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# Oil sands thickened froth treatment tailings exhibit acid rock drainage potential during evaporative drying



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#### HIGHLIGHTS

#### GRAPHICAL ABSTRACT

- First study that reports acid rock drainage (ARD) in thickened froth tailings (TT).
- Pyrite mineral in TT governs ARD through oxidation.
- Jarosite, a signature ARD mineral, was formed during pyrite oxidation.
- The results are important in making decisions about site closure and reclamation.



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#### ABSTRACT

Bitumen extraction from oil sands ores after surface mining produces different tailings waste streams: 'froth treatment tailings' are enriched in pyrite relative to other streams. Tailings treatment can include addition of organic polymers to produce thickened tailings (TT). TT may be further de-watered by deposition into geotechnical cells for evaporative drying to increase shear strength prior to reclamation. To examine the acid rock drainage (ARD) potential of TT, we performed predictive analyses and laboratory experiments on material from field trials of two types of thickened froth treatment tailings (TT1 and TT2). Acid-base accounting (ABA) of initial samples showed that both TT1 and TT2 initially had net acid-producing potential, with ABA values of -141 and -230 t CaCO<sub>3</sub> equiv. 1000 t<sup>-1</sup> of TT, respectively. In long-term kinetic experiments, duplicate ~2-kg samples of TT were incubated in shallow trays and intermittently irrigated under air flow for 459 days to simulate evaporative field drying. Leachates collected from both TT samples initially had pH ~ 6.8 that began decreasing after ~50 days (TT2) or ~250 days (TT1), stabilizing at pH ~ 2. Correspondingly, the redox potential of leachates increased from 100–200 mV to 500–580 mV and electrical conductivity increased from 2–5 dS  $m^{-1}$  to 26 dS  $m^{-1}$ , indicating dissolution of minerals during ARD. The rapid onset and prolonged ARD observed with TT2 is attributed to its greater pyrite (13.4%) and lower carbonate (1.4%) contents versus the slower onset of ARD in TT1 (initially 6.0% pyrite and 2.5% carbonates). 16S rRNA gene pyrosequencing analysis revealed rapid shift in microbial community when conditions became strongly acidic (pH ~ 2) favoring the enrichment of Acidithiobacillus and Sulfobacillus bacteria in TT.

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This is the first report showing ARD potential of TT and the results have significant implications for effective management of pyrite-enriched oil sands tailings streams/deposits.

#### 1. Introduction

Surface mining of oil sands ores and subsequent water-based extraction of bitumen in Alberta, Canada generates ~1 million m<sup>3</sup> of fluid tailings day<sup>-1</sup> (http://www.aer.ca/rules-and-regulations/directives/ tailings-plans-2012) in various waste streams that comprise different proportions of sand, water, fine clays, unrecovered solvent hydrocarbons and unextracted bitumen. "Froth flotation tailings" differ from other tailings streams in having different mineralogy, including greater proportions of iron-containing minerals like pyrite (Kaminsky et al., 2009). Most tailings are retained as colloidal suspensions in anaerobic ponds below a water layer, preventing oxidation of solids that have significant proportions of iron sulfide minerals (Siddique et al., 2014). However, recent government regulations (http://www.aer.ca/documents/directives/ Directive074.pdf) require the operators to reduce the volume and increase the shear strength of retained tailings in preparation for reclamation (Dobchuk et al., 2013; Badiozamani and Askari-Nasab, 2014). One such technology in use is polymer flocculation of the fine clays followed by deposition as thin layers on gentle slopes to de-water the tailings by evaporative drving and collection of runoff (http://www.suncor.com/: BGC Engineering Inc., 2010). Unless the drying tailings are constantly being covered by new layers of wet tailings, this technology potentially exposes the fine clays in these 'thickened tailings' to atmospheric oxygen  $(O_2)$  and natural precipitation (water;  $H_2O$ ).

Acid rock drainage (ARD), also called acid mine drainage, is the result of H<sub>2</sub>O, atmospheric O<sub>2</sub> and, typically, microorganisms interacting with metal sulfides, most commonly pyrite (FeS<sub>2</sub>); this process releases soluble Fe and other toxic metals and generates acidic leachates (Mason, 2002; Johnson, 2003). ARD is a global environmental problem, occurring when sulfide-containing rock is exposed naturally (Kwong et al., 2009; Graham and Kelley, 2009; Verplanck et al., 2009; Dold et al., 2013) or as a result of construction activity (Gusek et al., 2011) or mining (Egiebor and Oni, 2007; Geller et al., 1998). Thus, ARD is a potential consequence of pyrite-rich oil sands tailings undergoing evaporative drying.

The following equations comprising spontaneous and microbialmediated reactions describe this process, although additional reactions involving precipitation are also possible (Akcil and Koldas, 2006):

$$2FeS_2(s) + 7O_2(g) + 2H_2O = 2Fe^{2+}(aq) + 4H^+(aq) + 4SO_4^{2-}(aq)$$
(1)

$$4Fe^{2+}(aq) + O_2(g) + 4H^+(aq) = 4Fe^{3+}(aq) + 2H_2O(l)$$
(2)

$$\begin{aligned} FeS_2(s) + 14Fe^{3+}(aq) + 8H_2O(l) &= 15Fe^{2+}(aq) + 2SO_4^{2-}(aq) \\ &+ 16H^+(aq) \end{aligned} \tag{3}$$

The generation of Fe<sup>3+</sup> ions in solution significantly accelerates dissolution of pyrite and further acidification, which in turn solubilizes toxic heavy metals. Thus, waste rock, tailings and mine structures containing iron sulfide-aggregated rock have ARD potential (McLemore, 2008). Incursion of ARD into surface waters can significantly impact the chemistry and biology of natural and engineered ecosystems, reducing the value of the water for agricultural, recreational, or industrial uses, rendering it unsafe for human consumption and having a negative effect on the biota (Tripole et al., 2006). On the other hand, ARD potential can be balanced by the presence of minerals such as calcite and dolomite that can neutralize acidity (Johnson and Hallberg, 2005) and prevent or inhibit ARD.

Because of the large volumes of oil sands tailings that may be treated using evaporative drying technology, oil sands tailings pond managers are interested in predicting and pre-empting the potential for ARD generation. We received samples from field trials of two froth treatment thickened tailings (TT) having different pyrite and carbonate contents that were either pre-treated or not pre-treated with polymer (polyacrylamide) used as a flocculant. Here we used predictive chemical and mineralogical analyses of bulk TT to determine ARD potential (static tests) followed by demonstration of changes to leachate chemistry and solid phase during long-term laboratory incubation of TT in shallow irrigation trays (kinetic tests), generally following the approach described by Sapsford et al. (2009). The trays were incubated under continuous air flow to simulate evaporative drying, irrigated periodically using either artificial rainwater or distilled water and subjected to leachate collection over the period of incubation. Both leachate and solids were analyzed to observe the onset of ARD from these field materials.

#### 2. Material and methods

#### 2.1. Experimental approach

A field trial was established in late 2011 in the Athabasca region of northern Alberta, Canada to test evaporative drying of froth flotation thickened tailings (TT), investigate technical aspects of TT placement in drying cells and measure geotechnical performance of two different TT preparations; one was treated with a flocculant and the other remained untreated. Eight rectangular drying cells (surface earthen pits of ~7 m long, 2.5 m wide, 3.2–5.2 m deep and with steep wall slopes and base slopes of 0.7–4.3%) were constructed and instrumented for characterizing the performance of tailings deposits. TT samples were deposited in the drying cells up to 2 m thickness. Twenty-liter samples were collected in June 2012 after spring thaw from the upslope areas of Cell #1 (no flocculant treatment; TT1) and Cell #5 (treated with polyacrylamide as a flocculant; TT2). The pliant samples were wrapped in plastic bags with most air excluded and sealed inside polyethylene pails in the field; they were analyzed chemically immediately after receipt (Section 2.1.1) then stored approximately 1 month at room temperature in the laboratory until establishing the kinetic experiment (Section 2.1.2).

#### 2.1.1. Static test (initial bulk analyses) of TT to predict ARD potential

TT samples collected from the field trial were immediately subjected to standard physical (texture), chemical (pH and acid–base accounting; ABA) and mineralogical (sulfides and carbonates) analyses as described in Section 2.2. Numbers of acidophilic and neutrophilic sulfide-oxidizing microbes (ASOM and NSOM, respectively) were determined using the Most Probable Number (MPN) method and media with Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> described by Roberts et al. (2002) except that triplicate MPN tubes were used, and serial dilutions were performed in sterile potassium phosphate buffer.

#### 2.1.2. Kinetic laboratory experiment to determine ARD potential

A kinetic laboratory experiment was performed to determine the rates of dissolution of minerals (pyrite and carbonates) and acid generation from TT under controlled irrigation and air flow. The experiment was conducted in shallow polypropylene trays containing TT. The bottom of each tray ( $290 \times 150 \times 90$  mm; Cambro, USA) was perforated and placed into a second tray fitted with two ports: one for vacuum application to enable leachate recovery and the other for leachate collection (Fig. A1). Pre-weighed TT (1.5-2 kg wet weight) was gently

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