Diavik Waste Rock Project: Geochemistry of Low Sulfide Content Large-scale Waste-rock Test Piles

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Abstract
Sulfide minerals in waste-rock stockpiles can oxidize and generate acid mine drainage. Two waste-rock test piles were constructed at the Diavik diamond mine to evaluate the quality of effluent released from waste rock with differingsulfur contents. The Type I test pile contains ~ 0.035wt.%S and the Type III test pile ~ 0.058 wt. % S, both measure 15 m in height by 60 m wide and 50 m long at the base. On-going monitoring of the geochemistry of the test-pile porewater and effluent began in 2007. Drainage from the Type I test pile maintained a near-neutral pH (ranged from 5.8 to 8) with concentrations of SO_4< 500 mg/L. As air temperatures increased in spring and summer of each year, the measured pH in the Type III test pile drainage decreased from near-neutral in May (pH 7.5) to acidic conditions by October (ranged from 5 to 4.5). As the pH in the Type III test pile decreased, concentrations of SO_4 and other metals increased (e.g. SO_4>1500 mg/L) suggesting sulfide oxidation was occurring. The increase in SO_4 and most dissolved metals coincides with the decrease in pH to 4.5. Maximum concentrations of SO_4, Al, Zn, Ni, Co, and Cu were observed in 2009 during the first flush of water through the test pile.

Key Words: Arctic, waste rock, diamond mine, low sulfur content

Introduction
Waste rock is generated to gain access to an economically exploitable ore body and is generally stockpiled on the Earth's surface. Waste rock stockpiles at mine sites can range in size up to tens of hectares in area and tens of meters high (Ritchie, 1994). The generation of acid mine drainage (AMD) from these stockpiles is dependant on the concentrations of reactive minerals, such as pyrite or pyrrhotite. There is no recommended lower limit of % S in predicting AMD unless the neutralization potential is sufficient to neutralize the resulting acid (Price, 2009). The release of AMD from unsaturated waste rock piles with low sulfide content is not well documented.Furthermore, the effects of cold Arctic environments on the kinetics of these processes are not well documented.

The expansion of mining in northern Canada has increased the demand for information pertaining to long-term environmental impacts of mining in the Arctic, where unique climatic and physiographic conditions exist. Two of the objectives of this collaborative research project are to examine the quality of drainage from waste-rock piles and the role of bacteria in the biogeochemical evolution of waste-rock effluent. This paper summarizes the water quality from two experimental waste-rock piles (test piles), with low sulfide mineral content, that are located in a continuous permafrost region. Effluent and pore water samples were collected and analyzed for pH, Eh, EC, TDS, acidity/alkalinity, sulfate, major ions, and trace metals overtime to compare the effluent geochemistry from two test piles. Saturation indices (SI) for discrete mineral phases were calculated to assist in the interpretation of aqueous geochemistry.The design, construction and initial results are described by Smith *et al.* (2009, 2012), the thermal regime within the test piles is described by Pham *et al.* (2011), air flow through the Type III test pile is described by Amos *et*

al. (2009), and the hydrogeology is described by Fretz *et al*. 2011. Microbiology in the test piles is discussed by Bailey *et al.* in this volume (2012).

Site description

The Diavik diamond mine is located 300 km northeast of Yellowknife, NWT in the Slave geologic province and a continuous permafrost region (Figure 1). The mine-site facilities are located on an island in Lac de Gras, an oligotrophic lake. The open pit and underground mining operation will generate a 120Mt waste rock stockpile over the course of production. Host rocks consist mainly of granite and pegmatitic granitelithologies containing irregular xenoliths of biotite schist. These host rocks are cut by diabase dikes. Carbonates are present in the fractures of the granite (unpublished data). The granite and pegmatitic granite contain only trace sulfides and are considered non-acid generating with little neutralization potential (Smith *et al.*, 2012). The biotite schist contains locally disseminated pyrrhotite with trace amounts of other sulfides and is considered potentially acid generating with little neutralization potential (Smith *et al.*, 2012). Diavik segregates the host rock based on target sulfur content: Type I (target of <0.04 wt. % S), Type II (target of 0.04 wt. % S to 0.08 wt. % S), and Type III (target of > 0.08 wt. % S).

Figure 1.Location of the Diavik Diamond Mine.

Research facilities

Three large-scale waste-rock test piles were constructed as part of a multidisciplinary research program. Detailed construction and instrumentation of the research facilities are described by Blowes *et al*. (2006) and Smith*et al*. (2009). Each test pile was constructed on a graded and sloped base lined with high density polyethylene (HDPE). All infiltrating water reaching the base of the test piles was directed through heat-traced drainage lines to instrumentation trailers (Figure 2b).

Inside these trailers, water was collected in a series of three plexiglass flow-through cells (Figure 3): the first cell for collecting water samples (A), the second for continuous measurements of pH (B), and the

third cell for continuous measurements of conductivity and temperature (C). Water was then directed to a tipping bucket to measure the flow rate (D).

Figure 2. a) Graded and sloped base prior to HDPE liner placement b) drainage lines from the Type I basal drain to the instrumentation hut.

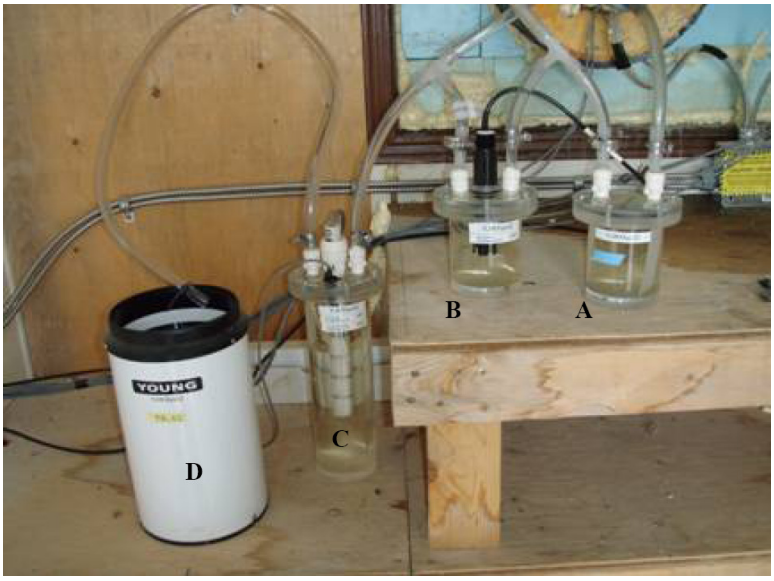

Figure 3. Flow through cell set-up A) water sampling cell B) pH measurements C) electrical conductivity measurements D) flow measurements

Two waste-rock test piles measure 15 m in height by 60 m by 50 m at the base; the Type I test pile consists of waste rock with 0.035 wt. % S (n= 242, σ=0.019) and the Type III test pile consists of waste rock with 0.053 wt. % S (n=270, σ=0.037) (Smith *et al.*, In press; Figure 4). The average carbon content of the Type I test pile was 0.028 (n= 60; σ=0.007) and the average carbon content of the Type III test pile was 0.030 (n= 208; σ=0.006). The third test pile, constructed based on a proposed reclamation concept, consists of Type III waste rock (0.082 wt % S, n=183, σ=0.053) resloped and capped with a lower permeability till layer and freeze-thaw layer (not discussed in this paper) (Smith *et al.*, In press; Figure 4).

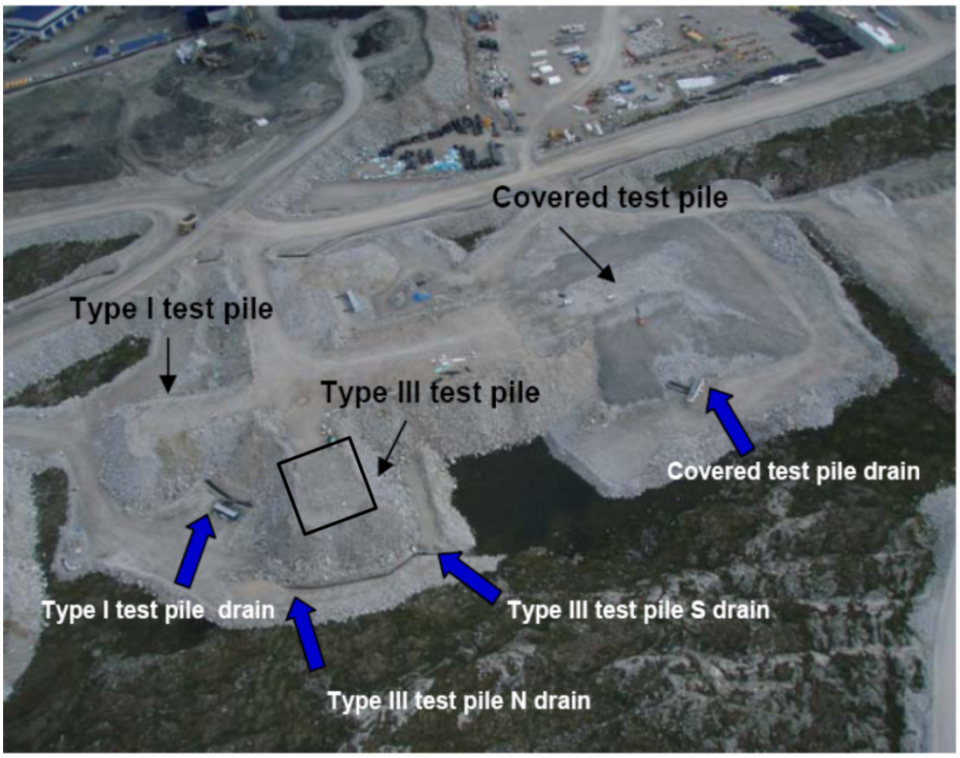

Figure 4. Test pile research facilities at Diavik.

Soil water solution samplers (SWSS) were installed at various depths in the test piles to extract pore-water samples from the unsaturated matrix. Construction and distribution of the SWSS in each test piles is described in detail by Smith *et al.* (2012). The SWSS consisted of a porous ceramic cup attached to a polyvinyl chloride (PVC) pipe capped at the top, with two 0.64 cm polyethylene (PE) tubing lines extending to the surface of the waste rock test pile (Figure 5). The SWSS were surrounded with fine-grained waste rock (< 25 mm fraction), either Type I or Type III, held in Nitex nylon screen bags (175 x 325 mm) to ensure hydraulic contact between the tip and matrix material (Figure 5). Tubing connecting the SWSS to the surface was strung through 50 mm flexible PVC protective conduit that contained heat trace.

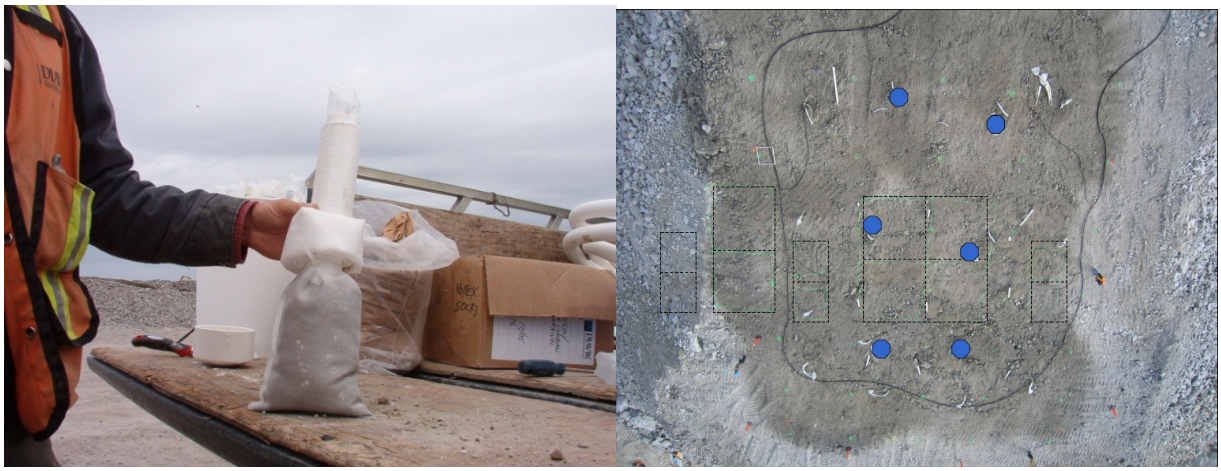
Figure 5.a) Constructed SWSS prior to placement in the waste rock test pile b) aerial view of the Type III test piles (black square in Figure 4) to show location of SWSS strings (blue dots)

Methods

Water samples

Effluent samples were collected from the Type I test-pile basal drain (Figure 4). The Type III test pile has two sampling locations; the Type III test-pile north and south basal drains(Figure 4). Water samples were collected from flow through cells using 0.64 cm PEtubing attached to a sterile 60 mL PE syringe. SWSS were used to extract pore water samples under a $N_{2(g)}$ atmosphere and an initial vacuum of 40-50 kPa. Water from the SWSS was collected through a flow-through cell and samples were retrieved with sterile PE syringes.

At each sampling location, the pH, E_h, EC, temperature, and alkalinity were determined for water collected from the sampling cell system. Field measurements were completed using a Hach spectrophotometer DR/8400 for the determination of o-PO_4, Fe(II), H_2S, and NH_3 concentrations (SMEWW, 2005). Concentrations of anions were determined from unacidified, 0.45 µm filtered samples and concentrations of total (unfiltered) and dissolved (filtered) cations were determined from acidified water samples.

Speciation calculations were conducted on samples collected from the Type I test-pile basal drain and Type III test-pile north and south basal drains with a complete suite of field and laboratory analyses in order to assist in the identification of mineral phases potentially controlling the composition of the aqueous phase. The equilibrium/mass-transfer model MINTEQA2 (Allison *et al*., 1990),with a modified database for consistency with the WATEQ4F (Ball and Nordstrom, 1991) database, was used to calculate the SI for discrete mineral phases.

Results and Discussion

Type I test pile

Flow first reported to the base of the Type I test pile in 2008 (Figure 6).Measurable alkalinity was present in the Type I test-pile effluent for the duration of this study; however, concentrations decreased through each field season with pH, reaching a minimum of < 5 mg/Lat the end of each field season. The Type I test-pile effluent maintained a near-neutral pH (ranged from 5.8 to 8) with low concentrations of SO_4 (< 500 mg/L), Fe (< 1.4 mg/L) and other metals,such as Ni and Zn, (Figure 7)from 2007 through 2009. In 2010, when the flowrate decreased at the end of the field season, the concentrations of SO_4 and NO_3increased. These higher concentrations probably were derived from blasting residuals (Bailey *et al*., 2012. The pH decreased each year, concurrently with increased concentrations of SO_4 and metals, as the internal temperature in the Type I test pile increased in the summer and as larger portions of the pile contributed to the outflow. The pore water extracted from SWSS at various depths show near neutral pH (6 to 7.5) and low concentrations of SO_4 (300 to 1100 mg/L), and dissolved metals. The concentrations from the SWSS were drawn largely from the matrix material not the macropores and thus, had higher concentrations than the basal drains.

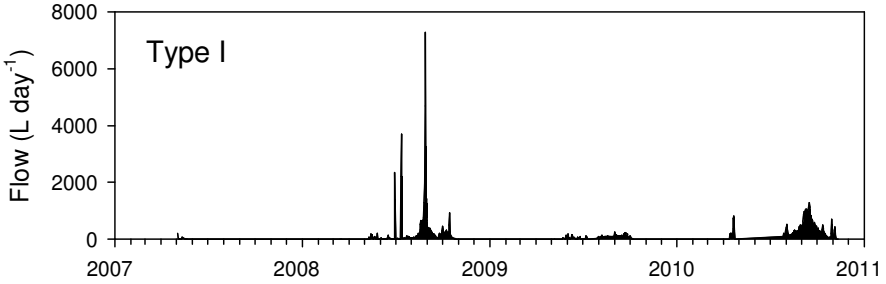

Figure 6.Flow (L day^{-1}) for each location from 2007 through 2010.

The first volume of water that moves through the total matrix porosity within a given volume of waste rock (known as the “first flush”) contains high concentrations of blasting residuals (Bailey *et al*., 2012).

After the first flush of water through the matrix material in the Type I test pile, SO_4 due to blasting is expected to have been flushed from the pile (Bailey *et al.*, 2012).

Geochemical equilibrium modeling suggests the Type I test-pile effluent was at equilibrium with respect to calcite at the beginning of 2008 for a short period of time and was undersaturated with respect to calcite from 2008 through to 2010 (Figure 8). The limited acid generating potential of this waste rock suggests the pH remained near neutral due to the modest alkalinity in the effluent, which has not been consumed by acid generating reactions. These results suggest that the initial pH values, near pH 7.0, were associated with the presence of carbonates in the waste rock and the lack of intense acid generation.

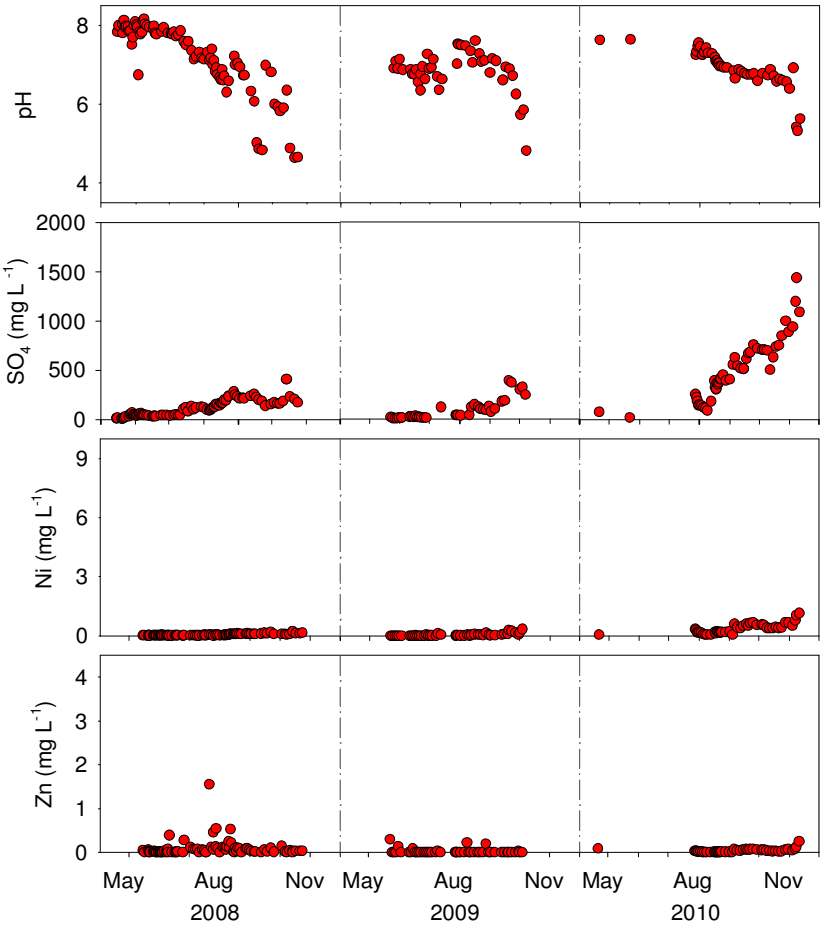

Figure 7. Drain geochemistry from Type I test-pile basal drains.

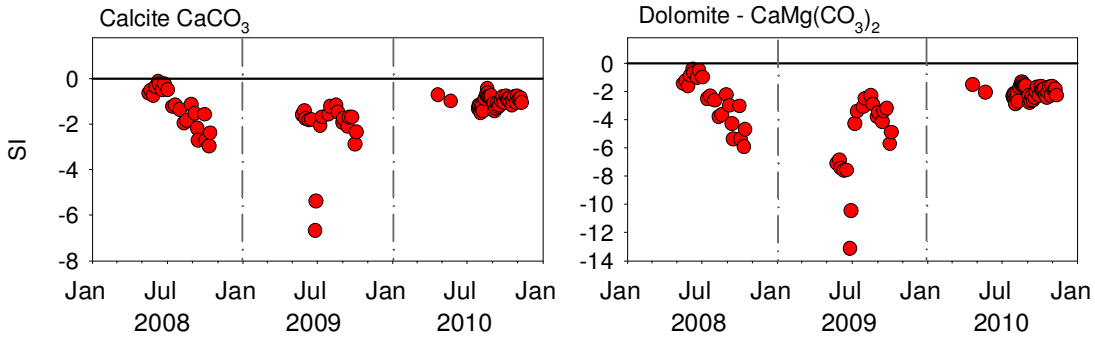

Figure 8. Saturation indices (SI) for calcite and dolomite from the Type I basal drain effluent.

Type III test pile

Flow first reported to the base of the Type III test pile in 2007 (Figure 9). Measurable alkalinity was detected in the Type III test-pile basal drains in 2007. Concentrations decreased along with decreasing pH through the end of the field season (Figure 10). The pH in the Type III test-pile basal drains decreased in 2007 from near-neutral in May to acidic conditions in October. A similar trend was observed in each subsequent year; however, the pH values observed in May decreased each year from 2008 through 2010.By the end of each field season, the rate of sulfide mineral oxidation exceeded the rate of carbonate mineral dissolutionalong the active flow paths.As the pH in the Type III test-pile basal drains decreased, concentrations of SO_4, Feand other metals increased, suggesting more intense sulfide oxidation was occurring. The increase in SO_4, Fe and most dissolved metals coincides with the decrease in pH to 4.5 (Figure 10). Maximum concentrations of Fe, SO_4, Al, Zn, Ni, Co, and Cu were observed in 2009 at the end of the first flush of water through the matrix material in the Type III test pile. Pore water in the Type III test pile containedhigh concentrations of SO_4 (4500 mg/L), Al (79 mg/L), Ni (25 mg/L), Cu (6.6 mg/L), Zn (18.5 mg/L), Co (5.5 mg/L) by 2010 in near surface pore water.

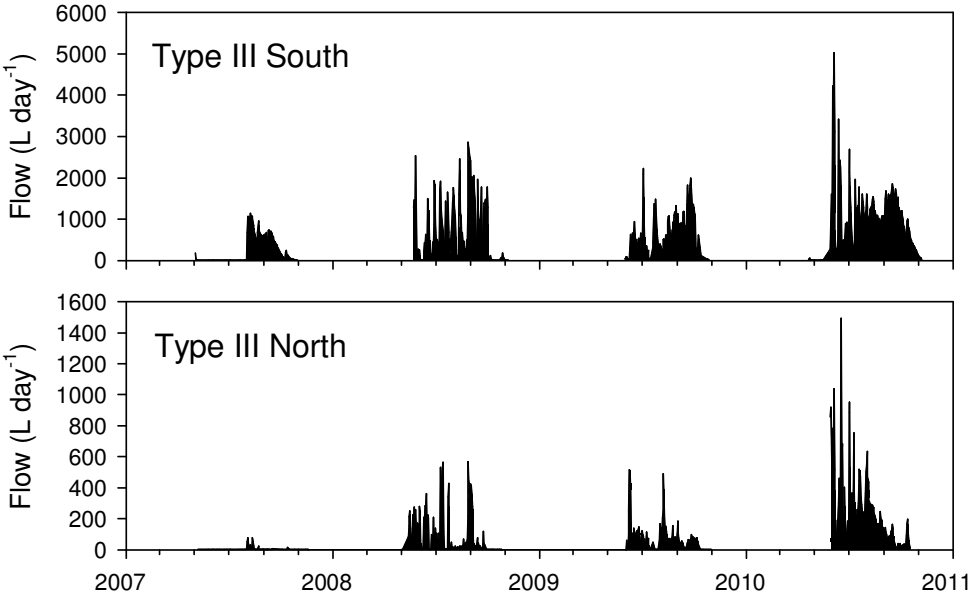

Figure 9. Flow (L day^{-1}) for the Type III north and South basal drains from 2007 through 2010.

The initial concentrations of SO_4 released in 2007 were well correlated to the concentrations of NO_3, suggesting that the oxidation of sulfide minerals during blasting was the principal source of SO_4, rather than *in situ* oxidation. In subsequent years, much of the SO_4 released from the Type III test pile was derived from *in situ* sulfide-mineral oxidation (Bailey *et al.*, 2012). An exception to this occurred at the end of each field season when the concentrations of SO_4 and NO_3 increased and were highly correlated. The correlation between SO_4 and NO_3 concentrations suggests that a portion of this SO_4 was derived from the oxidation of sulfide minerals during blasting. The observed lag in the release of blasting residuals suggests that there is only limited water flow within portions of the Type III test pile.

Geochemical equilibrium modeling suggests the Type III test pile effluent was undersaturated with respect to all carbonate minerals (Figure 11). It is likely that acid generation in the Type III test pile exceeded the neutralizing capacity available from carbonate minerals by the end of each field season. After the depletion of accessible carbonate minerals, the pH was controlled by the relative rate of Al- and Fe-hydroxide mineral dissolution.

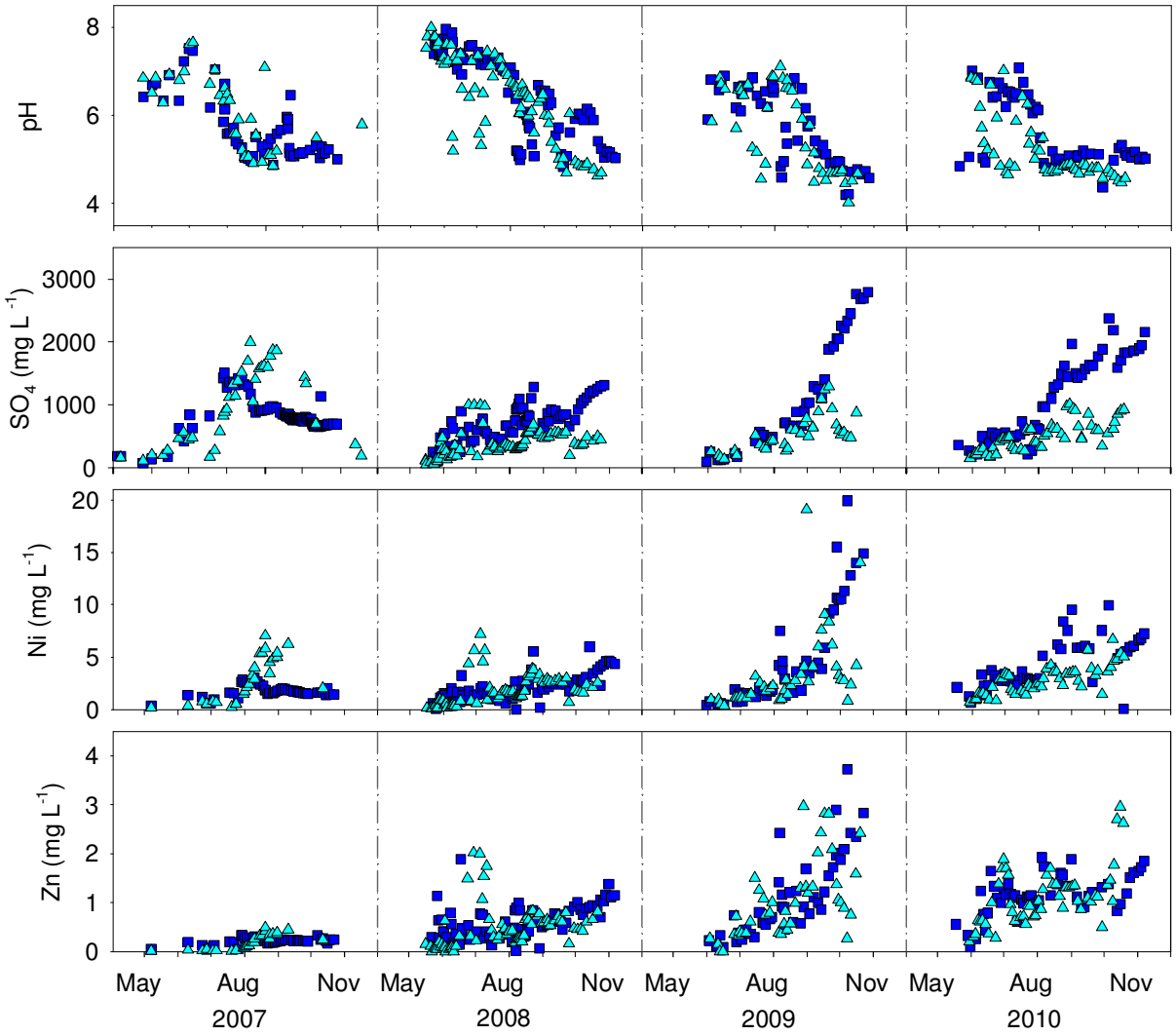

Figure 10.Effluent geochemistry from Type III north (triangle) and Type III south (square) test-pile basal drains.

In mill tailings impoundments, the dissolution of Al-hydroxides results in an increase in the release of Al and maintains the pore water pH to 4.0 – 4.5 (Jurjovec*et al.*, 2002). Each year, the pH of the Type III test-pile effluent decreased from near neutral to a pH near 5.0. The pH remained relatively constant at this value for several weeks, forming a plateau in the pH values, which corresponded to an increase in Al concentrations from < 2 mg/L in 2007 to a range of 6 to 16 mg/L. Geochemical equilibrium calculations suggest that this shift in pH is associated with the dissolution of Al-hydroxide minerals. Initially, the Type III test-pile effluent was supersaturated with respect to gibbsite and boehmite. Geochemical calculations indicate a shift to equilibrium with respect to gibbsite and boehmite as the pH decreased near the end of the field season. The Type III test-pile effluent remained supersaturated with respect to goethite throughout the monitoring period. Further mineralogical examination of these waste rock piles is required to substantiate the results from geochemical equilibrium modelling.

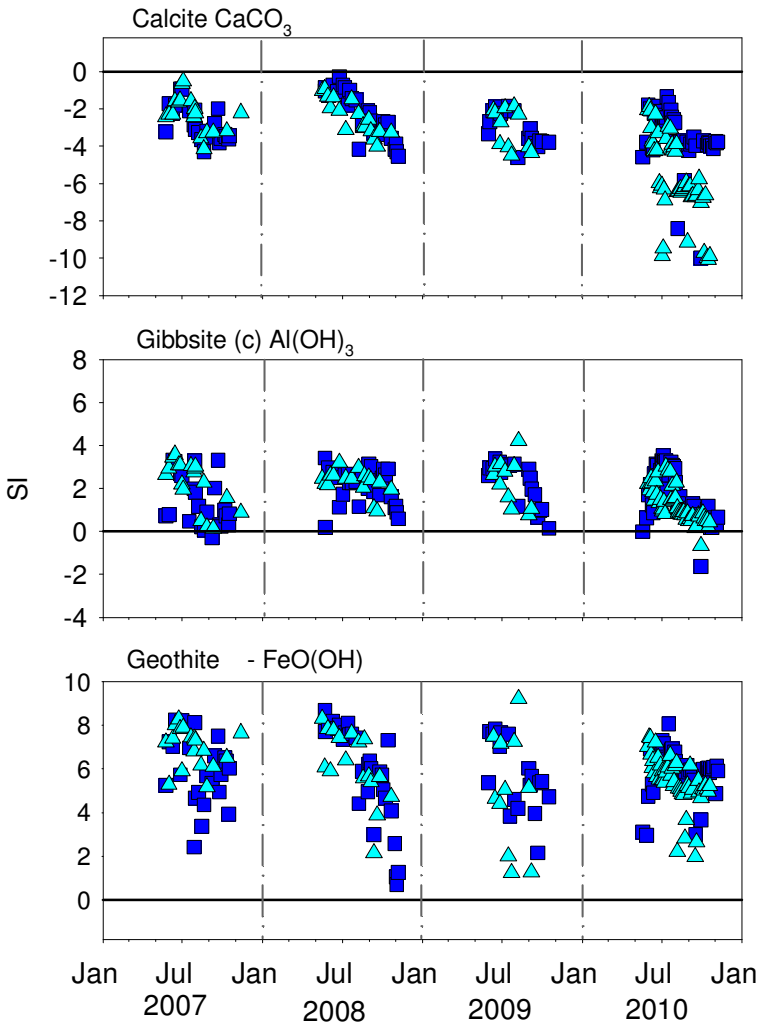

Figure 11. Saturation indices (SI) for the Type III north (triangle) and south (square) test –pile basal drain effluent.

Conclusions

The Type I test-pile effluent is characterized by near-neutral pH and low concentrations of SO_4 and dissolved metals. Sulfide mineral oxidation in the Type I test pile was balanced by acid neutralization through carbonate mineral dissolution. The effluent of the Type III testpileis characterized bya low pH and elevated concentrations of SO_4 and dissolved metals. The rate of sulfide mineral oxidation in the Type III testpile exceeds the rate of acid consumption by carbonate minerals, resulting in the generation of acidic drainagefrom waste rock with 0.058 wt. % S.

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