

EVALUATION OF METALS RELEASE FROM OIL SANDS COKE: AN
ECOTOXICOLOGICAL ASSESSMENT OF RISK AND HAZARD TO AQUATIC
INVERTEBRATES

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By

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ABSTRACT

The oil sands operations in northeast Alberta, Canada, employ unconventional processes to produce synthetic crude oil (SCO). Because the extracted bitumen, ‘the form of oil in oil sands’, is highly viscous, it requires thermal upgrading to produce SCO. Coking technology is used to convert heavy bitumen fractions to lighter volatile fractions. During this process, an enormous volume of solid coke is produced and the metal impurities (e.g. Al, Fe, Mn, Ni, Ti and V) present in bitumen fractions end-up in the coke particles. As coke demands significant space for storage, oil sands companies are exploring options for placing coke into reclamation landscapes for long term storage and recovery. However, coke holds appreciable amounts of potentially leachable metals that may impede the performance of reclamation landscapes. Although two previous coke leaching studies had showed that coke released metals into water at concentrations exceeding the Canadian guidelines for the protection of aquatic life, the ecotoxicological hazard and risk of these metals were not well characterized. Therefore, the overall goal of this research was to characterize the fate and toxicity of metals associated with coke.

In this research, the toxicity of coke leachates collected from oil sands field sites and those artificially generated in the laboratory were evaluated using a standard three-brood *Ceriodaphnia dubia* tests. Coke leachates (CLs) collected over a period of 20 months from two field lysimeters were found to be acutely toxic to *C. dubia*. Vanadium concentrations were significantly higher ($p \leq 0.05$) than concentrations of all other metals in CLs from both lysimeters, and also in leachates from a laboratory batch renewal leaching study. Furthermore, toxic unit (TU) calculations suggested that Ni and V were likely the cause of CL toxicity, but this was not explicitly proven. Therefore, a chronic

toxicity identification and evaluation (TIE) approach was adopted to identify and confirm the cause(s) of CL toxicity. Coke was subjected to a 15 day batch leaching process in the laboratory at pH 5.5 and 9.5 in order to characterize the effect of pH on metals release from coke, and to generate CLs for use in TIE tests. The 7-day LC50 estimates for *C. dubia* survival were 6.3% and 28.7% (v/v) for CLs generated at pH 5.5 and 9.5, respectively. The dissolved concentrations of Mn, Ni and Zn were high ($p \leq 0.05$) in pH 5.5 CL, whereas Al, Mo and V were high ($p \leq 0.05$) in pH 9.5 CL. Evidence gathered from a series of chronic TIE tests revealed that Ni and V were the cause of toxicity in pH 5.5 CL, whereas V was the primary cause of toxicity in pH 9.5 CL. Further, the influence of bicarbonate, chloride and sulfate ions on metals release, speciation and Ni and V toxicity was investigated. The type and amount of metals released from coke was significantly influenced by the ion type elevated in the leaching solution. Specifically, sulfate influenced mobilization of Ni, Fe, Mn and Zn from coke, whereas bicarbonate enhanced Al, Mo and V releases from coke. With respect to toxicity, increasing bicarbonate decreased the 7-day Ni^{2+} IC50 from 6.3 to 2.3 $\mu\text{g Ni}^{2+}/\text{L}$ suggesting enhanced Ni toxicity at high pH or alkalinity. Conversely, sulfate showed a protective effect against V toxicity to *C. dubia*.

The research presented in this thesis suggests that coke will not be inert when stored in reclamation landscapes and that metals, particularly Ni and V, could reach ecotoxicologically relevant levels in surface waters or substrate porewaters, under favourable leaching conditions. Operationally, efforts should focus on remediation and monitoring of metals released from coke, particularly Ni and V, in impacted wetlands, especially before discharging water into natural wetlands and/or local streams and rivers.

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DEDICATION

To the most wonderful people in my life

Amma, Bava and Guddu

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LIST OF ABBREVIATIONS

| | |
|---------------|--|
| ACS | American Chemical Society |
| AEUB | Alberta Energy and Utilities Board |
| ANOVA | Analysis of variance |
| AR | Anion resin |
| bbbl | billion barrels |
| BDL | Below detection limit |
| C | Celsius |
| CC | Coke cell |
| CC | Cold coke |
| CL | Coke leachate |
| cm | centimeter |
| CR | Cation resin |
| CWQG | Canadian Water Quality Guideline |
| d | days |
| DMG | Dimethyl glyoxime |
| DO | Dissolved oxygen |
| DOC | Dissolved organic carbon |
| EDTA | Ethylenediaminetetraacetic acid |
| ERCB | Energy Resources Conservation Board |
| g | grams |
| HRW | Hard reconstituted water |
| IC50 | Inhibition concentration |
| ICP-MS | Inductively coupled plasma mass spectrometer |
| K_{BL} | Biotic ligand affinity constant |
| kg | kilogram |
| km | kilometer |
| LC50 | Median lethal concentration |
| m | meter |
| μg | microgram |
| μm | micro meters |
| μM | micromolar |
| μS | micro Siemens |
| MFT | Mature fine tailing |
| mg | milligram |
| MHRW | Moderately hard reconstituted water |
| MJ | megajoules |
| MLSB | Mildred Lake Settling Basin |
| MOPS | Morpholinepropane sulfonic acid |
| <i>n</i> | number of replicate |
| Ni | Nickel |
| NMCP | North Mine Centre Pond |
| OSPW | Oil sand process water |
| <i>p</i> | probability |

| | |
|----------|--|
| PAH | Polycyclic aromatic hydrocarbon |
| PC | Product coke |
| pKa | Acid dissociation constant |
| PLF | Potential leachable fraction |
| ppb | parts per billion |
| ppm | parts per million |
| <i>r</i> | correlation of coefficient |
| SCO | Synthetic crude oil |
| SD | Standard deviation |
| SE | Standard error |
| SLRS | Standard reference material |
| SPE | Solid phase extraction |
| SRC | Saskatchewan Research Council |
| STS | Sodium thiosulfate |
| SWSD | Shallow Wetland South Ditch |
| TIE | Toxicity identification and evaluation |
| TOC | Total organic carbon |
| TU | Toxic unit |
| V | Vanadium |
| v/v | volume by volume |
| wt. | Weight |
| YCT | Yeast, cerophyll and trout-chow |

1. INTRODUCTION

1.1 Background

The oil sands deposits in north-eastern Alberta, Canada, represent the largest accumulation of bitumen resource in the world. Unconventional processes such as hot water extraction and thermal upgrading are employed by oil sands mining companies to produce synthetic crude oil (SCO). Because bitumen, ‘the form of oil in oil sands’, is highly viscous and composed of a high percentage (approximately 50 wt. %) of non-volatile, high molecular weight and high carbon containing amorphous fractions like asphaltenes and resins, it requires thermal upgrading to produce SCO. Coking technology is commonly used in the thermal upgrading process to generate the high temperatures (550 to 625 °C) required to thermally crack these heavy hydrocarbon fractions to lighter volatile fractions. The objective of bitumen upgrading is to increase the hydrogen to carbon ratio by removing carbon from the bitumen fractions like asphaltenes. During this thermal process, asphaltene fractions undergo only partial degradation and the high molecular weight components (n-heptane and cyclohexane) polymerize and condense to form a solid, carbonaceous, heterogeneous substance termed *coke* (Speight, 1998, 1999). Further, metal impurities (e.g. Al, Fe, Ni, Ti and V) present in bitumen fractions are undesirable as they deactivate the reaction catalysts used in bitumen upgrading and thus decrease SCO yield (Speight, 1999; Furimsky, 2009). The concentrations of Al, Fe, Ni, Ti and V in the asphaltene fractions are reported to be 640, 4000, 210, 1400 and 820 ppm, respectively (Zhao et al. 2001). These metals are preferentially removed from bitumen fractions and thus get enriched in the coke particles.

Bitumen upgrading has a high propensity for coke formation (Speight, 1986). Syncrude Canada Ltd., the largest oil sands mining company in Alberta operating since the 1970s, has produced more than 20 million tonnes of coke over the last decade at an average 2.5 million tonnes per year (ERCB, 2009). The rate of coke production (~7000 tonnes/day in 2008) exceeds what can be combusted and/or sold resulting in an enormous on-site coke inventory. Moreover, coke is considered a potential energy source and regulations set by the Energy Resources Conservation Board (ERCB) require oil sands companies to store coke on-site for the purpose of energy resource conservation and possible future use. However, use of coke as an alternative fuel source in the present energy market is precluded due to its high transportation costs and the availability of cheaper energy sources such as coal (Scott and Fedorak, 2004). In addition, the high sulphur content (6-8% wt), low combustibility (Bejarano et al. 2003), high metals content, low volatile fractions (Furimsky, 2000), and increased green house gas emissions compared to natural gas (McKellar et al. 2010) currently make coke an undesirable alternative source of energy. As a result, Syncrude has accumulated an estimated 40 million tonnes of coke in their on-site inventory (ERCB, 2009). Thus, a growing coke inventory, zero-discharge regulation and limited space for on-site storage prompted oil sands companies to assess the feasibility of integrating coke into reclamation landscapes for long-term storage and possible later recovery.

1.2 Research rationale

Syncrude, as part of their land reclamation strategy, are reviewing options for integrating coke into terrestrial and/or wet reclamation landscapes for long-term storage and future recovery. At mine closure, a significant portion of the final landscape could have coke stored in wet reclamation landscapes (C. Qualizza, personal communication). The purpose of these

reclamation landscapes is to achieve maintenance-free, self sustaining ecosystems with capabilities equivalent to or better than pre-disturbance conditions (Golder Associates Ltd. 2000). However, the interaction of coke and its constituents with these landscapes, especially constructed wetlands, is not well understood. Because several metals get enriched in coke during bitumen upgrading, coke could be viewed as a potential source of metals in such landscapes. These metals may diffuse into the overlying water under favourable geochemical (e.g. red-ox, pH, weathering, salinity, etc.) and biological (e.g. bioturbation, bioleaching, etc.) conditions thus presenting an ecotoxicological risk to aquatic biota and possibly impeding the performance of reclamation landscapes.

Previously, it was believed that metals in coke are virtually non-leachable and as such do not pose any significant hazard to the environment or groundwater when stored in reclamation landscapes (Chung et al. 1996). However, recent studies have shown that coke has the potential to release certain metals at concentrations exceeding Canadian water quality guidelines for the protection of aquatic life (Squires, 2005; Kessler and Hendry, 2006). Further, when bare coke was used as a substrate for growing plants, it was found that plant roots accumulated significant amounts of Mo and V, but when coke was capped with a soil layer, accumulated root metal concentrations remained at baseline or control levels (Nakata et al. 2011). When colonization potential by aquatic invertebrates was tested *in situ* in coke amended wetlands, it was found that metal tolerant Chironomidae species dominated in coke substrates, whereas the abundance of metal sensitive Cyclopoida species decreased (Baker, 2007). In another study, coke was found to inhibit methanogenesis – a process vital for the biodegradation of organic acids in the tailings ponds (Fedorak and Coy, 2006).

While these research findings show that coke is not inert in the environment and does affect biological function, the causes of such effects were not explicitly identified. In other words, the hazardous substance(s) associated with coke was not identified. Furthermore, the fate, speciation, bioavailability and toxicity of metals released from coke under natural and representative environmental conditions were not well addressed. Therefore, the overall goal of this research was to evaluate the ecotoxicological hazard and risk of metals released from coke. This thesis presents a series of experiments that identified the hazards and characterized the risk of metals using a model aquatic invertebrate, *Ceriodaphnia dubia*.

1.3 *Ceriodaphnia dubia* as a test species

An important aspect of risk assessment is to integrate the knowledge of exposure and effects assessment data in order to describe or estimate the risk (Suter et al. 2000). Toxicity testing integrates exposure and effects assessment data to establish a cause-effect relationship. This further guides the risk management process that generally includes reclamation and/or remediation of contaminated sites. Sensitive test species are often the choice of most hazard assessment studies. This is because if toxicity is noticeable in sensitive single-species tests, then the results are often good predictors of aquatic community level impacts (de Vlaming and Norberg-King, 1999; de Vlaming et al. 2000).

In the present research, *Ceriodaphnia dubia* was used for toxicity testing of coke leachates and also for the purpose of identifying the cause of coke leachate toxicity. A sensitive freshwater species was used because in previous coke research it was observed that trace metals released from coke had no measureable effect on larvae of *Chironomous dilutus* (a benthic invertebrate), despite the release of certain metals (Cu, Mn, Mo, Ni and V) from coke at

toxicologically relevant levels (Squires, 2005). Possible reasons for this observation could be the use of a test species that is generally known to be relatively tolerant to metal exposure and/or that the metals released from coke were not in bioavailable form. Therefore, to test whether the metals released from coke are bioavailable and toxic, a more sensitive species, *C. dubia*, was used in the present research.

Ceriodaphnia dubia is a freshwater microcrustacean species that belongs to the family Daphniidae. This species is ubiquitous in temperate freshwaters and their distribution is abundant in lakes, ponds, streams and rivers throughout North America (Environment Canada, 2007). It is one of the most commonly used species for toxicity testing of effluents, leachates, and individual contaminants. Advantages of using *C. dubia* as a test species is briefly described below.

- i. *Ecology*: their distribution is ubiquitous and abundant which makes them an important component of the diet of many larger freshwater species. Thus, they occupy an important link in the aquatic food web.
- ii. *Life-cycle*: their short life cycle is particularly advantageous in maintaining cultures in the laboratories for the continuous supply of neonates which allows for high-throughput toxicity testing.
- iii. *Toxicity testing*: a three-brood test can be completed in 7 or 8 days and the effect on sensitive endpoint such as reproduction can be assessed within this short exposure duration. Further, these organisms are routinely used in developing water quality guidelines.
- iv. *Sensitivity*: *C. dubia* is sensitive to several contaminants including metals even at low, environmentally relevant exposure levels.

- v. *Maintenance*: these organisms are easy to maintain in the laboratory and toxicity testing is cost-effective.

1.4 Thesis organization

This thesis contains a series of three manuscripts that have either been published or have been submitted for publication in peer reviewed scientific journals. Some repetition of introductory or methodological material is therefore unavoidable.

The thesis is presented in seven chapters, including the Introduction. Chapter 2 presents the research hypothesis, objectives, and a synthesis section that links the appendix chapters to rest of the thesis. Chapter 3 provides review of literature relevant to oil sands operations, coke production and reclamation practices, metals release from coke, toxicity of coke, and the fate and toxicity of metals of concern associated with coke. Chapters 4, 5 and 6 are research chapters and are presented in chronological order (as performed). A preface at the outset of each chapter provides an overview of the chapter and its context to the thesis. Chapter 7 presents the general discussion which integrates the research chapters and also links the observations made in these chapters and the appendix chapters. Conclusions, recommendations for coke reclamation and future research perspectives are presented in Chapter 7.

2. RESEARCH HYPOTHESIS AND OBJECTIVES

2.1 Hypothesis

The overall null hypothesis of this research was as follows:

Ho: *The metals released from coke under natural and representative environmental conditions are not bioavailable and thus not toxic to freshwater invertebrates.*

2.2 Objectives

To test this hypothesis, the following experimental objectives were designed:

- i. To evaluate the toxicity of coke leachate samples collected from several oil sand field locations and correlate toxicity responses with contaminant concentrations in the leachates.
- ii. To characterize, identify and confirm the cause(s) of toxicity of experimentally created coke leachates.
- iii. To determine the influence of inorganic ions on metals release from coke, assess the influence of inorganic ions on chronic toxicity of Ni and V, and examine the mixture toxicity of Ni and V.

2.3 Relation of appendix chapters to thesis

The research chapters presented in this thesis provide information about the fate and toxicity of metals released from coke. For coke stored in wetlands, the release of metals associated with coke into porewater and surface water depends on several biogeochemical (e.g. pH, red-ox, weathering, bioturbation, etc.) parameters. Further, under certain environmental

conditions metals released from coke could reach ecotoxicologically significant levels in the surface water. Therefore, to understand the ecotoxicological risk of storing coke in wet reclamation landscapes, it was important to evaluate the fate and toxicity of contaminants release from coke exposed to natural weathering conditions. Further, because coke comes in contact with oil sands process wastes (e.g. recycled process water, tailings) it was important to rule-out the confounding effects of these materials on coke leachate toxicity. Therefore, coke leaching studies were conducted in the laboratory using fresh coke that had no history of contact with oil sands process wastes under representative environmental conditions to help identify the toxicants associated with coke.

For coke stored in wetlands, a hypothetical scenario would be that metals associated with coke would diffuse into porewater spaces and/or overlying water column under certain environmental conditions. While the studies presented in Chapter 4, 5 and 6 evaluated the toxicity of coke leachates where coke was exposed to natural weathering or simulated leaching conditions in the laboratory, they did not assess the fate of contaminant release from coke an *in situ* wet reclamation set-up. It was hypothesized that metals present in coke porewaters would diffuse into the surface water under certain environmental conditions. Therefore, metals concentration in coke porewaters placed in a natural wetland with other reclamation covers was assessed using *in situ* porewater sampling devices such as the peepers. Thus, this study presented in Appendix A compares and contrasts how different metal contaminants behave under reclamation set-up exposed to natural field conditions and to coke subjected to leaching in the laboratory.

To optimize the duration for laboratory batch coke leaching experiments, preliminary coke leaching experiments were conducted to evaluate the kinetics of metals release from coke.

Time taken for metal concentrations to reach equilibrium between porewater and overlying water was chosen as the standard duration for coke leaching experiments presented in Chapters 5 and 6. The findings of this study are presented in Appendix B. One of the objectives of this study was to generate coke leachates that could be used to evaluate toxicity and also perform toxicity identification and evaluation experiments. However, because coke leachate volume was not sufficient to complete the full series of TIE tests another separate coke leaching study was initiated to complete the full TIE test series. This study is presented in Chapter 5. The findings from the two studies could be used to compare metal concentrations released from coke.

3. LITERATURE REVIEW

3.1 Oil sands deposits

The province of Alberta in western Canada is blessed with plentiful supply of different forms of non-renewable energy reserves including oil sands, conventional crude oil, natural gas and coal. Among these resources, the vast oil sands deposits in the northeastern part of the province show great promise to meet the future demand for fuel (ERCB, 2010). Including Alberta, the seven oil sand reserves in the world constitute about 98% of the world's heavy-oil reserves. Nearly 91% of the total world oil sand reserves are concentrated in Alberta, Canada, and Venezuela (Demaison, 1977). At present, oil sands deposits in Canada and Venezuela are being actively developed using unconventional methods for the production of crude oil.

Oil sands deposits in Alberta represent the largest accumulation of heavy hydrocarbons (i.e. bitumen) in the world. This deposit is spread across a total area of 142, 000 km² and is divided into three geologic regions including (i) Athabasca-Wabasca (ii) Peace River and (iii) Cold Lake deposits. Collectively, the Alberta oil sand resource is estimated to contain as much as 1.7 trillion barrels of bitumen of which nearly 170 billion barrels are estimated to be recoverable with existing technology (ERCB, 2010).

Currently, active development is concentrated in the Athabasca oil sands area north of Fort McMurray (Fig. 3.1). Oil sands deposits in the Athabasca oil sands area have an overburden thickness of less than 75 m and are thus suitable for recovery using surface mining techniques. Nearly 4, 200 km² of the Athabasca oil sands reserve is designated as a surface mineable area (Fig. 3.1). Oil sands companies have so far mined an area of 602 km² thus showing potential for more active development in the Athabasca oil sands reserve (Fig. 3.1).



Figure 3.1. Oil sands resource in Alberta

Source: Government of Alberta, 2009 (Reproduced with permission)

3.2 Oil sands operations

Oil sands, also called *tar sands* or *heavy oil*, is a mixture of oil, water and sand (clay particles). The key component of this mixture is *bitumen* which is a highly viscous, carbon rich hydrocarbon deposit. Bitumen is comprised of a complex mixtures of organic molecules ranging from simple methane to high molecular weight asphaltenes, containing carbon, sulfur, oxygen, nitrogen and organometals called porphyrins particularly nickel and vanadium (Strausz, 1977; Speight, 2001). The occurrence of bitumen in association with fine solids, its highly viscous

nature and complex chemical composition makes it un-suitable for use in conventional recovery and distillation processes. Instead, unconventional processes such as surface or open pit mining, *hot water* extraction and thermal upgrading are being used to obtain oil sands from the earth, separate bitumen from fine solids and upgrade bitumen to yield synthetic crude oil that is suitable for further refining. Oil sands operations are the largest earth excavation operations in the world (Mossop, 1980). These operations employ large industrial machineries, demand large volumes of freshwater and significantly change the environment. Individual oil sands mine sizes range from 150 to 200 km² (National Energy Board, 2006) which significantly alters the boreal landscape. Suncor Energy Inc. and Syncrude Canada Ltd., the two largest oil sands mining companies in Canada, have been actively mining the Athabasca oil sands deposit for more than 40 years. These deposits undergo three major operational processes (i.e. surface mining, extraction and upgrading) to produce commercial grade synthetic crude oil product (see Fig. 3.2).

3.2.1 Surface mining

Surface or open pit mining is economically feasible for recovering oil sands deposits that lie below 75 m or less of overburden material. A deposit that is deeper than 75 m or more is recovered using in situ mining technologies (e.g. steam assisted gravity drainage). In surface mining, vegetation cover (e.g. forests) is removed first to make way for earth excavation. Power shovels and large trucks assist in earth excavation which involves removing water-soaked muskeg and the overburden soil layer. Removing the overburden layer exposes the underlying oil sand deposit which are subsequently dug up and piled into huge trucks and sent to feeders and crushers where uniform grained sand particles are prepared and then sent to extraction units.

3.2.2 Extraction

The average composition of the mined oil sand is 10 % bitumen, 5 % water and 85 % solids, such as sand and clay particles. The primary objective of the extraction process is to separate the bitumen from the solids. This is achieved using a *hot water* extraction technique first developed by Dr. Karl Clark, who used a combination of hot water, steam and caustic to separate bitumen from the sand (FTFC, 1995). Mined oil sand along with hot water and caustic are fed into large rotating tumblers to form a slurry. This slurry mixture is then heated using steam and aerated which results in froth production. In the primary and secondary separation vessels, bitumen is separated as a froth which floats to the surface and the coarse sand that settles to the bottom are removed (FTFC, 1995). Surfactants such as naphtha are used in the froth treatment to decrease the froth thickness and viscosity which aids in the separation of bitumen from the fine clay solids. The rejects from the extraction unit are termed *tailings* which are a warm aqueous suspension of sand, silt, clay, residual bitumen and naphtha at a pH between 8 and 9 (FTFC, 1995). These tailings are pumped into large tailings settling ponds to aid in the separation of fine solids from the coarse sand and silts (Fig. 3.2).

3.2.3 Upgrading

Recovered bitumen is highly viscous, deficient in hydrogen, and contains impurities such as sulfur, nitrogen and metals particularly, nickel and vanadium. Thus, bitumen requires upgrading in order to produce synthetic crude oil that is suitable for use in refineries. Upgrading is the most complex process in oil sands operations and typically involves primary and secondary upgrading processes. In primary upgrading, also classified as the carbon-rejection or hydrogen-addition process, bitumen is heated at elevated temperatures using coking technology to reduce

bitumen viscosity and remove impurities such as metals and mineral content (AOSTRA, 1991). These impurities get enriched in coke which is an un-desired by-product of thermal upgrading of bitumen. Coke is removed from the upgrading units and stored on-site in large coke silos or cells (Fig. 3.2). Primary upgrading products require further processing to make it a suitable feedstock for refineries. This is achieved via catalytic hydro-processing in the secondary upgrading units to produce synthetic crude oil (SCO) that is shipped in pipelines to refineries to produce consumer products (e.g. diesel, fuel, kerosene).

3.2.4 Waste disposal

The oil sands operations continuously generate tailings, coke and sulfur as major waste products that are stockpiled on site owing to a zero discharge regulation (Fig. 3.2). A brief description of the composition, type and disposal of tailings is given here. Coke disposal practice at Syncrude is described later under the Oil Sands Coke section.

3.2.4.1 Tailings

The oil sands extraction process requires large volumes of water which eventually results in the production of large volumes of waste tailings (MacKinnon, 1989). Tailings are chiefly composed of process water, solids and unrecovered bitumen (Fig. 3.2). Depending on the size of the solid particles tailings can be grouped under two main types:

- i) *Coarse tailings* – these are uniform sand particles with a median grain size of 150 μm .

The coarse solids settle out to form dykes and beaches in the tailings pond (FTFC, 1995).

ii) *Fine tailings* – these are predominantly clay particles with particle size ranging between 0.05 to 45 μm . Fine tailings are about 85% water, 13% clay and 2% un-recovered bitumen, and have been found to be acutely toxic to fish (FTFC, 1995). The fine solids remain dispersed in water and undergo very slow settling. Consolidation of fine tailings to soft clay would take decades to centuries (List and Lord, 1997).

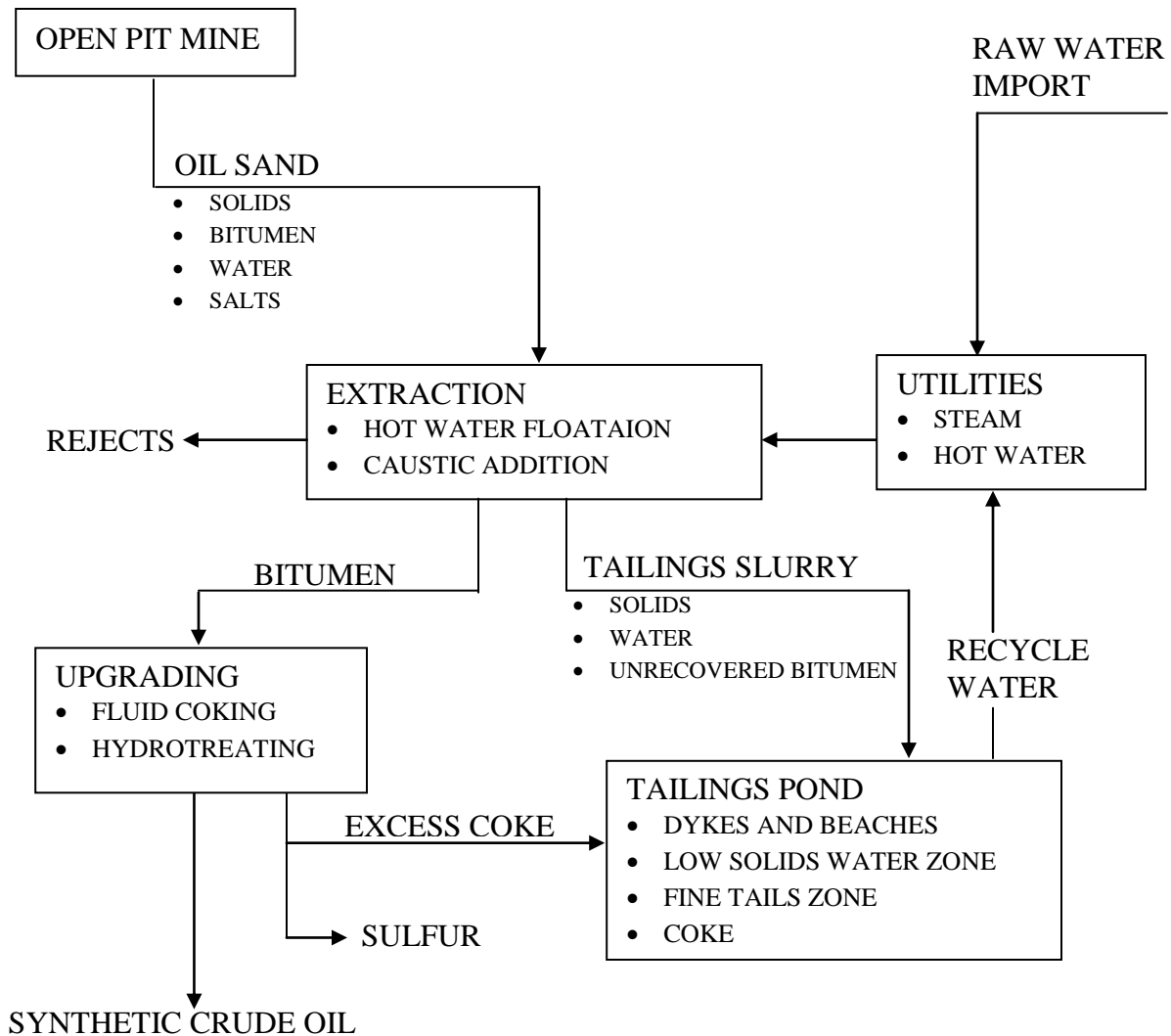


Figure 3.2. Generalized scheme of oil sands operations and waste disposal

Source: Modified from FTFC, 1995

At the Syncrude facility, tailings are disposed as slurry into the Mildred Lake Settling Basin (MLSB) which is a large tailings holding pond. The fine tailings consolidate over time to produce a dense mature fine tailing (MFT) leaving a large clarified water layer at the surface of the pond which is recovered and recycled as extraction process water (FTFC, 1995). Syncrude tailings pond water has an alkalinity of about 800 to 1000 mg/L HCO_3^- with a pH of 8.0 to 8.4; the total dissolved solids are dominated by sodium, bicarbonate, chloride and sulfate (Allen, 2008). The current tailings facilities in the Athabasca oil sands area covers about 130 km², which represents 22% of the 602 km² area disturbed by oil sands development (Alberta Environment, 2009). Thus, a significant portion of the oil sands disturbed landscape requires reclamation.

3.3 Oil sands coke

The sheer volume of coke produced during bitumen upgrading makes it one of the major oil sands process wastes that await integration into reclamation landscapes. Because reclamation landscapes are perceived to be self sustaining it is necessary that the interaction of coke with the environment is well understood. To this end, a brief review of literature on coke production, its interaction with the environment and the contaminants associated with coke is presented in the following sections.

3.3.1 Coke production

Bitumen is chiefly composed of four fractions namely saturates, aromatics, resins and asphaltenes. The asphaltene fractions of bitumen which are non-volatile, high molecular weight, high carbon containing amorphous substances are the primary precursors of coke formation. A major portion of oil sands bitumen are composed of asphaltene (~50 wt. %) fractions that cannot

be easily distilled (Gray, 2002). Thus, thermal upgrading of bitumen is necessary to convert heavy hydrocarbons to lighter crude oils to make it a suitable feedstock for downstream refineries. During bitumen upgrading, asphaltene fractions undergo only partial degradation and the high molecular weight components (n-heptane and cyclohexane) polymerize and condense to form solid coke (Speight, 1998). Thus, bitumen upgrading is regarded to have a high propensity for coke formation (Speight, 1986).

Coking technology is employed in thermal cracking of heavy bitumen fractions to obtain lighter hydrocarbons. The primary purpose of coking technology in bitumen upgrading is to provide a sufficient and continuous supply of heat required for thermal cracking of bitumen residue fractions into distillable lighter crudes (Furmisky, 2009). Chiefly, this is a carbon-rejection process in which carbon rejected from bitumen ends up as solid coke. In addition, undesirable bitumen impurities such as metals (e.g. Ni and V), sulfur and mineral matter are removed and get enriched with coke.

3.3.2 Fluid coking process

Syncrude employs a fluid coking process for the conversion of heavy bitumen into lighter fractions. Fluid coking chiefly consists of a burner vessel, a reactor vessel (coker unit) and a fractionation unit (Fig. 3.3). In the burner vessel, coke is combusted with air under O_2 starved condition in order to increase the temperatures of the coke particles to about $625\text{ }^\circ\text{C}$ (Furmisky, 2000). Hot coke is then circulated to the reactor vessel where it is maintained in a fluidized condition and hence the name fluid coking process (Fig. 3.3) (Scott and Fedorak, 2004). The fluidized coke bed supplies continuous heat required for thermal degradation of heavy bitumen fractions and also serves as the reaction sites for cracking of the residual to lighter fractions

(Rana et al. 2007). Inside the reactor vessel, highly dispersed bitumen feed is sprayed onto fluidized coke bed which is maintained at a temperature of 480 to 550 °C (Furmisky, 2000). Upon contact with hot coke, bitumen fractions undergo thermal degradation on reactive coke particle surfaces yielding distillable products, light gas and solid coke as the waste by-product (Gray, 2002). Distillable products and light gas pass through a cyclone scrubber which aids in the removal of fine grained coke particles trapped in the distillate products. The distillable products are further treated in fractionators to produce various crude oil fractions (e.g. naphtha, gasoline) that are now ready for transport in pipelines for downstream processing in refineries. Excess coke build up in reactor vessels is removed (called product coke (PC)) and then hydro-transported as a slurry mixed with recycled process water to storage facilities (Fig. 3.3). About 20% of cold coke (CC) from the reactor vessel is re-circulated back to the burner vessel for combustion and then sent back to the reactor vessel to supply heat and to act as a reactive surface site (Fig. 3.3). This process is continuous and coke production is an un-avoidable outcome of bitumen thermal upgrading. As of 2008, the on-site coke inventory of the Syncrude Mildred Lake operations is estimated to be more than 40 million tonnes (ERCB, 2009). Further, based on the current coke production rates (i.e. 2 million tones/year) the lifetime production of coke from oil sands operations is projected to reach nearly 1 billion m³ (Fedorak and Coy, 2006).

3.3.3 Properties of coke

Coke is a solid, carbonaceous, heterogeneous substance formed as the by-product of thermal upgrading of bitumen. The color varies from gray to black and it is insoluble in organic solvents (Speight, 1999). Syncrude fluid coke appears as a non-agglomerating, free flowing solid

because of their uniform size and spherical shape (Table 3.1) (Scott and Fedorak, 2004). This property of the coke makes it suitable for hydro-transport in pipelines to storage sites.

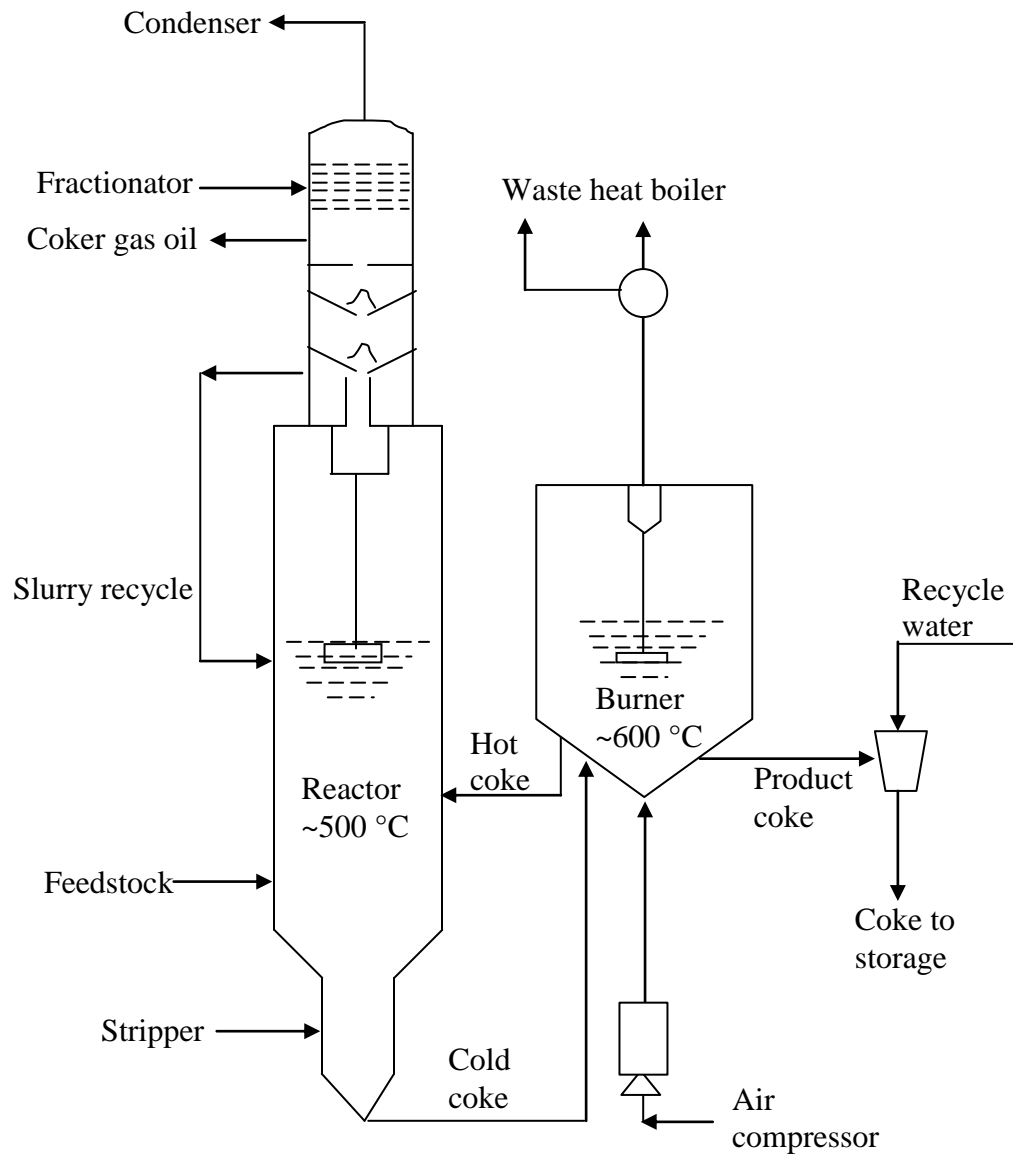


Figure 3.3. Simplified schematics of fluid coking process

Source: Modified from Furimsky, 2000.

Coke is chiefly comprised of inorganic carbon (~83 wt. %) which is the rejected carbon from asphaltene fractions during bitumen upgrading. Metal impurities such as Al, Fe, Ti, Ni and V present in bitumen are un-wanted and are expelled during bitumen upgrading and thus get enriched in the coke (Table 3.1).

Table 3.1. Physico-chemical properties of Syncrude coke

| Characteristic | Syncrude Coke |
|--|------------------------------------|
| <u>Physical properties^a</u> | |
| <i>Particle characteristics</i> | |
| Size | Uniform – medium to fine sand size |
| Shape | Round spheres |
| Structure | Onion-like layers |
| Surface area (m ² /g) | 10.7 to 12.2 |
| Mean particle diameter ^b (µm) | 170-240 |
| Particle density ^b (g/cm ³) | 1.52 |
| <u>Chemical properties^c</u> | |
| <i>Proximate analysis (wt. %)</i> | |
| Fixed carbon | 90.48 |
| Volatile | 3.93 |
| Ash | 0.31 |
| Moisture | 5.28 |
| <i>Ultimate analysis (wt. %)</i> | |
| Carbon | 82.28 |
| Hydrogen | 1.74 |
| Oxygen | 1.41 |
| Nitrogen | 1.83 |
| Sulfur | 5.32 |
| <i>Ash analysis (wt. %)</i> | |
| SiO ₂ | 23.6 |
| Al ₂ O ₃ | 9.4 |
| TiO ₂ | 0.4 |
| Fe ₂ O ₃ | 31.6 |
| NiO | 2.9 |
| V ₂ O ₅ | 19.7 |

^a Komex International Ltd. 1998.

^b Furmisky, 2000.

^c Bryers, 1995.

3.3.4 Commercial uses of coke

At present there is no commercial use for coke. The vast majority of coke produced is being stockpiled for future recovery and use because coke holds potential use as a future alternative energy source and regulations set by the Energy Resources Conservation Board (ERCB of Alberta) require oil sands companies to store coke on-site for the purpose of energy resource conservation. Coke is considered a potential “future” energy source because of its high heating value (29.5 MJ kg^{-1}) which is equivalent to the heating value of medium grade coal (Komex International Ltd., 1998). However, Coke is presently stockpiled because utilization of coke as an energy source is currently not economically feasible due to its high transportation cost and the availability of cheaper energy sources such as coal (Scott and Fedorak, 2004). Further, its high sulphur content (6-8 wt. %), low combustibility (Bejarno et al. 2003), high metal content, low volatile fractions (Furimsky, 2000) and high greenhouse gas emissions compared to natural gas (McKellar et al. 2010) currently make coke an undesirable source of energy.

While the use of coke as an energy source at present is limited, it has been found to be useful in tailings management and contaminant removal. Because the density of coke is low relative to high moisture fluid fines they are used as a low-density capping material to cover the fluid fines in the MLSB (Norwest Corporation, 2003). Further, the activated carbon derived from coke combustion has shown great potential for its use in contaminant removal. Coke derived activated carbon effectively removed significant amounts of color and chlorinated organics from pulp mill wastewater (Shawaa et al. 2001). More recently, use of coke directly without activation has been shown to remove naphthenic acids and vanadium from tailings pond waters (Zubot, 2010). Because naphthenic acids are known to be an acutely toxic component of the tailings water its removal from solution phase using coke would particularly benefit reclamation efforts.

3.3.5 Coke disposal

Thermal upgrading of bitumen generates large volumes of coke as a waste by-product and only a small portion of it (~20%) is retained for maintaining the temperatures in coker vessels. The rest is stockpiled on-site. In the last decade alone, Syncrude has stockpiled nearly 20 million tonnes of solid coke on-site at an average production of about 2 million tonnes every year (ERCB, 2009). In the past Syncrude used to store coke in mined out pits (i.e. coke cells) which was protected from overflow and leaching by dykes (impermeable soil structures) constructed from extraction rejects. However, with the increase in coke production, a growing coke inventory and limited space for storage has caused Syncrude to store coke in tailings ponds. At Syncrude, excess coke from coker drums are removed and are mixed with recycled process water to form a slurry and is then hydro-transported in pipelines to be deposited into the Mildred Lake Settling Basin (MLSB). Syncrude plans to stockpile coke at the MLSB for a few decades or until the basin reaches its full capacity (Scott and Fedorak, 2004). Eventually, this coke would become part of reclaimed landscapes that would have functional capabilities similar to pre-development landscapes.

3.4 Coke and the environment

The sheer volume of coke produced and the fact that it is stored exposed to the natural environment raises questions about its interaction with and impact on the natural environment. Because coke is energy-rich, high sulfur containing carbon material, initially there were concerns about the risk of coke undergoing spontaneous combustion, or combustion upon slow oxidation when stored exposed to the external environment. These concerns were subsequently investigated and it was found that coke was relatively stable and posed minimal risk of

combustion when stored in the environment (Scott and Fedorak, 2004). However, few studies have been performed in the past to evaluate the effects of coke on biota, possibly because coke was perceived to be an inert material. It was only in the recent past that oil sands industries started to assess the risks of storing coke in reclamation landscapes.

3.4.1 Coke reclamation

Because coke holds the potential for use as a future energy source, regulations set by the Alberta Energy Resources Conservation Board requires oil sands companies to store coke in such a manner that it can be recovered in the future. Integrating coke into reclamation landscapes would serve to comply with this regulation and also minimize the demand for storage space. Further, its sheer volume would make coke an integral part of the final reclamation landscape at mine closure. The main goal of these reclamation landscapes is to achieve maintenance-free, self-sustaining ecosystems with capabilities equivalent to or better than pre-disturbance conditions (Golder Associates Ltd. 2000). Both dry (i.e. terrestrial) and wet (i.e. aquatic) reclamation strategies are considered for long-term coke storage and recovery. The document describing the details of various options for integrating coke into final reclamation landscapes will be released by Syncrude in December 2011.

At Syncrude, the final reclaimed landscape is currently proposed to have three coke storage areas including coke cell 5, the Mildred Lake Settling Basin and the North Mine Centre Pond. Coke stored in coke cell 5 has been capped with soil (i.e. overburden material) overlain with a reclamation soil mixture that supports forest eco-sites (Scott and Fedorak, 2004). This strategy essentially forms the terrestrial reclamation practice. At present, coke is discharged into the Mildred Lake Settling Basin (MLSB) to cover mature fine tailings. Coke deposition will

continue along the west side of MLSB until approximately 2018 (ERCB, 2010). At completion of the Mildred Lake operation in 2018, the final volume of coke in the MLSB would be approximately 30.9 M m³. The North Mine Centre Pond (NMCP) will continue to receive coke produced after mine operations in the Mildred Lake facility nears completion (ERCB, 2010). The NMCP will include a combination of wet and dry reclamation landscapes. It will be filled with composite tailings and capped with coke, and a wetland created at the centre will receive drainage water from these deposits (C. Qualizza, personal communication). Eventually, drainage water from these three coke storage areas will be discharged into the Base Mine Lake or End Pit Lake. Wetlands would aid in remediation of contaminants released from coke and other oil sands process wastes. Integrating coke into wet reclamation landscapes is perceived to be a feasible option because coke is essentially carbon rich (~ 83 %) and as such could possibly support wetland ecosystem development. Thus, coke would become an integral part of the final reclamation landscapes, particularly the wet landscapes.

3.4.2 Coke contaminants

The source of metal contaminants in coke originates from the bitumen fractions (i.e. asphaltene) and bitumen solid impurities (clay particles). The asphaltene fraction, which is a precursor for coke formation, contains most of the metal impurities. For example, the concentrations of Al, Fe, Ni, Ti and V in the asphaltene fraction were found to be 640, 4000, 210, 1400 and 820 ppm, respectively (Zhao et al. 2001). In the bitumen complex, Al, Fe, Mn and Ti are primarily bound to inorganic impurities such as aluminosilicate clay particles, pyrite and TiO, while Ni and V are typically present as organometallic complexes called porphyrins (Zhao et al. 2001; Speight, 1999). Among these metal impurities, Ni and V bound as metalloporphyrins in the

asphaltene fraction are particularly undesirable as they deactivate the hydrotreatment catalysts and decrease the synthetic crude oil yield. Therefore, they are removed from bitumen and thus get enriched in coke (Furimsky, 2009). Organic contaminants such as the naphthenic acids are reported to be completely disintegrated at the high temperatures (~500 °C) used during the coking process and therefore are not associated with fluid coke (Schramm et al. 2000).

The sheer volume of coke produced, its high surface area and the loosely bound metal fractions in coke contribute to a sizeable amount of metal release from coke upon contact with water. Because several metals get enriched in coke during bitumen upgrading, coke could be viewed as a repository of trace metals when stored in wetlands. This issue has raised concerns about its suitability for use in reclamation landscapes particularly in wetlands. In a recent study it was reported that certain toxic metals (e.g. Ag, Cd, Pb, Hg, Ni and Zn) found in the Athabasca River near oil sands development exceeded the guidelines for the protection of aquatic life (Kelly et al. 2010). Upgrading of bitumen which involves coking, coke combustion and production of fly ash was believed to have contributed to the air-borne transport of these metals to the Athabasca River (Kelly et al. 2010).

3.4.3 Metals release from oil sands coke

Coke is viewed as a repository of several valuable metals (e.g. Fe, Ni, Ti and V) that could be suitable for extraction using hydrometallurgical procedures. These metals have the potential to generate secondary revenue and as a result several researchers have conducted leaching studies to recover metals from coke. For instance, fly ash derived from coke combustion was found to leach, under acidic conditions, significant amounts of Fe (5070 ppm), Ni (2488 ppm), Ti (500 ppm) and V (10750 ppm) (Jack et al. 1979). In another study, the potential for V

recovery from Suncor coke ash was found to be significantly higher than commercial grade V extraction from iron ores (Holloway and Estell, 2005). These studies tested metals release from coke under extreme leaching conditions suitable for metallurgical extraction, but such leaching conditions are not common when coke is exposed to the natural environment.

Previously, it was believed that trace metals in Syncrude coke were virtually non-leachable into the environment when stored in reclamation landscapes (Chung et al. 1996). However, more recently, two independent coke leaching studies showed that coke had the potential to release certain metals at concentrations exceeding Canadian guidelines for the protection of aquatic life (Squires, 2005; Kessler and Hendry, 2006). Squires (2005) investigated metal leachability from weathered Syncrude coke (i.e. coke cell 5) in a series of batch leaching tests and found that coke released certain metals (e.g. Al, Mn, Ni and V) at appreciable amounts immediately upon contact with water. Water chemistry, particularly pH, had a significant effect on the type and amount of metals released from the coke.

Both geochemical (e.g. sorption, weathering, red-ox, pH, ionic strength, etc.) and biological (e.g. red-ox, bioturbation, biosorption, etc.) factors could potentially influence the release of metals from coke stored in reclamation landscapes such as wetlands. In order to assess the effect of environmental variables on metals mobilization from coke, it is important to gain insight into the solid phase association of metals with various binding fractions (e.g. carbonates, oxides of Fe and Mn, sulphides, organic matter, and minerals) in solid coke. Generally, metals associated with carbonate minerals are bound by weak electrostatic forces. Consequently, these metals are easily mobilized via *ion exchange* mechanism by dominant ligands such as Na^+ , OH^- , H^+ , Mg^{2+} and Cl^- (Linge, 2008). Further, mild acidic conditions can enhance the mobility and bioavailability of metals bound to carbonate fractions, whereas strong acidic conditions could

result in the dissolution of metals bound to Fe oxides and sulphides (Linge, 2008). Conversely, metals complexed to organic matter undergo dissolution under oxidizing conditions (Filgueiras et al. 2002). Furthermore, alkaline pH and oxidizing conditions increases desorption of oxyanion metals (e.g. As, Cr, Mo and V) bound to organic matter because the binding sites become increasingly negative as pH increases thus enhancing the release of these metals (Langmuir et al. 2004). However, under the natural conditions existing in freshwater systems, metals are strongly bound to Fe and Mn oxides and organic matter. These metal fractions are not mobilized easily and hence are less bioavailable (Filgueiras et al. 2002). In deep lakes where sediments are generally in an anoxic and reducing state, metals may get entrapped in the crystal lattice during the mineralization process. Such metals are highly immobilized and are virtually non-bioavailable. Therefore, an understanding of the solid phase distribution of metals in coke is critical to assess and also predict the potential leachability and bioavailability of metals associated with coke.

Sequential extraction procedures are commonly used to describe the speciation of metals in solid samples such as soils and sediments. This approach provides useful information about a metals origin, mode of occurrence, biological and physicochemical availability, mobilization and transport, and also aids in the design of remediation process for contaminated sediments (Tessier et al. 1979; Filgueiras et al. 2002). Briefly, a soil or sediment sample is leached using a series of reagents (e.g. acetic acid, hydroxylammonium chloride, hydrogen peroxide, hydrofluoric acid) with increasing leaching strength that target specific metal binding phases (e.g. carbonates, oxides of Fe and Mn, sulphides, organic matter, and minerals). Metals mobilized by less reactive reagent are generally considered mobile and those mobilized by strong reactive reagents (e.g.

hydrogen peroxide) are generally considered highly immobilized and thus not available for uptake by aquatic biota.

To date, the sequential extraction experiment conducted by Kessler and Hendry (2006) is the only study that describes the solid phase distribution of metals in oil sands coke. Results revealed that several metals, including those that were previously identified as metals of concern (e.g. Al, Mn, Mo, Ni and V), were bound strongly to the coke matrix. For the metals of concern, more than 70% of their total metal content was present in the residual fraction (Table 3.2 and Fig. 3.4; Kessler and Hendry, 2006). Residual metal fractions are those that are mobilized only under aggressive leaching conditions (e.g. HNO₃ and HF digestion) and are considered virtually non-leachable and thus non-bioavailable under natural environmental conditions existing in coke reclaimed landscapes. Interestingly, the percentage of metals content in the residual fraction of aged and/or weathered (~10 years) coke was similar to freshly produced coke (Kessler and Hendry, 2006). This suggests that natural weathering of coke over a small geologic time scale of 10 years does not substantially alter the solid phase speciation of metals in coke. Therefore, metals release from coke which primarily occurs from the water soluble and/or carbonate bound fractions should decrease over time for coke stored in the external environment. This is because the water soluble (i.e. metals loosely bound to the coke surfaces) and carbonate bound fractions represent only a small fraction compared to other solid phase fractions (Table 3.2). Further, these metals fractions are reportedly desorbed immediately upon contact with water (Kessler and Hendry, 2006). Consequently, the water soluble and carbonate bound fractions hold particular relevance, at least in the short term, to the mobilization of metals from coke stored in reclamation landscapes such as wetlands. Although, the water soluble Mn, Mo and V fractions are small compared to their respective residual fractions (Table 3.2), the sheer volume and a higher surface

area of coke would mean that a significant amount of these metals would be released when coke comes in contact with water. Apart from their solid phase distribution, the aqueous speciation of metals is also important for understanding their leaching behaviors. For instance, using a cascade leaching test it was found that the rate of V release from coke was fastest compared to all other metals released from coke (Kessler and Hendry, 2006). Similarly, when coke was subjected to batch leaching under different pH conditions it was found that V reached peak concentration immediately upon coming in contact with water (Squires, 2005). This is because V has a strong tendency to associate with oxygen donor atoms, and its dissolution in aqueous solution increases with pH and oxygenation (Wherli and Stumm, 1989; Crans et al. 1998). Therefore, an understanding of aqueous speciation and solid phase distribution of metals associated with coke will provide critical information required to predict the leaching potential of metals from coke stored in final reclamation landscapes.

Table 3.2 Solid phase distribution of metals (% total concentration) in Syncrude fluid coke as determined using a sequential extraction scheme.

| Extractable fraction | Target solid phase | Al | Mn | Mo | Ni | V |
|-----------------------------|--------------------------|------|------|------|------|------|
| Water soluble | loosely bound to surface | 0.01 | 0.43 | 1.03 | 0.02 | 0.56 |
| Acid extractable | bound to carbonates | 0.26 | 0.79 | 0.06 | 0.19 | 0.17 |
| Reducible | bound to Fe-Mn oxides | 0.26 | 2.30 | 0.44 | 0.18 | 0.22 |
| Oxidizable | bound to organic matter | 16.8 | 20.7 | 24.3 | 22.9 | 15.5 |
| Residual | bound to matrix | 82.7 | 75.8 | 74.2 | 76.8 | 83.6 |
| Total concentration (mg/kg) | | 8467 | 266 | 87 | 549 | 1539 |

Source: Kessler and Hendry (2006).

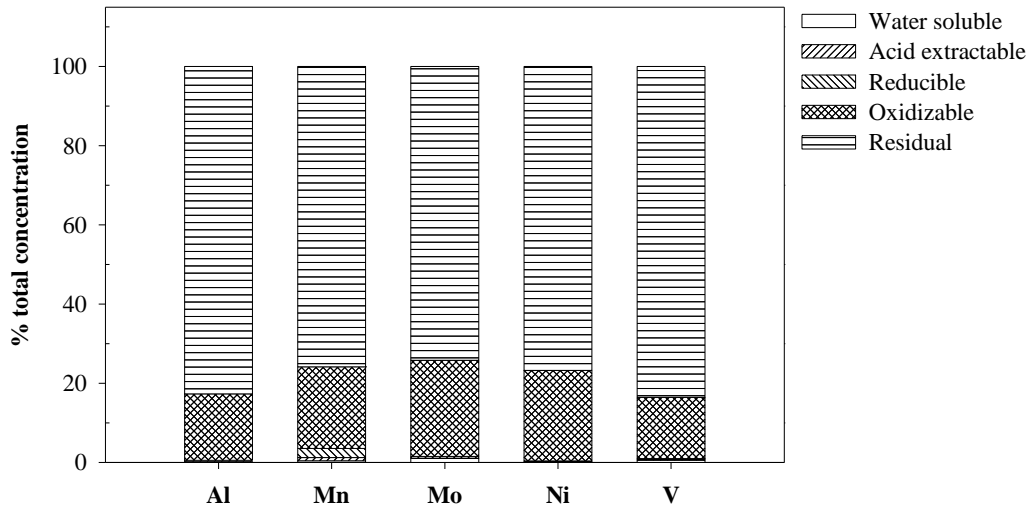


Figure 3.4 Distribution of metals of concern in Syncrude fluid coke in various ‘operationally’ defined solid phases (*Source: Kessler and Hendry, 2006*).

3.4.4 Toxicity of coke

To date, only four studies appear to have investigated the impact of coke and coke leachates on biota. Until now coke was believed to be inert when stored in the natural environment. Nakata et al. (2011) investigated the physiological response of two species of plants exposed to coke. It was found that plant roots accumulated significant amounts of Mo and V when grown in bare coke, but when coke was capped with a reclamation soil mixture accumulated root metal concentrations only reached baseline levels (Nakata et al. 2011). Further, when plants were grown in bare coke they suffered from water stress which was attributed to the physical composition of the coke (Nakata et al. 2011). In a separate field trial, Baker (2007) investigated the process of aquatic invertebrate colonization exposed *in situ* to coke substrates placed in a natural wetland that had no input of other oil sands process wastes. It was found that the invertebrate abundance decreased in coke substrate units compared to native sediment

substrate units. Further, it was observed that the invertebrate community colonizing Syncrude coke substrates had a predominance of metal tolerant Chironomidae species and a low abundance of sensitive invertebrates such as the Cyclopoida (Baker, 2007). While it was suggested that certain contaminants associated with coke could be responsible for the decline in abundance of sensitive invertebrate species, the toxicant(s) responsible for the observed effect was not identified. On the other hand, there was no significant effect on the survival and growth of benthic macroinvertebrate, *Chironomus dilutus*, when exposed to coke and its leachate, despite the fact that coke leached toxicologically significant levels of metals (Squires, 2005). The reason for the lack of toxic effects was hypothesized to be due to the use of a less sensitive test organism in the bioassays (compared to those used to develop the aquatic guideline) and/or that metals leached from coke were not present in a bioavailable form (Squires, 2005). In another study, coke was found to inhibit methanogenesis - a process vital for the bio-degradation of organic contaminants in the tailings ponds (Fedorak and Coy, 2006). While these research findings proved that coke is not inert in the environment and does affect biological function, the cause(s) of such effects was not explicitly identified.

3.5 Fate and toxicity of key metals

Nickel and vanadium have previously been identified as metals of concern in coke leachates obtained from natural weathering of coke and those generated in laboratory leaching experiments (e.g. Squires, 2005; Kessler and Hendry, 2006). Therefore, a brief description of the aqueous speciation, fate and toxicity of nickel and vanadium is provided.

3.5.1 Nickel

3.5.1.1 Speciation and environmental fate

Nickel is a *d*-block transition metal with an atomic number and weight of 28 and 58.68, respectively. It is the 9th most abundant metals in the earth's crust with an average soil concentration of 99 mg/kg (Langmuir et al. 2004). Nickel is a red-ox active element and generally exists in -1, 0, +1 and +2 oxidation states (Greenwood and Earnshaw, 1997). However, in aquatic systems the +2 oxidation state is the most dominant form and it forms stable complexes with both inorganic and organic ligands. Nickel is classified as a borderline acid that shows intermediate tendency to form bonds with –S, -N and –O electron donor groups which are abundant at the surfaces of biota (Nieboer et al. 1999; Langmuir et al 2004).

Fossil fuel combustion (e.g. coal and oil) accounts for a major source of Ni emissions to the environment (Pacyna and Pacyna, 2001). Dry and wet deposition, effluents from metal mining, smelters, refineries, electroplating, municipal waste incinerators, and natural bedrock weathering contribute to significant amounts of Ni to surface waters (Eisler, 1998). Environmental fate processes describe the relative distribution of contaminants among different environmental media and thus provide critical information regarding the aquo metal ion activity, bioavailability, toxicity, and transport. The fate of Ni in aquatic systems is largely controlled by physicochemical parameters including pH, red-ox potential, ionic strength, adsorption, chemisorption, precipitation, cation exchange capacity, and biosorption. In the absence of organic ligands (e.g. humic acids), Ni forms stable complexes with inorganic ligands in the order $\text{OH}^- > \text{SO}_4^{2-} > \text{Cl}^- > \text{NH}_3$, and the relative proportion of Ni-ligand complex increases with increasing levels of these ligands (Adriano, 2001). Under low pH conditions, high activity of H^+ displaces

cationic metals including Ni^{2+} by ligand exchange process from oxide and organic surfaces (Salomons and Forstner, 1984) which increases its mobility and bioavailability. Nickel sorption onto oxyhydroxides of Fe, Mn, aluminosilicate clays, and organic matter increases with increasing pH (McBride, 1994). Under the prevailing anoxic conditions in lake sediments, reduced Ni^{2+} forms insoluble complexes with sulphides thus greatly reducing its solubility and mobility.

3.5.1.2 Toxicity of nickel

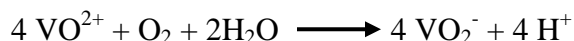
Nickel and its compounds are included in the priority substances list and are regulated under the Canadian Environment Protection Act (Hughes et al. 1994). At present, the Canadian Council of Ministers of the Environment (CCME) has included Ni on the priority list for development of water quality guidelines for the protection of aquatic life. Nickel compounds like Ni_3S_2 , NiS and NiO all generate reactive oxygen species resulting in acute Ni toxicity and carcinogenicity (Eisler, 1998). The essentiality of Ni to aquatic organisms is not completely established (Muyssen et al. 2004). However, recent observations on the down-regulation of gastrointestinal Ni uptake in rainbow trout upon pre-exposure to waterborne Ni has given indirect evidence for Ni essentiality in fish (Chowdhury et al. 2008). Nevertheless, the essentiality aspect of Ni in aquatic organisms is not fully understood. The mechanism of acute Ni toxicity differs between aquatic vertebrates and invertebrates. Acutely, Ni inhibits ion regulation, especially Mg^{2+} homeostasis, in *Daphnia magna*. In vertebrate species such as rainbow trout waterborne exposure to Ni depleted plasma O_2 and hemoglobin levels, thus acting as a respiratory toxicant (Pane et al. 2003; Pane et al. 2003). On the other hand, hardness cations (Ca and Mg) are known to inhibit waterborne Ni^{2+} uptake and thus protect against Ni toxicity in

daphnids (Deleebeeck et al. 2008). However, the influence of pH or alkalinity on Ni uptake and toxicity is not well understood (Deleebeeck et al. 2008; Kozlova et al. 2009). Thus, the Ni biotic ligand model (BLM) is not fully developed for many freshwater species.

3.5.2 Vanadium

3.5.2.1 Speciation and environmental fate

Vanadium is a *d*-block transition metal with an atomic number 23 and atomic weight of 50.9. It is the 7th most abundant metal in the earth's crust with an average soil concentration of 136 mg/kg (Langmuir et al. 2004). Vanadium occurs in +3, +4, +5 oxidation states, but V(V) is the most thermodynamically stable, mobile and dominant species in oxic waters. Its solubility in aqueous solution increases with its valance, pH and oxygenation (Wherli and Stumm, 1989; Crans et al. 1998). Under aerobic conditions, V(IV) is rapidly oxidized to V(V) according to the red-ox reaction shown here (Rehder, 1991).



In oxygenated surface waters, oxyanion species of V(V) (e.g. H_2VO_4^- and HVO_4^{2-}) dominate because of their strong tendency to associate with oxygen donor atoms (Crans et al. 1998; Crans et al. 2004). On the other hand, in acidic and reducing conditions, oxocation species of V(IV) (e.g. VO^{2+} and $\text{V}(\text{OH})_3^+$) are known to be thermodynamically stable (Wherli and Stumm, 1989).

Fossil fuel combustion (e.g. coal and oil) accounts for a major source of V emissions to the environment (Pacyna and Pacyna, 2001). Other anthropogenic sources of V input to surface waters include metallurgical, chemical, polymer, and petroleum processing industries. Because of their abundance in crude oils, V and Ni are commonly used as indicators of intentional or

unintentional crude oil spills and oil pollution. The environmental fate of V is strongly influenced by its red-ox behavior and other geochemical parameters including pH, Eh, precipitation/dissolution of V minerals, and sorption processes. Vanadium is a red-ox sensitive element, soluble under oxidizing conditions but precipitates or adsorbs under reducing conditions (Morford et al. 2005). Vanadium, especially the vanadyl cation (VO^{2+}), forms strong surface complexes with clay minerals, Al_2O_3 , Fe_2O_3 , TiO_2 and organic matter (Wherli and Stumm 1989; Peacock and Sherman, 2004). Therefore, oxidation of bound vanadyl oxocations could be viewed as a key process that controls V solubility and mobilization from soils or sediments.

3.5.2.2 Toxicity of vanadium

Vanadium is considered a possible essential metal for humans but certainly essential for other living organisms (Crans et al. 2004). The essentiality in humans is not completely established although V has shown great promises as an exogenic analogue for phosphorylation process owing to its structural and electronic similarities to phosphate (Rehder, 1991). Because of its similarity to phosphate, V regulates several metabolic processes by replacing phosphate groups in phosphorylated substrates and enzymes (e.g. NAD, ADP, GDP, glucose-6-phosphatae, Na/K-ATPase, Ca/Mg ATPase, alkaline phosphatases etc.) (Crans et al. 2004). Some marine phytoplanktons and ascidians are known to biologically regulate V. However, the biological role of V in freshwater organisms remains to be established (Watanabe et al. 1997).

Vanadium is not among the commonly observed or studied aquatic contaminants. Toxicity of V is governed by its oxidation state and generally the pentavalent V species (e.g. H_2VO_4^- and HVO_4^{2-}) are more toxic than V(IV) species (Barceloux, 1999; Mukherjee et al. 2004). In a study looking at the effect of water hardness and pH on V speciation and toxicity to

rainbow trout (*Oncorhynchus mykiss*), it was observed that V was less toxic at pH 5.5 and pH 6.6 when compared with pH 7.7. This difference in toxicity was attributed to the relative abundance of the more toxic vanadate (H_2VO_4^-) species (Stendahl and Sprague, 1982). In another study, V was found to be highly toxic relative to Se, Li, U and B to three species of endangered freshwater fish (Hamilton, 1995). Chronic exposure of leopard frogs to dietary V at environmentally relevant levels reduced larval growth rates, survival during metamorphosis and their capacity to store lipids in the form of energy (Rowe et al. 2009).

Mitochondria are the primary sites of V mediated toxic action in mammals and aquatic animals (Valko et al. 2005; Soares et al. 2007). Inorganic vanadate ions enter cells via anion transport pathways whereas the uptake of organically bound vanadyl complexes occurs by a simple diffusion process (Yang et al. 2003). Once inside the cell, V(V) is reduced to V(IV) by NADPH and the free vanadate species inhibits the electron transport system. This leads to the generation of reactive oxygen species inside mitochondria which subsequently results in cellular oxidative stress, DNA damage and cell death (Valko et al. 2005; Soares et al. 2007).

4. VARIATION IN TOXICITY RESPOSNE OF *CERIODAPHNIA DUBIA* TO ATHABASCA OIL SANDS COKE LEACHATES

Preface

The fate and toxicity of metals in oil sands coke exposed to natural weathering conditions is described in this chapter, including the influence of soil capping of coke on its leachate chemistry and toxicity. Considerations for soil capping of coke is a critical attribute of coke reclamation efforts as the cap layer may greatly retard metals transport or flux to the surrounding medium. From this research, it was found that the metals released from coke, especially Ni and V, were possible causes of leachate toxicity. However this study was not designed to specifically identify the cause(s) of leachate toxicity. In a subsequent study (chapter 5), therefore, coke leachate toxicants were identified explicitly. The influence of soil cover and process water chemistry on metals release from coke is briefly discussed here. A detailed description of this issue with respect to vanadium release from coke is given in chapter 7. The issue of process water chemistry was also addressed in a separate laboratory coke leaching experiment which is presented in chapter 6 and further discussed in chapter 7.

This chapter is published as a research article in the journal *Chemosphere*, 80: 489-497. The figures, tables and references cited in this article have been re-formatted here to thesis style. References cited in the text are listed in the reference section of this thesis (chapter 8).

4.1 Abstract

Coke from the Athabasca (Alberta, Canada) oil sands operations may someday be integrated into reclamation landscapes. It is hypothesized that the metals associated with the solid coke may leach into the surrounding environment. Therefore, the main objectives of this study were to characterize the toxicity and chemistry of coke leachates collected from two field lysimeters (i.e. shallow lysimeter and deep lysimeter) over a period of 20 months, as well as from other oil sands coke storage sites. In addition, a batch renewal leaching of coke was conducted to examine the rate of metals release. Chronic toxicity of key metals (e.g. Al, Mn, Ni and V) found in lysimeter coke leachate was evaluated separately. Toxicity test results revealed that whole coke leachates (100% v/v) were acutely toxic to *Ceriodaphnia dubia*; the 7-day LC50 values were always <25% v/v coke leachate. The deep lysimeter leachate was generally more toxic than the shallow lysimeter leachate, likely because of significantly higher concentrations of vanadium (V) found in the deep lysimeter leachate at all sampling times. Vanadium concentrations were higher than all other metals found in the leachate from both lysimeters, and in the batch renewal leaching study. Furthermore, V found in leachates collected from other oil sands field sites showed a concentration-response relationship with *C. dubia* survival. Mass balance calculations indicated that 94 to 98% of potentially leachable V fraction was still present in the coke from two field lysimeters. Evidence gathered from these assessments, including toxic unit (TU) calculations for the elements of concern, suggests that V was the likely cause of toxicity of the deep lysimeter leachate, whereas in the shallow lysimeter leachate both Ni and V could be responsible for the observed toxicity.

4.2 Introduction

The oil sands deposit in northeastern Alberta, Canada, holds the largest accumulation of bitumen resource in the world. The total volume of crude bitumen reserve in this deposit is estimated at $259.2 \times 10^9 \text{ m}^3$ with nearly $50 \times 10^9 \text{ m}^3$ (i.e. 315 billion barrels) considered potentially recoverable using existing technology (AEUB, 2002). Syncrude Canada Ltd. and Suncor Energy Inc. are the two major oil sands mining companies operating near Fort McMurray, Alberta. These two oil sands companies use surface mining methods in which earth is excavated to a depth of approximately 50-100 m to access the oil soaked sands. The mined oil sands are then mixed with hot water (79-93 °C) and caustic soda (sodium hydroxide) to extract bitumen from sand particles (Rogers et al. 2002). The extracted bitumen is then heated at elevated temperatures (approximately 500°C) through a complex process of coking and/or hydrocracking and catalytic hydrotreating that result in the production of synthetic crude oil with the formation of coke as the by-product (Scott and Fedorak, 2004). Coke is produced as a solid residue due to the removal of carbon from the heavy bitumen hydrocarbons (Bejarano et al. 2003). Based on the volume of bitumen processed, it is estimated that Syncrude and Suncor generated over 2 and 3 million tonnes of coke, respectively, in 2003. Further, the production of coke is projected to reach nearly 1 billion m^3 over the lifetime of the oil sands operations (Fedorak and Coy, 2006). Currently, the oil sands companies are stockpiling these vast amounts of coke because the regulations set by the Alberta Energy and Utilities Board (AEUB) require oil sands companies to store coke on-site for future recovery. Coke is considered a potential “future” energy source because of its high heating value ($\sim 29.5 \text{ MJ kg}^{-1}$) which is equivalent to the heating value of medium grade coal (Komex International Ltd. 1998). Coke is presently stockpiled because utilization of coke as an energy source is currently not economically feasible

due to its high transportation cost and the availability of cheaper sources of carbonaceous or asphaltenic materials (Scott and Fedorak, 2004). In addition, the properties of the coke, such as high sulfur content (6-8 % wt.) and low combustibility (Bejarano et al. 2003), makes it an undesirable energy source. Syncrude and Suncor thus stockpile the majority of their coke on site in large containment cells or coke piles which are exposed to the natural environment.

Some oil sands companies have been considering the integration of coke into terrestrial and aquatic landscapes as part of their closure plans and for long term storage and future recovery of the coke. Although, the aquatic reclamation option is under review, the oil sands companies have started to ascertain the possible effects of coke and its leachate on aquatic biota. As part of the scientific assessment of the feasibility of storing coke in reclamation landscapes, small instrumented watersheds were established in 2001 on coke field sites at both Syncrude and Suncor. A key component of the watershed monitoring instrumentation is large circular tank lysimeters installed in the reclaimed coke watersheds at each of the mine sites. The tank lysimeters permit collection of leachate water for assessment of water balance and determination of any toxicity associated with the coke leachate.

Certain metals (e.g. nickel and vanadium) that are complexed with petroleum porphyrins in bitumen end up in coke during the upgrading process (Har, 1981). Most recently, it was shown that oil sands coke has the potential to release metals at concentrations exceeding Canadian guidelines for the protection of aquatic life (Squires, 2005; Kessler and Hendry, 2006). Also, plants grown in coke over the long term suffered from water stress that was attributed to the physical composition of the coke (Nakata, 2007), and the use of coke as a substrate in a methanogenic bioassay showed that coke inhibited methane production (Fedorak and Coy, 2006). However, no studies had been conducted to assess the chronic toxicity of coke leachates

collected from various oil sands field sites and whether the potential toxicity of coke leachates changed over time (e.g. some natural environmental factors such as rainfall, freezing and drought might influence the release of trace metals from coke).

Therefore, the objectives of the studies described here were to assess the temporal variation in toxicity response, using the model aquatic invertebrate *Ceriodaphnia dubia*, of coke leachates collected at various times from two experimental tank lysimeters and from other oil sands coke storage sites, and to evaluate using the toxic unit (TU) approach the relative contributions of key metals released from coke to the coke leachate toxicity. In addition, a batch renewal leaching study was performed to determine the leaching rates of various metals released from coke.

4.3 Materials and methods

4.3.1 Tank lysimeters

In order to evaluate the field performance of reclamation soil layers capped over coke, two tank lysimeters were installed during September 2003 in a coke deposit located near the southeast shore of the Mildred Lake Settling Basin (MLSB) situated on the Syncrude Canada Ltd lease. Lysimeter installation was planned, designed and executed by O' Kane Consultants Inc of Calgary, AB, Canada. The circular tank lysimeters are made of prefabricated plastic with a diameter of 2.44 m and a height of 2.5 m (Fig. 4.1). Coke was excavated to a depth of approximately 2.5 m in the coke deposit and the lysimeters were placed into the excavated region and backfilled using the same coke. Conditions inside the tank lysimeters were carefully monitored during coke backfilling to create a profile that was as similar to outside the lysimeter

as possible. Inside each lysimeter there was a 2.5 m coke layer at the bottom overlain by two different depths of reclamation soil cover. The shallow lysimeter had an approximately 35 cm layer of glacial till overlain by a 15 cm peat mineral topsoil layer, for a total of approximately 50 cm of soil cover. The deep lysimeter had an approximately 80 cm layer of glacial till overlain by a 15 cm peat layer, for a total of approximately 1 m of soil cover (Fig. 4.1). Therefore, the ‘shallow’ and ‘deep’ nomenclature used to describe the two lysimeters refers to the two different soil cover depths on top of the coke layer and not to differing depths of coke or lysimeter installation. Each lysimeter was installed with a piezometer for the purpose of leachate collection and water level measurement. Also, in situ monitoring instruments were installed for the purpose of monitoring (by other research groups) changes in moisture storage and O₂/CO₂ gas concentrations (O’ Kane Consultants Inc. 2004). Lysimeters were open to the environment and the source of water percolating through the soil covers and the coke profile was either rainwater and/or snow-melt water.

4.3.2 Syncrude lysimeter coke leachate and recycle water collection

Coke leachates from both lysimeters were collected at various times from February 2005 to October 2006 and shipped from Syncrude Canada Ltd. (Fort McMurray, AB, Canada) to the Toxicology Centre, University of Saskatchewan (Saskatoon, SK, Canada) in 2 L HDPE Nalgene[®] bottles stored in coolers. Collection of leachate from the lysimeters was aided either by a manual bailer and/or a pump. The time of leachate collection from both lysimeters are listed in Table 4.1. Upon arrival at the Toxicology Centre 24 to 48 h after collection, leachates were stored at 4°C and sub-samples of leachate were analyzed for pH, total ammonia, dissolved oxygen content and water hardness before the initiation of toxicity tests. Leachate collection

from the lysimeters was dependent on the availability of leachate from the bottom of each lysimeter. A LC50 value could not be calculated for leachate collected from either lysimeters during February, August and November 2005 because of insufficient leachate volume to prepare test solutions of varying concentrations.

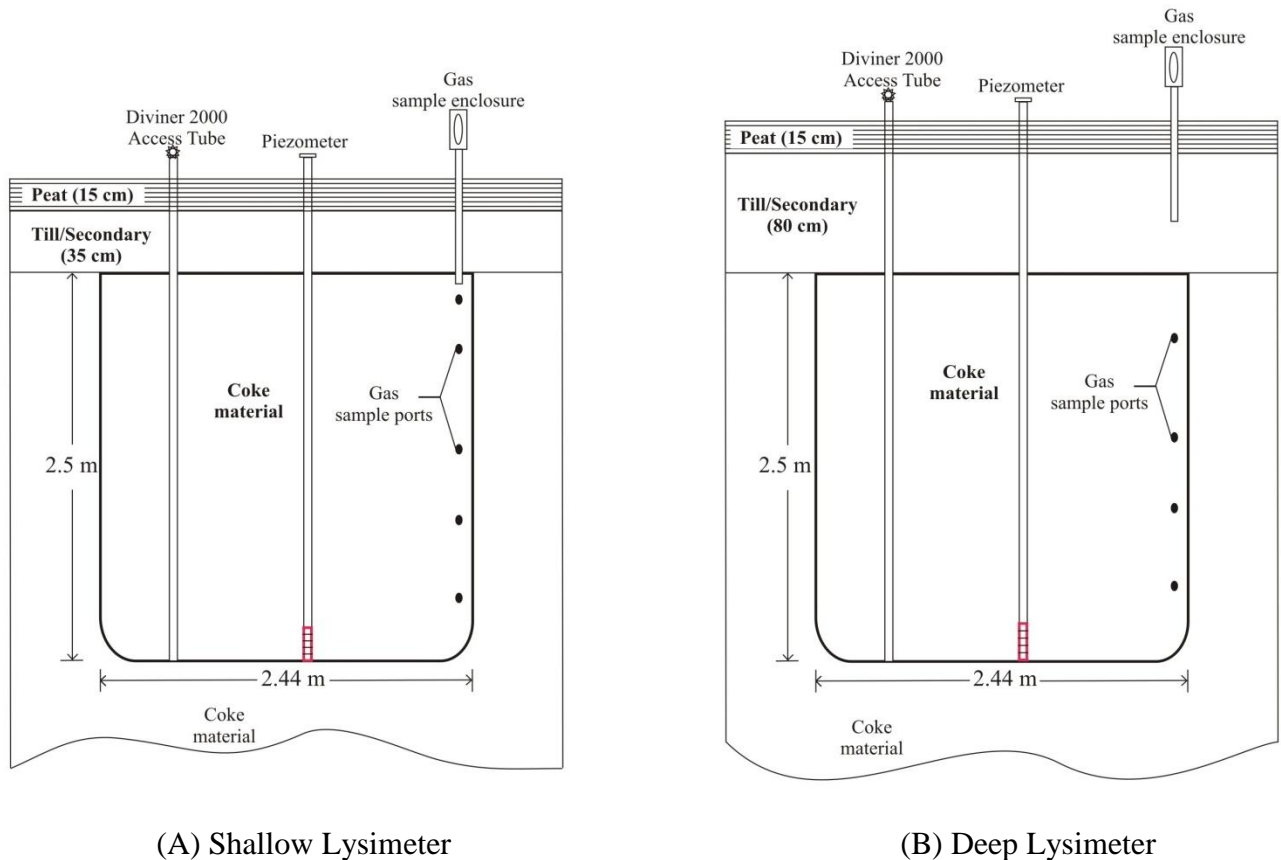


Figure 4.1. Cross-section view of two Syncrude tank lysimeters showing different soil cover depths. *Source:* Modified from O’Kane Consultants Inc., 2004.

A fresh sample of recycle water from Syncrude operations was collected in July 2006. It is hypothesized that recycle water would influence coke leachate toxicity since coke is being transported to storage sites (i.e. MLSB) hydraulically using recycle water. It was therefore

important to delineate the influence of recycle water on the toxicity of coke leachate from the lysimeters.

4.3.3 Coke leachate collection from other oil sands field sites

Coke leachate was also collected at various times from other coke storage sites located at Syncrude Canada Ltd. and Suncor Energy Inc. lease areas. During August 2006, leachate was collected through a piezometer from Syncrude coke cell 5 well 2 (CC5 well 2) and another tank lysimeter installed at the Suncor coke storage site. Surface water from Suncor Coke Pond, which holds the coke run-off water accumulated near the coke stockpile was collected during August 2006 and July 2007. The toxicity responses of various oil sands field collected leachates were compared with contaminant concentrations, especially with vanadium concentration, in their respective leachates. For a broader comparison of trace metal concentration and leachate toxicity, the leachate from Syncrude's shallow and deep lysimeter collected during September 2006 was selected.

4.3.4 Toxicity testing

Toxicity testing of all lysimeter leachates and other field collected leachates was conducted in a controlled environment chamber with an air temperature of 24.5 ± 0.5 °C and the photoperiod set to 16:8 h light:dark. The cladoceran, *Ceriodaphnia dubia*, was used as the test organism and maintained according to a standard culturing protocol in moderately hard reconstituted water (Environment Canada, 1992). Daphnids were fed a diet of *Pseudokirchneriella subcapitata* and YCT (yeast, cerophyll and trout-chow) mixture daily at a rate of 15 and 3 mL per 2 L of culture water, respectively. All toxicity tests were conducted

using unfiltered leachate since there were no visible suspended particles. Moderately hard reconstituted water (MHRW) used as dilution water in all tests was prepared using 96 mg/L of NaHCO₃, 60 mg/L of CaSO₄, 60 mg/L of MgSO₄, and 4 mg/L of KCl in deionized water (Environment Canada, 1992). Whole leachate was diluted using MHRW in a 0.5X dilution series to obtain desired test concentrations. Chemical characteristics of 100% leachate from the two Syncrude lysimeters and of dilution water used in preparing test solutions are shown in Table 4.1.

Chronic (7 or 8 d) *C. dubia* toxicity tests were conducted with ten replicates of single neonates (\leq 24 h old) placed in either 20 mL of control or test solution with renewal of test solutions every 24 h. A test was considered acceptable if 80% of control organisms survived and 60% of the surviving adults produced at least three broods with a total of at least 15 neonates per adult. All toxicity tests were performed in 30 mL glass beakers. Survival and reproduction were used as test endpoints.

4.3.5 Additional toxicity tests

In order to generate chronic toxicity values and calculate toxic units (TUs) for key metals found in coke leachates, additional 7-day chronic toxicity tests were conducted using *C. dubia*. Aluminum sulfate (99.99+% pure) and manganese (II) chloride hydrate (99.999% pure) were obtained from Sigma-Aldrich Inc. (St. Louis, MO, USA) and, nickel chloride hexahydrate (99.9985% pure) and sodium metavanadate (min. 96% pure) were obtained from Strem Chemicals (Newburyport, MA, USA). Test concentrations of Al, Mn and Ni covered the concentration range found in leachates from both the lysimeters (Table 4.2). However, for vanadium, the highest concentration tested was well below the levels usually found in the

leachates from both the lysimeters. Test concentrations were prepared using either 2.5X or 0.5X dilution series, with MHRW. Test solutions were prepared daily from stock solutions.

4.3.6 Chemical analyses of coke leachates

Dissolved concentrations of 26 elements in coke leachate were measured in-house using an inductively coupled plasma mass spectrometer (ICP-MS) equipped with collision cell technology (Thermo Fisher Scientific, Mississauga, ON, Canada). Internal standards of Li, Sc, In, Tb, and Bi were employed during the analysis (High-purity Standards, Charleston, SC, USA). Standard solutions of Ag, Al, As, B, Ba, Be, Bi, Cd, Cr, Co, Cu, Fe, Hg, Mn, Mo, Ni, Pb, Sb, Se, Sn, Sr, Tl, Ti, U, V and Zn were purchased from VWR International (Mississauga, ON, Canada). For evaluating the accuracy of ICP-MS measurements, a river water standard reference material (SLRS-4) and a natural water standard reference material (1640) were purchased from the National Research Council (Ottawa, ON, Canada) and the National Institute of Standards & Technology (Gaithersburg, MD, USA), respectively. Measurement of major ion composition of leachates was performed at ALS Laboratory Group (Saskatoon, SK, Canada). Routine water quality variables including pH, dissolved oxygen, conductivity, alkalinity, hardness and ammonia were measured in-house on day 0 and day 6 or 7 during the course of all toxicity tests.

4.3.7 Batch-renewal coke leaching experiment

Coke from Syncrude Canada Ltd. operations was collected in November 2007 from the Mildred Lake Coke Watershed site located in the MLSB, placed in two 20 L plastic buckets and shipped to the Toxicology Centre, University of Saskatchewan. Approximately 500 mL of coke were transferred into three replicate 2 L glass jars and 200 mL of MHRW added to each for

leaching. This volume of water was sufficient to saturate the pore spaces among the coke particles without forming any overlying water layer. The MHRW used for leaching was prepared as described in Section 2.4. The reason for leaching with MHRW was to ensure that the water hardness was similar to that of recycle water which is used to hydraulically transport coke to its deposit site (Table 4.1 and 4.3). All leaching jars were closed with air-tight plastic lids. Leaching water in all jars was renewed after 4 h of leaching on day 0, again after 24 h of leaching, followed by 24 h renewal cycles until day 10. After day 10, there was no pore water renewal until day 45 when the experiment was terminated. Sub-samples of MHRW were collected for water quality, major ion and trace element analysis on day 0 and day 10 of the leaching period. Coke leaching water (i.e. pore water) was extracted by vacuum filtration using 0.45 μm pore size membrane filters (Gelman Supor[®] - 450; Pallman Laboratories, Ann Arbor, MN, USA). Following each coke leaching water extraction, a 5 mL coke pore water sample was acidified using 2% high-purity HNO_3 to a $\text{pH} < 2$ for trace element analysis using ICP-MS. Separate coke leaching water sub-samples were also collected for major ion analysis and routine water quality measurements.

4.3.8 Statistics

All LC50 estimates and associated 95% confidence intervals were calculated using the trimmed Spearman-Kärber method, version 1.5 (US EPA, 1990). Differences in toxicity response between shallow and deep lysimeter leachate were considered significant if there was no overlap of the 95% confidence intervals. Reproduction data (7-8 d) were used to estimate the IC50 value for recycle water using the Inhibition Concentration (IC_p) approach, version 2.0 (US EPA, 1993). All other statistical analyses were performed using the computer program

SigmaStat[®], version 3.1 (SPSS, Chicago, IL, USA) with a 95% ($p \leq 0.05$) level of confidence. Independent student's *t*-tests were used to determine significant differences in element concentrations between shallow and deep lysimeter leachates collected at the same time. A concentration-response relationship was plotted for vanadium concentrations in leachate collected from different lysimeters and other oil sands coke storage sites versus *C. dubia* survival. Furthermore, vanadium leaching potential from coke in the two field lysimeters was calculated using mass balance calculations similar to those described in Shibata et al. (2007). Here, the potential leachable fraction of vanadium (PLF = 5.7 mg/kg) estimated by Kessler and Hendry (2006) for a similar coke sample was used. The initial mass of potential leachable V (mg) in the lysimeters was calculated from the product of the PLF of V in coke (mg/kg), the volume of coke (m³) in the lysimeters, and the bulk density of coke (kg/m³). The total mass of vanadium (mg) released from the lysimeters during the study period was estimated by integrating the regression equation obtained by plotting the concentration of V in coke leachate (mg/L) versus the cumulative volume of water pumped from the lysimeters (L).

A toxic unit (TU) approach was used to evaluate the relative significance of leached metals in lysimeter leachate toxicity. Toxic units were calculated for six metals (i.e. Al, Mn, Mo, Ni, V and Zn) that were considered to be of concern in relation to the toxicity of lysimeter coke leachates. Calculated metal concentrations at the leachate LC50 (% v/v) for the shallow and deep lysimeters at various times were divided by the metal-specific 7-d LC50 value ($TU = [M] \text{ at leachate LC50} / 7\text{-d LC50 [M]}$). Toxicity values (i.e. 7-d LC50) for Al, Mn, Ni and V were generated in-house using *C. dubia* as the test species following Environment Canada (1992) test guidelines. The 7-d LC50 values for Mo and Zn were obtained from Onikura et al. (2008),

determined at a water hardness of 130 mg/L as CaCO₃. This hardness value closely resembled the hardness of both lysimeter leachates (Table 4.1).

4.4 Results

4.4.1 Chemistry of lysimeter coke leachate

The pH and hardness of leachate from both lysimeters were within acceptable limits for toxicity testing using *C. dubia* (Table 4.1). Conductivity of the leachate from both lysimeters ranged from 1160 to 1813 µS/cm, but did not display any trend over time. Alkalinity was lower in the shallow lysimeter leachate when compared with deep lysimeter leachate at all times except in November 2005 (Table 4.1). Ammonia was below the detection limit (< 0.05 mg/L) at all times for both lysimeters. The ionic composition of leachate from both lysimeters at all times was dominated by sodium, sulfate and bicarbonate (Table 4.1). The concentrations of most major ions did not vary much between shallow and deep lysimeter leachates during the study period (Table 4.1). However, bicarbonate was an exception. The bicarbonate concentration was higher in the deep lysimeter leachate than in the shallow lysimeter leachate at all sampling times, except for leachate collected in November 2005 (Table 4.1).

Table 4.1. Chemical characteristics of dilution water used in toxicity testing and of the 100% leachate collected from two Syncrude tank lysimeters at various times.

| Parameter | Dilution water ^a | Lysimeter depth | Leachate collection (month, year) | | | | | | | |
|---|-----------------------------|-----------------|-----------------------------------|-----------|-----------|-----------|-----------|-----------|------------------------|------------------------|
| | | | Feb. 2005 | Aug. 2005 | Nov. 2005 | Feb. 2006 | Apr. 2006 | Aug. 2006 | Sep. 2006 ^b | Oct. 2006 ^c |
| <u>Water quality^d</u> | | | | | | | | | | |
| pH | 8.1±0.2 | Shallow | 7.1 | 7.2 | 7.3 | 7.6 | 7.1 | 7.0 | 7.4 | 7.2 |
| | | Deep | 7.6 | 7.2 | 7.1 | 7.9 | 7.8 | 7.7 | 8.1 | NA |
| Alkalinity (mg/L as CaCO ₃) | 63±4 | Shallow | 48 | 37 | 46 | 41 | 27 | 25 | 25 | 24 |
| | | Deep | 203 | 135 | 27 | 86 | 93 | 73 | 65 | NA |
| Conductivity (µS/cm) | 340±13 | Shallow | 1545 | 1350 | 1370 | 1390 | 1320 | 1280 | 1813 | 1320 |
| | | Deep | 1634 | 1160 | 1320 | 1350 | 1220 | 1220 | 1242 | NA |
| Hardness (mg/L as CaCO ₃) | 79±4 | Shallow | 93 | 63 | 83 | 90 | 108 | 123 | 125 | 132 |
| | | Deep | 38 | 27 | 108 | 167 | 115 | 124 | 152 | NA |
| <u>Major ions (mg/L)</u> | | | | | | | | | | |
| Ca | 15 | Shallow | 19 | 15 | 15 | 18 | 20 | 23 | -- | 25 |
| | | Deep | 9 | 7 | 20 | 28 | 18 | 20 | | NA |
| K | 2 | Shallow | 5 | 5 | 6 | 5 | 5 | 5 | -- | 6 |
| | | Deep | <5 | <5 | 5 | <5 | 4 | 5 | | NA |
| Mg | 14 | Shallow | 12 | 10 | 11 | 13 | 14 | 16 | -- | 17 |
| | | Deep | 5 | 5 | 14 | 28 | 17 | 18 | | NA |
| Na | 31 | Shallow | 288 | 279 | 274 | 277 | 242 | 230 | -- | 239 |
| | | Deep | 346 | 279 | 242 | 250 | 229 | 222 | | NA |
| Cl | 2 | Shallow | 8 | 7 | 10 | 11 | 9 | 8 | -- | 10 |
| | | Deep | 20 | 8 | 9 | 15 | 12 | 11 | | NA |
| HCO ₃ | 88 | Shallow | 82 | 67 | 57 | 48 | 32 | 31 | -- | 30 |
| | | Deep | 327 | 150 | 32 | 136 | 113 | 88 | | NA |
| SO ₄ | 87 | Shallow | 645 | 556 | 585 | 618 | 568 | 559 | -- | 576 |
| | | Deep | 520 | 462 | 568 | 562 | 467 | 478 | | NA |

^a Values are (mean ± SE, *n* = 8) pooled from the entire study period.

^b Leachate collected in September 2006 from both lysimeter was not analyzed (NA) for major ions.

^c Leachate from the deep lysimeter was not available (NA).

^d Total ammonia levels in dilution water and coke leachates were always less than 0.05 mg/L.

4.4.2 Toxicity of lysimeter coke leachate

Toxicity tests demonstrated that the undiluted (100%) leachates from both lysimeters were acutely toxic to *C. dubia* at all sampling times. The 7-day median lethal concentration (LC50) could not be calculated for leachates collected from both lysimeters during February, August and November 2005, since insufficient volumes of leachate were available to test concentrations below 25% dilution. When an LC50 was calculated, the lowest LC50 (12.5%) for shallow lysimeter leachate was recorded in February 2006 and September 2006, and the highest LC50 (21.8%) was recorded in August 2006 (Fig. 4.2). For deep lysimeter leachate, the lowest LC50 (7.2%) and the highest LC50 (14.4%) were recorded in April 2006 and August 2006, respectively (Fig. 4.2). Leachate toxicity (LC50 values) did not vary much over time. During the entire study period and for both lysimeter leachates, reproduction of *C. dubia* was inhibited at lower leachate concentrations than those inhibiting survival, when compared with control reproduction (data not shown).

4.4.3 Comparison of lysimeter leachate toxicity and contaminant concentrations

For leachate collection times where LC50s could be calculated, the deep lysimeter leachate always had a lower LC50 value than the shallow lysimeter leachate (Fig. 4.2). Correspondingly, the concentration of vanadium was always significantly higher in deep lysimeter leachate than in shallow lysimeter leachate ($p \leq 0.05$, Table 4.2), and the TU for vanadium in deep lysimeter leachate was higher than TUs for all other elements (Fig. 4.3b). At the beginning of this study (i.e. February 2005), the concentrations of molybdenum and vanadium in deep lysimeter leachate were highly elevated, but decreased gradually over subsequent collection times (Table 4.2). Conversely, molybdenum levels in the shallow lysimeter

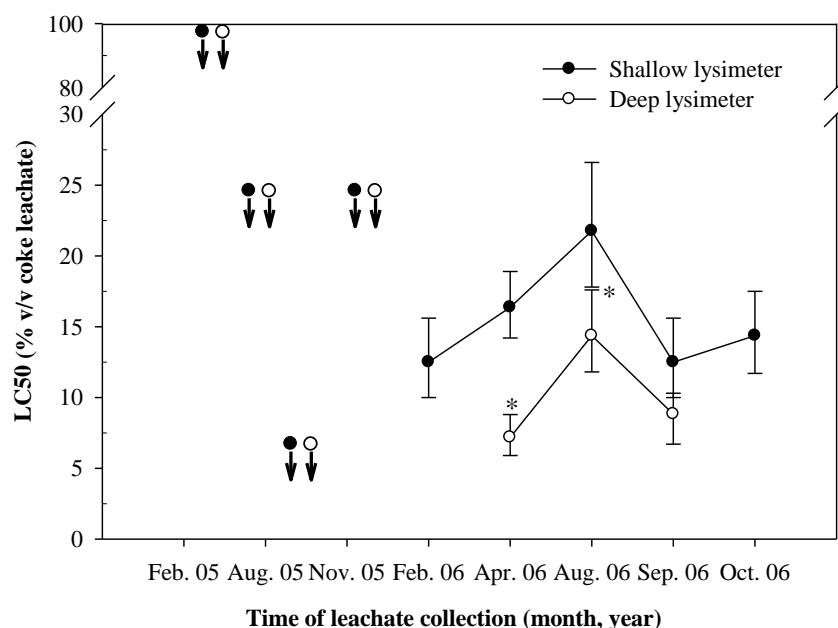


Figure 4.2. Temporal variation in toxicity response of *Ceriodaphnia dubia* exposed to coke leachate from the Syncrude shallow and deep lysimeters. Values are expressed as LC50s (% v/v coke leachate) with 95% confidence intervals. Arrow heads indicate LC50 values less than the lowest concentration tested (100%, 25%, or 6.25%). No leachate was available for toxicity testing from the deep lysimeter in October 2006. An asterisk (*) denotes a significant difference in toxicity response between shallow and deep lysimeter leachate.

leachate, increased steadily between February 2005 and February 2006, and then started to decrease thereafter reaching the lowest concentration of 1753 $\mu\text{g/L}$ in October 2006 (Table 4.2). The concentrations of vanadium and nickel in undiluted (100%) leachate from both lysimeters at all times were well above the in-house generated 7-day LC50 values of 550 and 3.8 $\mu\text{g/L}$, respectively (Table 4.2). These toxicity tests were conducted under similar experimental

conditions using the same stock of *C. dubia* in moderately hard reconstituted water. There were no definite trends in concentrations over time for other elements from either lysimeter leachate. Moreover, only nickel and vanadium, displayed concentrations above the estimated 7-d LC50 values for *C. dubia* (Table 4.2). The TUs for Ni and V were therefore higher than Al, Mn, Mo and Zn and hence dominated the toxic contribution towards the observed leachate toxicity in both lysimeter leachates (Fig. 4.3a and b).

Survival of *C. dubia* exposed to 100% leachate collected from other oil sands field sites, including the two Syncrude lysimeters, was compared with their vanadium concentration in those leachates. Leachates collected in 2006 from Syncrude coke cell 5 (CC5 well 2) and the Suncor tank lysimeter displayed 100% survival (Fig. 4.4). The corresponding concentrations of vanadium were 9.6 and 13.6 µg/L, respectively. These levels were much lower than the *C. dubia* LC50 value for vanadium. Furthermore, a 2007 sample from the Suncor coke pond had a vanadium concentration of 22.9 µg/L and showed 90% survival (Fig. 4.4). Concentrations of vanadium found in 2006 samples from the Suncor coke pond (41.1 µg/L), and the Syncrude shallow (2184 µg/L) and deep (5565 µg/L) lysimeters, all displayed 100% mortality (Fig. 4.4). A similar relationship of concentration dependent toxicity was not evident for any other element found in the leachates.

Table 4.2. Mean (\pm SD, $n = 3$) concentrations of dissolved trace elements in coke leachate water collected from the Syncrude shallow and deep lysimeters at various times.

| Element ^{a, b} ($\mu\text{g/L}$) | Lysimeter depth | Leachate collection (month, year) | | | | | | | | 7-d LC50 ^{c, d} ($\mu\text{g/L}$) |
|--|--------------------|-----------------------------------|----------------|----------------|-----------------|-----------------|-----------------|----------------|---------------|---|
| | | Feb. 2005 | Aug. 2005 | Nov. 2005 | Feb. 2006 | Apr. 2006 | Aug. 2006 | Sep. 2006 | Oct. 2006 | |
| Al | Shallow | 10.2 \pm 1.4* | 9.6 \pm 1.6* | 7.4 \pm 2.4 | 16 \pm 4.4 | 8.1 \pm 0.5 | 8.2 \pm 1.0 | 3.5 \pm 5 | 2.9 \pm 1.1 | 497 |
| | Deep | 22 \pm 1.5 | 18 \pm 1.8 | 10 \pm 1.6 | 11 \pm 0.3 | 6.6 \pm 0.5* | 6.1 \pm 0.5* | 3.5 \pm 2.2 | NA | |
| B | Shallow | 681 \pm 33 | 665 \pm 10 | 674 \pm 34 | 749 \pm 92 | 573 \pm 13 | 603 \pm 46 | 688 \pm 61 | 645 \pm 19 | 45500 ^e |
| | Deep | 581 \pm 6.6* | 553 \pm 17* | 512 \pm 57* | 541 \pm 18* | 495 \pm 6.4* | 497 \pm 13* | 541 \pm 42* | NA | |
| Ba | Shallow | 30 \pm 0.3 | 16 \pm 0.1 | 28 \pm 0.4 | 20 \pm 0.4* | 34 \pm 0.4 | 40 \pm 0.3 | 43 \pm 0.3 | 44 \pm 0.4 | ND |
| | Deep | 7.9 \pm 0.2* | 6.8 \pm 0.3* | 20 \pm 0.1* | 26 \pm 0.4 | 21 \pm 0.1* | 26 \pm 0.3* | 33 \pm 0.3* | NA | |
| Mn | Shallow | 183 \pm 2.2 | 65 \pm 0.6 | 169 \pm 3.8 | 171 \pm 1.5 | 212 \pm 1.7 | 266 \pm 2.7 | 302 \pm 1.1 | 231 \pm 3.2 | 12810 |
| | Deep | 3.5 \pm 0.3* | 22 \pm 0.2* | 73 \pm 0.6* | 90 \pm 0.3* | 69 \pm 0.6* | 80 \pm 1.5* | 110 \pm 1.4* | NA | |
| Mo | Shallow | 2735 \pm 23* | 2952 \pm 25 | 3285 \pm 26 | 3576 \pm 69 | 2054 \pm 13 | 1904 \pm 13 | 1987 \pm 15 | 1753 \pm 24 | 19700 |
| | Deep | 3470 \pm 64 | 2909 \pm 23 | 2346 \pm 25* | 1846 \pm 21* | 1969 \pm 7.8* | 1707 \pm 30* | 1800 \pm 7* | NA | |
| Ni | Shallow | 32 \pm 0.5 | 56 \pm 0.7 | 34 \pm 0.2 | 20 \pm 0.5 | 44 \pm 0.7 | 57 \pm 0.6 | 62 \pm 0.7 | 57 \pm 0.7 | 3.8 |
| | Deep | 14 \pm 0.7* | 14 \pm 0.5* | 17 \pm 0.3* | 18 \pm 0.7* | 15 \pm 0.2* | 16 \pm 0.5* | 22 \pm 0.7* | NA | |
| Sr | Shallow | 331 \pm 2.2 | 236 \pm 2.3 | 352 \pm 5.6 | 309 \pm 5.9* | 416 \pm 4.4 | 523 \pm 88 | 550 \pm 3.0 | 489 \pm 30 | ND |
| | Deep | 136 \pm 1.1* | 96 \pm 0.4* | 343 \pm 1.6 | 406 \pm 4.1 | 339 \pm 1.5* | 366 \pm 4.5* | 515 \pm 3.0* | NA | |
| V | Shallow | 2143 \pm 16* | 2342 \pm 25* | 2937 \pm 36* | 2380 \pm 62* | 1763 \pm 16* | 2046 \pm 0.3* | 2184 \pm 13* | 1774 \pm 19 | 550 |
| | Deep | 14680 \pm 241 | 9825 \pm 173 | 8974 \pm 84 | 7427 \pm 1826 | 6611 \pm 39 | 5238 \pm 88 | 5565 \pm 19 | NA | |
| Zn | Shallow | 11 \pm 4.6* | 62 \pm 6.4* | 25 \pm 10 | 8.3 \pm 2.7 | 32 \pm 13 | 6.6 \pm 2.6 | 15 \pm 10 | 125 \pm 91 | 165 |
| | Deep | 70 \pm 47 | 96 \pm 7.5 | 41 \pm 21 | 24 \pm 13 | 11 \pm 6.4 | 15 \pm 13 | 13 \pm 0.9 | NA | |

Note: All values > 10 µg/L are rounded off to the nearest µg/L for clarity of presentation

^aThe following elements were always below their detection limit ($\leq 0.01\mu\text{g/L}$): Ag, As, Be, Bi, Cd, Hg, Pb, Se, Sn, Ti, Tl, U.

^bThe following elements were $\leq 5\mu\text{g/L}$ at all times in both lysimeter leachates: Co, Cr, Cu, Fe and Sb.

^cToxicity data for elements Al, Mn, Ni and V were determined in-house.

^d7-d LC50 values for Mo and Zn obtained from Onikura et al. (2008).

^e48-h LC50 value for B was obtained from Dethloff et al. (2009).

NA = Leachate from the deep lysimeter was not available.

ND = Not determined

* Denotes a significant ($p\leq 0.05$) difference in trace element concentration between the two lysimeters tested at same time point.

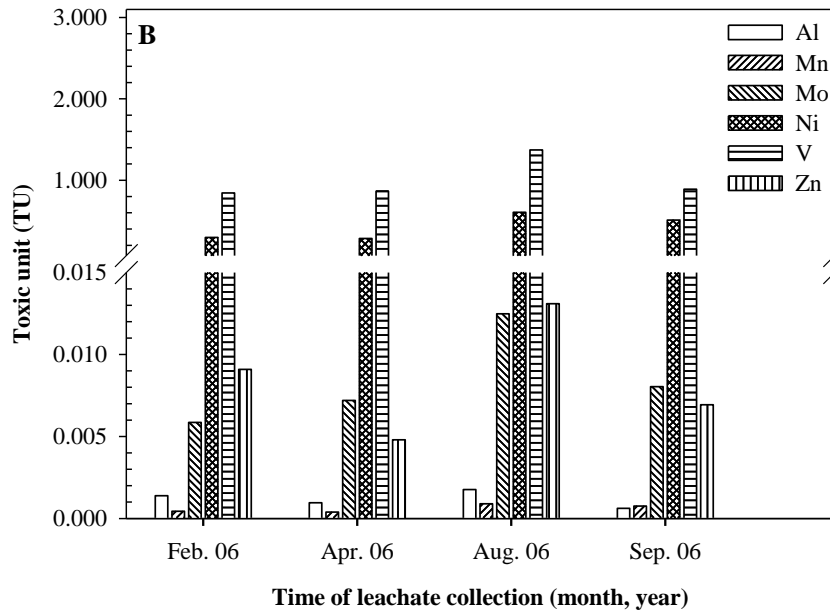
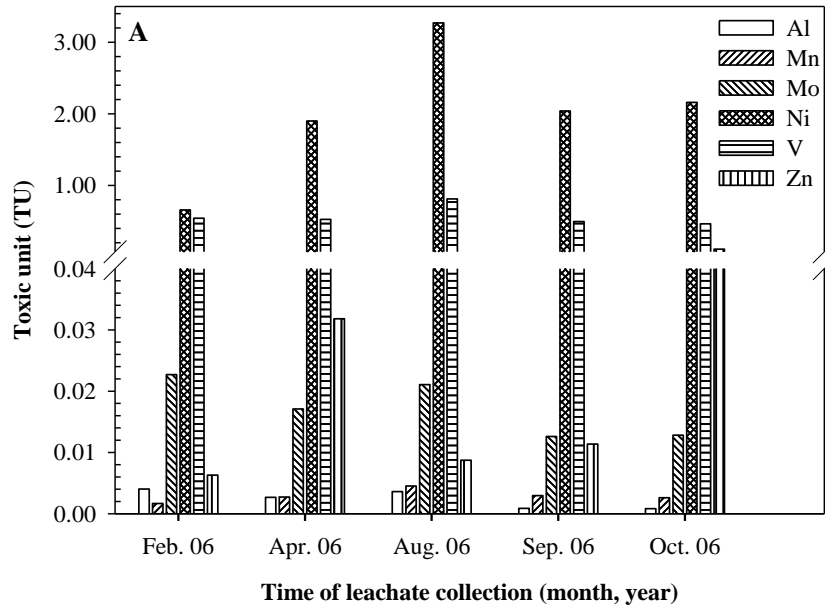


Figure 4.3. Relative toxic contribution of key metals to coke leachate toxicity expressed as toxic units (TU) at the LC50 concentration (% v/v) for leachates collected at different times from the (A) shallow and (B) deep lysimeters. Note: 6.25% was used for TU calculation for deep lysimeter leachate collected in February 2006.

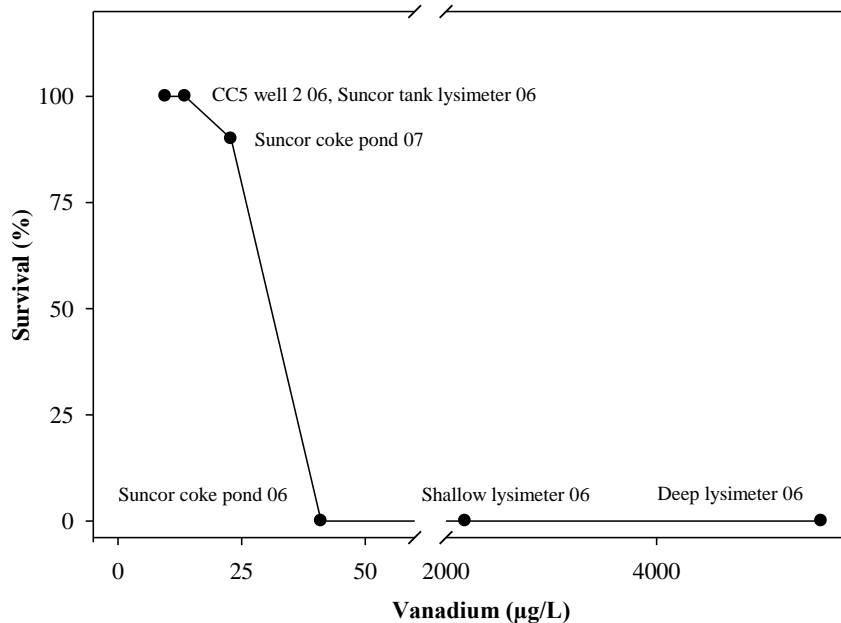


Figure 4.4. Relationship between survival of *Ceriodaphnia dubia* exposed to 100% coke leachate collected from various oil sand field locations and lysimeters, and associated vanadium concentration in that leachate.

4.4.4 Toxicity of Syncrude recycle water

The water chemistry of Syncrude recycle water was dominated by alkaline pH, elevated alkalinity and very high conductivity (Table 4.3). However, the water hardness was similar to MHRW, which was used as dilution water to prepare test solutions. Ammonia was not detected in 100% recycle water (Table 4.3). The estimated LC50 and IC50 values for *C. dubia* survival and reproduction in Syncrude recycle water were 70.7% and 49.4%, respectively. The concentrations of most trace elements were <10 µg/L except for boron, barium, strontium and zinc (Table 4.3).

Table 4.3. Toxicological and chemical characteristics (mean \pm SE, $n = 3$) of Syncrude recycle water without coke leachate influence. All values $> 10 \mu\text{g/L}$ are rounded off to the nearest $\mu\text{g/L}$ for clarity of presentation.

| Characteristic | Description |
|--|---------------------------------|
| <u>Toxicity end-points</u> | |
| LC50 (%) | 70.7 ^a |
| IC50 (%) | 49.4 (45.1 – 56.8) ^b |
| <u>Water quality</u> | |
| pH | 8.6 \pm 0.03 |
| Alkalinity (mg/L as CaCO ₃) | 538 \pm 9 |
| Hardness (mg/L as CaCO ₃) | 100 \pm 1 |
| Conductivity ($\mu\text{S/cm}$) | 3954 \pm 58 |
| Ammonia (mg/L) | BDL |
| <u>Element^{c, d} ($\mu\text{g/L}$)</u> | |
| Al | 7.3 \pm 3.2 |
| B | 2105 \pm 52 |
| Ba | 61 \pm 0.3 |
| Fe | 8.8 \pm 0.8 |
| Mn | 7.1 \pm 0.1 |
| Mo | 4.8 \pm 0.6 |
| Ni | 8.4 \pm 0.2 |
| Se | 8.9 \pm 0.9 |
| Sr | 449 \pm 1.7 |
| Zn | 50 \pm 18 |

BDL = below detection limit ($<0.05 \text{ mg/L}$).

^a 95% confidence interval not obtainable.

^b 95% confidence interval.

^c The following elements were below their detection limit ($\leq 0.01 \mu\text{g/L}$): Bi, Be, Cd, Hg and Sb.

^d The following elements were $\leq 5 \mu\text{g/L}$: Ag, As, Co, Cr, Cu, Pb, Sn, Ti, Tl, U and V.

4.4.5 Batch renewal leaching of Syncrude lysimeter coke

During the first 10 d of leaching water renewals, the leachate pH was 7.7 ± 0.3 , and mean alkalinity and hardness were 43 ± 9 and 65 ± 9 mg/L as CaCO_3 , respectively. The major ion concentrations in leachate water did not change significantly over the 10-d leaching period relative to dilution water (data not shown). Among the trace elements detected, vanadium concentrations were always higher than all other trace elements during the entire leaching period (Fig. 4.5a). The concentrations of vanadium, strontium, molybdenum and boron decreased steadily as the cumulative volume of water flushing the coke increased over the leaching period (Fig. 4.5a and b). After six water renewals, there was minimal change in the concentrations of these trace elements in the leachate from day 6 to 10; (Fig. 4.5a and b). However, concentrations of boron, molybdenum and vanadium reached peak values in the day 45 sample. The concentrations of aluminum increased during the first 6 days of leaching and then leveled off until day 45 (Fig. 4.5b).

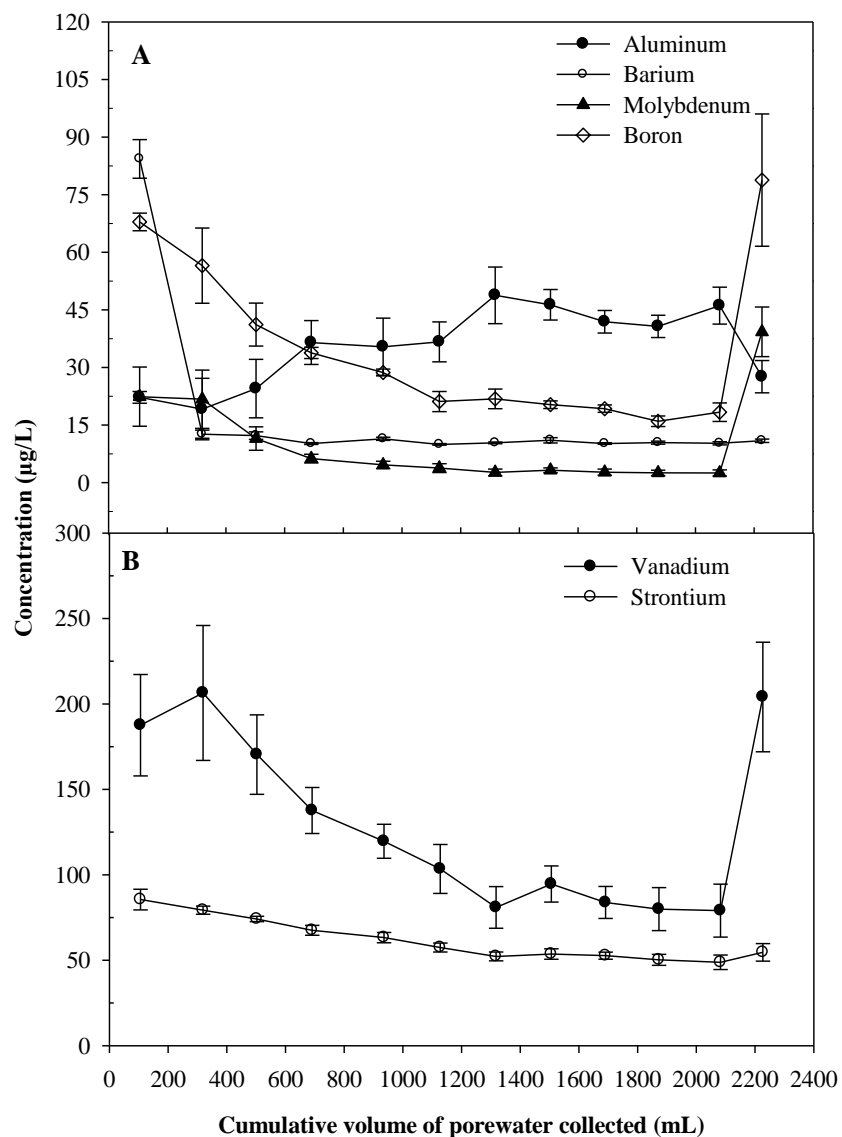


Figure 4.5. Mean (\pm SE, $n=3$) concentrations of trace elements released from representative Syncrude lysimeter coke as a function of cumulative volume of porewater collected during the batch-renewal coke leaching experiment. Cumulative volume of porewater on x -axis starting from 106 mL to 1967 mL corresponds to the first 10 days of the renewal period, and 2111 mL correspond to day 45 of the static period.

4.5 Discussion

Vanadium concentrations in the deep lysimeter leachate were found to be significantly higher than in the shallow lysimeter leachate at all sampling times. This is likely due to the slightly more alkaline pH of the deep lysimeter leachate. Vanadium is known to be more soluble under slightly alkaline pH and it has been shown that under slightly acidic condition, V solubility decreases due to a shift in speciation from V(V) to V(IV) (Wherli and Stumm, 1989). Further, it has been reported that the speciation of V in coke pore water from the Syncrude tank lysimeters was dominated by V(IV) in shallow lysimeter leachate and V(V) in deep lysimeter leachate (Li and Le, 2007). If correct, this suggests that the more soluble fraction of V(V) was readily released by coke in the deep lysimeters at slightly more alkaline pH. Conversely, for nickel, the concentration was higher in the shallow lysimeter when compared with the deep lysimeter; possibly due to the slightly less alkaline pH in the shallow lysimeter (Ni is more soluble under acidic conditions). This corresponds with the findings from our laboratory coke leaching experiments where Ni reached elevated concentration when leaching water pH was lowered from 9.5 to 5.5 (unpublished data). Other elements that were elevated in leachates from both lysimeters included Al, B, Mo, Mn, Sr and Zn. However, concentrations of most elements in coke leachate, except nickel and vanadium, were below the reported acute and/or chronic toxicity values for *C. dubia* (Table 4.2). Furthermore, TU calculations suggested that Ni and V significantly contributed to the observed leachate toxicity compared to Al, Mn, Mo and Zn in leachates from both lysimeters.

Based on the metal-specific 7-d LC50 values and the TUs estimated for the six metals of concern in coke leachates, the observed toxicity of coke leachate from both lysimeters could be attributed to trace elements, especially Ni and V, released from coke, rather than to the dissolved

constituents present in recycle water. This is especially the case at the leachate concentrations associated with the observed LC50 values ($\leq 25\%$ v/v coke leachate). At such leachate concentrations, levels of most major ions that could be attributed to the recycle water would be diluted substantially below levels that should result in significant *C. dubia* mortality.

Nevertheless, the observed mortality in 100% coke leachate may also have been influenced by the constituents present in recycle water. Despite the possibility that major ions (e.g. Na, SO₄, and Cl) contributed to the toxicity of 100% leachate, it is hypothesized that Ni and V were the primary cause of leachate toxicity at lower leachate concentrations ($< 25\%$ v/v).

The TUs calculated for V in deep lysimeter leachate were at least 0.5 TU higher than for Ni (Fig. 4.3B). This can be explained by the higher concentrations of the more toxic V(V) in the deep lysimeter. In a study looking at the effect of water hardness and pH on V speciation and toxicity to rainbow trout (*Oncorhynchus mykiss*), it was observed that V was less toxic at pH 5.5 and pH 6.6 when compared with pH 7.7. This difference in toxicity was attributed to the higher relative abundance of the more toxic metavanadate (V(V); H₂VO₄⁻) species (Stendahl and Sprague, 1982). Speciation of V can exist in a wide range of oxidation states from -2 to +5. In oxygenated surface waters at neutral and higher pH, V(V) is the predominant and mobile species. Conversely, V(IV) may be present as the vanadyl cation (VO²⁺) under reducing conditions at acidic pH. In addition, V(IV) readily oxidizes to V(V) in alkaline solution (Crans et al. 1998; Minelli et al. 2000). Toxicity is governed by the oxidation state of V species with the most toxic form of V being V(V) (Taylor and van Staden, 1994; Zhao et al. 2006).

Vanadium concentrations found in leachates from various oil sands field sites showed a concentration dependent relationship with *C. dubia* survival. A similar relationship was not observed for other elements found in these coke leachates (data not shown). Coke leachates

collected from various oil sands field sites such as CC5 well 2, the Suncor tank lysimeter and the Suncor coke pond (2007) showed 100% – 90% survival, with V levels in these leachates being well below the LC50 concentration of 550 µg/L estimated for *C. dubia*. On the other hand, Ni levels in samples from all of these sites were above the Ni LC50 of 3.8 µg/L estimated for *C. dubia*, suggesting that these leachates should have been toxic if Ni was the primary toxicant. An explanation for this observation is still lacking, but it is possible that an interaction exists between V and Ni toxicity, or Ni and other components of the leachates. These hypotheses need to be investigated.

Metal release from Syncrude lysimeter coke was also evaluated in the laboratory using a batch renewal leaching process in an effort to determine the number of pore water flushings required to substantially reduce leaching of metals from the coke. In a similar study looking at the leaching potential of dissolved solids from oil sands coke, it was found that the rate of release for V was higher than the rates for other metals. In addition, it was suggested that the initial peak in concentration of trace elements was associated with the solubilization of the readily available metal fraction found in the coke (Kessler and Hendry, 2006). This is supported by the findings from the present experiment, wherein V reached its peak concentration during the first two pore water renewals. Further, the total mass of V was highest relative to other elements released from coke during the entire leaching duration. In addition, the rise in concentrations of V, Mo and B on day 45 suggested that coke still held appreciable amounts of leachable metals after 10 pore water flushings.

The potential leachable fraction (PLF) of V associated with coke from the Syncrude MLSB site has been reported as 5.7 mg/kg (Kessler and Hendry, 2006). The coke used in the aforementioned study was from the same source as that used in the Syncrude tank lysimeters and

in the batch renewal leaching experiment described here. For the purpose of mass balance calculation for vanadium, the PLF of V for coke used in batch renewal leaching experiment and in two field lysimeters was assumed to be 5.7 mg/kg. The initial mass of V (mg) in the coke was calculated from the product of PLF of V (mg/kg), the volume of coke used in the experiment (m^3), and the density of coke (kg/m^3). Calculations show that 500 mL (or 0.527 kg) of coke contained 3 mg of potentially leachable V before starting the batch renewal leaching study. Further, the total mass of V released during the 45 d batch renewal leaching period was calculated by integrating the regression equation. Mass balance calculations revealed that only 9% of the PLF of V was released during the 45 d leaching period. Over 91% was still present in the coke in the potentially leachable form. This explains the continuous release of V during the initial 10 d renewal period and the rise in concentration of V on day 45 of the batch renewal leaching experiment (Fig. 4.5a).

With respect to the two Syncrude field lysimeters, the initial mass of the potentially leachable V (73969 mg) in each lysimeter was obtained from the product of the PLF of V (i.e. 5.7 mg/kg), the volume of coke in the lysimeters (i.e. 11.691 m^3), and the bulk density of the coke ($1,110 \text{ kg}/\text{m}^3$). The cumulative volume of water removed from the lysimeters between March 2005 and October 2006 was 488.2 L for the shallow lysimeter and 484.1 L for the deep lysimeter (Fenske, personal communication). The total mass of V released from coke in the two lysimeters between March 2005 and October 2006 was determined by integrating the regression equation between zero and the final volume of water removed from each lysimeter. Mass balance calculations for lysimeters show that only 2% and 6% of the total mass of V (i.e. 73969 mg) had leached from the shallow and deep lysimeters, respectively during the study period. This would easily explain the prolonged toxicity of leachate collected from both lysimeters at all sampling

times. At this rate, the two Syncrude lysimeters would presumably continue to leach V for many years at levels toxic to freshwater aquatic species such as *C. dubia*. Of course, this would be influenced by several other factors such as the pH of the infiltrating water, redox properties within coke profile in the lysimeters, and drainage and chemical properties of the soil cover. Moreover, if oil sands coke gets integrated into wet reclamation landscapes, it may potentially release V to the surrounding environment at levels toxic to aquatic invertebrates such as *C. dubia* for a considerable period of time.

5 IDENTIFYING THE CAUSES OF OIL SANDS COKE LEACHATE TOXICITY TO AQUATIC INVERTEBRATES

Preface

The objective of this study was to evaluate the influence of pH on metals release from coke and also to identify the toxicant associated with coke leachate. A toxicity identification and evaluation (TIE) approach was adopted to identify the toxicants. This study showed that pH has a profound influence on the type and amount of metals release from coke. Based on weight-of-evidence from a series of chronic TIE tests, Ni and V were identified as the cause of observed coke leachate toxicity. This helped design subsequent experiments in which the fate, speciation and toxicity of Ni and V were evaluated. Together, these studies provide information that could be useful in predicting the fate and toxicity of metals associated with coke stored in reclamation landscapes.

This chapter is accepted for publication in the journal *Environment Toxicology and Chemistry*. The revised version of the manuscript accepted by the journal is presented in this chapter. Figures and tables are re-formatted to fit thesis style. Supplementary material submitted as part of the revised manuscript is presented at the end of this chapter. References cited in this chapter are listed in the reference section of this thesis (chapter 8).

5.1 Abstract

In a previous study it was found that coke leachates (CL) collected from oil sands field sites were acutely toxic to *Ceriodaphnia dubia*; however, the cause of toxicity was not known. Therefore, the purpose of this study was to generate CL in the laboratory to evaluate the toxicity response of *C. dubia* and perform chronic toxicity identification evaluation (TIE) tests to identify the causes of CL toxicity. Coke was subjected to a 15 d batch leaching process at pH 5.5 and 9.5. Leachates were filtered on day 15 and used for chemical and toxicological characterization. The 7 d median lethal concentration (LC50) was 6.3 and 28.7% (v/v) for pH 5.5 and 9.5 CLs, respectively. Trace element characterization of the CLs showed Ni and V levels to be well above their respective 7 d LC50s for *C. dubia*. Addition of ethylenediaminetetraacetic acid (EDTA) significantly ($p \leq 0.05$) improved survival and reproduction in pH 5.5 CL, but not in pH 9.5 CL. Cationic and anionic resins removed toxicity of pH 5.5 CL only. Conversely, the toxicity of pH 9.5 CL was completely removed with an anion resin alone, suggesting that the pH 9.5 CL contained metals that formed oxyanions. Toxicity reappeared when Ni and V were added back to anion resin treated CLs. The TIE results combined with the trace element chemistry suggest that both Ni and V are the cause of toxicity in pH 5.5 CL, whereas V appears to be the primary cause of toxicity in pH 9.5 CL. Monitoring and risk assessments should therefore focus on the fate and toxicity of metals, especially Ni and V, in coke amended reclamation landscapes.

5.2 Introduction

The oil sands deposits in Alberta, Canada, are the world's largest reservoir of bitumen resource. An estimated $287 \times 10^9 \text{ m}^3$ of crude bitumen reserve (1804×10^9 barrels of crude oil) is spread across $142,000 \text{ km}^2$ of north-eastern Alberta, of which 2% ($6.2 \times 10^9 \text{ m}^3$ or 39×10^9

barrels of crude oil) is considered potentially recoverable using open-pit or surface mining (ERCB, 2010). Syncrude Canada Ltd., the largest oil sands mining company in Alberta operating since the 1970s, uses open-pit mining to access these oil-rich sands. Bitumen, the chief component of oil sands, is extracted from mined oil sands using hot water and caustic soda (NaOH) (Rogers et al. 2002). Because the extracted bitumen is highly viscous and deficient in hydrogen it is thermally upgraded via a complex fluid coking and/or hydro-cracking and catalytic hydro-treating process. In the fluid coking process, heavy bitumen is heated to approximately 500 °C which result in the production of lighter crude fractions with coke formed as a solid waste by-product (Scott and Fedorak, 2004). The objective of bitumen upgrading is to increase the hydrogen to carbon ratio by removing carbon from the bitumen, the carbon thus removed undergoes polymerization and condensation reactions to form a solid, carbonaceous, heterogeneous substance termed coke (Bejarano et al. 2003; Speight 1999). In addition, metal impurities present in the bitumen are undesirable as they deactivate reaction catalyst and decrease synthetic crude oil yield. Therefore these metals are removed from the bitumen and thus get enriched in the coke particles (Speight 1999; Furimsky, 2009). At an average of 2 million tonnes per year, Syncrude has produced nearly 20 million tonnes of coke over the last decade (ERCB, 2009). Because coke is considered a potential energy source, regulations set by the Energy Resources Conservation Board (ERCB) require oil sands companies to store coke on-site for the purpose of energy resource conservation. Nevertheless, use of coke as an alternative fuel source is presently precluded by high transportation costs and the availability of cheaper energy sources such as coal (Scott and Fedorak, 2004). In addition, high sulphur content (6-8% wt), low combustibility (Bejarano et al. 2003), high metal content, low volatile fractions (Furimsky, 2000) and increased green house gas emissions compared to natural gas (McKellar, 2010)

currently make coke an undesirable alternative source of energy. As a result, Syncrude has accumulated an estimated 40 million tonnes of coke in their on-site inventory (ERCB, 2009).

As part its mine closure plan, Syncrude is reviewing the option of integrating coke into terrestrial and/or aquatic reclamation landscapes for long-term storage and future recovery. In an effort to create sustainable reclamation landscapes, Syncrude initiated a multidisciplinary scientific assessment to study the fate and behaviour of coke in the environment. As part of this undertaking, two independent studies showed that concentrations of certain metals released from oil sands coke exceeded Canadian guidelines for the protection of aquatic life and those for livestock (Kessler and Hendry, 2006; Squires, 2005). In a previous study Puttaswamy et al. (2010) showed that coke leachates collected from Syncrude lysimeters were acutely toxic to the freshwater invertebrate, *Ceriodaphnia dubia*. However, the causes of coke leachate toxicity were not identified. To determine the ecotoxicological risk of integrating coke into reclaimed landscapes it is important to identify the toxic components.

For coke integrated into aquatic reclamation landscapes (e.g. wetlands) the fate and toxicity of metals associated with coke would be significantly influenced by pH. In a previous study it was found that certain metals (Al, Mn, Mo, Ni, V and Zn) mobilized from coke exposed to natural weathering differed significantly between the two lysimeters (Puttaswamy et al. 2010). Based on this study it was hypothesized that pH would significantly influence the type and amount of metals released from coke. Therefore, the objectives of the present study were to assess the influence of pH on metals release from coke and to identify the cause of leachate toxicity by performing a chronic toxicity identification and evaluation (TIE) using *Ceriodaphnia dubia* as the test species.

5.3 Materials and methods

5.3.1 Coke leachates

Fluid or fresh coke (coke produced from the fluid coking process) was collected directly from Syncrude Canada (AB, Canada) coker drums in July, 2006, and shipped to the Toxicology Centre, University of Saskatchewan (SK, Canada) in two 20 L pails (LDPE). At Syncrude operations, fluid coke is hydraulically transported in recycled process water to its place of storage. Recycled process water is characterized by high alkalinity and conductivity and, has been shown to be toxic to *C. dubia* (Puttaswamy et al. 2010). Because we were interested in identifying the toxicants associated with coke alone, we used coke obtained directly from the Syncrude fluid coker. This coke material had no history of contact with the recycled process water.

Coke was subjected to a 15 d, batch leaching process under two pH conditions (pH 5.5 and 9.5) with the coke:water ratio maintained at 1:4 (v/v). Batch leaching process was used to simulate wet reclamation scenario in which coke would be stored in constructed wetlands. This ratio best matched a proposed depth ratio of coke (0.5 to 0.75 m) to water (1 to 2 m) in shallow constructed wetlands (Squires, 2005). In the Athabasca oil sands region, pH values of 5.8 and 9.1 have been reported in a natural and a constructed wetland, respectively (Bendell-Young et al. 2000; Leung, 2001). It is thus likely that coke stored in wet reclamation landscapes could be exposed to such extreme pH conditions. Therefore, the objective of using two pH conditions for leaching coke was to assess the influence of this realistic range of environmental pH on metals release from coke, and to generate coke leachates with different trace metal chemistries to aid in full identification of potential toxicants. Prior to leaching, coke from two 20 L pails was

homogenized and 400 ml sub-samples poured into 2 L glass jars. Hard reconstituted water (HRW) was prepared for fluid coke leaching by adding 192 mg of NaHCO₃, 120 mg of CaSO₄, 120 mg of MgSO₄, and 8 mg of KCl to 1 L deionized water. The HRW used in this study best represented the water chemistries (e.g. hardness and alkalinity) of Syncrude lysimeter leachates and the recycled process water (Puttaswamy et al. 2010). The elemental composition of the HRW used for coke leaching and toxicity testing is given in Table S1 (supplementary material). The pH of the HRW was adjusted to pH 5.5 or 9.5 using either ultra-pure 1N HCl or 1N NaOH prior to addition to the jars. To each jar, 1.6 L of HRW was poured carefully against the side of the jar thereby avoiding suspension of coke particles. All jars were closed with air-tight lids to minimize pH fluctuation. The pH of the overlying water in individual leaching jars was monitored every day, and if pH drifted by more than ± 0.1 unit from the desired leaching pH of 5.5 or 9.5, then it was adjusted using either 1N HCl or 1N NaOH. On day 15, overlying water and porewater (collectively referred to as coke leachate) from each treatment group was extracted by vacuum filtration through 0.45 μm pore size membrane filters (Gelman Supor[®] 450; Pall Corporation). Coke leachates were pooled from all replicate jars from their respective treatment groups and stored in 20 L plastic containers at 4 °C until toxicity testing was initiated. Sub-samples of leachate were collected for trace element ($n=3$), major ion ($n=1$), polycyclic aromatic hydrocarbon (PAH, $n=1$), dissolved organic carbon (DOC, $n=3$) and general water chemistry analysis.

5.3.2 Toxicity testing procedures

All toxicity tests were conducted in a controlled environment chamber with an air temperature of 24.5 ± 0.5 °C and a photoperiod of 16:8 h light:dark. The cladoceran,

Ceriodaphnia dubia, was used in chronic (7 ± 1 d) toxicity tests to evaluate any changes in leachate toxicity associated with TIE manipulations. Daphnids were maintained in HRW and were fed daily a diet of *Pseudokirchneriella subcapitata* and YCT (yeast, cerophyll and trout-chow) mixture at a rate of 15 and 3 ml per 2 L of culture water, respectively (Environment Canada, 1992). Hard reconstituted water was used as dilution water for all toxicity tests. Tests were conducted with ten replicates ($n=10$) of single neonates (≤ 24 h old) placed in either 20 ml of control or test solution with renewal of test solutions every 24 h (Environment Canada, 1992). All toxicity tests were performed in 30 ml glass beakers and used survival and reproduction as test endpoints. The test was considered acceptable if 80% of control organisms survived and 60% of the surviving adults produced at least three broods with a total of at least 15 neonates per adult.

5.3.3 Initial toxicity test

Toxicity of coke leachates (CLs) was characterized, hereafter referred to as *initial toxicity test*, within 48 h of collection from leaching jars prior to any toxicity identification evaluation (TIE) tests (Fig. 5.1). The two filtered leachates had dissolved oxygen (DO) concentrations in the range of 5.4 to 5.7 mg/L and thus were aerated for 30 min to bring DO level to > 6.5 mg/L prior to toxicity testing. The water chemistry of the two leachates did not change substantially before and after aeration (see Table S2, supplementary material). Prior to exposing *C. dubia* to the leachates, the pH of the two leachates were adjusted to between 7.0 and 8.5 using either 1N HCl or 1N NaOH at each water renewal during all toxicity tests. After pH adjustment the two leachates (5.5 and 9.5) were tested separately for toxicity using a 0.5X dilution series (6.25, 12.5, 25, 50 and 100%) with daily water renewal. Water chemistry variables were measured three

times during the course of each toxicity test in the controls (dilution water only) and in the two leachates. Because the leachate dilutions (6.25, 12.5, 25 and 50 %) had similar water chemistry characteristics, for brevity, only the water chemistry data of whole leachates and the leachate concentration closest to their respective median lethal levels are presented in Table 5.1.

5.3.4 Phase I TIE: characterization tests

The objective of phase I TIE tests is to perform simple physical and chemical manipulations of leachates or effluents in order to characterize the class(es) of toxicants such as metals, nonpolar organics and/or ammonia that are often responsible for leachate or effluent toxicity (USEPA, 1991). Generally, phase I TIE manipulations are performed using the estimated median lethal concentration (e.g. LC50) from the initial toxicity tests. However in this study all phase I TIE manipulations were performed using 6.25% and 25% leachate concentrations for the pH 5.5 CL, and a 50% leachate concentration for the pH 9.5 CL, in both cases twice their respective LC50 concentration (Table 5.1). This was done to test the effectiveness of phase I TIE manipulations in removing the leachate toxicity. Based on water chemistry results from initial toxicity tests, specific phase I TIE tests were selected for both leachates. For example, because ammonia concentrations were below 0.05 mg/L in both 100% CLs (Table 5.1), a graduated pH test was not included in the phase I TIE scheme. Because CLs was filtered and aerated prior to initial toxicity testing, these manipulations were not repeated in the phase I TIE tests. A summary of the different TIE manipulations used to characterize, identify and confirm the cause of CL toxicity is shown in Figure 1. The overall goal of the phase I TIE tests was to achieve survival and reproduction in post-manipulated CLs that were similar to the negative controls (i.e. dilution water only treatment). Further, system blanks (TIE

manipulation of dilution water) were used in all phase I and II TIE tests to detect toxic artifacts (should they occur) resulting from physicochemical manipulations of the leachates.

Ethylenediaminetetraacetic acid (EDTA) was added to two CLs at each water renewal to yield final concentrations of 3 and 8 mg/L in order to determine if CL toxicity was due to chelatable cationic metals. To determine whether oxidative compounds or trace metals were the cause of CL toxicity, sodium thiosulfate (STS, $\text{Na}_2\text{S}_2\text{O}_3$) was added to subsets of the two CLs at each water renewal to yield a final concentration of 10 mg STS/L. Sodium thiosulfate addition reduces strong oxidants like chlorine and also binds certain cationic metals like Ni ($\log K = 2.06$) although to a lesser extent than EDTA ($\log K = 18.6$) (Hockett and Mount, 1996). The volumes of EDTA and STS added to CLs were not more than 5% of the total test volumes. To determine whether nonpolar organics were the toxic components in the leachates, the two CLs were filtered through Empore[®] high performance, C 18 solid phase extraction (SPE) disks (3M) by vacuum filtration at a rate of 100 ml/min. Prior to filtration, the C 18 SPE disks were preconditioned with methanol and water (USEPA, 1991). To further test if the CLs contained any ionizable organics (e.g. naphthenic acids), the pH of the two CLs was adjusted to approximately 3 and then filtered through C 18 disks. Post-SPE CLs were pH adjusted back to between 7 and 8.5 prior to toxicity testing.

5.3.5 Phase II TIE: identification tests

The objective of phase II TIE tests is to identify the specific suspect toxicant(s) within the classes of compounds characterized in phase I tests. A general approach for phase II TIE manipulations consists of chemical separation followed by toxicity characterization in order to

identify the toxicant(s) (USEPA, 1993). All phase II and III (described below) TIE manipulations were performed using whole (i.e. 100%) leachates.

Ion exchange resins (both anionic and cationic) were used to determine if anionic and/or cationic metals were responsible for leachate toxicity. The anionic resin (AR) used was AG[®] 1-X8 resin, a strongly basic anion exchanger having a counter ion (OH⁻) attached to a quarternary ammonium group (R-CH₂N-(CH₃)₃⁺) supported on 1 mm spherical, styrene beads cross-linked with divinyl benzene. The cationic resin (CR) used was AG[®] 50W-X8 resin, a strongly acidic, cation exchanger having a counter ion (H⁺) attached to a sulfonic acid group (R-SO₃⁻) that was coated onto 1 mm spherical styrene beads and cross-linked with divinyl benzene. Both ion exchange resins are thermally stable, resistant to solvents, reducing agents and oxidizing agents (Bio-Rad Laboratories). Preliminary experiments were conducted to determine the effective concentration of each resin having no-effect on *C. dubia* reproduction while reducing metal concentrations in the leachate (data not shown). Furthermore, a critical exercise of this preliminary experiment was to determine appropriate salt additions required to balance the loss of important ions, especially Ca²⁺, Mg²⁺ and SO₄²⁻, from both leachates due to ion exchange. Based on results from preliminary experiments, we used 5 g/L and 2.5 g/L of AR and CR, respectively. Resins were added directly into either dilution water or the 100% CLs (at their initial pH), and stirred for 1 h on a magnetic plate. Leachates were then vacuum-filtered through a 0.45 μm membrane and pH adjusted to between 7 and 8.5. Calcium sulfate (≥99% pure, Sigma-Aldrich) and MgSO₄ (≥99.5% pure, Sigma-Aldrich) were added to post-resin samples at 100 and 120 mg/L, respectively, to replenish Ca²⁺, Mg²⁺ and SO₄²⁻ ions in CLs. Toxicity tests were initiated using resin manipulated and un-manipulated CLs as well as dilution water.

Because Ni was identified as one of the suspect toxicant from phase II CR and AR tests, dimethylglyoxime (DMG, a Ni specific chelator) was used to remove dissolved Ni in the pH 5.5 CL. Onikura et al. (2008) showed that 30 mg of DMG/L was effective in reducing Ni toxicity and therefore suggested that DMG was useful in identifying Ni related toxicity in TIE tests. However, in the present study, DMG removed only 40% of the dissolved Ni from pH 5.5 CL and thus the CL was still acutely toxic to *C. dubia* (data not shown). Moreover, the use of 30 mg/L of DMG affected *C. dubia* fecundity and survival. Given that the DMG test was inconclusive, the DMG results are not presented here.

5.3.6 Phase III TIE: confirmation tests

Based on chemical and toxicological characterizations of resin-manipulated leachates, AR was the most effective in reducing the toxicities of both pH 5.5 and 9.5 CLs. Therefore, suspect trace metals (Ni and V) identified from phase II TIE tests were spiked back into the post-AR leachates at their original concentrations (individually and in mixture) and these solutions then tested for toxicity (see Fig. 5.1). A re-appearance of comparable toxicity would serve to confirm the role of suspect metals as being the cause of CL toxicity.

5.3.7 Analytical chemistry

Chemical characterization of dilution water and leachates was performed in-house at the Toxicology Centre, University of Saskatchewan. Routine water chemistry variables including pH, dissolved oxygen, conductivity, alkalinity, hardness and ammonia were measured in triplicate on days 0 and 15 of the coke leaching study, and on days 0, 3 and 7 of all toxicity tests. The dissolved concentrations of inorganic cations (Ca^{2+} , Mg^{2+} , Na^{+} and K^{+}) and anions (Cl^{-} , HCO_3^{-} , SO_4^{2-}) in dilution water and CLs were measured using a dual ion chromatography system

equipped with a dual ion exchange column (Dionex ICS-3000) following the EPA 300.1 method. Dissolved organic carbon was measured with a total organic carbon analyser 5050A (Shimadzu). Prior to elemental analyses, filtered (0.45 μm) leachate samples were acidified to 2% acid concentration with high-purity HNO_3 (Omnitrace ultra, EM Science). Dissolved concentrations of 26 elements in coke leachates were analyzed using an inductively coupled plasma mass spectrometer (ICP-MS) equipped with collision cell technology (X Series II, Thermo Electron). All samples were spiked with internal standards containing Bi, In and Tb (ICP-MS-IS-2, High-Purity Standards) to check for possible instrument drift and sample matrix effects. Standard solutions of Ag, Al, As, B, Ba, Be, Bi, Cd, Cr, Co, Cu, Fe, Hg, Mn, Mo, Ni, Pb, Sb, Se, Sn, Sr, Tl, Ti, U, V and Zn (BDH Aristar®) in a dilute HNO_3 matrix were used as external calibration standards to calculate element concentrations. Accuracy and precision of the analytical procedure was monitored by including two certified reference materials (CRMs), procedural blanks and sample duplicates at each analytical run. The CRMs consisted of a river water sample (SLRS-4, National Research Council) and a natural freshwater sample (1640, National Institute of Standards and Technology); accuracy relative to certified mean values ranged from 90.7 to 113.4% for SLRS-4 and from 87.5 to 99.6% for CRM 1640. At the end of the coke leaching study, a single sample of pH 5.5 and 9.5 CL was also analyzed for polycyclic aromatic hydrocarbons (PAHs) following a modified EPA 8270C method at the Saskatchewan Research Council (SRC) analytical laboratory. Target analytes in sample extracts were analyzed by a HP 6890 gas chromatography system (GC)/HP 5973 with a mass selective detector (MSD) run in the selective ion monitoring (SIM) mode.

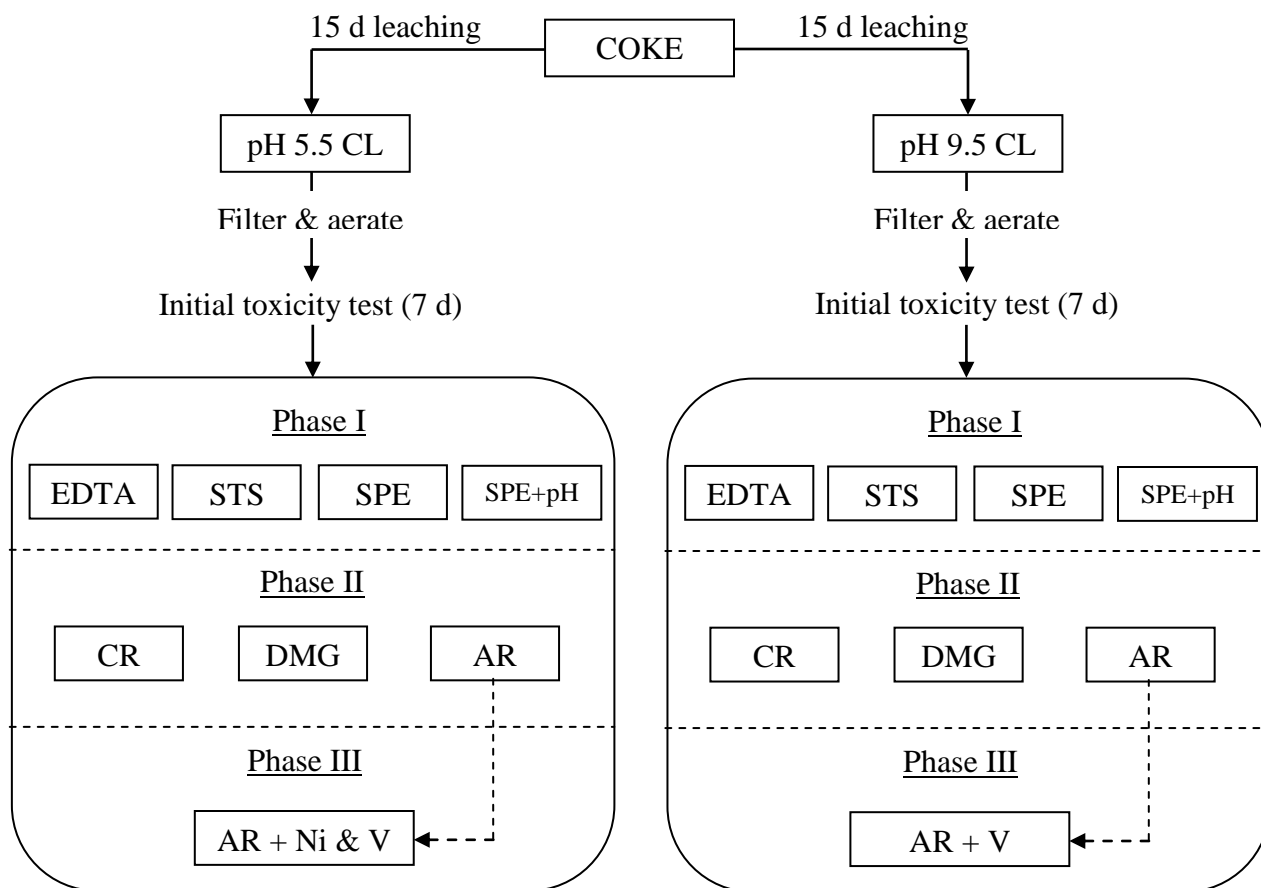


Figure 5.1. Overview of the performed coke leachate toxicity identification and evaluation (TIE) tests.

Acronyms are as follows:

CL–coke leachate
 EDTA–ethylenediaminetetraacetic acid
 STS–sodium thiosulfate
 SPE–solid phase extraction

CR–cation resin
 DMG –dimethyl glyoxime
 AR–anion resin
 Ni–nickel; V–vanadium.

5.3.8 Statistical analysis

Chronic median lethal concentration (LC50) for survival and inhibition concentration (IC50) for reproduction, the associated 95% confidence intervals, were calculated using the trimmed Spearman-Kärber method, version 1.5 (USEPA, 1990) and the inhibition concentration

(IC_p) approach, version 2.0 (USEPA, 1993). For all chronic TIE tests, the mean number of neonates produced per live *C. dubia* was used as the test endpoint. Statistical analyses were performed using SigmaPlot[®], version 11.0 (Systat Software, Inc.) with a 95% ($p \leq 0.05$) level of confidence. Reproduction data were analyzed using one-way analysis of variance (ANOVA). If data were not normally distributed and/or failed the equal variance test, non-parametric analysis was performed using a Kruskal-Wallis one-way analysis of variance on ranks. Post-hoc multiple comparisons were performed using Dunnett's or Dunn's test. Difference in metal concentrations between un-manipulated pH 5.5 and 9.5 CLs was analyzed using Student's *t*-test.

5.4 Results

5.4.1 Effect of pH on metals release from coke

The pH had a significant effect on the type and the concentration of metals released from coke. In general, pH 5.5 favored release of cationic metals (Ni, Mn, Fe and Zn) and pH 9.5 favored the release of metals, which form oxyanions (Al, V and Mo) in solutions (Table 5.2). Further, the concentration of V in pH 9.5 CL was at least an order of magnitude higher compared to all other metals (Table 5.2). However, the V concentration in pH 5.5 CL was more than three times lower (688 $\mu\text{g/L}$) than that in the pH 9.5 CL (2205 $\mu\text{g/L}$) (Table 5.2). Aside from changes in metal concentrations it is important to note that coke did not substantially alter the ionic composition of the two CLs. For example, concentrations of Ca^{2+} , Mg^{2+} and SO_4^{2-} in pH 5.5 and 9.5 CLs were comparable to those of the dilution water (Table 5.3). Only, HCO_3^- levels were at least an order of magnitude lower in pH 5.5 CL compared to the dilution water (HRW) and pH 9.5 CL (Table 5.3), presumably due to the direct influence of pH on aqueous speciation of

carbon dioxide. The concentrations of each of the 16 priority polycyclic aromatic hydrocarbons listed by the U.S. Environmental Protection Agency were all less than 0.05 µg/L in both leachates (see Table S3, supplementary material).

5.4.2 Initial toxicity test and water chemistry

Prior to toxicity testing, CLs were filtered, aerated and pH-adjusted to match the dilution water pH. Further, the water chemistry of dilution water and pH 5.5 and pH 9.5 CLs were measured on day 0, 3 and 6 during initial toxicity testing. The majority of the water chemistry variables in both CLs were within the standard toxicity testing conditions, most importantly pH and total hardness (Table 5.1) as these two variables strongly influence metal bioavailability and hence toxicity. However, the total alkalinity of the whole pH 5.5 CL (100%) was an order of magnitude lower compared to both dilution water and whole pH 9.5 CL (Table 5.1). Ammonia was below the detection limit (< 0.05 mg/L) in dilution water and in both leachates at their 100% concentration at all times during testing (Table 5.1). Dissolved organic carbon (DOC) concentrations in both leachates were similar to dilution water DOC levels (Table 5.1). Both leachates were acutely toxic to *C. dubia* at 100% concentration; 100% mortality was observed within 24 to 48 h of exposure. The 7 d LC50 estimates for pH 5.5 and pH 9.5 CLs were 6.3% and 28.7% (v/v), respectively (Table 5.1). Assessment using both survival and reproduction as test end-points showed that pH 5.5 CL was more toxic than pH 9.5 CL (Table 5.1).

Table 5.1. Chemical characteristics (mean \pm SE, $n = 3$) and toxicity endpoints for pH 5.5 and 9.5 coke leachates from the initial toxicity test.

| Characteristic | Dilution water (HRW) | pH 5.5 coke leachate (CL) | | pH 9.5 coke leachate (CL) | |
|---|-------------------------|---------------------------|-------------------|---------------------------|--------------------------------|
| | | 6.25% CL | 100% CL | 25% CL | 100% CL |
| Dissolved oxygen (mg/L) | 7.24 \pm 0.04 | 7.8 \pm 1.3 | 6.9 \pm 0.04 | 7.8 \pm 1.1 | 7.1 \pm 0.01 |
| pH | 8.25 \pm 0.02 | 8.3 \pm 0.04 | 7.2 \pm 0.02 | 8.3 \pm 0.1 | 8.24 \pm 0.02 |
| Alkalinity (mg/L as CaCO ₃) | 98 \pm 2 | 94 \pm 2 | 8 \pm 1 | 107 \pm 2 | 130 \pm 1 |
| Hardness (mg/L as CaCO ₃) | 141 \pm 2 | 152 \pm 8 | 164 \pm 1 | 150 \pm 9 | 153 \pm 2 |
| Ammonia (mg/L) | BDL | -- ^a | BDL | -- | BDL |
| Conductivity (μ S/cm) | 576 \pm 1 | 587 \pm 13 | 669 \pm 1 | 620 \pm 6 | 721 \pm 1 |
| Dissolved organic carbon (mg/L) | 3.9 \pm 0.1 | -- | 3.4 \pm 0.2 | -- | 3.5 \pm 0.1 |
| <u>Toxicity endpoints</u> | | | | | |
| LC50 (% v/v CL) | NA | NA | 6.3% ^b | NA | 28.7% (23.5-35.1) ^c |
| IC50 (% v/v CL) | NA | NA | <6.25% | NA | 31.3% (26.3-35.5) |

BDL = below detection limit (<0.05 mg/L).

NA = not applicable.

LC50 = median concentration lethal to 50% test population.

IC50 = concentration estimated to cause 50% inhibition in mean reproduction.

^a Ammonia and dissolved organic carbon not measured in 6.25% and 25% coke leachates.

^b 95% confidence interval not obtainable.

^c Values in parenthesis are 95% confidence intervals.

Table 5.2. Trace element concentrations (mean \pm SE, $n = 3$) in un-manipulated (*no resin*) and resin-manipulated (*cationic resin, CR and anionic resin, AR*) pH 5.5 and 9.5 coke leachates, and the 7 d median lethal concentrations (LC50) for metals estimated using *C. dubia* as the test species.

| Elements ^{a, b} ($\mu\text{g/L}$) | pH 5.5 coke leachate | | | pH 9.5 coke leachate | | | 7 d LC50 ($\mu\text{g/L}$) |
|---|----------------------|----------------|----------------|----------------------|----------------|---------------|---------------------------------|
| | No resin | Cation resin | Anion resin | No resin | Cation resin | Anion resin | |
| Al | 28 \pm 4.6* | 1.6 \pm 0.6 | 1.2 \pm 0.02 | 206 \pm 42 | 2.8 \pm 2.1 | 0.6 \pm 0.8 | 497 ^c |
| B | 174 \pm 15 | 192 \pm 2.8 | 157 \pm 1.6 | 179 \pm 6.2 | 247 \pm 28 | 174 \pm 10 | 45 500 ^d |
| Ba | 46 \pm 2.8 | 0.6 \pm 0.2 | 49 \pm 0.3 | 43 \pm 1.1 | 1.5 \pm 0.7 | 5.3 \pm 4.4 | 10 024 ^e |
| Fe | 8.9 \pm 4.2 | 1.5 \pm 0.7 | 3.0 \pm 1.5 | 19 \pm 17 | 5.8 \pm 2.5 | 1.5 \pm 0.2 | NA |
| Mn | 776 \pm 146 | 5.5 \pm 0.1 | BDL | 2.9 \pm 1.1* | 0.4 \pm 0.2 | BDL | 12 810 ^c |
| Mo | 106 \pm 28* | 114 \pm 1.2 | 2.7 \pm 2.4 | 218 \pm 7.8 | 298 \pm 28 | 5.2 \pm 0.2 | 19 700 ^f |
| Ni | 145 \pm 31* | 1.2 \pm 0.1 | 0.2 \pm 0.2 | 0.2 \pm 0.1 | 0.8 \pm 0.5 | 0.5 \pm 0.5 | 3.8 ^c |
| Sr | 146 \pm 20 | 0.7 \pm 0.2 | 159 \pm 3 | 178 \pm 6.4 | 3.8 \pm 1.3 | 42 \pm 29 | NA |
| V | 688 \pm 105* | 361 \pm 7.3 | 36 \pm 26 | 2205 \pm 69 | 1922 \pm 174 | 251 \pm 11 | 550 ^c |
| Zn | 27 \pm 4.8 | 2.9 \pm 0.01 | 1.2 \pm 0.2 | 3.5 \pm 0.8* | BDL | 4.2 \pm 0.9 | 165 ^f |

BDL = below detection limit ($\leq 0.01 \mu\text{g/L}$).

NA = not applicable.

* denotes a significant difference ($p \leq 0.05$) between un-manipulated pH 5.5 and 9.5 CLs.

^a The following elements were $\leq 0.01 \mu\text{g/L}$: Ag, Be, Bi, Hg, Pb, Se, Sn, Ti, Tl and U.

^b The following elements were $\leq 5 \mu\text{g/L}$: As, Cd, Cu, Co, Cr and Sb.

^c Median 7 d LC50 for Al, Mn, Ni and V (Puttaswamy et al. 2010).

^d Median 48 h LC50 for B (Dethloff et al. 2009).

^e 7 d IC25 for Ba (Brix et al. 2010).

^f Median 7 d LC50 for Mo and Zn (Onikura et al. 2008).

Table 5.3. Ionic composition of dilution water, pH 5.5 and 9.5 coke leachates, before and after resin treatment (*anionic, AR and cationic, CR*) and salt addition^a.

| Sample Type | Anions (mg/L) | | | Cations (mg/L) | | | |
|---------------------------|-----------------|-------------------------------|-------------------------------|------------------|----------------|------------------|-----------------|
| | Cl ⁻ | HCO ₃ ⁻ | SO ₄ ²⁻ | Ca ²⁺ | K ⁺ | Mg ²⁺ | Na ⁺ |
| Dilution water (HRW) | 5 | 127 | 180 | 18 | 3 | 23 | 50 |
| HRW + AR | 6 | 50 | 3 | 8 | 4 | 0 | 50 |
| HRW + AR + Salt | 107 | 22 | 157 | 26 | 6 | 21 | 50 |
| HRW + CR | 8 | 13 | 161 | 1 | 2 | 0 | 25 |
| HRW + CR + Salt | 87 | 18 | 323 | 25 | 8 | 27 | 123 |
| <u>Coke Leachate (CL)</u> | | | | | | | |
| pH 5.5 CL | 72 | 12 | 192 | 27 | 4 | 27 | 52 |
| pH 5.5 CL + AR | 149 | 17 | 1 | 21 | 5 | 0 | 49 |
| pH 5.5 CL + AR + Salt | 156 | 14 | 156 | 21 | 12 | 42 | 47 |
| pH 5.5 CL + CR | 73 | 14 | 193 | 1 | 3 | 1 | 31 |
| pH 5.5 CL + CR + Salt | 88 | 24 | 373 | 33 | 9 | 33 | 139 |
| pH 9.5 CL | 7 | 207 | 175 | 25 | 4 | 26 | 84 |
| pH 9.5 CL + AR | 5 | 51 | 13 | 9 | 4 | 1 | 73 |
| pH 9.5 CL + AR + Salt | 136 | 71 | 170 | 34 | 6 | 23 | 72 |
| pH 9.5 CL + CR | 7 | 14 | 167 | 0 | 1 | 0 | 40 |
| pH 9.5 CL + CR + Salt | 19 | 27 | 333 | 30 | 4 | 24 | 93 |

^a CaSO₄ (100 mg/L) and MgSO₄ (120 mg/L) were added to post-resin treated HRW and coke leachates to restore Ca²⁺, Mg²⁺ and SO₄²⁻ ion concentrations (referred to as “+Salt”) prior to toxicity testing.

5.4.3 Phase I TIE: characterization tests

Selection of relevant phase I characterization tests were based on the initial results of leachate toxicity testing and associated water chemistry analyses. For example, because ammonia levels were below the detection limit in the two leachate concentrations tested (Table 5.1), a graduated pH test to detect ammonia toxicity was not included in the TIE. The goal of TIE tests was to achieve a non-significant difference in mean *C. dubia* reproduction between TIE manipulated leachates and the negative control. None of the TIE manipulations substantially influenced water chemistry variables, particularly pH and total hardness (data not shown).

Among the four phase I TIE manipulations employed, only EDTA addition reduced chronic toxicity in pH 5.5 CL. A dose-dependent increase in *C. dubia* reproduction was observed with increasing EDTA concentration in pH 5.5 CL (Fig. 5.2). Neither EDTA concentrations (3 and 8 mg/L) were lethal or affected *C. dubia* reproduction in control groups (Fig. 5.2). Further, *C. dubia* reproduction in the 6.25% CL + 8 mg/L EDTA group approached that of the controls (Fig. 5.2). There was 100% mortality in the un-manipulated 25% leachate; however, EDTA addition improved both survival and reproduction (Fig. 5.2). Fecundity in the 25% + 8 mg/L EDTA group was significantly different from the control (Fig. 5.2). Sodium thiosulfate (STS) addition did not reduce toxicity in either 6.25% or 25% pH 5.5 CLs; the mean reproduction of STS manipulated leachate groups was still significantly different from control reproduction (Fig. 5.3a). Further, solid phase extraction combined with pH manipulation did not improve *C. dubia* fecundity in pH 5.5 CL (Fig. 5.3b).

None of the phase I TIE manipulation tests substantially reduced the toxicity of pH 9.5 CL (Fig. 5.4). Phase I TIE results thus indicated that cationic metals could be at least partially responsible for pH 5.5 CL toxicity. With respect to pH 9.5 CL, phase I TIE tests suggested that

cationic metals, non-polar organics and ionizable organics were not the primary cause of leachate toxicity.

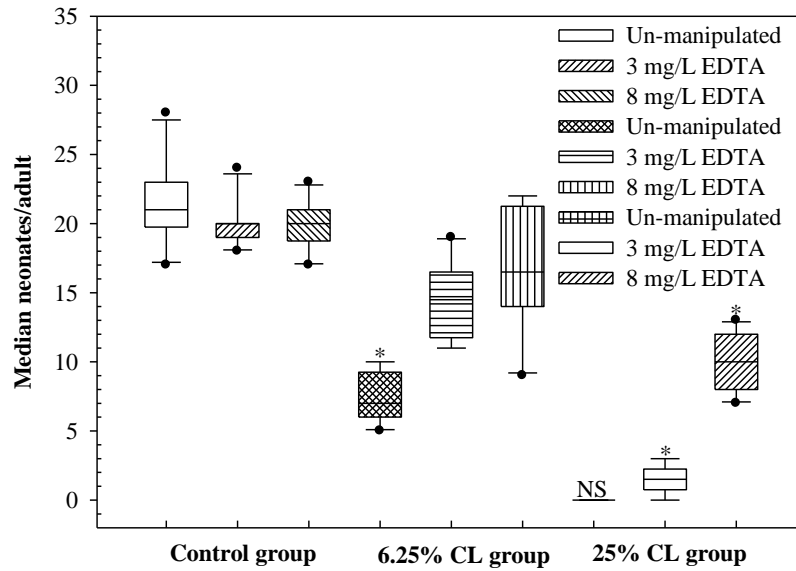


Figure 5.2. Median number of neonates per *Ceriodaphnia dubia* exposed to two concentrations of pH 5.5 coke leachate (6.25% and 25%), with and without ethylenediaminetetraacetic acid (EDTA) addition (3 and 8 mg/L). An asterisk (*) denotes a significant difference ($p \leq 0.05$) between the control and pH 5.5 coke leachate groups. *NS*—*No survival*.

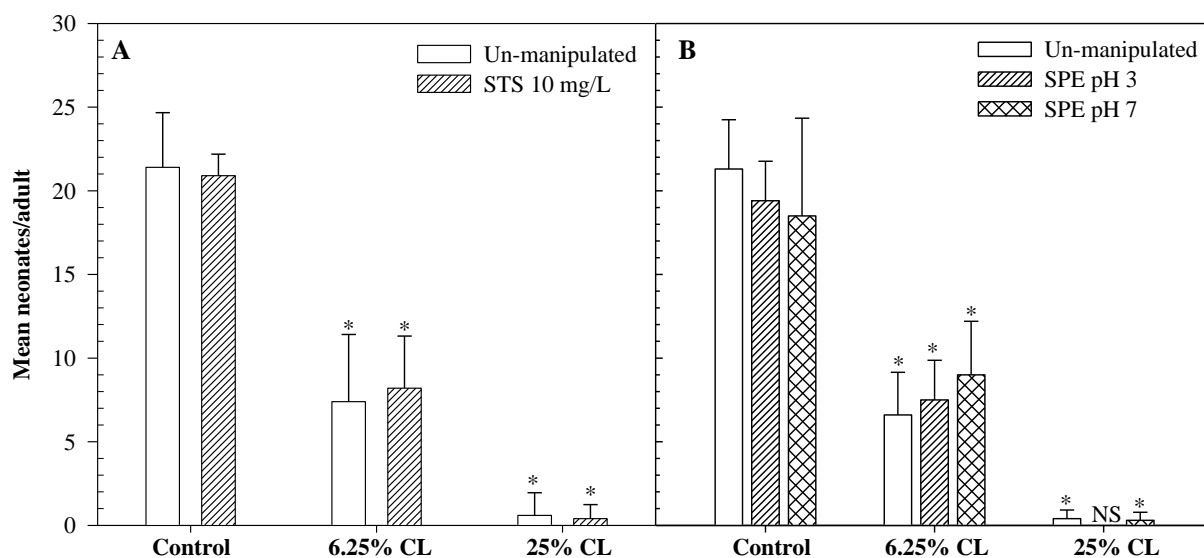


Figure 5.3. Mean (\pm SD, $n = 10$) number of neonates per *Ceriodaphnia dubia* exposed to two concentrations of pH 5.5 coke leachate (6.25% and 25%), with and without (A) 10 mg/L sodium thiosulfate addition (STS) and (B) solid-phase extraction using C18 disks at pH 3 and 7. An asterisk (*) denotes a significant difference ($p \leq 0.05$) between the control and treatment groups. NS—No survival.

5.4.4 Phase II TIE: toxicity identification and chemistry

To increase confidence in TIE results, all phase II and III TIE tests were performed using whole CLs (100%). Based on the weight-of-evidence from phase I tests, metals were suspected as the cause of CL toxicity. Further, Ni and V concentration in pH 5.5 CL and V in pH 9.5 CL were well above their individual *C. dubia* LC50s (Table 5.2). The concentrations of all other measured trace metals were either below their respective detection limit, or considerably lower than their individual LC50s (Table 5.2).

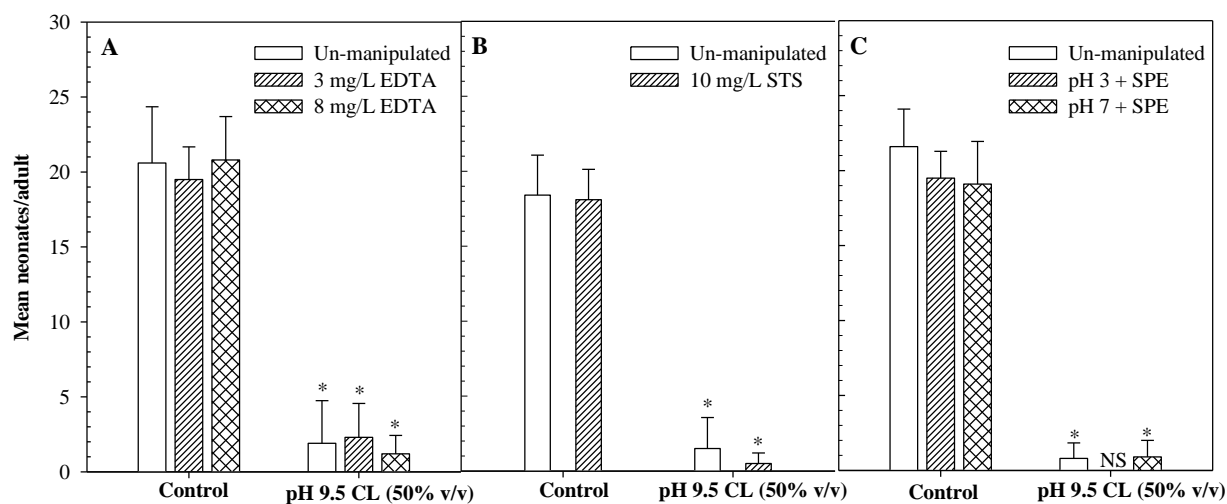


Figure 5.4. Mean (\pm SD, $n = 10$) number of neonates per *Ceriodaphnia dubia* exposed to pH 9.5 coke leachate (50% v/v), with and without (A) 3 or 8 mg/L ethylenediaminetetraacetic acid (EDTA) addition, (B) 10 mg/L sodium thiosulfate addition (STS), and (C) solid-phase extraction using C-18 disks at pH 3 and 7. An asterisk (*) denotes a significant difference ($p \leq 0.05$) between control and pH 9.5 CL groups. NS—No survival.

Cation resin (CR) and anion resin (AR) were used to test if Ni and V were responsible for leachate toxicity. Because 7 d survival and reproduction of *C. dubia* in dilution water that had been passed through these resins were comparable to those in the negative control, it was concluded that they were non-toxic at the resin concentrations tested (Fig. 5.5). Of the two resins used, AR was effective in removing dissolved Ni and V, and also toxicity, in both leachates. Dissolved concentrations of Ni and V in AR-treated leachates were reduced to less than 10% of their original concentrations in both leachates (Table 5.2). On the other hand, CR removed 99%

of dissolved Ni in pH 5.5 CL but only 52 and 23% of dissolved V in pH 5.5 and 9.5 CLs, respectively (Table 5.2). Furthermore, AR significantly reduced dissolved Ni and V concentrations in pH 5.5 CL to approximately an order of magnitude lower than their respective *C. dubia* LC50s (Table 5.2). Consequently, *C. dubia* reproduction and survival increased significantly in AR-treated pH 5.5 CL compared to the un-manipulated CL (Fig. 5.5). Moreover, fecundity in AR-treated pH 5.5 CL was similar to that in the control group (Fig. 5.5). With CR, fecundity of *C. dubia* increased considerably in pH 5.5 CL compared to the un-manipulated CL, but was still significantly lower compared to the control (Fig. 5.5). For pH 9.5 CL, AR completely removed toxicity and the 7 d *C. dubia* fecundity was comparable to that of the control group (Fig. 5.5). Correspondingly, the dissolved concentration of the only suspect toxicant, V, was reduced significantly, to a level below its toxicity threshold (Table 5.2). Conversely, CR did not reduce toxicity and there was 100% mortality in manipulated and un-manipulated pH 9.5 CL (Fig. 5.5). Furthermore, CR was not as effective as AR in removing dissolved V from pH 9.5 CL; the concentration of V in CR-treated 9.5 CL was nearly 3.5 times higher than the 7 d *C. dubia* LC50 for V (Table 5.2).

Use of ion exchange resins substantially changed the ionic composition of HRW (dilution water) and both CLs. Generally, AR additions removed bicarbonate and sulfate from HRW and pH 9.5 CL, but only sulfate in pH 5.5 CL (Table 5.3). In addition, AR substantially removed Ca and Mg from HRW and pH 9.5 CL, and Mg from pH 5.5 CL (Table 5.3). Conversely, CR effectively removed all cations and only bicarbonate from HRW, pH 5.5 CL and pH 9.5 CL (Table 5.3). However, addition of CaSO₄ (100 mg/L) and MgSO₄ (120 mg/L) to post-resin treated waters and leachates restored Ca²⁺, Mg²⁺ and SO₄²⁻ concentrations (Table 5.3).

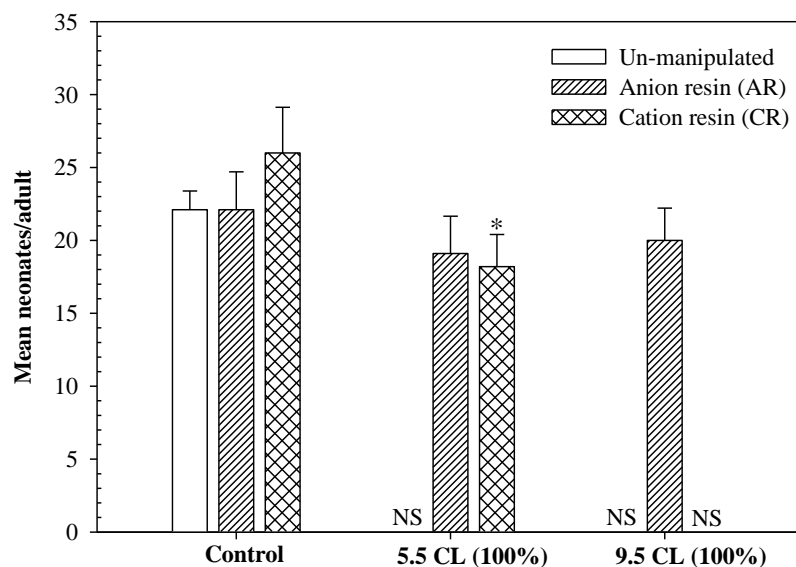


Figure 5.5. Mean (\pm SD, $n = 10$) number of neonates per *Ceriodaphnia dubia* exposed to whole (100% v/v) pH 5.5 and pH 9.5 coke leachate with and without either anion or cation resin treatment. An asterisk (*) denotes a significant difference ($p \leq 0.05$) between the control and resin manipulated groups. NS-No survival.

In the phase II tests, AR effectively removed toxicity in both pH 5.5 and 9.5 CLs. Toxicity (100% mortality) re-appeared within 48 h when Ni and V were added (to approximately initial levels) either individually or in combination to post-AR treated pH 5.5 CL (Fig. 6). Vanadium was the only element identified as being responsible for toxicity in pH 9.5 CL. Toxicity re-appeared, when V was added to post-AR treated pH 9.5 CL, confirming the role of V in leachate toxicity (Fig. 6).

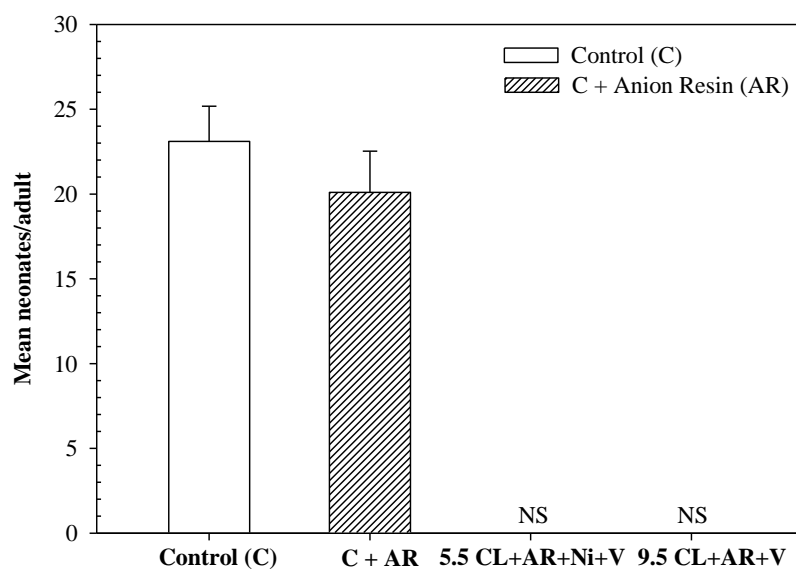


Figure 5.6. Mean (\pm SD, $n = 10$) number of neonates per *Ceriodaphnia dubia* exposed to pH 5.5 post-anion resin (AR) coke leachate spiked with both Ni and V and pH 9.5 post-anion resin coke leachate spiked with only V. NS–No survival (100% mortality) of the test organisms in both pH 5.5 and 9.5 post-anion resin (AR) coke leachates spiked with metals.

5.5 Discussion

In a previous study it was found that coke exposed to natural weathering processes in two lysimeters released several metals (Al, B, Mn, Mo, Ni, V and Zn) and that the leachates collected over a period of 20 months were acutely toxic to *C. dubia* (Puttaswamy et al. 2010). However, the cause of leachate toxicity was not identified. In the present study, the effect of pH on metals release from similar coke was assessed and a chronic toxicity identification evaluation (TIE) approach used to identify the cause(s) of coke leachate toxicity. Based on TIE manipulations and a weight-of-evidence approach, Ni and V were identified as the toxic components of coke leachates.

As expected, pH had a significant influence on the type and amount of metals released from coke. Leaching at pH 5.5 favored the release of cationic metals (Ni, Mn, Fe and Zn) whereas leaching at pH 9.5 favored the release of metals that form oxyanions (Al, V and Mo) in solutions. It is well known that pH is a key variable affecting metal mobility with cationic metals generally mobilized under acidic conditions and anionic metals mobilized under alkaline conditions (Forstner, 1993). The concentration of Ni in pH 5.5 CL (145 µg/L) was high compared to that in pH 9.5 CL (0.2 µg/L). Nickel solubility is shown to decrease under alkaline pH conditions due to formation of insoluble Ni(OH)_{2(s)} precipitates (Ji and Cooper, 1996). It is therefore possible that under alkaline leaching conditions, Ni dissolution was limited due to formation of insoluble Ni hydroxide precipitates. In a similar batch leaching study using Syncrude stock-piled coke, it was observed that Ni concentrations decreased significantly (from 258 µg/L to 7.3 µg/L) when pH of the leaching water was increased from 5.5 to 10 (A. Squires, 2005, MSc thesis, University of Saskatchewan, Saskatoon, SK, Canada).

The concentration of V in pH 9.5 CL was highest of all metals released from coke under these leaching conditions. Moreover, V concentrations in both leachates were above the 7 d *C. dubia* LC50 of 550 µg/L. This indicates that Syncrude coke contains appreciable amounts of V that can be readily mobilized under alkaline leaching conditions. Similarly, in a previous study it was reported that due to slightly alkaline pH (> 7.6) conditions, V concentrations were consistently elevated in leachates obtained from a lysimeter installed in the Syncrude Mildred Lake Settling Basin (Puttaswamy et al. 2010). Vanadium is known to be more soluble under alkaline pH conditions and its solubility decreases under acidic condition due to a shift in speciation from V(V) to V(IV) (Wherli and Stumm, 1989). Furthermore, Ni and V are the two

chief metallic components associated with bitumen as porphyrin forms (Speight, 1999). Because their presence lowers fuel quality and poisons the catalysts, Ni and V are preferentially removed from bitumen during its upgrading and thus end up in the coke (Furimsky, 2009). Therefore, for coke stored in constructed wetlands or other landscapes, it is speculated that release of Ni and V from the coke would be strongly influenced by pH of the surrounding water. The majority of the dissolved ions in both pH 5.5 CL and 9.5 CL were similar to the HRW ionic composition, suggesting that coke does not release substantial amounts of Ca^{2+} , Mg^{2+} , Na^+ , Cl^- , HCO_3^- or SO_4^{2-} .

From the initial toxicity tests it was found that both leachates were acutely toxic to *C. dubia* at 100% leachate concentrations. However, based on their individual LC50s, pH 5.5 CL was more toxic than pH 9.5 CL (Table 5.1). The higher toxicity of pH 5.5 CL could be attributable to the presence of high Ni compared to 9.5 CL. Species sensitivity distribution show *C. dubia* to be highly sensitive among other freshwater species to Ni exposure (Keithly et al. 2004). Further, the V concentration at the LC50 value (6.3% v/v) of pH 5.5 CL is calculated to be 43 $\mu\text{g/L}$. This value is well below the *C. dubia* 7 d LC50 value for V (550 $\mu\text{g/L}$). Nevertheless, because their individual concentrations are well above their respective LC50s (Table 5.2), toxicity at 100% pH 5.5 CL could be due to both Ni and V. Therefore, for phase II TIE tests it was important to use 100% leachate to account for the possible toxicity of both Ni and V.

Of the four phase I TIE tests, only EDTA addition reduced toxicity of pH 5.5 CL. A reduction in toxicity due to EDTA addition suggests that divalent cationic metals are, or contribute to, the cause of toxicity (Hockett and Mount, 1996). In the present study, it was observed that acidic leaching influenced the release of many cationic metals from fluid coke.

However, only the concentration of Ni (145 µg/L) was well above its *C. dubia* 7 d LC50 of 3.8 µg/L (Table 5.2). Concentrations of other divalent cationic metals such as Cu, Cd, Pb, Hg and Co were all less than 0.01 µg/L. Further, the two EDTA levels used were in stoichiometric excess of dissolved Ni concentrations and other divalent cationic metals, suggesting that dissolved Ni should have been fully chelated by EDTA. In addition, the [Ni-EDTA]⁻ complex has the highest stability (log *K* = 20.4) compared to other major cations in pH 5.5 CL including Ca, Mg, Sr, Fe, Ba and Zn (Morel, 1993). Moreover, the ability of a metal ion to complex with the greatest amount of ligand (e.g. EDTA) at equilibrium depends on the product of *K* multiplied by the concentration of free metal ion (Nowack, 2002). In pH 5.5 CL, the concentration of dissolved Ni was high compared to most divalent cationic metals (Table 5.2). As a result, Ni in the pH 5.5 CL (6.25% and 25% v/v) should be completely chelated by EDTA and therefore not available for uptake by *C. dubia*. Nevertheless, there was residual toxicity (i.e. decreased fecundity) in 25% + 8 mg/L pH 5.5 CL group compared to the control (Fig. 5.2). This toxicity could be attributable to V for two reasons. First, at the pH of the EDTA addition experiment (7.2 to 8.2), V species would be predominantly present as oxyanions and thus may not bind to EDTA. At neutral pH and under most environmental conditions V is predominantly present as oxyanion species (Crans et al. 1998). Only at low pH (<5) do cationic V species exist (VO²⁺ and VO⁺²) that can form strong complexes with EDTA⁴⁻ (Jen et al. 1997; Chen and Naidu, 2002). Second, the V concentration in the EDTA-manipulated 25% pH 5.5 CL group was calculated to be 172 µg/L, which should be sufficient to cause reproductive effects in *C. dubia*.

Solid phase extraction tests did not reduce pH 5.5 CL toxicity (Fig. 5.3b). Generally, when post-SPE samples are no longer toxic, nonpolar organic compounds are thought to be present and a subsequent methanol elution test is performed to recover and confirm toxicity

(Norberg-King, 2005). In the present study, a methanol elution test was not performed because post-SPE leachates remained toxic. Furthermore, analysis of both CLs revealed concentrations of all PAHs quantified to be below the detection limit (see Table S3, supplementary material). Therefore, nonpolar organics were not among the suspect toxicants. Initially, it was suspected that naphthenic acids, which are often an acutely toxic component of oil sands process waters (Clemente and Fedorak, 2005; Nero et al. 2006), could be present in coke leachates. Naphthenic acids are pH sensitive and at an aqueous pH below their acid dissociation constant ($pK_a = 5$ to 6) they are largely protonated (Headley and McMartin, 2004). To rule out toxicity due to ionizable organics (such as naphthenic acids), a pH adjustment to 3 followed by SPE (using C 18 disks) was performed. The pH 3 manipulated post-SPE leachate remained toxic, suggesting that naphthenic acids were not the cause of coke leachate toxicity (Fig. 5.3b and Fig. 5.4c). Moreover, naphthenic acids are reported to be completely disintegrated at the high temperatures ($500\text{ }^\circ\text{C}$) during the coking process and thus should not be associated with fluid coke (Schramm et al. 2000). None of the phase I TIE tests reduced the toxicity of pH 9.5 CL (Fig. 4), suggesting that cationic metals, organics, and oxidizable compound were not the primary cause of toxicity of pH 9.5 CL.

Overall, phase I TIE results provided limited success in characterizing leachate toxicity. Therefore, to identify suspect toxicants and to guide further TIE tests, chemical characterization of leachates was performed as part of the phase II TIE. Based on the weight-of-evidence from the phase I TIE results, trace metal concentrations in the whole leachates (phase II analyses), and metal-specific LC50 values for *C. dubia*, Ni and V were identified as suspect toxicants in the coke leachates. Cationic resin (CR) and anionic resin (AR) manipulations, along with trace element characterization of the post-resin leachates, were therefore used to further assess if Ni

and V were the cause(s) of leachate toxicity. Chelating resins are useful in determining the cause of toxicity from both cation and anion forming metal species (Burgess et al. 2000; Burgess 2007). In the present study, CR partially reduced the toxicity of pH 5.5 CL (Fig. 5). This reduction was likely due to a reduction in dissolved Ni concentration, however, residual toxicity in pH 5.5 CL was suspected to be due to V. The V concentration in pH 5.5 post-CR leachate (361 µg/L) remained sufficient to potentially impair *C. dubia* reproduction (Table 5.2). In a previous study, the IC50 and IC20 for V (based on 7 d *C. dubia* reproduction) were estimated to be 490 µg/L and 125 µg/L, respectively (Puttaswamy et al. 2010).

After passage through an anion resin, toxicity disappeared in pH 5.5 CL, and there was a concomitant reduction of dissolved Ni and V to concentrations below their respective toxicity thresholds (Fig. 5 and Table 5.2). When Ni and V were added back to the pH 5.5 post-AR CL, toxicity reappeared (Fig. 6). These observations strongly suggest that Ni and V could both be acting as toxicants in pH 5.5 CL. It was interesting to note that AR was more effective than CR in removing both cationic and anionic forming metals from coke leachates (Table 5.2). Similar observations were made by Burgess et al. (2007), where an arsenic selective anionic resin, with a chloride (Cl⁻) counter ion attached to a positively charged amine functional group (R-N-(CH₃)₃⁺), significantly reduced the concentrations of several cationic metals (e.g. Cd, Ni, Zn, Cu and Pb). Further, it was suggested that the positively charged amine functional groups on the anionic resin were effective ligands for Cd, Ni and Zn because of their smaller complex stabilities compared to Cu and Pb (Burgess et al. 2007). In the present study, AR used had a similar functional group (i.e. R-CH₂N-(CH₃)₃⁺) to the one used by Burgess et al. (Burgess et al. (2007), but having (OH⁻) as the counter ion. As a result, the pH of the post-AR leachates reached to ~12 due to

exchangeable hydroxyl (OH^-) ions. It is highly likely that at this extremely alkaline pH (~12), Ni would precipitate as insoluble nickel hydroxide $\text{Ni}(\text{OH})_{2(s)}$ (Ji and Cooper, 1996).

For pH 9.5 CL, CR treatment failed to reduce toxicity. Moreover, CR did not reduce V levels in the post-CR leachate to concentration below its 7 d LC50 (Table 5.2). At pH 6 and above, V is predominantly present as oxyanions ($\text{VO}_2(\text{OH})^{2-}$ and VO_3OH^-) (Peacock and Sherman, 2004). Therefore, the negatively charged sulfonic acid (R-SO_3^-) functional group on the CR used likely repelled the negatively charged V oxyanion species. Conversely, AR treatment was effective in removing dissolved V and completely removed toxicity in pH 9.5 CL (Table 5.2 and Fig. 5.5). Adding V back to pH 9.5 post-AR CL at a nominal concentration of 2000 $\mu\text{g/L}$ resulted in 100% mortality of *C. dubia* (Fig. 6). These results confirm that vanadium must have been the primary cause of toxicity in pH 9.5 CL. In conclusion, Syncrude coke has the potential to release metals at toxicologically relevant concentrations under a range of pH conditions. Results from toxicity identification evaluation and chemical analyses suggested that Ni and V were the primary causes of Syncrude coke leachate toxicity. Further research should be undertaken to examine metals mobilization from coke stored in actual reclamation landscapes (e.g. wetlands) and to better understand the fate, transport and bioavailability of these metals in such landscapes, especially where other oil sands materials such as tailings water may be present.

5.6 Supplementary material

Table S 5.1. Elemental composition of dilution water (HRW) used for coke leaching and TIE manipulations.

| Elements ^a | Concentration (µg/L) |
|-----------------------|-------------------------|
| As | 0.5 |
| B | 22.5 |
| Cd | 0.02 |
| Cu | 0.1 |
| Hg | 0 |
| Mn | 0.6 |
| Ni | 0.3 |
| Pb | 0.08 |
| Se | 0.1 |
| Sn | 0.8 |
| Sr | 2.5 |
| Tl | 0.04 |
| Zn | 2.5 |

^a The following elements were below detection limit (≤ 0.01 µg/L): Ag, Al, Ba, Be, Bi, Co, Cr, Fe, Sb, Ti, U and V.

Table S 5.2. Effect on water chemistry (mean±SE, n=3) before and after aeration of the filtered coke leachates (CL).

| Characteristic | pH 5.5 CL | | pH 9.5 CL | |
|---|-----------|---------|-----------|----------|
| | Before | After | Before | After |
| Dissolved oxygen (mg/L) | 5.4±0.1 | 6.6±0.3 | 5.7±0.2 | 6.8±0.01 |
| pH | 5.7±0.3 | 5.9±0.4 | 9.1±0.01 | 8.8±0.3 |
| Hardness (mg/L as CaCO ₃) | 151±2 | 154±3 | 149±2 | 151±2 |
| Alkalinity (mg/L as CaCO ₃) | 7±1 | 8±2 | 140±2 | 138±3 |

Table S 5.3. Concentrations of polynuclear aromatic hydrocarbons (PAHs) measured in the two coke leachates.

| Analyte (µg/L) | pH 5.5 CL | pH 9.5 CL |
|-----------------------------|-----------|-----------|
| Acenaphthene | <0.05 | <0.05 |
| Acenaphthylene | <0.05 | <0.05 |
| Anthracene | <0.05 | <0.05 |
| Benzo (a) anthracene | <0.1 | <0.1 |
| Benzo (a) pyrene | <0.01 | <0.01 |
| Benzo (b) fluoranthene | <0.5 | <0.5 |
| Benzo (e) pyrene | <0.5 | <0.5 |
| Benzo (g, h, i) perylene | <0.5 | <0.5 |
| Benzo (k) fluoranthene | <0.5 | <0.5 |
| Chrysene | <0.1 | <0.1 |
| Dibenzo (a, h) anthracene | <0.5 | <0.5 |
| Fluoranthene | <0.05 | <0.05 |
| Fluorene | <0.05 | <0.05 |
| Indeno (1, 2, 3-c,d) pyrene | <0.5 | <0.5 |
| Naphthalene | <0.05 | <0.05 |
| Perylene | <0.5 | <0.5 |
| Phenanthrene | <0.05 | <0.05 |
| Pyrene | <0.05 | <0.05 |

**6 INFLUENCE OF INORGANIC ANIONS ON METALS RELEASE FROM COKE
AND ON TOXICITY OF NICKEL AND VANADIUM TO *CERIODAPHNIA*
*DUBIA***

Preface

Coke comes in contact with oil sands process water during its hydro-transport and possibly in the final reclamation landscapes where process water could be used to ‘water cap’ coke stored in constructed wetlands. This process water has elevated levels of ions, especially bicarbonate, chloride and sulfate ions. Therefore, it was of interest to examine the influence of these ions on metals speciation and mobility from coke, and on the toxicity of the two primary metals of interest, Ni and V. This would provide critical information about the possible interaction of coke with its surroundings in constructed landscapes. The research presented in this chapter showed that the type and amount of metals released from coke was significantly influenced by the anion that dominated in the leaching solution. Specifically, sulfate influenced mobilization of Ni, Fe, Mn and Zn from coke, whereas bicarbonate enhanced the release of Al, Mo and V from coke. In separate studies, important interactions were noted between Ni toxicity and bicarbonate, and V toxicity and sulfate. These findings can be utilized in planning effective reclamation landscapes with respect to metals fate and toxicity. This aspect is further discussed in chapter 7.

This manuscript is accepted for publication in the journal *Chemosphere* with revisions pending. The submitted version of the manuscript is presented in this chapter. Figures and tables are re-formatted to fit thesis style. Supplementary material which was part of the submission is

presented at the end of this chapter. References cited in this chapter are listed in the reference section of this thesis (chapter 8).

6.1 Abstract

Previously it was shown that pH significantly influences the release of various trace metals from oil sands coke particularly Ni and V at toxicologically relevant concentrations. Coke comes in contact with oil sands process water (OSPW) during its transport and long term storage in reclamation landscapes. Interaction of coke with OSPW dominant inorganic anions (i.e. HCO_3^- , Cl^- and SO_4^{2-}) has not been characterized before. Therefore, the objective of this study was to characterize the influence of inorganic anions on metals release from coke and on speciation and toxicity of Ni and V. Also, mixture toxicity of Ni and V was determined. Coke was subjected to batch leaching process at L/S ratio of 1:4 at four levels of HCO_3^- , Cl^- and SO_4^{2-} for 15 days in 2 L glass jars. Further, the effect of each anion (i.e. HCO_3^- , Cl^- and SO_4^{2-}) on Ni and V toxicity and the mixture toxicity of Ni and V was assessed using a 7 day *Ceriodaphnia dubia* reproduction test. The type and amount of metals released from coke were significantly influenced by the anion type. Specifically, sulfate influenced mobilization of Ni, Fe, Mn and Zn whereas bicarbonate enhanced Al, Mo and V releases from coke. With respect to toxicity, increasing bicarbonate decreased the 7 day Ni^{2+} IC50 from 6.3 to 2.3 $\mu\text{g Ni}^{2+}/\text{L}$. On the other hand, sulfate showed an ameliorative effect against V toxicity. In combination, Ni and V act additively at their highest sub-lethal concentrations. The fate and toxicity of Ni and V, the two most toxicologically relevant metals associated with coke, were generally influenced by inorganic anions. Aqueous chemistry and toxicity of Ni and V are discussed in detail that will provide critical information for the reclamation efforts at the oil sands.

6.2 Introduction

The oil sands deposit in Alberta, Canada, holds the largest accumulation of surface mineable heavy hydrocarbon (i.e. bitumen) reserves in the world. Bitumen is recovered from mined oil sands and is processed in upgrading facilities using coking technology to yield synthetic crude oil (SCO). In 2009, the upgrading facilities in Alberta produced $122 \times 10^3 \text{ m}^3/\text{d}$ (~ 0.8 million bbl/day) of SCO and by 2019, SCO production is forecast to almost double to $215 \times 10^3 \text{ m}^3/\text{d}$ (~ 1.3 million bbl/day) (ERCB, 2010). Syncrude Canada Ltd., an oil sands mining company in Alberta, has one of the largest upgrading facilities that uses coking technology to upgrade raw bitumen to SCO. In the upgrading facility, finely dispersed bitumen feedstock is sprayed onto hot fluidized bed of coke particles in the coker vessels which are maintained at elevated temperatures of about 500° C (Furmisky, 2000). Thermal treatment increases the H/C ratio of bitumen and removes carbon from bitumen that ends up in the bottoms of coker vessels as a solid carbonaceous residue termed coke (Bejarno et al. 2003). Generally, large volumes of solid coke is generated during bitumen upgrading and only a small portion of it (~20%) is retained for maintaining the temperatures in coker vessels and the rest is stockpiled on-site into the already growing coke inventory. In the last decade alone, Syncrude has stockpiled nearly 20 million tonnes of solid coke on-site at an average production of 2 million tonnes every year (ERCB, 2009). Regulations set by the Energy Resource Conservation Board (ERCB) require Syncrude to store coke on-site until a feasible technology allows it to be used as an alternative energy source. At present, its use as an alternative energy source is precluded because of its high transportation costs and availability of cheaper energy sources such as coal (Scott and Fedorak, 2004), high sulphur content (6-8% wt.), low combustibility (Bejarno et al. 2003), high metal content (Furmisky, 2009) and increased green house gas emissions compared to natural gas

(McKellar et al. 2010). For these reasons, Syncrude has been stockpiling coke and as a result its coke inventory till date has reached over 40 million tonnes (ERCB, 2009).

Because Syncrude coke particles have uniform size and a spherical shape they aid in hydro-transport from its site of production to storage facility. Coke is mixed with recycled process water to form slurry and is then hydro-transported in pipelines to be deposited into the Mildred Lake Settling Basin (MLSB) a large tailings holding pond. Syncrude plans to stockpile coke at the MLSB for next few decades or until the basin reaches its full capacity (Scott and Fedorak, 2004). Eventually, this coke would become part of reclaimed landscapes (i.e. *dry landscape*– forests and/or *wet landscape* – end-pit lake). Wet landscapes are a reclamation strategy used for long-term storage and treatment of oil sands process materials (e.g. coke, tailings and process water-cap) in ‘constructed wetlands’ created in geotechnically-secure mine pits with the intention of supporting self-sustaining wetlands (Leung et al. 2003). As part of a multidisciplinary scientific assessment investigating the feasibility of storing coke in reclamation landscapes, this study assessed the ecotoxicological risk of storing coke in wet reclamation landscapes.

During the upgrading process several trace metals especially Ni and V present in the bitumen feedstock end up with coke and get enriched (Furmisky, 2009, Speight, 1999). Coke leachates collected from field lysimeters and those generated in the laboratory leaching studies under varying conditions (e.g. pH, weathering, red-ox, L/S ratio etc.) showed that coke releases several metals upon contact with water with some reaching toxicologically relevant concentrations (Puttaswamy et al. 2010; Squires, 2005; Kessler and Hendry, 2006). Further, using a chronic toxicity identification and evaluation (TIE tests) we identified Ni and V as the primary cause of coke leachate toxicity (Puttaswamy and Liber, 2011, accepted). In wet

reclamation landscapes, oil sands process water (OSPW) used for water-capped landforms may interact with coke and influence the fate and toxicity of metals released from coke. Further, the dissolved solids in OSPW are generally dominated by elevated levels of sodium (500 to 700 mg/L), bicarbonate, chloride (75 to 550 mg/L) and sulfate (200 to 300 mg/L) (Allen, 2008). It was hypothesized that these inorganic anions (i.e. bicarbonate, chloride and sulfate) could influence metals release from coke and also the toxicity of Ni and V – two metals that will be of toxicological relevance to reclamation efforts. Therefore, the objectives of this study were twofold. First, investigate the influence of bicarbonate, chloride and sulfate on metals release and speciation from coke. Second, assess the effect of bicarbonate, chloride and sulfate on Ni and V chronic toxicity using *Ceriodaphnia dubia*. Also, the mixture toxicity of Ni and V was assessed since the concentrations of these two metals in the field collected coke leachates were found to be generally above their chronic toxicity thresholds.

6.3 Materials and methods

6.3.1 Influence of anions on metals release from fluid coke

At Syncrude operations, fluid coke (i.e. coke produced from the fluid coking process) from coker drums is hydraulically transported in pipelines mixed with recycled tailings pond water and discharged into the Mildred Lake Settling Basin (MLSB) for long term storage and later recovery. The interaction of coke with MLSB water is unavoidable both during its hydro-transport and long term storage. To assess the influence of inorganic anions on metals mobilization and speciation from of coke batch leaching experiments were conducted.

Fluid coke was collected from the Syncrude Canada Ltd. (AB, Canada) in July, 2006, and shipped to the Toxicology Centre, University of Saskatchewan (SK, Canada) in two 20-L pails. This coke material was collected directly from the coker drums and hence had no history of contact with recycle tailings pond water. Coke was subjected to a 15 day batch leaching process at a coke:water ratio of 1:4 in 2 L glass jars at five levels (0, 50, 150, 450 and 1250 mg/L) of individual anion solution. Appropriate amounts of NaHCO_3 (Sigma-Aldrich, St. Louis, MO), NaCl (BDH Inc., Toronto, ON) and Na_2SO_4 (EMD chemicals, Gibbstown, NJ) were dissolved in de-ionized water to yield desired levels of bicarbonate, chloride and sulfate, respectively. Salts used were of analytical grade reagent type and fulfill American Chemical Society (ACS) specifications. Coke was leached using 0 (no salt), 50, 150, 450 and 1250 mg/L of each anion with three replicate jars per treatment group. De-ionized (Milli-Q quality) water was used for leaching coke at the 0 mg/L treatment (i.e. no salt group). Water chemistry variables were measured before (day 0) and after (day 15) coke leaching and ionic composition of the coke leachates was measured for samples collected on day 15 (Table S6.1, supplementary material). Prior to leaching, coke from the two 20 L pails was mixed and 400 mL sub-sample of coke was poured into 2 L glass jars. To each jar, 1.6 L of the leaching water previously prepared for each anion group was poured carefully against the sides of the jar avoiding suspension of coke particles. All jars were closed with air-tight lids to minimize water loss due to evaporation. On day 15, overlying water and porewater from each treatment group was extracted by vacuum filtration through 0.45 μm pore size membrane filters (Gelman Supor[®] 450; Pallman Laboratories, Ann Arbor, MN, USA). Coke leachates were pooled from all replicate jars from their respective treatment groups and stored in 5 L plastic containers at 4 °C. Sub-samples of

leachate collected on day 15 were analyzed for trace element, major ion and general water chemistry.

6.3.2 Influence of anions on toxicity of Ni and V

In a previous study, we applied a chronic toxicity identification and evaluation (TIEs) approach to coke leachates generated in the laboratory and successfully identified Ni and V as the primary cause of oil sands coke leachate toxicity (Puttaswamy and Liber, 2011, accepted). Therefore, an understanding of the influence of OSPW dominant inorganic anions (i.e. bicarbonate, chloride and sulfate) on Ni and V speciation and chronic toxicity would provide important information for the success of reclamation efforts.

Chronic toxicity of Ni and V to *C. dubia* was assessed at three levels of bicarbonate (50, 150 and 250 mg/L), chloride (4, 80 and 250 mg/L) and sulfate (0, 96 and 300 mg/L) concentrations, referred to in the rest of the text, and in all three cases as low, medium and high. All nine test waters were prepared in medium hard reconstituted water (MHRW) with an average pH of 7.9 ± 0.1 , hardness of 90 ± 3 mg/L as CaCO₃, and conductivity of 304 ± 5 μ S/cm. First, MHRW was prepared in de-ionized water by adding 96 mg/L NaHCO₃ (EMD chemicals, Gibbstown, NJ), 60 mg/L CaSO₄ (99%, Sigma-Aldrich, St. Louis, Mo), 60 mg/L MgSO₄ (Sigma-Aldrich, St. Louis, MO) and 4 mg/L KCl (EMD chemicals, Gibbstown, NJ) (Environment Canada, 2007). Desired levels of bicarbonate test waters were then prepared by varying the amounts of NaHCO₃ and KCl in the MHRW salt recipe. To obtain medium and high chloride test waters, NaCl was added at appropriate amounts to MHRW salt recipe. To prepare low (i.e. 0 mg/L) sulfate test water, CaSO₄ and MgSO₄ in the MHRW salt recipe was replaced with CaCl₂·2H₂O (Sigma, St. Louis, MO) and MgCO₃ (BDH chemicals, Poole, UK) and for high

sulfate water, Na_2SO_4 was added at 290 mg/L to MHRW salt recipe. The Ca:Mg ratio was held constant (1:1.2) on a molar basis in all nine dilution water types to maintain the water hardness between 80-100 mg/L as CaCO_3 . Test waters (i.e. dilution water) were prepared in 50 L Nalgene[®] carboys and were aerated continuously at-least one week prior to initiating any toxicity test. Toxicity of Ni and V to *C. dubia* was tested at the same time for each ion at all three levels. Dilution water was used as negative salt control. Test concentrations of Ni (0, 0.5, 1.25, 3 and 8 $\mu\text{g/L}$) and V (0, 0.25, 0.5, 0.75 and 2 mg/L) were prepared daily from stock solutions of nickel chloride hexahydrate (99.99% pure) and sodium metavanadate (min. 96% pure) salts purchased Strem Chemicals (Newburyport, MA, USA). Concentrations of all major ions and, Ni and V were measured during toxicity testing and the measured concentrations were used in estimating test end-points and in speciation modelling.

6.3.3 Mixture toxicity of Ni and V

The interactive effect of Ni and V to *C. dubia* was tested in a complete factorial design ($4^2 = 16$ treatments, $n = 10$) at four sub-lethal concentrations of each metal following the methods described in Naddy et al. (1999). Three inhibition concentrations (i.e. IC12.5, IC25 and IC50) of Ni and V estimated in a previous study (Puttaswamy et al. 2010) were used to prepare the binary mixtures. A control treatment of only the dilution water was used as the fourth treatment group. Test concentrations of Ni and V were prepared daily from the stock solutions and were measured during toxicity tests.

6.3.4 Toxicity testing

All toxicity tests were conducted in a controlled environment chamber with an air temperature of 24.5 ± 0.5 °C and a photoperiod of 16:8-h light:dark. The cladoceran,

Ceriodaphnia dubia, was used in 7-or 8-d chronic toxicity tests to assess the influence of bicarbonate, chloride and sulfate ions on the toxicity of Ni and V. Daphnid cultures were maintained in MHRW and were fed a diet of *Pseudokirchneriella subcapitata* and YCT (yeast, cerophyll and trout-chow) mixture daily at a rate of 15 and 3 mL per 2 L of culture water, respectively (Environment Canada, 2007). The third clutch of neonates from the MHRW cultures were transferred to anion specific dilution water and held for a week for acclimation prior to toxicity testing. Chronic (7 or 8 d) *C. dubia* toxicity tests were conducted with ten replicates of single neonates (≤ 24 h old) placed in either 20 mL of control or test solution with renewal of test solutions every 24 h (Environment Canada, 2007). The test was considered acceptable if 80% of control organisms survived and 60% of the surviving adults produced at least three broods with a total of at least 15 neonates per adult. All toxicity tests were performed in 30-mL glass beakers and used survival and reproduction as test endpoints.

6.3.5 Chemical analyses

Dissolved concentrations of 26 elements in the coke leachates and concentrations of only Ni and V in toxicity test waters were measured in-house using an inductively coupled plasma mass spectrometer (ICP-MS) equipped with collision cell technology (Thermo Fisher Scientific, Mississauga, ON, Canada). Internal standards of Li, Sc, In, Tb, and Bi were employed during the analysis (High-purity Standards, Charleston, SC, USA). Standard solutions of Ag, Al, As, B, Ba, Be, Bi, Cd, Cr, Co, Cu, Fe, Hg, Mn, Mo, Ni, Pb, Sb, Se, Sn, Sr, Tl, Ti, U, V and Zn were purchased from VWR International (Mississauga, ON, Canada). For evaluating the accuracy of ICP-MS measurements, a river water standard reference material (SLRS-4) and a natural water standard reference material (1640) were purchased from the National Research Council (Ottawa,

ON, Canada) and the National Institute of Standards & Technology (Gaithersburg, MD, USA), respectively. The dissolved concentrations of inorganic cations (Ca^{2+} , Mg^{2+} , Na^+ and K^+) and anions (Cl^- , HCO_3^- , SO_4^{2-}) in coke leachates and in all dilution waters were measured in-house using a dual ion chromatography system equipped with a dual ion exchange column (Dionex ICS-3000, Sunnyvale, CA, USA) following US EPA method 300.1. Routine water quality variables including pH, dissolved oxygen, conductivity, alkalinity, hardness and ammonia were measured on day 0, 3 and 7 during the course of all toxicity tests.

6.3.6 Statistics

Toxicity test estimates for survival (LC50) and reproduction (IC50), and the associated 95% confidence intervals, were calculated using measured concentrations of Ni and V by trimmed Spearman-Kärber method, version 1.5 (US EPA, 1990) and the Inhibition Concentration (IC_p) approach, version 2.0 (US EPA, 1993). All other statistical analyses were performed using SigmaPlot[®], version 11.0 (Systat Software, Inc., Chicago, IL, USA) with a 95% ($p \leq 0.05$) level of confidence. Fecundity of *C. dubia* or mean neonates per adult was used as the test endpoint for all chronic toxicity tests. A two-way ANOVA was performed on *C. dubia* fecundity data to assess the influence of anion on Ni or V toxicity (factor: anion and metals) and the interactive effects of Ni and V mixtures. If data were not normally distributed and/or failed the equal variance test, a non-parametric two-way ANOVA (Scheirer-Ray-Hare extensions of the Kruskal-Wallis test) was performed on ranked data as described in Sokal and Rohlf (1995). Post-hoc multiple comparisons were performed using Tukey's test to identify significant differences in treatments groups. The effect of bicarbonate on Ni toxicity and, sulfate on V toxicity was tested using regression analysis.

Aqueous speciation estimates for Ni and V were calculated using the MINEQL+ model, a chemical equilibrium modeling system (Schecher and McAvoy, 2001). Only Ni and V speciation data are presented because these two metals have been identified as the primary cause of coke leachate toxicity (Puttaswamy and Liber, 2011; accepted) and therefore are of interest here for further investigation with respect to their mobility, speciation, and bioavailability. Measured concentrations of all water chemistry variables and metals from the coke leaching experiment (Table 6.1 and Table S6.1, supplementary material) and the IC50 concentration of Ni or V from toxicity experiment (Table 6.3) were used as input components for Ni and V speciation calculation. Since the two experiments performed were kept closed to the atmosphere, speciation calculations were done with user input pH and carbonate (calculated from pH and alkalinity values) for a system closed to the atmosphere. Aqueous species distribution of Ni and V in coke leachates and in toxicity experiments as influenced by different anions are presented as the percentage (%) of total concentration of each metal.

6.4 Results

6.4.1 Influence of anions on metals release from coke

Water chemistry of the coke leachates measured on day 15 of coke leaching revealed that coke does not release significant amounts of major ions especially hardness cations Ca^{2+} and Mg^{2+} (see Table S6.1, supplementary material). On the other hand, the ionic composition of the leaching water had a significant influence on the type and concentration of the trace metals released from coke. Exceptions to this rule were B, Ba, Mo and Sr (Table 6.1). With respect to the type of metals, sulfate had the greatest influence on the release of cationic metals (i.e. Fe,

Mn, Ni and Zn) compared to bicarbonate and chloride (Table 6.1 and Fig. 6.1a). On the other hand, the release of metals (i.e. Al, Mo and V) that form oxyanions from coke was significantly influenced by bicarbonate leaching more than sulfate and chloride (Table 6.1 and Fig. 6.1b). The concentrations of most trace metals in the chloride group were either similar or lower compared to bicarbonate or sulfate groups (Table 6.1). Within each anion leaching group, the concentrations of Al, Mo and V increased whereas concentrations of Mn and Ni decreased with increasing level of bicarbonate concentration (Table 6.1, Fig. 6.1a and 6.1b). On the other hand, the concentrations of Mn, Ni, Sr and Zn increased with increasing level of sulfate (Table 6.1 and Fig. 6.1b). Highest concentrations of As (8 µg/L), Cd (3.2 µg/L), Cr (2 µg/L) and Se (2.2 µg/L) were observed under bicarbonate leaching and Pb (1.3 µg/L) under all three anion groups. Since the concentrations of these priority metals were ≤ 10 µg/L in coke leachates, their individual concentrations are not shown in Table 6.1 for clarity of presentation. The concentrations of Ni and V released from coke under all salt groups (except for Ni in bicarbonate group) were well above the chronic *C. dubia* IC50s or LC50s estimated in this study (Table 6.1 and 6.4). Speciation analysis for dissolved Ni and V was performed using a thermodynamic equilibrium model (MINEQL+) with calculated ionic strength input. Bicarbonate and sulfate significantly altered free Ni²⁺ species distribution in the coke leachates. Specifically, free Ni²⁺ concentration decreased and NiCO₃ and NiSO₄ formation increased with increasing levels of bicarbonate and sulfate, respectively (see Fig. S6.1a and c, supplementary material). Conversely, free Ni²⁺ was the dominant species at all levels of chloride with only minor portion of NiCl formation at high chloride level (see Fig. S6.1b, supplementary material). For vanadium, the vanadate (+5) oxyanion H₂VO₄⁻ was the dominant species (more than 75%) in both chloride and sulfate groups (see Fig. S6.1e and f, supplementary material). On contrary, the relative concentration of the two

most dominant vanadate oxyanion species (i.e. H_2VO_4^- and HVO_4^{2-}) varied with increasing bicarbonate levels (see Fig. S6.1d, supplementary material).

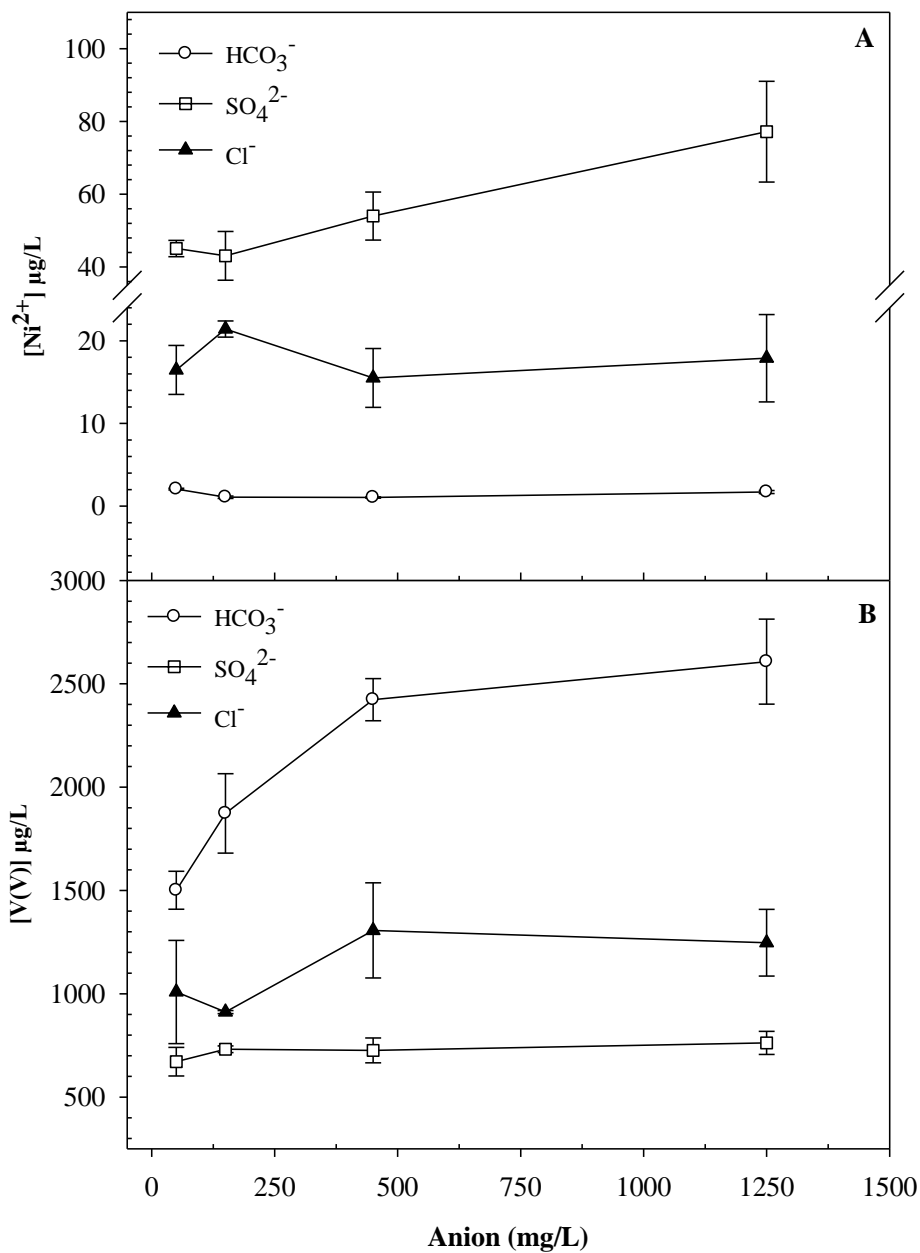


Figure 6.1. Influence of inorganic anions (HCO_3^- , Cl^- and SO_4^{2-}) on the release of (A) Ni^{2+} and (B) V(V) from coke during 15 day batch leaching. Values are mean \pm SE, $n = 3$.

Table 6.1. Influence of anions (HCO_3^- , Cl^- and SO_4^{2-}) on trace metals (mean \pm SE, $n=3$) release from Syncrude coke during a 15 day batch leaching process.

| Anion (mg/L) | Elements ^{a, b, c} ($\mu\text{g/L}$) | | | | | | | | | |
|--------------------|---|---------------|---------------|---------------|---------------|---------------|---------------|--------------|----------------|---------------|
| | Al | B | Ba | Fe | Mn | Mo | Ni | Sr | V | Zn |
| No salt | 1.9 \pm 1.0 | 104 \pm 2.6 | 13 \pm 1.3 | 0.8 \pm 0.1 | 145 \pm 17 | 185 \pm 16 | 16 \pm 4.1 | 48 \pm 0.7 | 1079 \pm 67 | 5.8 \pm 1.4 |
| <u>Bicarbonate</u> | | | | | | | | | | |
| 50 | 47 \pm 8.8 | 115 \pm 1.6 | 7.8 \pm 1.5 | 1.6 \pm 0.5 | 47 \pm 0.6 | 218 \pm 6.6 | 2.1 \pm 0.1 | 46 \pm 6.5 | 1501 \pm 91 | 1.9 \pm 0.1 |
| 150 | 117 \pm 31 | 121 \pm 4.0 | 6.7 \pm 2.4 | 1.2 \pm 0.2 | 24 \pm 2.6 | 237 \pm 6.1 | 1.1 \pm 0.1 | 46 \pm 14 | 1873 \pm 192 | 2.7 \pm 1.3 |
| 450 | 240 \pm 8 | 133 \pm 3.7 | 8.6 \pm 0.3 | 1.2 \pm 0.0 | 19 \pm 0.4 | 268 \pm 10 | 1.0 \pm 0.1 | 62 \pm 2.0 | 2424 \pm 101 | 1.5 \pm 0.2 |
| 1250 | 282 \pm 31 | 127 \pm 2.4 | 7.2 \pm 2.0 | 3.3 \pm 0.3 | 18 \pm 1.4 | 268 \pm 2.5 | 1.7 \pm 0.2 | 53 \pm 11 | 2607 \pm 205 | 7.9 \pm 2.4 |
| <u>Chloride</u> | | | | | | | | | | |
| 50 | 2.2 \pm 1.3 | 119 \pm 4.7 | 13 \pm 0.7 | 7.8 \pm 3.8 | 163 \pm 15 | 214 \pm 30 | 16 \pm 3.0 | 47 \pm 3.8 | 1009 \pm 249 | 5.7 \pm 1.0 |
| 150 | 1.1 \pm 0.1 | 114 \pm 8.3 | 14 \pm 0.7 | 2.3 \pm 1.2 | 200 \pm 4.2 | 161 \pm 6.9 | 21 \pm 1.0 | 41 \pm 0.7 | 912 \pm 7.6 | 6.6 \pm 0.3 |
| 450 | 3.8 \pm 2.1 | 141 \pm 0.5 | 18 \pm 2.0 | 2.2 \pm 1.0 | 180 \pm 23 | 245 \pm 32 | 16 \pm 3.6 | 58 \pm 6.6 | 1307 \pm 230 | 4.7 \pm 9.7 |
| 1250 | 5.8 \pm 1.4 | 131 \pm 9.6 | 26 \pm 0.3 | 6.0 \pm 3.5 | 172 \pm 25 | 238 \pm 30 | 18 \pm 5.3 | 63 \pm 5.6 | 1247 \pm 161 | 10 \pm 2.9 |
| <u>Sulfate</u> | | | | | | | | | | |
| 50 | 1.2 \pm 0.1 | 111 \pm 6.1 | 23 \pm 1.0 | 14 \pm 12 | 268 \pm 5.7 | 108 \pm 16 | 45 \pm 2.2 | 54 \pm 0.4 | 672 \pm 69 | 16 \pm 1.2 |
| 150 | 3.3 \pm 1.1 | 121 \pm 3.3 | 20 \pm 1.6 | 43 \pm 20 | 245 \pm 27 | 137 \pm 19 | 43 \pm 6.7 | 52 \pm 2.9 | 732 \pm 16 | 15 \pm 2.5 |
| 450 | 9.2 \pm 2.4 | 147 \pm 8.1 | 21 \pm 0.8 | 74 \pm 32 | 286 \pm 12 | 149 \pm 27 | 54 \pm 6.6 | 68 \pm 5.1 | 726 \pm 60 | 19 \pm 1.7 |
| 1250 | 13 \pm 3.7 | 149 \pm 15 | 21 \pm 1.2 | 145 \pm 109 | 324 \pm 45 | 153 \pm 26 | 77 \pm 13 | 72 \pm 4.8 | 762 \pm 55 | 32 \pm 3.6 |

^aThe following trace elements were below their detection limit ($\leq 0.01 \mu\text{g/L}$): Ag and Sn.

^b Trace elements with concentration $\leq 1 \mu\text{g/L}$: Be, Cu, Hg, Sb and U.

^c Trace elements with concentration $1 \geq 10 \mu\text{g/L}$: As, Cd, Co, Cr, Pb, Se and Tl, but not listed here for clarity of data presentation.

6.4.2 Influence of anions on toxicity of Ni and V

There was no considerable change in the pH and hardness of the dilution water used for toxicity testing within each anion group (Table 6.2). However, the water hardness in the high bicarbonate group decreased to 57 ± 3 mg/L as CaCO_3 , with a concomitant decrease in Ca^{2+} concentration compared to low and medium bicarbonate groups (Table 6.2). The concentrations of bicarbonate (50, 150 and 250 mg/L), chloride (4, 80 and 250 mg/L) and sulfate (only 96 and 300 mg/L) used in toxicity tests had no effect on *C. dubia* survival and fecundity (Fig. 6.2a to f).

However, in low sulfate (i.e. $\text{SO}_4^{2-}=0$ mg/L) controls, *C. dubia* fecundity significantly decreased ($p = 0.001$) compared to high sulfate control treatment (Fig. 6.2c and f). Further, in the presence of V both *C. dubia* survival (data not shown) and fecundity were significantly ($p < 0.001$) affected in the low sulfate compared to medium and high sulfate groups (Fig. 6.2f). However, with increasing sulfate concentrations, *C. dubia* fecundity improved and the 7 day IC50 for V increased by a factor of about 6 between low and high sulfate groups (Table 6.3 and Fig. 6.2f). Further, there was a significant relationship between sulfate and V toxicity which decreased with increasing sulfate concentrations in the test waters (Fig. 6.3b). Although, increasing sulfate concentration showed a protective effect against chronic V toxicity, the speciation of V remained un-changed (see Fig. S6.2b, supplementary material). On the other hand, presence of Ni in low sulfate water had no significant effect on *C. dubia* fecundity except at the highest Ni concentration (Fig. 6.2c). The 7 day IC50 for Ni in sulfate group was similar to those estimated for the chloride group (Table 6.3). Interestingly, predicted free Ni^{2+} species remained un-changed at around 60% in both sulfate and chloride waters (data not shown). In bicarbonate test waters, a concentration-dependent decrease in *C. dubia* fecundity was observed in the presence of Ni or V (Fig. 6.2a and d).

Table 6.2. Water chemistry (mean \pm SE, $n = 3$) of different dilution waters measured during toxicity testing.

| Anion (mg/L) | pH | Conductivity (μ S/cm) | Alkalinity (mg CaCO ₃ /L) | Hardness (mg CaCO ₃ /L) | Major Ions (mg/L) | | | | | | |
|--------------------|-----|-------------------------------|---|---------------------------------------|-------------------|------------------|------------------|----------------|-----------------|-------------------------------|-------------------------------|
| | | | | | Na ⁺ | Ca ²⁺ | Mg ²⁺ | K ⁺ | Cl ⁻ | SO ₄ ²⁻ | HCO ₃ ⁻ |
| <u>Bicarbonate</u> | | | | | | | | | | | |
| 50 | 7.9 | 313 \pm 3 | 59 \pm 2 | 81 \pm 4 | 23 | 18 | 15 | 2 | 2 | 97 | 52 |
| 150 | 8.3 | 433 \pm 3 | 129 \pm 2 | 83 \pm 3 | 65 | 10 | 14 | 2 | 2 | 93 | 122 |
| 250 | 8.6 | 564 \pm 6 | 197 \pm 3 | 57 \pm 3 | 107 | 7 | 15 | 1 | 2 | 84 | 173 |
| <u>Chloride</u> | | | | | | | | | | | |
| 4 | 8.0 | 292 \pm 6 | 69 \pm 1 | 83 \pm 2 | 40 | 22 | 18 | 2 | 3 | 120 | 85 |
| 80 | 7.9 | 593 \pm 1 | 63 \pm 1 | 86 \pm 1 | 128 | 22 | 21 | – ^a | 133 | 142 | 92 |
| 250 | 8.0 | 1176 \pm 0 | 64 \pm 1 | 88 \pm 1 | 305 | 20 | 20 | – | 409 | 141 | 57 |
| <u>Sulfate</u> | | | | | | | | | | | |
| 0 | 8.1 | 270 \pm 3 | 68 \pm 3 | 107 \pm 2 | 30 | 9 | 15 | 2 | 24 | 1 | 94 |
| 96 | 7.9 | 336 \pm 2 | 74 \pm 1 | 84 \pm 2 | 31 | 20 | 14 | 2 | 2 | 93 | 56 |
| 300 | 7.9 | 807 \pm 14 | 71 \pm 2 | 83 \pm 1 | 135 | 15 | 13 | – | 2 | 303 | 68 |

^a below method detection limit.

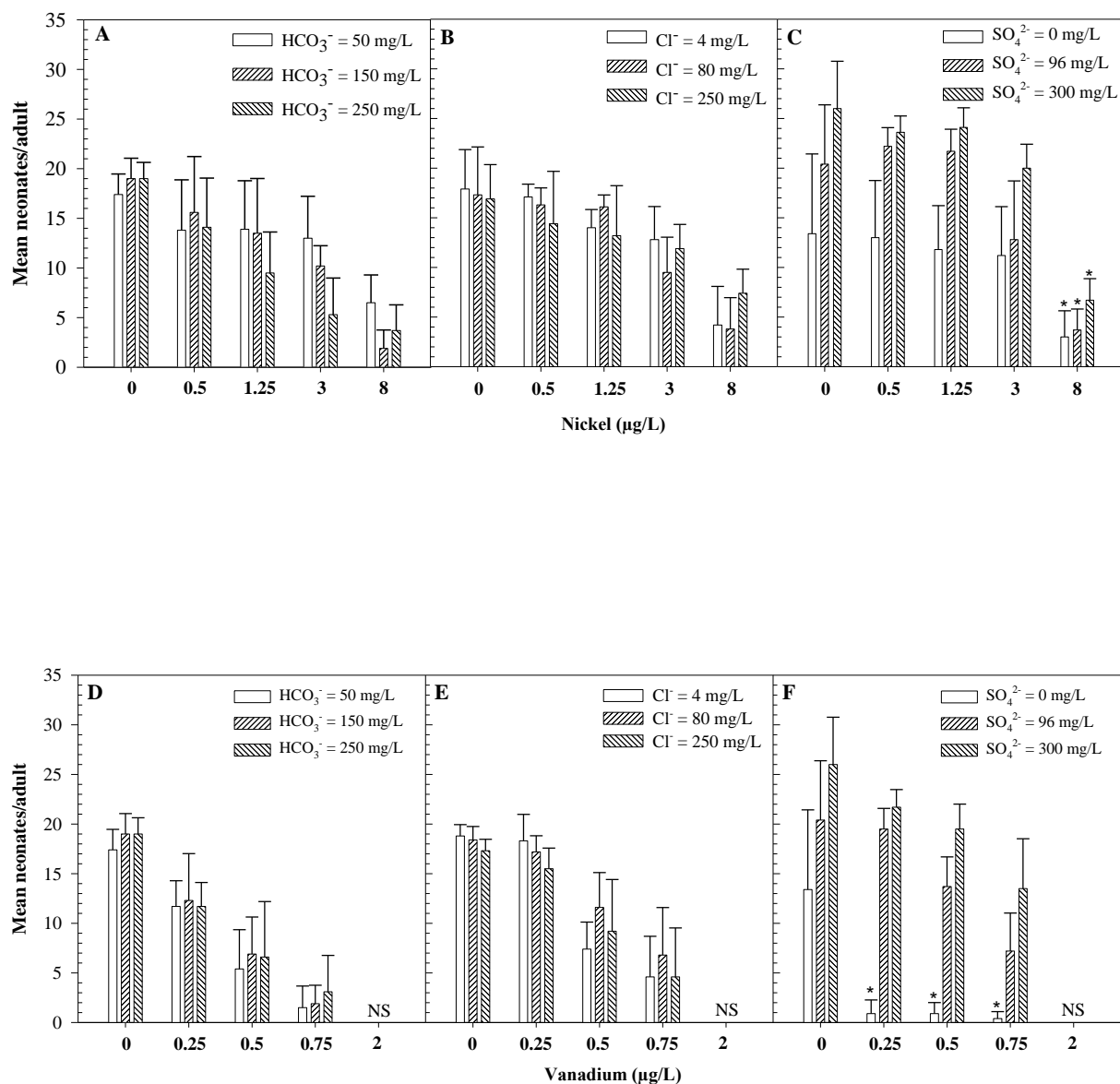


Figure 6.2. Influence of bicarbonate, chloride and sulfate on chronic toxicity of (A to C) Ni²⁺ and (D to E) V(V) to *C. dubia*. An asterisk (*) denotes significant difference within each treatment. NS – 100% mortality of test organism. Values represent mean±SD, n = 10.

Table 6.3. Influence of inorganic anions (HCO₃⁻, Cl⁻ and SO₄²⁻) on chronic toxicity of Ni and V to *C. dubia*.

| Anion (mg/L) | Nickel (µg/L) | | Vanadium (µg/L) | |
|--------------------|---------------|----------------|-----------------|------------------|
| | IC50 | LC50 | IC50 | LC50 |
| <u>Bicarbonate</u> | | | | |
| 50 | 6.3 (NC) | – ^a | 375 (309-432) | 438 (340-565) |
| 150 | 3.7 (3.1-4.3) | 6.7 (4.5-9.9) | 385 (289-505) | 364 (276-477) |
| 250 | 2.3 (1.8-2.6) | 3.4 (2.3-4.9) | 362 (292-523) | 424 (358-502) |
| <u>Chloride</u> | | | | |
| 4 | 5.9 (5.1-6.4) | 5.9 (4.9-7) | 456 (423-490) | 484 (390-598) |
| 80 | 4.3 (3.4-5.2) | 6.7 (5.7-7.8) | 609 (532-686) | 665 (538-822) |
| 250 | 7 (5.3-8.3) | 8 (5.9-10.8) | 529 (432-599) | 598 (495-724) |
| <u>Sulfate</u> | | | | |
| 0 | 6 (4.5-6.5) | – | 129 (124-138) | – |
| 96 | 5 (4.1-5.8) | – | 612 (554-690) | 879 (682-1132) |
| 300 | 6 (5.6-6.4) | 7.6 (NC) | 770 (641-1043) | 1155 (1004-1328) |

^a LC50 not calculable because % trim required is too large.

NC – 95% confidence interval not calculable.

IC50 – Reproduction inhibition concentration in 50% of test population.

LC50 – Lethal concentration to 50% of test population.

The 7 day IC50 or LC50 for V estimated in the bicarbonate group was at its lowest (i.e. more toxic) compared to sulfate (except 0 mg/L) and chloride groups (Table 6.3). While there was no particular relationship of bicarbonate effect on V toxicity, the relative distribution of V species changed (Table 6.3 and Fig. S6.2b, supplementary material). On the other hand, the 7 d IC50 for Ni decreased by a factor of about 3 between low and high bicarbonate groups (Table 6.3). In other words, an increase in bicarbonate concentration increased Ni bioavailability and/or toxicity to *C. dubia* (Table 6.3 and Fig. 6.3a). Interestingly, the predicted free Ni²⁺ concentration at the observed Ni²⁺ IC50 decreased with increasing bicarbonate level and the formation of aqueous NiCO₃⁰ species increased (see Fig. S6.2a, supplementary material). Generally, among

the three anions used for toxicity testing, chloride had no or the least effect on Ni or V toxicity and speciation (Table 6.3 and Fig 6.2b and 6.2e).

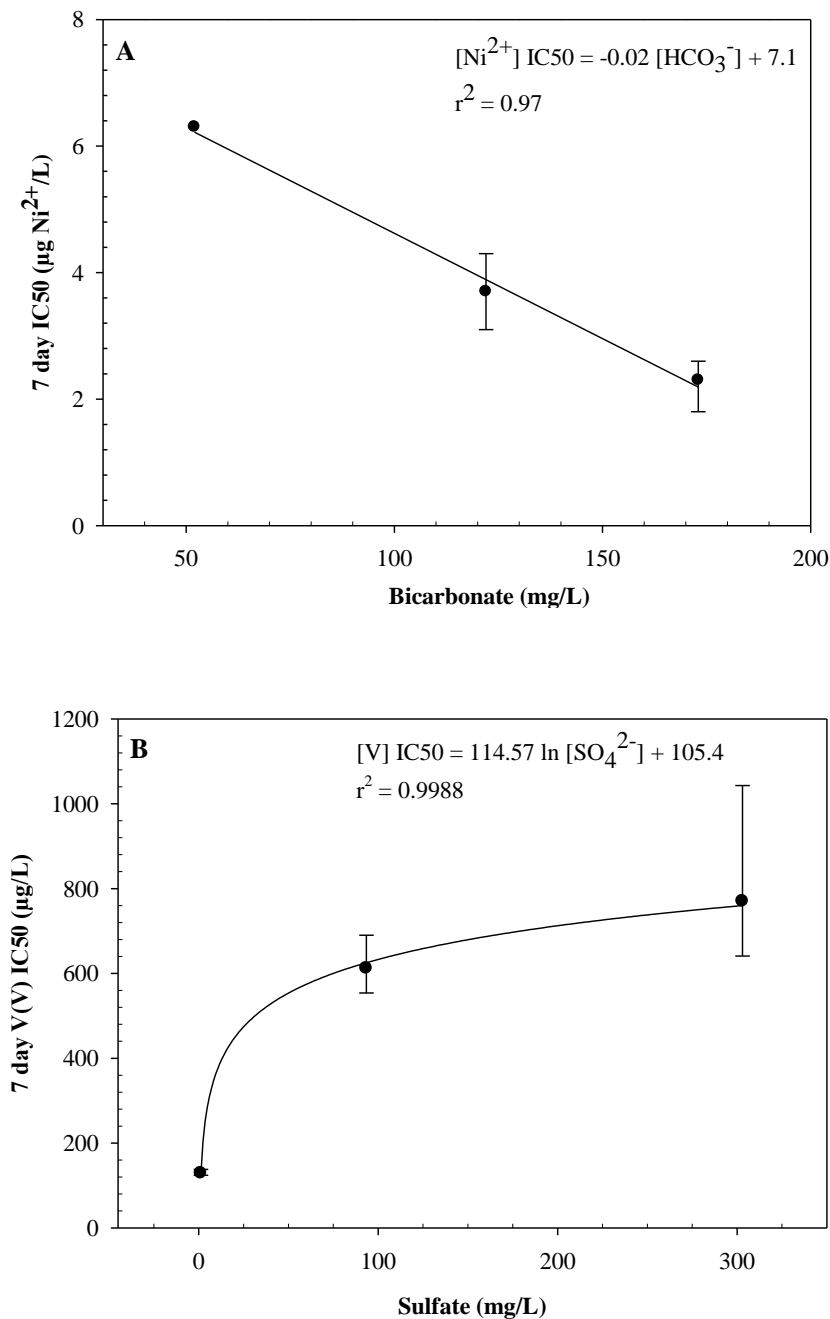


Figure 6.3. Relationship between anion type and the observed 7 day IC₅₀ for (A) Ni²⁺ vs. bicarbonate and (B) V(V) vs. sulfate. Error bars are 95% confidence intervals.

6.4.3 Mixture toxicity

There was a significant interactive effect ($p < 0.001$) of sub-lethal concentrations of Ni and V on *C. dubia* fecundity (Fig. 6.4). In the Ni only group, there was 100% survival (data not shown) at all three Ni test concentrations by the end of 7 days of exposure whereas the mean reproduction decreased concentration-dependently with a significant reduction compared to controls (Fig. 6.4). On the other hand, in the V only group, survival was 70% in the high V (i.e. 500 $\mu\text{g/L}$) group and the mean number of neonates significantly decreased by approximately 2 times compared to control (Fig. 6.4). Generally, there was a concentration-dependent decrease in *C. dubia* fecundity at all combinations of Ni and V mixture. The fecundity of *C. dubia* in either Ni (2.25 $\mu\text{g/L}$) or V (500 $\mu\text{g/L}$) alone was about 11 neonates per adult but when exposed in combination, *C. dubia* fecundity significantly decreased ($p < 0.001$) by 3 times compared to their individual levels (Fig. 6.4). An additive effect of Ni and V was apparent only at their highest combination (Ni 2.25 x V 500 $\mu\text{g/L}$) which showed reduced survival and fecundity compared to all other groups (Fig. 6.4).

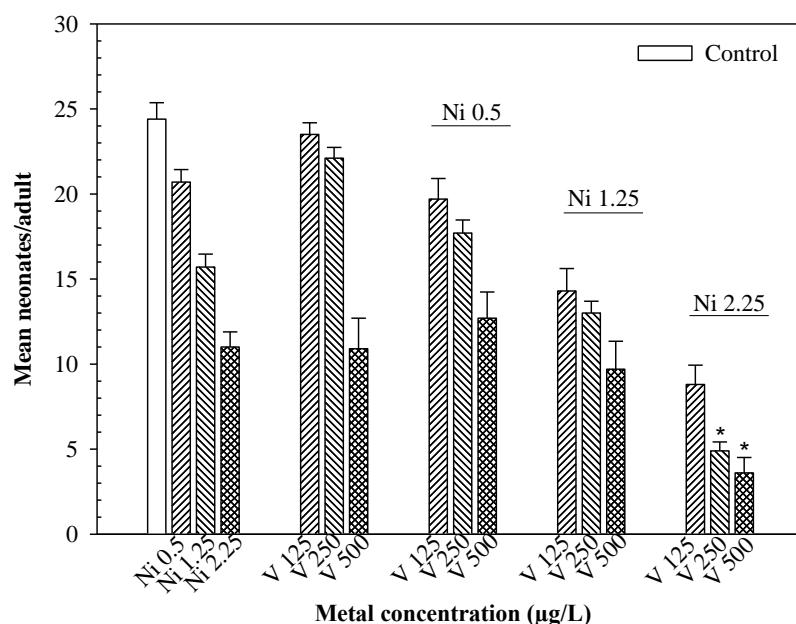


Figure 6.4. Interactive effect of sub-lethal doses of Ni and V on *C. dubia* fecundity (mean±SD, n=10). An asterisk (*) denotes significant difference ($p\leq 0.05$) from rest of the treatment combinations.

6.5 Discussion

Oil sands coke releases several trace metals upon contact with fresh water, particularly Ni and V at toxicologically relevant levels (Puttaswamy et al. 2010; Puttaswamy and Liber, 2011; accepted). Interaction of coke with inorganic constituents of oil sands process water (OSPW), during its long term storage in the Mildred Lake Settling Basin (MLSB), may influence the fate and toxicity of metals associated with coke. For the purpose of brevity, discussion will focus on only Ni and V released from coke and where appropriate other trace elements will be mentioned.

6.5.1 Influence of anions on metals release from coke

The type and concentration of trace elements released from coke was significantly influenced by the salt type and its level. Among several trace metals released under de-ionized water (i.e. no salt group) leaching, only the concentrations of Ni and V were above their 7-day LC50s (Table 6.1 and 6.4). Nickel and V are the two chief metallic components associated with raw bitumen in porphyrin forms and because their presence lowers fuel quality and poisons the catalysts, these metals are removed during bitumen upgrading and get concentrated in the coke matrix (Speight, 1999; Furimsky, 2009). Release of Ni and V under de-ionized water leaching indicates that the two metals are loosely bound to the coke surface and that the dissolution occurs immediately upon contact with water. In a similar study, when coke was pre-washed with de-ionized water at L/S ratio of 1:40, the concentration of Ni and V released from Syncrude coke reached 120 and 8610 $\mu\text{g/L}$, respectively (Kessler and Hendry, 2006). This suggests that the metal fractions ionically bound to coke are easily mobilized. Under bicarbonate leaching, the concentration of V released from coke increased significantly by a factor of about 1.2 at each increasing level (3-fold) of bicarbonate (Table 6.1 and Fig. 6.1b). Also, there was a concomitant increase in the pH from 8.33 to 8.80 with increasing bicarbonate level which likely favored increased V mobilization from coke. Vanadium occurs in several oxidation states (+3, +4 and +5), but V(V) is the most mobile and dominant species in natural systems and its dissolution in aqueous solution increases with pH and oxygenation (Wherli and Stumm, 1989; Crans et al. 1998). Speciation calculation of V revealed two stable vanadate oxyanion species (i.e. H_2VO_4^- and HVO_4^{2-}) dominant in all salt groups (see Fig. S6.1d to f, supplementary material). These two species are the hydrolysis products of vanadate cation (VO_2^+), and both vanadate cation (VO_2^+) and anion (HVO_4^{2-}) are known to form coordinative complexes with metal hydrous surfaces

(>MOH; e.g. TiO_2 , $\delta\text{-Al}_2\text{O}_3$, $\alpha\text{-FeOOH}$) (Wherli and Stumm, 1989; Peacock and Sherman, 2003). This suggests that the solid phase association of V in coke could possibly be a vanadate cation or anion species which may be adsorbed to metal oxide surfaces found in coke. The chemical composition of Syncrude coke has revealed important metal oxides (e.g. TiO_2 , Fe_2O_3 and Al_2O_3) at amounts ranging from 20.9 to 2.8 (wt. %) (Scott and Fedorak, 2004). Generally, the (V) oxidation state of V in minerals (e.g. vanadinite, haggite) is more soluble and easily leached from soils into water (Crans et al. 1998). Therefore, it is hypothesized that V(V) species are mobilized easily from coke under the standard batch leaching conditions. The concentration of V released was lowest in sulfate group compared to no salt, bicarbonate and chloride groups (Table 6.1 and Fig. 6.1b). Further, speciation calculation for V in the sulfate group showed the dominance of vanadate species (i.e. H_2VO_4^- and HVO_4^{2-}) but no precipitates (see Fig. S 6.1f, supplementary material). Sulfate forms several stable complexes with the vanadyl (VO^{2+}) cation at low pH but has lower affinity to the vanadate (VO_2^+) cation which is the dominant species in aqueous solutions (Crans et al. 2004). Therefore, it is speculated that in the sulfate group, free sulfate which was the dominant inorganic ligand formed very few stable aqueous complexes with vanadate oxyanions and as a result V(V) release from coke remained low in the sulfate group.

The concentration of Ni released from coke was lowest in the bicarbonate compared to sulfate and chloride groups (Table 6.1 and Fig.6.1a). In the absence of organic ligands, Ni^{2+} forms stable complexes with inorganic ligands in the order $\text{OH}^- > \text{SO}_4^{2-} > \text{Cl}^- > \text{NH}_3$ and the relative proportion of the Ni-ligand complex increase with increasing levels of these inorganic ligands (Adriano, 2001). As sulfate level increased there was an increase in the concentration of Ni released from coke and also the formation of NiSO_4^0 ($\log K = 2.3$) complex (Table 6.1, Fig. 6.1a

and Fig. S 6.1c, supplementary material). On the other hand, the chloride group had the second highest level of Ni released from coke. Similarly, this could be due to the increasing concentration of Cl⁻ ligands. Chloride can increase Ni mobility or decrease its sorption due to NiCl complex formation (Adriano, 2001). However, the alkaline pH in the bicarbonate group is suspected to have resulted in low Ni mobilization from coke. Solubility of Ni decreases markedly in the alkaline pH range, and generally above pH 6 chemisorptions on oxides, noncrystalline aluminosilicates and layer silicate clays is favored rendering it less mobile (McBride, 1994).

6.5.2 Influence of anions on toxicity of Ni and V

The concentrations of all three anions and Ni and V used in this experiment are generally below the levels usually found in OSPW and coke leachates. In general, the measured water chemistry variables in all tests were within the acceptable limits for chronic *C. dubia* toxicity testing (Environment Canada, 2007). Moreover, the anion composition used did not impact *C. dubia* survival and/or fecundity except in the low (i.e. 0 mg/L) sulfate groups (Fig. 6.2c and 6.2f). The highest concentrations of bicarbonate, chloride and sulphate used in this study were well below their respective toxicity thresholds as reported in the literature. For example, the reported 7-day *C. dubia* IC50s for bicarbonate, chloride and sulfate in moderately hard water are 725 mg/L, 697 mg/L and 1129 mg/L respectively (Lasier and Hardin, 2010; Elphick et al. 2011a, b). Control *C. dubia* fecundity in the low sulfate group was significantly reduced (by about 50%) compared to high sulfate (Fig. 6.2c and f). In a similar experiment, *D. magna* exposed to 0 ‰ salinity water with a conductivity of 310 µS/cm showed lower growth, reproduction and high respiration rate indicating higher energy allocation for maintaining

osmoregulatory process (Arner and Koivisto, 1993). In this study, the conductivity of the zero sulfate groups was 270 $\mu\text{S}/\text{cm}$ and a decreased fecundity in the controls could be a physiological adaptation to sulfate induced osmotic stress. Sulfate is an important osmolyte and freshwater eels have been shown to retain high concentration of sulfate to regulate their serum osmolality (Nakada et al. 2005). Daphnids are hyperosmotic to the external medium and as a result they actively regulate major ions into their haemolymph to maintain ion homeostasis (Aladin and Potts, 1995; Rainbow, 1997). Therefore, it is speculated here that to overcome osmotic stress due to the absence of an osmolyte like sulfate, daphnids may have increased their ion uptake by allocating less energy for reproduction.

6.5.2.1 Vanadium

When V was present in zero sulfate waters it acted as an additional stressor resulting in a significant reduction in fecundity and 100% mortality at all V test concentrations (Fig. 6.2f) . Interestingly, when Ni was present in zero sulfate waters, *C. dubia* fecundity remained constant at around 12 neonates/adult at Ni concentrations up to 3 $\mu\text{g}/\text{L}$ and showed no sign of additional stress (Fig. 6.2c and f). In fact, the 7-day IC50 or LC50 for V in zero sulfate waters was lowest compared to thresholds estimated in other salt groups (Table 6.3). However, with increasing sulfate concentration both fecundity and survival improved dramatically in V exposure treatments (Fig. 6.2f). Concurrently, the 7 day V IC50 increased significantly with increasing sulfate levels by a factor of about 5 to 6 between low and high sulfate groups showing a vanadate-sulfate interaction (Table 6.3 and Fig. 6.3b). Similar relationships were not observed for V toxicity and bicarbonate and/or chloride test waters (Table 6.3) indicating non-interaction between V and bicarbonate and/or chloride. Sulfate is essential to all organisms for many cellular

functions including ion homeostasis and a large group of solute carrier transporters (SLC group) which transport sulfate anion are known to occur in non-mammalian systems (Schaechinger and Oliver, 2007; Pilsyk and Paszewski, 2009). Similarly, anion-anion interaction has been noted between sulfate and selenate (+5), an oxyanion (Se_2O_3^-) forming element similar in structure to vanadate, in *C. dubia* and *H. azteca* (Brix et al. 2001), *D. magna* (Hansen et al. 1993) and *C. reinhardtii* (Morlon et al. 2006). Further, the V speciation calculation showed H_2VO_4^- and HVO_4^{2-} as the two dominant oxyanion species at the measured IC50 concentrations at all levels of bicarbonate; sulfate and chloride test waters between the pH range of 7.9 and 8.6 (see Fig. S 6.2b, supplementary material). In a study investigating the effects of pH and hardness on V lethality to rainbow trout, toxicity was attributed to H_2VO_4^- and HVO_4^{2-} oxyanion species which were predicted to be the dominant species between the pH range of 6.6 and 8.8 (Stendahl and Sprague, 1982). In oxic waters the hydrolysis products of vanadate (V) (i.e. H_2VO_4^- and HVO_4^{2-}) dominate which have a pKa of 7.8 and 12.7, respectively (Wherli and Stumm, 1989; Crans et al. 2004). These vanadate species are structurally similar to sulfate, selenate, phosphate, arsenate, chromate, molybdate and, that molybdate and vanadate are said to mimic sulfate and phosphate ions and enter through anion channels (Bridges and Zalups, 2005; Rainbow, 1997). Therefore, based on the observed sulfate-vanadate interaction, predicted V speciation and the ionic mimicry analogy we hypothesize that the vanadate species (i.e. H_2VO_4^- and HVO_4^{2-}) may be taken up via a putative sulfate (anion) transporting pathway in daphnids.

6.5.2.2 Nickel

Among bicarbonate, chloride and sulfate waters, daphnids were most sensitive to Ni exposure in the bicarbonate test waters (Table 6.3). Increasing chloride or sulfate concentrations had no effect on the chronic Ni toxicity to *C. dubia* and the IC50s were quite similar between

these two groups (Table 6.3). Similarly, chloride had no effect on acute Ni toxicity to *D. pulex* and further, Ni exposure did not disrupt Cl⁻ balance in *D. magna* (Kozlova et al. 2009; Pane et al. 2003). Presence of Ni²⁺ in the low sulfate group did not act as an additional stressor unlike V which significantly impaired *C. dubia* fecundity (Fig. 6.2c). This suggests that Ni²⁺ uptake is not inhibited by anions (chloride and sulfate) and it is exclusively taken up via cation transport pathways. Based on Ni²⁺-Mg²⁺ antagonism in *D. magna*, the mechanism of Ni²⁺ uptake was suggested to occur via a putative Mg²⁺ channel (Pane et al. 2003). The two lowest Ni IC50s of 2.3 and 3.7 µg Ni²⁺/L were observed in medium and high bicarbonate water (Table 6.3). Further, with an increasing pH or bicarbonate level the chronic Ni IC50 decreased (i.e. toxicity increased) (Table 6.3 and Fig. 6.3a). Similar observations have also been made in other studies where increasing {H⁺} activity enhanced Ni²⁺ toxicity in both *D. magna* and *C. dubia* (Deleebeeck et al. 2007; Schubauer-Bergian et al. 1993). Further, it was observed that Ca²⁺ but not Mg²⁺ had a protective effect against Ni²⁺ toxicity in the bicarbonate group (see Fig. S 6.3a and b, supplementary material). Although our intention was to assess the effect of bicarbonate on chronic Ni²⁺ toxicity by keeping Ca:Mg molar ratio constant (1:1.2) in all test waters, it was observed that Ca²⁺ but not Mg²⁺ significantly decreased in the high bicarbonate group due to slightly alkaline pH and/or alkalinity (Table 6.2). Under slightly alkaline pH (~8.2), presence of carbonate (CO₃²⁻) ligand increases the formation of the solid calcite [CaCO_{3(s)}] as follows (Ruiz-Agudo et al. 2011; Plummer and Busenberg, 1982).



Therefore, low Ca²⁺ concentration in the high bicarbonate waters (i.e. 250 mg/L) could be due to the formation of calcite precipitates. Nevertheless, it is argued here that the observed decrease in Ni²⁺ IC50 was primarily due to either bicarbonate or pH effect than Ca²⁺ and/or Mg²⁺. First, the

chronic Ni IC50 decreased (i.e. toxicity increased) by a factor of 2 between low and medium bicarbonate (i.e. 50 and 150 mg/L) groups even when their respective hardness remained constant (Table 6.2 and 6. 4). Second, the chronic Ni IC50 decreased by a factor of about 3 between high bicarbonate (i.e. 250 mg/L) and low sulfate (i.e. 0 mg/L) groups even when their respective Ca^{2+} and Mg^{2+} concentrations was similar (Table 6.2 and 6.4). Third, Ca^{2+} and Mg^{2+} have similar importance towards chronic Ni toxicity because of their identical K_{CaBL} (3.53) and K_{MgBL} (3.57) (K_{BL} = biotic ligand affinity constant) and the mechanism of chronic Ni toxicity is shown to be primarily due to the disruption of Mg^{2+} homeostasis in *D. magna* (Deleebeeck et al. 2008; Pane et al. 2003). Based on these arguments we speculate that the observed decrease in Ni IC50 in the bicarbonate group (at least in 50 and 150 mg/L) was primarily due to pH or bicarbonate effects.

Speciation calculations revealed that the free Ni^{2+} activity decreased from 68% to 24% and the formation of NiCO_3^0 complex ($\log K = 4.57$) increased from 10% to 60% as pH or alkalinity increased between low and high bicarbonate groups (see Fig. S 6.2a, supplementary material). It was observed that between predicted free Ni^{2+} and NiCO_3^0 , the relationship for predicted NiCO_3^0 complex vs. observed chronic Ni^{2+} IC50 was similar to the relationship of pH or bicarbonate effect on Ni^{2+} toxicity to *C. dubia* (Fig. 6.3a and 6.6c). This suggests that with increasing pH or alkalinity, NiCO_3^0 complex becomes more bioavailable to daphnids than the free Ni^{2+} ion. Hoang et al. (2004) and Deleebeeck et al. (2008a, b) made similar observations and suggested that the enhanced toxicity of Ni^{2+} at high alkalinity and/or pH (~8.1) could be due to the more dominant NiHCO_3^+ and NiCO_3^0 complexes than free Ni^{2+} . It was proposed that Ni-carboante complexes would dissociate at the gill micro-environment yielding free Ni^{2+} which could then be taken up via a putative electro-neutral $\text{Mg}^{2+}/\text{HCO}_3^-$ symporter thereby increasing

the toxicity of Ni^{2+} at higher pH or alkalinity (Deleebeeck et al. 2008a, b). Further, there are evidence that suggests Pb-carbonate complex uptake via $\text{Cl}^-/\text{HCO}_3^-$ exchangers in human red cells is stimulated in the presence of HCO_3^- (Simons, 1986). Interestingly, when MOPS (3-morpholinepropanesulfonic acid) was used to control test solution pH, the 48-h EC_{50} for Ni^{2+} increased (i.e. toxicity decreased) by a factor of about 2 (from 37 to 67 μM) between the pH range of 7 to 8.3 and when NaHCO_3 was used to control test solution pH, the 48-h EC_{50} for Ni^{2+} showed a decreasing trend (26 to 23 μM) between the pH range of 7.6 to 8.0 (Kozlova et al. 2009). Also, when biological buffers were used to control solution pH, free Ni^{2+} uptake rates was highest at pH 6 and was suppressed at pH 7 and 8 (Komjarova and Blust, 2009). These observations support the hypothesis that bicarbonate stimulates Ni toxicity (as observed in our study) and that the formation of Ni-carbonate complexes increases the chances of Ni^{2+} activity at the gill micro-environment and its uptake via the putative $\text{Mg}^{2+}/\text{HCO}_3^-$ symporter as proposed by Deleebeeck et al. (2008a, b). Clearly, the mechanism of enhanced Ni toxicity in freshwater invertebrates as a function of pH and/or bicarbonate/carbonate alkalinity needs further attention (Deleebeeck et al. 2008a; Kozlova et al. 2009).

In combination, Ni and V at their highest sub-lethal dose (2.25+500 $\mu\text{g}/\text{L}$) were found to affect *C. dubia* survival and fecundity additively (Fig. 6.4). Based on the molar mass of each metal it becomes obvious that Ni is more toxic than V at low levels. Among freshwater organisms, *C. dubia* is most sensitive to Ni exposure even at low $\mu\text{g}/\text{L}$ levels (Keithly et al. 2004). Conversely, V is toxic to *C. dubia* at high $\mu\text{g}/\text{L}$ levels, but in vertebrates at mg/L levels. However, the highest sub-lethal doses of Ni (2.25 $\mu\text{g}/\text{L}$) and V (500 $\mu\text{g}/\text{L}$) used in this study are generally 5 to 10 times lower than those found in experimentally-generated oil sands coke leachates (Puttaswamy and Liber, 2011; accepted). This suggests that Ni and V in combination

could potentially affect reproduction of aquatic invertebrates such as *C. dubia* in wet reclamation landscapes. Further, based on their aqueous chemistry it is speculated that the mode of action of each metal is different.

6.6 Conclusion

Inorganic anions (i.e. HCO_3^- , Cl^- and SO_4^{2-}) can significantly influence the mobilization, speciation and toxicity of Ni and V associated with oil sands coke. Specifically, sulfate influences cationic metals (e.g. Ni, Fe, Mn and Zn) release and bicarbonate enhances the release of metals that form oxyanions (e.g. Al and V) from coke. Further, bicarbonate or pH increases Ni bioavailability and toxicity, and sulfate appeared to offer protection against V toxicity. In combination, Ni and V at their sub-lethal doses can act additively. Overall, interaction of coke with inorganic anions commonly found in oil sands process water may have important implications for the performance of reclamation landscapes (e.g. end-pit lake).

6.7 Supplementary material

Table S 6.1. Water chemistry of coke leachates measured on day 15 of batch leaching. Values are mean±SE, n = 3.

| Anion (mg/L) | pH | Conductivity (μS/cm) | Alkalinity (mg CaCO ₃ /L) | Hardness (mg CaCO ₃ /L) | Major Ions (mg/L) | | | | | | |
|--------------------|-----|-------------------------|---|---------------------------------------|-------------------|------------------|------------------|----------------|-----------------|-------------------------------|-------------------------------|
| | | | | | Na ⁺ | Ca ²⁺ | Mg ²⁺ | K ⁺ | Cl ⁻ | SO ₄ ²⁻ | HCO ₃ ⁻ |
| No salt | 7.9 | 38 ± 0.4 | 10 ± 0.6 | 4 ± 0 | 1.4 | – ^a | – | – | 0.1 | 0.4 | 6 |
| <u>Bicarbonate</u> | | | | | | | | | | | |
| 50 | 8.3 | 146 ± 0.4 | 32 ± 13 | 3 ± 0 | 22 | – | – | – | 0.2 | – | 61 |
| 150 | 8.4 | 351 ± 2 | 160 ± 2 | 3 ± 0 | 59 | – | – | – | 0.3 | – | 155 |
| 450 | 8.5 | 677 ± 3 | 531 ± 2 | 4 ± 0 | 173 | – | – | – | 0.4 | – | 453 |
| 1250 | 8.8 | 2282 ± 3 | 1020 ± 1 | 4 ± 0 | 480 | – | – | – | 0.7 | – | 1120 |
| <u>Chloride</u> | | | | | | | | | | | |
| 50 | 7.8 | 255 ± 19 | 8 ± 0 | 5 ± 0 | 34 | – | – | – | 50 | – | – |
| 150 | 7.8 | 683 ± 8 | 7 ± 1 | 5 ± 0 | 100 | – | – | – | 155 | – | – |
| 450 | 7.9 | 2103 ± 2 | 7 ± 1 | 6 ± 0 | 288 | – | – | – | 456 | – | – |
| 1250 | 7.9 | 3963 ± 0 | 7 ± 1 | 5 ± 0 | 828 | – | – | – | 1314 | – | – |
| <u>Sulfate</u> | | | | | | | | | | | |
| 50 | 7.9 | 177 ± 1 | 10 ± 1 | 5 ± 0 | 25 | – | – | – | – | 51 | – |
| 150 | 7.9 | 416 ± 1 | 11 ± 1 | 5 ± 1 | 72 | – | – | – | – | 152 | – |
| 450 | 7.9 | 1116 ± 1 | 9 ± 0 | 6 ± 0 | 214 | – | – | – | – | 457 | – |
| 1250 | 7.9 | 3887 ± 0 | 9 ± 1 | 5 ± 0 | 596 | – | – | – | – | 1286 | – |

^a below method detection limit.

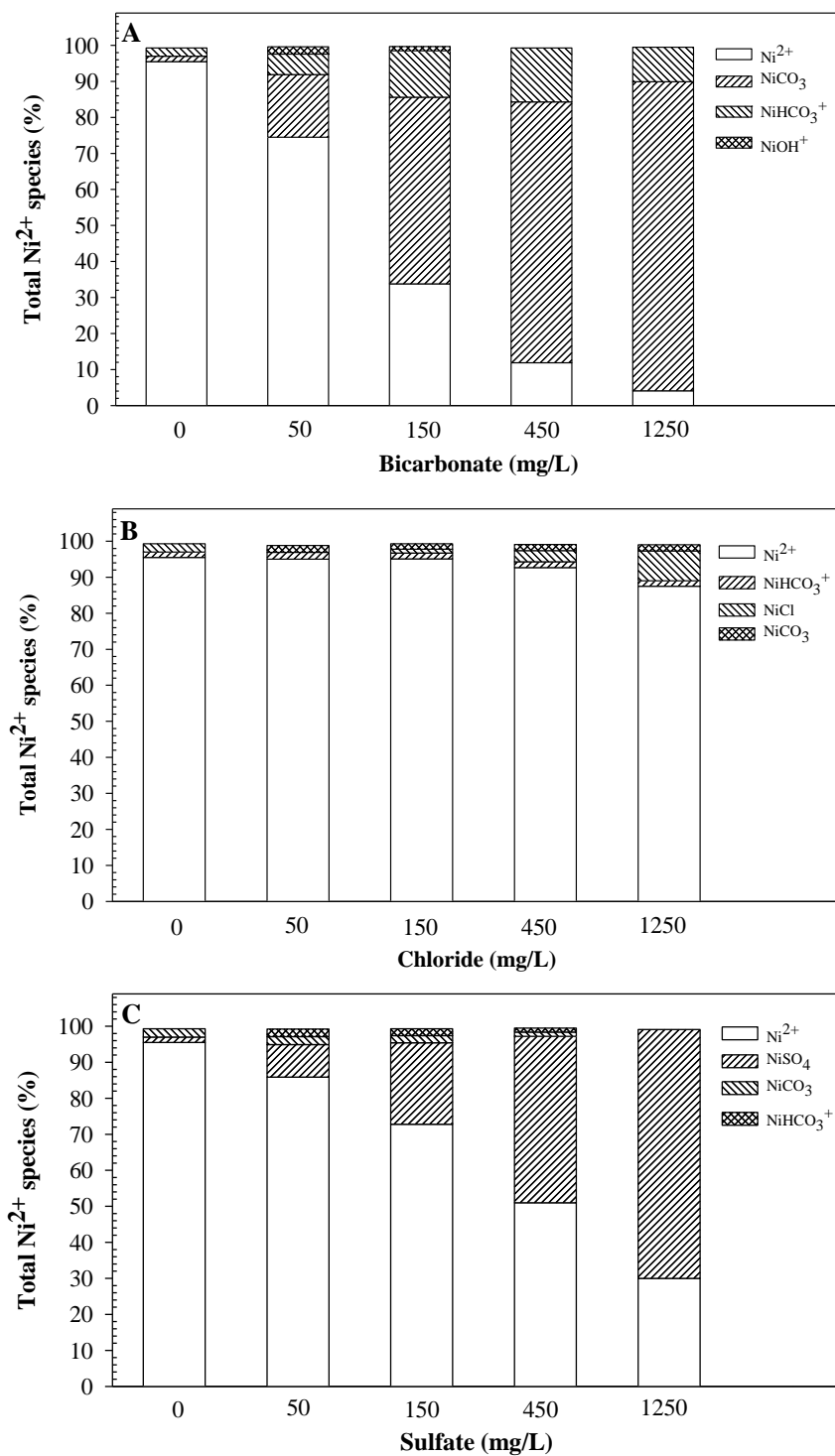


Figure S 6.1. Influence of bicarbonate, chloride and sulfate on aqueous speciation of nickel (A to C) in coke leachates.

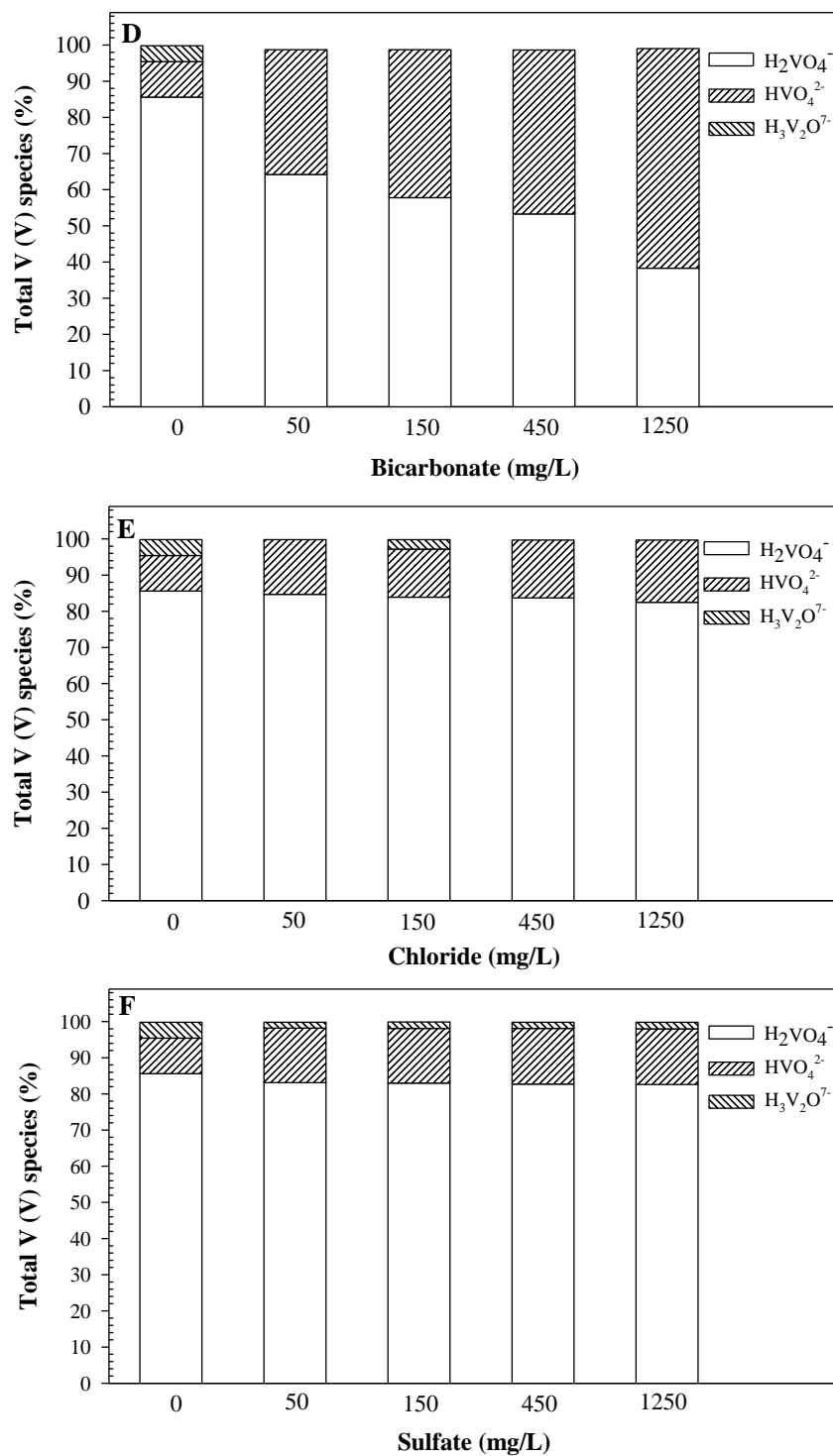


Figure S 6.1. Influence of bicarbonate, chloride and sulfate on aqueous speciation of vanadium (D to F) in coke leachates.

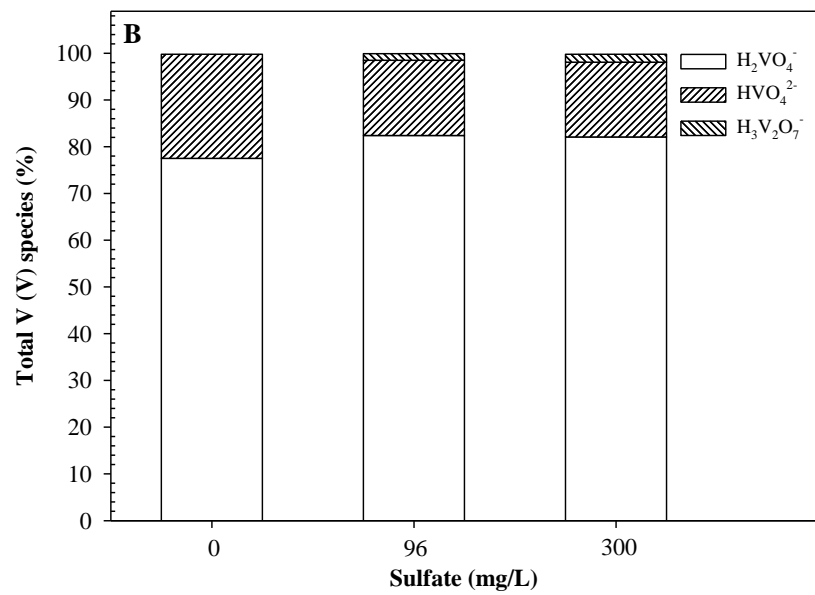
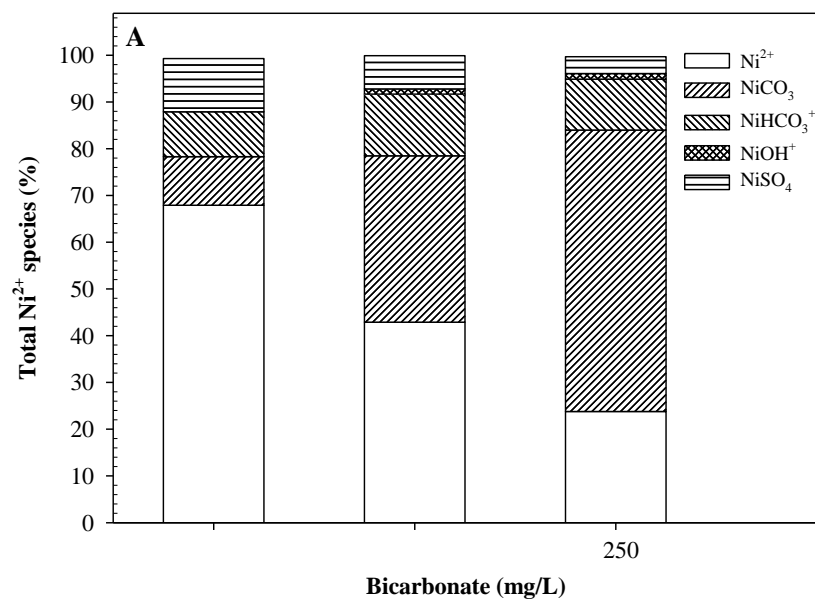


Figure S 6.2. Influence of bicarbonate on aqueous speciation of (A) Ni²⁺ and, sulfate on aqueous speciation of (B) V calculated at the IC50 concentration using MINEQL+.

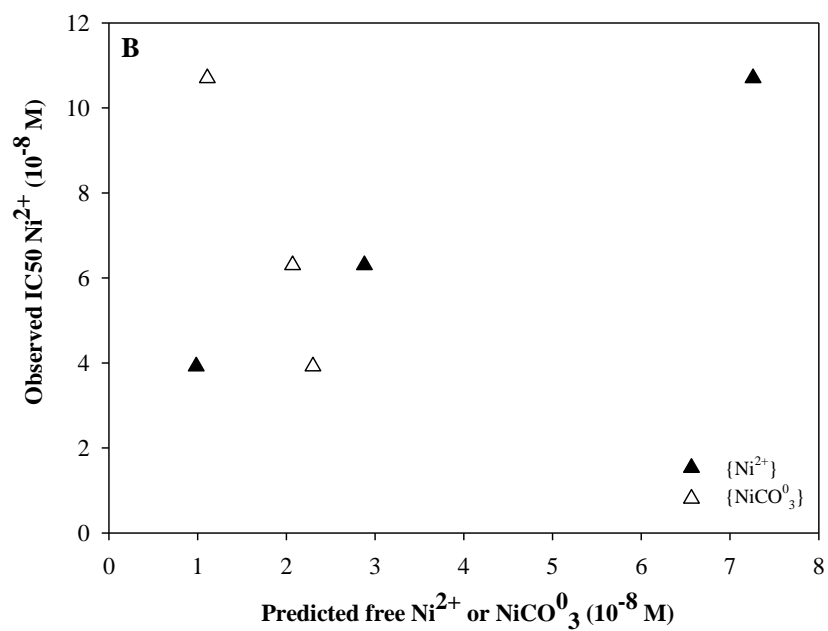
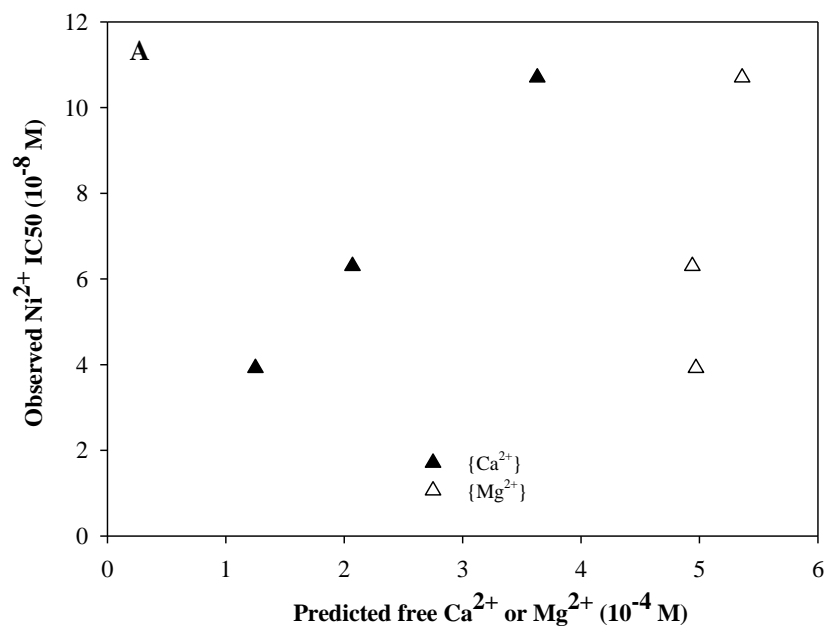


Figure S 6.3. Relationships between (A) predicted Ca^{2+} or Mg^{2+} vs. observed Ni^{2+} IC50 and (B) predicted Ni^{2+} or NiCO_3^0 vs. observed Ni^{2+} IC50, for Ni^{2+} toxicity tests done in bicarbonate waters.

7. GENERAL DISCUSSION

Canadian oil sands mining companies use coking technology to upgrade heavy bitumen to synthetic crude oil (SCO). A consequence of this process is the production of enormous volumes of solid coke as a waste by-product. Further, the trace metals (e.g. Al, Fe, Ni, Ti and V) present in the bitumen as impurities are undesirable as they deactivate the catalysts used in hydroprocessing and decrease SCO yield. Consequently, they are removed from the bitumen and thus get enriched in coke (Zhao et al. 2001; Furimsky, 2009). In 2008, Syncrude Canada Ltd. produced an estimated 2.7 million tonnes of solid coke from just one upgrading facility, adding to their already growing cumulative coke inventory of over 40 million tonnes (ERCB, 2009). Currently, Syncrude stockpiles all of the produced coke on-site in coke cells and/or in the Mildred Lake Settling Basin (MLSB) which awaits reclamation. This practice occurs because the coke production rate (i.e. ~7000 tonnes per day) is greater than what can be combusted and/or sold as an alternative fuel in the current energy market. Thus, a growing coke inventory, zero-discharge regulation and limited space for on-site storage prompted oil sands companies a few years ago to assess the feasibility of integrating coke as a substrate amendment in wet reclamation landscapes (i.e. constructed wetlands). The main goal of these reclamation landscapes was to achieve maintenance-free, self-sustaining ecosystems with capabilities equivalent to or better than pre-disturbance conditions (Golder Associates Ltd., 2000). However, trace metals present in coke were hypothesized to impede the performance of wet reclamation landscapes if they are released into the overlying water column in forms bioavailable to aquatic biota. Therefore, for effective management or remediation of metals released from coke, a better understanding of their fate and toxicity was warranted.

Previously, it was believed that trace metals in Syncrude coke were virtually non-leachable into the environment when stored in reclamation landscapes (Chung et al. 1996). However, in recent times, two independent coke leaching studies have showed that coke had the potential to release certain metals at concentrations exceeding Canadian guidelines for the protection of aquatic life (Squires, 2005; Kessler and Hendry, 2006). Furthermore, plants grown using coke as a substrate suffered from water stress that was attributed to the physical composition of the coke (Nakata et al. 2011), benthic invertebrate abundance decreased when coke was used as a substrate for colonization in a constructed wetland (Baker, 2007), and coke was found to inhibit methanogenesis - a process vital for the bio-degradation of organic contaminants in tailings ponds (Fedorak and Coy, 2006). While these research findings proved that coke is not inert in the environment and does affect biological processes, the causes of such effects were not explicitly identified. Furthermore, the fate, speciation and toxicity of trace metals released from coke under natural conditions were not well characterized. Therefore, the overall goal of this research was to assess if coke could pose an ecotoxicological risk to aquatic invertebrates when used as a substrate amendment in wet reclamation landscapes. Research findings presented in this thesis identified Ni and V as the primary toxicants associated with coke and further characterized their speciation and toxicity under conditions relevant to reclamation landscapes. Other metals identified as potential concern to the performance of wetlands include Al, As, Mo and Zn. The fate, speciation and toxicity of Ni and V are discussed in detail with reference to wet reclamation landscapes; the concerns of other metals are only briefly discussed.

7.1 Fate of metals released from coke

For coke integrated into wet reclamation landscapes, the environmental fate, transport, bioavailability and toxicity of trace metals associated with coke depends on the solid phase

distribution of metals in coke and on geochemical (e.g. pH, red-ox, sorption, weathering, re-suspension etc.) and biological (e.g. red-ox, bioturbation etc.) parameters. Almost all of the metals that become enriched in coke during upgrading basically originate from the natural bitumen impurities. In the bitumen complex, Al, Fe, Mn and Ti are primarily bound to inorganic impurities such as aluminosilicate clay particles, pyrite and TiO₂, while Ni and V are typically present as organometallic complexes called porphyrins (Zhao et al. 2001; Speight, 1999). However, during bitumen combustion at elevated temperature (~500°C) the solid phase association of these metals in coke may change considerably which would then influence their mobility and aqueous speciation. Because several metals get enriched in coke during bitumen upgrading, coke could be viewed as a repository of trace metals when stored in wetlands.

In the present research it was found that Ni and V released from coke were the primary source of coke leachate toxicity to a model aquatic invertebrate. Moreover, the concentrations of V released from coke in all leaching experiments, as well as in coke leachates collected from field lysimeters, were consistently higher than all other trace metals released from coke (Chapter 4, 5 and 6). In addition, V in the overlying water reached a peak concentration within a very short period (~4 h) of contact with water (Chapter 4 and Appendix B). These results indicate that a significant fraction of V is loosely bound to the coke surface, and that this V desorbs immediately upon contact with water. Kessler and Hendry (2006) determined the solid phase partitioning of V in coke and found that the total V (1539 mg/kg) partitioned in various 'operationally' defined fractions decreased in the order: residual (83.5%) > bound to organic (15.5%) > water soluble (0.6%) > bound to sulphides (0.2%) ≈ bound to oxides (0.2%). Although the more labile water soluble and oxide bound fractions are significantly small compared to the residual fraction (i.e. non-leachable), the sheer volume and a high surface area

of coke would mean that a significant amount of V dissolution would occur from these two fractions under favorable leaching conditions.

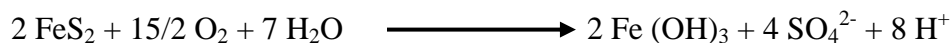
Vanadium mobilization from coke, exposed to natural weathering process in field lysimeters and laboratory batch leaching process, was greatly enhanced under alkaline pH and bicarbonate enriched leaching conditions, but not under acidic pH or sulfate enriched leaching conditions (Chapter 4, 5, and 6). Further, the measured dissolved oxygen level at room temperature (25°C) in these leaching experiments was generally between 7 and 10 mg/L. Under oxic and alkaline leaching conditions, high concentrations of OH^- and HCO_3^- would displace loosely bound or adsorbed V from the coke surface via ligand exchange. Furthermore, V has a high affinity for oxygen atoms and thus forms stable oxyanion complexes in aqueous solution. Therefore, in wet reclamation landscapes, conditions such as alkaline pH, oxic waters and a positive red-ox (Eh) status at the coke-water interface are expected to favor V release from coke into the porewater and overlying water column. These conditions may occur in shallow wetlands or in the littoral zone of constructed lakes and wetlands where the water column would be well oxygenated due to mixing. Ozonation which has been discussed as a treatment option for reduction of naphthenic acids in tailings water could similarly enhance V release from coke. This aspect should be investigated in future studies. On the other hand, under sub-oxic and reducing conditions in coke porewaters, the dissolved V concentration was generally found to be lower (Appendix A). This suggests that V mobilization to overlying water would be greatly retarded under reducing conditions possibly due to V sorption onto various solid phases.

In reclamation landscapes containing coke, the chemistry of the soil cover and that of the recycled process water will greatly influence the fate of metals associated with coke. In the present research it was found that the concentration of V released from coke in the deep lysimeter was 2 to 7 times higher than the concentrations measured in the shallow lysimeter

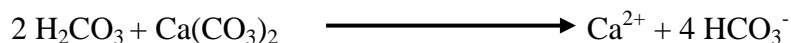
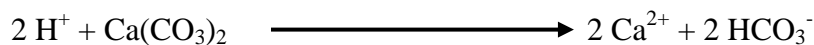
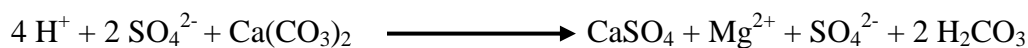
leachate (Table 4.2). The only major difference between the two lysimeters was their soil cover depth (Fig. 4.1). The chemistries of the soil cover and the recycled water were hypothesized to have caused the higher release of V from the deep lysimeter. Among the parameters known to enhance V mobilization (e.g. alkaline pH, O₂ and bicarbonate), it was found that pH and bicarbonate levels were elevated in the deep lysimeter relative to shallow lysimeter leachate (Table 4.1). Furthermore, a positive relationship was observed between bicarbonate level and V release from coke in the deep lysimeter but not in the shallow lysimeter (Fig. 7.1). A similar relationship (Fig. 7.1) was observed in the coke leaching study (chapter 6).

Although coke in the two lysimeters was covered with similar soil, the depth of the soil cover differed between the two lysimeters (Fig. 4.1). The soil used to cap the coke was comprised of a top layer of peat soil and a secondary layer of glacial mineral soil (sub soil), a sandy loam-clay soil. The glacial mineral soil is rich in pyrite and carbonate minerals and, pyrite oxidation generates increased acidity in these soils (Kessler, 2007). The acidity generated is neutralized by the dissolution of carbonate minerals (calcite, dolomite and magnesite) yielding bicarbonate (Pokrovsky et al. 2009). Therefore, a thicker soil cover is speculated to have generated higher bicarbonate in the deep lysimeter compared to shallow lysimeter leachate.

Pyrite oxidation and acidification



Carbonate mineral dissolution



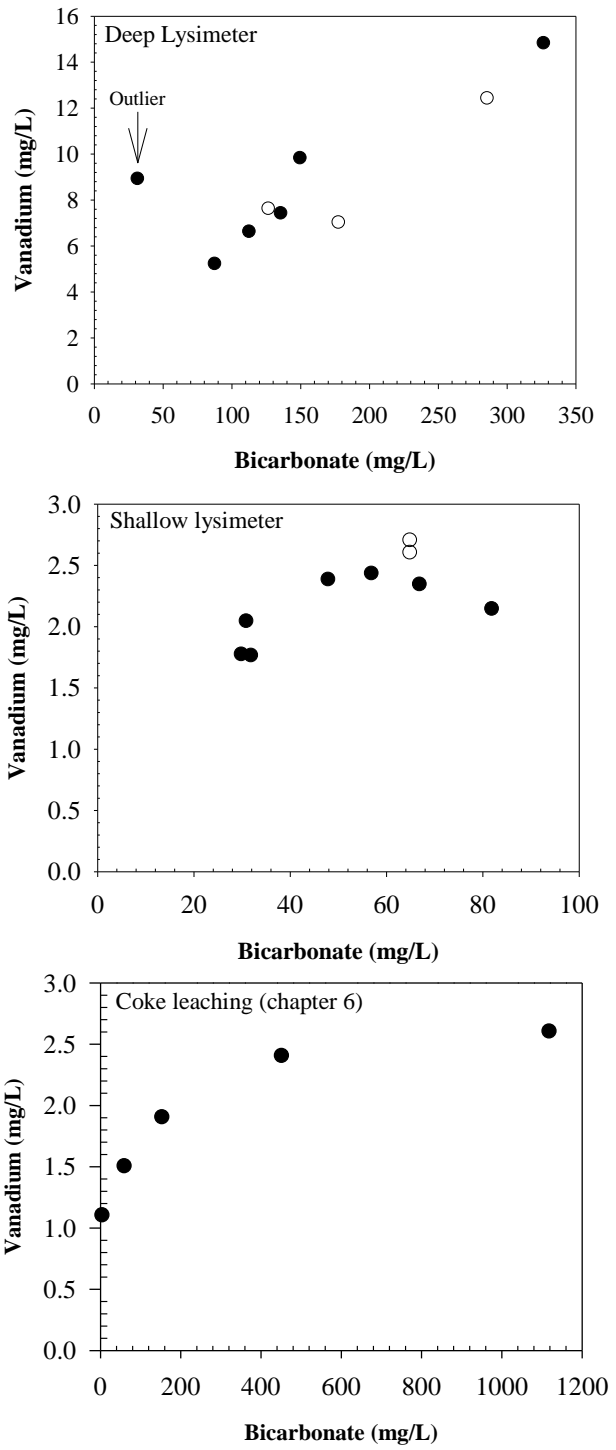


Figure 7.1 Influence of bicarbonate ion on vanadium release from coke. Values shown are from chapter 3 and 5. Data for open circles are from H. Rodger (2006, pers. comm.).

Coke particles have a high concentration of metal oxide surfaces (e.g. Al_2O_3 , Fe_2O_3 and TiO_2) and clay minerals which can scavenge dissolved V species effectively in the porewaters. Since V has a strong tendency to associate with oxygen donor atoms, both oxocation (VO^{2+} and VO_2^+) and oxoanion (H_2VO_4^- and HVO_4^{2-}) species of V can form strong surface complexes with Al_2O_3 , Fe_2O_3 and TiO_2 (Wherli and Stumm, 1989; Peacock and Sherman, 2004). Therefore, a likely scenario in a deep end-pit lake (water cap: 65 to 100 m) where bottom substrates (e.g. reclamation soil cover, coke and mature fine tailings) would typically be in an anoxic state, it is possible that V release from coke would be retarded due to sorption onto abundant hydrous oxide and mineral surfaces. A relatively impermeable reclamation cover may further retard V diffusion into the overlying water column.

Together with vanadium, Ni was identified as one of the primary metals responsible for the observed coke leachate toxicity for leachates obtained from both field lysimeters and those generated in the laboratory (Chapter 4 and 5). Nickel is present in high concentration in coke and because of its high toxicity to aquatic invertebrates it could potentially pose an ecotoxicological risk if released into the water column at appreciable amounts. Leaching experiments showed that Ni mobilization from coke was enhanced under acidic and sulfate-enriched leaching conditions, but was significantly reduced under alkaline and bicarbonate-enriched leaching conditions (Chapter 4, 5 and 6). Under low pH conditions, high activity of H^+ displaces cationic metals (e.g. Ni^{2+}) by a ligand exchange process from oxide and organic surfaces (Salomons and Forstner, 1984). Again, from the work of Kessler and Hendry (2006), partitioning of total Ni (549 mg/kg) in coke was shown to decrease in the order residual (76.8%) > bound to organic (22.8%) > bound to oxides (0.18%) \approx bound to sulphides (0.17%) \gg loosely bound to coke surface (0.02%). It is possible that during coke leaching under acidic condition (pH 5.5; Chapter 5), increased H^+ activity in the solution promoted Ni^{2+} desorption exclusively from the oxide and/or organic

bound fractions of the coke. However, in the present research, the design of the static coke leaching experiments did not allow this hypothesis to be tested explicitly. On the other hand, increased sulfate levels were found to enhance Ni^{2+} mobilization from coke with a concomitant increase in NiSO_4 complex formation ($\log K = 2.3$) (Chapter 6). In the absence of organic ligands, Ni^{2+} forms stable complexes with inorganic ligands in the order $\text{OH}^- > \text{SO}_4^{2-} > \text{Cl}^- > \text{NH}_3$, and the relative proportion of the Ni-ligand complex increases with increasing levels of these inorganic ligands (Adriano, 2001). Therefore, it is speculated that at high ligand (SO_4^{2-}) and exchangeable cation (Na^+) concentrations which are typical properties of process water used for ‘water-capping’ coke, Ni could be displaced from coke via an ion exchange process. However, under alkaline and bicarbonate-enriched leaching conditions, Ni release from coke was significantly reduced (Chapter 5 and 6). This is likely because cationic metal sorption onto oxide and/or organic surfaces generally increases with increasing pH, and the solubility and mobility of Ni in alkaline soils is known to decrease due to chemisorptions onto oxides, aluminosilicates and clays (Salomons and Forstner, 1984; McBride, 1994). Based on these observations, it can be expected that in end-pit lakes, Ni solubility and mobility could generally be retarded due to (i) prevailing reducing conditions at the coke-water or coke-tailings interface, (ii) abundant particulate adsorbents that can bind Ni, and (iii) the slightly alkaline pH of the process water used for water-capping coke, all of which would enhance Ni sorption. While it was found that pH has an opposite effect on Ni and V release from coke, it is the reducing condition in coke substrates that would commonly retard the release of these two metals and thus significantly dictate their fate and toxicity in aquatic reclamation landscapes, including end-pit lakes.

Other trace metals released from coke that could pose an ecotoxicological concern include Al, As, Mo and Zn. In the present research, the Canadian water quality guideline for the protection of aquatic life for Al (100 $\mu\text{g/L}$), As (5 $\mu\text{g/L}$), Mo (73 $\mu\text{g/L}$) and Zn (30 $\mu\text{g/L}$) was

exceeded by these metals at least once in the coke leaching experiments (Chapter 4, 5 and 6, Appendix B). However, none of these metals were identified as the primary toxicants in the coke leachates because their concentrations were generally below toxicity thresholds for *C. dubia* (Chapter 5). Nevertheless, in wet reclamation landscapes cycling of these metals between coke substrate and the water column may affect the performance of wetland ecosystems. It was found that oxic and alkaline pH leaching conditions favored the release of Al, As and Mo, and that acidic pH and sulfate-enriched leaching conditions favored Zn release from coke (Chapter 4, 5 and 6, Appendix B). Aluminum solubility and bioavailability in the water column are greatly enhanced under acidic (pH<6.0) or alkaline (pH>8.0) conditions (Driscoll and Schecher, 1990). However, in the neutral pH range (6 to 8) Al is highly insoluble and precipitates to form amorphous oxides that could scavenge both cation and anion forming metals. Thus, in wet reclamation landscapes, Al would play a dual role as either a metal scavenger or a potential toxicant depending upon the pH, labile Al concentration and red-ox conditions. In oxic environments, arsenate (AsO_4^{3-}) and molybdate (MoO_4^{2-}) oxyanion species dominate and their sorption onto Fe and Al oxide surfaces increases at low pH (McBride, 1994; Fox and Doner, 2003). Because microorganisms mediate the reduction of less-toxic As(V) to highly toxic As(III) in the sediment, it is important with respect to wet reclamation landscape performance to understand if microbes in wetlands could reduce As associated with coke to the highly soluble, mobile and more toxic As(III). Zinc likely would not be of ecotoxicological concern in end-pit lakes and other aquatic reclamation landscapes because (i) the majority of Zn in coke is present in the residual or non-leachable fraction (Kessler and Hendry, 2006), (ii) Zn has a high affinity for many solid phases (e.g. sulphides, metal oxides and clay surface), and (iii) the slightly alkaline pH of the process water used for water-capping coke should increase sorption and thus retard Zn solubility and bioavailability to aquatic organisms.

7.2 Toxicity of metals released from coke

In previous research, it was observed that trace metals released from coke had no measurable effect on larval *Chironomous dilutus* (a benthic invertebrate), despite the release of certain metals (Cu, Mn, Mo, Ni and V) from coke at toxicologically relevant levels (Squires, 2005). Possible reasons for this observation could be the use of a test species that is generally known to be relatively tolerant to many metals and/or that the metals released from coke were not in a bioavailable form. In the present research, however, a freshwater zooplankton species, *Ceriodaphnia dubia*, an organism commonly used in toxicity testing, was selected to evaluate the bioavailability and toxicity of trace metals released from coke. Daphnids are known to be sensitive to trace metal exposure and because of their short life-cycle and ease of handling they are ideal test organisms for chronic toxicity testing. Moreover, it has been suggested that if toxicity is noticeable in a sensitive single-species tests such as the *C. dubia* test, then the results are often good predictors of aquatic level impacts (de Vlaming and Norberg-King, 1999; de Vlaming et al. 2000). Thus, use of a sensitive test species such as *C. dubia* to evaluate bioavailability and toxicity of trace metals released from coke would provide a good model for predicting the potential ecotoxicological risk of storing coke in wet reclamation landscapes.

The 7-d median lethal concentration (LC50) estimated for *C. dubia* exposed to coke leachates collected from two field lysimeters was consistently below 25% (v/v) over the 20 month monitoring period (Chapter 4). This prolonged acute toxicity was attributed to trace metals released from the coke under semi-natural field conditions. However, due to insufficient volumes of leachate being available at each sampling time, a full series of toxicity identification and evaluation (TIE) tests could not be performed to identify the cause of lysimeter coke leachate toxicity. Instead, a toxic unit (TU) approach was used to estimate the relative significance of metals of concern released from coke, thus identifying and ranking suspect

toxicants. While the TU method ranks the relative importance of each metal in relation to the observed toxicity, it does not explicitly identify the toxicants. Based on calculated TUs and metal-specific LC50s, Ni and V were identified as the suspect toxicants in the lysimeter leachates (Chapter 4). In addition, the cause of prolonged acute toxicity of coke leachates from both lysimeters was concluded to be due to the continued release of Ni and V from coke at concentrations above their respective toxicity thresholds for the entire 20 month period of monitoring (Chapter 4). Further, at all sampling times, V concentrations in the two lysimeters especially in deep lysimeter leachate were significantly higher than the concentrations of all other trace metals (Chapter 4). As discussed earlier, alkaline pH and oxic conditions are known to favor V mobilization from coke, particularly the water soluble or loosely bound V fraction. While it was known that the pH of the deep lysimeter coke leachate was slightly alkaline (7.1 to 8.1), it is speculated based on the measured dissolved oxygen levels (6.8 to 8.3 mg/L) of the coke leachates in the laboratory that oxic conditions may have prevailed inside the deep lysimeter, despite the 1 m thick reclamation soil cover placed over the coke which favored increased V dissolution. This suggests that in shallow or littoral wetlands (water cap: 5 to 10 m), where mixing of water column would occur, oxic conditions may prevail in coke substrate thus promoting the release of V as well as the release of other metals such as Al, As, and Mo. Nickel release from coke in the two lysimeters followed a different-pattern. The concentration of Ni in the deep lysimeter leachate (14 to 22 µg/L) was low compared to the shallow lysimeter (20 to 62 µg/L) possibly due to the slightly alkaline pH of the water in the deep lysimeter (Chapter 4). Nevertheless, these Ni concentrations are high enough to be toxic to many freshwater invertebrates including *C. dubia* which are sensitive to low levels of Ni exposure (Keithly et al. 2004). It is likely that only the water soluble Ni fraction was mobilized from the coke in the lysimeters and that the Ni present as oxides and complexed to the organic fraction was not

released under the slightly more alkaline leaching conditions in the deep lysimeter. Similarly, when coke was leached under alkaline pH conditions (pH 9.5) in separate laboratory experiments, Ni levels in the leaching water were significantly (~30 times) lower than levels measured under acidic leaching condition (Appendix B).

In an effort to understand the ecotoxicological risk of storing coke in wetlands, it was important that the trace metals responsible for the observed field lysimeter coke leachate toxicity were identified and confirmed. Consequently, a chronic toxicity identification and evaluation (TIE) approach was applied to coke leachates generated via a batch leaching process in the laboratory. A batch leaching was used to mimic coke stored in a wetland where transport of metals into the overlying water column would be largely controlled by diffusion. The coke: water ratio of 1:4 used in all leaching studies best matches an earlier proposed ratio of coke (0.5 to 0.75 m) and water (1 to 2 m) depths in shallow or littoral wetlands (MacKinnon, 2002). Further, this ratio allowed for direct comparison of results to similar leaching experiments performed under different leaching conditions such as pH, freeze-thaw and dissolved oxygen (Squires, 2005).

Coke was leached under two pH conditions (i.e. 5.5 and 9.5) to generate leachates with different trace metal chemistries so that the TIE manipulations could identify if different metals were acting as toxicants in the two coke leachates. Coke leachates from both pH treatments were found to be acutely toxic to *C. dubia* at a 100% leachate concentration (Chapter 5). As expected, pH had a significant influence on the type and concentration of metals released from coke. For example, acidic pH favored the release of cationic metals (Mn, Ni and Zn) and alkaline pH favored the release of metals that form oxyanions (Al, Mo and V) in solution. While trace metals were believed to be the cause of coke leachate toxicity based on lysimeter leachate chemistry, the role of other classes of compounds (e.g. ammonia and organic compounds) were ruled out by

specific TIE manipulation tests (Chapter 5). The application of ion exchange resins in TIEs was of great benefit in identifying the toxicants since coke leachates were comprised of mixtures of metals in both cationic and anionic forms. Resins remove both essential and toxic cations (cation resin) and/or anions (anion resin) from solution. Therefore, major ions removed by resins that are essential for *C. dubia* survival and reproduction (e.g. Na^+ , Ca^{2+} , Mg^{2+} , SO_4^{2-}) were added back to post-resin leachates at appropriately initial amounts to minimize or remove toxic effects caused due to the removal of essential ions. Using a series of preliminary experiments, the optimal resin strength (2.5 g/L for cationic resin and 5 g/L for anionic resin) and major ion balance (i.e. CaSO_4 and MgSO_4 salts) were developed for use in chronic coke leachate TIEs using *C. dubia*. With the anion resin treatment, toxicity was removed in both pH 5.5 and 9.5 coke leachates, and toxicity re-appeared when Ni and V were added back to post-resin pH 5.5 leachate and with V addition to post-resin pH 9.5 leachate (Chapter 5). Based on metal chemistry and toxicity assessment of post-resin leachates it was concluded that Ni and V are the primary cause of coke leachate toxicity in acidic leachates and V alone in alkaline leachates. Other metals released from coke that could be of possible concern include Al, As, Mn and Mo (Chapter 5 and Appendix B). These findings would assist in coke reclamation efforts particularly in undertaking metal remediation strategies and long-term monitoring programs.

Based on the results presented in Chapters 4 and 5, it was hypothesized that if coke was added as a substrate in shallow wetlands, Ni and V would become metals of potential concern. Because coke comes in contact with recycled process water during its hydro-transport and long-term storage in wetlands, it was of interest to examine whether the dominant inorganic anions (i.e. bicarbonate, chloride and sulfate) in the process water would influence the speciation and toxicity of Ni and V released from coke. Results presented in Chapter 6 provide evidence that chronic toxicity of Ni and V is influenced by individual inorganic anions, and that there are the

interactive toxic effects of Ni and V on *C. dubia*. While these results do not provide a complete picture of the mechanistic aspects of Ni and V uptake and toxicity, they present some important testable hypotheses that, if tested, would advance the understanding of Ni and V bioavailability and toxicity mechanisms. Specifically, two interesting observations were made about Ni and V toxicity to *C. dubia*.

First, increasing bicarbonate concentrations were found to increase Ni toxicity to *C. dubia* (Chapter 6). However, Ni speciation calculations showed that the free Ni^{2+} concentration was low (24%) relative to the NiCO_3 (60%) complex concentration in high bicarbonate water where Ni was found to be highly toxic. A commonly accepted tenet in metal toxicology is that the free aquo ion $\{\text{M}^{+n}\}$ is the most bioavailable species of a metal that causes toxicity. The findings presented provided in Chapter 6, however, indicate that at high bicarbonate levels, NiCO_3 , not the free Ni^{2+} , could have been more toxic. Similar observations have been made by other researchers using different test organisms (Hoang et al. 2004; Deleebeeck et al. 2008; Kozlova et al. 2009). Therefore, further investigation of bicarbonate influence on Ni uptake and toxicity to aquatic invertebrates is warranted.

Second, increasing sulfate levels in test waters were protective against V toxicity (Chapter 6). Further, the vanadate oxyanion (HVO_4^{2-}) was found to be the dominant V species in all sulfate (0, 150 and 250 mg/L) test waters. Because the vanadate oxyanion is structurally similar to sulfate and phosphate (Bridges and Zalups, 2005), and based on ionic mimicry analogy, it is hypothesized that vanadate may be taken up via a sulfate or anion transporter in aquatic invertebrates. Clearly, this hypothesis also requires further investigation. One of the limitations of this experiment was that whole body Ni and V in adult *C. dubia* could not be accurately measured because of their small size and mass. This greatly limited the ability to integrate metal speciation and bioaccumulation data.

7.3 Conclusions

The overall objective of this research was to examine whether metals released from oil sands coke are bioavailable and toxic to aquatic invertebrates. While it was found that coke releases several trace metals at different concentrations depending on the leaching condition (i.e. pH and ionic strength), only Ni and V were identified as the primary toxicants of concern associated with coke leachate. This conclusion was consistent for both field collected and laboratory generated leachates, and for different leaching conditions (e.g. liquid/solid ratio, pH, dissolved oxygen, ionic composition, flow-through and static type, and duration of leaching). Bicarbonate and alkaline pH conditions enhance V release from coke, whereas sulfate and acidic pH conditions increase Ni release from coke. Further, the geochemistry of the soil cover and the chemistry of the recycled process water influence the fate and release of metals associated with coke, especially Ni and V. Speciation modeling of Ni and V in coke leachates revealed that these two metals are present in bioavailable forms and thus would result in toxicity. Other metals released from coke that could be of potential ecotoxicological concern include Al, As, Mn, Mo and Zn.

7.4 Recommendations for coke reclamation

Based on the observations and knowledge derived from this research, a hypothetical scenario for metals cycling in coke amended wetlands is briefly described here.

Metals fate and transport

- Maintaining coke substrates under anoxic and reducing conditions is preferable. This would greatly retard metals flux to overlying water. Under reducing conditions, red-ox sensitive metals in coke such as As, Fe, Mn, Ni, Mo, Sn and V are immobilized by

sorption onto sulphides, organic matter and clay minerals. For instance, reducing condition decreases V mobilization by enhancing adsorption and precipitation.

- Integrating coke in deep wetlands rather than shallow wetlands is recommended. This should avoid fluctuations in oxygen and water level, thus maintaining anoxic conditions in coke substrates.
- Reactive geochemical barriers that allow minimal oxygen flux and are resistant to pH fluctuations should be used to cover coke in order to retard metals flux from coke to overlying water.
- Elevated levels of sulfate in the recycled process water may promote increased sulphide formation by sulfate reducing bacteria. Sulphides would result in the precipitation of some cationic metals (e.g. Fe, Mn, Ni, Sn and Zn) associated with coke and thus reduce their bioavailability. While the use of recycled process water for water capping coke is recommended, presence of other contaminants such as naphthenic acids in the recycled water may impede the ecological performance of reclamation landscapes. Therefore, use of pre-treated (e.g. ozonation) recycled process water may be a suitable option for water capping coke in constructed wetlands.

Metals bioavailability and toxicity

- High sulfate concentration in the overlying water will reduce V toxicity to aquatic invertebrates. Therefore, water capping coke using recycled process water could prove beneficial with respect to V bioavailability and toxicity.
- The colloid facilitated transport of metals from coke substrates may increase metals concentration in drainage waters. Therefore, drainage from coke amended wetlands should be avoided or should undergo remediation treatments.

7.5 Future research

Future research should include field-based studies to examine the effect of natural weathering processes on speciation, fate, transport and toxicity of metals associated with coke. Creation of representative reclamation landscapes, both in the field and in the laboratory, would provide opportunities to better understand and predict metal cycling in final reclamation landscapes. Some specific research needs are highlighted here.

- Further evaluation of salinity effects on Ni and V aqueous speciation and toxicity would be relevant to future reclamation landscape settings.
- Knowledge about V toxicity to freshwater organisms is limited. Therefore, future research should focus on developing a better understanding of V exposure and effect to different aquatic organisms. In addition, the effect of water quality conditions such as pH, sulfate, nutrients (e.g. phosphate) and organic matter that are representative of recycled process water on V toxicokinetics (i.e. uptake, distribution and elimination) should be evaluated.
- A multidisciplinary research initiative could be undertaken to examine the effect of soil cover geochemistry on metals fate, transport and bioavailability in potential reclamation landscapes. Further, an understanding of the performance (e.g. sorptive strength, diffusion and dispersivity) of active barrier systems (e.g. natural zeolites and ferric hydrites) and their suitability to contain oxyanion metals (e.g. As, Cr, Mo and V) and organic acids (e.g. naphthenic acids) could be of interest to coke reclamation efforts.
- Laboratory experiments could be designed to evaluate colloid facilitated transport of metals in reclamation landscapes. *In situ* probes, such as peepers and diffusion gradients in thin films (DGTs), could be used to characterize the diffusion of bioavailable metal fraction in coke amended wetlands and other landscapes.

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APPENDIX A

IN SITU MEASUREMENT OF POREWATER METAL CONCENTRATIONS IN EXPERIMENTAL RECLAMATION SUBSTRATES PLACED IN A NATURAL WETLAND

Introduction

Formation of solid coke as a by-product during bitumen upgrading is part of the oil sands operations. Syncrude Canada Ltd. alone produces an average of 2.5 million tonnes of coke per year (ERCB, 2009). The growing coke inventory has prompted oil sands companies to consider placing coke in constructed wetlands due to limited terrestrial storage space. It was originally believed that coke was relatively inert when placed in the surrounding environment and therefore it could be used as a substrate in wetlands to support colonization by wetland biota, in particular benthic invertebrates. To assess the feasibility of using coke as a substrate in wetlands, small in situ experimental enclosures amended with peat, coke and native sediments were placed in the Shallow Wetland South Ditch (SWSD) at the Syncrude wetlands research site. It was hypothesized that trace metals associated with coke may become mobilized into the substrate porewater under natural weathering conditions. Therefore, the objective of this study was to collect and determine the porewater concentration of metal contaminants released from coke in these experimental enclosures under natural environmental conditions.

Dissolved metal concentrations in contaminated sediment porewaters are generally elevated compared to the overlying water concentrations. Further, porewater metal concentrations are regarded as good predictors of metal bioavailability and toxicity to sediment dwelling organisms compared to total sediment metal concentrations (Luoma and Rainbow,

2008). Therefore, sampling the dissolved phase of metals in coke porewaters using an *in situ* dialysis device (i.e. peepers) should provide a good estimate of the bioavailable metal fraction released from coke under natural weathering conditions. Peepers are commonly used for *in situ* porewater sampling to determine the dissolved metal concentrations. Peepers operate on the basis of a diffusion-controlled transport mechanism where concentrated porewater solutes diffuse into the peeper chambers holding low or no solutes through a filter membrane (Adams et al. 2003).

Materials and Method

***In situ* enclosures**

In 2002 and 2004, experimental enclosure units (i.e. different combinations of test reclamation covers) consisting of peat over native sediment and peat over Syncrude or Suncor coke were placed in the Shallow Wetland South Ditch (SWSD) located in the Syncrude wetland research facility by excavating 40 cm diameter x 10 cm holes in the wetland. The bottom layer (8 cm) was either native sediment, Syncrude coke or Suncor coke overlain on top by peat (2 cm) material (Baker, 2007). The purpose of these experimental enclosure units was to assess the feasibility of storing coke in constructed wetlands and to better understand the fate and toxicity of metals released from coke under natural weathering conditions. Details of the *in situ* test units used for sampling porewater for this study are provided in Table 1.

***In situ* porewater sampling**

A schematic of the peeper design used for *in situ* sampling of porewater in the test enclosures is shown in Figure 1. Prior to deploying the peepers in the field, peeper cells were

filled with de-ionized water and a 0.2 µm semipermeable polysulfone membrane (Pall Corporation, MI, USA) covering the cells held in place between the face plate and base (Fig. 5.1).

Table 1. *In situ* enclosure units installed in the Syncrude Shallow wetland used for collection of porewater.

| <i>In situ</i> enclosure ID ¹ | Substrate combination (10 cm) | | Installed |
|--|-------------------------------|-----------------|------------------|
| | Top (2 cm) | Bottom (8 cm) | |
| 34, 53 and 86 | Peat | Native sediment | July 2002 |
| 24, 78 and 104 | Peat | Syncrude coke | July 2002 |
| 28, 49 and 106 | Peat | Suncor coke | July-August 2002 |
| 08, 68 and 97 | Peat | Syncrude coke | July 2004 |

¹As per Baker (2007).

A total of 12 peepers, three per enclosure unit, were deployed in August 2005 at the SWSD. Peepers were left undisturbed in the enclosure units for 15 days to equilibrate. An equilibration time of 15 to 20 days is recommended for larger peepers that are commonly used in field investigations (Adams et al. 2003). Peepers were retrieved from their respective enclosure units on day 15 and the porewater in the peeper cells was collected using a clean pipette tip and transferred into Nalgene® sample bottles and shipped to Toxicology Centre, University of Saskatchewan stored in an ice-packed cooler. Porewater samples were acidified using 2% high purity HNO₃ in the laboratory before submitting for analysis. Measurement of porewater pH and conductivity was done on a sub-set sample and are shown in Table 2. However, at the time of porewater collection, red-ox measurements could not be made because of electrode malfunction, thus limiting the interpretation of the porewater metal concentrations data.

Analytical chemistry

Porewater from only those chambers that were in direct contact with native sediment or coke substrate were selected for determining the trace metals concentrations. All samples were analyzed at the Prairie Diagnostic Services, Western College of Veterinary Medicine, University of Saskatchewan, using Inductively Coupled Plasma-Mass Spectrometer (ICP-MS). Trace metal concentrations are presented as mean \pm SE ($n = 3$) in $\mu\text{g/L}$ units (Table 2).

Table 2. Porewater chemistry (mean \pm SE, $n = 3$) of de-ionized water and *in situ* enclosure units.

| Enclosure units | pH | Conductivity ($\mu\text{S/cm}$) |
|--------------------|----------------|-----------------------------------|
| De-ionized water | 7.1 ± 0.02 | 0 |
| Native sediment | 7.8 ± 0.2 | 0.7 ± 0.02 |
| Syncrude coke 2002 | 9.1 ± 0.1 | 0.6 ± 0.1 |
| Syncrude coke 2004 | 9.2 ± 0.1 | 0.7 ± 0.1 |
| Suncor coke 2002 | 9.7 ± 0.3 | 0.7 ± 0.1 |

Results and Discussion

Peeper cells corresponding to native sediment or coke substrates were identified upon retrieval from the *in situ* enclosure units based on coloration of the filter membranes. Generally, contact with coke turned the filter membranes black and contact with native sediment turned the filters brown or yellow. Peeper cells in contact with enclosure units were located approximately between 10 and 22 cm (Fig. 5.1). Since red-ox potential of porewater was not measured during this study, it was inferred instead from changes in the levels of dissolved Fe and Mn in porewaters that the substrate layers could have been partially anoxic (Table 3). Under anoxic

condition partially anoxic conditions in the sediments, reduction of Fe^{3+} and Mn^{4+} oxides results in the formation of soluble Fe^{2+} and Mn^{2+} species (Salomons and Forstner, 1984).

Porewater elemental concentration differed significantly among enclosure types. For example, heavy metals like Hg and Pb were higher in coke porewater compared to native sediment (Table 3). While Hg levels were elevated in all coke porewaters, concentrations were particularly elevated in Suncor coke porewaters (Table 3). On contrary, Sn was high in Syncrude coke porewaters compared to native sediment or Suncor coke porewaters (Table 3). Porewater concentrations of Ag, Al, Fe, Mn and Sn decreased in Syncrude 2002 coke compared to Syncrude 2004 coke (Table 3). This is likely because Syncrude coke placed in the Shallow wetland in 2002 underwent longer weathering and leaching compared to Syncrude coke placed in 2004. This suggests that as coke ages in a wetland the rate of metals release declines and as a result the porewater metal concentrations decrease over time. Interestingly, Ni and V concentrations in Syncrude coke porewaters were low and similar to native sediment porewater levels (Table 3). Coke leaching studies have shown that Ni and V reach peak concentrations in the overlying water immediately (within first 4 h) upon contact with water (see Appendix B). It is therefore possible that Ni and V bound to Syncrude coke got mobilized into the porewater and subsequently to the overlying water column immediately after placing them in the Shallow wetland in 2002 and 2004. Also, it is possible that under the prevailing reducing conditions in the coke substrates, Ni and V were strongly bound to amorphous oxide surfaces and thus not released to the porewater.

Conclusion

Coke releases certain toxic metals (e.g. Al, Hg, Pb and Sn) into the porewater compartment at relatively high concentrations under natural weathering conditions. Nickel and V

concentrations in the coke porewaters were generally lower although they were found to be metals of primary concern in Syncrude fluid coke. This study did not characterize the total metal content in coke or sediments, the overlying water metal concentrations and also the solid metal binding phases (e.g. organic matter, sulphides) associated with the enclosure units which limit the interpretation of metals fate in porewaters. Future studies should consider collecting samples of the overlying water, native sediment and coke for analysis and also measure *in situ* red-ox conditions in the enclosure units at various depths.

Table 3. Porewater concentration of elements in *in situ* enclosure units.

| Element ^a (µg/L) | Native sediment | Syncrude coke 2002 | Syncrude coke 2004 | Suncor coke 2002 |
|--------------------------------|-----------------|-----------------------|-----------------------|---------------------|
| Ag | BDL | 21 ± 4 | 114 ± 36 | BDL |
| Al | 746 ± 49 | 1433 ± 17 | 1390 ± 20 | 1560 ± 21 |
| As | 2 ± 0.5 | 2 ± 1 | 1.2 ± 0.4 | 4 ± 1 |
| B | 387 ± 73 | 278 ± 24 | 371 ± 108 | 283 ± 32 |
| Ba | 580 ± 230 | 483 ± 23 | 508 ± 101 | 410 ± 35 |
| Be | 0.1 ± 0.03 | 0.02 ± 0.01 | 0.03 ± 0.01 | 0.05 ± 0.01 |
| Ca | 85607 ± 6948 | 55280 ± 5049 | 94740 ± 35630 | 119690 ± 35068 |
| Co | 0.4 ± 0.2 | 0.3 ± 0.01 | 0.4 ± 0.3 | 1 ± 0.3 |
| Cr | 0.4 ± 0.05 | 1 ± 0.1 | 1 ± 0.2 | 1 ± 0.3 |
| Cu | 1 ± 0.2 | 1.3 ± 0.1 | 1.4 ± 0.5 | 1 ± 0.2 |
| Fe | 4261 ± 2499 | 1119 ± 421 | 807 ± 649 | 2614 ± 766 |
| Hg | BDL | 2573 ± 1141 | 3155 ± 547 | 24130 ± 3670 |
| Li | 44 ± 6 | 39 ± 6 | 44 ± 12 | 41 ± 7 |
| Mn | 1614 ± 504 | 1052 ± 472 | 515 ± 466 | 1317 ± 181 |
| Mo | 1 ± 0.3 | 1 ± 0.2 | 2 ± 1 | 0.4 ± 0.1 |
| Ni | 3 ± 0.5 | 2 ± 0.2 | 4 ± 2 | 2 ± 0.02 |
| Pb | BDL | 36 ± 6 | 32 ± 0.1 | 23 ± 2 |
| Sb | 0.1 ± 0.01 | 0.1 ± 0.01 | 0.1 ± 0.01 | 0.1 ± 0.01 |
| Se | 0.1 ± 0.1 | 0.2 ± 0.03 | 0.1 ± 0.04 | 0.1 ± 0.05 |
| Si | 5787 ± 1466 | 7414 ± 2622 | 8223 ± 1430 | 8707 ± 2321 |
| Sn | BDL | 9509 ± 845 | 10910 ± 226 | 4 ± 0.5 |
| Sr | 424 ± 96 | 391 ± 127 | 437 ± 125 | 488 ± 138 |
| Tl | 0.03 ± 0.01 | 0.02 ± 0 | 0.02 ± 0 | 0.01 ± 0 |
| V | 1 ± 0.3 | 2.5 ± 1 | 2.5 ± 0.5 | 1.1 ± 0.2 |
| Zn | BDL | 423 ± 5 | 405 ± 20 | 347 ± 34 |

BDL: below detection limit (≤ 0.01 µg/L).

^a Element concentration < 0.01 µg/L: Bi, Ce and Cd.

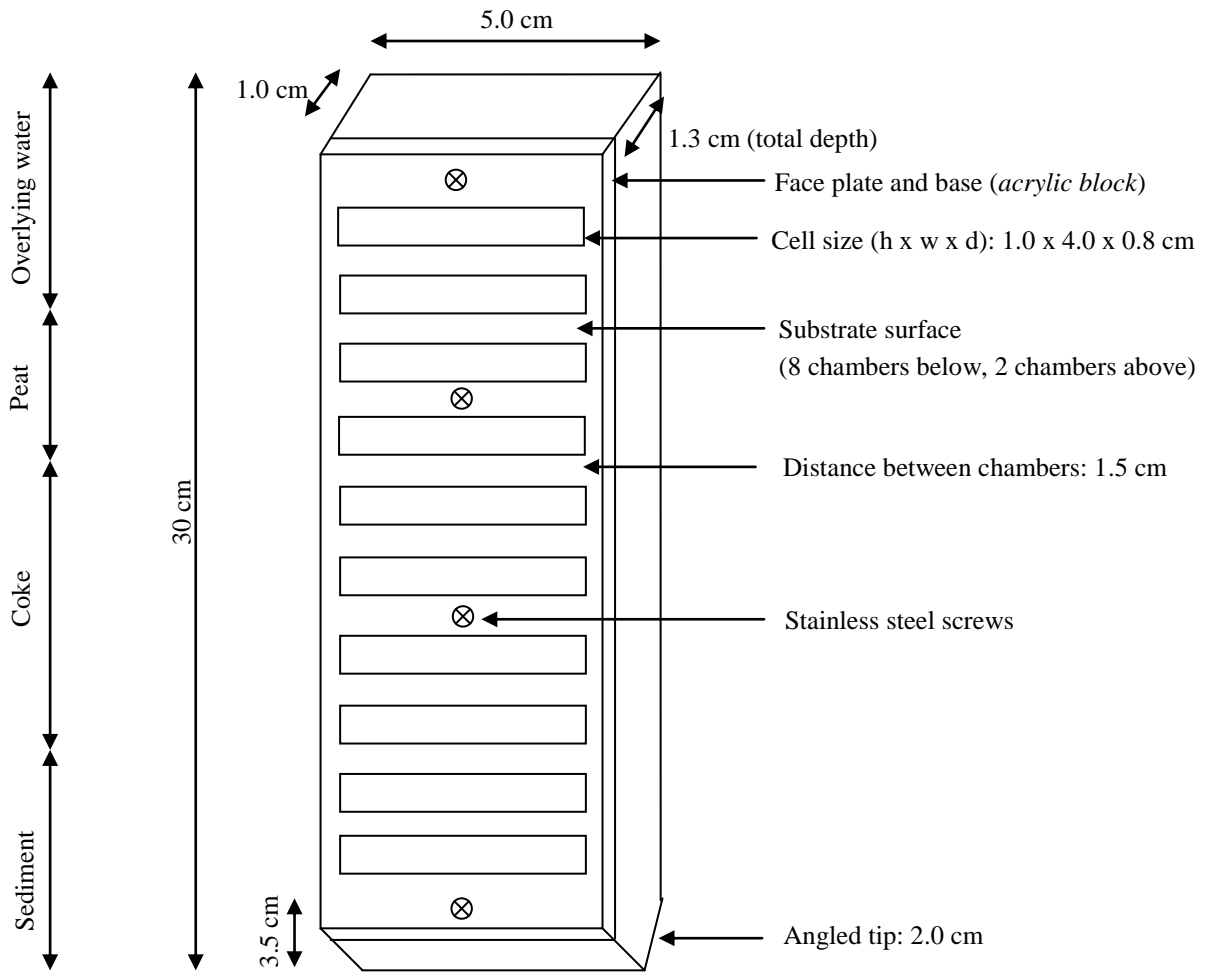


Figure 1. Schematic diagram of the peeper used for *in situ* porewater sampling (Not drawn to scale).

APPENDIX B

INFLUENCE OF pH ON METALS RELEASE FROM SYNCRUDE COKE

Introduction

Coke leachates collected from Syncrude tank lysimeters over a period of 20 month were found to be acutely toxic to *Ceriodaphnia dubia* (Puttaswamy et al. 2010). Trace metals released from coke were originally thought to be responsible for the observed coke leachate toxicity. However, the type of metal that caused coke leachate toxicity was not identified. Therefore, the objective of this study was to generate coke leachates in the laboratory under varying pH conditions to determine the influence of pH on metals release from coke and to identify the toxicants in the leachate using a chronic toxicity identification and evaluation (TIE) approach.

Materials and Methods

Coke leachates

Fluid coke (i.e. coke generated from a fluid coking technique) was collected from Syncrude Canada Ltd. (AB, Canada) coker drums in July, 2006, and shipped to the Toxicology Centre, University of Saskatchewan (SK, Canada) in two 20 L pails. In the laboratory, coke was subjected to a 45 day batch leaching process under two pH conditions (5.5 and 9.5) with the coke:water ratio maintained at 1:4 (v/v). Into a 2 L glass jar, 400 mL of coke was poured and 1.6 L of hard reconstituted water (HRW) was added into each jar. The HRW used for leaching coke best represents the water chemistries (i.e. hardness and alkalinity) of Syncrude lysimeter leachates and the Syncrude recycle water (Puttaswamy et al. 2010). The pH of the HRW was

adjusted to pH 5.5 or 9.5 using ultra-pure 1N HCl or 1N NaOH prior to addition to the leaching jars. All jars were closed with air-tight lids to minimize pH fluctuation. The pH of the overlying water was monitored daily and adjusted to pH 5.5 or 9.5 using either 1N HCl or 1N NaOH as necessary. On day 0 (4 h), 15 and 45, overlying water and porewater from each pH treatment group ($n = 3$) was extracted by vacuum filtration through 0.45 μm pore size membrane filters (Gelman Supor[®] 450; Pallman Laboratories, Ann Arbor, MN, USA). On day 45, coke leachates were pooled from all replicate jars from their respective treatment groups and stored in 10 L plastic containers at 4 °C until subsequent toxicity testing could be performed. Sub-samples of the leachates were collected for trace metal and general water chemistry analysis.

The total volume of coke leachate (~10 L) generated under each pH leaching group in this study was exhausted mid-way through the toxicity identification and evaluation (TIE) tests. As a result, a full TIE test series could not be completed and a new leaching study was initiated with an intention of generating sufficient volumes of coke leachate to run the full TIE test series (Chapter 5). Therefore, only the trace metals data measured in overlying water and coke porewater at different times during the batch leaching study is presented in this appendix chapter.

Analytical chemistry

Trace metal concentrations in the coke leachates were analyzed in-house at the Toxicology Centre, University of Saskatchewan using an inductively coupled plasma mass spectrometer (ICP-MS) equipped with collision cell technology (Thermo Fisher Scientific, Mississauga, ON, Canada). Trace metal concentrations are presented as mean \pm SE ($n = 3$) in $\mu\text{g/L}$ units.

Results and Discussion

As expected, pH had a significant influence on the type and concentration of trace metals released from coke. Generally, acidic pH (5.5) favored the release of cationic metals (e.g. Fe, Ni, Mn and Zn) and alkaline pH (9.5) favored the release of metals (e.g. Al, Mo and V) that form oxyanions in solutions (Table 1 and 2). Further, within the first 4 h of leaching (day 0), concentrations of most metals (e.g. Al, Mn, Ni, V and Zn) reached a peak in overlying water and in the porewater under both pH leaching conditions (Table 1, 2 and Fig. 1, 2). This indicates that metals that are loosely bound to the coke surface are released immediately upon contact with water. Concentrations of several metals including Al, As, Cd, Cr, Mo, Ni and V released from coke was found to be elevated compared to the Canadian guideline for the protection of aquatic life or agriculture and livestock (Table 1 and 2). Further, vanadium concentrations released from coke under both pH leaching conditions were highest compared to all other metals (Table 1 and 2). Similar results were observed for V concentrations in coke leachate collected from two Syncrude field lysimeters (Puttaswamy et al. 2010). Moreover, concentrations of several metals (e.g. Mn, Mo, Ni, V and Zn) in the overlying water reached a steady state between day 15 and 45 under both pH leaching condition (Table 1, 2 and Fig. 1, 2). Based on this observation, a 15 day coke leaching duration was adopted in all other leaching studies (Chapter 5 and 6).

Conclusion

Metals released from coke were significantly influenced by the solution pH. Most metals (e.g. Al, Mn, Ni, V and Zn) reached a peak concentration in the overlying water within few hours of contact with water. Further, the concentrations of several metals in the overlying water under both pH leaching condition reached a steady state concentration between days 15 and 45.

Table 1. Trace metal concentrations (mean \pm SE, $n = 3$) in overlying water and porewater measured on day 0 (within 4 h), 15 and 45 under pH 5.5 leaching conditions.

| Element ($\mu\text{g/L}$) | Overlying water | | | Porewater | | | CWQG ^a ($\mu\text{g/L}$) |
|--------------------------------|-----------------|----------------|----------------|----------------|-----------------|----------------|--|
| | day 0 | day 15 | day 45 | day 0 | day 15 | day 45 | |
| Al | 8 \pm 0.6 | 8 \pm 1.2 | 13 \pm 1.4 | 13 \pm 3 | 11 \pm 2 | 8 \pm 0.4 | 100 |
| As | 3 \pm 0.1 | 3 \pm 0.04 | 2.3 \pm 0.3 | 12 \pm 0.3 | 5 \pm 0.3 | 2 \pm 0.2 | 5 |
| Ag | BDL | BDL | BDL | BDL | BDL | BDL | 0.1 |
| B | 50 \pm 2 | 90 \pm 0.5 | 147 \pm 1 | 295 \pm 8 | 334 \pm 24 | 236 \pm 21 | NA |
| Be | BDL | 0.1 \pm 0.1 | 0.1 \pm 0.1 | 0.1 \pm 0.1 | BDL | BDL | 100 ^b |
| Ba | 36 \pm 2 | 42 \pm 1 | 54 \pm 1.4 | 83 \pm 3 | 73 \pm 5 | 66 \pm 2 | NA |
| Cd | 0.2 \pm 0.01 | 0.1 \pm 0.02 | 0.1 \pm 0.02 | 0.3 \pm 0.02 | 0.2 \pm 0.02 | 0.2 \pm 0.01 | 0.017 |
| Cu | 1 \pm 0.03 | 1 \pm 0.2 | 0.3 \pm 0.05 | 0.4 \pm 0.03 | 0.5 \pm 0.2 | 0.4 \pm 0.05 | 4 |
| Co | 4 \pm 0.5 | 3 \pm 0.1 | 2 \pm 0.4 | 8 \pm 0.3 | 3 \pm 0.4 | 2 \pm 1 | NA |
| Cr | 1 \pm 0.3 | 0.4 \pm 0.1 | 1 \pm 0.2 | 0.9 \pm 0.1 | 0.6 \pm 0.02 | 1 \pm 0.8 | 1 Cr (VI) |
| Fe | 4 \pm 1.4 | 4 \pm 0.4 | 3 \pm 0.4 | 9 \pm 2 | 9 \pm 2 | 18 \pm 3 | 300 |
| Hg | 0.02 \pm 0 | BDL | BDL | 0.02 \pm 0 | BDL | BDL | 0.026 |
| Mn | 606 \pm 73 | 359 \pm 16 | 316 \pm 57 | 1738 \pm 60 | 661 \pm 72 | 563 \pm 20 | 200 ^b |
| Mo | 92 \pm 3 | 217 \pm 4 | 291 \pm 6 | 615 \pm 38 | 772 \pm 71 | 394 \pm 36 | 73 |
| Ni | 96 \pm 11 | 42 \pm 4 | 45 \pm 4 | 135 \pm 8 | 42 \pm 5 | 44 \pm 2 | 150 |
| Pb | 0.1 \pm 0 | BDL | BDL | 0.1 \pm 0.01 | 0.03 \pm 0.01 | 0.05 \pm 0 | 7 |
| Sb | 0.2 \pm 0 | 0.3 \pm 0.01 | 0.4 \pm 0 | 1.1 \pm 0.02 | 1 \pm 0.1 | 0.6 \pm 0.03 | NA |
| Sn | 0.1 \pm 0.01 | 0.02 \pm 0 | BDL | 0.1 \pm 0.01 | BDL | BDL | NA |
| Se | 0.3 \pm 0.02 | 0.3 \pm 0.01 | 0.3 \pm 0.03 | 0.5 \pm 0.02 | 0.4 \pm 0.03 | 0.3 \pm 0.01 | 1 |
| Sr | 87 \pm 4 | 102 \pm 2 | 183 \pm 4 | 363 \pm 5 | 344 \pm 22 | 352 \pm 21 | NA |
| Ti | 1 \pm 0.02 | 2 \pm 0.04 | 4 \pm 0.1 | 4 \pm 0.2 | 8 \pm 0.8 | 6 \pm 1 | NA |
| Tl | 0.03 \pm 0 | 0.03 \pm 0 | 0.02 \pm 0 | 0.03 \pm 0 | BDL | BDL | 0.8 |
| V | 751 \pm 11 | 1178 \pm 45 | 1136 \pm 64 | 2356 \pm 199 | 2222 \pm 114 | 966 \pm 70 | 100 ^b |
| Zn | 13 \pm 2 | 9 \pm 06 | 9 \pm 1.4 | 23 \pm 2 | 7 \pm 1 | 9 \pm 0.2 | 30 |
| U | 0.02 \pm 0 | BDL | BDL | BDL | BDL | BDL | 15 |

BDL: below detection limit ($\leq 0.01 \mu\text{g/L}$).

^a Canadian Water Quality Guideline for the protection of freshwater aquatic life.

^b Canadian Water Quality Guideline for the protection of livestock and agriculture.

Table 2: Trace metal concentrations (mean \pm SE, $n = 3$) in overlying water and porewater measured on day 0 (within 4 h), 15 and 45 under pH 9.5 leaching conditions.

| Element ($\mu\text{g/L}$) | Overlying water | | | Porewater | | | CWQG ^a ($\mu\text{g/L}$) |
|--------------------------------|-----------------|----------------|----------------|----------------|----------------|----------------|--|
| | day 0 | day 15 | day 45 | day 0 | day 15 | day 45 | |
| Al | 105 \pm 13 | 152 \pm 30 | 308 \pm 3 | 473 \pm 31 | 302 \pm 9 | 176 \pm 21 | 100 |
| As | 3 \pm 0.2 | 4 \pm 0.4 | 4 \pm 0.1 | 7 \pm 1 | 10 \pm 1 | 6 \pm 0.2 | 5 |
| Ag | BDL | BDL | BDL | BDL | BDL | BDL | 0.1 |
| B | 33 \pm 4 | 68 \pm 6 | 115 \pm 1 | 86 \pm 3 | 264 \pm 10 | 297 \pm 5 | NA |
| Be | BDL | 0.1 \pm 0.1 | 0.1 \pm 0.1 | BDL | 0.1 \pm 0.1 | 0.1 \pm 0.1 | 100 ^b |
| Ba | 24 \pm 3 | 35 \pm 1 | 51 \pm 2 | 49 \pm 3 | 65 \pm 1.2 | 75 \pm 3 | NA |
| Cd | 0.1 \pm 0.01 | 0.1 \pm 0 | 0.1 \pm 0.01 | 0.1 \pm 0.01 | 0.2 \pm 0.02 | 0.2 \pm 0.02 | 0.017 |
| Cu | 0.5 \pm 0 | 0.3 \pm 0.02 | 0.3 \pm 0.04 | 0.4 \pm 0.1 | 0.2 \pm 0.1 | 1 \pm 0.1 | 4 |
| Co | 0.2 \pm 0.01 | 0.2 \pm 0.01 | 0.5 \pm 0.1 | 0.2 \pm 0.01 | 0.4 \pm 0.01 | 1 \pm 0.02 | NA |
| Cr | 2 \pm 0.1 | 2 \pm 1 | 1 \pm 0.1 | 3 \pm 0.1 | 0.6 \pm 0.1 | 1 \pm 0.1 | 1 Cr (VI) |
| Fe | 4 \pm 0.3 | 4 \pm 1 | 2 \pm 1 | 5 \pm 0.5 | 3 \pm 0.3 | 4 \pm 1 | 300 |
| Hg | BDL | BDL | BDL | 0.02 \pm 0 | 0.03 \pm 0 | 0.04 \pm 0.0 | 0.026 |
| Mn | 34 \pm 4 | 8 \pm 3 | 14 \pm 10 | 88 \pm 11 | 129 \pm 10 | 93 \pm 38 | 200 ^b |
| Mo | 85 \pm 8 | 163 \pm 16 | 206 \pm 3 | 235 \pm 21 | 553 \pm 22 | 474 \pm 16 | 73 |
| Ni | 3 \pm 0.2 | 1 \pm 0.1 | 3 \pm 0.5 | 4 \pm 0.3 | 4 \pm 0.05 | 6 \pm 1 | 150 |
| Pb | BDL | BDL | BDL | 0.05 \pm 0 | 0.0 \pm 0.0 | 0.1 \pm 0.01 | 7 |
| Sb | 0.3 \pm 0.03 | 0.4 \pm 0.03 | 1 \pm 0 | 1 \pm 0.1 | 1.3 \pm 0.05 | 1 \pm 0.03 | NA |
| Sn | 0.1 \pm 0.01 | BDL | BDL | 0.3 \pm 0.2 | BDL | 0.1 \pm 0.01 | NA |
| Se | 0.3 \pm 0.01 | 0.3 \pm 0.02 | 0.4 \pm 0.02 | 0.5 \pm 0.02 | 0.5 \pm 0.03 | 0.4 \pm 0.01 | 1 |
| Sr | 43 \pm 5 | 131 \pm 5 | 206 \pm 4 | 195 \pm 15 | 465 \pm 15 | 463 \pm 11 | NA |
| Ti | 1 \pm 0.1 | 35 \pm 33 | 3 \pm 0.1 | 2 \pm 0.1 | 5 \pm 0.2 | 5 \pm 0.1 | NA |
| Tl | 0.0 \pm 0.0 | 0.0 \pm 0.0 | 0.0 \pm 0.0 | 0.0 \pm 0.0 | 0.0 \pm 0.0 | 0.0 \pm 0.0 | 0.8 |
| V | 953 \pm 94 | 1382 \pm 110 | 1450 \pm 34 | 2441 \pm 84 | 3118 \pm 183 | 1767 \pm 22 | 100 ^b |
| Zn | 5 \pm 3 | 3 \pm 2 | 0.1 \pm 0.01 | 5 \pm 2 | 2.4 \pm 2 | 9 \pm 1.6 | 30 |
| U | 0.3 \pm 0.04 | 0.4 \pm 0.05 | 0.5 \pm 0.02 | 1.2 \pm 0.1 | 1 \pm 0.1 | 1 \pm 0.01 | 15 |

BDL – below detection limit ($\leq 0.01 \mu\text{g/L}$)

^a Canadian Water Quality Guideline for the protection of freshwater aquatic life.

^b Canadian Water Quality Guideline for the protection of livestock and agriculture.

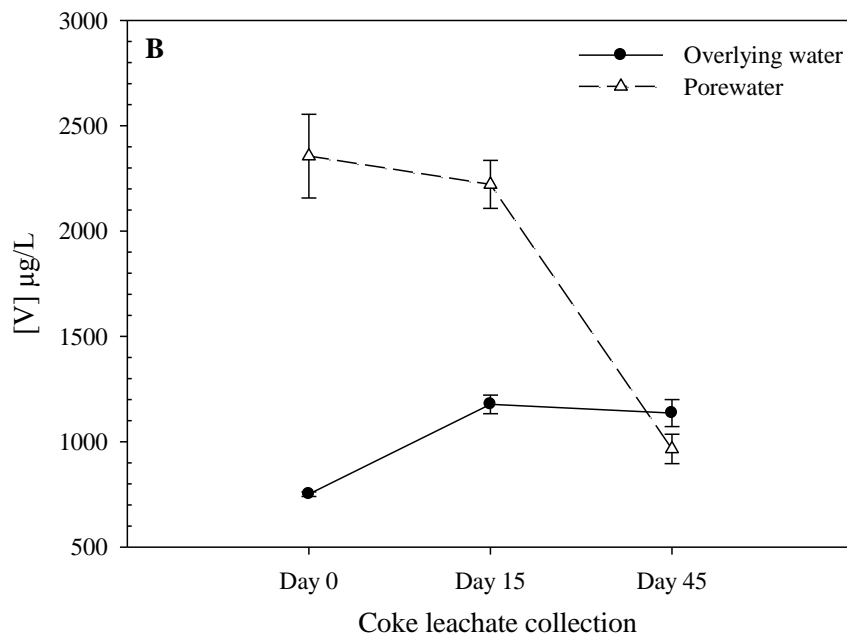
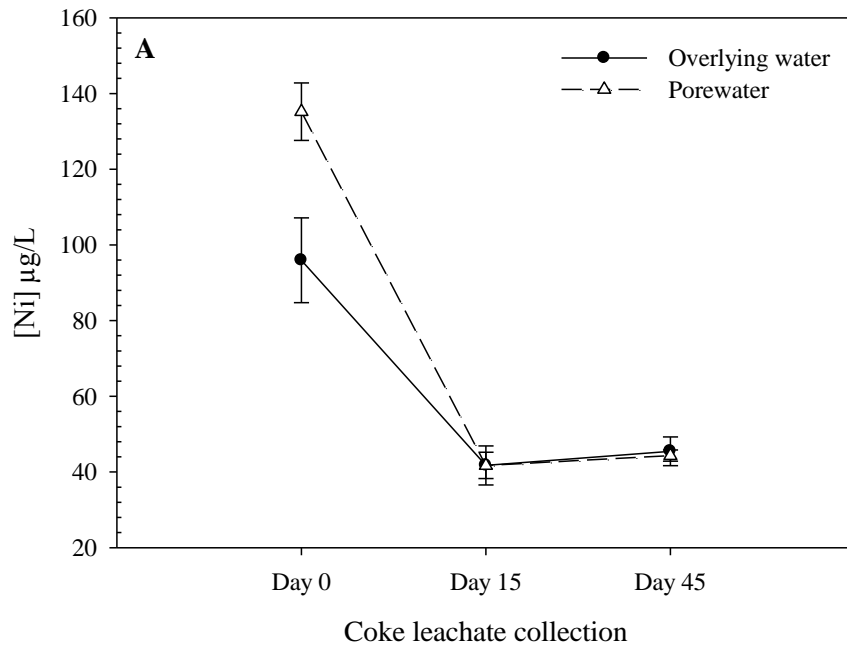


Figure 1. Concentrations of (A) Ni and (B) V in overlying water and porewater collected at three different times from pH 5.5 (acidic) coke leaching.

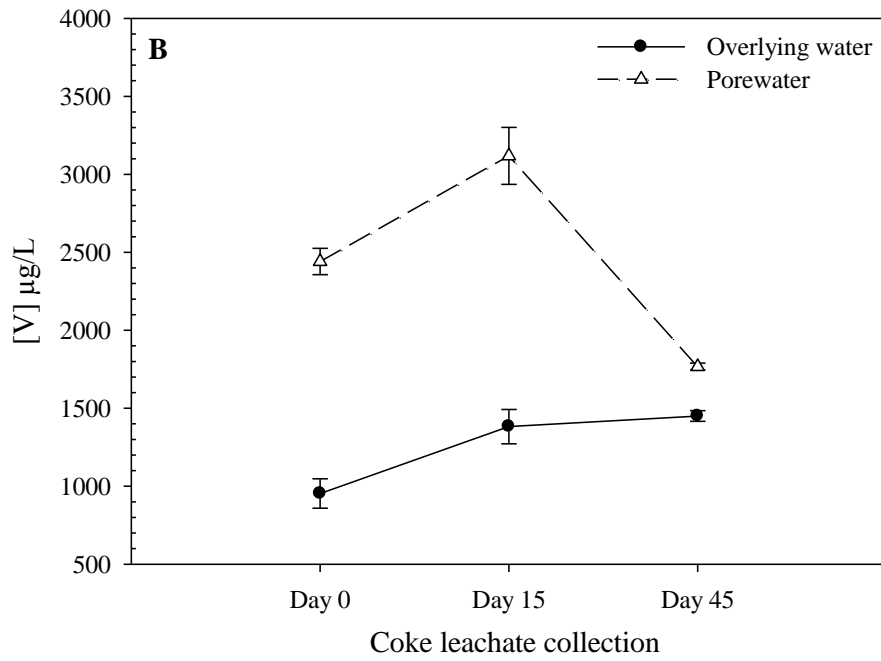
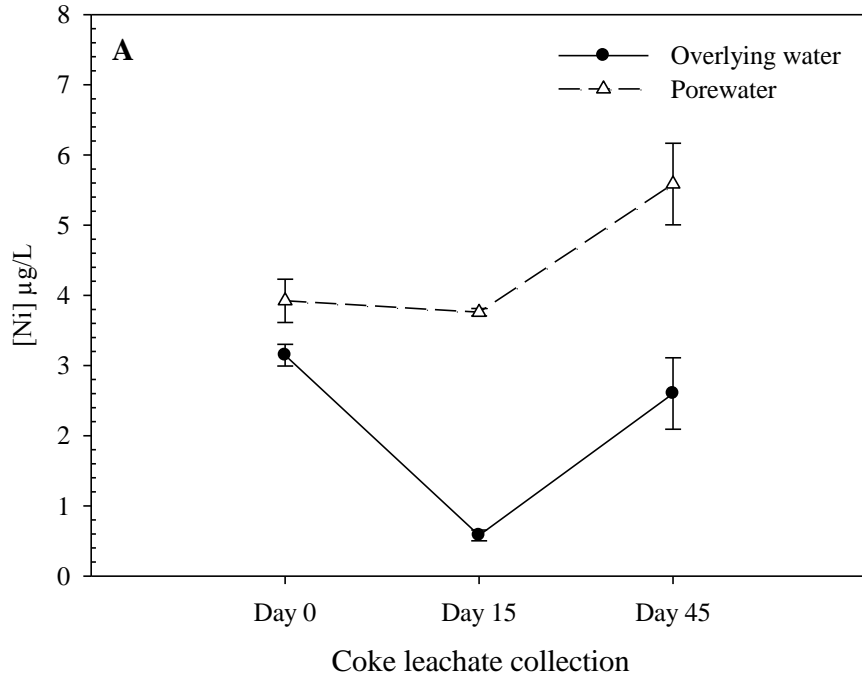


Figure 2. Concentrations of (A) Ni and (B) V in overlying water and porewater collected at three different times from pH 9.5 (alkaline) coke leaching.