

Neutral mine drainage water-quality impacts from a former taconite mine

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ABSTRACT: Surface waters at the site of a former Minnesota taconite mine were reported to have solute concentrations elevated with respect to water-quality standards. Waste rock and ore generated from past mining were primarily from open pit mining of the Biwabik Iron Formation (BIF). The BIF is a variably bedded iron formation composed of inter-bedded cherty and slaty iron silicate and iron carbonate rich beds. A geochemical characterization was conducted to identify potential constituents of interest (COI), facilitate understanding of mechanisms controlling their environmental behavior at the site, and guide future site activities. Primary COI were determined to be SO_4 , hardness (predominantly from Mg), alkalinity, Fe, Mn, and Al. BIF waste rock from the Lower Slaty member appears to be the primary source for the identified COI. Mechanisms of release are primarily attributed to pyrite oxidation and subsequent neutralization by dissolution of mixed-composition (Ca-, Mg-, Fe-, and Mn-bearing) siderite and ankerite.

1 INTRODUCTION

Open-pit mining of taconite ore has led to the formation of several mine pit lakes at a former taconite mine on the Mesabi Iron Range, in northeastern Minnesota. Water quality from the site, was evaluated during preliminary studies associated with redevelopment of the property and found to have elevated solute concentrations with respect to water-quality standards or regional background concentrations (e.g. for SO_4 , hardness, and alkalinity). A geochemical characterization was initiated at that time to assess the sources of the elevated concentrations and guide environmental planning. As part of this characterization, a variety of geochemical tests have been conducted on waste rock and waste rock leachate to help identify potential constituents of interest (COI) and facilitate understanding of the mechanisms controlling their release and subsequent behavior in the environment. This paper summarizes the methods, results, and conclusions from the geochemical characterization and presents the basis of a geochemical conceptual model that can be used to guide future management and development of the site.

2 SITE GEOLOGY

The site is located at the eastern end of the Biwabik Iron Formation (BIF). The BIF dips gently to the southeast, although the geology of the site is complicated by local folding and faulting. The BIF is classified into two types of iron formation: cherty iron formation, which is granular, massive, and typically rich in quartz and iron oxides, and slaty materials, which are generally finely laminated, fine-grained, and contain iron silicates and/or iron carbonates.

Wolff (1917) divided the BIF into four informal members: the Lower Cherty, Lower Slaty, Upper Cherty, and Upper Slaty. The Upper Cherty and Lower Cherty members comprise the primary ore zones due to their higher concentrations of magnetite and cherty silicate taconite, whereas the Lower Slaty and the Upper Slaty members are largely waste rock. The Lower Slaty member is approximately 75 feet to 85 feet thick. The P submember comprises the upper 60 feet to 75 feet and is a fine-grained, finely-laminated, dark gray to black slate containing some disseminated pyrite. At the base of the P submember is approximately 10 feet to 15 feet of the Intermediate Slate (locally

referred to as the Q submember). The Q submember is typically a black to dark-gray graphitic silicate- and quartz bearing ash-fall tuff containing up to 5% disseminated ultra fine-grained pyrite (Morey, 1993). Due to an erosional unconformity, the Upper Slaty member is absent from most of the site, and therefore the Lower Slaty member comprises the majority of the approximately 2×10^{11} kg of waste rock on site, particularly in areas of notable water quality.

3 METHODS

Samples of waste rock were recovered from stockpile drilling and selected for testing. Most samples were subjected to modified acid-base accounting, Synthetic Precipitation Leaching Procedure (SPLP) testing, aqua regia digestion, humidity cell testing, analysis of pore-water chemistry (for samples collected from the saturated zone), and (for a subset) X-ray diffraction analysis (XRD). Samples of diamond drill core were subjected to modified acid-base accounting, SPLP, aqua regia digestion, and (for a subset of samples) humidity cell testing and petrographic analysis. Detailed descriptions of the methods utilized in the collection and analysis of these samples are provided below.

3.1 Sample collection

3.1.1 Waste rock

Three boreholes were advanced in each of three stockpiles that together comprise more than 35% of the Lower Slaty waste rock on site. Sonic drilling methods were used to recover waste rock material from the stockpiles without the use of water. A 4-inch diameter core barrel was advanced 20 feet ahead of the 6-inch diameter casing while drilling above the level of the pit water, and was reduced to 10-foot runs below the water level. Samples were shaken out of the core barrel into 6-mil plastic sample bag sleeves. Samples were generally collected from three positions within the borehole: the surface directly below any cover materials present, just above the water level, and just above the bedrock. Samples were crushed to less than 1/4-inch diameter using a jaw crusher, after being allowed to air-dry overnight where necessary. The crusher was cleaned using brushes and jetted air between samples. After crushing, the samples were homogenized and split using the cone and quarter technique (Pitard, 1993). Samples were shipped overnight, under chain of custody, to Northeast Technical Services (NTS) in Virginia, MN and CANTEST, Ltd. in Burnaby, BC, for testing and chemical analyses.

Continuous diamond drill core through the Upper Slaty, Lower Slaty, and the Lower Cherty submembers immediately underlying the Lower Slaty was obtained from standard NQ diamond drilling core from three boreholes from mining activities. Samples for chemical analyses were collected from the Upper Slaty, Lower Slaty member of the Biwabik Iron Formation: submembers P and Q and the 20-foot interval underlying the Q submember (identified as the R submember of the Lower Cherty member). Samples taken for chemical analyses within these submembers were determined based on detailed geologic logging. Sample interval lengths were modified as necessary to ensure that geologic contacts were honored, with only one geologic stratum comprising any sample. Samples were shipped overnight, under chain of custody, to CANTEST, Ltd. in Burnaby, BC and to ACZ for testing and chemical analyses.

3.1.2 Existing water quality

Site water-quality monitoring has been conducted as part of an ongoing monitoring program. Groundwater samples to be analyzed for dissolved metals were filtered in the field using an in-line 45- μ m disposable filter, following the low flow purging procedure (EPA, 1996). Surface-water samples collected for dissolved metals were collected in unpreserved containers and were filtered and preserved (within 48 hours) upon receipt at the laboratory. Each sample container was labeled with a unique sample identification number, placed in a cooler with ice, and submitted to the laboratory for analysis. At each surface-water sampling site, sample bottles were filled using a clean sample bottle. Field blanks and field duplicate samples were collected at a ratio of one per sampling event. Samples were sent under chain of custody to NTS for chemical analyses for general parameters and metals (total and dissolved) by standard EPA methods (EPA, 2007).

Pore water was collected from waste rock stockpile boreholes using either a disposable bailer or a submersible pump. Several gallons were purged from the borehole prior to sampling with the disposable bailer. Between 20 and 30 gallons were purged prior to sampling with the pump. A total of 15 pore-water samples were analyzed for general parameters and metals (total and dissolved) by standard EPA methods. Samples were filtered in the field with a 0.45-micron vacuum filter and preserved with HNO_3 (for metals) and H_2SO_4 (for cations) in laboratory-provided sampling containers.

3.2 Mineralogy

The mineralogy of waste rock was evaluated using a combination of XRD, scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), and optical microscopy. The XRD analyses included standard qualitative analysis to identify the minerals present as well as quantitative phase analysis by Rietveld refinements for select samples to identify not only the minerals present, but also their relative abundance. The SEM and optical microscopy work was performed to identify the modes of occurrence of the carbonate and sulfide minerals, including their texture, grain size, morphology, and mineral association. The EDS analyses were conducted to determine the chemical composition of the carbonate and sulfide minerals.

3.2.1 XRD

Six samples of sonic drill core of the waste rock stockpiles were submitted for quantitative XRD analysis at The University of British Columbia Dept. of Earth and Ocean Sciences. Samples were ground at CANTEST, Ltd. to $<10\ \mu\text{m}$ under ethanol in a vibratory McCrone Micronising Mill for seven minutes. Step-scan X-ray powder-diffraction data were collected over a range of 3° to $80^\circ\ 2\theta$ with $\text{CoK}\alpha$ radiation on a standard Siemens D5000 Bragg-Brentano diffractometer. The resulting X-ray diffractograms were analyzed using Search-Match software, refined with the Reitveld program Topas 3. Fifteen samples collected from diamond drill core were submitted to the Michigan Technological University Department of Material Science and Engineering for qualitative XRD analysis. Samples were ground, and step-scan X-ray powder-diffraction data collected over a range of 5° to $45^\circ\ 2\theta$ with a Scintag XDS 2000 Diffractometer. Background was subtracted and crystalline phases were identified using Scintag Diffraction Management System for NT (DMSNT) software.

3.2.2 SEM and EDS

SEM was used to investigate the physical characteristics of the minerals present in fifteen samples collected from diamond drill core. In addition to the physical characteristics, the chemistry of the carbonate minerals was analyzed using EDS in conjunction with the SEM.

Samples representing the range of modes of occurrence of sulfides and carbonates, as well as the stratigraphic units encountered, were selected from the core at the time of detailed logging. These samples were polished, mounted, and carbon-coated and then examined using a JEOL 840-JXA SEM equipped with a Kevex Sigma EDS system. EDS spectra were collected at an accelerating voltage of 20 kV for 120 seconds, maintaining a dead time of approximately 25%.

3.3 Acid base accounting

Acid-base accounting (ABA) provides a measure of the balance between the acid-producing capability and acid-neutralizing capacity of mine wastes. Modified ABA was conducted on 25 samples of waste rock (CANTEST, Ltd.) and 21 samples of diamond drill core (ACZ). Modified ABA testing utilized partial-decomposition by wet-chemical-leach speciation methods for identification of sulfur and carbon forms by combustion-infrared spectrophotometer, including:

- HCl-extractable sulfur (total sulfur from untreated sample minus total sulfur after extraction with 40% HCl), which is attributed to SO_4 -sulfur,
- HNO_3 -extractable sulfur (total sulfur after HCl extraction minus total sulfur after extraction with 14% HNO_3), which is attributed to pyritic sulfide-sulfur,
- Non-extractable sulfur (total sulfur from untreated sample minus total sulfur after HNO_3 extraction), which is attributed to organic sulfur,

- Total carbon after extraction with 15% HCl, which is attributed to organic carbon, and
- Total inorganic carbon (carbonate), which is calculated as the difference in total carbon and total carbon after HCl extraction.

NP was measured with the method of Lawrence as described in MEND (1991), which is summarized below.

Two grams of sample were pulverized to < 250 μm (minus-60 mesh) and digested at room temperature with 0.1 N HCl over a 24-hour period under mechanical agitation to achieve a pH of approximately 2. Subsequently, samples were titrated with 0.1 N NaOH to reach the endpoint pH, typically 8.3. However, in this case additional "endpoint" pH values of 4.5, 6.0, and 10 were also recorded.

3.4 SPLP

Twenty-five samples of waste rock and 21 samples of diamond drill core were submitted to CAN-TEST, Ltd. and ACZ, respectively, for SPLP extraction and analysis (EPA, 2007). Both labs utilized extraction fluid number 3, which is deionized reagent water with no added acidity. The solid phase was extracted with an amount of extraction fluid equal to 20 times the weight of the solid phase. Samples were agitated in an end-over-end rotary agitator with the extraction fluid for a period of 18 hours.

3.5 Aqua regia digestion

Twenty-five samples of waste rock and 21 samples of diamond drill core were submitted to CAN-TEST, Ltd. and ACZ, respectively, for aqua regia digestion and analysis to evaluate the solid-phase chemical composition. Digestate was analyzed by inductively coupled plasma-atomic emission spectrometry (ICP), inductively coupled plasma mass spectrometry (ICP-MS), and cold vapor atomic absorption (CVAA), to determine solid-phase elemental concentrations of select metals, metalloids, and non-metals. Analyzed constituents included Ag, Al, As, Au, B, Ba, Bi, Ca, Cd, Co, Cr, Cu, Fe, Ga, Hg, K, La, Mg, Mn, Mo, Na, Ni, P, Pb, Sb, Se, Sr, Th, Ti, Tl, U, V, W, and Zn.

3.6 Humidity cells

Humidity cells are designed to enhance the release of acidity/alkalinity, metals, and other constituents from solid materials by providing conditions conducive to sample oxidation and then leaching with a fixed volume of water on a weekly basis. Samples of waste rock and diamond drill core were submitted to CANTEST, Ltd. for humidity cell testing following the ASTM method D5744-07, Option A (ASTM, 2007). Humidity cell tests were conducted for 25 samples of waste rock and for 12 samples of diamond drill core. For each humidity cell, one kg of rock was placed in a clear acrylic cell and was initially flushed with 750 mL of deionized water. The waste rock stockpile sample cells had an inner diameter of 11 cm and a 20-cm height from the base. Diamond drill core samples had an inner diameter of 20 cm and height from the base of 11 cm. Subsequently, cells were subjected to a weekly cycle composed of three days of dry air followed by three days of water-saturated air and then a 500 mL flush with deionized water in a climate-controlled facility. Humidity cell effluent was collected and analyzed for pH, electrical conductivity, oxidation/reduction potential, SO_4 , acidity and/or alkalinity, and dissolved metals by ICP and ICP-MS. Analytical frequency was initially weekly, but was later reduced following leachate concentration stabilization.

4 RESULTS AND DISCUSSION

4.1 Borehole observations

In general, waste rock encountered in the stockpile boring profiles was black, fine-grained, slaty or cherty iron formation, which was variously magnetic and consisted of coarse-grained gravel to cobble-sized clasts, with various amounts of sand and silt, some of which was a result of

Table 1. Summary of average water chemistry by site.

	pH	TDS	Alkalinity	Hardness	SO ₄	Ca	Mg	Fe	Mn	Al	As	Co	Cu	Sb	Se
Site	mg/L		mg/L CaCO ₃		mg/L						µg/L				
GW1	6.8	450	320	440	120	60	70	1.5	0.62	51.3	0.9	1.0	1.4	0.02	0.4
GW3	7.2	760	300	640	320	110	90	20	0.65	109	5.2	0.4	0.5	0.02	0.3
GW4	6.4	780	230	610	340	100	90	30	3.7	474	2.6	0.8	1.2	0.1	0.4
GW5	6.8	2110	480	1700	1220	150	320	10	1.0	343	1.6	1.0	1.9	0.03	1.6
GW6	7.4	370	140	290	150	60	30	3.1	0.61	1169	0.8	1.6	3.3	0.2	0.3
Stream	8.0	676	290	650	330	40	130	0.80	0.16	23.4	2.0	0.4	0.4	0.1	0.6
Pit 1	8.1	860	370	780	390	40	160	0.03	1.2	12.5	1.1	0.9	0.6	0.03	0.6
Pit 2	8.5	440	320	400	110	30	80	0.03	0.01	12.5	4.1	0.3	0.6	0.1	0.5
Pit 3	7.9	2040	570	1660	1150	50	370	0.04	2.3	12.5	2.0	4.1	1.0	0.1	2.4
Pit 4	8.3	760	320	710	350	30	150	0.03	0.03	12.5	1.1	0.4	0.5	0.04	0.8

pulverization of the rock during drilling. Disseminated pyrite or similar sulfide minerals were occasionally noted in the samples after being crushed and dried. Pyrite also occurred as thin partings or vein-fillings in some samples.

Diamond drill core from boreholes associated with mining operations was evaluated from three boreholes to obtain additional information on the materials comprising the waste rock at the site. In general the holes encountered 40–50 feet of overburden, 55–65 feet of the Upper Cherty member, 66–71 feet of the P submember of the Lower Slaty member, 11–13 feet of the Q submember of the Lower Slaty member, and 140–145 feet of the Lower Cherty member. One hole also intersected the Upper Slaty member. In general, pyrite was commonly visible in the P and Q submembers. Dominant modes of pyrite included disseminated and veinlet occurrences, with veinlets generally occurring either parallel to or cross-cutting bedding.

4.2 Site water chemistry

Site water chemistry (summarized in Table 1) provides an indication of potential water-quality concerns and is useful for evaluating the potential for mobilization of constituents under various environmental conditions. Average concentrations of Al, Fe, and Mn exceed drinking water-quality standards in all groundwater monitoring wells. Background concentrations for these constituents are elevated regionally (MPCA, 1999). GW03, GW04, and GW05 also exceed drinking water standards for TDS and SO₄. GW01, GW03, and GW05 also exceed discharge standards for alkalinity.

Concentrations of Al, Fe, and Mn are generally lower in surface waters than in the groundwater monitoring wells. Average concentrations of Al and Fe are below water-quality standards for each of the pit lakes on site. Pit lakes exceed the discharge standard of 250 mg/L for alkalinity, the discharge standard of 500 mg/L for hardness, and the discharge and secondary drinking water standards for TDS. SO₄ concentrations are elevated in the pit lakes 1, 3, and 4 (390 mg/L, 1150 mg/L, and 350 mg/L, respectively) compared to the secondary (aesthetic) drinking water standard of 250 mg/L.

The tendency for Al, Fe, and (to a lesser extent) Mn to precipitate from solution in circumneutral to alkaline oxygenated waters is consistent with their concentration trends at the site; they are elevated in groundwater, but have much lower concentrations in surface waters. Al does not need to be oxidized prior to hydrolysis and precipitation from solution, and iron oxidation at the mildly alkaline pH of site waters is rapid (Eary and Schramke, 1990). However, slower oxidation kinetics for Mn²⁺, particularly in the presence of elevated SO₄ and bicarbonate concentrations can allow it to accumulate in solution (Hem, 1963).

The elevated concentrations of solutes in the pit lakes are consistent with the mechanisms discussed previously. The (Ca+Mg):SO₄ and (Ca+Mg):HCO₃⁻ ratios from waters on and near the site are also consistent with the pyrite oxidation and neutralization mechanisms and relative rates observed in the humidity cells.

Pore-water chemistry is notably consistent, with pH from 7.4 to 8.0 and SO₄ concentrations ranging from 1040 to 1420 mg/L for all but one sample. That sample was collected at the phreatic

Table 2. Quantitative XRD results in wt%.

Mineral	Ideal Formula	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Average
Quartz	SiO ₂	40.4	46.8	37.6	33.9	36.5	39
Siderite	Fe ²⁺ CO ₃	31.6	17.5	26.2	30.2	22.5	26
Clinochlore	(Mg,Fe ²⁺) ₅ Al(Si ₃ Al)O ₁₀ (OH) ₈	15.3	0	20.6	18.1	0	11
Stilpnomelane	K(Fe,Mg) ₈ (Si,Al) ₁₂ (O,OH) ₂₇	2.4	2.2	1.2	2.5	13.2	4.3
Magnetite	Fe ₃ O ₄	4.3	6.5	6.2	3.5	0	4.1
Minnesotaitite	(Fe ²⁺ ,Mg) ₃ Si ₄ O ₁₀ (OH) ₂	3.7	1.8	4.2	8	0	3.5
Goethite	α-Fe ³⁺ O(OH)	0	6.1	0	3.2	8	3.5
Greenalite	(Fe ²⁺ ,Fe ³⁺) ₂₋₃ Si ₂ O ₅ (OH) ₄	0	4.7	0	0	11	3.1
Hematite	α-Fe ₂ O ₃	0	5.6	0	0	4.2	2.0
Ankerite	Ca(Fe ²⁺ ,Mg,Mn)(CO ₃) ₂	0	5.1	0.7	0.6	1.3	1.5
Pyrite	FeS ₂	2.4	0	3.3	0	0	1.1
Talc	Mg ₃ Si ₄ O ₁₀ (OH) ₂	0	3.3	0	0	0	0.7
Plagioclase	NaAlSi ₃ O ₈ -CaAl ₂ Si ₂ O ₈	0	0	0	0	3.3	0.7
Calcite	CaCO ₃	0	0.4	0	0	0	0.1

surface and had a SO₄ concentration of 2270 mg/L. The quality of pore water clearly does not represent either drinking water or discharge water quality. Nonetheless, comparison of pore-water concentrations with water-quality standards can provide an indication of constituents that merit further consideration when evaluating COI. Comparison of the dissolved fraction of pore-water samples to surface-water discharge and drinking water standards indicates that alkalinity, hardness, TDS, SO₄, and Mn were greater than standards in all samples, and that Co and Fe exceeded water quality standards in one or more samples. Dissolved (Ca+Mg):SO₄ ratios in pore water ranged from 1.2 to 1.6, and (Ca+Mg):HCO₃⁻ ratios ranged from 1.4 to 2.6, consistent with partial degassing of CO₂ occurring during neutralization of acidity from sulfide oxidation.

4.3 Mineralogy

Results of the quantitative XRD analyses are provided in Table 2 and are consistent with the qualitative XRD analyses. Rocks of the Biwabik Iron Formation evaluated as part of this study generally contain trace to moderate pyrite (< 0.02 to 5 wt% as pyrite) and abundant Mg-rich siderite (average of 24 wt%). The minerals stipnomelane, greenalite, clinochlore, and, tentatively, magnesite were also identified in the Lower Slaty P and Q submembers. Ankerite, calcite, and chamosite were also identified in the Upper Cherty sample. Quartz, minnesotaitite, talc, stipnomelane, greenalite, magnetite, and ankerite were also identified in the Lower Cherty.

Two general modes of occurrence were identified for pyrite: disseminated and veinlets (Fig. 1). Disseminated pyrite is generally present as euhedral grains (with an average size of approximately 5 μm), as generally < 20 μm individual grains comprising aggregates, or as sieve-textured grains (small idiomorphs lying within larger xenoblasts) up to approximately 300 μm. Pyrite veinlets were observed in samples from the Lower Slaty (P and Q submembers), generally as aggregates of individual euhedral grains ranging from 20 μm to 300 μm. Two orientations were common for the pyrite veinlets: parallel to bedding and cross-cutting. A tendency toward separation along these pyritiferous veins and bedding was noted. Both modes of occurrence are generally concurrent, with the disseminated variety comprising the majority of the pyrite in all cases. Pyrite in the Lower Cherty and Upper Cherty was less abundant than in the Lower Slaty and, where present, was disseminated. One grain of arsenopyrite was observed in a sample from the P submember of the Lower Slaty (identified with SEM/EDS, but below XRD detection limits).

Siderite was the primary carbonate mineral identified in this study, although ankerite and subordinate calcite were observed in the Upper Slaty and in trace amounts in the Lower Cherty and waste rock stockpiles. Based on EDS, the siderite has a consistent chemical composition

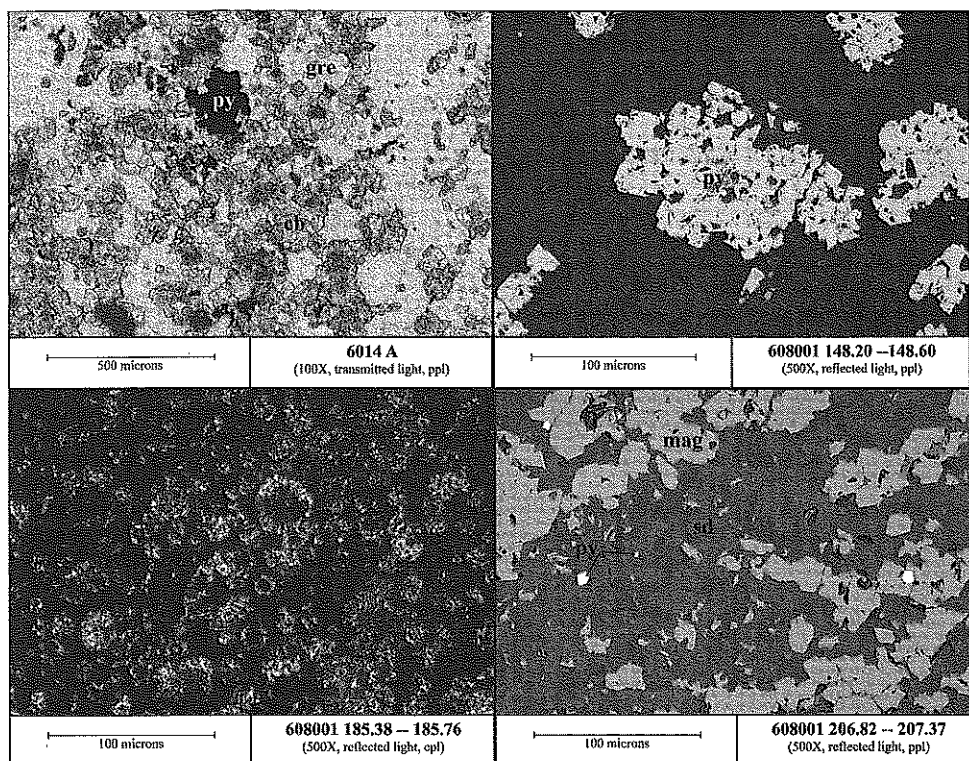


Figure 1. Photomicrographs of a) decussate greenalite, idiomorphic carbonate, and xenoblastic sieve textured pyrite, b) idiomorphic to subidiomorphic sieve textured pyrite in a siderite-rich matrix, c) atoll textured siderite with disseminated pyrite, and d) disseminated pyrite in a granoblastic siderite and magnetite matrix.

of approximately $\text{Ca}_{0.03}\text{Mg}_{0.20}\text{Fe}_{0.73}\text{Mn}_{0.04}\text{CO}_3$. Siderite in the P submember has a disseminated idiomorphic to xenoblastic mode of occurrence (Fig. 1). Siderite in the Q submember is also disseminated, but with a smaller grain size (approximately $25\ \mu\text{m}$). Siderite in the Lower Cherty is generally present as a granular aggregate with a grain size ranging from $<25\ \mu\text{m}$ to $>300\ \mu\text{m}$.

4.4 Acid base accounting

Sulfide content of all samples ranges from 0.01 to 2.73 wt% S, with average values of 0.24 and 0.66 wt% for the waste rock and diamond drill core samples, respectively. Carbonate content ranges from 0.11 wt% C to 8.3 wt% C, with average values of 2.5 and 3.1 wt% for the waste rock and diamond drill core, respectively. If all carbonate is assumed to be the Mg-rich siderite described previously, this would correspond to an average content of 24 wt% siderite, which is in excellent agreement with the quantitative XRD results (26% siderite, Table 1) and the qualitative XRD, which consistently identified siderite as a major constituent.

The difference in composition of waste rock and diamond core is attributed to the sampling bias toward sulfidic zones (e.g. the Q submember, relative to the P submember and Lower Cherty) in the diamond core samples, and to the partial oxidation of the waste rock samples. Sulfide concentrations are substantially higher in rocks from the Lower Slaty Q submember (average 2.68 wt%) than from any other rock types tested. Sulfides are present at much lower concentrations in rocks from the Lower Slaty P submember (average 0.14 wt%), and the Lower Cherty R submember (average 0.16 wt%). Sulfide concentrations in the P and R submembers appear to increase with proximity to the Q submember. Sulfide generally comprises $>95\%$ of total sulfur for the diamond core and $>75\%$ of total sulfur for the waste rock. The lower relative sulfide fraction observed in the

Table 3. Acid base accounting results.

Sample type	n	Net neutralization potential* kg CaCO ₃ per tonne			NP to AP ratio**		
		Minimum	Maximum	Average	Minimum	Maximum	Average
Waste rock	25	-11	58	22	0.59	166	21
Lower Slaty (P)	8	23	91	51	5.6	38	20
Lower Slaty (Q)	4	-43	-12	-31	0.51	0.87	0.63
Lower Cherty	6	15	68	42	5.6	46	17
Upper Slaty	1	-	-	648	-	-	84

*Net neutralization potential calculated as the difference in the modified NP to pH 8.3 and acid generation potential calculated based on sulfide plus non-extractable sulfur.

**Ratio of modified neutralization potential to pH 8.3 and acid generation potential calculated based on sulfide plus non-extractable sulfur.

waste samples is due to the presence of non-extractable (acid-insoluble) sulfur. For the purpose of this characterization, the acid-insoluble fraction has conservatively been included with the sulfide fraction in the calculation of acid-generating potential.

For the purpose of this characterization, the NP values to an endpoint of 8.3 were used for ABA determinations. ABA results are summarized in Table 3. Net neutralization potentials (NNP) across all samples range from -43 to 91 kg CaCO₃ per tonne with an average NNP of 22 kg CaCO₃ per tonne for waste rock. One sample of waste rock and five samples of diamond drill core have NNP < 0, indicating acid-generating potential. Ten samples of waste rock and two samples of diamond drill core have 0 < NNP < 20, indicating potential uncertainty regarding classification of these samples as non acid-generating, depending on the criteria applied.

The NP to AP ratio for all samples ranges from 0.51 to 166 with an average of 19 and a median of 6.8. One sample of waste rock and four samples of diamond drill core (all from the Q submember of the Lower Slaty) had NP to AP ratios < 1, indicating the potential for acid generation for those samples. Seven samples of waste rock and one of diamond drill core have 1 < NP:AP < 4, indicating potential uncertainty regarding their acid-generating capacity classification, depending on the criteria applied. The approach of determining a site-specific appropriate NP to AP ratio for designation of potentially acid-generating materials (Ferguson and Morin, 1991; Morin and Hutt, 1994) has been applied to the site. As is presented below, observed (Ca + Mg):SO₄ ratios for the impacted areas of the site are approximately 1.4. Thus, an NP to AP ratio of 2 provides an additional factor of safety when applied to classification of site materials as potentially acid-generating.

To assess the applicability of the NP values from the Modified ABA, empirical NP values were compared to theoretical mineralogic NP based on observed siderite composition. Comparison with theoretical mineralogic NP (Fig. 2) indicates that the Modified ABA to an endpoint pH of 8.3 provided a generally conservative representation of the NP, consistent with published results obtained for similar siderite samples using the SobPer method (Jambor et al., 2003).

A final consideration relating to ABA is that of mineral availability. Two of the primary factors controlling mineral availability are the particle size distribution and the armoring or encapsulation of mineral grains. Both of these factors can be evaluated based on consideration of the mineralogical evaluation. For example, because the surface area of a particle increases exponentially as its particle size decreases, the actual reactivity will be a function of both the abundance of acid-generating and acid-neutralizing materials and their respective particle size. Similarly, the presence of mineral coatings (such as ferric hydroxides on calcite or sulfates on pyrite) can preclude these minerals from participating in acid neutralization or generation (EPA, 2003).

As described above, grain sizes of pyrite and siderite range from < 5 µm to approximately 300 µm and from < 25 µm to approximately 300 µm, respectively. Furthermore, the general tendency is for the larger carbonate grains to occur conjointly with the larger pyrite grains and, likewise, for the smaller carbonate and pyrite grains to occur conjointly (e.g. see Fig. 1). None of the mineralogic or petrographic analyses provided any indication of localized occurrences of pyrite in the absence of carbonate minerals. Because of the semi-consolidated to poorly-consolidated sedimentary nature

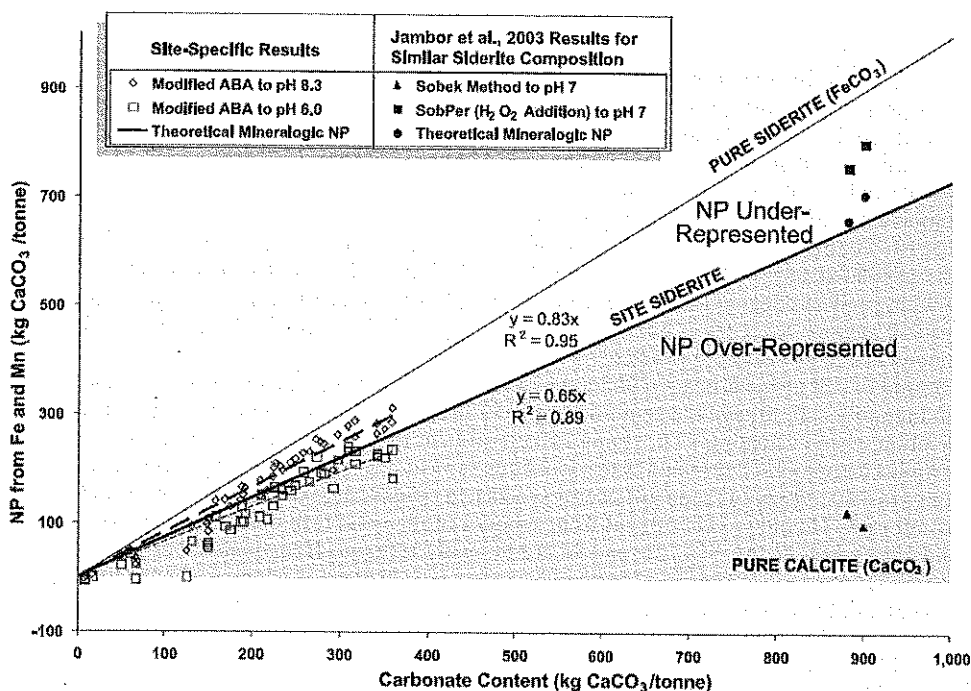


Figure 2. Comparison of mineralogic NP with NP measured using the Modified NP to pH 8.3.

of the deposits, the mineral grain sizes are small regardless of the size of the aggregate particles and the porosity and friability are high relative to typical hard rock mines, particularly for the slaty rock types. Hence, the overall abundance of carbonate and sulfide is interpreted to provide a reasonable indication of the extent of their respective surface areas. Furthermore, none of the petrologic or mineralogic evaluations of waste rock provided any indication of encapsulation, armoring, or alteration rims that could potentially inhibit the reactivity of the sulfide or carbonate surfaces.

4.5 SPLP

SPLP leachate solute concentrations were generally low and pH was circumneutral to mildly alkaline (pH 7.3 to 9.0) for all samples. Specific conductance ranged from 28 to 236 $\mu\text{S}/\text{cm}$ and SO_4 from 1 to 87 mg/L in the waste rock samples and from 47 to 112 $\mu\text{S}/\text{cm}$ and <1 to 9 mg/L, respectively, in the diamond core samples. Comparison of extract concentrations can provide an indication of constituents that merit further consideration when evaluating COI. Comparison of SPLP extract pH and solute concentrations with various Minnesota water-quality standards for surface-water discharge and drinking water indicates that the extracts from one or more samples exceeded water-quality standards for Al, Cu, Fe, Mn, and Se.

4.6 Aqua regia digestion

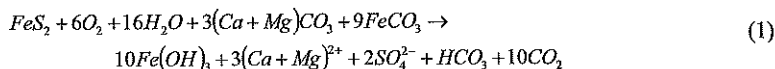
Aqua regia digestion is a strong acid digestion that will dissolve almost all elements that could become environmentally available. However, it does not necessarily indicate that constituents will become environmentally available (EPA, 2007). Constituents released at the highest concentrations were Fe, Mg, Al, Mn, and Ca. Average concentrations exceeded the crustal average abundances (Price, 1997) for Mo, Ag, Mn, Fe, As, Cd, Sb, Bi, W, Hg and Se and were in excess of ten times average crustal abundances for Mn, As, Bi, and Se. However, average extract concentrations for Sb and Hg were below the average concentration for shale (Price, 1997). Only Ag was present at an average concentration greater than the average concentration for shale.

4.7 Humidity Cells

Humidity cell effluent pH ranged from 6.7 to 9.5 for the waste rock samples and from 6.9 to 8.3 for the drill core samples. After effluent concentrations stabilized, SO_4 concentrations ranged from <1 to approximately 200 mg/L, well below saturation with respect to the common SO_4 minerals, which indicates that observed SO_4 release rates are not affected by precipitation of secondary minerals and are likely a good indicator of the sulfide oxidation rates occurring in the cells. SO_4 release rates from the waste rock samples calculated using weeks 15 to 26 range from 3.2×10^{-9} to 4.2×10^{-8} kg of SO_4 per kg of sulfide per second, with an average value of 1.5×10^{-8} . Although these calculated rates vary by a factor of 13, most variability is from cells with low SO_4 production. Excluding cells producing less than or equal to 5 mg/L in week 26, the remaining (average weekly) rates still average 1.5×10^{-8} , but are all within a factor of 2.9. Similarly, SO_4 release rates from diamond drill core samples averaged 7.1×10^{-9} .

Humidity cell effluent is not a direct measure of ultimate water quality. However, constituents with humidity cell effluent concentrations greater than water-quality standards merit further consideration when evaluating COI. Humidity cell effluent from one or more samples of waste rock stockpiles has exceeded drinking water standards for Mn, Fe, Al, SO_4 , As (from one cell), and Cu (from one cell). Discharge standards were exceeded in effluent for hardness, and for Cu and Se from one cell each. Humidity cell effluent from samples of diamond drill core exceeded water-quality standards for Mn, Fe, Al, SO_4 , Cu, and Se. Additionally, effluents from diamond drill core samples from the Q submember of the Lower Slaty have also exceeded the drinking water-quality standard for Sb and effluent from the R submember of the Lower Cherty and the Virginia Formation have exceeded the discharge water-quality standard for Co.

Humidity cell leachate chemistry was evaluated using $(\text{Ca}+\text{Mg}):\text{SO}_4$ and $(\text{Ca}+\text{Mg}):\text{HCO}_3^-$ ratios to identify relative acid-generation and acid-neutralization rates occurring in the humidity cells. The aggregate overall behavior was assessed by summing the Ca, Mg, SO_4 , and bicarbonate concentrations for all cells through 26 weeks. The resulting overall $(\text{Ca}+\text{Mg}):\text{SO}_4$ ratios were 1.5 and 1.3 and the overall $(\text{Ca}+\text{Mg}):\text{HCO}_3^-$ ratios were 0.80 and 0.70 for humidity cells on the waste rock and diamond drill core samples, respectively. The overall ratios from the humidity cell tests are similar to field averages for the pit lakes of $(\text{Ca}+\text{Mg}):\text{SO}_4 = 1.3$ and $(\text{Ca}+\text{Mg}):\text{HCO}_3^- = 1.5$. The overall behavior of acid neutralization by siderite can be represented by Equation 1, which represents approximately 80% CO_2 degassing.



The acid-neutralizing consumption rate appears to be approximately 1.4 times faster than the acid-generating rate, both in the humidity cells and in the field.

4.8 Geochemical conceptual model

Primary COI include: SO_4 , hardness (Ca and Mg), alkalinity, Fe, Mn, and Al. These constituents have been consistently observed at elevated concentrations with respect to water-quality standards in site water and geochemical test effluent. Secondary COI include Co, Cu, As, and Se. These constituents have been sporadically detected at elevated concentrations with respect to water-quality standards in site water and/or geochemical test effluent, but are not readily mobilized under prevailing conditions at the site. However, these constituents are present and can potentially be mobilized under certain conditions (such as reducing conditions or elevated pH).

Primary constituents of interest (COI) are associated with pyrite oxidation and subsequent acid neutralization, primarily by siderite and ankerite. Calcite equilibrium has been shown to control the relationship between pH and pCO_2 in many carbonate aquifers (e.g. Langmuir, 1971; Plummer, 1976). Similarly, the relationship between pCO_2 and pH in the site pit lakes and waste rock stockpiles appears to be controlled by dissolution of siderite (and ankerite) in response to the amount of sulfide oxidation occurring. In order to evaluate the conceptual model, these geochemical controls, including equilibration with atmospheric oxygen, progressive degassing of CO_2 , precipitation of calcite, precipitation of ferrihydrite, dissolution of pyrite, dissolution of siderite (with the aforementioned chemical composition) to the extent necessary to yield observed site $\text{Ca}+\text{Mg}:\text{SO}_4$ ratios,

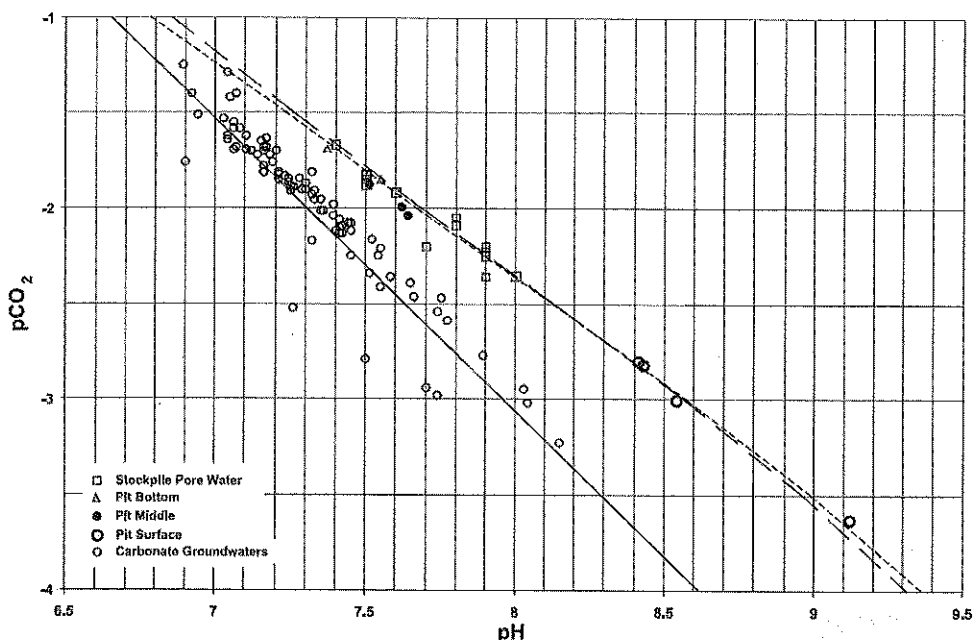


Figure 3. Simulated relationship between pH and $p\text{CO}_2$ defined by calcite equilibrium (solid line) from Langmuir (1971) and Plummer (1976) and defined by dissolution of site siderite in response to pyrite oxidation with subsequent precipitation of calcite and ferrihydrite.

and the pH resulting from thermodynamic equilibrium with the aforementioned controls) were simulated in Phreeqc (Parkhurst, 1999). Comparison of the simulated results with pore-water and lake-water chemistry is shown on Figure 3. The model provides excellent agreement with measured conditions at the site, indicating that the conceptual model provides a consistent explanation of the behavior of primary COI at the site.

5 CONCLUSIONS

Waste rock from the Lower Slaty member of the BIF has impacted water quality at the site as a result of pyrite oxidation and subsequent neutralization by Mg-rich siderite and ankerite, resulting primarily in elevated SO_4 , alkalinity, and hardness. Sulfide concentrations are roughly an order of magnitude higher in rocks from the Lower Slaty Q submember (average 2.7 wt%) than from any other rock types tested. The Q submember of the Lower Slaty is potentially acid-generating, whereas the P submember of the Lower Slaty, the R submember of the Lower Cherty, and the top of the Upper Slaty are non acid-generating. However, the aggregated waste rock present in site stockpiles appears to be net neutralizing as long as the relative rates of release of acid generating and acid neutralizing minerals are maintained over the long term. Select humidity cells are being continued for long-term testing to provide additional information regarding these relative rates of release. Alternatives for management of waste rock to limit oxidation and infiltration are being investigated as a means to ameliorate site water-quality.

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