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Initial geochemical characteristics of fluid fine tailings in an oil sands end pit lake

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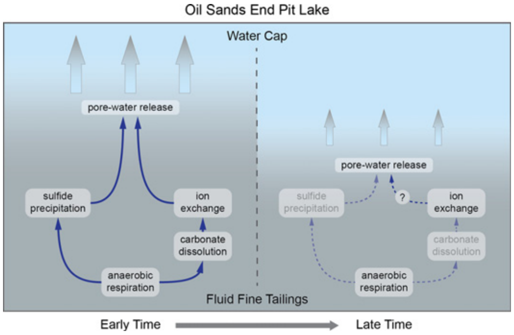
HIGHLIGHTS

- First study of fluid fine tailings geochemistry in oil sands end pit lake
- Carbonate dissolution has promoted ion exchange reactions.
- Microbial iron and sulfate reduction influence pore-water chemistry.
- Biogeochemical processes have likely enhanced tailings settlement.
- Long-term geochemical evolution of oil sands end pit lakes remains unknown.

GRAPHICAL ABSTRACT



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ABSTRACT

Geochemical characteristics of fluid fine tailings (FFT) were examined in Base Mine Lake (BML), which is the first full-scale demonstration oil sands end pit lake (EPL) in northern Alberta, Canada. Approximately 186 Mm^3 of FFT was deposited between 1994 and 2012, before BML was established on December 31, 2012. Bulk FFT samples ($n = 588$) were collected in July and August 2013 at various depths at 15 sampling sites. Temperature, solid content, electrical conductivity (EC), pH, Eh and alkalinity were measured for all samples. Detailed geochemical analyses were performed on a subset of samples ($n = 284$). Pore-water pH decreased with depth by approximately 0.5 within the upper 10 m of the FFT. Major pore-water constituents included Na (880 ± 96 mg L^{-1}) and Cl (560 ± 95 mg L^{-1}); Ca (19 ± 4.1 mg L^{-1}), Mg (11 ± 2.0 mg L^{-1}), K (16 ± 2.3 mg L^{-1}) and NH_3 (9.9 ± 4.7 mg L^{-1}) were consistently observed. Iron and Mn concentrations were low within FFT pore water, whereas SO_4 concentrations decreased sharply across the FFT–water interface. Geochemical modeling indicated that $FeS_{(s)}$ precipitation was favoured under SO_4-reducing conditions. Pore water was also under-saturated with respect to gypsum [$CaSO_4 \cdot 2H_2O$], and near saturation with respect to calcite [$CaCO_3$], dolomite [$CaMg(CO_3)_2$] and siderite [$FeCO_3$]. X-ray diffraction (XRD) suggested that carbonate-mineral dissolution largely depleted calcite and dolomite. X-ray absorption near edge structure (XANES) spectroscopy revealed the presence of $FeS_{(s)}$, pyrite [FeS_2], and siderite. Carbonate-mineral dissolution and secondary mineral precipitation have likely contributed to FFT dewatering and settlement. However, the long-term importance of these processes within EPLs remains unknown. These results provide a reference for assessing the long-term geochemical evolution of oil sands EPLs, and offer insight into the chemistry of pore water released from FFT to the overlying water cover.

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1. Introduction

Oil sands mining operations in northern Alberta, Canada, develop large open pits to access bitumen hosted in Cretaceous sand and sandstone of the McMurray formation. Heated water and sodium hydroxide (NaOH) are added to extracted oil sand ore to produce a slurry from which bitumen is extracted by flotation (Masliyah et al., 2004). The residual tailings slurry contains solids and dissolved salts from the ore combined with oil sands process-affected water (OSPW). Differential settlement of tailings particles occurs following discharge of this slurry into tailings ponds. The sand-sized fraction, with particles >44 μm in diameter, is dominated by quartz [SiO_2] grains that settle rapidly. Particles measuring <44 μm in diameter settle much more slowly, with those <2 μm remaining suspended for extended times. This fraction is largely comprised of clay minerals, which form an aqueous matrix within tailings ponds referred to as fluid fine tailings (FFT). This matrix initially contains 25 to 35% (w/w) solids, of which at least 90% (w/w) are typically <44 μm in diameter and 30% (w/w) are <2 μm in diameter. The remaining FFT matrix is comprised of OSPW, which generally contains high concentrations of dissolved salts, naphthenic acids (NAs), petroleum hydrocarbons (PHCs), and unrecovered bitumen (Allen, 2008; Kavanagh et al., 2011). Suspended clay particles exhibit low settlement rates due to the relatively thick electrical double layer (EDL) that develops on the surfaces of clay minerals when they equilibrate with high Na concentrations in OSPW. Consequently, FFT is typically stored in tailings ponds for several years to facilitate dewatering, settlement and reuse of released water in the bitumen extraction process. Dewatering and associated settlement rates for FFT are typically greatest within the first year following deposition; however, low densities may persist for many years thereafter (Kasperski and Mikula, 2011).

In early 2015, the government of Alberta introduced a Tailings Management Framework (TMF) to provide guidance for managing FFT in the Athabasca Oil Sands Region (AOSR; Government of Alberta, 2015). The TMF includes site-specific thresholds for FFT volumes over the life of an oil sands mine, and requires that the entire FFT inventory of a project must reach an acceptable state within 10 years of the end of bitumen mining. Various strategies are under development to address these objectives and, more generally, to facilitate incorporation of FFT into oil sands mine closure landscapes. End pit lakes (EPLs) are referenced in the TMF as a potential technology for reducing FFT inventories within tailings ponds, and for facilitating FFT integration into mine closure landscapes.

End pit lakes are comprised of thick FFT deposits stored below a water cover within decommissioned open pits. The initial chemical composition of the water cover is dominated by OSPW. However, fresh water inputs and in situ (bio)geochemical processes are expected to improve the quality of the water cover over time. The oil sands industry anticipates that fresh water inputs, including precipitation and runoff from adjacent reclaimed and undisturbed areas, and in situ biogeochemical process will support improvements in EPL water quality over time. These improvements – to meet yet-to-be defined criteria – will be essential before future discharge of EPL cover water to natural water bodies in the AOSR could be approved. However, long-term pore-water release during FFT dewatering and settlement will likely contribute OSPW-derived constituents to EPL water covers for many years. Consequently, a thorough understanding of FFT pore-water geochemistry and relationships between geochemical processes and FFT settlement are critical for anticipating the long-term evolution of this water quality.

Methanogenesis is a principal mode of hydrocarbon degradation within FFT deposits (Fedorak et al., 2003; Siddique et al., 2006, 2007, 2011; Stasik et al., 2014; Stasik and Wendt-Potthoff, 2014) and has been linked to increased dewatering and settlement (Holowenko et al., 2000; Bordenave et al., 2010; Siddique et al., 2014a). Anaerobic degradation of hydrocarbons including *n*-alkanes and monoaromatics (i.e., benzene, toluene, ethylbenzene, xylenes) under methanogenic conditions produces CH_4 and CO_2 (Siddique et al., 2006, 2007, 2011). Associated increase in dissolved CO_2 promotes carbonate-mineral dissolution and releases divalent cations (i.e., Ca^{2+}, Mg^{2+}) to FFT pore water (Siddique et al., 2014a). Subsequent exchange for monovalent cations (i.e., Na^{+}) at clay-mineral surfaces can enhance FFT dewatering and settlement by reducing the EDL thickness (Brown et al., 2013; Siddique et al., 2014a).

Microbial SO_4 and Fe reduction are important anaerobic respiration processes in oil sands FFT deposits (Chen et al., 2013; Stasik et al., 2014; Stasik and Wendt-Potthoff, 2014). Reduction of SO_4 and Fe^{3+} coupled with organic carbon oxidation generates H_2S and Fe^{2+}, and can promote the precipitation of secondary Fe^{2+} sulfides (Chi Fru et al., 2013; Chen et al., 2013; Siddique et al., 2014b; Stasik et al., 2014). Increases in dissolved Fe^{2+} concentrations may also promote siderite [$FeCO_3$] precipitation within FFT deposits. Siddique et al. (2014b) proposed that formation of these secondary phases at clay particle surfaces will mask surface charge and promote aggregation.

This study examines the initial geochemical characteristics of FFT stored in the first of more than 30 EPLs proposed for the AOSR (Prakash et al., 2011). A detailed sampling program was conducted during the summer of 2013 to examine the physical properties, pore-water geochemistry, mineralogy, and solid-phase geochemistry of FFT stored in this EPL. Results help to constrain initial controls on FFT pore-water geochemistry and to assess the potential geochemical influence of FFT pore water on the water cover. These data also serve as a reference for assessing the long-term geochemical evolution of FFT pore water, which is critical for assessing the performance of EPLs as an oil sands mine closure strategy. Consequently, this research contributes to the ongoing assessment of this approach to oil sands mine closure.

2. Site description

The Mildred Lake Mine is located approximately 35 km north of Fort McMurray, Alberta, Canada. The mine lease covers an area of approximately 1000 km^2 and is among the largest mining operations worldwide. The regional climate is considered to be sub-humid continental with short summers and long cold winters (Carey, 2008). Minimum and maximum mean daily temperatures of -39.8 °C (January 18, 1996) and 26.3 °C (August 1, 2003), respectively, have been measured at the Mildred Lake weather station adjacent to the mine site (Environment Canada, 2015). Mean annual precipitation is approximately 400 mm with 30% falling as snow between September and May. A majority of rainfall occurs during May, June, July, and August when average monthly rainfall is approximately 50 mm (Environment Canada, 2015).

Surface mining at the Mildred Lake Mine began in 1978 and a total of 2.4×10^9 barrels of synthetic crude oil were produced by the end of 2013. Ore contains an average of 12% (w/w) bitumen, 3 to 6% (w/w) water, and 84 to 86% (w/w) solids, which are comprised principally of quartz sand with a small clay fraction (Chalaturnyk et al., 2002). Bitumen is separated from these solids with the introduction of heated water to reduce viscosity, and NaOH to disperse clay particles (Caughill et al., 1993; Masliyah et al., 2004; Han et al., 2009). The resulting bitumen froth is recovered for upgrading, while the residual sand–clay slurry is pumped to various tailings impoundments, including the Mildred Lake Settling Basin, for storage.

From 1994 until 2012, a portion of FFT and recycled OSPW generated at the Mildred Lake Mine were placed in West In-Pit (WIP), which was the precursor to BML. This depleted open pit received approximately 186 Mm^3 of FFT, some coarse tailings along the east wall of the pit, and minor amounts of petroleum coke over this time. As of October 2012, the FFT deposit had reached a maximum thickness of 48 m and was submerged under a 52 Mm^3 water cover, with a surface area of approximately 8 km^2 and average depth of 6.5 m. The FFT–water interface exhibited an average elevation of 302.5 m above sea level (masl) as of October 2012 when FFT placement ceased (Fig. 1).