Process water treatment in Canada's oil sands industry: I. Target pollutants and treatment objectives

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Abstract: Process water treatment has become a critical issue for Canada's oil sands industry. Continuous recycling of tailings pond water (TPW) has contributed to a decline in water quality that has consequences for bitumen recovery, water consumption, and reclamation efforts. Potential roles for water treatment were assessed through a review of process water quality and toxicity data from two long-term oil sands operations. Target pollutants were identified according to exceedances of environmental and industrial water quality guidelines. From 1980 to 2001, the salinity of TPW increased at a rate of 75 mg/L per year. Recent increases in hardness, sulphate, chloride, and ammonia have raised concerns over scaling and corrosion. Naphthenic acids released during bitumen extraction are the primary source of toxicity in TPW. Biodegradation of naphthenic acids has been demonstrated in pond experiments; however, recalcitrant compounds may contribute to chronic toxicity in reclaimed environments. Water treatment objectives established in this review provide benchmarks for the selection of candidate water treatment technologies.

Key words: oil sands, tailings ponds, naphthenic acids, toxicity, reclamation.

Résumé : Le traitement des eaux de procédé est devenu une question très importante pour l'industrie canadienne des sables bitumineux. Le recyclage continu de l'eau des parcs à résidus (TPW) contribue à diminuer la qualité de l'eau, ce qui impacte la récupération du bitume, la consommation d'eau et les efforts de remise en état. Les rôles potentiels du traitement de l'eau ont été évalués par un examen de la qualité de l'eau de procédé et des données de toxicité pour deux exploitations à long terme de sables bitumineux. Les polluants ciblés ont été identifiés selon les excédents aux lignes directrices environnementales et industrielles sur la qualité de l'eau. Entre 1980 et 2001, la salinité de la TPW a augmenté à un rythme de 75 mg/L par an. Les récentes augmentations en dureté, en sulfates, en chlorures et en ammoniac ont soulevé des inquiétudes quant à l'incrustation et la corrosion. Les acides naphténiques libérés durant l'extraction du bitume sont la principale source de toxicité dans la TPW. La biodégradation des acides naphténiques a été démontrée dans des expériences dans les parcs à résidus; toutefois, les composés récalcitrants peuvent contribuer à une toxicité chronique dans les environnements remis en état. Les objectifs du traitement de l'eau établis dans cette revue fournissent des points de référence pour la sélection des technologies de traitement des eaux.

Mots-clés : sables bitumineux, parcs à résidus, acides naphténiques, toxicité, remise en état.

[Traduit par la Rédaction]

Introduction

The oil sands in northern Alberta, Canada, represent one of the largest oil deposits in the world, with proven reserves of 174 billion barrels of bitumen (Alberta Energy and Utilities Board 2005). As an unconventional fossil fuel, bitumen is more costly to recover and process than conventional oil and gas; however, increased global demand for oil coupled with technological advances in bitumen production have triggered rapid growth in the industry. Oil production from the oil sands has reached 1 million barrels per day, and is projected to triple over the next decade (National Energy Board 2006).

Rapid expansion of Alberta's oil sands industry presents several challenges with respect to the protection of local freshwater resources such as the Athabasca River basin (Griffiths et al. 2006). Oil sands mines consume large volumes of water, importing an average of 3 barrels of river water for every barrel of oil produced (Syncrude Canada Limited 2005; Shell Canada 2005*b*; Suncor Energy Incorporated 2005*b*). While only a small fraction (<2%) of the river's annual flow is currently allocated to the oil sands, it remains unclear whether or not low winter flows can support the expected increase in water consumption over the next decade (Peachey 2005).

Most of the freshwater imported by oil sands mines is used in hot water extraction, a flotation process that separates bitumen from sand and clay. The resulting process water is alkaline, slightly brackish, and acutely toxic to aquatic biota due to high concentrations of organic acids leached from the bitumen during extraction (MacKinnon and Sethi 1993). Under a zero discharge policy, oil sands

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producers are required to store all process waters and tailings on-site, a condition that has led to the construction of over 70 km^2 of tailings ponds (Dominski 2007) and a significant inventory of waste. The volume of impounded process water at Syncrude's Lease 17/22 was approaching 1 billion m^3 in 2004, (MacKinnon 2004); the current total volume of impounded tailings sludge (among all operators) has exceeded 700 million m^3 (Dominski 2007). At mine closure, process water and tailings will be reintegrated in the landscape through various reclamation scenarios, with the intent of restoring sustainable aquatic and terrestrial ecosystems.

While oil sands producers have made improvements in water use efficiency and have invested in reclamation research, the industry still faces several hurdles related to water use. Recycling of tailings pond water (TPW) has slowed the increase in freshwater withdrawals (Syncrude Canada Limited 2005), but has contributed to a long-term decline in process water quality that threatens to affect bitumen recovery through disruption of extraction chemistry (Kasperski 2003) and scaling and corrosion of extraction facilities (Rogers 2004). Tailings treatments such as consolidated tailings (CT), whereby calcium sulphate is added to mature fine tailings and sand, further enhance the salinity and hardness of process water (Marr et al. 1996). As producers become increasingly dependent on process water recycling, the decline in water quality may reduce bitumen recovery rates, leading to increased demand for water.

Many of the operational and environmental challenges related to the management of oil sands process water could be addressed through the selection of appropriate water treatment technology. Process water treatment could allow operators to regulate water quality to suit the bitumen extraction process, reduce the need for freshwater withdrawals by recycling TPW for utilities and other operational uses, offset withdrawals through discharges of treated water, promote bioremediation through the removal of pollutants that contribute to acute and chronic toxicity in aquatic biota, and ensure that downstream sites meet water quality guidelines for the protection of aquatic ecosystems (e.g., CCME 2005).

Water treatment technologies are rapidly evolving to meet the water management needs of the oil industry, yet the viability of these emerging technologies for oil sands operations remains unclear. As a prerequisite to the evaluation of process water treatment options, process water quality and toxicity data from two long-term oil sands mining projects were reviewed to identify target pollutants and establish water treatment priorities. Target pollutants were identified based on their exceedance of environmental and industrial water quality criteria. Process water quality data were compiled from published papers, reports, and conference presentations.

Oil sands overview

There are three major oil sand deposits in the province of Alberta covering over 140 000 km^2 in the northern half of the province (Alberta Department of Energy 2005) (Fig. 1). Oil sands deposits are situated at varying depths beneath an overburden of muskeg, glacial tills, sandstone, and shale. Shallow oil sand deposits (i.e., up to 75 m) are accessed via surface mines, and account for only 18% of the total recoverable bitumen, most of which is in the Athabasca deposit (Alberta Department of Energy 2005). For deeper deposits, bitumen is extracted via in situ processes in which steam is injected into a well to heat and loosen the bitumen so that it can be pumped to the surface through a production well. Surface mining currently accounts for 65% of total production from the oil sands, and is forecast to remain at this level through 2010 (Alberta Department of Energy 2005). At present, there are three major producers in mineable oil sands: Suncor Energy Corp. (Suncor), Syncrude Canada Ltd. (Syncrude), and Albian Sands Inc. (Albian).

Surface mined oil sands are transported as a slurry from the mine to the extraction plant. Bitumen extraction follows modified versions of the Clark Hot Water Process, in which bitumen is separated from sand and clay particles by a combination of mechanical energy, heat, and the presence of surfactants leached from the bitumen (Kasperski 2003). Historically, caustic soda (NaOH) was added to promote the release of surfactants and improve bitumen separation. Downstream effects of alkalinity on water chemistry and tailings formation (e.g., MacKinnon 2001) has led some operators to reconsider this method.

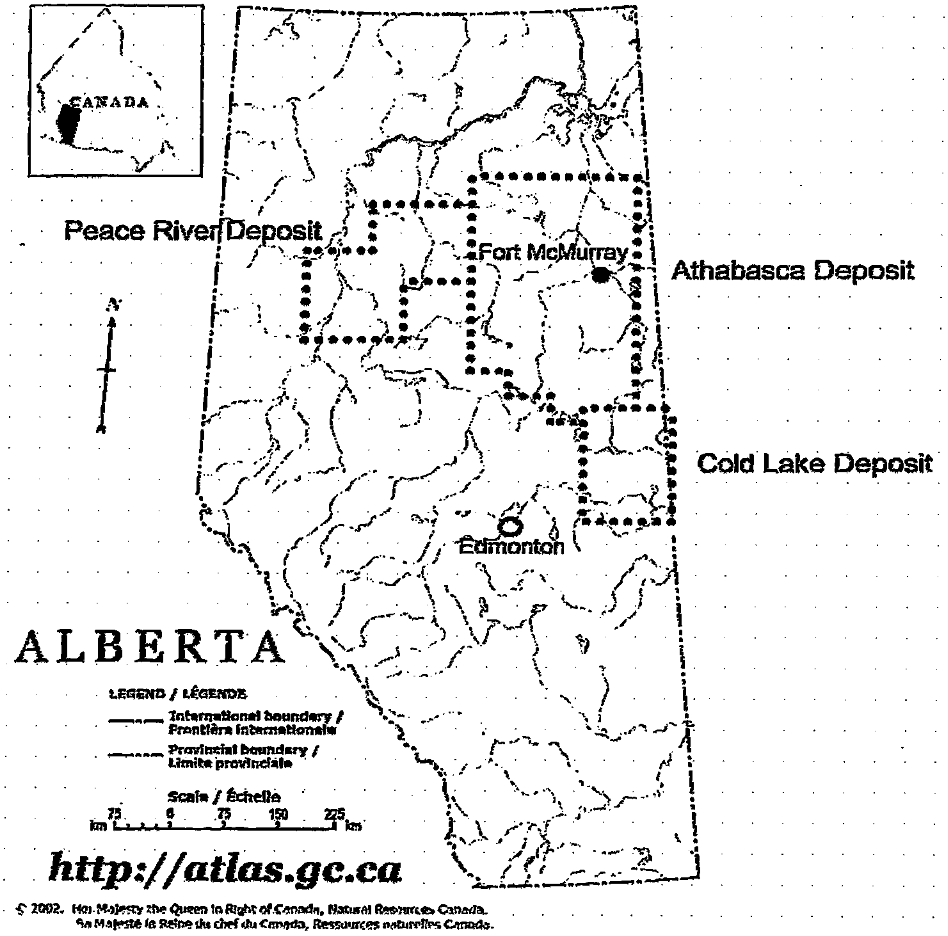
The aerated slurry is then piped into the primary separation vessel, where bitumen separated via flotation (froth) is skimmed from the surface and pumped to a froth treatment plant after which it is sent to be upgraded to synthetic sweet crude oil. Residual bitumen is recovered from the middlings of the primary separation vessel. Depending on ore quality, approximately 1 m^3 of oil sand is required to produce 1 barrel of oil (Scott et al. 1985). A simplified flow diagram and materials balance for an oil sands mining operation is presented in Fig. 2.

Tailings

Tailings composed of water, dissolved salts, organics, minerals, and bitumen are pumped from separation vessels and froth treatment facilities to a series of settling basins and tailings ponds. The composition of oil sands tailings varies with ore quality, source, extraction processes, and age, but generally contain ~70 to 80 wt% water, ~20 to 30 wt% solids (i.e., sand, silt, and clays) and ~1–3 wt% bitumen (Kasperski 1992). Upon delivery to settling basins, tailings divide into three fractions: (*i*) rapidly-settling sand particles; (*ii*) an aqueous suspension of fine particles (silt and clay); and (*iii*) a clarified surface water layer (total suspended solids = ~15–70 mg/L) with residual bitumen (MacKinnon and Sethi 1993). The fine tailings settle to 20 wt% solids within a few weeks, but require several years to reach 30–35 wt% solids, at which point consolidation slows considerably and the sludge is designated as mature fine tailings (MFT) (Scott et al. 1985). Evidence from Syncrude tailings ponds suggests that MFT is settling 30% faster than predicted, but still requires 10 years to consolidate to 44% solids (MacKinnon 2001).

Enhancement of settling rates has been demonstrated with centrifugation, pH adjustment, lime, inorganic coagulants, organic flocculants and other methods (Kasperski 1992; MacKinnon 2001), although only a few of these approaches have been applied at a commercial scale (e.g., CT, paste technology). The CT process increases the settling rate of the solids, but releases a particle-free pore water with ele-

Fig. 1. Major oil sands areas in Alberta, Canada.



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Sa Majesté la Reine du chef du Canada, Ressources naturelles Canada.

vated concentrations of TDS and hardness (Marr et al. 1996). The use of calcium sulphate as a settling aid requires careful control of calcium levels to prevent scaling of heat exchangers and losses in bitumen extraction efficiency (Kasperski and Mikula 2003). Paste technology is another recently implemented process, in which flocculants are added to thicken and reduce the volume of tailings (Shell Canada 2007).

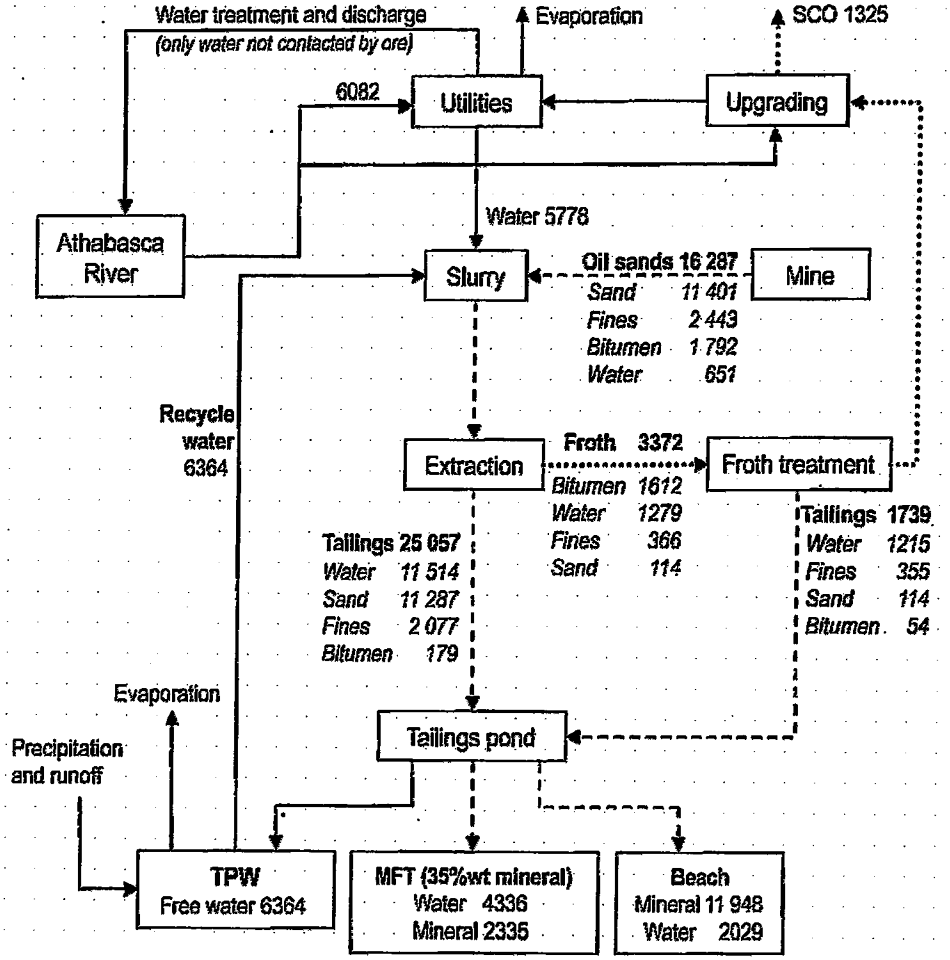
Water usage

The Athabasca River is the primary source of water for oil sands producers in the Athabasca deposit. Other important sources of water include groundwater, site runoff, overburden drainage, and water contained in oil sands (connate water). In 2004, annual freshwater imports by the three major oil sands mining companies totaled 114 million m^3, which corresponds to an average of 3.1 barrels of water per barrel of oil produced (Syncrude Canada Limited 2005; Shell Canada 2005*b*; Suncor Energy Incorporated 2005*a*). The actual volume of water used in extraction is considerably higher, given that the process relies largely on recycled water from tailings ponds. In 2004, Syncrude recycled the equivalent of 16.4 barrels of water per barrel of oil produced (228 million m^3; Syncrude Canada Limited 2005). Recycled water accounts for approximately 80%–85% of the water used in extraction processes (Syncrude Canada Limited 2005; Suncor Energy Incorporated 2005*a*).

Given the large fraction of process water retained in tailings after extraction, achieving the levels of freshwater use intensity and process water recycling reported by oil sands producers likely requires a large inventory of process water and (or) the implementation of CT and other technologies to recover process water. This can be demonstrated by calculating the flow rates for a hypothetical oil sands operation where the amount of recycled water available is limited to the free water that forms above tailings, which results in a higher water use intensity and a lower percentage of process water recycled (Fig. 2). Note that flow rates will vary among operations depending on ore quality, extraction and upgrading techniques, and tailings treatment.

As of 2005, the total allocation of Athabasca River flow for oil sands producers was 360 million m^3 per year (11.4 m^3/s), roughly 1.7% of the river's annual flow (Peachey 2005). While the annual flow far exceeds allocation, there are concerns that low winter flows (e.g., 75 m^3/s, Dec. 2001) (Alberta Environment 2004) may not support the water demand of a rapidly expanding industry. Where impacts to aquatic ecosystems are expected, Alberta Environment may limit withdrawals to 10% of natural flow (Alberta Environment 2006). Allocated withdrawals for ex-

Fig. 2. Simplified flow diagram (t/h) for an oil sands mining operation (solid lines = aqueous streams; dashed lines = oil sands and tailings; dotted lines = bitumen/oil; SCO, synthetic crude oil; TPW, tailings pond water; MFT, mature fine tailings). The calculated values for water, tailings, and bitumen are based on the following assumptions: oil production of 200 000 bpd; ore composition: bitumen (11 wt%), sand (70 wt%), fines (15%), water (4 wt%); fraction of imported freshwater used in extraction = 95%; water content in slurry = 45 wt%; bitumen extraction efficiency = 87%, upgrading efficiency = 85%. It was also assumed that the only sources of water were the Athabasca River, water contained in the ore, and the free water recovered from tailings. Consolidated tailings or other tailings treatments were not considered in the calculations. Flow rates and paths were based on data compiled from Kasperski (1992), Kasperski (2003), Shell Canada (2005*a*), Syncrude Canada Limited (2005), and Suncor Energy Incorporated (2005*b*).



isting and planned operations on the Athabasca River correspond to an instantaneous pumping rate of 22.3 m^3/s, which may account for up 30% of the river volume during low flow periods (Sawatsky 2004).

Tailings pond water quality

Inorganic chemistry

Tailings pond water is moderately hard (15–25 mg/L Ca^{2+}, 5–10 mg/L Mg^{2+}) with a pH of 8.0–8.4 and an alkalinity of ~800–1000 mg/L HCO_3^- (Table 1). Total dissolved solids (TDS) concentrations (2000 to 2500 mg/L) are in the slightly brackish range, having increased in both Syncrude and Suncor's tailings ponds at a rate of 75 mg/L per year between 1980 and 2000 (MacKinnon and Retallack 1981; Nix 1983; MacKinnon and Sethi 1993; Kasperski 2001; MacKinnon 2004) (Fig. 3). Dissolved solids are dominated by sodium (~500 to 700 mg/L), bicarbonate, chloride (~75 to 550 mg/L), and sulphate (~200 to 300 mg/L). At Syncrude, chloride and hardness concentrations in the Mildred Lake Settling Basin (MLSB) increased sharply throughout the 1990s, whereas Suncor experienced a rapid increase in sulphate concentration in the same period. Increases in bicarbonate concentrations appear to have leveled off during the early- to mid-nineties, and both operators have reported declining concentrations in recent years. Syncrude have also reported a slight decline in TDS concentrations beginning in 2000 (MacKinnon 2001). Similar to the dominant ions, ammonia concentrations in MLSB have increased by 3.5-fold, from an initial concentration of 4 mg/L in 1980 to 14 mg/L in 2001 (MacKinnon 2001). Dissolved solids are considerably more concentrated in TPW than in local surface waters: sodium, chloride, sul-

Table 1. Inorganic water chemistry of oil sands process waters, the Athabasca River, and regional lakes.

Variable (mg/L unless otherwise noted)	Syncrude MLSB (2003)[a]	Syncrude demonstration ponds (1997)[b]	Suncor TPW (2000)[c]	Suncor CT release water (1996–97)[d]	Suncor CT Pond seepage (1996–97)[d]	Athabasca River (2001)[e]	Regional lakes (2001)[e]
TDS	2221	400–1792	1887	1551	1164	170	80–190
COND ($\mu S \cdot cm^{-1}$)	2400[f]	486–2283	1113–1160[f]	1700	1130	280	70–226
pH	8.2[g]	8.25–8.8	8.4	8.1	7.7	8.2	7–8.6
Sodium	659	99–608	520	363	254	16	<1–10
Calcium	17	15–41	25	72	36	30	2–25
Magnesium	8	9–22	12	15	15	8.5	1–8
Chloride	540	40–258	80	52	18	6	<1–2
Bicarbonate	775	219–667	950	470	780	115	9–133
Sulphate	218	70–513	290	564	50	22	1–6
Ammonia	14[g]	0.03–0.16	14[f]	0.35	3.4	0.06	<0.05–0.57

Note: MLSB, Mildred Lake Settling Basin; TPW, tailings pond water; CT, consolidated tailings; TDS, total dissolved solids; COND, conductivity; data represent mean values from samples collected during the year indicated; ranges indicate mean values for multiple sites.

[a] (MacKinnon 2004).

[b] (Siwik et al. 2000).

[c] (Kasperski 2001).

[d] (Farrell et al. 2004).

[e] (Golder Associates Limited 2002).

[f] (MacKinnon and Sethi 1993).

[g] (MacKinnon 2001).

phate, bicarbonate, and ammonia concentrations exceed Athabasca River values by up to 40-, 90-, 30-, 8-, and 200-fold, respectively (Golder Associates Limited 2002).

Organic chemistry

Organic compounds detected in tailings pond water include bitumen, naphthenic acids (NAs), asphaltenes, benzene, creosols, humic and fulvic acids, phenols, phthalates, polycyclic aromatic hydrocarbons (PAHs), and toluene (Strosher and Peake 1978; MacKinnon and Retallack 1981; Gulley 1992; MacKinnon and Sethi 1993; Madill et al. 2001; Rogers et al. 2002*b*). A wide range of bitumen concentrations (measured as oil and grease) have been detected in tailings ponds. Nix (1983) reported concentrations of 9, 31, and 12 mg/L in Suncor ponds 1A, 1, and 2 respectively; Gulley (1992) later reported 92 mg/L in Pond 1A. MacKinnon and Boerger (1986) reported an oil and grease concentration of 25 mg/L in MLSB. Dissolved organic matter (DOM) ranges in concentration from 50 to 100 mg/L, and is mostly comprised of organic acids, 80% of which are NAs (Nelson et al. 1993).

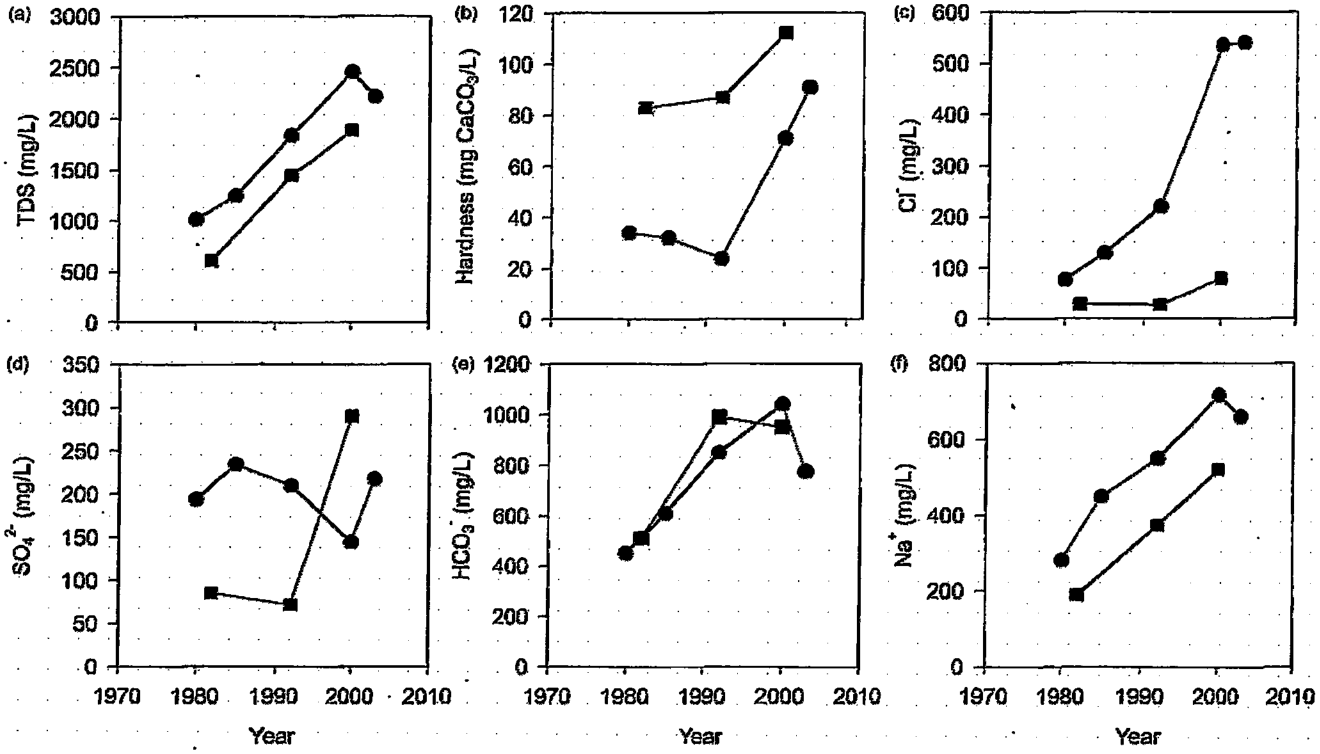
Naphthenic acids are alkyl-substituted cyclic and aliphatic carboxylic acids that are removed from bitumen during the extraction process. Concentrations of NAs range from 40 to 70 mg/L in tailings ponds, but can be has high as 130 mg/L in fresh tailings water (Holowenko et al. 2002; MacKinnon 2004). Naphthenic acids are the main source of acute toxicity in TPW (Verbeek et al. 1993) and depending on their composition and age, can have toxic effects at relatively low concentrations. For example, Holowenko et al. (2002) reported a Microtox® IC_{50} value of 32 vol% for MLSB water; the corresponding NA concentration was 16 mg/L (based on 49 mg/L NA in the original sample). Natural degradation processes have caused NA concentrations in MFT pore water (10–15 m depth) to decline over time, from 73 mg/L in 1995 to 33 mg/L in 2003, although concentrations in dike seepage have remained relatively high (~75 mg/L) (MacKinnon 2004). Background concentrations of NAs in surface water are typically less than 1 mg/L (Headley and McMartin 2004).

Among the aromatic compounds detected in process water are several toxicants of concern including benzene, toluene, phenol, and PAHs (Table 2). Historical concentrations of benzene and toluene in Suncor process water (e.g., >0.6–6.3 and 1–3 mg/L, respectively; Gulley 1992) have in some cases far exceeded CCME guidelines for the protection of aquatic life (0.37 and 0.002 mg/L, respectively) (CCME 2005). More recent data from Syncrude indicate much lower concentrations of these and other compounds; for example, surface water concentrations of BTEX (benzene, toluene, ethylbenzene, and xylene) in MLSB were below detection levels (i.e., <0.010 mg/L) in 1998 (Rogers et al. 2002*b*). Total phenol concentrations in MLSB appear to have declined over time, ranging from 0.3 mg/L in 1981, to 0.15 mg/L in 1985, 0.02–0.04 mg/L in 1992, and 0.008 mg/L in 1998 (MacKinnon and Retallack 1981; MacKinnon and Benson 1985; Nelson et al. 1993; Rogers et al. 2002*b*).

Toxicity

The toxic effects of oil sands process water on aquatic biota have been documented since the early stages of oil sands development. In 1975, it was reported that drainage water from the Great Canadian Oil Sands (GCOS, the precursor to Suncor) lease was acutely toxic to rainbow trout (*Oncorhynchus mykiss*), with an LC_{50} of less than 20% (Hrudey 1975). MacKinnon and Retallack (1981) described the environmental hazards associated with the Syncrude tailings ponds after 3 years of operation, including toxicity to aquatic biota (e.g., 96 h LC_{50} = 10% for rainbow trout), poor water quality, floating bitumen mats, and the risk of infiltration of TPW

Fig. 3. Temporal changes in the concentrations of inorganic ions in tailings pond water at Syncrude Canada Ltd. (circles) and Suncor Energy Corp. (squares); note that Suncor began to implement consolidated tailings (CT) treatment ca. 1997 (data sources: MacKinnon and Retallack 1981; Nix 1983; MacKinnon and Boerger 1986; MacKinnon and Sethi 1993; Kasperski 2001; MacKinnon 2001; MacKinnon 2004).



into groundwater. Between 1981 and 1992, Microtox® LC_{50} values in MLSB ranged from 25% to 43% (Nelson et al. 1993).

Early speculation that organic acids were the primary source of toxicity (MacKinnon and Retallack 1981) was confirmed by Verbeek et al. (1993) with the Environmental Protection Agency (EPA) Toxicity Identification and Evaluation (TIE) protocol. Acute toxicity in MLSB water was removed by adjustment of pH to 2.5 followed by centrifugation, or by reverse phase solid phase extraction with C_{18}, indicating that the toxicants were organic acids with a non-polar component (NAs). Toxicity in Suncor Pond 1A was completely removed by extraction of organic compounds with a non-polar component; however, sparging with nitrogen removed 20%–35% of acute toxicity, indicating the contribution of volatile organic compounds (light hydrocarbon mixtures released into the tailings as diluent) to acute toxicity (Verbeek et al. 1993).

While earlier studies focused mainly on the acute toxicity of TPW, more recent studies have addressed the chronic effects of process waters on aquatic and terrestrial biota in constructed wetlands and ponds (e.g., van den Heuvel et al. 1999*b*, 2000; Siwik et al. 2000; Bendell-Young et al. 2000; Pollet and Bendell-Young 2000; Leung et al. 2001; Colavecchia et al. 2004) (for a summary see Table 3). This research will be discussed in greater detail after a brief review of the land reclamation options currently under consideration.

Wet landscape reclamation

As part of their licensing agreement with the government of Alberta, oil sands operators must reclaim tailings ponds, mining sites, and other disturbed land to self-sustaining ecosystems with a land use equivalent to the original landscape (Alberta Department of Energy 1995). Reclamation plans include dry and wet landscape options. For the dry landscape option, fine tailings will be dewatered, mixed with sand, buried, and capped with soil. The wet landscape option will feature end-pit lakes (EPLs) in mined-out areas, in which fluid fine tails will be capped with a layer of process water and river water (FTFC 1995). Natural sedimentation in the EPLs is expected to provide a buffer layer at the water:tailings interface to reduce the transfer of contaminants from the tailings to the water column. Lake morphometry will be designed to resist water column mixing during wind events.

The reclamation plans are supported by ongoing research on the viability of EPLs and treatment wetlands to form sustainable ecosystems and provide effective remediation of NAs and other pollutants. Both Suncor and Syncrude began to conduct research on wet reclamation in the 1980s, building a series of prototype ponds in which mature fine tailings were capped with water (e.g., Nix 1983). Most studies have demonstrated that small, isolated ponds begin to detoxify naturally over a period of several months to 2 years, and are eventually colonized by aquatic plants (e.g., Nix 1983; Boerger et al. 1992; Nix and Martin 1992; Gulley and

Table 2. Organic chemistry of oil sands process water, the Athabasca River, and regional lakes.

Variable (mg/L)	Syncrude MLSB (1985–1998)	Syncrude demonstration ponds (1996–97)[a]	Suncor tailings ponds (1982–1998)	Athabasca River (2001)[b]	Regional lakes (2001)[b]
DOC	58[c]	26–58	62–67[c]	7	14–27
BOD	25[d]	-	<10–70[e]	<2	-
COD	350[d]	-	86–525[f] 260–973[e]	40[d]	-
OG	25[d]	-	9–31[f] 92[e]	<0.5	-
NA	49[g]	3–59	68[g]	<1	1–2
Phenols	0.008[h]	0.001–0.003	0.03–1.8[f] 0.03–1.4[e]	<0.001	0.002–0.004
Cyanide	0.5[d]	-	0.01–0.04[e]	0.004[d]	-
PAHs	0.01[h]	-	-	-	-
Toluene	-	-	1–3[e]	-	-
Benzene	-	-	<0.6–6[e]	-	-
BTEX	<0.01[h]	-	-	-	-

Note: DOC, dissolved organic carbon; BOD, biochemical oxygen demand; COD, chemical oxygen demand; OG, oil and grease; NA, naphthenic acids; PAH, polycyclic aromatic hydrocarbon; BTEX, benzene, toluene, ethylbenzene, xylene; MLSB, Mildred Lake Settling Basin; data represent mean values from samples collected during the year indicated; ranges indicate mean values for multiple sites.

[a] (Siwik et al. 2000).

[b] (Golder Associates Limited 2002).

[c] (MacKinnon and Sethi 1993); MLSB and Suncor Ponds 1–3.

[d] (MacKinnon and Boerger 1986).

[e] (Gulley 1992); Suncor Ponds 1A, 4.

[f] (Nix 1983); Suncor Ponds 1A, 1, and 2.

[g] (Holowenko et al. 2002): MLSB and Suncor Pond 5.

[h] (Rogers et al. 2002*b*).

MacKinnon 1993; Alberta Department of Energy 1995; MacKinnon et al. 2001). The degradation of NAs in isolated TPW has been shown to occur at a rate of 16% per year over the first 5 years (130 to 24 mg/L) (MacKinnon 2004). The same study showed that further degradation of NAs beyond 5 years was negligible, but that the toxicity of the sample (Microtox® IC_{20}) continued to decline, reaching 100 vol% at 10 years. Aeration and nutrient additions have been shown to increase detoxification rates by stimulating natural microbial populations that degrade NAs (Nix 1983).

There is conflicting evidence as to whether or not wet landscape environments formed from reclaimed tailings and process water can sustain fish populations and other aquatic biota. Although natural detoxification of process water has been demonstrated in small ponds, there is some evidence that larger systems may not detoxify as rapidly. For example, after being dormant for 5 years, Suncor's Pond 1A remained highly toxic to brook trout (*Salvelinus fontinalis*) (96 h $LC_{50} = 24\%$), although some detoxification had occurred (<10% LC_{50} values are typical for active tailings ponds) (Nix 1983). In a study by Boerger et al. (1992), it was demonstrated that fine tailings retain their toxicity beyond 2 years (e.g., Microtox® EC_{50} of 59%), but do not transfer toxicity to the freshwater surface layer.

Another concern is the persistence of chronic toxicity after natural degradation has removed the acutely toxic fraction of naphthenic acids. For example, yellow perch (*Perca flavescens*) stocked in experimental reclamation ponds (MFT capped with surface runoff) for 3 to 10 months suffered increased mortality rates, gill lesions, tumors, and fin erosion (van den Heuvel et al. 2000). In a related study however, yellow perch exhibited positive effects after being stocked for 5 to 11 months in the same demonstration pond, including increased fecundity and body condition, though this may have been linked to reduced competition in the reclamation ponds relative to reference sites (van den Heuvel et al. 1999*b*). Normal growth rates were reported for larval fathead minnows (*Pimephales promelas*) raised in experimental reclamation ponds for 59 days, although elevated mortality rates were detected at certain sites (Siwik et al. 2000).

Tailings amendment processes such as CT treatment may also contribute to the chronic toxicity of process water. Fathead minnows exposed to CT release water and dike seepage from a Suncor CT pond all died within 28 days (Farrell et al. 2004). Bendell-Young et al. (2000) reported low species diversity among benthic fauna in wetlands receiving dike seepage water, CT release water, or phosphate-amended CT water. The authors also found that fish in the wetlands receiving process waters exhibited signs of stress (based on changes in blood chemistry), and in the case of a wetland receiving dilute dike seepage waters, died within 14 days of capture.

Concerns over the viability of proposed wet reclamation options focus on the lengthy residence time required to degrade naphthenic acids and the incomplete degradation of recalcitrant compounds (Quagraine et al. 2005*b*). Researchers have made considerable progress in their attempts to characterize the hundreds of individual NAs in oil sands process water, and to isolate the fraction responsible for toxicity (Holowenko et al. 2001, 2002; Rogers et al. 2002*b*; Lo et al. 2003; Hao et al. 2005). A critical finding was that NA compounds vary in terms of toxicity and biodegradability.

Table 3. Summary of recent studies on experimental reclamation ponds and treatment wetlands in the oil sands.

Study objective	Findings	Reference
Toxicity of tailings pond sediments to early life stages of fathead minnows (*Pimephales promelas*)	Fathead minnows hatched over sediments from oil sands deposits and tailings ponds (treatments ranged from 0.05 to 25 g sediment/L) exhibited increased mortality, malformations, and reduced size; toxic effects may be related to PAHs where sediment total PAH concentrations > 500 μg/L	(Colavecchia et al. 2004)
Toxicity of dike seepage to wetland plants	Plants exposed to oil sands effluent had higher photosynthetic rates than plants in reference wetlands; accumulation of stress related proteins in cattail roots may reflect osmotic stress from high salinity; concluded that cattail and clover can adapt to oil sands effluent (in the form of dike seepage)	(Crowe et al. 2001)
Effects of oil sands wetland outflow on terrestrial plant growth	Effluents from a naturally-formed dike seepage wetland and a CT pond inhibited the germination of terrestrial plant species such as rye, wheat, pea, canary grass, and clover	(Crowe et al. 2002)
Effects of CT water on survival of fathead minnows	Fathead minnows exposed to CT release water and dike seepage water did not survive beyond 28 days, and experienced gill hyperplasia and decreased lymphocytes; concluded that wastewater will require amelioration to support fish populations	(Farrell et al. 2004)
Effects of process water on phytoplankton biomass and community composition	Phytoplankton communities were sampled in 10 water bodies across the oil sands region; biomass was not correlated with either NAs or major ions; NA and major ion concentrations explained 40% of the variability in the phytoplankton community	(Leung et al. 2003)
Effects of process water on phytoplankton community	Microcosm experiments showed effects of process waters (<5 years old, [NA] > 20 mg/L) on phytoplankton community composition; the greatest changes occurred in the microcosms with the highest NA concentrations and salinity	(Leung et al. 2001)
Mutagenicity of polyaromatic compounds in tailings porewater	Pore water extracts were not mutagenic based on Ames *Salmonella* assay	(Madill et al. 2001)
Effects of seepage ponds and wetlands on growth, development, and survival of frogs	Tadpoles (*Bufo boreas* and *Rana sylvatica*) in wetlands receiving effluent exhibited reduced growth, prolonged developmental time, and decreased survival compared to reference sites	(Pollet and Bendell-Young 2000)
Acute and subchronic toxicity of NAs to rodents	Exposure of rats to a wide range of NA dosages (0.6–300 mg/kg) indicated hepatotoxicity, but worst-case scenario exposure in tailings pond water should not cause acute toxicity; subchronic exposure may cause health problems	(Rogers et al. 2002*a*)
Growth effects on larval fathead minnows	Fathead minnow larvae exposed to water from Syncrude demonstration ponds (5- to 9-year old capping experiments) showed no evidence of impeded growth at 7 d or 56 d, although increased mortality was detected at several sites	(Siwik et al. 2000)
Physiological endpoints in swallows inhabiting process water wetlands	Found no differences in reproductive success, growth rate, or immune response between swallows inhabiting oil sands wetlands and reference sites; elevated hepatic ethoxyresorufin-*O*-deethylase (EROD) activity in nestlings living on reclaimed sites indicated the presence of xenobiotics in their diet, which were likely derived from contaminants associated with oil sands processing	(Smits et al. 2000)
Effects of aromatic compounds on fish hormone levels	At river sites within the Athabasca oil sands deposit and adjacent to oil sands development, fish had lower steroid production and higher activity of a hepatic enzyme relative to reference sites, suggesting exposure to aromatic compounds; PAHs could potentially cause endocrine disruption in aquatic biota	(Tetreault et al. 2003)
Chemical indicators of exposure to process waters in fish	Yellow perch in experimental reclamation ponds (i.e., water capped tailings) had elevated mixed-function oxygenase (MFO) activity and PAH concentrations relative to reference sites; however, these chemical endpoints did not appear to be linked to physiological responses in the fish	(van den Heuvel et al. 1999*a*)
Effects of reclamation pond water on fish physiology	Yellow perch living in experimental reclamation ponds had increased gonad size, fecundity, and condition factors (at 5 and 11 months) relative to a reference lake; this may have reflected greater resource availability or reduced inter- and intraspecific competition in the experimental ponds	(van den Heuvel et al. 1999*b*)

Table 3 (*concluded*).

Study objective	Findings	Reference
Effects of long-term (3–10 months) exposure of yellow perch (*Perca flavescens*) to reclamation ponds	Increased occurrence of disease and gill lesions in yellow perch from experimental reclamation ponds may be related to immune system suppression; incidence of disease was positively correlated with concentrations of oil sands-related compounds, did not identify a specific substance as the stressor	(van den Heuvel et al. 2000)

Naphthenates in fresh TPW are dominated by a group of compounds with carbon numbers 13–16; however, if the water is isolated and aged for several years, the composition of the mixture shifts towards larger molecules (i.e., C_{22+}) (Holowenko et al. 2002). Toxicity has been shown to decrease with increasing relative abundance of C_{22+} compounds, suggesting that the smaller compounds (C_{13-16}) not only degrade faster, but are more toxic than the larger molecules (Holowenko et al. 2002). Subsequent research has shown that NAs with a high number of multi-ring structures are less toxic and more resistant to microbial degradation than less complex structures (Lo et al. 2006).

Due to the variable toxicity among NA compounds, decreases in acute toxicity may not necessarily correlate with changes in total NA concentration. For example, CT treatment has been shown to significantly reduce toxicity (i.e., from IC_{50} of 20%–30% in pond water to 70%–100% in CT release water) despite only a slight reduction (25%) in NA concentration (Marr et al. 1996). Similarly, a 38% reduction in NA concentration in 1-year old process water (from 129 to 81 mg/L) eliminated LC_{50} toxicity for trout, zooplankton, and Microtox® (LC_{50}) (MacKinnon et al. 2001), even though much lower NA concentrations in "fresh" tailings water have proven to be acutely toxic to aquatic biota.

Polycyclic aromatic hydrocarbons may also contribute to chronic toxicity in process water. Although water column concentrations of PAHs are predicted to be low in reclaimed environments (Gulley 1992), the potential for chronic effects on aquatic biota (e.g., endocrine disruption, behavioural and growth effects) remains a concern. Tetreault et al. (2003) sampled fish populations in two rivers that drain into the Athabasca River near major oil sands developments, and found evidence of reduced steroid production and increased exposure to natural oil sands compounds (based on hepatic enzyme activity) at sites within the oil sands deposit and adjacent to an oil sands development, compared to reference sites. The authors suggested that PAHs detected in river sediments and water may contribute to endocrine disruption, which is supported by numerous studies on the physiological effects of PAH exposure on fish in other regions (e.g., Lintelmann et al. 2003). Other studies have reported evidence of PAH exposure among fish populations in demonstration ponds (van den Heuvel et al. 1999*a*), and cited PAHs as potential stressors causing increased mortality and malformations in fish (Colavecchia et al. 2004).

Salinity concentrations in process water are currently insufficient to be acutely toxic, but may influence biological productivity, community composition, or act as a stressor that increases the toxicity of other compounds to biota in reclaimed environments. Crowe et al.'s (2001) study on plant growth in process water reported the production of dehydrin-related proteins in cattail roots that may have been indicative of osmotic stress caused by the high salinity. Significant shifts in phytoplankton species composition have been linked to elevated concentrations of salinity and NAs in oil sands process waters (Leung et al. 2001). A subsequent study found no correlation between phytoplankton biomass and NA or major ion concentrations, and concluded that major ions had at least as much of an ecological effect as NAs (Leung et al. 2003).

Water treatment objectives

Process water recycling

With the exception of chemical additives to promote the settling of fine clay particles, TPW is not treated prior to reuse in the extraction process. The consequent decline in process water quality has raised concerns over the effects of water chemistry on bitumen recovery, scaling, corrosion, and fouling of extraction plant infrastructure. Given that the proposed expansion of mining projects may lead to restrictions on freshwater imports, operators may eventually need to consider treatment of TPW and other process waters to meet the operational requirements currently served by the Athabasca River (e.g., extraction, boiler feedwater, upgrading, drinking water, and other domestic uses). In the following sections, potential treatment objectives for the industrial reuse of tailings pond water are established based on water quality criteria for bitumen extraction and boiler feedwater treatment.

Bitumen extraction chemistry

Process water chemistry strongly influences bitumen extraction and froth quality. Bitumen recovery is optimized at alkaline pH due to increased activity of surfactants, negative charges on clay and sand surfaces, and reduced interfacial tension between bitumen droplets and solids (Kasperski 2003). Where needed (e.g., low or moderate grade ores), process water pH is controlled through the addition of alkaline reagents such as sodium hydroxide (Schramm et al. 1985). Changes in process water pH or alkalinity as a result of water treatment would thus affect the sodium hydroxide dosage, and should be taken into consideration when selecting treatment technologies.

Divalent cations interfere with bitumen recovery by increasing the adhesion of bitumen to sand and clay particles, reducing the adhesion of bitumen to air bubbles, neutralizing surfactants, and increasing the coagulation of clay particles (Kasperski 2003). While bitumen recovery rate has been negatively correlated with calcium + magnesium concentration (over a range of ~0.1 to 10 mmol/L), the effect is not consistent across ore types (Cuddy et al. 2000). Much of the variability in bitumen recovery at different calcium concentrations may be attributable to differences in fines content and ore chemistry (Kasperski 2003).

Table 4. Hypothetical treatment objectives for industrial reuse of oil sands tailings pond water.

Variable (mg/L unless otherwise noted)	Oil sands tailings pond water	Industrial water quality guidelines (mg/L)			Treatment objective (% removal)
		Conventional boiler (900–1500 psi)[a]	Once-through steam generator[b]	Bitumen extraction[c]	
Alkalinity	635–779[d]	100	-	-	>85
Calcium	17–25[d]	0.005	0.05	~50–140	>99
COND (μS cm^{-1})	1506–2400[e]	150–1000	-	-	33–94
Copper	0.7[f]	0.015	-	-	98
DO	-	0.007	0.04	-	-
Hardness	91–112[d]	n.d.-0.05	0.5	-	>99
Iron	0.08[e]-2.4[f]	0.02	0.05	-	37–92
Oil	25[g]-92[h]	1	1	-	96–99
pH	8.2–8.4[i]	8.5–9.5	9–9.5	7–9	-
Silica	1.75[g]	2–8	50	-	-
TDS	1900–2221[d]	100–650	8000	-	52–95
TSS (%)	0.7[e]	-	0	0.5–2	100

Note: TPW, tailings pond water; COND, conductivity; DO, dissolved oxygen; TDS, total dissolved solids; TSS, total suspended solids; MLSB, Mildred Lake Settling Basin; ASME, American Society of Mechanical Engineers; OTSG, once through steam generator.

[a] (ASME 1994).

[b] (Zaidi and Constable 1994).

[c] (Hall and Tollefson 1979; Kasperski 2003).

[d] (Kasperski 2001; MacKinnon 2004).

[e] (MacKinnon and Sethi 1993).

[f] (Nix 1983).

[g] (MacKinnon and Boerger 1986).

[h] (Gulley 1992).

[i] (MacKinnon 2001).

Where hardness concentrations are prohibitive to bitumen extraction, treatment of process water to precipitate calcium carbonate has proven to be effective at preventing the decline in bitumen recovery. Magnetic treatment of process water with a total hardness of 235 ppm improved bitumen recovery from 45% to 65%, and appeared to reduce the binding of cations to clay particles, possibly as a result of increased precipitation of calcium carbonate (Amiri 2006).

High concentrations of sodium chloride (1000–2000 mg/L and 3000–6000 mg/L) have also been shown to reduce bitumen recovery, albeit in low grade ores only (see Kasperski 2003). A positive effect on bitumen recovery was reported for sodium chloride additions up to 1149 mg/L, which is within the range of reported values from tailings ponds. Additional water quality requirements for bitumen extraction include low clay content (suspended solids of 0.5% to 2% are sufficient for extraction process), removal of substances that could flocculate clays, and removal of particulate or dissolved substances that might deposit on heat exchange surfaces (Hall and Tollefson 1979).

Based on the process water quality data reviewed herein, there are no significant exceedances of bitumen extraction criteria in process water. Current hardness concentrations are insufficient to reduce bitumen extraction, although long-term trends in TPW quality, coupled with expansion plans and the potential for increased reliance on tailings release water and other streams with high water hardness (e.g., site runoff, basal aquifer water) point towards an eventual need for water treatment.

Scaling, fouling, and corrosion

Prevention of scaling, fouling, and corrosion are major concerns for oil sands operators, particularly at in situ operations where produced water is recycled for steam generation (e.g., Zalewski and Bulkowski 1998; Hart 2002), although problems related to scale formation and fouling have also been reported at the extraction facilities of mining operations (pers. comm., K. Kasperski 2006). Recent increases in hardness and pH in TPW have translated into significant increases in the Langelier Saturation Index (a scaling index for calcium carbonate), necessitating the use of anti-scalants (Rose and Rideout 2001). Common components of scales formed from produced water include carbonate, silica, sulphate, phosphate, and iron oxides (CH2M Hill Canada 1981; Zalewski and Bulkowski 1998).

Chemicals of concern with respect to process water corrosivity include TDS, sulphate, chloride, bicarbonate, ammonium, NAs, copper, and dissolved oxygen (CONRAD 1998; Rogers 2004). As previously noted, concentrations of these chemicals, as well as water hardness, have increased considerably in the tailings ponds. Applying the strict guidelines of conventional boiler feedwater treatment to prevent scaling, corrosion, and fouling in TPW would require up to 100% removal of suspended solids, >95% removal of bitumen, 99% removal of hardness, 85% removal of alkalinity, 98% removal of copper, 33%–94% reduction in conductivity, and 37%–92% removal of iron (Table 4), although less aggressive treatments would be sufficient to prevent scaling and fouling of hot water extraction facilities.

Table 5. Hypothetical treatment objectives for environmental discharge of oil sands process water.

Pollutant (mg/L)	Oil sands tailings pond water[a]	Environmental guideline (mg/L)				Treatment objective (% removal)
		CEQG[b]	EPEA[c]	USEPA[d]	Other	
Inorganic						
Ammonia	14	1.4	5	0.8–1.3[e]	-	64–93
Bicarbonate	775–950	-	-	-	500[f]	50
Chloride	80–540	-	250–500		150[g]	70
Sulphate	218–290	-	-		50[g]	80
TDS	1900–2221	-	-	-	1340[h]	50–60
Organic						
Benzene	<0.01–6.3	0.37	-	-	-	<99
BOD	<10–70	-	25	-	-	<65
COD	86–973	-	200	-	-	<80
Cyanide	0.01–0.5	0.005	-	0.005	-	50–99
Naphthenic acids	50–70	-	-	-	30[i]	20–74
					5[j]	90
					1[k]	99
Oil and grease	9–92	no odour or visible sheen	5–10	1% of 96-h LC_{50} for selected biota	35[l]	<90
Phenols	0.02–1.5	0.004	1	0.001	-	33–99.7
Toluene	<0.01–3	0.002	-	1.3[m]	-	<99
PAHs	0.01	0.00001–0.00006[n]	-	-	-	>99
Trace metals						
Aluminum	0.07–0.5	0.1	-	0.75	-	<80
Arsenic	0.006–0.015	0.005	-	0.15	-	<67
Chromium	0.003–2	-	-	0.074[o]	-	<63
Copper	0.002–0.9	0.002	-	0.009[o]	-	>95–99
Iron	0.8–3	0.3	3.5	1	-	<50
Lead	0.04–0.19	-	-	0.0025[o]	-	94–99
Nickel	0.006–2.8	-	-	0.052[o]	-	93–99
Zinc	0.01–3.2	-	-	0.12[o]	-	96

Note: TDS, total dissolved solids; BOD, biochemical oxygen demand; COD, chemical oxygen demand; PAH, polycyclic aromatic hydrocarbons.

[a] (MacKinnon and Boerger 1986; Gulley 1992; Siwik et al. 2000; Leung et al. 2001; Kasperski 2001; MacKinnon 2004).

[b] CEQG, Canadian Environmental Quality Guidelines; surface water quality guidelines for the protection of aquatic life (CCME 2005).

[c] EPEA, Environmental Protection and Enhancement Act; example maximum discharge limits for various Alberta industries (Alberta Environment 1999); monthly average guideline for BOD (Alberta Environment 1997).

[d] USEPA, United States Environmental Protection Agency; water quality criteria for the protection of aquatic life; (USEPA 1999).

[e] USEPA 30-day average concentration at pH 8.0–8.3.

[f] $NaHCO_3$ toxicity (zooplankton) of 10 mequiv. HCO_3/L (Mount et al. 1997).

[g] Ambient water quality guidelines (Government of British Columbia 2000).

[h] General guideline cited by SETAC (2004); effects vary with ionic composition.

[i] Microtox® LC_{50} value for a commercial mixture of naphthenic acids (Herman et al. 1994).

[j] Toxicity to fish from a commercial mixture of naphthenic acids (Patrick et al. 1968).

[k] Background concentration in surface waters (Headley and McMartin 2004).

[l] USEPA Efluent Limitation Guideline, Agriculture and Wildlife Category, National Pollutant Discharge Elimination System (NPDES).

[m] USEPA drinking water guideline.

[n] Criteria for individual compounds.

[o] Continuous concentration at hardness = 100 mg/L $CaCO_3$.

Environmental discharge and reclamation

For the purposes of environmental discharge and (or) reclamation, the goal of water treatment would be to remove toxicity and ensure that biota in reclaimed and downstream aquatic systems are not affected by acute or chronic effects of chemicals associated with oil sands processing. Poor water quality in EPLs could hinder recolonization of reclaimed environments and bioremediation of pollutants (Quagraine et al. 2005*b*). Although oil sands operators are currently bound to a zero discharge policy, treatment and discharge of process waters could represent an option to offset water consumption. To identify target pollutants and determine hypothetical treatment objectives, TPW quality data were compared to environmental water quality benchmarks such as the CCME's surface water quality guidelines for the protection of aquatic life (CCME 2005), industrial discharge limits under Alberta's Environmental Protection and Enhancement Act (EPEA) (Alberta Environment 1999), and background concentrations in local surface waters (Golder Associates Limited 2002). Treatment objectives based on exceedances of these criteria were then determined for target chemicals (Table 5).

Naphthenic acids

As the principal source of toxicity in the tailings ponds, NAs represent the main pollutant of concern with respect to reclamation or environmental discharge. Although the acutely toxic fraction of NAs have been shown to degrade naturally over time in experimental pits and wetlands, the lengthy water residence time required for degradation may not be practical where the direct discharge of water is required. Also, high molecular weight NA compounds appear to be resistant to biodegradation and could persist in reclaimed environments. Further research is needed to determine if recalcitrant NAs in reclaimed environments pose a chronic toxicity risk. Since concentration-based limits have not been established in Canada, background concentrations in local surface- and groundwater (i.e., ~1–5 mg/L) are suggested as a target for NA removal. Given typical NA concentrations of 50–70 mg/L in TPW, the corresponding water treatment objective would be 90%–99% removal.

Bitumen

Residual bitumen in the tailings ponds poses a hazard to aquatic biota, and its biodegradation could be a source of NAs in EPLs (Quagraine et al. 2005*a*). Bitumen slicks would not only interfere with the establishment of aquatic communities in reclamation ponds, but would also contribute to the fouling of advanced treatment technologies. Previously reported bitumen concentrations in tailings ponds water have been at least 2.5- to 9-fold higher than the EPEA maximum discharge limit of 10 mg/L (Table 5), thus up to 90% removal may be required.

Volatile organic compounds

Based on historical data, concentrations of benzene, cyanide, PAHs, phenols, and toluene in TPW have previously exceeded CCME guidelines for the protection of aquatic ecosystems by at least an order of magnitude (Table 5). While there is little evidence that aromatic compounds contribute significantly to acute toxicity in process waters, certain compounds have been detected in fish (van den Heuvel et al. 1999*a*) and there are concerns over endocrine disruption and other chronic effects (Tetreault et al. 2003). To reduce aromatic hydrocarbon concentrations in process water below CCME guidelines, removal rates of up to 99% may be required. Volatilization, dilution, and natural degradation may sufficiently reduce the concentrations of certain compounds in proposed wet landscape systems; for example, total phenol concentrations in demonstration ponds (0.001–0.003 mg/L; Siwik et al. 2000) are well below the EPEA discharge limit (1 mg/L) and slightly below the CCME surface water quality guideline (0.004 mg/L).

Total dissolved solids

High concentrations of TDS in process water may affect zooplankton community structure and contribute to acute or chronic toxicity in aquatic biota. Total dissolved solids concentrations in excess of 1340 mg/L are generally considered sufficient to cause toxicity in aquatic biota due to ion imbalance (SETAC 2004). Ion imbalance refers to a condition in which common ions occur in different ratios or at concentrations above or below tolerance levels for aquatic biota, which can induce chronic stress that impairs normal metabolic functions. As such, the toxic effects of TDS are strongly dependent on the ionic composition of the water (e.g., Mount et al. 1997).

The dominant ions in tailings pond water exceed several water quality criteria. Current concentrations of chloride and sulphate in TPW exceed water quality guidelines for the protection of aquatic life by 3- to 4-fold (USEPA 1999; Government of British Columbia 2000), and sodium chloride concentrations may be sufficient to induce chronic effects in zooplankton (Harmon et al. 2003). In other systems, sodium bicarbonate concentrations comparable to those of TPW have been shown to cause acute toxicity in zooplankton (Mount et al. 1997). To date, evidence of toxic effects from salinity levels in TPW has been limited to osmotic stress in plants (Crowe et al. 2001) and shifts in phytoplankton community structure (Leung et al. 2003). Salinity could contribute to the acute toxicity of TPW because osmotic stress is an important component of the toxic effect of NAs on aquatic biota (see Quagraine et al. 2005*b*). Based on current concentration, removal rates of up to 50%–60% for TDS, 70% for chloride, and 80% for sulphate would be required to meet the criteria cited above.

Ammonia

Ammonia is highly toxic to fish and other aquatic biota. Total ammonia nitrogen concentrations of 14 mg/L in TPW (MacKinnon 2004) exceed both the USEPA's criterion continuous concentration (0.8–1.3 mg/L for pH range of 8.0–8.3), which is a guideline for long-term exposure (i.e., 30-day average) (USEPA 1999), and the EPEA maximum daily discharge limit for refineries in Alberta (5 mg/L) (Table 5). For TPW, ammonia removal rates of 64%–93% would be required to meet surface water guidelines.

Trace metals

Trace metals detected in TPW include aluminum (Al), arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), iron (Fe), lead (Pb), molybdenum (Mo), titanium (Ti), vanadium (V), and zinc (Zn) (Hall and Tollefson 1979; MacKinnon and Retallack 1981; MacKinnon 1981; Nix 1983; Gulley 1992; FTFC 1995; Siwik et al. 2000). Among these elements are toxic metals that have been labeled as priority pollutants under the USEPA's Clean Water Act (e.g., As, Cd, Cr, Cu, Ni, Pb, and Zn) (USEPA 2006). Historical data from tailings ponds indicate some exceedances of CCME water quality guidelines for trace metals (Table 5), however the scarcity of recent data makes it difficult to determine if current concentrations are problematic. Trace metal concentrations in experimental reclamation ponds do not exceed surface water quality guidelines (e.g., Siwik et al. 2000; Farrell et al. 2004). Trace metals that have previously exceeded CCME guidelines in oil sands process water include Al, As, Cr, Cu, Fe, Pb, Ni, and Zn (exceedances ranging from 50% to 100%) (MacKinnon and Retallack 1981; Nix 1983; Gulley 1992).

Conclusions

Target pollutants for the operational reuse of oil sands process water include suspended solids, bitumen, hardness, sulphate, chloride, ammonium, and iron. Increasing concentrations of water hardness in recycled water may eventually exceed bitumen extraction criteria and saturation points for scaling, necessitating some form of water treatment to sustain bitumen recovery without increasing the consumption of freshwater.

Chemicals of environmental concern in oil sands process water include NAs, bitumen, ammonia, sulphate, chloride, aromatic hydrocarbons, and trace metals. While NAs are the main contributors of acute toxicity to aquatic biota, various compounds have exceeded CCME water quality guidelines at some point during oil sands operations and could contribute to chronic toxicity in reclaimed aquatic environments. Proposed reclamation procedures rely on natural processes to ameliorate the process water quality in proposed artificial aquatic ecosystems comprised of mature fine tailings capped with process water. Small-scale versions of the proposed systems have demonstrated natural detoxification over a period of months; however, it remains unclear whether or not full-scale systems will be as effective, or how residual pollutants will affect aquatic and terrestrial food webs in the reclaimed landscape. Alternative forms of water treatment may offer more effective and rapid removal of environmental contaminants. The target pollutants and treatment objectives proposed herein provide a framework for the assessment of emerging water treatment technologies and their potential to minimize environmental impacts while optimizing bitumen production from oil sands deposits.

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