will not accurately represent ambient conditions • No aerial colonization • High construction cost • Long experimental periods require higher operational costs

The recommended mobile artificial stream facility consists of an indoor trailer where fish experiments requiring controlled temperature and light are conducted and an outdoor mobile facility that includes mesocosms for benthic invertebrate and periphyton community experiments and associated equipment. This facility will give oil sands operators the ability to identify potential acute and chronic effects of mine waters on benthic invertebrates and individual fish in the Athabasca River, or its tributaries. The results from the experiments will provide a level of effects testing that is currently used for alternative EEM for other effluents in Canada. The data from the studies will be directly comparable across the industry and could be used before release—to test different treatment technologies and evaluate treated mine waters for potential return—or after release as part of biological monitoring. Because the mobile facility is based on existing facilities that use commercially available components, it will require limited engineering design and construction and would be operational within a fairly short time.

PRESENTATIONS AND PUBLICATIONS

No public presentations or publications.

RESEARCH TEAM AND COLLABORATORS

Institution: Alberta Innovates – Technology Futures (Now InnoTech Alberta)

Principal Investigator: Jean Birks (InnoTech)

Research Collaborators: Don Burn, University of Waterloo; George Dixon, University of Waterloo; Andrea Farwell, University of Waterloo

Regional Substance Loading Allocation Study

COSIA Project Number: WE0009

COSIA GAP/Opportunity Area: Regional Substance Loading Allocation Study

Research Provider: Four Elements Consulting

Industry Champion: Suncor Energy Inc.

Industry Collaborators: Canadian Natural Resources Limited, Imperial Oil Resources Limited, Syncrude Canada Ltd., Teck Resources Limited, Total E&P Canada Inc.

Status: Completed

PROJECT SUMMARY

A Regional Substance Load Allocation Study for the Athabasca River (RSLA) was undertaken by Canada's Oil Sands Innovation Alliance (COSIA). The study demonstrates how technical aspects of Alberta Environment and Sustainable Resource Development (now the Alberta Energy Regulator) policies for water quality protection could be implemented using a regional, collaborative, and equitable approach to determine acceptable substance levels and cumulative effects for hypothetical oil sands water releases to the Athabasca River. It builds on previous undertakings in this area by oil sands industry members, with a focus on a regional approach to watershed management that supports understanding the cumulative impacts of oil sands development.

The study considers a hypothetical future operational period between 2020 and 2040 in which seven companies representing 13 oil sands operations could seek authorization to release treated tailings water or other operational waters to the Athabasca River. Currently, water used for mining and extraction of bitumen at oil sands sites is recycled, resulting in a growing inventory of water and increasing salt concentrations up until mine closure (i.e., no water in the recycle loop is released to the natural environment during operations). The existing plan is to release this lower quality water at mine closure through pit lakes, but this study contemplates an alternative. Instead of releasing stored water when a mine is closed, it may be preferable to return it to the environment while the mine is still operational, as part of a sustainable water management framework. This would reduce the footprint of water inventories, manage the build-up of salts in recycle circuits, manage the quality of water that must ultimately be returned to the receiving environment, and potentially reduce the net water demand on the river.

The Substance Load Allocation (SLA), which is the amount of a stream's total permissible substance load that is allocated to one operation, was derived for each of the 13 oil sands operations simultaneously. SLAs were calculated such that site-specific instream thresholds associated with chronic effects to aquatic life would not be exceeded for "worst-case" (lowest flow) conditions in the receiving environment.

The outfall location and bitumen production capacity of each operation are key factors to consider. The outfalls from the 13 oil sands operations range from 20 km to 116 km downstream of Fort McMurray. Bitumen production capacity ranges from 157,000 barrels per day to 501,000 barrels per day. The location, timing, water quality, and toxicity of the hypothetical releases being considered are not fully defined. Therefore, 90 release configurations and many scenarios of release (between one and 13 simultaneous releases with different SLAs) were considered, resulting in thousands of modelling scenarios. A total of fifty-two water quality parameters are included in the model such as TSS, TDS, toxicity units, a suite of metals (e.g.,. lead, copper, chromium), anions (e.g., chloride, ammonia, sulphate), and a suite of PAHs (anthracene, fluoranthene etc.).

The Athabasca River Model (ARM) was used for predictive water quality modelling. The ARM has been used previously for similar studies as well as all oil sands mine Environmental Impact Assessments (EIAs) and is an accepted means of modeling multiple releases to a watershed in Canada, the United States and Europe. The model accounts for water withdrawals and point and non-point sources as well as local mixing characteristics for each release. It also includes loading from natural upstream sources and tributaries as well as existing releases that have been identified in EIAs. The ARM is capable of efficiently implementing and analysing many scenarios. The ARM calculates SLAs automatically using an optimization routine to determine release loads that will achieve instream thresholds for several outfall locations simultaneously.

The procedures for determining SLAs were developed for industrial releases that have constant flows determined by process equipment. Therefore, constant release flows are typically assumed in the calculation of SLAs. However, the high on-site storage available to oil sands operations also enables the application of variable SLAs to the region. This flexibility was leveraged to derive a number of SLAs corresponding to potential flow management approaches, for example:

- Constant SLAs derived for ice-cover worst-case (7Q10, the lowest 7-day average flow expected to occur during open-water season once every 10 years) flow conditions and applied throughout the year
- Seasonal SLAs derived for ice-cover and open-water worst-case (7Q10, the lowest 7-day average flow expected to occur during open-water season once every 10 years) flow conditions and applied in their respective season (note that ice-cover seasonal SLAs are the same as constant SLAs)
- Flow-dependent SLAs derived as a function of historical daily flows in the Athabasca River. The flow levels used were low (i.e., 7Q10), mean, and high river flows

Together, these approaches have increased the number of available water management options for operators while minimizing the potential for cumulative impacts of multiple releases.

PROGRESS AND ACHIEVEMENTS

The study demonstrates how technical aspects of Alberta Environment and Sustainable Resource Development (now the Alberta Energy Regulator) guidance for water quality protection could be implemented using a collaborative and equitable approach to determine acceptable substance levels for oil sands water releases to the Athabasca River.

In this analysis, the ARM was used to calculate SLAs for 13 oil sands operations, with a focus on chloride and chronic toxicity. Within this analysis alone, thousands of release scenarios were modelled for the substances of interest; however, the tool is capable of modelling an almost unlimited number of scenarios, by accounting for various release configurations and many substances of interest beyond those featured in this study. This powerful flexibility enables the study of load allocations to ensure there are no adverse effects from cumulative impacts within the Athabasca River.

LESSONS LEARNED

Calculating SLAs simultaneously for all 13 operations results in approximately half of the overall loading allocation that would occur if the loading allocations are calculated on a case-by-case basis without accounting for other sources. The limited mixing in the Athabasca River results in an overall restriction in the derived SLAs that is protective of the river and results in reserve capacity at the downstream boundary of the reach.

Even for the worst-case modelling conditions used, substance concentrations are predicted to be elevated only in a small area downstream of the release outfalls. Additional modelling was completed to characterize potential changes in water quality for more representative conditions of river flow and release water quality. For representative conditions, only a small change in substance concentrations in the Athabasca River was predicted, even directly downstream of the outfall. Continuous probabilistic modelling was undertaken to confirm that the required compliance frequencies for the instream thresholds would be achieved. Predicted concentrations are consistently below the instream threshold over the modelled flow record. These results demonstrate that the modelling approach used to derive the SLAs is conservative with respect to instream threshold compliance.

Use of existing on-site water storage capacity would allow oil sands operators to control release flows seasonally and therefore application of seasonally variable SLAs would be appropriate for the oil sands sector. Flow-dependent SLAs corresponding to an instream target of twice the LARP trigger and seasonal SLAs based on the CEB would both achieve the desired level of compliance with the chronic instream threshold at the regulatory mixing zone boundary and achieve the LARP trigger at Old Fort with a similar frequency to background concentrations.

The flow-dependent SLAs typically result in lower chloride concentrations at the regulatory mixing zone boundary and fewer exceedances of the LARP trigger at Old Fort for the ice-cover period. Additionally, the flow-dependent SLAs allow for higher overall loading to the Athabasca River. Active management of release flows through flow-dependent SLAs could be used to allow for higher overall load and to further minimize changes in substance concentrations in the Athabasca River relative to more conventional constant SLAs.

The release limits derived from SLAs may not, for every substance, dictate acceptable release rates. When an operation applies for an actual water release, a detailed and site-specific assessment will be completed. The assessment may reveal additional factors that modify acceptable release rates.

PRESENTATIONS AND PUBLICATIONS

Presentations

Regional Collaboration in Water Management – RSLA Study. COSIA Innovation Summit 2017. Please contact COSIA for a copy of this presentation.

Publications

COSIA 2018. *Regional Substance Loading Allocation Summary Report.* 22 pages. (https://cosia.ca/sites/default/files/attachments/AthabascaRiver.pdf)

RESEARCH TEAM AND COLLABORATORS

Institution: Four Elements Consulting, LLC

Principal Investigator: Tammy Rosner

NATURAL AND ANTHROPOGENIC INPUTS TO THE ATHABASCA WATERSHED

Impacts of Atmospheric Dust Deposition on the Speciation of Trace Elements in Snowmelt and Peatland Surface Waters

COSIA Project Number: WE0018

COSIA GAP/Opportunity Area: Aerial deposition of polycyclic aromatic hydrocarbons and metals

Research Provider: University of Alberta

Industry Champion: Canadian Natural Resources Limited

Industry Collaborators: Imperial Oil Resources Limited, Suncor Energy Inc., Syncrude Canada Ltd., Teck Resources Limited

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 open pit mining process and upgrading, but from wind erosion of dry tailings, light and heavy haul roads, construction activities, and quarries, in addition to natural sources such as wind erosion from exposed soils, river banks 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). There are also ongoing concerns about potentially heavy metals as particulate being released to the atmosphere from bitumen mining and upgrading, but the extent of these sources and their ecological significance is unclear. 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 extraction and 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 microns 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 in soluble form .

PROGRESS AND ACHIEVEMENTS

Snowpack samples are being studied to characterize atmospheric deposition of dusts and trace elements (TEs) during winter. Snow collected near industry presents several challenges. First, large dust particles are abundant but the concentrations of TEs in the filterable (< 0.45 µm) fraction tend to be low (measured in nanograms per litre). Second, physical separation of particles from the matrix requires melting, but this presents a risk of TE adsorption to container walls because, to avoid particle dissolution, the meltwater is not acidified. A method optimization is in progress to improve sample handling and processing so as to reliably distinguish between total concentrations of TEs and those in the filterable fraction. Lab experiments are underway to understand TE leaching and adsorption to the walls of the sample containers. Briefly, snow samples and high purity water were spiked with 200 ng/L of TEs (Ag, Al, Cd, Pb, Tl and Y), incubated under both acidified and non-acidified conditions for periods ranging from one hour to one month. Preliminary results of TE adsorption indicate that Ag was the only TE that adsorbed to the bottle wall in snow samples that were not acidified; the other TEs were stable in solution up to one month. The snow samples collected to date were obtained using polypropylene bottles. Examination of this polymer using scanning electron microscopy has revealed an open porous structure which might trap particulate matter smaller than 10 µm; possible losses of PM_{10} through adsorption onto container walls is also being investigated. A manuscript is in preparation which describes improved methods for processing snow samples for chemical analysis of TEs and characterization of dust particles.

In previous independently-funded studies of TEs in wild berries from the Athabasca Bituminous Sands (ABS) region, the research team developed a geochemical approach to clearly distinguish between TEs supplied exclusively by dust (e.g., Al, Cr, Fe, La, Pb, Th, V, Y) and TEs taken up by roots (e.g., Cd, Cu, Mn, Ni, Zn). As a first estimate of the chemical reactivity of TE in dust particles, Labrador Tea (*Rhododendron groenlandicum*) samples were collected from the ABS region as well as from other parts of Alberta and Canada (BC and Ontario), including from some commercial suppliers. Concentrations of TEs were determined in acid digests as well as hot water extracts (105^{o}C, 50 bar). For TEs that are associated mainly with dust particles (e.g., Al, La, Fe, Pb, V), the concentrations in the hot water extracts were approximately 1% of the total concentrations. In contrast, for elements that are supplied to the plants primarily from root uptake (e.g., Mn and Zn), the concentrations in the hot water extracts were roughly 50% of the total concentrations. Additional work is required to clearly distinguish between liberation of dust particles from the plant surface and particle dissolution.

Preliminary measurements have been undertaken of total and dissolved (< 0.45 µm) TE concentrations in peat bog surface waters from a control location (Avenir, near Lac La Biche). Bog water differs significantly from Athabasca River water. Specifically, dissolved Sr is about ten times lower in the bog water, while Fe is about ten times higher; Pb and Zn levels in the bog water are five to ten times higher, but Cr, Cu and Ni are all below detectable levels. The relative abundance of these elements is very different from typical freshwaters, and it is already apparent that a complex series of biogeochemical processes is regulating their composition.

LESSONS LEARNED

With respect to snowpack sampling near industrial operations, it seems unlikely that the very low concentrations of TEs being measured in the filterable fraction are due to losses caused by adsorption to container walls. The only obvious exception to this general rule may be Ag, but with the concentrations of Ag as low as they are, this element has no real environmental relevance. Regarding atmospheric deposition onto plants, whether the material being sampled in peat bogs is *Sphagnum* moss or Labrador Tea or cranberries, the samples collected nearest industry are certainly impacted by dust. However, the chemical reactivity of the dusts, as indicated by hot water extracts, appears to be rather limited, even at elevated pressure. Elements with the greatest tendency to leach are not associated with the dust particles, but rather with the plant material itself. With respect to TEs in bog surface waters, their chemical composition is not simply the result of mineral dissolution reactions; other processes may be far more important for several elements of environmental concern.

PRESENTATIONS AND PUBLICATIONS

Presentations

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

Shotyk, W. 2019. *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 presentation, plus 13 page paper for the published Proceedings).

Shotyk, W. 2019. *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 3-7, 2019. Invited keynote speaker.

Shotyk, W. 2019. *Metals versus Minerals in the Mining Environment: Misconceptions and Misunderstandings.* Mining and the Environment Conference, Sudbury, Ontario, Canada, June 23-28, 2019. Invited keynote speaker.

Publications

Manuscripts Submitted

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, Special Issue on Atmospheric Deposition and Forest Health (revised manuscript in review).

Manuscripts in Preparation

Javed, M.B., Cuss, C.W., Noernberg, T., Zheng, J., and Shotyk, W. *An optimized contamination-free method for sample collection, handling and processing for trace and ultra-trace elements in snow*.

Shotyk, W. *Trace elements in wild, native berries from reclaimed lands: bioindicators of contamination by atmospheric dust*.

Shotyk, W., Javed, M.B., and Noernberg, T. *Trace elements in Labrador Tea* (Rhododendron groenlandicum): *a medicinal plant and bioindicator of atmospheric dust and associated trace elements*.

RESEARCH TEAM AND COLLABORATORS

Institution: University of Alberta

Principal Investigator: Dr. William Shotyk

Name	Institution or Company	Degree or Job Title	Degree Start Date (Students Only)	Degree Completion Date (Students Only)
Dr. Muhammad Javed	University of Alberta	Post-Doctoral Fellow		
Tommy Noernberg	University of Alberta	Mechanical Engineer and Field Specialist		
Tracy Gartner	University of Alberta	Project Manager		
Karen Lund	University of Alberta	Lab technician		

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Water Quality in the Lower Athabasca River

COSIA Project Number: WE0058

COSIA GAP/Opportunity Area: Environmental Effects Monitoring of Treated Oil Sands Process-Affected Water and Depressurization Water Releases to the Athabasca River

Research Provider: University of Alberta

Industry Champion: Canadian Natural Resources Limited

Industry Collaborators: Imperial Oil Resources Limited, Suncor Energy Inc, Syncrude Canada Ltd., Teck Resources Limited

Status: Year 2 of 3

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. 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 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 TEs 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.

The research team proposes to address these industry 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 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 and 2018, 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, including the Horse, Clearwater, Steepbank and Muskeg Rivers. These inputs mix slowly from the east to the west side of the LAR from upstream to downstream, taking as much as 50-70 km for complete mixing (in the case of 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, the mixing of tributaries was not delayed for as long 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.

Progress has been made in four areas to date:

- 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 current analytical method can measure the distribution of TEs among major colloidal species from 1 nm to 0.45 µm. Progress on the second size range has been limited by the lack of suitable students to undertake the work. A prospective PhD student has been identified and recruitment is underway.
- Samples have been collected for three seasons and analyzed for two of these seasons. Laboratory and data analysis for the remaining samples is underway, and researchers will return to the river for a fourth sampling campaign in May-June, 2019.
- Preliminary assessment of filtration and storage artefacts has been conducted using a small sample set. Progress on the larger study has been limited by the lack of suitable students to help with the research. An MSc student was recruited in September 2018 and is being trained, and a prospective PhD student has been identified and recruitment is underway.

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. Any such attributions require re-assessment and 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

Oral Presentations

Cuss, C.W. 2018. *Separation of nanominerals and colloids into bioaccessibility-based fractions using FFF-ICPMS*. Presented at Nanolytica Conference, Simon Fraser University, Vancouver, British Columbia, May 3, 2018. Invited speaker.

Cuss, C.W. 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.* Presented at the International Conference on Field- and Flow-based Separations, Columbia, South Carolina, May 14-17, 2018.

Cuss, C.W. 2018. *Dynamics of dissolved (< 0.45 µm) trace elements and organic matter in tributary mixing zones of the lower Athabasca River, Alberta.* Presented at Canadian Society for Chemistry Conference, Edmonton, Alberta, May 28-30, 2018. Invited speaker.

Cuss, C.W. 2018. *Measuring the distribution of metals and metalloids amongst dissolved colloidal species using AF4-UV-ICPMS*. Presented at Canadian Society for Chemistry Conference, Edmonton, Alberta, May 28-30, 2018.

Cuss, C.W. 2018. *Routine analysis of trace element distributions among major dissolved colloidal species using AF4-UV-ICPMS (with applications).* Presented at International Conference on Heavy Metals in the Environment, Athens, Georgia, July 21-25, 2018. Invited speaker.

Cuss, C.W. 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, Park City, Utah, January 5, 2018. Invited speaker.

Cuss, C.W. 2017. *AF4-ICPMS in the SWAMP: Challenges, strategies, and applications for routine analysis with the 300-Dalton membrane.* Presented at Postnova User's Meeting, Park City, Utah, September 15, 2017. Invited speaker.

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, Alberta, March 27-29, 2019 (invited speaker, plus 13 page paper for the published Proceedings).

Poster Presentations

Ghotbizadeh, M., Cuss, C.W., Noernberg, T., and Shotyk, W. 2018. *Spatial variation in the composition, size and morphology of dissolved colloids along the Athabasca River.* Presented at Canadian Society for Chemistry Conference, Edmonton, Alberta, May 28-30, 2018.

Ghotbizadeh, M., Cuss, C.W., Noernberg, T., and Shotyk, W. 2018. *Measuring spatial variation in the speciation, composition, and morphology of trace element-bearing colloids in the lower Athabasca River and its tributaries*. Presented at COSIA Oil Sands Innovation Summit, Calgary, Alberta, June 6-8, 2018.

Publications

Manuscripts in Preparation

Cuss, C.W., Ghotbizadeh, M., Grant-Weaver, I., Javed, M.B., Noernberg, T., and Shotyk, W. *Influence of tributaries on the concentrations and speciation of trace elements in a large boreal rIver: implications for representative sampling.*

Ghotbizadeh, M., Grant-Weaver, I., Markov, A., Noernberg, T., Ulrich, A., and Shotyk, W. *Spatial variation, speciation and source apportionment of trace elements along the Lower Athabasca River.*

Ghotbizadeh, M., Grant-Weaver, I., Markov, A., Noernberg, T., Ulrich, A., and Shotyk, W. *Temporal variation, speciation and source apportionment of trace elements along the Lower Athabasca River.*

Noernberg, T., Ghotbizadeh, M., Cuss, C.W., and Shotyk, W. *The SWAMP FISH: A metal-free water sampling device for use in large rivers.*

Theses in Preparation

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

Xue, J. *Geochemistry and Speciation of Bitumen-derived Trace Elements along the Lower Athabasca River, and Implications for Assessing Environmental Impacts.* MSc thesis.

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 (Students Only)	Degree Completion Date (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	Post-Doctoral Fellow		
Marjan Ghotbizadeh	University of Alberta	MSc Student	2018	2019
Jinping Xue	University of Alberta	MSc Student	2019	2021
Karen Lund	University of Alberta	Lab Technician		
Iain Grant-Weaver	University of Alberta	Lab Technician		
Acacia Markov	Guelph University	Summer Student		

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Current Knowledge of Oil Sands Process-Affected Water (OSPW) Seepage from Tailings Ponds and its Environmental Influence in Northeastern Alberta

COSIA Project Number: WE0059

COSIA GAP/Opportunity Area: OSPW Chemistry and Effects: Natural and Anthropogenic Effects in the Watershed

Research Provider: Integrated Sustainability Consultants Ltd., Kilgour and Associates

Industry Champion: Teck Resources Limited

Industry Collaborators: Canadian Natural Resources Limited, Imperial Oil Resources Limited, Suncor Energy Inc., Syncrude Canada Ltd.

Status: Completed

PROJECT SUMMARY

Northeastern Alberta, Canada is rich in bitumen. At the mines north of Fort McMurray, the unconventional oil is separated from the bituminous sands by hot water extraction which generates a by-product mixture known as tailings. Seepage and toxicity of the liquids, known as oil sands process-affected water (OSPW), from the ponds is a commonly cited concern among stakeholders. Effects of undifferentiated OSPW (Lari et al. 2016) or constituents, such as sodium, chloride, and sulphate (Zubot et al. 2012), metals and trace elements such as arsenic (Donner et al. 2017), and polyaromatic compounds (Gagné et al. 2011) on a variety of receptors, including mammalian cell lines (Fu et al. 2017), fishes (Marentette et al. 2015a, b), and invertebrates (Lari et al. 2016) have been documented. Additional work suggests OSPW has migrated beyond containment at some sites (Frank et al. 2014), but few comprehensive treatments exploring the issue are widely available to evaluate the relevance of the threat to the region. Using descriptions of the local and regional hydrogeological setting and chemical and toxicological information available in the primary literature, the current knowledge of seepage from tailings ponds was reviewed, based on more than 100 sources.

The information was summarized and presented in a risk framework of source-pathway-receptor. Source information on the ponds includes their type (in-pit vs. external tailings facilities) and an overview of the compounds contained in the ponds, including classical naphthenic acids and other polar organics that are often present. Pathway information included the regional and local hydrogeological settings and the distance to the nearest surface waterbody. Receptor information was the richest and included comparing the chemical fingerprinting of OSPW with natural surface- and groundwater influenced by bitumen, and with other water surveys in the region. Toxicological characterization of OSPW was also examined as were results of field monitoring, in situ exposures in test end-pit lakes, and controlled laboratory experiments.

PROGRESS AND ACHIEVEMENTS

In most cases no evidence of seepage is apparent in surface waters, suggesting the containment and interception systems and approaches are functioning as designed (e.g., Ross et al. 2012; Sun et al. 2017). However, some data suggests seepage has occurred in local groundwater near older ponds and possibly into sediments of the Athabasca River near these facilities (Frank et al. 2014; Roy et al. 2016). Although data also suggests OSPW may be present in McLean Creek and Beaver River, two tributaries adjacent to tailings ponds (MacKinnon et al. 2005; Ross et al. 2012; Sun et al. 2017), the physical migratory pathways for possible seepage into McLean Creek have not been established and the results are ambiguous. Researchers have also suggested some data shows similarities between OSPW and surface water in tributaries (Arens et al. 2017), but the degree to which these signatures are attributable to natural discharge of groundwater influenced by bitumen observed regionally is not clear. Regional groundwater samples suggest that many OSPW-like signatures in surface water identified at these locations originate from widespread and patchy natural contamination of thoroughly established groundwater seeps throughout the lower Athabasca region, influenced by bitumen and discharged from the deep Devonian formations (Gibson et al. 2013; Gue et al. 2015; Birks et al. 2018), including some sites far from development (Sun et al. 2017).

Toxicologically, the impacts of OSPW in laboratories are clear, but evidence from field studies is less conclusive. Irrespective of the possible source, or sources, of seepage-inferred constituents, research suggests concentrations of classical naphthenic acids estimated using reliable methods in all surface waterbodies assessed (i.e., Ross et al. 2012; Sun et al. 2017) are below effect thresholds of standard toxicological measurements calculated from the results of laboratory studies (e.g., Marentette et al. 2015a,b). However, much of the information must be evaluated cautiously as chemical methods have changed over time and some methods, such as Fourier Transform Infrared and gas-chromatography-mass spectrometry often overestimate the presence of classical naphthenic acids (Hughes et al. 2017a), which is the fraction of polar organics present in OSPW to which most of the toxicity has been attributed (Morandi et al. 2015; Hughes et al. 2017b). A risk assessment of possible OSPW seepage into the sediments of the Athabasca River is not different from groundwater seeps sampled (Roy et al. 2016). Finally, no biological effects consistent with exposure to OSPW seepage have been observed in the surface waters of the region (Culp et al. 2018; McMaster et al. 2018). This risk assessment suggests the threat of seepage is present, but definitive impacts have not been observed.

Debate continues regarding the occurrence, extent, and relevance of seepage from tailings ponds to the aquatic ecosystem of the minable oil sands region.

LESSONS LEARNED

Although a holistic assessment based on widely available and accessible sources of information is lacking, information compiled through this review suggests the risk of impacts of OSPW seepage on local waterbodies is low. Analytical methodology must be evaluated cautiously as some methods can overestimate the occurrence of classical naphthenic acids.

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Hughes, S.A., Mahaffey, A., Shore, B., Baker, J., Kilgour, B., Brown, C., Peru, K.M., Headley, J.V. and Bailey, H.C. 2017a. *Using ultrahigh-resolution mass spectrometry and toxicity identification techniques to characterize the toxicity of oil sands process-affected water: The case for classical naphthenic acids.* Environmental Toxicology and Chemistry, 36(11), 3148-3157.

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PRESENTATIONS AND PUBLICATIONS

Publications

Manuscript Pending

Arciszewski, T., Fennell, J. 2019. *Current knowledge of oil sands process-affected water seepage from tailings ponds and its environmental impact in northeastern Alberta*. Science of the Total Environment.

RESEARCH TEAM AND COLLABORATORS

Name	Institution or Company	Degree or Job Title	Degree Start Date (Students Only)	Degree Completion Date (Students Only)
Jon Fennell	Integrated Sustainability Consultants Ltd.	Senior Hydrogeologist		
Tim Arciszewski	Kilgour and Associates	Research Scientist		

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

COSIA Project Number: WJ0017

COSIA GAP/Opportunity Area: Receiving Water Criteria

Research Provider: University of Alberta

Industry Champion: Syncrude Canada Ltd.

Industry Collaborators: Canadian Natural Resources Limited, Shell Canada Ltd., Imperial Oil Resources Limited, Suncor Energy Inc., Teck Resources Limited

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:

1. 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.
2. Likely sources of spatiotemporal variation, such as the channelization of the LAR and seasonality of inputs, have not been assessed.
3. Changes in the geochemical behaviour of TEs caused by the input of considerable dissolved organic matter (DOM) and iron oxyhydroxide (FeO(OH)) by tributaries have not been quantified.
4. 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.
5. 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.

We propose to address these industry concerns while developing new technologies and knowledge, including:

1. Apparatus and methods for collecting samples across transects of the LAR, at several depths, under metal-free conditions.
2. 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.
3. Measuring the impacts of seasonal differences and high-DOM, high-Fe inputs on the geochemical behaviour of TEs in the LAR.
4. 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 and 2018, 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, including the Horse, Clearwater, Steepbank and Muskeg rivers. These inputs mix slowly from the east to the west side of the LAR from upstream to downstream, taking as much as 50 km - 70 km for complete mixing (as in the case of 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, the mixing of tributaries was not delayed for as long 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.

Progress to date includes:

1. 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).
2. 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 has been identified and recruitment is underway.
3. Samples have been collected for three seasons, and they have been analyzed for two of these seasons. Laboratory and data analysis for the remaining samples are underway. A fourth sampling campaign will occur May - June, 2019.
4. Preliminary assessment of filtration and storage artefacts has been conducted using a small sample set. Progress on the larger study has been limited by the lack of suitable students; however, an MSc student is currently being trained (recruited in September 2018), and a prospective PhD student has been identified and recruitment is underway.

Data analysis and visualization are underway.

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

Conference Presentations/Posters

Separation of nanominerals and colloids into bioaccessibility-based fractions using FFF-ICPMS. 2018. Presented at Nanolytica, Simon Fraser University, British Columbia.

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. 2018. Presented at the International Conference on Field- and Flow-based Separations, South Carolina, USA.

Dynamics of dissolved (< 0.45 µm) trace elements and organic matter in tributary mixing zones of the lower Athabasca River, Alberta

Measuring the distribution of metals and metalloids amongst dissolved colloidal species using AF4-UV-ICPMS Spatial variation in the composition, size and morphology of dissolved colloids along the Athabasca River (poster)

Measuring spatial variation in the speciation, composition, and morphology of trace element-bearing colloids in the lower Athabasca River and its tributaries. 2018. Poster presented at Alberta Innovates Water Innovation Forum, Calgary.

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

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

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.

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. 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

Publications

Published Theses

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

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

Journal Publications

Cuss, C.W. et al. *Influence of tributaries on the concentrations and speciation of trace elements in a large boreal rIver: implications for representative 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).

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.* Alberta Institute of Agrologists, Annual General Meeting, Banff, AB, March 27-29 (invited oral presentation, 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 (Students Only)	Degree Completion Date (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	Post-Doctoral Fellow		
Marjan Ghotbizadeh	University of Alberta	BSc (MSc Candidate)	2018	2019
Jinping Xue	University of Alberta	BSc (MSc Candidate)	2019	2021
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).

OIL SANDS PROCESS-AFFECTED WATER CHEMISTRY AND TOXICITY

Oil Sands Process-Affected Water (OSPW) Typology

COSIA Project Number: WE0011

COSIA GAP/Opportunity Area: OSPW Chemistry and Effects

Research Provider: Alberta Innovates – Technology Futures (Now InnoTech Alberta)

Industry Champion: Total Canada E&P Ltd.

Industry Collaborators: Canadian Natural Resources Limited, Suncor Energy Inc., Syncrude Canada Ltd.

Status: Completed

PROJECT SUMMARY

Compile and review existing data provided by individual operators on the composition and toxicity of OSPW and OSPW porewater to identify whether the existing data are sufficient to do a comprehensive OSPW typology suitable for risk assessment. The available geochemistry and toxicity data were critically reviewed to identify comparability issues and to see if any preliminary typologies are evident. Data on the geochemistry and toxicity of OSPW free water and OSPW porewater were compiled using: the COSIA Substance Load Allocation study database, water quality and toxicity sampling results from 2010 to 2012 provided by Canadian Natural, Suncor and Syncrude, and for 2012 provided by Total specifically for this project. In total the combined database includes geochemistry and/or toxicity data from 14 tailings ponds. These include data for samples obtained from the free water zone of the tailings pond (OSPW free water) and from depth within the fluid fine tailings (OSPW porewater).

An OSPW "typology" for risk assessment is essentially a classification scheme that differentiates OSPW according to major types or subtypes that need to be considered differently in risk scenarios. The overarching goal of this typology project is to identify whether there are major groupings, in terms of both composition and toxicity, within OSPW free waters and porewaters across the oil sands industry. A typology for OSPW is needed to assess and mitigate environmental risk, to help guide treatment technology development and for communication to regulators and stakeholders.

PROGRESS AND ACHIEVEMENTS

The project was completed in November 2014. While OSPW toxicity has been extensively studied by academics and scientists in Canada and around the world, these studies did not involve a large number of tailings pond samples that varied both spatially and temporally. Most operators conduct basic geochemical characterization of OSPW routinely but typically do not include toxicological assessments as a routine part of the suite of tests. This made comparing data between operating sites more challenging.

LESSONS LEARNED

The main requirement for developing an OSPW typology for risk assessment is the availability of comparable geochemistry and toxicity data over the full spectrum of OSPWs. Our literature review, data review and gap analysis have identified categories of OSPW where there appears to be limited data available, and incompatibilities in some of the existing data that prevent their comparison on a regional basis. Some of the gaps include:

Ecotoxicity Data:

In general, we found that characterizing the toxicological properties of OSPW has lagged behind the geochemical characterizations. There is in general a lack of toxicity data (number and type of tests), and more specifically chronic and sublethal toxicity data.

Geochemical Characterization:

There are some species of organics and organometals that have been identified in the literature as being potential controls on toxicity that were not widely available in any of the existing datasets (naphthenic acid speciation, organometals, and comparable PAH data).

OSPW Porewater Data:

The limited data on porewater composition and porewater toxicity is a major data gap. Only one operator has an on-going program of sampling and analyzing the composition of fluid fine tailings (FFT). Of particular interest are OSPW porewaters that result from some of the newer tailings reduction technologies.

Our compiled database does show the large number of analyses conducted by individual operators characterizing the composition of their OSPW; however, lack of toxicity data in general and lack of consistency between the various monitoring programs result in a much smaller pool of data available for inter-operator comparisons and understanding relationships between toxicity and substance concentration. Some of the data issues that limited our ability to use existing data included:

- Water quality and ecotoxicity testing are often not synchronized (water quality and ecotoxicity samples collected at different times up to a month apart)
- Inadequate test concentrations and inconsistent reporting of percentage effect concentrations (LC/EC/IC values and 95% confidence intervals) for ecotoxicity tests
- Different suites of ecotoxicity tests and procedures among operators/sites/years
- Different pre-aeration times prior to testing for different bioassays
- Different suites of organic characterization and procedures among operators/sites/years
- Variation in sample processing techniques including filtering (i.e., dissolved/total) and centrifuging prior to analysis
- Differences in sample matrix and analytical methods used between operators

These data issues do not indicate poor data quality or limitations in the design of the different monitoring programs; most are simply because the various datasets were not designed with the objective of facilitating inter-operator comparisons or developing a cross-industry typology. However, the net result of these data issues is that only a small subset of the existing data can be used for direct comparisons of OSPW free water between operators.

PRESENTATION AND PUBLICATIONS

No public presentations or publications.

RESEARCH TEAM AND COLLABORATORS

Institution: Alberta Innovates – Technology Futures (Now InnoTech Alberta)

Principal Investigator: Andrews Takyi (Total E&P Canada Ltd.)

Toxicity of Ozone-Treated and Untreated Oil Sands Process-Affected Water (OSPW)

COSIA Project Number: WE0016

COSIA GAP/Opportunity Area: Water Return

Research Provider: University of Alberta

Industry Champion: Canadian Natural Resources Limited

Industry Collaborators: Imperial Oil Resources Limited, Suncor Energy Inc., Syncrude Canada Ltd., Teck Resources Limited, Total E&P Canada Ltd.

Status: Completed

PROJECT SUMMARY

Large volumes of oil sands process-affected water (OSPW) have been produced during the bitumen extraction process from the oil sands industry in the Alberta oil sands region. Compared to natural surface waters, OSPW contains elevated concentrations of total dissolved solids (TDS, mostly salts and bicarbonates) and organic compounds naturally present in bitumen. OSPW is currently stored in tailings ponds for its reuse in the bitumen extraction process, process cooling, and material hydro-transport. As a part of the industry's reclamation plan, OSPW in tailings ponds will be treated and eventually developed into terrestrial and/or aquatic habitat upon mine closure.

The main objective of this COSIA Environmental Priority Area (EPA) study was for University of Alberta professors, Dr. Mohamed Gamal El-Din and Dr. Keith Tierney, to document the possible toxic effects of the whole organic fraction of oil sands process-affected water (OSPW-OF) of two different OSPW waters on the development and reproduction of zebrafish (*Danio rerio*). The second objective was to determine whether advanced oxidation treatment ameliorates possible toxic effects of the two OSPW-OF.

PROGRESS AND ACHIEVEMENTS

The study started with the characterization of OSPW before and after treatment by determining the main physico-chemical parameters. In addition, the acid-extractable fraction (AEF) in OSPW was analyzed by Fourier transform infrared spectroscopy (FTIR), while classical naphthenic acids (NAs) (i.e., O_{2}-NAs) and oxidized NAs (Ox-NAs) were quantified by ultra-performance liquid chromatography time-offlight mass spectrometry (UPLC-TOF-MS). Ion mobility spectroscopy (IMS) was applied to raw and treated OSPWs to provide qualitative information of NA species. UPLC-TOF-MS results indicated that the organics in raw OSPW mainly contained classical NAs, oxidized NAs and sulphur containing NA species (S-NAs). The dominant oxidized species in raw OSPW were O_{3}-NAs (i.e., NAs with an additional oxygen atom) and O_{4}-NAs (i.e., NAs with two additional oxygen atoms). Based on Fourier-transform ion cyclotron resonance mass spectrometry (FTICR-MS) results, the dominant species in raw OSPW with an AEF of 41 mg/ L were O_2 (30.3%), O_3 (27.9%), and O_4 (24.9%). O_2S (2.7%), O_3S (4.8%), and O_4S (2.1%)

were the major sulphur-containing species. O_2N accounted for only 0.6% of the total intensity, while N_2Ox accounted for 3.9% of the total intensity. The FTICR-MS results also showed that ozonation was effective to transform the Ox species in OSPW. After ozonation with 50 mg/L utilized O_3 dose, the abundance of O_2 was reduced to 16.6%. However, the O_3, O_4, O_5, and O_6 species increased to 33.4%, 35.1%, 8.2% and 0.8%, respectively, indicating a significant shift of organic species distribution to more oxygen-rich species. The ozonation process also reduced the relative abundance of O_2S species, which were not detected after ozonation. In terms of transformation of nitrogen-containing species, a decrease of the relative abundance of N_2Ox to 0.6% after ozonation was found.

LESSONS LEARNED

Ozonation and a peroxone process (i.e., hydrogen peroxide/ozone; H_2O_2:O_3) using mild-ozone doses of 30 mg/L and 50 mg/L were investigated. Although the results indicated that 1:2 peroxone was the optimum dose based on its high degradation of NAs, no significant difference in terms of NA degradation was found between peroxone and ozonation. The finding also showed that the NA degradation rates increased with increased carbon and hydrogen deficiency (Z) numbers. Suppressing the hydroxyl radical (•OH) pathway by adding tert-butyl alcohol (TBA) reduced the NA degradation in all treatments, while molecular ozone contribution was 50% and 34% for classical NAs and oxidized NAs, respectively. Our results indicated that both molecular ozone and •OH were important pathways for the degradation of NA species.

In terms of toxicity, the studies found that developmental OSPW exposure was not overtly toxic to zebrafish embryos. Survival, growth and reproduction were not affected by exposure and the expression of many target genes remained unaffected. The embryos appeared to be able to recover relatively quickly after the exposure ended (using biotransformation enzyme expression as a measure of recovery). The results showed a few indications of slight endocrine disruption from OSPW exposure (decreased pigmentation, and GR and Sox9b expression), but more research would be needed to support these findings.

Though the exposed fish grew and reproduced normally, there were changes in multiple behavior endpoints. Some of these endpoints showed lasting behavioral changes into adulthood resulting in a change in behavioral phenotypes within the test populations. The ‘behavioral bottleneck’ observed in the first-generation fish did not exist in the second generation embryos, indicating that perhaps this change in behavioral phenotypes is not heritable. The environmental implications of these changes in behavior and the mechanisms through which they occur are not known.

PRESENTATIONS AND PUBLICATIONS

Presentations

Mohamed Gamal El-Din, Keith Tierney, Danielle Lyons, Danielle Philibert. *Effects of raw and ozonated OSPW exposure on embryonic zebrafish*. Presentation on OSPW to COSIA.

Publications

Fu L., Li C., Gamal El-Din M., Belosevic M., and Stafford J.L. 2017. *Comparison of the acute immunotoxicity of non-fractionated and fractionated oil sands process-affected water in mammalian macrophages.* Environmental Science & Technology 2017; 51:8624-8634.

Garcia-Garcia E., Pun J., Perez-Estrada L.C., Gamal El-Din M., Smith D. W., Martin J.W., and Belosevic M. 2012. *Commercial naphthenic acids and the organic fraction of oil sands process water induce different effects on pro-inflammatory gene expression and macrophage phagocytosis in mice.* Journal of Applied Toxicology 2012; 32:968-979.

Garcia-Garcia E., Pun J., Perez-Estrada L.A., Gamal El-Din M., Smith D. W., Martin J.W., and Belosevic M. 2011. *Commercial naphthenic acids and the organic fraction of oil sands process water downregulate pro-inflammatory gene expression and macrophage antimicrobial responses.* Toxicology Letters 2011; 202:62-73.

Garcia-Garcia E., Ge J.Q., Oladiran A., Montgomery B., Gamal El-Din M., Perez-Estrada L.C., Stafford J.L., Martin J.W., and Belosevic M. 2011. *Ozone treatment ameliorates oil sands process water toxicity in mammals.* Water Research; 2011; 45:5489-5857.

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Hagen M.O., Garcia-Garcia E., Oladiran A., Karpman, M., Mitchell S., Gamal El-Din M., Martin J.W., and Belosevic M. 2012. *The acute and sub-chronic exposures of goldfish to naphthenic acids induce different host defense responses.* Aquatic Toxicology 2012; 109:143-149.

Klamerth N., Moreira J., Li C., Singh A., McPhedran K.N., Chelme-Ayala P., Belosevic M., and Gamal El-Din M. 2015. *Effects of ozonation on naphthenic acid speciation and toxicity of pH-dependent organic fractions of oil sands process-affected water.* Science of the Total Environment 2015; 506-507: 66-75.

Li C., Fu L., Stafford J.L., Belosevic M., and Gamal-El Din M. 2017. *The composition and toxicity of oil sands process-affected water (OSPW): a critical review.* Science of the Total Environment 2017; 601-602: 1785-1802.

Lyons D.D., Philibert D.A., Zablocki T., Qin R., Huang R., Gamal El-Din M., and Tierney K.B. 2018 *Assessment of developmental effects of oil sands process-affected water exposure on zebrafish: Linking morphological changes with gene expression.* Accepted 3 February, to Environmental Pollution, 241 (2018): 959–968.

Lyons D.D., Morrison C., Philibert D.A., Gamal El-Din M., and Tierney K.B. 2018. *Growth and recovery of zebrafish embryos after developmental exposure to raw and ozonated oil sands process-affected water.* Accepted 3 May to Chemosphere, MS# CHEM-52106, 32 p.

Reichert M., Blunt B., Gabruch T., Zerulla T., Ralph A., Gamal El-Din M., Sutherland B.R., and Tierney K.B. 2017. *Sensory and behavioral responses of a model fish to oil sands process-affected water with and without treatment.* Environmental Science & Technology. 51 (12): 7128–7137.

Sun N., Chelme-Ayala P., Klamerth N., Md. Shahinoor Islam, Perez-Estrada L., Drzewicz P., Blunt B.L., Reichert M., Hagen M.O., Tierney K.B., Belosevic M., and Gamal El-Din M. 2014. *Advanced analytical mass spectrometric techniques and bioassays to characterize untreated and ozonated oil sands process-affected water.* Environmental Science & Technology 2014; 48:11090-11099.

Wang C., Klamerth N., Messele S.A., Singh A., Belosevic M., and Gamal El-Din M. 2016. *Comparison of UV/hydrogen peroxide, potassium ferrate, and ozone in oxidizing the organic fraction of oil sands process-affected water (OSPW).* Water Research 2016; 100:476-485.

Wang N., Chelme-Ayala P., Perez-Estrada E.L., Garcia-Garcia E., Pun J., Anderson J., Wiseman S., Giesy J.P., Martin J.W., Belosevic M., and Gamal El-Din M. 2013. *Impact of ozonation on naphthenic acid speciation and toxicity of oil sands process-affected water to* Vibrio fischeri *and mammalian immune system.* Environmental Science & Technology 2013; 47:6518-6526.

RESEARCH TEAM AND COLLABORATORS

Institution: University of Alberta

Principal Investigators: Dr. Mohamed Gamal El-Din and Dr. Keith Tierney

Literature Review and Evaluation of Dissolved Chloride for Treated Oil Sands Process-Affected Water (OSPW) Return

COSIA Project Number: WE0037

COSIA GAP/Opportunity Area: Receiving Water Criteria

Research Provider: University of Alberta

Industry Champion: Syncrude Canada Ltd.

Industry Collaborators: COSIA Water Environmental Priority Area Members

Status: Completed

PROJECT SUMMARY

For the better part of two decades, surface water discharges of dissolved chloride in Alberta were guided by the 1999 Alberta Environment short-term limit of 860 mg/L. The 2011 adoption of the Canadian Council of Ministers of the Environment (CCME) short-term limit of 640 mg/L, in theory, was intended to lead to better protection of aquatic organisms in surface waters and streams. As with any environmental guideline that trends in this direction (i.e., downward), it is worthwhile to take a closer look at what, if any, benefits have been achieved. Consequently, Canada's Oil Sands Innovation Alliance undertook an exploratory study of specific dissolved chloride issues to:

1. Review recent scientific literature to better understand the science and limitations behind the establishment of the CCME short-term limit of 640 mg/L for dissolved chloride.
2. Investigate the life cycle aspects of desalination as it relates to removing dissolved chloride from oil sands process-affected water (OSPW).

PROGRESS AND ACHIEVEMENTS

1. Toxicity endpoint dose descriptors for sensitive aquatic species (LC50 and EC50 toxicity values) are used to derive the short-term limit for dissolved chloride (Cl^-) in surface waters. Standardized aquatic toxicity tests used to establish these endpoints are far from being an exact science. Variabilities in test outcomes for LC50 and EC50 toxicity endpoints are reported to range from 30% to almost 5,000% in extreme cases.
2. The 640 mg/L short-term limit is mostly based on toxicity test results using nontolerant laboratory organisms rather than acclimated (tolerant) organisms from natural aquatic settings. This gap between the idealized, simulated laboratory and the real world conditions (in this case the Athabasca River setting in the oil sands region) limits the ability to translate standard laboratory toxicity test results to the Athabasca River setting because of different modifying factor conditions.
3. Evidence of the eight most potentially sensitive aquatic species to Cl^- indicates that most of these species (excluding *Ceriodaphnia dubia*, water flea) would not be present in the Athabasca River oil sands region. This raises a valid concern about application of the 640 mg/L short term limit to the Athabasca River oil sands region.

4. Of the remaining seven aquatic species that would not be present in the Athabasca River oil sands region, six are key species in the development of the short-term limit as their LC50/EC50 toxicity endpoints are lower than the endpoint for the water flea. In particular, these six species have a dominant role in anchoring the lower end of the sensitive species distribution curve used in deriving the short-term limit of 640 mg/L. This is an important source of confounding in applying the short-term limit for the site-specific conditions in the Athabasca River oil sands region.
5. Dissolution of natural salt deposits over long periods of time has resulted in the collapse of subsurface strata in several geological formations (Cretaceous Clearwater, McMurray and Devonian formations) in the Athabasca River oil sands region. This has created a complex hydrogeological system with connections between surface and subsurface water resources in the region. It is well documented that naturally saline (dissolved sodium chloride) water discharge occurs in the Athabasca River oil sands region thru numerous springs, riverbed seepage and fens. Historic records and oral tradition indicate that saline spring discharges into the Athabasca and Clearwater rivers have been occurring continuously for hundreds of years over a 125 km reach from Fort McMurray to the Firebag River.
6. Sampling of nine natural springs (two in the Athabasca River and seven in the Clearwater River) that were discharging saline water to both rivers showed Cl^- concentrations well above the short-term limit of 640 mg/L. Dissolved chloride concentrations in the nine spring water samples ranged from 3,690 mg/L to 27,400 mg/L (median 9,800 mg/L). The natural spring with the highest Cl^- concentration (27,400 mg/L) was adjacent to the Syncrude Canada Ltd. main oil sands development.
7. Estimates of Cl^- flux from saline spring and groundwater discharges in the oil sands region to the Athabasca and Clearwater rivers were made:
8. For the Athabasca River, saline spring and groundwater discharges to the river are estimated to contribute 12,000,000 kg to 36,000,000 kg annually (33 tonne/day to 98 tonne/day)
9. For the Clearwater River, saline spring and groundwater discharges to the river are estimated to contribute 11,800,000 kg to 35,600,000 kg annually (32 tonne/day to 97 tonne/day)
10. Assessments of Na^+, Cl^- and $SO42^-$ ion inputs to the Athabasca River using Alberta Environment data for the period 1990 - 1993 (before major oil sands development expansion or any major tailings placement or reclamation) show that NaCl from saline basal water inputs are the most likely and plausible source of inputs to the Athabasca River, rather than anything associated with oil sands developments. Another estimate of incremental Cl^- mass flux to the Athabasca River was made using this data. Estimated daily incremental Cl^- mass flux to the Athabasca River based on this data is 1,100,000 kg/day or 1,100 tonne/day from saline spring and groundwater water contributions to the river. Estimated Cl^- mass flux quantities described above are not trivial amounts. These mass flux quantities support a position that aquatic organisms in the Athabasca River oil sands region are well acclimated (tolerant) to dissolved chloride.
11. This review identified an absence of information in scientific literature describing demonstrated desalination technologies at or near full-scale, focusing on Cl^- removal from wastewaters similar in characteristics to OSPW and/or with product water intended for water return end use. Different desalination technologies were identified that only have potential application for removing Cl^- from OSPW for water return end use.

12. Due to their energy and cost intensive nature, desalination technologies require careful analysis for Cl^- removal. While literature is scarce for desalination applications in the oil and gas industry, and the Alberta oil sands industry, the technology is still promoted for use. With respect to the latter (application to OSPW from the surface mining stream for water return end use), the entire information base in scientific literature only exists at the lab/pilot scale. This information, in effect, requires considerable assumptions to be made about technological and economic aspects for scale−up. This severely limits any practical analysis of life cycle aspects for this technology for specific application in the oil sands industry.
13. If desalination technologies were considered applicable and appropriate by oil sands developments for Cl^- removal from OSPW, numerous data and information needs exist before any practical analysis of life cycle aspects for this technology could be undertaken.

LESSONS LEARNED

Regulation of chloride in treated water needs to consider sources which contain elevated concentrations that are naturally occurring. Daily incremental chloride mass fluxes to the Athabasca River are estimated to be about 1100 tonne/day and are not trivial.

PRESENTATIONS AND PUBLICATIONS

Publication

Kindzierski, Warren, Aynul Bari, Md. 2018. *Literature review and evaluation of dissolved chloride for treated OSPW water return*.

RESEARCH TEAM AND COLLABORATORS

Institution: University of Alberta

Principal Investigator: Warren Kindzierski

Investigations of the Bioaccumulation Potential of Dissolved Organics in Oil Sands Process-Affected Water (OSPW): A Review

COSIA Project Number: WE0049

COSIA GAP/Opportunity Area: Receiving Water Criteria

Research Provider: WaterSMART Solutions Ltd.

Industry Champion: Syncrude Canada Ltd.

Industry Collaborators: COSIA Mine Members

Status: Completed

PROJECT SUMMARY

Bitumen recovery in the Athabasca region of Alberta generates large quantities of oil sands process-affected water (OSPW). Toxicity of OSPW has been studied extensively and naphthenic acids (NAs) have been consistently implicated as the primary driver of aquatic toxicity. Proposed lease closure options include treated OSPW waters in reclaimed landscapes. Consequently, in addition to quantifying the potential toxic effects of OSPWs, it is crucial to determine whether NAs and other dissolved organics in OSPW are likely to bioaccumulate or biomagnify in these environments.

PROGRESS AND ACHIEVEMENTS

Reported bioconcentration factors (BCFs) for NAs indicate limited potential for accumulation in fish and amphibians. Most quantitative assessments of NA bioaccumulation potential evaluated commercial NA mixtures (e.g., refined Merichem) as a surrogate for OSPW. Additionally, the majority of NA bioaccumulation studies to date employed a method of single-ion monitoring for measuring NA concentrations, resulting in BCF values that reflect only a single NA isomer class (i.e., NA isomers having the formula $C_{13}H_{22}O_2$). These measurements do not necessarily represent the behavior of all NAs or the complex mixture of other dissolved organics found in OSPWs. Using an advanced analytical technique, one study was able to more comprehensively characterize OSPW constituents, identifying several heteroatomic isomer classes within the dissolved organics profile. The same study conducted experiments to simulate bioaccumulation of OSPW dissolved organics in biological storage lipids, determining that the extent of partitioning was low. Using the same analytical technique, a subsequent study reported a range of BCFs for OSPW NAs from 0.7 L/kg to 53 L/kg wet weight based on in vivo fish exposures. Dissolved organics that contained SO or NO functional groups had BCFs from 0.6 L/kg to 28 L/kg wet weight. Another validated biomimetic method using synthetic cell membranes, coupled with Quantitative Structure-Activity Relationship (QSAR) modelling, could be used as an additional tool to estimate the bioaccumulation potential of dissolved organics in OSPW samples from a variety of sources. In situ testing (i.e., testing in actual tailings ponds) could further validate bioaccumulation potential, particularly because it would ensure that the effects of other oil sands process materials are not overlooked.

LESSONS LEARNED

Based on the work completed to date, reported BCF ranges are below the Canadian Environmental Protection Agency (CEPA) threshold for classifying a substance as bioaccumulative (i.e., BCF ≥ 5000).

PRESENTATIONS AND PUBLICATIONS

Publications

Scott, Angela. 2018. *Investigations of the bioaccumulation potential of dissolved organics in oil sands process-affected water – a review*. Prepared for the Canadian Oil Sands Innovation Alliance.

RESEARCH TEAM AND COLLABORATORS

Institution: Unaffiliated

Principal Investigator: Angela Scott

Vanadium Toxicity to Aquatic Organisms Representative of the Athabasca Oil Sands Region

COSIA Project Number: WJ0024

COSIA GAP/Opportunity Area: Receiving Water Criteria

Research Provider: University of Saskatchewan

Industry Champion: Syncrude Canada Ltd.

Industry Collaborators: COSIA Water Environmental Priority Area Members

Status: Completed

PROJECT SUMMARY

Vanadium (V) is one of the most abundant trace elements in crude oils, making it an element of potential concern in aquatic ecosystems surrounding various industries, such as the Athabasca Oil Sands (AOS) industry in northeastern Alberta. When bitumen from the AOS region is upgraded to synthetic crude oil, V is removed and enriched at elevated concentrations (> 1000 mg V/kg) into the by-product petroleum coke. This coke is stored on site of some major oil sands companies' leased land, until more practical ways of utilizing or storing it becomes available. The overall goal of this research was to evaluate the toxicity of V (as vanadate oxyanions) to a diverse suite of aquatic organisms regionally relevant to the AOS region to generate the data needed to derive sound V water quality benchmarks for the region. To achieve this goal, acute and chronic toxicity tests were conducted using comparable laboratory standard test organisms and organisms more regionally relevant to northern Alberta. Selected test-species included: four zooplankton species (*Daphnia pulex, D. dentifera, Simocephalus serrulatus,* and *Ceriodaphnia quadrangula*; 2-d and 8-d to 21-d studies), two unicellular green algae species (*Pseudokirchneriella subcapitata* and *Scenedesmus quadricauda*; 72-h cell growth studies), two benthic invertebrates (*Chironomus dilutus* and *C. riparius*; 4-d and 30-d to 40-d studies), and two freshwater fish species (*Oncorhynchus mykiss* and *Pimephales promelas*; 4-d and 28-d studies).

PROGRESS AND ACHIEVEMENTS

The acute toxicity of V was 52.0 mg/L, 63.2 mg/L for C. dilutus and C. riparius, respectively, and 4.0 mgV/L and 14.8 mgV/L for P. promelas and O. mykiss, respectively. Vanadium exposure significantly impaired adult emergence of C. dilutus and C. riparius at concentrations of 16.7 (31.6% reduction) and 8.3 (18% reduction) mg/L, respectively. Chronic toxicity in fish presented as lethality, with chronic 28-d LC50s of 0.5 mg/L and 4.3 mg/L for P. promelas and O. mykiss, respectively. These data were combined with data from peer-reviewed literature, and separate acute and chronic species sensitivity distributions (SSDs) were constructed. The acute and chronic hazardous concentrations endangering only 5% of species (HC5) were estimated as 0.64 mgV/L and 0.05 mgV/L, respectively.

LESSONS LEARNED

These new data for V toxicity to aquatic organisms ensure that there are now adequate data available for regulatory agencies to develop appropriate water quality guidelines for use in the Athabasca Oil Sands region and elsewhere. Until then, the HC5 values presented in the present study could serve as interim benchmarks for the protection of aquatic life from exposure to hazardous levels of V in local aquatic environments.

PRESENTATIONS AND PUBLICATIONS

Publications

Published Thesis

Schiffler, S. 2016. *Toxicity of vanadium to freshwater organisms representative of the Athabasca oil sands region.* University of Saskatchewan, Saskatoon, Saskatchewan, Canada.

Journal Publications

Schiffer, S., Liber, K. 2017. *Estimation of vanadium water quality benchmarks for the protection of aquatic life with relevance to the Athabasca oil sands region using species sensitivity distributions.* Environmental Toxicology and Chemistry. Vol. 36, No. 11, pp. 3034-3044.

Schiffer, S., Liber, K. 2017. *Toxicity of aqueous vanadium to zooplankton and phytoplankton species of relevance to the Athabasca oil sands region.* Ecotoxicological and Environmental Safety. 137(2017) 1-11.

RESEARCH TEAM AND COLLABORATORS

Institution: University of Saskatchewan

Principal Investigator: Karsten Liber

Name	Institution or Company	Degree or Job Title	Degree Start Date (Students Only)	Degree Completion Date (Students Only)
Stephanie Schiffer	University of Saskatchewan	MSc	2014	2017

The Base Mine Lake Toxicity Identification and Evaluation Study

COSIA Project Number: WJ0025

COSIA GAP/Opportunity Area: Biological Estimated Rates and Water Quality Trajectory

Research Provider: University of Alberta, University of Saskatchewan

Industry Champion: Syncrude Canada Ltd.

Industry Collaborators: Canadian Natural Resources Limited, Imperial Oil Resources Limited, Suncor Energy Inc., Teck Resources Limited, Total E&P Canada Ltd.

Status: Completed

PROJECT SUMMARY

End pit lakes (EPLs) are a key strategy for large-scale and long-term remediation of oil sands process-affected water (OSPW). The industry's first EPL, Base Mine Lake (BML), was commissioned at Syncrude in December 2012. The main objective of this study was to identify the most toxic chemicals in OSPW by an approach that combines concepts of effects directed analysis (EDA) and toxicity identification and evaluation (TIE). At the same time, experiments were set up to determine the most persistent and bioaccumulative chemicals. In practical terms, the project was based on strategic and large-scale fractionation of the toxic, complex mixture of organic compounds in BML (5,000-10,000 distinct chemical species belonging to 15 to 30 chemical groups) into sub-fractions. These primary fractions are chemically characterized by HPLC Orbitrap Mass Spectrometry (HPLC-Orbitrap MS) and tested for their aquatic toxicity and mode of toxic action by a battery of in vitro and in vivo assays. This process is then repeated by taking the most toxic primary fraction(s) and strategically sub-fractionating these into secondary fractions, which are themselves chemically characterized by HPLC-Orbitrap MS, and tested again for their aquatic toxicity and mode of toxic action. In this manner, the sub-fractionation of the most toxic fraction(s) continues until the source of the toxicity can be narrowed down to one, or a few, chemical groups. Together, the identification of the most toxic, persistent, and bioaccumulative compounds in BML will allow focused monitoring and water management strategies to evolve.

The research program was an effective collaboration between the Martin Group at the University of Alberta and the Giesy Group at the University of Saskatchewan. Extraction, fractionation, and detailed chemical characterization of OSPW was largely performed by the Martin Group, while aquatic toxicity testing of these fractions was conducted by the Giesy Group.

PROGRESS AND ACHIEVEMENTS

In the four years of this project, the most toxic chemicals in OSPW have been identified, including new chemical families that were not previously known and are not routinely monitored by any oil sands company, or provincial monitoring or regulatory agencies. Highly qualified personnel trained in this project are now employed by the provincial government (e.g., Alberta Innovates) and methods developed in this project to monitor for these chemicals in tailings ponds, EPLs, and natural water have been effectively transferred to the public domain for service to Canadian industry and public monitoring agencies. Through Canada's Oil Sands Innovation Alliance (COSIA), the results have been shared directly with all Canadian oil sands companies, and findings communicated in peer-reviewed journals for public information. This work will allow focused monitoring and water management strategies for OSPW to evolve.

LESSONS LEARNED

Lessons learned include the following:

- The project demonstrated the first empirical evidence that, indeed, classical naphthenic acids (O_{2-} species) are a primary source of toxicity in OSPW. Nevertheless, evidence that other (non-acid) organic species are also toxic at similar concentrations means that future regulatory and monitoring activities cannot ignore other chemicals in OSPW of related effluent from mine sites. Future research related to detoxification of water in EPLs should include comprehensive analysis by ultrahigh resolution mass spectrometry.
- This project produced the first comprehensive analysis of the aquatic bioconcentration potential for thousands of organic species in OSPW. Japanese medaka (*Oryzias latipes*) were exposed to 10% OSPW, and measured BCFs were evaluated against predicted BCFs from octanol–water distribution ratios (DOW) and phospholipid membrane–water distribution ratios (DMW). Only SO+, NO+, and O2– species were detectable in medaka exposed to OSPW, and BCFs for SO+ and NO+ species ranged from 0.6 L/kg to 28 L/kg, lower than predicted (i.e., 1.4 – 1.7 × 103 L/kg), possibly because of biotransformation of these hydrophobic substances. BCFs of O2– species ranged from 0.7 L/kg to 53 L/kg, similar to predicted values and indicating that phospholipid partitioning was an important bioconcentration mechanism. Interestingly, the same chemicals that cause acute toxicity also accumulate to the greatest extent in fish, or in biomimetic polymers (PDMS and phospholipids). This work furthermore demonstrates that fish tissue can be analyzed for evidence of OSPW exposure, which may be useful in future fish monitoring programs.
- The field monitoring campaign shows that classic naphthenic acids have largely disappeared over time. In Syncrude's experimental ponds set up in 1989 and 1992, the relative effect of dilution, versus biodegradation, is difficult to judge. In controlled laboratory studies over nine months there was no measurable evidence that BML OSPW could be (bio)degraded, but amendment by nutrients showed evidence for biostimulation. This may be a consideration for managing EPLs in the future, to accelerate their capacities for in situ biodegradation.

PRESENTATIONS AND PUBLICATIONS

Presentations

Morandi, G.D., Wiseman, S., Sun, C., Martin, J., and Giesy, J.P. 2016. *Assessing the reproductive toxicity of dissolved organic chemicals in OSPW by use of the fathead minnow 21-day reproductive bioassay.* Presented at SETAC PNC 2016.

Publications

Journal Publications

Alharbi, H., Morandi, G., Giesy, J.P., and Wiseman, S.B. 2016c. *Effect of oil sands process-affected water on toxicity of retene to early life-stages of Japanese medaka* (Oryzias latipes). Aquatic Toxicology 176: 1-9.

Morandi, G.D., Wiseman, S., Pereira, A.D.S., Mankidy, R., Gault, I.G., Martin, J.W., and Giesy, J.P. 2015. *Effects-directed analysis of dissolved organic compounds in oil sands process-affected water (OSPW).* Environmental Science & Technology 49(20):12395-404.

Morandi, G.D., Zhang, K., Wiseman, S.B., Pereira, A., Martin, J.W. and Giesy, J.P. 2016. *Effect of lipid partitioning on predictions of acute toxicity of oil sands process-affected water to embryos of fathead minnow* (Pimephales promelas). Environmental Science & Technology 50(16), 8858.

Peng, H., Sun, J., Alharbi, H.A., Jones, P.D., Giesy J.P., and Wiseman S. 2016. *Peroxisome proliferator-activated receptor γ is a sensitive target for oil sands process-affected water: effects on adipogenesis and identification of ligands.* Environmental Science & Technology 50, 7816–7824.

Zetouni N.C., Siraki A.G., Weinfeld M., Pereira A., and Martin J.W. 2017. *Screening of genotoxicity and mutagenicity in extractable organics from oil sands process-affected water*. Environmental Toxicology and Chemistry. 36:1397–1404.

Zhang, K., Pereira, A., and Martin, J.W. 2015. *Estimates of octanol-water partitioning for thousands of dissolved organic species in oil sands process-affected water.* Environmental Science & Technology 49: 8907-8913.

Zhang, K., Wiseman, S.B., Giesy, J.P., and Martin, J.W. 2016. *Bioconcentration of dissolved organic compounds from oil sands process-affected water by medaka* (Oryzias latipes): *importance of partitioning to phospholipids*. Environmental Science & Technology 50: 6574–6582.

RESEARCH TEAM AND COLLABORATORS

Institution: University of Alberta

Principal Investigator: Jon Martin

Name	Institution or Company	Degree or Job Title	Degree Start Date (Students Only)	Degree Completion Date (Students Only)
John Giesy	University of Saskatchewan	Professor		

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

COSIA GAP/Opportunity Area: Water Return

Research Provider: ExxonMobil Biomedical Sciences, Inc.

Industry Champion: Imperial Oil Resources Limited

Industry Collaborators: Canadian Natural Resources Limited, Teck Resourced Limited., Suncor Energy Inc., Syncrude Canada Ltd.

Status: Year 4 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 released back to the environment. AEOs represent a complex mixture that varies in composition in different OSPW, altering aquatic toxicity and complicating the development of water quality criteria. Defendable numerical criteria for AEOs are lacking, which limits the ability to consistently evaluate the effectiveness of OSPW treatment options and the potential suitability of OSPW for eventual discharge to the environment. In order to ensure long-term, responsible management of OSPW, industry needs to develop water quality criteria for AEOs.

The first objective of this research was to use the Target Lipid Model (TLM) 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). These data were 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 final objective was to integrate study findings into recommendations on developing BE-based water quality benchmarks for OSPW.

PROGRESS AND ACHIEVEMENTS

The major outcome of this research was the development of passive sampler methods to support the derivation of water quality benchmarks for organic constituents in OSPW. Thresholds based on BE were developed for several invertebrates and fishes exposed to organics extracted from OSPW (Redman et al., 2018). These data form the basis of an initial SSD 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. Additional data on sensitive species and, importantly, data on OSPW from a range of operations and ages, are needed to improve the technical basis for applying this approach.

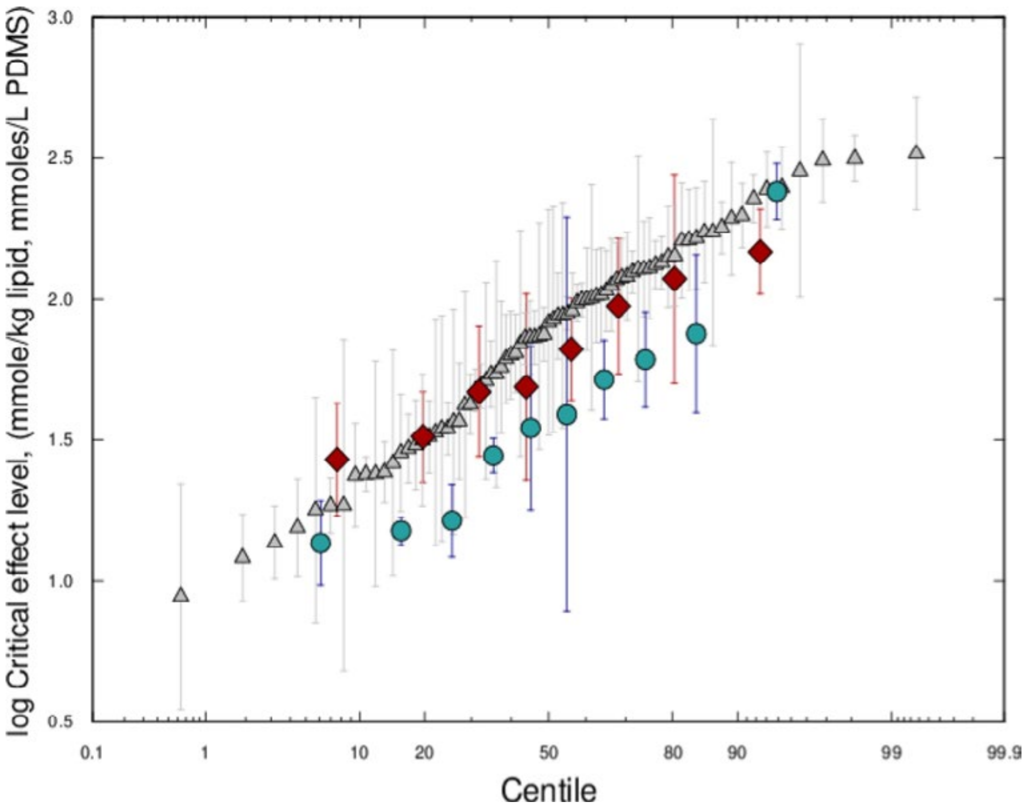

Figure 1: Comparing critical fiber concentrations and standard errors (mmol/L polydimethylsiloxane (PDMS)) derived for hydrocarbons (●), and organic acids (♦), and target lipid model (TLM)-derived tissue-based effect concentrations (mmol/kg lipid, ▲).

LESSONS LEARNED

The BE method could serve as a rapid 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). Therefore, BE measurements have the potential to streamline the water quality assessment of treated OSPW effluents by providing timely and cost-effective data on the predicted toxicity of organics in a given effluent. 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, and residual solvent) and organic acids, respectively.

LITERATURE CITED

Redman, A.; Butler, J.; Letinski, D.; Di Toro, D.; Leon Paumen, M.; Parkerton, T. *Technical basis for using passive sampling as a biomimetic extraction procedure to assess bioavailability and predict toxicity of petroleum substances.* Chemosphere 2018, 199, 585−594.

McGrath, J.A.; Fanelli, C.J.; Di Toro, D. M.; Parkerton, T.F.; Redman, A. D.; Paumen, M.L.; Comber, M.; Eadsforth, C.V.; den Haan, K. *Re-evaluation of Target Lipid Model-Derived HC5 Predictions for Hydrocarbons.* Environ. Toxicol. Chem. 2018, 37, 1579.

PRESENTATIONS AND PUBLICATIONS

Presentations

Redman, A., D. Letinski, A. Bekele, T. Parkerton. 2018. *Passive sampler-based approach to derive water quality criteria for organics in oil sands process water.* Canada's Oil Sands Innovation Alliance (COSIA) Innovation Summit Calgary, Alberta, June 7-8, 2018.

Publications

Redman A.D., Parkerton T.F., Butler J.D., Letinski D.J., Frank R.A., Hewitt L.M., Bartlett A.J., Gillis P.L., Marentette J.R., Parrott J.L., Hughes S.A., Guest R., Bekele A., Zhang K., Morandi G., Wiseman S., Giesy J.P. 2018. *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 Investigator: Dr. Aaron Redman

Name	Institution or Company	Degree or Job Title	Degree Start Date (Students Only)	Degree Completion Date (Students Only)
Daniel Letinski	ExxonMobil Biomedical Sciences, Inc.	Sr. Scientific Associate		

Analytical and Toxicological Evaluation of Bioavailable Naphthenic Acids from Oil Sands Process-Affected Water (OSPW) and Groundwater Using Biomimetic Extraction – Solid Phase Microextraction

COSIA Project Number: WJ0113

COSIA GAP/Opportunity Area: Water Return

Research Provider: University of Alberta

Industry Champion: Imperial Oil Resources Limited

Status: Completed

PROJECT SUMMARY

Large volumes of oil sands process-affected water (OSPW) have been generated during the bitumen extraction process from northern Alberta oil sands developments. OSPW is currently stored in tailing ponds and is not discharged into the environment. As a part of future reclamation plans, OSPW in tailing ponds will be treated and the ponds will eventually be developed into terrestrial and/or aquatic habitat upon mine closure. Naphthenic acids (NAs), as primary organic constituents of OSPW, have been shown to be toxic to aquatic organisms. Due to their complexity, NAs have been investigated using high resolution mass spectrometry to characterize and determine NAs from raw and treated OSPW and other natural water samples (Huang et al., 2018; Pereira et al., 2013). However, an analytical tool used to improve the understanding of the bioavailability of the organic constituents in OSPW is still needed.

Biomimetic extraction - solid phase micro-extraction (BE-SPME) method can be used as a surrogate measurement of the bioavailability of organics to aquatic organisms (Leslie et al., 2002). In a biomimetic extraction process, a small portion of the freely dissolved fraction of hydrophobic organic chemicals is extracted from water samples by a surrogate hydrophobic phase, typically the polydimethylsiloxane (PDMS) polymer (Letinski et al., 2014). Compared to exhaustive extractions, such as solid phase extraction (SPE), a biomimetic extraction is designed to not deplete the toxicant concentration in the sample. It is similar to the natural situation where uptake by biota does not affect environmental concentrations. Solid phase micro-extraction (SPME) fibres have been used as a suitable hydrophobic phase for biomimetic extractions of polycyclic aromatic hydrocarbons (PAHs) (Redman et al., 2014). The total molar concentration of the chemicals extracted by SPME can be analyzed by gas chromatography flame ionization detector (GC-FID) or gas chromatography mass spectrometry (GC-MS). An important advantage of BE-SPME is that only the bioavailable fraction of the toxicants that partition to the fibre is measured. In both fibres and biota, the accumulation potential of each compound in a sample also depends on its hydrophobicity (or log K_{ow}). Thus, hydrophobic compounds present in mixtures at low concentrations can make a relatively large contribution to total body residues (TBRs) in biota or to the fibre concentration. SPME provides a reasonable surrogate for bioconcentration in biota.

The objective of this project was to build the capacity of SPME experience in the region to support expanded water quality assessments and to characterize the composition of organics in OSPW that contribute to its toxicity. A BE-SPME method was applied to extract organic constituents from acidified raw and ozonated OSPW samples. SPME fibres were then analyzed using GC-FID for quantification, and atmospheric pressure gas chromatography time-of-flight mass spectrometry (APGC-TOF-MS) was used for compositional analysis. 2,3-demethylnaphthelene was used for developing external calibration curves for GC-FID quantification. Microtox assays were applied to assess the acute toxicity of raw and ozonated OSPW samples and to compare with the SPME analysis results. Raw and ozone-treated OSPW samples were sent to ExxonMobil Biomedical Sciences, Inc. (EMBSI), for independent BE-SPME analysis using GC-FID and to compare with our analysis.

PROGRESS AND ACHIEVEMENTS

In this research, a new set of SPME preparation methods coupled with GC-FID and APGC-TOF-MS analysis methods were developed to characterize and determine the potentially bioavailable nonpolar organic constituents from raw and treated OSPW samples.

The results indicated an impact of the sample pH on the SPME method. For the extraction of NAs from OSPW, the pH of a sample was adjusted to 2.0 to protonate NA ions to form NA molecules, while for the extraction of nonpolar compounds (such as hydrocarbons), pH adjustment of the sample was not necessary. Much less organics were extracted at natural pH condition and these organics could primarily be nonpolar compounds.

It was also observed that after ozonation with an applied ozone dosage of 80 mg/L, the peak of abundant organics was almost completely removed, achieving about 90% removal. It was also found that the GC-FID and Microtox results followed a similar trend with low toxicity observed at low concentrations on the SPME fibre. For individual samples, the correlation of GC-FID and Microtox results was also related to the composition of organic species in raw and treated samples.

In addition, the results from ExxonMobil Biomedical Sciences, Inc. (EMBSI) for the same sample sets were compared with the University of Alberta (U of A) results. While the difference in operational conditions made a direct comparison difficult, the BE-SPME analysis results from EMBSI and the U of A laboratory showed a similar trend. The results of manual SPME extraction at the U of A were 2-3 times the automated SPME extraction used at EMBSI.

The next phase of this research will continue under Dr. Mohamed Gamal El-Din's NSERC Senior Industrial Research Chair in Oil Sands Tailings Water Treatment, focusing on the application of automated SPME and optimization of the APGC-TOF-MS method.

LESSONS LEARNED

The lessons learned from this study are outlined below.

- This research lays the foundation for developing the capacity in the region to employ the SPME methodology for rapidly evaluating the bioavailability of organics in OSPW.
- The BE-SPME method presented in this study could serve as a rapid and convenient analytical screening tool for estimating the toxicity of raw and treated OSPW.

- The BE-SPME measurements can be used for water quality assessment of treated OSPW effluents by providing timely and cost-effective data on the predicted toxicity of the organic compounds.
- The BE-SPME method can be applied to treated OSPW to characterize relative contributions from hydrocarbons at ambient pH and from organic acids such as NAs under acidified conditions.
- APGC-TOF-MS can be used for simultaneous analysis of hydrocarbons and NAs in OSPW.
- To produce consistent results, some operational conditions are recommended, such as the use of 2,3-dimethylnaphthelene as standard for GC-FID quantification, and manual baseline integration for samples at low concentrations.

LITERATURE CITED

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PRESENTATIONS AND PUBLICATIONS

Presentations

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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 (Students Only)	Degree Completion Date (Students Only)
Rongfu Huang	University of Alberta	Research Associate		
Pamela Chelme-Ayala	University of Alberta	Research Associate		
Zhi Fang	University of Alberta	PhD Student	2014	2018
Shimiao Dong	University of Alberta	Research Assistant	2017	2018

Development of Microbial Fuel Cell Biosensor for Detection of Naphthenic Acids

COSIA Project Number: WJ0116

COSIA GAP/Opportunity Area: Water Return

Research Provider: University of Alberta

Industry Champion: Imperial Oil Resources Limited

Status: Year 2 of 3

PROJECT SUMMARY

Naphthenic acids (NAs) have been identified as one of the primary sources of acute toxicity and endocrine-disrupting potential of refinery wastewater and oil sands process-affected water (OSPW). Oil sands mining operations in northern Alberta produce large volumes of OSPW through hot water bitumen extraction processes. There is, therefore, a growing concern over NA intrusion into surrounding surface water and groundwater, and subsequent adverse impacts on aquatic ecosystems and the environment. Hence, monitoring of NAs in these wastewaters are crucial for oil sands, crude oil production and refining industries. Analytical tools commonly used for measurements of NAs include Fourier transform infrared (FTIR) spectroscopy, gas chromatography-mass spectrometry (GC-MS), and high-performance liquid chromatography (HPLC). However, analysis of NAs with these methods is time consuming and expensive, and samples need to be sent to an analytical laboratory. Development of a low-cost and fast analytical method for in situ quantification and/or in situ monitoring of NAs will help to address these challenges.

The objective of this research is to develop a self-powered microbial fuel cell (MFC)-based biosensor for in situ detection and quantification of NAs in OSPW samples. We envision that the development of a biosensor can provide a cost-effective way for in situ quantification and real-time monitoring of NAs, which will alleviate the need for off-site analysis of NAs. Furthermore, biosensors can be deployed in engineered remediation systems (e.g., constructed treatment wetlands, end pit lakes) for in situ monitoring of NAs.

Specific project objectives include:

- Understanding interactions among various NAs and environmental parameters.
- Examining the long-term performance of the biosensor with real OSPW samples.
- Development of a miniaturized MFC-based biosensor for field application.

PROGRESS AND ACHIEVEMENTS

To date, we have investigated dual-chamber biosensors with various NA model compounds, such as cyclohexanecarboxylic acid and cyclohexanebutyric acid. Biofilms enriched with different inoculum sources, such as municipal waste activated sludge, OSPW, and matured file tailings (MFT), showed reasonably comparable electrical responses to varying concentrations of these model NAs. Moreover, electrical signals from biosensors proportionally increased with the increase in the concentrations of model NAs (Figure 1c). However, we observed a significant difference in electrical signals with similar concentrations of various model NAs; thus, the electrical response appeared to be dependent upon the molecular structures of NAs.

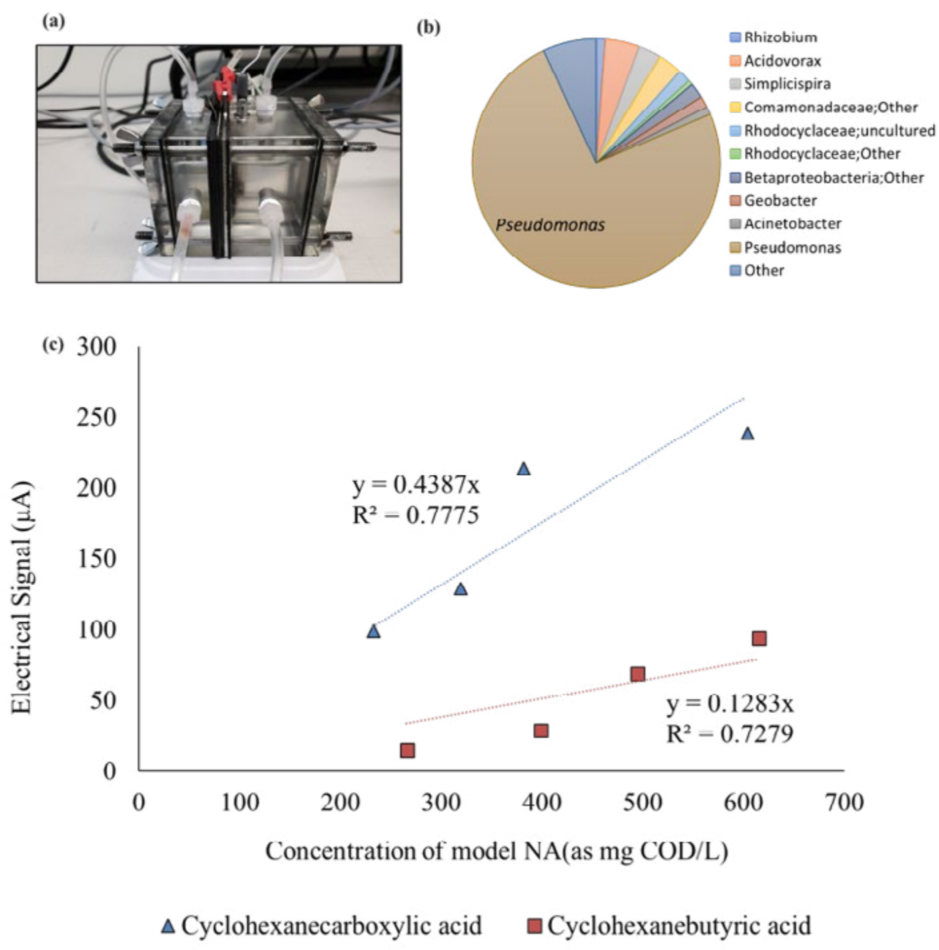

Figure 1: (a) photograph of a bench-scale dual-chamber biosensor; (b) microbial community structure in biosensor, (c) electrical signal from biosensors at different concentrations of two model NAs.

LESSONS LEARNED

The results from preliminary tests suggest that MFC-based sensors can be further developed for in situ quantification/monitoring of NA concentrations. The team will continue working on further development and optimization of biosensor design and testing towards practical implementation.

PRESENTATIONS AND PUBLICATIONS

Presentations

Barua, S., Zakaria, B. S., and Dhar, B. R. 2018. *Development of a self-powered biosensor for real-time monitoring of naphthenic acids*. Poster presented at Canada's Oil Sands Innovation Alliance (COSIA) Innovation Summit, June 7-8, Calgary, AB, Canada.

Barua, S., Zakaria, B. S., and Dhar, B.R. 2018. *Development of bioelectrochemical sensing device for naphthenic acids.* Poster presented at 53rd Central Canadian Symposium on Water Quality Research, February 22, Toronto, ON, Canada.

RESEARCH TEAM AND COLLABORATORS

Institution: University of Alberta

Principal Investigator: Dr. Bipro Dhar

Name	Institution or Company	Degree or Job Title	Degree Start Date (Students Only)	Degree Completion Date (Students Only)
Tae Chung	University of Alberta	MSc Student	2018	2020
Sajib Barua	University of Alberta	MSc Student	2017	2019
Basem Zakaria	University of Alberta	PhD Student	2017	2021

PIT LAKES

Lake Miwasin (Formerly PASS Demonstration Pit Lake)

COSIA Project Number: WJ0091

COSIA GAP/Opportunity Area: Pit Lakes

Industry Champion: Suncor Energy Inc.

Industry Collaborators: Canadian Natural Resources Limited, Syncrude Canada Ltd.

Status: Year 1 of 5

Lake Miwasin is a scaled down demonstration of Suncor's commercial scale pit lake at Dedicated Disposal Area 3 (DDA3, the future Upper Pit Lake (UPL)). Suncor uses the Permanent Aquatic Storage Structure (PASS) process, an inline tailings treatment process 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 lead to a self-sustaining boreal lake ecosystem. Specific objectives of the Research & Monitoring Plan are to: (1) test assumptions in the pit lake design and; (2) address critical gaps in the pit lake design. To meet the goal and objectives, research and monitoring activities are planned to take place over a 15-year period (2018-2033).

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 (~2019 to ~2021)
- Phase 4: Water return under natural flow (~2022)

PROGRESS AND ACHIEVEMENTS

The Lake Miwasin project has completed Phase 1 and Phase 2 operations by end of 2018. Construction and instrumentation of the pilot lake started in summer 2017 and treated FT were deposited in the lake in October 2017. Major work undertaken in 2018 included:

- placement of aquatic cover between August and early October;
- revegetation of the upland area (June) and the riparian and littoral zones (late August);
- baseline testing in March, August and October 2018 to characterize the treated tailings and water quality performance under the ice and during open water season (both prior to and immediately after aquatic cover placement); and
- groundwater (water level and chemistry) and soil monitoring.

Baseline testing in 2018 included sampling of treated FT, pore water, surface water, groundwater (level and chemistry), and sediment. Field collected samples were sent to commercial labs for tailings characterization, water chemistry and toxicity, and sediment quality and toxicity testing. Water samples were also provided to research labs at University of Alberta for UPLC-TOF-MS and BE-SPME analyses (Dr. Gamal El-Din), and for fish toxicity analysis (Dr. Belosevic). The SWAMP lab at University of Alberta also performed trace element analysis of tailings, water, and plant tissue samples collected at Lake Miwasin, following sampling and analytical protocol for trace and ultra-trace level heavy metals and metalloids.

An RFP for a 5-year Lake Miwasin research and monitoring program was issued for bid in November 2018. This program will be initiated in 2019.

LESSONS LEARNED

2018 represents the first year of this 15+ year pilot pit lake study. Preliminary observation and baseline testing results at Lake Miwasin indicated that:

- The final aquatic cover is composed of 57% process affected water and 43% fresh water, generally (and more conservatively) representing the anticipated DDA3/Upper Pit Lake water cap composition.
- Tailings and water quality conditions generally met performance expectations.
- No groundwater seepage has been observed.

PRESENTATIONS AND PUBLICATIONS

No public presentations or publications.

RESEARCH TEAM AND COLLABORATORS

Institution: Suncor Energy Inc.

Principal Investigator: Rodney Guest

Research Collaborators: Dr. Mohamed Gamal El-Din and Dr. Mike Belosevic, University of Alberta

Base Mine Lake Monitoring and Research Program

COSIA Project Number: WJ0121

COSIA GAP/Opportunity Area: Demonstration of Acceptable Configuration Including MFT as a Lake Substrate, Demonstration of Adaptive Management Techniques, Scale Up, Biological Establishment Rates and Water Quality Trajectory

Research Provider: Multiple Researchers and Institutions

Industry Champion: Syncrude Canada Ltd.

Industry Collaborators: Canadian Natural Resources Limited, Imperial Oil Resources Limited, Suncor Energy Inc., Teck Resources Limited

Status: Multi-year project, ongoing (summary includes information and data up to and including 2016).

PROJECT SUMMARY

Base Mine Lake (BML) is the first commercial-scale demonstration of end pit lake (EPL) technology in the oil sands industry. An oil sands EPL is an area where overburden and oil sands have 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 fine fluid tailings (FFT), treated fluid tailings (FT) or other solids (e.g., coarse tailings sand or overburden).

BML is located in the former West In-Pit (WIP) of the Syncrude Canada Ltd. Mildred Lake (Base Lease) operation. It consists of a mined-out oil sands pit filled with FFT (silt, clay, process-affected water and residual bitumen) that sits 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 FFT (or other tailings) will remain sequestered below the water cap.

Infrastructure has been installed to pump water in from Beaver Creek Reservoir (BCR) and pump water out to the tailings recycle water system (RCW) until a more substantial upstream surface watershed is reclaimed and connected to BML and outflow is established into the Athabasca River. This process dilutes the BML water cap over time.

Placement of FFT began in 1995, was completed in late 2012, and BML was commissioned as of December 31, 2012. No tailings solids were added or removed after this time. During 2013, fresh water and OSPW were added to the existing OSPW upper layer to attain a final water elevation of 308.7 m above sea level.

The objective of the BML Monitoring and Research Program (BML MRP) is to validate WCTT for an FFT-filled lake. The outcomes from the BML MRP will be useful for other pit lakes that may contain other tailings materials, including treated tailings. At the same time, the BML MRP establishes a baseline of biophysical data to assess the state of the lake at certification, including water quality and other lake processes. The BML Monitoring Program is designed to track trends in the lake both seasonally and annually and measure these trends against some key performance metrics. The BML 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 BML Monitoring Program. In other words, the BML Monitoring Program tracks the trends in the lake through time, and the BML Research Program investigates why those changes are occurring.

Syncrude recognizes three categories of monitoring described:

1. *Compliance Monitoring*. Compliance monitoring is data collection used to support compliance with regulatory approvals or other policy requirements (including certification assessments).
2. *Adaptive Management/Validation Monitoring*. This refers to data collection to support plan stewardship and adaptive management actions and is critical to support technology validation. It also tracks rates of progress towards certification criteria and permits early intervention when there are performance deviations.
3. *Continuous Improvement Research and Monitoring*. Continuous improvement research and monitoring involves a combination of monitoring, assessments and focused studies. This includes the learnings from results of compliance monitoring, plan stewardship and adaptive management monitoring.

These three categories are integrated, such that lessons learned from research would inform future monitoring programs as well as support validation and corrective/preventive measures processes. Trends and information obtained from the compliance monitoring program will guide priorities for the research program.

This integrated BML MRP supports the adaptive management of BML performance to ensure attainment of certification criteria. Adaptive management is a decision-making process that allows for adjustments as outcomes from management actions and other events are better understood. The BML MRP also provides knowledge and guidance valuable to the integration of other pit lakes in the region.

The specific objective of the BML Monitoring Program is to provide information that supports the validation of WCTT as a viable tailings management and reclamation option. In the early stages, the BML Monitoring Program will demonstrate that FFT is sequestered and that the water quality in the lake is improving. The BML 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 BML Monitoring Program is key component in the adaptive management of BML, and the BML Monitoring Program supports regulatory compliance. The physical, chemical and biological components of the BML Monitoring Program are summarized in Table 1.

Table 1. BML Monitoring Program components.

Physical	Chemical	Biological
FFT Assessment	Water Balance Assessment	Aquatic Biology Assessment
Shoreline Erosion Assessment	Surface Water Quality Assessment	
Physical Limnology Assessment	Groundwater Assessment	
Meteorological Monitoring		

The BML Research Program uses a multi-university, multi- and interdisciplinary 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 identifying and quantifying the processes and properties in BML that are responsible for the trends observed in the BML Monitoring Program. The various components comprising the BML MRP are closely linked.

The current focus of the BML Research Program is to support the demonstration of the 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 are focused on key parameters influencing early BML development.

The BML Research Program has two overarching themes. The first theme is validating WCTT. Several research programs are quantifying fluxes from the FFT to the water column, including chemical, geochemical, mineral, gas and heat. Physical, biological and chemical mechanisms driving these fluxes are also investigated.

The second (and related) theme relates to the oxygen dynamics in the lake. The focus of this theme is on understanding the oxygen balance and process of oxygen consumption (e.g., methanotrophy) and oxygen production (photosynthesis).

PROGRESS AND ACHIEVEMENTS

BML Monitoring Program

Key findings from the Base Mine Lake Monitoring Program since 2013 (Syncrude Canada Ltd., 2017) include the following:

Fine Fluid Tailings (FFT) Assessment Summary

- The top of FFT surface elevation is variable across the lake, generally lower where the FFT is thicker, and generally corresponds to the original pit topography.
- FFT is settling as expected, up to 5 m in maximum thickness of FFT.
- There is a sub-basin developing in the northeast area of the lake. Settlement in this area is faster than expected.
- The FFT-water interface is very sharp over 20 cm. The water at the interface is very turbid.
- The FFT mudline density is generally 10 wt. % - 20 wt. % nearest the mudline and 30 wt. % - 40 wt. % approximately 1 m below the mudline.
- Particle size in the first metre of the top of the FFT contains 13% - 23% <1µm.
- 2016 sampling indicates average bitumen concentration in the FFT is generally <2% within 1 m below the mudline.
- There is generally good agreement between the sonar-determined mudline and the visually-observed mudline from fixed-interval samples at 10 cm intervals.
- Sonar methods determine the top of the FFT surface with an accuracy of +/- 21 cm, and precision estimates indicate measurements are repeatable 95% of the time.

Wind Wave-Induced Shoreline Erosion Assessment Summary

- All BML shorelines are susceptible to wind wave-related erosion processes.
- Winds blow across BML from all directions, but are most frequent from the west-northwest and east-northeast.
- Exploratory modelling indicates common waves in BML have significant heights of 0.3 m.
- By September 2014, a maximum of approximately 1.2 m retrogression was observed at some locations.
- As expected, many shoreline segments (especially engineered structures) do not show evidence of erosion.

BML Physical Limnology Assessment Summary

Lake Thermal Dynamics

- In 2016, BML underwent many of the same physical processes that are generally observed in natural lakes, including: summer thermal stratification, spring and fall turnovers, reverse thermal stratification (warmer water below cooler) in the winter, wind-driven thermocline tilting and wind-driven mixing. These processes were also observed in 2013-15.
- In one sensor location in BML, the water column remained oxic (5-20% saturation) until ice-off. Other locations became anoxic before ice-off.
- In 2016, spring turnover was less complete than fall turnover. This is attributed to the stabilizing influence of a slightly fresh layer near the air-water interface as the ice melts.
- Similar to 2014 and 2015, BML exhibited summer and winter thermal stratification that is typical of temperate and northern lakes.

Lake Turbidity Dynamics

- Turbidity drops lake wide within days of ice-on. The rate of decline in turbidity after ice-on is faster than at any other time during the year.
- Despite the rapid initial drop following ice-on, the turbidity stopped declining around January 1, 2016. The 2016 winter minimum turbidity (70 NTU to 100 NTU, depending on depth and location) is greater than any previous summer minimum (5 NTU to 30 NTU) since commissioning of BML in 2013.
- In September 2016, alum was added to the lake to manage turbidity. New sensors were deployed to track changes in the lake in real-time.
- After 12 days of alum addition, turbidity values reduced from 15 NTU to 20 NTU to as low as 5 NTU.
- Turbidity remained low (~5-10 NTU) post-alum addition and during fall turnover up to ice-on in December. In previous years, turbidity increased steadily throughout the fall turnover period to reach as high as 300 NTU in 2015.

Water Balance Assessment Key Learnings

- Net balance in 2014 = -51 mm; 2015 = -203 mm; 2016 = -79 mm.
- Change in storage in BML since November 1, 2013 = -335 mm.

BML Surface Water Quality Monitoring Program Summary

- Approximately 170 individual variables are measured.
- Water quality in BML has been generally improving since lake commissioning.
- Concentrations of naphthenic acids (NAs) at BML deep and littoral stations were similar (median concentration ~30 mg/L). There were no discernible seasonal or depth variations in NA concentrations in 2016. Concentrations of NAs from 2016 are not directly comparable with historical data due to an improvement in the analytical method.
- Most surface water quality parameters from 2013 - 2016 are consistently passing long- and short-term Alberta Environment and Parks (AEP) guidelines for the protection of aquatic life (AESRD 2014).
- Turbidity in BML was generally lower in 2016 compared to previous years, even prior to alum addition.
- Total suspended solids (TSS) and turbidity data collected during the summer and fall of 2016 indicate low concentrations of particulates at deep and littoral stations (median concentrations <1 mg/L to 3 mg/L TSS and 10 NTU to 47 NTU turbidity). Concentrations in summer were higher than fall, and increased with lake depth. Concentrations of both variables were much lower in 2016 than previous years.
- Alum dosage reduced turbidity in the lake to <20 NTU at all sampled depths.
- Major ion concentrations are generally consistent with depth and season.
- Dissolved oxygen (DO) concentrations increased post-alum addition, and was consistent across all sampling depths.
- DO saturation stabilized throughout the water column post-alum addition at ~70 %, however, response of the lake to the alum addition is confounded by fall turnover.
- Concentrations of total polycyclic aromatic hydrocarbons (PAHs) include 27 parent and 28 alkylated PAH species; approximately 90% of the total PAHs in BML are contributed by alkylated species, while most of the parent PAH species were below method detection limits (<0.005 µg/L).
- Total PAHs were slightly higher in deep than littoral stations, and summer concentrations were slightly lower than fall at both deep and littoral stations in 2016.
- PAH concentrations remained stable with depth to 6 m, then consistently increased down to the water-FFT interface.
- With respect to PAHs, only pyrene exceeded AEP guidelines in 2016 (summer only), compared to five parent PAH species that have exceeded the respective AEP guidelines in at least one historical sample. Total PAHs were lower in 2016 than in previous years of monitoring.
- Median metal concentrations BML were generally lower in 2016 than previous years with the following exceptions: the median concentration of strontium was slightly higher at all stations during both seasons in 2016, and total mercury was higher at deep stations in the fall of 2016.
- Most metals are below AEP chronic water quality guidelines for the protection of aquatic life. Concentrations of metals that were above AEP chronic water quality guidelines for the protection of aquatic life in BML on at least one occasion in 2016 included dissolved aluminum, dissolved iron, total boron, total chromium, total cobalt, total copper, total lead, total mercury, total selenium, and total silver. Although these metals have occasional exceedances, their median concentration is reduced in 2016 compared to previous years.

BML Groundwater Assessment Key Learnings

- Groundwater levels continue to show variability with location around BML.
- Groundwater flows vary in direction depending on geologic units in which wells are screened.
- Groundwater wells indicate water quality typical of the geologic units in which the wells are screened:
  - Shallow to intermediate depth groundwater, located within fill soils (e.g., dam shell and core, dragline rejects, dump and Clearwater fills) is a sodium sulphate or sodium bicarbonate type water and generally exhibits higher magnesium, calcium and sulphate concentrations than deeper groundwater.
  - Deeper groundwater, located with the Basal Water Sands or Devonian Limestone, is a sodium chloride type water and generally exhibits higher total dissolved solids (TDS), sodium and chloride than shallower groundwater.
  - Deeper groundwater, within the Km Pond Mud, exhibits similar proportions of major ions to other deep groundwater, but at much higher sodium, calcium, magnesium and chloride concentrations.
- Oxygen isotopes indicate that shallow fill deposits around BML are affected by recharge from local rainfall, and deeper water in the Basal Water Sands is more isolated from surface and local recharge.
- There do not appear to be significant changes in the concentrations of key water quality parameters (i.e., pH, sodium, chloride, copper, iron, NAs) over time.
- These relatively stable concentrations suggest that there has not been a significant impact on groundwater quality from BML water.

BML Aquatic Biology Assessment Summary

Periphyton and Phytoplankton

- Mean periphyton taxonomic richness has increased every year since monitoring began (ranged from 3 taxa to 7 taxa in 2013, 5 taxa to 7 taxa in 2014, 9 taxa to 11 taxa in 2015, and 6 taxa to 19 taxa in 2016).
- Total taxonomic richness of phytoplankton communities in BML was lowest in 2013 and peaked between 2014 and 2015.
- Phytoplankton richness in 2016 was similar to previous years, but some stations had historically-low abundance and biomass.
- Taxonomic richness has ranged from 3 taxa to 35 taxa at the platform stations and from 3 taxa to 33 taxa at the littoral stations since monitoring began in 2013.
- In 2016, phytoplankton richness at the littoral stations (11 taxa to 17 taxa) was slightly higher than the platform stations (6 taxa to 9 taxa).

Zooplankton

- Total taxonomic richness of zooplankton in BML has been variable (ranged from 4 taxa to 7 taxa in 2013 and 2014, 4 taxa to 17 taxa in 2015, and 5 taxa to 7 taxa in 2016).
- Despite having the lowest total abundance and biomass, taxonomic richness was highest in 2015 compared to all other years.
- The majority of identified taxa were Rotifera, followed by Cyclopoida and Cladocera.

Benthic Invertebrates

- Benthic invertebrate communities at littoral and shoreline stations have been dominated by midge larvae (Chironomidae) since monitoring began in 2014. In 2016, midge larvae represented a minimum of 87% of the total abundance at all BML stations.
- Fall 2016 was the first time that EPT (Ephemeroptera, Plecoptera, and Trichoptera) taxa were documented at the littoral stations.
- Chironomidae accounted for a minimum of 75% of the total biomass measured at each of the littoral and shoreline stations. Odonata and Oligochaeta were also substantial biomass contributors, but only to a subset of the littoral and near-shore stations.
- Similar to abundance, the taxonomic richness of benthic invertebrate communities in BML has been highly variable over time, ranging from 3 taxa to 28 taxa per sample across all years at littoral stations, and 3 taxa to 18 taxa per sample at the shoreline.
- Median richness at littoral stations was highest in 2016 (15 taxa), followed by 2014 (8 taxa) and 2015 (3 taxa).
- Median richness at shoreline stations declined from 15 taxa (2014 and 2015) to 10 (2016).
- At both shoreline and littoral stations, the majority of identified taxa belonged to Diptera (Chironomidae).

Sediment Quality

- In 2016, concentrations of sediment quality variables were generally below the Alberta Sediment Quality Guidelines for the Protection of Aquatic Life (AESRD 2014).
- Concentrations of eight parent PAHs also exceeded the probable effects level.

Water Toxicity

Acute Toxicity

- In 2016, BML water had no effect on the survival of zooplankton (*Daphnia magna*) or the two test fish species, fathead minnow (Pimephales promelas) and rainbow trout (*Oncorhynchus mykiss*), with all LC50 values >100% v/v BML water.
- Acute toxicity (survival) effects were observed in the zooplankton test (*Ceriodaphnia dubia*) in at least one of the three testing periods for all three platform stations. *C. dubia* showed the greatest response to water samples collected in July, with LC50 results ranging from 77% to 89%.
- *Ceriodaphnia* is known to be intolerant of salinity and this is reflected in the acute toxicity response. Samples collected from all stations in August and September showed no LC50 effect on *C. dubia* survival (i.e., ≥100%).

- Overall, the zooplankton and fish tests have shown a reduction in the acute responses to BML water in the last two years of monitoring (i.e., 2015 and 2016), reflective of water quality improvements.

Chronic Toxicity

- The 72-hour growth inhibition tests for freshwater algae (*Pseudokirchneriella subcapitata*) showed high month-to-month variation in 2016. The results from this test in 2016 were generally consistent with historical results.
- The 7-day macrophyte (*Lemna minor*) growth tests showed no significant effects of BML water on dry weight, but frond number showed a strong negative response to BML water in all 2016 test periods.
- The *L. minor* growth tests on frond number have shown extremely high monthly and annual variability since testing began in 2014.
- 7-day growth tests on fathead minnow (*P. promelas*) did not identify any toxic effect related to BML water exposure in 2016 (i.e., all IC25 values were >100%), and this test has not shown any toxic response to BML water since July 2014.
- The *Vibrio fischeri* bioluminescence test showed minimal monthly variation in 2016. The IC20 results indicated significant toxicity at all three platform stations, with a median LC20 of 29%.
- Results of the bioluminescence testing have been highly variable since sampling began in 2013, with no clear temporal trends observed.
- The *C. dubia* reproduction tests completed in 2016 indicated a significant toxic effect from BML water with a median IC25 of 39%.
- The *C. dubia* reproduction tests showed high temporal and spatial variability; however, moderate to high toxicity has been recorded every year since 2013.

BML Research Program

The following is a summary of research programs underway on Base Mine Lake (Syncrude Canada Ltd., 2017).

Research Component	Primary Objective	University	Researchers / Principal Investigators (PIs)
Physical limnology of BML and the potential for meromixis.	To understand the circulation of BML and its potential for meromixis.	University of British Columbia	Greg Lawrence Ted Tedford Roger Pieters
Characterization of controls on mass loading to an oil sands end pit lake.	To define mass loading to BML by characterizing the mechanisms and distribution of heat and mass transfer from the tailings column to the overlying water column.	University of Saskatchewan	Lee Barbour Matt Lindsay
Laboratory studies investigating chemical flux across tailings-cap water zones, simulating an EPL in the Athabasca oil sands region.	To quantify physical and biogeochemical processes in a laboratory system simulating an EPL.	University of Alberta	Ania Ulrich Morris Flynn Tariq Siddique
Laboratory studies investigating light penetration in Syncrude's BML water.	To understand water column turbidity and mitigation in laboratory mesocosms.	University of Alberta	Ania Ulrich (PI)
Field investigation of BML water cap oxygen concentrations, consumption rates, and key Biological Oxygen Demand/ Chemical Oxygen Demand (BOD/ COD) constituents affecting oxic zone development.	To establish temporal and spatial variability in in situ BML water cap oxygen concentrations and oxygen consumption rates, and identify the biogeochemical processes linked to its consumption from the FFT-water interface to the BML water surface.	University of Toronto McMaster University	Lesley Warren Greg Slater
Microbial communities and methane oxidation processes in BML.	To study BOD in the lake, especially the contributions of methane oxidation and nitrification; examine a potential role of methanotrophs in the degradation of NAs; and examine the microbial community in BML, how the community changes over time with changes in lake chemistry, and the potential use of community analyses as an indicator of reclamation.	University of Calgary	Peter Dunfield
Understanding air-water exchanges and the long-term hydrological viability of BML.	To measure and improve understanding of the physical mechanisms controlling CH_4 and CO_2 fluxes across the air-water interface, determine the factors that control evaporation from BML, and understand the long-term water balance of BML	McMaster University Carleton University	Sean Carey Elyn Humphreys

LESSONS LEARNED

Key learnings from the BML MRP include the following:

- The FFT mudline is distinct.
- The FFT is settling as expected.
- The water column exhibits conventional boreal lake dimixis.
- Water quality is improving with time.
- Residual fines created a turbid water column, and alum dosage was successful in clearing the water.
- A wide variety of biological communities (algae, zooplankton, macroinvertebrates, macrophyte) are developing.
- Bitumen is present in the water and on the shoreline. Mitigation is underway.
- An adaptive management approach to pit lake reclamation is beneficial to steward EPLs toward target outcomes.

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Syncrude Canada Ltd. 2017. 2016 Summary Report: Base Mine Lake Monitoring and Research Program. Submitted to AER 31 March 2017. 96 pp.

PRESENTATIONS AND PUBLICATIONS

Presentations

Conference Presentations/Posters

Arriaga, D., Morris, P., Risacher, F., Goad, C., Slater, G.F., and Warren, L.A. 2017. *Physical and geochemical processes affecting water cap oxygen concentrations within Base Mine Lake, the first oil sands end pit lake*. Canadian Geophysical Union (CGU) Meetings, Vancouver, Canada.

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Goad, C., Slater, G.F, Arriaga, D., Risacher, F., Morris, P., Lindsay, M., and Warren, L.A. 2017. *Methane biogeochemical cycling over seasonal and annual scales in an oil sands tailings end pit lake*. Canadian Geophysical Union (CGU) Meetings, Vancouver, Canada.

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Jessen, G.L, Mori, J., Colenbrander Nelson, T., Krukenberg, V., Hatzenpichler, R., Slater, G.F., and Warren, L.A. 2018. *Elucidating the relationship of geochemistry and microbes in Canada's first oil sands pilot pit lake*. Resources for Future Generations, Vancouver Canada.

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Poon, H.Y., Brandon, J.T., and Ulrich, A. 2017. *A mechanistic study of CO_2-induced turbidity reduction in water capped tailings*. CGU and CSAFM Joint Annual Scientific Meeting, Vancouver, B.C. (Poster)

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Published Theses

Arriaga, D. 2018. *The interplay of physical and biogeochemical processes in determining water cap oxygen concentrations within Base Mine Lake, the first oil sands pit lake*. PhD., McMaster University.

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Dompierre, K. 2016. *Controls on mass and thermal loading to an oil sands end pit lake from underlying fluid fine tailings*. PhD., University of Saskatchewan.

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Aguilar, M., Richardson, E., Tan, B., Walker, G., Dunfield, P.F., Bass, D, Nesbø, C., Foght, J., and Dacks, J.B. 2016. *Next-generation sequencing assessment of eukaryotic diversity in oil sands tailings ponds sediments and surface water*. J. Eukaryotic Microbiology, 63:732-743.

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RESEARCH TEAM AND COLLABORATORS

Name	Institution or Company	Degree or Job Title	Degree Start Date (Students Only)	Degree Completion Date (Students Only)
Dr. Ania Ulrich	University of Alberta	Professor		
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Dr. Morris Flynn	University of Alberta	Professor		
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Chelsea Benally	University of Alberta	Post-Doctoral Fellow		
Stanley Poon	University of Alberta	PhD	2014	2019
Xiaoxuan (Lily) Yu	University of Alberta	PhD	2014	2019
Najmeh Samadi	University of Alberta	MSc	2013	2019
Lesley Warren	University of Toronto	Professor		
Greg Slater	McMaster University	Professor		
Jill Banfield	University of California			
Berkeley	Professor			
Tara Colenbrander Nelson	University of Toronto	Field Researcher		
Jennie Kirby	McMaster University	Laboratory Researcher		

Dr. Gerdhard Jessen	McMaster University / University of Toronto	Post-Doctoral Fellow	2017	2019
Dr. Jiro Mori	McMaster University / University of Toronto	Post-Doctoral Fellow	2017	2019
Dr. Lin-xing Chen	UC Berkeley	Post-Doctoral Fellow	2017	2019
David Bowman	McMaster University	PhD	2013	2017
Daniel Arriaga	McMaster University	PhD Candidate	2012	2018
Mohamed El-Waraky	McMaster University	PhD Candidate	2016	2020
Florent Risacher	McMaster University	MSc	2015	2017
Patrick Morris	McMaster University	MSc	2015	2017
Corey Goad	McMaster University	MSc	2015	2017
Robbyn Darling	McMaster University	MSc	2017	2019
Kevin Yang	McMaster University	Undergraduate Thesis Student	2016	2017
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Sarah Kumar	University of Toronto	Undergraduate Research Assistant	2019	2020
Anthony Bozzo	University of Toronto	Undergraduate Research Assistant	2019	2020
Katherine Norris	University of Toronto	Undergraduate Research Assistant	2019	2020
Karen Chu	University of Toronto	Undergraduate Research Assistant	2019	2020
Julia Reman	McMaster University	Undergraduate Research Assistant	2018	2018
Mike Dereviankin	McMaster University	MSc	2019	2021
Sean Carey	McMaster University	Professor		
Elyn Humphreys	Carleton University	Professor		
Dr. Mike Treberg	Carleton University	Research Associate		
Dr. Gordon Drewitt	Carleton University	Research Associate		
Dr. Graham Clark	Carleton University	Post-Doctoral Fellow		
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		
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Sarah Chang	University of British Columbia	MSc Candidate	2016	2019
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Yixiang Zhang	UBC	Undergrad		
Karin Huang	UBC	Undergrad		
Colleen Qiu	UBC	Undergrad		
Peter Dunfield	University of Calgary	PI		
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Felix Nwosu	University of Calgary	PhD	2015	2018 (expected)
Chunzi Wang	University of Calgary	BSc	2012	2016
Azriel Abraham López Jáuregui	University of Calgary	BSc	2013	2018 (expected)
Lisa Gieg	University of Calgary	Co-PI		
Joel Dacks	University of Alberta	Collaborator		
Fauziah Rochman	University of Calgary	PhD	2011	2016
Gul Zeb	University of Calgary	MSc	2015	2018 (expected)
Tobin Verbeke	University of Calgary	Post-Doctoral Fellow		
Dr. Matt Lindsay	University of Saskatchewan	Professor		
Dr. Lee Barbour	University of Saskatchewan	Professor Emeritus		
Kathryn Dompierre	University of Saskatchewan	PhD	2012	2016
Qingyang Liu	University of Saskatchewan	MSc (switched to PhD, 2016)	2014	2018 (Withdrew)
Sarah Rudderham	University of Saskatchewan	MSc	2016	2019
Daniel Francis	University of Saskatchewan	MSc	2017	2019
Spencer Chad (Spencer is supported by Dr. Barbour's IRC related funds, but his research now has a BML focus)	University of Saskatchewan	MSc	2016	2019

Mattea Cowell	University of Saskatchewan	Undergrad Summer Research Assistant	2015	2015
Carlo Cilia	University of Saskatchewan	Undergrad Summer Research Assistant	2015	2015
Jared Robertson	University of Saskatchewan	Post-Doctoral Fellow	2017	2018
Noel Galuschik	University of Saskatchewan	Research Technician	-	-
Brenda Bews	University of Saskatchewan	Research Engineer	-	-
Rebecca North	University of Saskatchewan	Research Assistant	-	-
Stephanie Villeneuve	University of Saskatchewan	Research Assistant	-	-
Julie Zettl	University of Saskatchewan	Research Engineer	-	-

REGIONAL WATER PROJECTS

Regional Water Management Initiative

COSIA Project Number: WE0005

COSIA GAP/Opportunity Area: Regional Water Management

Industry Champion: Suncor Energy Inc.

Industry Collaborators: Canadian Natural Resources Limited, Imperial Oil Resources Limited, Syncrude Canada Ltd., Teck Resources Limited, Total E&P Canada Inc., BP Canada, Conoco Phillips Canada, Devon Canada, Nexen Inc, Shell Canada, Statoil Canada

Status: Completed

PROJECT SUMMARY

The Regional Water Management Initiative project was carried out by Canada's Oil Sands Innovation Alliance (COSIA) Water Environmental Priority Area project team between 2012 and 2015. The project's objective was to explore opportunities to manage water in the Athabasca Oil Sands production region, seeking opportunities to minimize negative environmental net effects through the development of regional water reuse networks. The project was intended to extend the body of knowledge and the development of tools necessary to evaluate regional solutions, work that has been underway since 2009; initially through the Oil Sands Leadership Initiative (OSLI). Inside a sustainable water management framework for the oil sands, the regionalization of water systems represents one potential type of reuse application to be evaluated against a range of alternatives.

The project looked at three types of potential collaborative networks:

- Oil Sands Mine Oil Sands Process-Affected Water (OSPW) to In Situ Make-up
- In Situ Blowdown Regional Disposal
- Oil Sands Mine Depressurization Deep Well Disposal

Potential screening scenarios were developed based on in situ water demand and oil sands mine water supply volumes using data provided by operators. Scenario development assumed that there would be equal supply volumes from all five oil sands mines and that water treatment would be done at each oil sands mine site to prepare the water for delivery by pipeline to the recipients.

Elements considered in selecting the scenarios for analysis were:

- Broad participation categories
- Individual project timing
- Probabilistic adjustment of participation by category
- Project schedule slip volume adjustments
- In situ supply level of total dissolved solids (TDS)

For each of the three networks being studied, scenarios based on different assumptions were analyzed:

- A scenario in which two sets of facilities participated in the project
- A scenario where projects with a later start-up were de-emphasized and a risked scenario where they were not
- Scenarios with a most likely participation rate and a conservative participation rate
- Scenarios with two different OSPW water qualities

The combination of three potential regional networks with four scenarios for each resulted in twelve scenarios. The two conservative cases of the late project scenario were discarded, reducing the number of scenarios to ten. Of those ten, the six most probable scenarios (based on the elements considered above) were analyzed in detail. While the Regional Water Management Initiative (RWMI) project team felt these were representative scenario alternatives for the purposes of the current project scoping, the models developed for the analysis could be easily adjusted to examine other scenarios.

PROGRESS AND ACHIEVEMENTS

In agreement with past work, the RWMI project confirmed that regional solutions focused on the Athabasca oil sands production region as a whole are technically viable opportunities that can be engineered. However, participation drivers are complex and depend on many factors. While there are clear drivers for in situ operators to consider participating in regional networks, oil sands mining participation drivers are weak at best and potentially negative, due largely to a finite amount of excess legacy OSPW needing to be moved offsite. Consequently, the primary water supply for in situ operators would eventually be the Athabasca River once the excess OSPW was used up. This has implications for stakeholders in the region; especially local Indigenous communities.

Overall, the RWMI project successfully developed the concept and tools to provide operators with information necessary to evaluate regional options as part of their overall water management strategy. Due to the complex nature of each operator's site asset base and operational history, it would not be beneficial to further develop a conceptual regional solution based on assumptions.Individual operators with strong drivers will need to assess and develop sub-regional solutions and collaborations to advance the engineering and produce technical, economic, and environmental risk assessments for enabling project sanction decisions. While there are no definitive next steps for the RWMI project, COSIA's Joint Industry Project model can be used to launch ensuing sub-regional network projects.

LESSONS LEARNED

The lessons learned from this study are outlined below:

- Regionalization of oil sands water systems should be considered by operators as part of their overall water management strategies.
- The complex nature of all drivers for operators to participate in regional water management is considerable and requires very specific information that cannot be generalized.
- The tools and models developed in this project can be used by operators to assess regional water management systems as normal course of business

A detailed summary of the work and scenarios has been created and published on the COSIA website (COSIA 2018).

PRESENTATIONS AND PUBLICATIONS

Presentations

Regional Water Management Initiative. COSIA Water Conference 2014.

Regional Water Management Initiative. COSIA Innovation Summit 2015.

Regional Water Management Initiative Workshop. COSIA Water Conference 2016

Publications

COSIA 2018. *Regional Water Management Initiative Summary Report.* 17 pages. (https://cosia.ca/sites/default/files/attachments/COSIA%20-%20Water%20-%20Public%20RWMI%20Summary%20Report.pdf)

RESEARCH TEAM AND COLLABORATORS

Institution: Suncor Energy Inc.

Principal Investigators: David Van Den Assem, Rodney Guest

Athabasca River Watershed Project

COSIA Project Number: WE0006

COSIA GAP/Opportunity Area: Integrated Water Management

Research Provider: WaterSMART Solutions Ltd.

Industry Champion: Total E&P Canada Ltd.

Industry Collaborators: Canadian Natural Resources Limited, Imperial Oil Resources Limited, Suncor Energy Inc., Syncrude Canada Ltd., Teck Resources Limited

Status: Completed

PROJECT SUMMARY

The Athabasca River Watershed Project is a summary of the state of knowledge for surface water quantity in the Athabasca River watershed, with a focus on the Lower Athabasca Region (LAR). It is intended to serve as a knowledge reference tool for Canada's Oil Sands Innovation Alliance (COSIA) members and others. Study questions were developed by project working group members to capture frequently asked questions, assess current knowledge and identify knowledge gaps related to the oil sands industry's use of water (quantity) from the Athabasca River. The key questions were organized according to seven themes: Climate and Hydrology; Water Usage; Implications of Climate Change on Flows; Water Storage Options; Legislation, Policy and Regulation; Traditional Ecological Knowledge; and Basin Stewardship Groups. These themes were chosen because they reflect all existing knowledge areas relevant to surface water quantity management for existing and planned operations. Each theme features one or more questions, and each of the 27 questions is addressed by providing a response, sources of information and identified knowledge gaps. A summary of knowledge gaps is provided in the last chapter.

PROGRESS AND ACHIEVEMENTS

The project was completed in December 2013. A total of six knowledge gaps (listed in Lessons Learned) were identified although some of these have been addressed since the report was finalized in 2013.

LESSONS LEARNED

Build on the network of stream gauging stations: There is a fairly good network of streamflow gauging stations for basins in the LAR with a drainage area greater than 200 km^2, but the network for small natural basins and disturbed land types is relatively weak. For example, 6% of Regional Aquatic Monitoring Program (RAMP) stations have drainage areas less than 20 km^2. It is recommended that a good streamflow gauging network be developed for small basins and disturbed land types, particularly for cleared, muskeg drainage, mine pit, reclamation material storage, tailings and reclaimed areas.

Flow variations and trends in the Athabasca River flows: Based on the information available, adequate information exists. However, to properly assess natural variation in a system, much longer records (i.e., more than 100 years) are needed to account for longer climate cycles. Long-term variability in basin hydrology may be determined based on the tree ring analysis approach such as that used by Dr. David Sauchyn and his team at the University of Regina to estimate historical annual stream flows in Alberta.

Typical regional runoff variation for land types in the Lower Athabasca River: The several gauged natural basins in the watershed provide good flow records to determine the runoff coefficients for some land types. However, there appears to be a knowledge gap for small watersheds as most gauged basins have a drainage area greater than 200 km2. There is limited understanding of runoff coefficients for disturbed land types, particularly for cleared, muskeg drainage, mine pit, reclamation material storage, tailings and reclaimed areas. To address this knowledge gap, the streamflow gauging network could be improved for small basins and developed for disturbed land types.

Current annual and seasonal water consumption by sector (municipal, agriculture, industry, forestry, etc.) in the Athabasca River watershed sub-basins: Although ESRD (now AEP) collects reported water use data, data are not regularly collated and reported on a sub-watershed, industry-by-industry basis.

Fresh water consumption in the Lower Athabasca Region: Mining companies have been diligent at reporting water use numbers, but as of 2012 several small SAGD projects and companies either had not submitted their numbers or their numbers are yet to be posted on the oil sands information portal (ESRD, 2012). While not noted in the report, as of 2018 the average fresh water use intensity in the In Situ sector is about 0.2 bbl water / bbl bitumen, so the vast majority of fresh water use in the oil sands is attributable to mining operations.

Water Storage Options: Water storage can have both positive and negative effects on river flows. While many assessments of different water storage options on Athabasca River flows have been completed, there appears to be a gap in assessing a regional water storage system on the Athabasca River. Such a system would not only provide water for oil sands operators but could be used for hydro power generation, recreation, augmentation of flows during low flow periods to improve aquatic conditions, navigation improvement in the delta channels and flood mitigation.

PRESENTATIONS AND PUBLICATIONS

No public presentations or publications.

RESEARCH TEAM AND COLLABORATORS

Institution: Total E&P Canada Ltd.

Principal Investigator: Femi Ade

Research Collaborators: Alberta Environment and Sustainable Resource Development (now Alberta Environment and Parks), WaterSMART Solutions Ltd.

WATER TREATMENT

Organics Treatment of Oil Sands Process-Affected Water (OSPW)

COSIA Project Number: WE0014

COSIA GAP/Opportunity Area: Passive Treatment Technologies, Active Treatment Technologies

Research Provider: AECOM Canada Ltd.

Industry Champion: Syncrude Canada Ltd.

Industry Collaborators: COSIA Water Environmental Priority Area Members

Status: Completed

PROJECT SUMMARY

Oil sands process-affected water (OSPW) is generated from surface mining of bitumen. The purpose of this study was to evaluate treatment options that would make OSPW suitable for discharge to surface water (e.g., discharge to the Athabasca River). Removal of organics was identified as the primary treatment objective for evaluation in this study. Among the organic species, a particular focus on removal of acid extractable organics (AEOs), such as naphthenic acids (NAs), was based on results from earlier investigations of toxicity in OSPW (results that suggested NAs and other AEOs contribute to toxicity). The purpose of OSPW treatment in the context of this study is to produce treated water that is visually clean (without color), with suspended solids concentrations lower than those found in Athabasca River water, and no or very low levels of hydrocarbons (less than 100 mg/L chemical oxygen demand [COD] and less than 1 mg/L oil and grease). Based on regulatory criteria for discharge of other wastewater streams to the Athabasca River, it was assumed that the treated OSPW must pass a 96-hour trout toxicity test.

This study considered both novel and commercial (or near commercial) technologies. Technologies that operate on a variety of principles were examined, including biological degradation, advanced oxidation, sorption processes, membrane separation and passive treatment. Technologies were assessed according to their capabilities and expected performance. As well, the treatment technologies were compared relative to each other. The assessment also considered the impact of cold wastewater and ambient temperatures to understand the potential impacts of the winter climate in the Athabasca oil sands region. Previous bench and pilot-scale testing data using OSPW, collected for evaluation of these technologies, were used in the preparation of this report.

PROGRESS AND ACHIEVEMENTS

Although 53 options were reviewed as part of this study, seven technologies were chosen for further evaluation based on performance during bench and pilot studies and other operational considerations.

The selected technologies for further evaluation include:

- Membrane Bioreactor (MBR)
- Hydrogen Peroxide/Ozone (HiPOx)

- Granular Activated Carbon (GAC)
- Constructed Wetlands
- Petroleum Coke
- Electrochemical Oxidation (AXINE)
- Aerobic Granular Reactor

Comparison of the selected technologies focused on removal of organic acids such as NAs. The anticipated performance of each technology is summarized in Table 1. The data includes bench and pilot tests. When bench or pilot test data were unavailable, vendor data or external literature was included.

Table 1. Performance comparison of organics removal technologies.

Technology/Train	Water Tested	Test Type	Feed Concentrations[2]	Removals[1,2]
MBR	Tailings Pond 2/3	Pilot	COD_T – 356 mg/L AEOs – 36 mg/L Toxicity – 3.0 TUa, 16 TUc	COD_T – 43% AEOs – 54% Toxicity – <1 TUa, <1 TUc
Ozone/Peroxide AOP (HiPOx)	Tailings Pond 2/3	Pilot	COD_T – 344 mg/L AEOs – 30 mg/L Toxicity – 59 TUa	COD_T – 17% AEOs – 86% Toxicity – 1 TUa
GAC[3]	Pond C	Pilot	COD_T – 19 mg/L	COD_T – 66%
		Pilot	COD_T – 18 mg/L Toxicity – 1.4 TUa, 1.0 TUc	COD_T – 66% Toxicity – 1 TUa
	Tailings Pond 2/3	Bench	COD_T – 332 mg/L AEOs – 35 mg/L Toxicity – 53 TUa	COD_T – 81% AEOs – 91% 1 TUa
Constructed Wetlands	N/A	Outside Literature	COD_T – 470 mg/L AEOs – 54 mg/L	COD_T – 46% AEOs – 44%
Petroleum Coke	N/A Tailings	Outside Literature Outside Literature	AEOs – 50-80 mg/L	DOC – 13-90% AEOs – 70-90%
AXINE	Tailings	Vendor Estimation	COD_T – 962 mg/L	COD_T – 85%
	Phenol Contaminated	Vendor Data	COD_T – 1148 mg/L	COD_T – 82%
	Formic Acid Contaminated	Vendor Data	COD_T – 841 mg/L	COD_T – 90%
Aerobic Granular Reactor	Municipal Wastewater	Outside Literature	COD_T – 400 mg/L	COD_T – 90%
	Pretreated Landfill Leachate	Outside Literature	COD_T – 24400 mg/L	COD_T – 78%

Notes: 1 COD_T indicates total COD and CODS indicates soluble/dissolved COD.
2 AEO denotes acid extractable organics, including naphthenic acids.
3 For GAC_2 COD_T was calculated from TOC concentrations (TOC x 2.67)

LESSONS LEARNED

Key results include:

- MBR, HiPOx, GAC, fluidized petroleum coke, and constructed wetlands are recommended for further consideration. Subject to site-specific constraints, combinations of treatment technologies may provide the most economical options for efficient treatment of OSPW to meet discharge goals.
- Combining treatment technologies would allow for removal of COD and NAs, while potentially reducing overall equipment size and cost. For example, biotreatment could be used as a first step followed by GAC for polishing only.

PRESENTATIONS AND PUBLICATIONS

Publications

Leaver, J., and Woodhull, J. 2014. *Oil sands process-affected water (OSPW) – evaluation of treatment options*. Prepared for the Canadian Oil Sands Innovation Alliance (COSIA). Project No. 60319361.

RESEARCH TEAM AND COLLABORATORS

Institution: AECOM Canada Ltd.

Principal Investigators: Julianne Leaver, John Woodhull

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

COSIA Project Number: WE0025

COSIA GAP/Opportunity Area: Passive Treatment Technologies

Research Provider: University of Alberta

Industry Champion: Syncrude Canada Ltd.

Industry Collaborators: Canadian Natural Resources Limited, Imperial Oil Resources Limited, Suncor Energy Inc., Teck Resources Limited

Status: Year 2 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-affected water (OSPW), which is generated from the extraction process, is currently stored in tailings ponds that occupy more than 170 km^2. OSPW is a highly complex mixture of salts, ammonia organic compounds (e.g., residual bitumen, naphthenic acids [NAs], polyaromatic hydrocarbons [PAHs], and humic and fulvic acids), and trace metals. To effectively manage water during operations, support progressive reclamation, and allow for final closure, there is a need to discharge treated 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 OSPW quality is safe for release into the environment.

Project Scope and Objectives

From 2011 to 2016, the NSERC Senior Industrial Research Chair (IRC) Program in Oil Sands Tailings Water Treatment - First Term made several important advancements in the fundamental understanding of treatment/reclamation strategies for OSPW. However, there are still important research and knowledge gaps concerning the release of treated/reclaimed OSPW into the environment. In addition, more green and low-cost treatment alternatives are needed, along with cost analysis of the different strategies. As such, 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 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:

1) Understand the fundamentals of semi-passive and engineered passive treatment processes.
2) Conduct life-cycle assessments and cost analyses of different treatment approaches.
3) Assess the performance of selected treatment processes at the pilot-scale level.
4) Assess the performance of four large field pilots on active mine sites.
5) 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:

1) Train highly qualified personnel with the skills necessary to promote and protect environmental and public health.
2) Support current research programs focused on the treatment/reclamation of OSPW by facilitating the transfer of knowledge and new discoveries.
3) 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	Biological Treatments	Coupling of Solar-Driven Photocatalysts and Biofilm Degradation for Treating OSPW
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

Significance of the Research to Industry

There are concerns about the environmental and public health impacts resulting from possible future releases of OSPW into the environment. The NSERC IRC Program - Second Term aligns with ongoing efforts for the economic development of Alberta oil sands resources, and enhances the leadership and stewardship roles of scientists and Alberta government policy makers. Assessment of the various types of 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 has 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.

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. [redacted]

[redacted] 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 developed in this program 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. [redacted]

- 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

Presentations

Oral Presentations

Gamal El-Din, M., L. Zhang and Y. Zhang. 2018. *Degradation of naphthenic acids from oil sands process water by a semi-passive biofiltration process*. Presented at the 18th European Congress on Biotechnology (ECB), Geneva, Switzerland, July 1-4.

Gamal El-Din, M. 2018. *Water treatment and reclamation strategies for oil sands process water using passive approaches*. Presented at Canada's Oil Sands Innovation Alliance (COSIA) Innovation Summit 2018, Calgary, Alberta, June 7-8.

Gamal El-Din, M. 2018. *Water treatment and reclamation approaches in the Canadian oil sands*. Presented at the Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing. Invited Speaker. March 27.

Gamal El-Din, M. 2018. *Water treatment and reclamation approaches in the Canadian oil sands*. Presented at the State key Laboratory of Heavy Oil Processing, China University of Petroleum, Beijing. Invited Speaker. March 26.

Gamal El-Din, M. 2017. *Water treatment and reclamation approaches in the Canadian oil sands*. Presented at ICEPC 2017 - The International Conference on Environmental Pollution Control, Vancouver, British Columbia. Keynote Speaker. October 8-12.

Gamal El-Din, M. 2017. *Overview of treatment studies on OSPW*. Presented at Canada's Oil Sands Innovation Alliance (COSIA) OSPW Science Workshop, Calgary, Alberta, September 6-7.

Messele, S.A., and M. Gamal El-Din. 2018. *Catalytic ozonation of naphthenic acid model compound in the presence of carbon materials*. Presented at the First Annual Future Energy Systems (FES) Research Symposium, University of Alberta, March 14.

Messele, S.A., and M. Gamal El-Din. 2017. *Application of adsorption and catalytic oxidation process for water reclamation*. Presented at Tsinghua University-University of Alberta Joint Student Colloquia on Energy and Environment, University of Alberta, October 6.

Phillips, N., D. Lillico, R. Qin, R. Huang, J. Stafford, M. Belosevic, and M. Gamal El-Din. 2018. *Toxicity of oil sands process-affected water (OSPW) and its fractions using mammalian immune cells*. Presented at Canada's Oil Sands Innovation Alliance (COSIA) Innovation Summit, Calgary, Alberta, June 7-8. (Presentation related to NSERC IRC First Term).

Qin, R., S. Messele, and M. Gamal El-Din. 2018. *The effect of oil sands process water (OSPW) inorganic matrix on the photodegradation of naphthenic acids*. Presented at Canada's Oil Sands Innovation Alliance (COSIA) Innovation Summit 2018, Calgary, Alberta, June 7-8.

Xue, J., Y. Zhang, Y. Liu, and M. Gamal El-Din. 2018. *Membrane bioreactor with ozonation pretreatment: a competent candidate for recalcitrant industrial wastewater treatment*. Presented at Euromembrane 2018 Conference, Valencia, Spain, July 9-13. (Presentation related to NSERC IRC First Term).

Zhang, L., Y. Zhang, and M. Gamal El-Din. 2018. *Degradation of naphthenic acids from oil sands process water by a semi-passive biofiltration process*. Presented at Canada's Oil Sands Innovation Alliance (COSIA) Innovation Summit 2018, Calgary, Alberta, June 7-8.

Poster Presentations

Abdalrhman, A.S., and M. Gamal El-Din. 2018. *Degradation of naphthenic acids (nas) under low-current electro-oxidation on graphite*. Presented at the First Annual Future Energy Systems (FES) Research Symposium, University of Alberta, March 14.

Abdalrhman, A., and M. Gamal El-Din. 2018. *Treatment of oil sands process water by electro-oxidation on dimensionally stable anode (DSA)*. Presented at Canada's Oil Sands Innovation Alliance (COSIA) Innovation Summit 2018, Calgary, Alberta, June 7-8.

Benally, C., S.A. Messele, and M. Gamal El-Din. 2018. *Use of carbon xerogel for adsorption of organic materials in oil sands process water*. Presented at the First Annual Future Energy Systems (FES) Research Symposium, University of Alberta, March 14.

Huang, R., F. Zhi, P. Chelme-Ayala, and M. Gamal El-Din. 2018. *Characterization of bioavailable naphthenic acids from oil sands process water using biomimetic solid phase microextraction*. Presented at Canada's Oil Sands Innovation Alliance (COSIA) Innovation Summit, Calgary, Alberta, June 7-8.

Huang, R., Z. Fang, P. Chelme-Ayala, and M. Gamal El-Din. 2018. *Analytical and toxicological evaluation of bioavailable naphthenic acids from oil sands process water using biomimetic extraction - solid phase microextraction*. Presented at the First Annual Future Energy Systems (FES) Research Symposium, University of Alberta, March 14.

Li, M., Y. Boluk, and M. Gamal El-Din. 2018. *Cellulose nanofibers for selective ion removal from OSPW*. Presented at Canada's Oil Sands Innovation Alliance (COSIA) Innovation Summit, Calgary, Alberta, June 7-8.

Li, M., Y. Boluk, and M. Gamal El-Din. 2018. *Industrial applications of cellulose nanofibers for water reclamation*. Presented at the First Annual Future Energy Systems (FES) Research Symposium, University of Alberta, March 14.

Qin, R., and M. Gamal El-Din. 2018. *The effect of oil sands process water inorganic matrix on the photodegradation of naphthenic acids*. Presented at SPEA10, 10th European Meeting on Solar Chemistry and Photocatalysis: Environmental Applications, Almeria, Spain, June 4-8.

Qin, R., and M. Gamal El-Din. 2018. *The effect of oil sands process water inorganic matrix on the photodegradation of organic contaminants*. Presented at the Future Energy Systems (FES) Research Symposium, University of Alberta, March 14.

Zhang, L., Y.Y. Zhang, and M. Gamal El-Din. 2018. *Biofiltration as a semi-passive approach to treat process water*. Presented at the First Annual Future Energy Systems (FES) Research Symposium, University of Alberta, March 14.

Zhang, L., Y. Zhang, and M. Gamal El-Din. 2018. *Systematic analysis of the microbial community in a fixed-bed biofilm reactor for oil sands process water (OSPW) treatment*. Presented at the 18th European Congress on Biotechnology (ECB), Geneva, Switzerland, July 1-4.

Zhu, S., L. Xiang, M. Li, H. Zeng, and M. Gamal El-Din. 2018. *The rejection and the fouling behaviour of naphthenic acids in oil sands process water forward osmosis filtration*. Presented at Euromembrane 2018 Conference, Valencia, Spain, July 9-13. (Poster related to NSERC IRC First term).

Publications

Manuscripts in Preparation

Fang, Z., R. Huang, P. Chelme-Ayala, Q. Shi, C. Xu, and M. Gamal El-Din. *Comparison of uv/persulfate and uv/H_2O_2 for for removal of naphthenic acids and acute toxicity towards* Vibrio fischeri *from petroleum industrial process water*. To be submitted to Science of the Total Environment.

Huang, R., Z. Fang, S.A. Messele, P. Chelme-Ayala, A. Bekele, D.J. Letinski, A.D. Redman, and M. Gamal El-Din. *Simultaneous analysis of hydrocarbons and naphthenic acids from petroleum industrial process water using atmospheric pressure gas chromatography time-of-flight mass spectrometry*. To be submitted to Environmental Science & Technology Letters.

Huang, R., C. Wang, P. Chelme-Ayala, Z. Fang, Q. Shi, C. Xu, and M. Gamal El-Din. *Ferrate oxidation of individual naphthenic acids species isolated from process water of unconventional petroleum industry*. To be submitted to Science of Total Environment.

Manuscripts Under Review

Abdalrhman, A.S., S.O. Ganiyu, and M. Gamal El-Din. *Degradation kinetics and structure-reactivity relation of naphthenic acids during anodic oxidation on graphite electrodes*. Submitted to Chemical Engineering Journal on January 10, 2019 (Manuscript ID: CEJ-D-19-00450).

Abdalrhman, A.S., Y. Zhang, and M. Gamal El-Din. *Electro-oxidation by graphite anode for naphthenic acids degradation, biodegradability enhancement and toxicity reduction*. Submitted to Science of the Total Environment on September 20, 2018 (Manuscript ID: STOTEN-D-18-10356).

Li, C., L. Fu, D.M.E. Lillico, M. Belosevic, J.L. Stafford, and M. Gamal El-Din. *Exposure to environmentally relevant concentrations of oil sands process-affected water organic fraction does not significantly affect pregnancy and lactation in mice*. Submitted to Environmental Science & Technology on January 16, 2019 (Manuscript ID: es-2019-00332p; Manuscript related to NSERC IRC First Term.)

Li, M., Y. Boluk, and M. Gamal El-Din. *Isolated cellulose nanofibers for Cu (ii) and Zn (ii) removal: performance and mechanisms*. Submitted to carbohydrate Polymers on February 6, 2019 (Manuscript ID: CARBPOL-D-19-00545).

Messele, S.A., P. Chelme-Ayala, and M. Gamal El-Din. *Efficient catalytic ozonation of hydrocarbon contaminated water in the presence of carbon-based metal-free catalysts*. Submitted to Water Research on January 23, 2019 (Manuscript ID: WR48190).

Rashed, Y., S.A. Messele, H. Zeng, and M. Gamal El-Din. *Mesoporous carbon xerogel material for the adsorption of model naphthenic acids: structure effect and kinetics modeling*. Submitted to Journal Environmental Technology on September 17, 2018 (Manuscript ID: TENT-TENT-2018-1281).

Zhang, L., Y. Zhang, J. Patterson, Y. Zhang, and M. Gamal El-Din. *Transformation of indigenous microbial community leads to enhanced naphthenic acids biodegradation through benzoate degradation pathway*. Submitted to Water Research on January 31, 2019 (Manuscript ID: WR48190).

Zhang, L. Y. Zhang, and M. Gamal El-Din. *Integrated mild ozonation with biofiltration can effectively enhance the removal of naphthenic acids from hydrocarbon-contaminated water*. Submitted to Science of the Total Environment on February 7, 2019 (Manuscript ID: STOTEN-D-19-01853).

Published Papers

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.

Benally, C., M. Li, and M. Gamal El-Din. 2018. *The effect of carboxyl multi-walled carbon nanotubes content on the structure and performance of polysulfone membranes for oil sands process-affected water treatment*. Sep. Purif. Technol., 199, 170-181. (Manuscript related to NSER IRC First Term.)

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Huang, R., R. Qin, P. Chelme-Ayala, C. Wang, and M. Gamal El-Din. 2019. *Assessment of ozonation reactivity of aromatic and oxidized naphthenic acids species separated using a silver-ion solid phase extraction method*. Chemosphere, 219, 313-320.

Huang, R., Y. Chen, M.N.A. Meshref, P. Chelme-Ayala, S. Dong, M.D. Ibrahim, C. Wang, N. Klamerth, S.A. Hughes, J.V. Headley, K.M. Peru, C. Brown, A. Mahaffey, and M. Gamal El-Din. 2018. *Monitoring of classical, oxidized, and heteroatomic naphthenic acids species in oil sands process water and groundwater from the active oil sands operation area*. Sci. Total Environment, 645, 277-285. (Manuscript related to NSER IRC First Term).

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Hughes, S., R. Huang, A. Mahaffey, P. Chelme-Ayala, N. Klamerth, M. Meshref, M, Ibrahim, C. Brown, K. Peru, J. Headley, and M. Gamal El-Din. 2017. *Comparison of methods for determination of total oil sands-derived naphthenic acids in water samples*. Chemosphere, 187, 376-384. (Manuscript related to NSER IRC First Term.)

Islam, Md.S., K.N. McPhedran, S.A. Messele, Y. Liu and M. Gamal El-Din. 2018. *Isotherm and kinetic studies on adsorption of oil sands process-affected water organic compounds using granular activated carbon*. Chemosphere, 202, 716-725. (Manuscript related to NSER IRC First Term.)

Lyons, D., C. Morrison, D.A. Philibert, M. Gamal El-Din, K.B. Tierney. 2018. *Growth and recovery of zebrafish embryos after developmental exposure to raw and ozonated oil sands process-affected water*. Chemosphere, 206, 405-413. (Manuscript related to NSER IRC First Term.)

Lyons, D., D. Philibert, T. Zablocki, R. Qin, R. Huang, M. Gamal El-Din, and K. Tierney. 2018. *Assessment of raw and ozonated oil sands process-affected water exposure in developing zebrafish: associating morphological changes with gene expression*. Environ. Pollut., 241, 959-968. (Manuscript related to NSER IRC First Term.)

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RESEARCH TEAM AND COLLABORATORS

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Non-COSIA Collaborators:

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

Calcium Naphthenate

COSIA Project Number: WJ0042

COSIA GAP/Opportunity Area: Water Return: Active Treatment Technologies

Research Provider: Maxxam Analytics

Industry Champion: Teck Resources Limited

Industry Collaborators: Suncor Energy Inc.

Status: Completed

PROJECT SUMMARY

Naturally-occurring naphthenic acids in bitumen dissolve in process water to form naphthenates. High levels of naphthenates are found in oil sands process-affected water (OSPW). Naphthenates are useful as a process aid for bitumen extraction but they are acutely toxic to fish and other aquatic life forms. Naphthenates do naturally degrade over time and become much less toxic, but their removal from the water would be beneficial for meeting water release criteria.

Calcium naphthenates have been problematic in the oil industry for decades. Under certain conditions, naphthenic acids present in acidic crude oil will precipitate with Ca^{2+} ions that are present in the co-produced water and form calcium naphthenates. They are insoluble in both phases and are deposited at oil-water interfaces, causing serious problems for the oil industry. Project results showed that calcium naphthenates are produced together with calcium sulphate and calcium carbonate under different pHs. Calcium naphthenates also have an inverse solubility; that is, as temperature increases, solubility goes down, and they become insoluble at ~60°C. This has been seen in heat exchangers in the oil sands extraction plant where an insoluble layer of calcium naphthenate along with other hydrocarbons and mineral solids is deposited.

The objectives of this work are to:

- determine if calcium naphthenate can be precipitated out with available high calcium process water from the flue gas desulphurization, reducing the requirements for water treatment before potential release to the environment
- utilize process waters with high levels of calcium to add to OSPW to facilitate naphthenate removal
- look at the effects of temperature and process waters ratios
- determine residual levels of naphthenates and toxicity

PROGRESS AND ACHIEVEMENTS

Suncor provided the OSPW that was shipped to Maxxam Analytics (Maxxam) in Edmonton. Maxxam completed Phase I and II of the experiment but did not complete Phase III in light of results from Phases I and II.

Stock solutions of three synthetic waters with 40, 70 and 100 ppm calcium using calcium chloride were created. Two industry water sources with variable calcium concentrations were used with full chemical analysis conducted. The industry waters were mixed with the synthetic calcium waters at a ratio of 10%, 20% and 30%. These mixtures were mixed at 20°C, 40°C and 60°C for 20 minutes.

A total of 27 samples plus one OSPW duplicate were analysed using the Syncrude IR method scan to determine the naphthenate concentration after filtering through a 0.1 micron filter. Water chemistry was also determined with a focus on pH and calcium concentrations.

Phase I evaluated naphthenate reduction of the 27 samples via the calcium solutions at 20°C, 40°C and 60°C temperature changes.

Phase II evaluated naphthenate reduction with the addition of bentonite. Clays are known to absorb both calcium and naphthenates to their surfaces. Calcium bentonite was added at 0.5%.

LESSONS LEARNED

Phase I

At 20°C there was no decrease in calcium except for dilution. At 40°C, there was a slight decrease, whereas at 60°C a significant decrease in concentration was observed.

Naphthenate reduction appears to work better at 40°C (23% to 44%) than at 60°C (20% to 27%). This may be because there is increased competition with calcite precipitation at high temperatures. This technique requires a 100% reduction to be effective.

Phase II

With the addition of the calcium bentonite, only 20% to 30% of the naphthenates were removed, similar to Phase I results. The sludge and gel created with the calcium bentonite additive would require disposal.

PRESENTATIONS AND PUBLICATIONS

No public presentations or publications.

RESEARCH TEAM AND COLLABORATORS

Institution: Teck Resources Limited

Principal Investigator: Brad Komishke

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Research Collaborators: Maxxam Analytics

Calcite Treatment

COSIA Project Number: WJ0042

COSIA GAP/Opportunity Area: Water Return: Active Treatment Technologies

Research Provider: Teck Coal ART

Industry Champion: Teck Resources Limited

Status: Completed

PROJECT SUMMARY

Bench and Desktop Work

Two studies were undertaken to determine the precipitation of calcite by passive and semi-passive treatment methods. These studies provide treatment options for inorganic species removal in Oil Sands Process Waters if required.

Study 1: Emerging Selenium and Calcite Treatment Technologies Evaluation – Phase I

This study involved scouting assessments for three technologies. The first project examined the use of Magnetic Graphene Oxide (MGO) to remove selenium from water streams. The second project evaluated the use of sodium tripolyphosphate (STPP) to remove gypsum, calcite and selenium. STPP can be used to create nucleation sites to promote the removal of total dissolved solids (TDS) from solutions and to evaluate the potential of these technologies as an option for water treatment for Coal Operations. The third project was a literature review for bio-reduction of selenium, which identified multiple strains that could be tested in biological reactors.

Study 2: Calcite Treatment of Mine-impacted Water from Coal Operations

This study examined passive and semi-passive treatments to avoid or control calcite deposition. These tests provided proof of concept and baseline tests to decrease the alkalinity of the water. The program continued with experiments at the mini-pilot scale. The conceptual treatment model involved acidification of the stream followed by mechanical aeration and off-gassing.

Mini Pilot/Offsite Work

Three pilot studies were conducted to assess calcite treatment strategies.

Study 1: Continuous Bench Project: Testing Kroff Antiscalant on Mine-impacted Water

This project was done to assess the efficacy of antiscalants in preventing and dissolving calcite precipitation on river water, and to determine the required reagent concentrations. The location was selected because previous work had been done in the same stream using acid addition to inhibit calcite deposition; using the same site would allow for an accurate comparison of the different technologies.

Study 2: Calcite Pilot Plant: Treatment of Creek 1 at Site 1 Operations

A pilot plant was built at Site 1 Operations to test the effect of acid addition and cascading on calcite precipitation. The plant was also used to demonstrate the saturation index potential (SI_{pot}) method and its ability to predict calcite deposition.

Study 3: Calcite Pilot Plant: Calcite Precipitation Prevention using Antiscalants

Objectives of study 3 were to test for the prevention and removal of calcite precipitation using antiscalants, evaluate changes in phosphorus and cadmium concentration as a result of antiscalant addition and/or calcite precipitation, and confirm that no acute toxicity occurred.

PROGRESS AND ACHIEVEMENTS

Bench and Desktop Work

Study 1: Emerging Selenium and Calcite Treatment Technologies Evaluation – Phase I

Results yielded concentration below 20 µg/L but did remove about 50% of the selenium in solution at pH below 2. The results with synthetic process water from zinc mine operations were not encouraging as the calcium concentration in solution did not decrease. This review was the background for changing the scope of the project to include the study of fluidized bed reactors at bench scale.

Study 2: Calcite Treatment of Mine-impacted Water from Coal Operations

The values of Langmuir Saturation Index (LSI) from the solution were reduced significantly, to below zero, which indicates that the water chemistry has been modified enough to avoid calcite precipitation. Further analysis is needed to find the final LSI after pH equilibration. Hydrochloric acid gave the best results in terms of alkalinity and LSI reduction versus dosage. Aeration increased carbon dioxide off-gassing of the treated streams, but did not affect alkalinity or LSI.

Mini Pilot/Offsite Work

Study 1: Continuous Bench Project: Testing Kroff Antiscalant on Mine-impacted Water

This project increased understanding of antiscalants and their ability to treat mine-affected water for calcite deposition by testing the vendor's dosage for the prevention and dissolution of calcite. Alkalinity measurements showed possible precipitation in the control stream followed by dissolution in the dissolve stream, and deposition rate was lower in the dissolve stream than in the control stream. A residue containing magnesium, sulphur and calcium formed in the prevent stream on the deposition tiles. pH measurements showed an increase at stream start compared to stream end. There was an average increase in phosphorus concentration in treated water of 0.072 mg for every milligram of antiscalant added. CO_2 measurements are being collected along the individual streams to determine whether cascades or streams are more proficient in off-gassing.

Study 2: Calcite Pilot Plant: Treatment of Creek 1 at Site 1 Operations

Calcite deposition prevention using acid addition and cascading were studied. The control stream behaved similarly to Creek 1 with respect to pH profile and calcite deposition. The SI_{pot} calculations corresponded well with observations, with calcite forming in the control stream, and very little forming in the treated streams as predicted by the calculations. Correlations between SI_{pot} and acid addition for hydrochloric and citric acid were developed.

Study 3: Calcite Pilot Plant: Calcite Precipitation Prevention using Antiscalants

Tests showed little evidence of calcite dissolution. Visual inspection of the stream showed flakes shed from the walls of the pilot streams during the removal tests.

LESSONS LEARNED

Bench and Desktop Work

Study 1: Emerging Selenium and Calcite Treatment Technologies Evaluation – Phase I

This work pointed out the need to continue the study of STPP through a Natural Sciences and Engineering Research Council project to understand the mechanism for TDS removal. Other lessons learned included the need to evaluate MGO for use in brine treatment and for phosphate treatment. More work is also needed to better understand the mechanisms of iron chloride precipitation in the residue stream for selenium removal.

Study 2: Calcite Treatment of Mine-impacted Water from Coal Operations

This study underscored the need for an onsite test program to, among other things, improve understanding of the fluidized bed reactor performance and optimization. As well, economic analysis is needed to evaluate the use of different acids and the optimal pH target. Finally, determining SI_{pot} for the samples and targets for alkalinity could affect the treatment operational variables.

Mini Pilot/Offsite Work

Study 1: Continuous Bench Project: Testing Kroff Antiscalant on Mine-impacted Water

Results of this work highlighted the need to recreate the project on a pilot scale with focus on:

- determining the efficacy of antiscalants as a treatment option for calcite on a larger scale (pilot)
- measuring the conductivity profile of each of the streams to determine if the parameter can be used as an indicator in future testing

Study 2: Calcite Pilot Plant: Treatment of Creek 1 at Site 1 Operations

Sampling and measurement methods were refined over the course of the project.

Study 3: Calcite Pilot Plant: Calcite Precipitation Prevention using Antiscalants

The ranking of antiscalants for further use to control calcite deposition was developed. In-stream testing for one year could document the seasonality of calcite precipitation to optimize treatment.

LITERATURE CITED

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Teck Resources Ltd. 2013. *Calcite Pilot Plant: Treatment of Creek 1 at Site 1*

PRESENTATIONS AND PUBLICATIONS

No public presentations or publications.

RESEARCH TEAM AND COLLABORATORS

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Technology Scanning Evaluation

COSIA Project Number: WJ0042

COSIA GAP/Opportunity Area: Water Return: Active Treatment Technologies

Research Provider: Teck Resources Limited Advanced Research Technologies

Industry Champion: Teck Resources Limited

Status: Completed

PROJECT SUMMARY

Completed bench and desktop work includes eight studies, which are summarized below. These studies provide treatment options for inorganic species removal in Oil Sands Process Waters if required.

Study 1: Bench Scale Evaluation of Paques' SULFATEQTM Process for Selenium Treatment

Pond 1 water from Site 1 was sent to The Netherlands in September 2013 to evaluate a bench-scale set up of Paques' SULFATEQTM process for selenate, sulphate, nitrate and cadmium treatment.

Study 2: High Density Sludge Treatment of Electrodialysis Reversal-Reverse Osmosis Brines

A high density sludge (HDS) process was examined as an alternative option for treating brines coming from an electrodialysis reversal-reverse osmosis process (EDR-RO). The purpose was to obtain data for preliminary equipment sizing and to evaluate the feasibility of operating an HDS process on the EDR-RO brines.

Study 3: Review of Historical Performance of Packed Bed Reactor Plants

This study documented and summarized performance information from four existing full-scale packed bed reactor systems to address Teck Coal selenium and nitrate water treatment requirements.

Study 4: Bench Scale Evaluation of InnoTech Alberta's Electro-Biochemical Reactor Process for Selenium Treatment

Bench scale tests were performed to evaluate InnoTech Alberta's Electro-Biochemical Reactor (EBR) process for selenium treatment on mine-impacted water.

Study 5: Integration of Nested EDR–RO Stages to Treat HDS Brine Produced from Primary EDR-RO Treatment of Mine-impacted Water

The EDR-RO process was piloted at Site 1. This study focused on treating gypsum-saturated brine produced after treating the primary brine from the EDR-RO process using an HDS process.

Study 6: Constituents of Interest Release Modelling from Past and Present Coal Operations

An empirical water quality model was developed using data from specific coal mine waste rock dumps to predict monthly selenium, sulphate and nitrate generation rates and stream loadings, which were compared to the current modelling system.

Study 7: Open Innovation Challenge: Water Treatment

NineSigma, which specializes in conducting open innovation challenges and technology landscaping studies, was contracted to help identify potential technologies to treat constituents of interest. The technical team shortlisted thirteen proposals and six were selected for further evaluation.

Study 8: Scoping Assessment of Active Water Treatment Technology Options

Seven active water treatment facility flowsheet options were identified as alternatives to the incumbent biological flowsheet. The assessment indicated that a non-biological process would achieve lower effluent selenium than the existing biological flowsheet and would also remove sulphate.

PROGRESS AND ACHIEVEMENTS

Study 1: Bench Scale Evaluation of Paques' SULFATEQTM Process for Selenium Treatment

A three-month bench scale evaluation of process revealed that selenate, nitrate and sulphate were reduced in the hydrogen-fed, continuously-mixed bioreactor. The process consistently and reliably reduced nitrate, but selenate reduction was not as robust. Total selenium concentrations fluctuated in the effluents of both the anaerobic reactor and the partial oxidation reactor.

Study 2: High Density Sludge Treatment of EDR-RO Brines

Low sulphate tenors could be achieved, typically less than 600 mg/L as sulphur. Metal impurity removal was good. Cadmium was generally removed to levels below 0.1 µg/L, which is the detection limit of the assay. The solid-liquid separation properties of the residue were excellent (achieving high 380 g/L solids) levels on average.

Study 3: Review of Historical Performance of Packed Bed Reactor Plants

The packed bed reactor systems were shown to tolerate fluctuations in the feed following acclimation, and could be operated to withstand shutdowns of extended periods. The packed bed reactor process consistently removed selenium to levels less than 10 µg/L.

Study 4: Bench Scale Evaluation of InnoTech's EBR Process for Selenium Treatment

The EBR process consistently and reliably reduced selenate to less than 2 µg/L and completely removed nitrate with a 12-hour hydraulic retention time.

Study 5: Integration of Nested EDR–RO Stages to Treat HDS Brine Produced from Primary EDR-RO Treatment of Mine-impacted Water

A mass balance concluded that a fully integrated EDR-RO system can achieve an overall water recovery rate of 98.5% while producing a clean permeate that could meet the discharge target guidelines.

Study 6: Constituents of Interest Release Modelling from Past and Present Coal Operations

Some waste rock dumps were found to be more reactive than others, with selenium and sulphate generation accelerating at most of the monitoring stations studied. Nitrate generation increased due to washing from dumps where waste rock is being placed.

Study 7: Open Innovation Challenge: Water Treatment

Two of the six technologies were based on adsorptive methods (AbTech and Nalco). A key feature of these technologies is the potential to decrease the mass of residuals. Three of the technologies were biologically-based.

Study 8: Scoping Assessment of Active Water Treatment Technology Options

Three new non-biological options were introduced based on EDR-RO technology. Two flowsheets were identified that would achieve the selenium target of less than 2 µg/L.

LESSONS LEARNED

Study 1: Bench Scale Evaluation of Paques' SULFATEQTM Process for Selenium Treatment

Paques efficiently demonstrated removal of nitrate (to less than 10 mg/L) and of selenium to less than 50 µg/L in a one-reactor configuration. It may be possible to achieve these levels from brines containing up to 1100 mg/L nitrate and 2 mg/L of selenium.

Study 2: High Density Sludge Treatment of EDR-RO Brines

There was some evidence that selenium was adsorbing on the residue in the underflow, but it appeared to be removed during washing infiltration. The EDR-RO-HDS biological option should be gated so it can be compared to other treatment options; such comparisons should be fast-tracked to determine technology for this option and evaluate it for operations.

Study 3: Review of Historical Performance of Packed Bed Reactor Plants

The Packed Bed Reactor process can mitigate fluctuations in influent such as temperature, flow rate, and water chemistry, Therefore, having equalization capacity in the feed to bioreactors, such as a chemical precipitation pre-treatment system and/or a settling/feed equalization pond, is recommended.

Study 4: Bench Scale Evaluation of InnoTech's EBR Process for Selenium Treatment

A six-hour hydraulic retention time (HRT) did not affect selenium removal but negatively impacted nitrate removal. The mechanism of the EBR technology is not well understood, but the process has been successfully piloted at other sites.

Study 5: Integration of Nested EDR-RO Stages to Treat HDS Brine Produced from Primary EDR-RO Treatment of Mine-impacted Water

This study showed the need to identify economically viable, environmentally practicable options to treat the residual brine after HDS and nested EDR-RO processes. Stable products from the brine are necessary since disposal of residues containing water-soluble nitrate and selenium salts is not feasible.

Study 6: Constituents of Interest Release Modelling from Past and Present Coal Operations

The rate controlling factors that determine waste rock dump behaviour need to be identified and used to manage and control selenium release.

Study 7: Open Innovation Challenge: Water Treatment

The six technologies featured in this study should be evaluated at laboratory scale to minimize costs while still obtaining the required engineering data.

Study 8: Scoping Assessment of Active Water Treatment Technology Options

Given the preference for the biological flowsheet, bolt-on technologies to remove sulphate need to be further evaluated.

LITERATURE CITED

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Teck Resources Limited 2014. *Bench Scale Evaluation of InnoTech's EBR Process for Se Treatment.*

Teck Resources Limited 2014. *Se Technology Scanning Evaluation, 2014.*

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Teck Resources Limited 2014. *Teck's Open Innovation Challenge: Water Treatment for the Elk Valley.*

PRESENTATIONS AND PUBLICATIONS

No public presentations or publications.

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Chendi Wu	Teck Resources Limited	Process Engineer		
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Farid Vaezi	Teck Resources Limited	Process Engineer		
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Selenium Treatment

COSIA Project Number: WJ0042

COSIA GAP/Opportunity Area: Water Return: Active Treatment Technologies

Research Provider: Teck Resources Limited Advanced Research Technologies

Industry Champion: Teck Resources Limited

Status: Completed

PROJECT SUMMARY

Bench and Desktop Work

Study 1: Site 1 Selenium Water Treatment Review

Findings from previous Site 1-based selenium removal investigations and current studies were incorporated into the review. Selenium removal at Site 1 Operations is complicated by the high treatment volumes, short discharge season, high concentrations of total dissolved solids (TDS) in the tailings impoundment water, and low water temperature.

Study 2: Preventing Selenium Release from Coal Wastes

Selenium is a naturally occurring element that is an essential nutrient, but outside a narrow concentration range, it becomes harmful to the environment. The study reviewed ways to prevent the release of selenium from waste rock.

Study 3: Accelerated Selenium Program 2013 to Mid-2014 Review

This study investigated alternative active water treatment options to the incumbent Fluidized Bed Reactor (FBR) technology and associated bolt-on options considered for selenium removal and for other constituents of interest.

Study 4: In Situ Treatment to Prevent Release of Selenium, Nitrate, and Sulphate

This study examined a selenium management strategy that integrates three processes to prevent release of selenium, nitrate, and sulphate.

Study 5: Performance Summary Report – 2013 Pilot Plant Studies at Site 2 Operations

A scoping study was completed in early 2013 for an active water treatment facility (AWTF) at Site 2. The objectives were to evaluate a) the FBR treatment system focused on selenium and phosphorus removal, and b) a membrane step focused on sulphate removal for an AWTF at this site.

Study 6: 2015 Site 2 Operations Pilot Program Status and Recovery Plan

Three options were shortlisted for the study, all of which include post treatment consisting of a moving bed biofilm reactor (MBBR) to remove residual biological oxygen demand/chemical oxygen demand (BOD/COD), sulphide, and ammonia from the upstream biological reactors, and a Continuous Backwash Sand Filter (CBSF) to remove phosphorus associated with operation of the MBBR.

Study 7: Pre-Scoping Assessment of Active Water Treatment Options for Site 3 Operations

Thirteen options for an AWTF at Site 3 Operations were identified.

Study 8: Stability of Advanced Oxidation Process (AOP) treated Site 4 Effluent

A three-day test program was conducted at Lab 1 to investigate sample speciation stability.

Mini Pilot/ Offsite Work

Study 1: Ion Exchange (IX) Technology Development for Teck Coal Active Water Treatment

This study evaluated IX technology to reduce selenium concentration from 500 µg/L to below 5 µg/L in the treated water, and reduce nitrate from mine-impacted water. The study sought to confirm generation of a low-volume/high-concentration stable selenium residue; validate the mass and energy balances; validate plant design assumptions for estimating capital and operating costs; determine technology limitations with regard to other constituents of interest; and confirm that the treated water conforms to discharge regulations, especially aquatic toxicity requirements.

Study 2: Microbiology Program 2017

The current flowsheet in operation in Site 3 includes bioreactors for nitrate and selenium reduction, and for phosphorus and COD removal. Understanding the microbial population inside the bioreactors will provide insight on process control and optimization as well as reduce overall environmental risk from the operations. Some of the program's general objectives are to determine whether the structure of bacterial communities in the bioreactors changes over time, develop protocols for assessing bioreactor health and guide future management decisions, determine impact of microbiology on selenium remobilization, and determine speciation of unaccounted-for selenium species.

Onsite Pilots

Study 1: EDR-RO Pilot Program for AWTF

The electrodialysis-reversal-reverse osmosis (EDR-RO) process was piloted to determine the capability and feasibility of the EDR-RO technology and generate enough brine solution to evaluate bench scale evaporation crystallization to generate disposable salt crystals.

Study 2: Evaluation of Treatment Technology for Selenium Removal at Site 2 Operations

The program evaluated the Packed Bed Reactor process for selenium and nitrate removal.

Study 3: Review of 2013 Active Water Treatment Pilot Program at Site 2 Operations

Five pilot systems were tested at Site 2 from September 2013 through February 2014:

- Pilot FBR – two-stage FBR, ballasted sand clarifier, and MBBR
- Pilot Nano-Filtration (NF) – microfiltration (MF) and NF (as a stand-alone process and as tertiary treatment to the FBR system)
- Pilot RO – softener reactor clarifier (SRC), MF, and RO
- FBR bench – two-stage FBR (to treat RO membrane brine)
- Pilot EDR plus RO – EDR-RO by two vendors and low temperature crystallizer by one vendor

Study 4: Site 2 Operations Active Water Treatment Pilot Program 2015-2016

A pilot program was carried out to overcome technical uncertainties and determine the technical feasibility of complete-train flowsheets to meet end-of-pipe guidance values. Three technology options with six configurations using combinations were tested. A number of studies were executed in parallel with the pilot plant operation to understand microbiology, selenium reduction kinetics, selenium reoxidation, and selenium speciation, and to obtain geochemical and geotechnical properties of the residuals.

PROGRESS AND ACHIEVEMENTS

Bench and Desktop Work

Study 1: Site 1 Selenium Water Treatment Review

Methods that successfully decrease selenium loading include microbial treatment of in situ mine developed waterbodies, exploitation of the annual freeze-thaw cycle, adding biosolids to the tailings impoundment water, and natural processes in the tailings impoundment.

Study 2: Preventing Selenium Release from Coal Wastes

The addition of organic carbon as a cover reduces overall selenium release by nearly 40% in water rock piles. Six distinct pools of selenium were identified in the evaluated sample.

Study 3: Accelerated Selenium Program 2013 to Mid-2014 Review

Several technologies, such as membranes, bioreactors, packed bed reactor and ion exchange, were identified as options that could significantly decrease water treatment costs.

Study 4: In Situ Treatment to Prevent Release of Selenium, Nitrate, and Sulphate

An 85% reduction in selenium released was observed in waste rock irrigated with treated water. Nitrate was not detectable in the treated column leachates, but they did have average sulphate concentrations of 5.3 mg/L and 3.2 mg/L. The control column leachate released an average of 84 mg/L.

Study 5: Performance Summary Report – 2013 Pilot Plant Studies at Site 2 Operations

The pilot program included four major process technologies, one biological and three membrane-based. Some of the RO brine produced in the pilot system was treated on-site using a bench-scale FBR system to investigate an alternative to evaporation-crystallization.

Study 6: 2015 Site 2 Operations Pilot Program Status and Recovery Plan

Phase 1 for the two-stage FBR followed by membrane ultrafiltration to separate the FBR residuals from the treated water (Option 2) is as likely to satisfy the must-have criteria as the other treatment trains that were investigated.

Study 7: Pre-Scoping Assessment of Active Water Treatment Options for Site 3 Operations

Six options were short-listed for pre-scoping evaluation of capital and operating costs.

Study 8: Stability of AOP-treated Site 4 Effluent

For samples that were fully oxidized as received or that were spiked, no material change in the selenium species matrix occurred during aeration, chemical quenching, and combined chemical quenching-aeration steps, nor on standing for two overnight periods. Test results showed that at least three minutes of ozonation, with hydrogen peroxide dosed either before or after ozonation, were needed for complete oxidation.

Mini Pilot/ Offsite Work

Study 1: Ion Exchange Technology Development for Active Water Treatment

The flow sheet originally proposed with an electro-coagulation (EC) step was not able to remove selenium in a closed-loop system due to the failure of the EC to reduce selenate to selenite. The IX process was tested in an open-circuit configuration and achieved the following concentrations in the treated water:

- Selenium removal to < 10 µg/L
- Nitrate removal to 35 mg/L (as N)
- Increased sulphate concentration in effluent by approximately 100 mg/L.

The next step is to compare the IX-based process with other technologies available to remove selenium.

Study 2: Microbiology Program 2017

The population baseline inside biological reactors (FBR and MBBR) was developed after eight weeks of weekly sampling. Nitrate will buffer the bioreactor in a more oxidized state. These conditions assist with sulphide control, but also buffer against selenium reduction. The MBBR demonstrated greater fluctuations in microbial population compared to the other bioreactors. The MBBR stored selenium on the media, and the bacteria on the biowheels contributed to selenium changes in the MBBR.

Onsite Pilots

Study 1: EDR-RO Pilot Program for AWTF

EDR-RO technology successfully treated the water, with 82% water recovery in the EDR phase and 37% recovery in the RO phase. Blending of RO permeate with EDR product was required to reconstitute the treated water prior to discharge.

Study 2: Evaluation of Treatment Technology for Selenium Removal at Site 2 Operations

The nitrate effluent target was consistently achieved in the overall process. The total selenium effluent target was achieved in 13% of the samples. The packed bed reactor process achieved the selenium target at the end of the program.

Study 3: Review of 2013 Active Water Treatment Pilot Program at Site 2 Operations

- FBR – Nitrate removal to less than the target 3 mg/L as N was achieved after the acclimation period.
- NF – As a stand-alone technology, NF treated selenium, cadmium, sulphate, and some calcium but not nitrate.
- RO – Treated all five constituents of interest at >70% water recovery.
- FBR bench – Achieved very little dissolved selenium reduction, from 1,740 µg/L to 1,580 µg/L, observed.
- EDR-RO – Both EDR-RO systems produced similar quality product water that treated all five constituents of interest.

Study 4: Site 2 Operations Active Water Treatment Pilot Program 2015-2016

Only two flowsheet options met the selenium target before post-treatment steps. The other flowsheets needed the final CBSF to remove a fraction of the selenium still present in order to meet the final selenium target. Hydrochloric acid and antiscalant effectively managed alkalinity and calcium in the influent water to mitigate precipitation of carbonate-containing minerals.

LESSONS LEARNED

Bench and Desktop Work

Study 1: Site 1 Selenium Water Treatment Review

Methods to decrease the selenium inventory offer the greatest chance to decrease selenium discharge concentration over the short term. The investigation of long-term source control using mitigation methods should be continued.

Study 2: Preventing Selenium Release from Coal Wastes

During the experiment, it became clear that selenium was being released from sources other than pyrite. Adding organic carbon facilitates the consumption of dissolved oxygen within the waste rock pile and also provides a source of carbon for indigenous bacterial populations to reduce problematic oxyanions such as nitrate, selenate, and sulphate.

Study 3: Accelerated Selenium Program 2013 to Mid-2014 Review

The accelerated selenium program addressed a pressing need to identify alternative treatment technologies for the constituents of interest.

Study 4: In Situ Treatment to Prevent Release of Selenium, Nitrate, and Sulphate

The greatest unknown with in situ treatment concepts is whether selenium release will be prevented over the long term. Selenium concentrations did not increase in the effluent when nutrient addition was stopped.

Study 5: Performance Summary Report – 2013 Pilot Plant Studies at Site 2 Operations

Biological processes are likely appropriate when only nitrate and selenium removal are required. A longer acclimation period is recommended for FBR-based water treatment systems.

Study 6: 2015 Site 2 Pilot Program Status and Recovery Plan

Several key technical uncertainties remained that needed further investigation. Specifically, the flowsheets needed to demonstrate that a non-toxic effluent, which achieved the discharge limits for the constituents of interest, could be consistently produced.

Study 7: Pre-Scoping Assessment of Active Water Treatment Options for Site 3 Operations

Three options, AnMBBR-AnMBR, Packed Bed Reactor(X), and AnMBBR have lower capital and operating costs than the flowsheet option selected for the Site 2 south active water treatment facility.

Study 8: Stability of AOP-treated Site 4 Effluent

Samples that were partially oxidized (non-selenate species) as-received and spiked, underwent some changes in selenium speciation after the first 12 hours. Chemical quenching did not prevent changes in the selenium species matrix, but rather changed the selenium species matrix further.

Mini Pilot/ Offsite Work

Study 1: Ion Exchange Technology Development for Teck Coal Active Water Treatment

The selenium-only process is much further developed than the selenium + nitrate process. The residue generated during the test was not representative of the process; therefore, it was not possible to calculate volumes of residuals or their composition, or to perform toxicity characteristic leaching procedure (TCLP) tests.

Study 2: Microbiology Program 2017

The microbial population in FBR#2 was more diverse than FBR#1, which was likely due to the different carbon sources being used in the reactors. As a nitrogen nutrient source, nitrate would be a poor choice compared with ammonia. Acetic acid appeared to generate lower selenium concentration in treated water and less diversity in selenium speciation at the bench scale.

Onsite Pilots

Study 1: EDR-RO Pilot Program for AWTF

The solids formed failed TCLP tests for leachable selenium. EDR-RO technology is recommended as a feasible option for treatment of mine-affected water, especially if sulphate removal is needed. Additional brine treatment work is needed.

Study 2: Evaluation of Treatment Technology for Selenium Removal at Site 2 Operations

Further work may be helpful to build more confidence in the process capability and to explore operational and/or design modifications.

Study 3: Review of 2013 Active Water Treatment Pilot Program at Site 2 Operations

- FBR – The four-month test period did not consistently produce targeted total selenium values. Optimization of key input variables and effective integration of the different unit operations in the FBR system were not completed.
- NF – Operation at 70% water recovery was negatively affected by NF membrane scaling
- RO – Turndown of the SRC to throughput values needed to test high water recovery in the RO required modifications in the process equipment that delayed testing and were challenging to operate.
- FBR bench – Mechanical limitations related to the turndown capability of equipment prevented optimization of conditions to reach lower filtered selenium values from high TDS brine.
- EDR-RO – The evaporation/crystallization phase of this treatment needs further development to ensure long-term stability of the salt produced.

Study 4: Site 2 Operations Active Water Treatment Pilot Program 2015-2016

Acetic acid showed advantages over other electron donors in the FBR, including lower biological yield, shorter acclimation time, and rapid recovery from process upsets. A chemical softening step at the front of the process was demonstrated as an alternative to hydrochloric acid and antiscalant addition to manage precipitation of carbonate-containing minerals, but was operationally challenging

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PRESENTATIONS AND PUBLICATIONS

No public presentations or publications.

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Sludge Treatment

COSIA Project Number: WJ0042

COSIA GAP/Opportunity Area: Water Return: Active Treatment Technologies

Research Provider: Teck Advanced Research Technologies

Industry Champion: Teck Resources Limited

Status: Completed

PROJECT SUMMARY

Bench and Desktop Work

2017 Site 1 and Site 2 Residuals Management Study

The project objective was to optimize the current amendment recipe for landfill and investigate alternative options for residuals dewatering at Site 1. Amendment and geotechnical tests were carried out at both laboratory and field scales. Site 1 thickened sludge (filter press feed) was dewatered using a decanter centrifuge as opposed to filter press at site.

Mini Pilot/ Offsite Work

Eight studies focusing on residual treatment from bench and lab work and off-site pilots were undertaken.

Study 1: Suitability Assessment for Disposal of Residuals from 2013 Site 2 Pilot Program

Residuals from pilot-scale treatments of Site 2 Pond water in 2013 were characterized and mineralogical analyses were completed on the residuals for interpretation of geochemical stability.

Study 2: Handling Options for Selenium Water Treatment Residues

Development of residual handling plans for the active water treatment facilities (AWTF) to be implemented under the Water Quality Plan were studied. The purpose was to remove selenium and other potential constituents of interest including cadmium, calcium, carbonate, nitrate, and sulphate from surface waterbodies affected by mining practices..

Study 3: Chemical Stability Evaluation of Fluidized Bed Reactor (FBR) Residue

Residue created in the biological treatment will likely be disposed of in a separate open air landfill. A residue column program was designed to identify potential areas of risk to be mitigated in the final disposal method.

Study 4: FBR Residuals Geochemical Stability Evaluation

A laboratory test program was conducted to determine the stability of bioresiduals.

Study 5: Failure Modes and Effects Analysis (FMEA) and Residuals Characterization for the Site 1 AWTF Landfill

A FMEA was done on the bioferric residual material expected to be produced and landfilled from the AWTF.

Study 6: Accelerated Selenium Program (ASP) Residuals 2013 to 2014 Summary

Technical assessments on the residuals expected from Site 1 AWTF were provided for waste classification, anticipated leachate quality, and third-party waste operator selection for off-site disposal considerations.

Study 7: Test Work on Packed Bed Reactor Sludge and Solid Residuals Generated

Test work was conducted on available backwash sludge and solid residuals samples collected during the 2014 packed bed reactor pilot.

Study 8: Site 2 AWTF Selenium Pilot Plant Residual Phase II Project

A Phase II project to investigate amendment options for residuals from AWTF was carried out.

PROGRESS AND ACHIEVEMENTS

Bench and Desktop Work

2017 Site 1 and Site 2 Residuals Management Study

The geotechnical strength of residual materials increased with soil and lime addition, higher compaction, and moisture loss. A ratio of 3:1 residuals to soil and 1% lime by mass was recommended as an amendment.

Mini Pilot/ Offsite Work

Study 1: Suitability Assessment for Disposal of Residuals from 2013 Site 2 Pilot Program

Land application of residuals from selenium-targeted treatment is unlikely without further treatment. Composting of Envirogen FBR residuals for agricultural use is unlikely because of low carbon-to-nitrogen ratio.

Study 2: Handling Options for Selenium Water Treatment Residues

The immediate handling option for the bioresiduals is to chemically stabilize the selenium residue as a precautionary measure and then dispose of the material in an onsite engineered landfill. Regulatory frameworks introduce another layer of consideration to any option that requires the movement of selenium residue out of the province.

Study 3: Chemical Stability Evaluation of FBR Residue

Over seven weeks, approximately 2% of the initial selenium in residue was observed in the leachate with minimal oxidized selenium identified. Dissolved selenium and ammonia concentrations showed a positive correlation, suggesting greater selenium release as the biomass decomposed. The concentration of iron in the leachate suggested the ferric iron may be reduced to the more soluble ferrous form.

Study 4: FBR Residuals Geochemical Stability Evaluation

Untreated FBR residuals will not create the reducing environment required to ensure long-term geochemical stability of selenium. Lime treatment of the FBR residuals should be avoided to decrease the mobilization of selenium. Landfill leachate from FBR residuals will likely require treatment.

Study 5: FMEA and Residuals Characterization for the Site 1 AWTF Landfill

The FMEA identified the following risks associated with the residuals and their handling:

- geotechnical stability (insufficient strength, potential for liquefaction)
- geochemical stability (remobilization of selenium and other compounds)
- potential evolution of problematic gases (such as ammonia, hydrogen sulphide and dimethyl selenide)
- the composition and volume of the recycled leachate
- plugging between the liners
- other potential risks associated with the closure plan

Study 6: ASP Residuals 2013 to 2014 Summary

The coupled FBR/ferric process produced residuals with the highest selenium concentration among the technologies piloted at Site 2 in 2013. The residuals were classified as non-hazardous waste.

Study 7: Test Work on Packed Bed Reactor Sludge and Solid Residuals Generated

Due to the lower than expected total suspended solids in the backwash residuals sludge, insufficient sample was collected for a complete characterization.

Study 8: Site 2 AWTF Selenium Pilot Plant Residual Phase II Project

Three amendment options were selected and evaluated: Site 2 residuals + Site 1 soil + lime, Site 2 residuals + Site 1 residual cakes + Site 1 soil + lime, and Site 2 residuals + softener underflow. It was found that the amended Site 2 residuals using tested amendment options could be classified as non-hazardous waste and therefore could be disposed of in a secure landfill.

LESSONS LEARNED

Bench and Desktop Work

2017 Site 1 and Site 2 Residuals Management Study

Cake obtained from centrifuge tests generally contained lower solids content compared with the filter cake. More soil and lime were needed to achieve the strength target for landfill disposal. The proposed amendment method will reduce landfill airspace and soil consumption. Given the promising preliminary results, a centrifuge should be considered to support the design of future water treatment facilities.

Mini Pilot/ Offsite Work

Study 1: Suitability Assessment for Disposal of Residuals from 2013 Site 2 Pilot Program

Thermogravimetric analysis of electrodialysis reversal-reverse osmosis (EDR-RO) brine showed that reasonable mass reduction by incineration would vaporize selenium into the off-gas. The FBR process produced residuals with the highest selenium concentration that passed as non-leachable toxic waste. Treatments of EDR-RO brine produced solids that exceeded the selenium and nitrate+nitrite limits, and will be classified as hazardous waste. The electrocoagulation-based processes produced iron-rich sludge that was likely to be classified as a toxic waste because of the soluble selenate content.

Study 2: Handling Options for Selenium Water Treatment Residues

Movement of selenium residue should be minimized and factored into the decision process for handling options. Sub-aqueous disposal of selenium residue should be considered as a long-term alternative to avoid the cost of pre-treatment before the amended residue is placed in a landfill.

Study 3: Chemical Stability Evaluation of FBR Residue

Results confirm that a landfill liner and leachate collection system are required to impound the biosolids. Conditions that minimize biomass decomposition and maintain microbial activity will likely reduce selenium concentrations in leachate.

Study 4: FBR Residuals Geochemical Stability Evaluation

This study showed that, to limit selenium mobilization, FBR residuals should be prevented from contacting precipitation. The FBR residuals should be allowed to dry to promote biomass decomposition and decrease water content, and dried FBR residuals should be disposed of in small cells to facilitate progressive closure.

Study 5: FMEA and Residuals Characterization for the Site 1 AWTF Landfill

A thorough examination of alternative handling options for the residuals is recommended. Gaps can be managed by following the proposed test plan developed by Applied Research and Technology (ART).

Study 6: ASP Residuals 2013 to 2014 Summary

The properties of the Site 1 AWTF residuals should be confirmed once they become available. A practice to allow the FBR/ferric residuals to dry prior to disposal in a covered system is recommended. Handling options for residuals from the Site 2 AWTF should be evaluated after technology selection.

Study 7: Test Work on Packed Bed Reactor Sludge and Solid Residuals Generated

Distinct variations in concentrations of constituents of interest were seen among the different batches of backwash sludge and solid residuals samples, and these would likely be classified as non-hazardous waste. The supernatant will exceed BC MOE requirements for discharge and will require re-treatment.

Study 8: Site 2 AWTF Selenium Pilot Plant Residual Phase II Project

Results suggested that high moisture content in the amended residuals was likely the main cause for low shear strength. Optimization of the dewatering process is recommended to maximize solids content of the cake.

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Teck Resources Ltd. 2014. *ASP Residuals 2013 to 2014 Summary.*

PRESENTATIONS AND PUBLICATIONS

No public presentations or publications.

RESEARCH TEAM AND COLLABORATORS

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Other Treatments

COSIA Project Number: WJ0042

COSIA GAP/ Opportunity Area: Water Return: Active Treatment Technologies

Research Provider: Teck Advanced Research Technologies

Industry Champion: Teck Resources Limited

Status: Completed

PROJECT SUMMARY

Six studies, described below, were undertaken as part of this project to evaluate treatment technologies in the removal of constituents of concern, including phosphorus and gypsum. These studies provide treatment options for inorganic species removal in Oil Sands Process Waters if required.

Study 1: Phosphorus Removal Options for Site 1 Active Water Treatment Facility

Six treatment options were considered for long-term phosphorus removal from treated Site 1 water.

Study 2: Constituents of Interest Release Modelling from Past and Present Coal Operations

An empirical model was developed using water quality data from specific coal mine waste rock dumps to predict selenium, sulphate, and nitrate generation rates and stream loadings by month. These predictions were compared with data from the water quality model current at the time the work was done.

Study 3: Review of Gypsum Removal Methods for Site 1: Part 1

A review was undertaken to summarize in one document all work completed to date to remove gypsum at this site and identify any promising leads that may still yield a reduction in levels of total dissolved solids (TDS) in the treated water.

Study 4: Review of Gypsum Removal Methods for Site 1: Part 2

A review was done of external literature relevant to TDS reduction in treated water from Site 1 mine water treatment plans (WTPs).

Study 5: Site 1 Water Treatment Bench Testing 2016

This study investigated various water sources for the lime make-up system and their effect on lime consumption in the WTPs.

Study 6: Examination of Total Dissolved Solids in Reclaim Water at Site 1 Operations

Tests were done to identify potential methods to decrease the overall TDS concentration in treated water.

PROGRESS AND ACHIEVEMENTS

Study 1: Phosphorus Removal Options for Site 1 Active Water Treatment Facility

The study found there are many commercially available options for treating phosphorus, and the most cost-effective options involve the addition of ferric chloride.

Study 2: Constituents of Interest Release Modelling from Past and Present Coal Operations

The empirical model developed in this project predicts that the sulphate guideline for Site 1 will be exceeded in some months of the year starting sometime between 2021 and 2030.

Study 3: Review of Gypsum Removal Methods for Site 1: Part 1

The review found that addition of WTP#3 solids, which are predominately gypsum, to reclaim water showed a decrease in TDS concentrations. As well, higher gypsum addition rates decreased TDS in the clarifier overflow.

Study 4: Review of Gypsum Removal Methods for Site 1: Part 2

Several options were found that may decrease gypsum concentration in the treated reclaim water. It is possible that the antiscalant added to the process and cooling water is contributing to gypsum supersaturation in the tailings impoundment.

Study 5: Site 1 Water Treatment Bench Testing 2016

This work showed a 28% increase in lime consumption when fresh antiscalant was added to the lime make-up water.

Study 6: Examination of Total Dissolved Solids in Reclaim Water at Site 1 Operations

Historical reclaim water data shows that gypsum is no longer supersaturated in the technology scanning evaluation, and there is a decrease in calcium, sulphate, and TDS concentrations in the reclaim water.

LESSONS LEARNED

Study 1: Phosphorus Removal Options for Site 1 Active Water Treatment Facility

If ferric chloride polishing proves insufficient, membrane systems could be used to remove phosphorus. Possible long-term phosphorus removal strategies should be evaluated.

Study 2: Constituents of Interest Release Modelling from Past and Present Coal Operations

A study is required to understand why some waste rock dumps are more active than others and why selenium generation is accelerating in some other dumps. The rate-controlling factors that determine waste rock dump behaviour need to be identified.

Study 3: Review of Gypsum Removal Methods for Site 1: Part 1

The problem has been further refined to consider methods to precipitate supersaturated gypsum to equilibrium levels to minimize TDS concentrations in the treated water. While a few promising leads were identified, the review of past work was useful to trigger thinking about potential mechanisms that may be impeding gypsum precipitation.

Study 4: Review of Gypsum Removal Methods for Site 1: Part 2

This review showed the need to develop a relevant technical program to investigate whether antiscalant may be inhibiting gypsum precipitation.

Study 5: Site 1 Water Treatment Bench Testing 2016

This study led to a recommendation to increase the WTP pH target to 11.5 to remove an additional 1300 mg/L of TDS as magnesium sulphate monohydrate. The return of process water containing antiscalant to the tailings storage facility (TSF) is believed to have adverse effects on the ability of gypsum to precipitate in treated water.

Study 6: Examination of Total Dissolved Solids in Reclaim Water at Site 1 Operations

Returning gypsum solids to the TSF is believed to have a beneficial impact by decreasing the overall TDS concentration. Calcite was tested as a seeding agent and did not show an improvement over current treatment methods.

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PRESENTATIONS AND PUBLICATIONS

No public presentations or publications.

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Wetland Treatment of Oil Sands Process-Affected Water (OSPW)

COSIA Project Number: WJ0046

COSIA GAP/Opportunity Area: Water Return

Research Provider: Simon Fraser University

Industry Champion: Imperial Oil Resources Limited

Status: Ongoing

PROJECT SUMMARY

Large volumes of oil sands process-affected water (OSPW) have been generated through mining operations and bitumen extraction in the Canadian oil sands. Ongoing efforts to find feasible treatment solutions have identified several technologies with the potential to improve water quality of OSPW, to enable return of treated OSPW to the Athabasca River watershed. 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 in Canada has not yet been fully investigated. To investigate the application of treatment wetlands in the oil and gas industry, a 1-ha surface-flow wetland - the Kearl Treatment Wetland (KTW) - was constructed on Imperial's Kearl oil sands site.

The overall goal of this study is to improve the science of treatment wetland technology in Canada. 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 was applied and tested for neutral organic contaminants. A contaminant-fate model will be used to assess the feasibility of treatment wetlands for 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:

1. investigate the ability of the KTW to treat OSPW from the Kearl oil sands site (Imperial Oil Resources Limited) in northern Alberta;
2. apply, test, and calibrate a contaminant-fate model of the KTW;
3. measure toxicity of wetland influent (OSPW) and effluent (treated OSPW); and
4. correlate this toxicity data with the profile of OSPW contaminants.

PROGRESS AND ACHIEVEMENTS

In 2017, polyethylene (passive) samplers (PES) were deployed in three locations throughout the KTW to measure freely dissolved PAH concentrations. OSPW entering the KTW consisted of runoff from an overburden disposal area which contained relatively low concentrations of PAHs (i.e., C_{max} = 8.55 ng/L). Two deployments were completed for ~30 days each in 2017: (1) July 21 – August 28, and (2) August 28 – September 28. Results from the 2017 operation showed a statistically significant ($p < 0.05$) decline in dissolved concentration through the KTW for 16 PAHs during deployment one and 20 PAHs during deployment two. The first deployment measured a mean removal efficiency (E_C) of 75.4% (SD 18.2%) for 19 PAHs, and the total concentration for Σ (19 PAHs) provides an E_C of 82.4% through the KTW. The second deployment measured a mean E_C of 36.7% (SD 30.2%) for 25 PAHs, and the total concentration for Σ (25 PAHs) gives an E_C of 57.0% through the KTW.

Model parameterization to the KTW was completed to set up model application and testing. Figure 1 illustrates 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 (MB = 1.01; CI 0.75 – 1.39). The model estimates the contributions of various biogeochemical removal mechanisms. Further testing and model applications will contribute to a better understanding of wetland treatment dynamics for various chemicals.

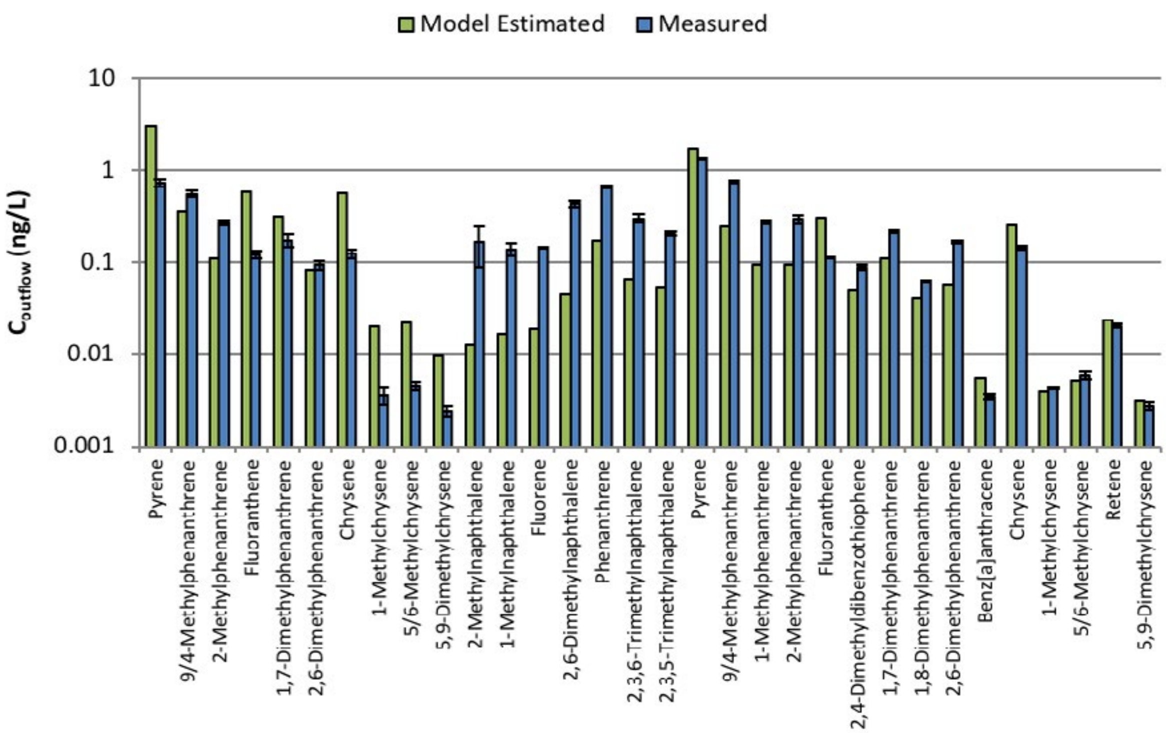

Figure 1: Comparison of model estimated and measured dissolved PAH concentrations in the effluent of the Kearl Treatment Wetland (KTW).

In 2018, the study scope was expanded to include passive sampling of NAs using POCIS in addition to PE sampling of PAHs. OSPW from drainage pond 1A was introduced into the KTW on August 25, 2018. Water was 100% recycled through the wetland, i.e., water from the final deep pool was pumped back into the wetland forebay cell. Therefore, in addition to passive sampling, grab samples were collected at specified frequencies throughout the duration of the study (August 25 to October 8, 2018). Calibration of these samplers to quantify the freely dissolved concentrations of PAHs and NAs must still be completed.

The data collected from the 2017-2018 campaign for the KTW allows investigation of the treatment efficiency for PAHs and NAs (objective 1). The contaminant-fate model has been developed for neutral organic contaminants (i.e., PAHs) but needs further development to apply and test for ionisable organic contaminants (i.e., NAs; part of objective 2). Efforts to investigate OSPW toxicity entering and leaving the KTW will begin in 2019 and continue through the course of the project. In conjunction, the model can be developed to incorporate this data and thereby contribute to a better understanding of changes to OSPW toxicity through wetland treatment.

LESSONS LEARNED

The results from the 2017-18 investigations demonstrate the capacity for the KTW to reduce concentrations of PAHs and NAs in OSPW. Our results show that specific congeners of NAs are more susceptible to wetland degradation. Higher concentration reductions are shown for NAs that are fully hydrogenated compared to other NAs within the same carbon group. Exploration of this phenomenon is ongoing.

Our data suggest treatment wetlands may be effective tools in helping to 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 2017-18 study, a successful sampling plan has been established to measure contaminants of concern in OSPW using polyethylene and POCIS passive samplers. Our investigative approach will continue to build upon these lessons as we prepare for the 2019 study.

PRESENTATIONS AND PUBLICATIONS

Presentations

Cancelli, A. M., Gobas, F. A.P.C. 2018. A model of contaminant removal from oil sands process-affected waters in the Kearl Treatment Wetland. Society of Environmental Toxicology and Chemistry, 39th North American Annual Meeting, Sacramento, CA.

Cancelli, A. M., Gobas, F. A.P.C. 2018. Quantifying the removal of polycyclic aromatic hydrocarbons in the Kearl Treatment Wetland. Canadian Oil Sands Innovation Alliance, Oil Sands Innovation Summit, Calgary, AB.

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RESEARCH TEAM AND COLLABORATORS

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H2nanO Treatment of Oil Sands Process-Affected Water (OSPW)

COSIA Project Number: WJ0096

Research Provider: H2nanO Inc.

Industry Champion: Canadian Natural Resources Limited

Industry Collaborators: Imperial Oil Resources Limited, Suncor Energy Inc., Syncrude Canada Ltd., Teck Resources Limited

Status: Completed

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 to enable its safe discharge to the environment. Towards this, COSIA issued a challenge for "Passive Organics Treatment Technology" that will deliver scalable and low-input OSPW treatment.

H2nanO Inc., (a water treatment technology company), in partnership with the University of Waterloo, has developed a sunlight-activated, reusable treatment process for passive organics treatment. This treatment, called Solar Pass, uses a proprietary buoyant photocatalyst that, when mixed with water, continuously treats and eliminates organics in water.

The purpose of this project was to evaluate photocatalysis treatment using H2nanO's Solar Pass as a method to passively treat dissolved organics in OSPW to water return quality.

Effective removal of these organics from OSPW has been studied extensively. While a number of potentially successful treatment technologies have been identified, most require relatively high energy to operate, are relatively costly, and cannot be easily deployed in the reclamation landscape.

This project had four objectives:

1. Determine the maximum treatment rates of photocatalysts with respect to removing acute and chronic water toxicity.
2. Test engineering features on particle retrieval and reuse.
3. Develop the ability to perform water treatment in the turbidity of untreated OSPW.
4. Determine the presence of by-products from photo-oxidation, engineering parameters, and the toxicity profile of the buoyant photocatalysts.

To achieve these objectives, oil sands operators provided H2nanO and the University of Waterloo with multiple samples of OSPW, which were tested using prototype Solar Pass ponds to evaluate treatment rates and efficacy, as well as bench-scale testing systems to study key parameters (e.g., treatment in turbid water). The project evaluated

both chemical and toxicological indicators in order to characterize and assess the treatment process and optimize it for an OSPW application. These tests were completed using both artificial and natural sunlight selected to simulate the treatment conditions in northern Alberta at a scale up to 650 L batches.

This project builds upon prior work by Professor Frank Gu's research group at the University of Waterloo, which demonstrated that treatment under natural sunlight was sufficient to eliminate naphthenic acids and acute toxicity to *Vibrio fischeri* in raw OSPW (Leshuk et al., February 2016). Follow up studies investigated the effect of water matrix ions, temperature, pH, and dissolved oxygen on the treatment kinetics (Leshuk et al., December 2016). Studies focused on other methods of OSPW treatment have shown that toxicity can be reduced through oxidative chemical treatments (He et al., 2012; Zubot et al., 2012), however the promise of photocatalysis is to be able to deliver the same treatments in a more passive, low-input process (Leshuk et al., September 2018; Leshuk et al., February 2018). This study aimed to evaluate whether that outcome could be realized.

The study addresses knowledge gaps related to photocatalytic OSPW treatment and its ultimate use for deployment as pre-treatment to remediation wetlands or for in-pond deployment. The Solar Pass' unique buoyant and reusable features may enable accelerated dissolved organics treatment to improve the rate of water return and maintain water quality in water-capped tailings storage systems. Photocatalysis has potential to improve the effectiveness of other closure technology and further strategic management of OSPW.

The project will result in research publications, knowledge sharing presentations, and improved technical and engineering knowledge on implementing photocatalysis in the Canadian oil sands. High quality professionals were trained during the project and have developed industry-specific expertise on OSPW treatment (including three graduate and seven undergraduate researchers) while engaging industry professionals to advance the evaluation of H2nanO's treatment process for use in the Canadian oil sands.

PROGRESS AND ACHIEVEMENTS

Pre-2018 Results and Progress

- Demonstrated heterogeneous photocatalysis using nanoparticle titanium dioxide (TiO_2) can destroy dissolved organics in OSPW using sunlight.
- Treatment with photocatalysts eliminated acute toxicity for *V. fischeri* in raw OSPW.
- Photocatalysis preferentially degrades heavier and more cyclic naphthenic acids in OSPW, which are the more environmentally-persistent fraction.
- The presence of different water matrix ions changed the rate of organics treatment in OSPW, and dissolved oxygen was critical to the treatment process.
- Differences in OSPW pH and temperature were not strong factors in the rate of treatment.

This work demonstrated that photocatalysis could passively degrade organics in OSPW to achieve key treatment metrics such as degradation of persistent naphthenic acids and elimination of toxic effects. These primary results motivated further study to assess factors relevant to the operational setting (such as turbidity) and reduced toxicity on standard bioassays.

2018 Results and Progress

Using H2nanO's buoyant photocatalyst media and the Solar Pass process, project results in 2018 demonstrated:

- Photocatalysis eliminated acute toxicity to Rainbow Trout with four days or less of sunlight energy, meeting a key quality requirement of the COSIA challenge.
- Analytical chemistry analysis demonstrated that photocatalysis specifically targets a minority of dissolved organics classes that contribute to toxicity, eliminating them in the first stages of treatment.
- The treatment by-products of oxidation are shorter chain organics that correlate with lower toxicity and higher biodegradability.
- The buoyant Solar Pass photocatalysts were advantageous, demonstrating no loss in efficacy in raw OSPW with elevated turbidity, and were durable through accelerated wear and fouling tests.
- Buoyant recovery was effective to deploy and recover the photocatalysts for reuse, and the composites had no acute or chronic toxicity to assays tested for OSPW toxicity.
- The Solar Pass process can treat organics in both gently mixed and unmixed environments, enabling potential treatment in both semi-passive and fully passive modes.

LESSONS LEARNED

H2nanO Solar Pass can passively treat OSPW to pass acute and chronic bioassays using only sunlight.
(Gu et al., 2018)

The project team demonstrated treatment of raw OSPW samples from "acutely toxic" to "no effect" in four days or less of sunlight energy using standard Rainbow Trout assays, and "chronically toxic" to "no effect" in ten days or less using Fathead Minnow assays. H2nanO's Solar Pass process requires only sunlight and its reusable treatment media to conduct passive treatment of dissolved organics.

This treatment shortens the time required for dissolved organics remediation and may enhance the overall process of water treatment for return to the watershed.

H2nanO Solar Pass preferentially targets the more persistent, toxicity-correlated dissolved organics and generates shorter chain organics that are lower toxicity and more biodegradable.
(Leshuk et al., September 2018)

Chemical analysis of the OSPW treatment identified that the Solar Pass process treats more biologically-persistent and toxicity-correlated long-chain organics faster. This enables accelerated treatment to remove adverse aquatic effects that are slow to be naturally attenuated.

The by-product of partially treated dissolved organics are shorter chain molecules that could be treated by biological processes. This provides the potential for a fast, pre-treatment (via photocatalysis) before natural remediation for return, accelerating the overall return process.

H2nanO can detoxify OSPW using only a partial, targeted treatment.
(Leshuk et al., February 2016; Leshuk et al., September 2018)

The targeted treatment analysis shows that Solar Pass can uniquely detoxify dissolved organics without fully destroying the compounds. This accelerates treatment, as a more extensive destruction of organics takes more energy and time.

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PRESENTATIONS AND PUBLICATIONS

Presentations

Conference Presentations/Posters

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.

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.

RESEARCH TEAM AND COLLABORATORS

Institution: H2nanO Incorporated, University of Waterloo, University of Toronto

Principal Investigator: Dr. Frank Gu

Name	Institution or Company	Degree or Job Title	Degree Start Date (Students Only)	Degree Completion Date (Students Only)
Dr. Tim Leshuk	University of Waterloo University of Toronto H2nanO Inc.	PhD, Chemical Engineering Post-Doctoral Fellow Co-Founder & CTO	2013 2018	2018 -
Zac Young	University of Waterloo H2nanO Inc.	MASc Chemical Engineering Co-Founder & COO	2016	2018
Brad Wilson	H2nanO Inc.	Lead Process Engineer		
Danielle Smith	H2nanO Inc. / University of Waterloo	Undergraduate Co-op Intern, Nanotechnology Engineering	2014	2019
Corin Seeleman	H2nanO Inc. / University of Waterloo	Undergraduate Co-op Intern, Nanotechnology Engineering	2014	2019
Zi Qi Chen	H2nanO Inc. / University of Waterloo	Undergraduate Co-op Intern, Chemical Engineering	2016	2021
Matthew Lam	H2nanO Inc. / University of Waterloo	Undergraduate Co-op Intern, Chemical Engineering	2016	2021
Greg Lazaris	H2nanO Inc. / University of Waterloo	Undergraduate Co-op Intern, Nanotechnology Engineering	2016	2021
Mary Gopanchuk	H2nanO Inc. / University of Waterloo	Undergraduate Co-op Intern, Materials and Nanoscience	2014	2018
Sean McLay	H2nanO Inc. / University of Waterloo	Undergraduate Co-op Intern, Nanotechnology Engineering	2015	2020
Michelle Si	University of Waterloo	MASc Science, Chemical Engineering	2017	2019

Research Collaborators:

- ExxonMobil. Collaboration on rapid detection and analysis tool for measuring aquatic toxicity towards potential use as an additional sensing technique in OSPW treatment.
- InnoTech Alberta. Collaboration on chemical analysis for OSPW treatment to identify and elucidate the benefits of the photocatalytic treatment process.

Demonstration-Scale Constructed Wetland Treatment System for Oil Sands Process-Affected Water (OSPW)

COSIA Project Number: WJ0142

COSIA GAP/Opportunity Area: Treatment for detoxification using passive (low energy) treatment technologies for OSPW

Research Provider: Suncor Energy Inc.

Industry Champion: Suncor Energy Inc.

Industry Collaborators: Canadian Natural Resources Limited

Status: Year 1 of 5

PROJECT SUMMARY

Between 2014 and 2016, Shell Canada Ltd. (former operator of Albian Sands, now operated by Canadian Natural Resources Limited) and Suncor Energy Inc. jointly funded research to evaluate the efficacy of different constructed wetland treatment system (CWTS) designs to treat chemicals of concern (COCs), such as metals, metalloids, petroleum related organics, and salts, in OSPW using desktop, bench- and pilot-scale studies (Rodgers and Castle 2015a, 2015b, and 2015c). Overall, pilot-scale CWTSs were capable of mitigating risks associated with OSPW and achieving numeric and narrative water quality criteria. Specifically, pilot CWTSs reduced concentrations of most inorganic (e.g., metals) and organic (naphthenic acids [NAs], oil and grease) constituents to below water quality guidelines and/or detection limits, and removed toxicity of OSPW to sentinel aquatic organisms (Rogers and Castle 2016). Based on the results observed at the pilot scale, design recommendations for a demonstration-scale CWTS were provided. As untreated OSPW would be considered the most difficult to treat, other available water streams are considered treatable within the conservative design limitations.

Building on this research, the goal of the Demonstration CWTS is to confirm the potential of a commercial-scale CWTS design to treat industrial wastewater for safe return to the environment. Specific objectives of the program are to:

1. Determine the rate and extent of COCs removal from OSPW streams by CWTS, as well as the ability of CWTS to meet performance goals (i.e., numeric and narrative treatment criteria).
2. Identify the seasonal rates and operating limits of the CWTS in the Athabasca oil sands region.
3. Evaluate the suitability of substrates and materials available in the Athabasca oil sands region for the construction of treatment wetlands.
4. Quantify the rate and extent of COCs bioaccumulation in plants to assess potential risk to wildlife.

Initially, the Demonstration CWTS will operate as a closed-loop system and water will be recycled within the existing operations (no water will be returned to the environment). Once performance monitoring has demonstrated CWTS treated water meets water quality criteria, Suncor Energy Inc. will seek approval to trial water return to the Athabasca River.

PROGRESS AND ACHIEVEMENTS

In 2016, the COSIA Water Environmental Priority Area initiated a study to facilitate the scoping of a multi-year program to design and construct a demonstration-scale CWTS. Outcomes from this work were then directly incorporated into the development of a research and monitoring plan for the Demonstration CWTS.

In addition, as a component of the Lake Miwasin Demonstration Pit Lake (LM-DPL) project, the Demonstration CWTS has been highlighted to both First Nations and Métis organizations engaged throughout the development of the LM-DPL Project. Focused discussions on the Demonstration CWTS were held at meetings in December 2017 and February 2018, and feedback received during these meetings was incorporated into the Demonstration CWTS research and monitoring plan. A three-day workshop on the LM-DPL/CWTS was held in April 2018 with community technical representatives, Elders and land users. A detailed workshop report was prepared and further informed the research and monitoring plan.

Suncor Energy Inc. also provided regular Demonstration CWTS project design and planning updates to the Alberta Energy Regulator (AER) as part of regular meetings on the DPL Project (e.g., November 21, 2017, and March 5, 2018). In June 2018, a draft research and monitoring plan was submitted to the AER. Construction activities for the Demonstration CWTS are planned to occur August - October 2018 and spring, 2019.

LESSONS LEARNED

This project is in early stages and there are no lessons learned to report at this time.

LITERATURE CITED

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PRESENTATIONS AND PUBLICATIONS

No public presentations or publications.

RESEARCH TEAM AND COLLABORATORS

Institution: Suncor Energy Inc.

Research Collaborators: John Rodgers Jr. and Dr. James Castle, Clemson University

Constructed Wetland Treatment System: Summary

COSIA Project Number: WJ0067

COSIA GAP/Opportunity Area: Treatment for detoxification using passive (low energy) treatment technologies for OSPW

Research Provider: Suncor Energy Inc.

Industry Champion: Suncor Energy Inc.

Industry Collaborators: COSIA Water and Environmental Priority Area Members

Status: Completed

PROJECT SUMMARY

Previous work evaluating the efficacy and performance of pilot-scale constructed wetland treatment systems (CWTSs) to treat oil sands process-affected water (OSPW) supported moving forward with the design, construction and monitoring of a demonstration-scale hybrid CWTSs. In 2017, the COSIA Water Environmental Priority Area (EPA) initiated a study to facilitate the scoping of a multi-year program to design and construct a demonstration-scale CWTS. The objectives of this study included identification of the Demonstration CWTS goal and objectives, performance measures of success, site identification and source water selection.

PROGRESS AND ACHIEVEMENTS

A two-day workshop (COSIA Water EPA Pilot Treatment Wetland Scoping Workshop, November 16 – 17, 2016) solicited feedback from leading researchers and service providers in CWTS design, monitoring and operation. This multi-sectoral workshop, attended by a large audience of multidisciplinary experts, was very interactive and allowed for productive discussions. The workshop succeeded in identifying additional knowledge gaps and design and monitoring considerations.

Based on workshop feedback and outcomes, industry representatives worked collaboratively to scope the goal and objectives of a CWTS field pilot and select a site location. Suncor Energy Inc. land was selected for the Demonstration CWTS, with the project goal of confirming the potential of a commercial-scale CWTS design to treat industrial wastewater for safe return to the environment. Specific objectives were to:

1. Determine the rate and extent of chemicals of concern (COCs) removal from various Oil Sands Process-Affected Water (OSPW) streams by CWTS, as well as the ability of CWTS to meet performance goals (i.e., numeric and narrative treatment criteria).
2. Identify the seasonal rates and operating limits of the CWTS in the Athabasca oil sands region.
3. Evaluate the suitability of substrates and materials available in the Athabasca oil sands region for the construction of treatment wetlands.
4. Quantify the rate and extent of COCs bioaccumulation in plants to assess potential risk to wildlife.

Using both numeric, chemical-specific and narrative, biological criteria, an integrative approach to monitor and measure the performance of the Demonstration CWTS was proposed. The performance measures of success were:

1. Performance in a northern climate.
2. Being a passive (i.e., low energy) system requiring minimal operation or maintenance.
3. Treating all identified COCs to below already-established water quality guidelines (e.g., CCME 1999, USEP 2002, ESRD 2014) with quality appropriate for discharge to the natural environment.
4. Eliminating or reducing acute and chronic toxicity to sentinel organisms including *Ceriodaphnia dubia*, *Pimaphales promelas*, and *Oncorhynchus mykiss*.

LESSONS LEARNED

Outcomes from this study were directly incorporated into the research and monitoring plan for the Demonstration CWTS, including the goal, objectives and measures of success.

PRESENTATIONS AND PUBLICATIONS

No public presentations or publications.

RESEARCH TEAM AND COLLABORATORS

Institution: Suncor Energy Inc.

Principal Investigator: Joshua Martin

Research Collaborators: Dr. John Rodgers Jr. and Dr. James Castle, Clemson University

Biotechnology Opportunities in the Oil Sands - Literature Study

COSIA Project Number: WJ0068

COSIA GAP/Opportunity Area: Water Treatment

Research Provider: OPE Group

Industry Champion: Nexen Inc.

Status: Completed

PROJECT SUMMARY

Biotechnology, the use of organisms or living systems to make or modify products or processes holds promise for a range of applications in the oil sands, as several activities related to oil sands mining directly or indirectly involve the natural environment. Advances in biotechnology have wide potential to enhance the environmental and economic performance of the Canadian oil sands industry, by, for example, improving tailings pond water quality or reducing greenhouse gas intensity.

Initial work completed by the Oil Sands Leadership Initiative (OSLI) identified research priorities and direction for synthetic biology and petroleum microbiology for the Oil Sands in 2013. To gain additional subject matter expert insights, the OPE Group was asked to review the work completed by OSLI and conduct a literature review of biotechnology opportunities in the oil sands. The specific objectives of this study were to:

1. Evaluate the most promising biotechnology opportunities for the oil sands,
2. Identify the current Technology Readiness Level (TRL) of each opportunity, and
3. Provide recommendations on how to direct research and development efforts towards applications.

While the study did not identify any currently commercial biotechnological applications for the oil sands that can be implemented directly at full scale, several potential applications were identified which are currently under investigation.

PROGRESS AND ACHIEVEMENTS

Most Promising Biotechnology Opportunities for the Oil Sands

- Several applications for biotechnology were identified including accelerated treatment of tailings pond water, enhanced bitumen recovery, corrosion management, and waste reduction. These applications were investigated in turn for each of the following types of organisms:
    - Environmental biotechnology (natural organisms) – natural organisms currently in the environment,
    - Genetically Modified Organisms – organisms whose genetic makeup has been modified in a laboratory setting, and
    - Synthetic Organisms – organisms whose genetic makeup has been partially or entirely engineered.

- The enhancement of wastewater treatment in tailings ponds using natural organisms was identified as a high potential application.

Technology Readiness Level of Biotechnology Opportunities

- None of the biotechnological opportunities identified can implemented directly at full scale at this time.
- Environmental Biotechnology (natural organisms) research, with a TRL of 5, is closest to oil sands application; GMOs and Synthetic Organisms are far from oil sands applications with a TRL of 2 and 0, respectively (Figure 1).

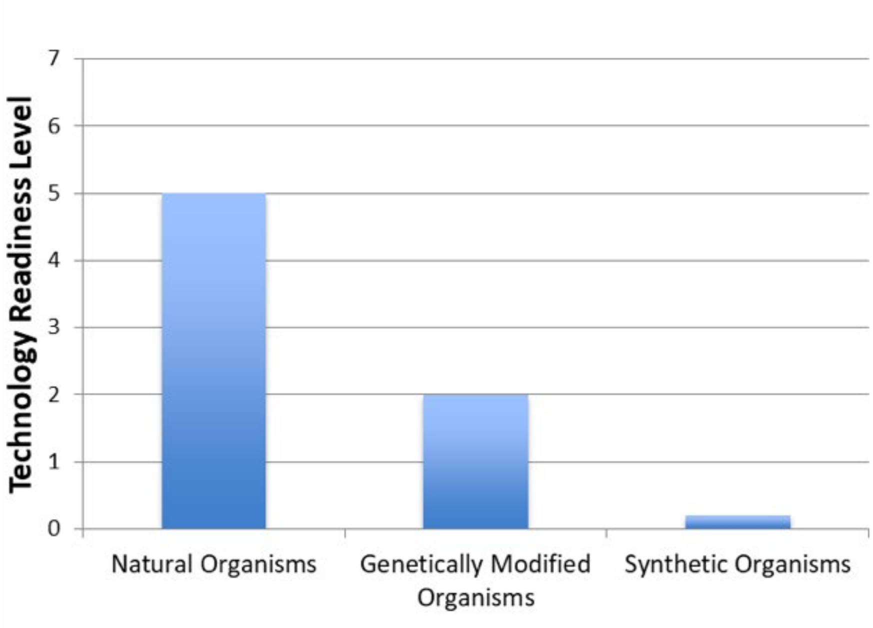

Figure 1: Comparison of the TRL of the most promising biotechnology research fields for the oil sands industry identified in the study.

Expected Progress

- Environmental Biotechnology (natural organisms) – bench testing is proceeding to investigate the potential for natural organisms to treat tailings pond water.
- Genetically Modified Organisms – far from commercial application; no projects are currently planned.
- Synthetic Biology – research applications are predominantly theoretical and academic; no projects are currently planned.

Impact on Industry

- Learnings from the environmental biotechnology research are now being applied to the COSIA Passive Organics Treatment Challenge, to enhance and accelerate the treatment of tailings pond water. Commercial deployment is possible within less than 5 years.

LESSONS LEARNED

The literature review did not identify any current commercial applications for biotechnology. However, initial work suggests that organisms that are naturally occurring in the environment could be cultured to enhance their ability to treat wastewater. COSIA continues to work with OPE to explore the application of environmental biotechnology using natural organisms to enhance the treatment of tailings pond water at the bench scale, which if successful, will proceed to field trials. This work may lead to accelerated treatment of tailings pond water and a reduction in the area required for treatment.

PRESENTATIONS AND PUBLICATIONS

No public presentations or publications.

RESEARCH TEAM AND COLLABORATORS

Institution: OPE Group

Principal Investigator: M. Martens

Name	Institution or Company	Degree or Job Title	Degree Start Date (Students Only)	Degree Completion Date (Students Only)
Mathijs Martens	OPE Group	MSc		
Paul Spelt	OPE Group	MSc		
Gerben Stouten	OPE Group	PhD		