



Influence of a tundra freeze–thaw cycle on sulfide oxidation and metal leaching in a low sulfur, granitic waste rock[☆]



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ABSTRACT

Drill cuttings were collected at 1 m depths from an instrumented, low sulfur, experimental waste rock pile containing a 4C-pyrrhotite that had been exposed to the extreme freeze–thaw cycle of a tundra climate. Boreholes were drilled from the top to base in the center of the pile and near the core–batter transition. Waste rock samples were analyzed for carbon, sulfur, and metal concentrations; sulfide oxidation states; and variation in iron and nickel forms due to oxidative dissolution of pyrrhotite. Results from X-ray absorption spectroscopy and aqueous extraction experiments were used to relatively compare samples from various depths in the boreholes, which indicate sulfide weathering fronts that decrease in intensity from the top to core to base at the center of the pile and from the core–batter transition to the center of the pile. The tundra climate and waste pile configuration produce a permafrost base, a seasonally frozen core, and an atmospheric-like zone near the surface. The fluctuation of the freeze–thaw cycle caused the greatest sulfide weathering near the surface and lesser weathering in the core and base of the pile. Metal- and sulfur-rich leachate from the higher weathering zone likely is collecting on a variable and seasonal frozen surface beneath the surface layer that causes metals and S to precipitate and (or) sorb during a portion of the year. The accumulation of sulfur and metals with the flux of this frozen surface produces a nickel and possibly an iron and sulfur enrichment zone beneath the surface layer in the center of the pile. The weathering front from the top to core to base of the pile and from core–batter transition to the core corresponds to a previously formulated leachate model, but the enrichment zone below the surface zone is unique to this conceptual waste-rock weathering model for this tundra climate.

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1. Introduction

The expansion of hard-rock mining in permafrost regions has created new questions concerning the generation of acid rock drainage (ARD) from sulfidic waste rock and the protection of natural environments (Dawson and Morin, 1996; Lemly, 1994; Mine Environment Neutral Drainage, 1998). The release of sulfate (SO_4^{2-}) and transition metals (e.g., Co, Cu, Fe, Ni, Zn) in ARD can be a

significant environmental concern, particularly in sensitive regions such as the tundra of northern Canada. The generation of ARD is affected by microscale properties, such as mineral composition and surface area that influence oxidation and dissolution processes (Blowes et al., 2003; White and Peterson, 1990), as well as macroscale properties, such as precipitation and temperature that influence transport processes (Kyhn and Elberling, 2001; Ritchie, 1994). The freeze–thaw cycle of a tundra climate can have microscale influences, such as changes in microbial populations and reduced chemical reactions, as well as macroscale influences, such as restricted leaching because of seasonal ice or permafrost conditions (Langman et al., 2016). The Diavik Waste Rock Project was implemented to examine the potential for and extent of ARD from run-of-mine (ROM) waste rock in a permafrost environment. A

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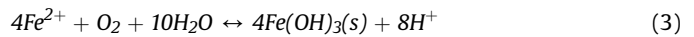
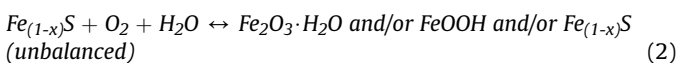
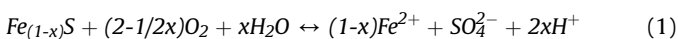
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significant part of the project included the long-term (years) monitoring of leachate, porewater, temperature, atmospheric conditions, and collection of periodic mineral/rock samples at a mine-site, experimental, waste-rock pile (pile) constructed of a low sulfur, granitic waste rock (site designation: Type III test pile).

The limited sulfide in the Diavik waste rock has been sufficient to generate acidic leachate and release significant SO_4^{2-} and Ni^{2+} ions (Bailey et al., 2016; Langman et al., 2014, 2015a; Sinclair et al., 2015; Smith et al., 2013a). From solute concentrations in porewater (interstitial water) and leachate (percolated water), Sinclair et al. (2015) formulated a conceptual model of the pile's annual leachate cycle. This leachate model consists of a seasonal divide of primarily large volume, low solute concentration leachate from near surface (surface zone) and batter areas during the early thaw period of late spring to early summer (snowmelt) and a small volume, high solute concentration leachate from the core and base (ice melt + precipitation) during the late thaw period of late summer and early fall (Fig. 1). Although the core and near surface zones are exposed to similar amounts of time above freezing (Pham et al., 2013; Sinclair, 2014), the two areas represent different environments—an extreme and quickly changing environment in the surface zone and batters and a moderated environment in the core. The solute load is nearly evenly divided between these two periods, which are followed by cessation of leachate from mid-fall to late spring (Sinclair, 2014). As part of the Diavik project, waste rock samples were collected from two boreholes in the pile to evaluate the leachate model at the mineral scale and the retention/release of the sulfide elements—Fe, Ni, and S—with weathering in the tundra's freeze-thaw cycle.

The oxidation of sulfide minerals in waste rock is initially rapid because of their high reactivity under atmospheric conditions, but subsequent oxidation and dissolution may be constrained by the formation of oxidized zones around a shrinking sulfide core and the availability of oxygen and water (Blowes et al., 2003; Mayer et al., 2002; Nordstrom and Alpers, 1999). This shrinking core concept of Fe-sulfide oxidation (Mayer et al., 2002; Wunderly et al., 1996) may produce alteration rims of oxidized S and Fe and on-grain precipitates (Belzile et al., 2004; Cruz et al., 2005; Mycroft et al., 1995) or non-grain but proximate Fe (oxyhydr)oxide precipitates (distal precipitates) (Langman et al., 2015b). Continued oxidation of the sulfide core occurs with diffusion of oxidants through the potentially mixed Fe-phase oxidized zones and the diffusion of oxidized S from the core to solution (Davis and Ritchie, 1986; Ritchie, 1994; Wunderly et al., 1996). The Fe oxidized zones may contain other metals, such as Ni, that were Fe substitutes in the original sulfide minerals, and their sorption to the Fe (oxyhydr)oxides can inhibit their release from the weathering sulfide (Belzile et al., 2004; Langman et al., 2015b). The leaching of fully oxidized S as hydrophilic SO_4^{2-} (Eq. (1)) and retention of Fe (Eqs. (2) and (3)) can produce various Fe (oxyhydr)oxides, such as goethite [α -FeO(OH)], lepidocrocite [γ -FeO(OH)], magnetite [$\text{Fe}^{2+}\text{Fe}^{3+}_2\text{O}_4$], ferrihydrite [$\text{Fe}_2\text{O}_3 \cdot 0.5\text{H}_2\text{O}$], and hematite [Fe_2O_3] with associated substitute metals potentially sorbed to these Fe (oxyhydr)oxides or incorporated into the Fe mineral phases. Sorption of other metals such as Ni can occur at near-neutral pH in the presence of α -FeO(OH) (Bruemmer et al., 1988; Rose and Bianchi-Mosquera, 1993), amorphous Fe(OH)₃ (Green-Pedersen et al., 1997), $\text{Fe}^{2+}\text{Fe}^{3+}_2\text{O}_4$ (Nassar, 2012), $\text{Fe}_2\text{O}_3 \cdot 0.5\text{H}_2\text{O}$ (Stumm and Morgan, 1996), Fe_2O_3 (McKenzie, 1980), and Fe oxide nanoparticles (Nassar, 2012; Salmani et al., 2013).



The formation of Fe oxidized zones and Fe distal precipitates is balanced by the reduction of these zones through hydrolysis and dissolution (Mycroft et al., 1995; Thomas et al., 1998, 2001). The extreme environment of the tundra climate hinders our prediction of the formation of ARD because the freeze-thaw cycle influences oxidative dissolution of the sulfide minerals at the microscale and inhibits the movement of water at the macroscale. Results of the experiments conducted for this study were used to determine the influence of the freeze-thaw cycle on sulfide weathering between early thaw areas (surface zone and batters) and late thaw areas (central core and base) of the pile. The early thaw areas represent the first portions of the pile to contribute to leachate released from the pile (large volume, low concentration solute) but also the first areas to freeze (Fig. 1). Examination of spatial differences in solute reservoirs between early and late thaw areas will elucidate potential differences in sulfide weathering in this tundra climate and potential permafrost conditions in the waste rock pile. Results of this study will further resolve the Sinclair et al. (2015) leachate model and allow for improved reaction and leachate parametrization for ARD prediction under such extreme freeze-thaw conditions.

1.1. Climate and waste rock characteristics

The Diavik Diamond Mine is located on an island in Lac de Gras, Northwest Territories, Canada (Fig. 2), in the Canadian Arctic—a permafrost, tundra-climate area with an annual precipitation of less than 300 mm (40% as rain, 60% as snow) and average minimum, mean, and maximum monthly temperatures of -31 , -9 , and 18 °C (Environment Canada, 2013). An active freeze-thaw zone extends 4 m into the bedrock, and deeper into unconsolidated materials (Pham et al., 2013). The waste rock is composed of about 75% granite, 14% pegmatitic granite (pegmatite), 10% biotite schist, and 1% diabase (Blowes and Logsdon, 1998). The Archean granite and pegmatite are massive and moderately to coarsely crystalline, and the metasedimentary schist occurs as xenoliths within the granite. The granites are primarily quartz [SiO_2], K-feldspar [KAlSi_3O_8], and albite [$\text{NaAlSi}_3\text{O}_8$] (Jambor, 1997). The biotite schist is composed of albite (35–55%), quartz (20–50%), and biotite [$\text{K}(\text{Mg},\text{Fe})_3\text{AlSi}_3\text{O}_{10}(\text{OH})_2$] (10–25%) with a mean sulfide content of 0.24 wt % S (range 0.02–0.42 wt % S). The waste rock pile is poorly sorted and composed of boulders to very fine grain material with a possible granule mean grain size (Chi et al., 2013).

The sulfide component of the waste rock is mostly (>70%) a 4C-pyrrhotite [Fe_7S_8] ranging from 50 to 200 μm in diameter, but traces of pyrite [FeS_2], chalcocopyrite [CuFeS_2], and sphalerite [(Zn,Fe)S] are present (Bailey et al., 2016; Jambor, 1997). The pyrrhotite contains traces of Ni and Co [($\text{Fe}_{0.852}\text{Ni}_{0.004}\text{Co}_{0.001}\text{S}_{\Sigma 0.857}\text{S}$)] (Jambor, 1997), and pentlandite [(Fe,Ni)₉S₈] lamellae have been found in a minority of grains (Langman et al., 2015b). An examination of weathered pyrrhotite in Diavik waste rock indicates a thiosulfate pathway of sulfide oxidation and correlation of Ni and SO_4^{2-} release with weathering (Langman et al., 2015b). Well-oxygenated conditions, which are prevalent in the pile (Amos et al., 2009; Langman et al., 2015a; Neuner et al., 2013; Smith et al., 2013a), tend to favor the thiosulfate pathway (Druschel et al., 2003; Schippers and Sand, 1999; Suzuki, 1999). The average leachate velocity is about 0.3–0.5 m per month (Krentz, 2014). Monitoring of leachate from the pile indicates seasonal changes in S and metal concentrations because of the freeze-thaw cycle, as described in the Sinclair et al. (2015) leachate model. Pile leachate collected between 2008 and 2012 contained significant concentrations of Ni ($\mu = 30 \text{ mg L}^{-1}$) but only small concentrations of Fe ($\mu < 2 \text{ mg L}^{-1}$) (Sinclair et al., 2015).

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