Waste Rock Sulfate Release Rates at a Former Taconite Mine, Laboratory and Field-Scale Studies

Braden Hanna[1] and Kim Lapakko[2]

[1]Itasca Denver, Inc., Lakewood, CO, USA bhanna@itascadenver.com
[2]Minnesota Department of Natural Resources, Lands and Minerals Division, St. Paul, MN, USA, Kim.Lapakko@state.mn.us

Abstract
New mining has been proposed at a former taconite mine near Hoyt Lakes, MN, USA, where previous open-pit mining generated approximately 160 million metric tons of sulfide-bearing waste rock that also contains abundant carbonate minerals. This existing waste rock is the primary source of sulfate, hardness, and alkalinity in the neutral drainage from the site. Because leaching of these constituents from waste rock has resulted in concentrations exceeding water-quality standards in the area, the potential extent of future solute releases is of concern. This paper describes an investigation of sulfate loading that was performed to address these concerns. Sulfate masses present in an existing pit were calculated and used to estimate rates of release from waste rock in the pit watershed. Waste rock release rates were also estimated for several pit-watersheds based on fluxes measured in streams draining the watersheds. These estimated field-scale rates were compared to each other and to rates observed in laboratory studies using humidity cells. Average rates of sulfate release ranged from approximately 8 to 28 g SO_4 per kg FeS_2 per year in the field and averaged 22 g SO_4 per kg FeS_2 per year for humidity cell tests on six drill core samples. This yielded field:laboratory sulfate rate scaling factors ranging from 0.3 to 1.2.

Key Words: sulfide oxidation, scaling factor, field scale, waste rock, case study

Introduction
Open-pit taconite mining occurred from 1954 through 2000 at a site on the Mesabi Iron Range near Hoyt Lakes, MN, USA. Following cessation of mining the open pits filled with water impacted by waste rock in the associated watersheds. Preliminary studies in 2008, related to a proposal to reopen the mine, identified elevated concentrations of sulfate, hardness, and alkalinity in the circumneutral water in the pit lakes and in a stream downgradient from the pits. Geochemical characterization indicated that sulfidic waste rock was the primary sulfate source (Hanna 2010).When Area 1 and Area 6 Pits fill, outflow reports to Second Creek via a constructed overflow channel and/or shallow groundwater seepage through surficial glacial till that comprises the uppermost layer of the pit walls (Adams *et al*. 2004, Barr Engineering 2009).

Subsequent evaluations, which are presented here, were performed with the objectives of determining sulfate release rates from waste rock in the field, determining sulfate release rates from drill core simulating unweathered waste rock in humidity cell tests, and determining the relationship between field and laboratory rates. These evaluations focused on the Area 1 and Area 6 pit lakes. The focus on these two lakes is due to several factors, including the abundance of waste rock stockpiles in these two pit watersheds (and the associated water-quality concerns), and the availability of quantitative data regarding: masses and sulfur contents of waste rock, hydrologic budgets, and depth profiles for chemical constituents in the water column. A map of the site is provided in Figure 1, which illustrates the spatial relationship between the Area 1 and Area 6 Pits and Second Creek and the waste rock stockpiles contributing sulfate to each pit.

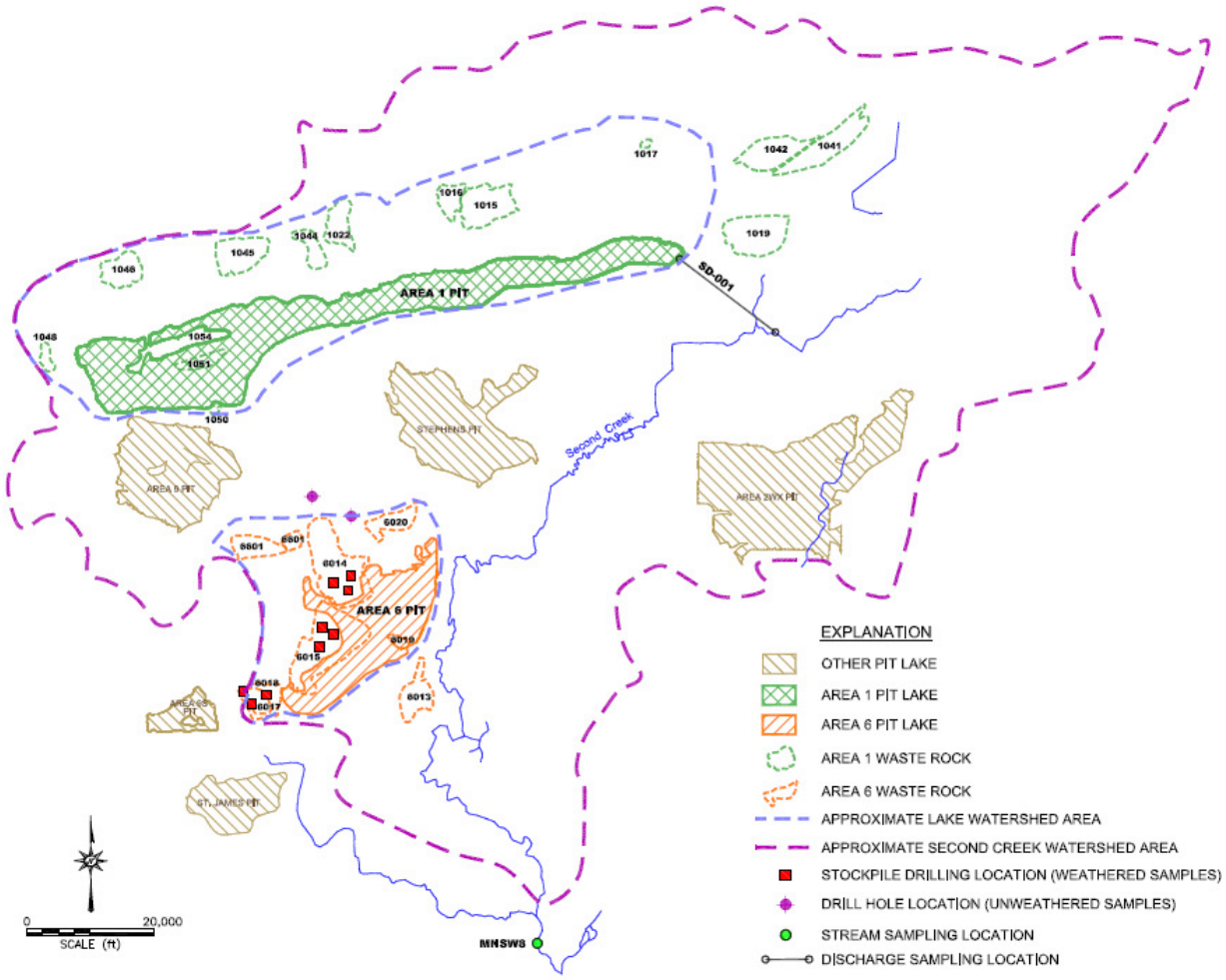

Figure 1. Study area location map.

Geologic Overview

The site is located at the eastern end of the Biwabik Iron Formation (BIF), a stratiform sedimentary deposit that dips gently to the southeast. The BIF is classified into two types of materials: cherty iron formation, which is granular, massive, and typically rich in quartz and iron oxides but absent visible sulfides; and slaty materials, which are generally finely laminated, fine-grained, and contain iron silicates, iron carbonates, and visible pyrite. The cherty beds are more abundant locally and typically comprise the ore, whereas the slaty beds typically report as waste rock. In Area 1 and Area 6 Pits, the P and Q submembers of the Lower Slaty and the Lower Cherty beds contribute approximately 65%, 21%, and 14% of the waste rock, respectively.

Previous characterization (Hanna 2010) indicated that the weathered waste rock was typically net-neutralizing and produced circumneutral leachate with low trace-metal content but elevated sulfate, hardness, and alkalinity. Sulfate release was attributed to pyrite oxidation and neutralization potential was attributed to magnesian siderite and ankerite. Petrographic analyses of the weathered samples indicated similar modes of occurrence for pyrite and carbonate minerals as described below for the unweathered samples.

Methods

Sample collection

Two types of samples were collected and evaluated for their environmental characteristics: weathered samples and unweathered samples. Two core holes were drilled to collect core samples of unweathered rock and three rotosonic holes were drilled in each of the 6014, 6015, and 6017 stockpiles to collect rock samples subjected to environmental weathering for 8 to 42 years. All coring was near pit 6 (Figure 1). The two drillholes north of the Area 6 Pit were located with the intention of intersecting the entire Lower Slaty and Lower Cherty members of the BIF. Drill core was logged by visual examination and samples of weathered and unweathered waste rock were recovered from drilling and selected for testing. Samples from drilling were subjected to humidity cell tests and mineralogical and petrographic analysis.

Analyses

Total sulfur and carbon were determined by combustion followed by infrared spectrophotometry (ASTM E 1915-07a [2007a], commonly referred to as LECO™). Sulfide content was measured using the difference between total sulfur and sulfur remaining after HCl-extraction.

Twelve unweathered samples from the intervals utilized in the humidity cell tests were subjected to petrologic/mineralogical analyses (HCItasca 2010). These analyses were conducted by Rod Johnson & Associates using optical microscopy, x-ray diffraction (Scintag XDS 2000), and a JEOL 840-JXA scanning electron microscope. Another 76 samples of weathered rock were sent to Twin Ports Testing for analysis of total sulfur by combustion infrared spectrophotometer (ASTM E 1915-07a [2007a], commonly referred to as LECO™) and were used to confirm that the samples selected for detailed testing were representative. Particle size-distribution of the humidity cell samples was determined using sieve analysis.

Humidity cells

The analysis of laboratory-based loading rates presented below is based on the unweathered rock samples collected from drill core. Characterization methods were similar and results for the weathered samples are described in detail in Hanna (2010) and HCItasca (2010). Seven samples of unweathered Lower Slaty rock were subjected to humidity cell testing by CANTEST, Ltd. using ASTM D5744-07, Option A (ASTM 2007b). Particle size reduction was achieved using staged crushing with a jaw crusher, and was inadvertently reduced to less than 2 mm, rather than the 6.3 mm top size recommended in the method. Perhaps due to the slightly-reduced particle size, the lab elected to use 20-cm diameter cells suggested by the method for materials less than 0.15-mm. The alternative cell geometry is not anticipated to have affected results, whereas the slightly reduced particle size may have resulted in accelerated sulfide oxidation rates if the liberated surface area of pyrite increased accordingly. A sample mass of 1.0 kg was used for all but one sample, which was from an interval with low core recovery and for which 0.6 kg was used. Temperature in the climate-controlled facility was maintained at 18-24 ^{o}C and a 500 ml weekly rinse volume was used following the 750 ml initial rinse. Humidity cell effluent was collected and analyzed for composition, including pH and sulfate. Analytical frequency was initially weekly, but was later reduced following leachate concentration stabilization. Because the primary testing objective was to obtain sulfate, calcium, and magnesium solute release data for comparison of unweathered rock testing with testing of weathered rock samples, the duration of the humidity cell tests on unweathered samples was limited to 26 weeks; however, long-term tests (>150 weeks) on previously weathered samples are ongoing to assess the long-term leaching character of the waste rock. Furthermore, the extensive data available for field-scale evaluation of weathering and leaching at the site provides substantial information for future mine characterization.

Laboratory release rates

Laboratory-based sulfate release rates for unweathered rock were calculated from the humidity cell results. Weekly constituent release rates were calculated following guidance provided in the ASTM standard

(Section 12.9.4 of ASTM D-5744-07 [2007b]) and normalized for pyrite content, assuming all sulfide was present as pyrite (Equation 1).

$$L_e = \frac{C_e * V_e * 0.052}{\mathrm{Py} * \mathrm{M}} \qquad \text{(Equation 1)}$$

Where:
L_e = loading rate in the effluent in g SO_4 per kg FeS_2 per year,
C_e = SO_4 concentration in the effluent in mg/L,
V_e = volume of the weekly collected effluent in L,
Py = the average pyrite fraction of the waste rock (calculated as 1.87*wt % sulfide/100),
M = mass of waste rock in the cell in kg, and
0.052 = a combined unit conversion factor (g*wk per mg per year).

The resulting weekly sulfate release rates were then averaged for weeks 15 through 26, the period for which release rates had generally stabilized.

Field release rates
Field release rate calculations required quantifications of rock mass and sulfate release for a specified period. The sulfide content of the rock was also needed for comparison with laboratory rates.

Waste rock mass
Because field rates were calculated based on sulfate generated in watersheds of specific pits, it was necessary to assess which stockpiles are contributing solutes to each pit. The stockpiles were evaluated based on the location of the stockpile, the surface watershed delineations, the bedrock topography, and the hydrologic conceptual model. The stockpiles (or portions thereof) concluded to be contributing solutes to each pit are illustrated in Figure 1. The estimated loading from pit walls, assuming a 1-m thick rind exposed to fully-oxidizing conditions, was less than 1% of that from the waste rock and was not included in the calculations.

Three independent data sets were used to estimate the waste rock mass: 1) operational records detailing overburden stripping and stockpiling, 2) geologic block model and pit bathymetry data, and 3) aerial survey topography before and after stockpile placement. The waste rock volumes determined in 1 and 2 were *in situ* volumes and were converted to mass using an *in situ* density of 3.07 g/cc (grams per cubic centimeter) based on operational experience at the site. The aerial survey was conducted by Aerometric and yielded stockpile elevations that were accurate within approximately 10 ft for the historical surveys (before placement) and 1 ft for the recent surveys (after placement). The volume of stockpiles was converted to mass assuming a porosity range of 0.28 to 0.35 after 5 to 15% compaction from settling (Roy 2006).

Lower bounds, best estimates, and upper bounds were calculated for exposed waste rock mass under both pit-empty (no water) and pit-full conditions. The best estimate was based on the volumes measured using aerial survey topography, the bulk density of 1.93 g/cc (derived from regression of the observed bulked stockpile volumes against the recorded *in situ* volumes), and the assumption that a small mine beneath stockpiles 6017 and 6018 (that may or may not have been backfilled with waste rock) was not backfilled with waste rock. The lower bound mass was based on the volumes measured using aerial survey topography minus 5%, a bulk density of 1.89 g/cc (the low end of the bulk-density range), and the assumption that the small mine was not backfilled with waste rock. The upper bound mass was based on the volumes measured using aerial survey topography plus 5%, a bulk density of 2.21 g/cc (the upper end of the bulk-density range), and the assumption that the small mine was backfilled with waste rock.

Pyrite content
Pyrite contents were based on pyrite contents measured in weathered and unweathered samples. The value for Area 6 was based on the average content measured in 101 samples of weathered waste rock collected from drill core (Figure 1). No direct measurements of pyrite content were available for Area 1 Pit. The pyrite value for Area 1 was estimated from average sulfide contents of each waste rock unit from the drill core from unweathered rock (Figure 1), weighted by relative abundance of the waste rock units in the Area 1 Pit, and adjusted for duration of exposure and oxidation rates. For comparison, pyrite contents were also estimated for each area based on average sulfide contents of each waste rock unit from the drill core from unweathered rock weighted by relative abundance of the waste rock units in each area (but not adjusted for time of exposure and oxidation rate).

Sulfate release to Second Creek
One set of field-based sulfate release rates was derived based on solute loading rates observed in Second Creek (the receiving water body for Area 1 and Area 6 Pit outflows). Based on the water balance, minimal outflow is believed to occur from Area 6 bedrock. Outflow from the Area 6 Pit to Second Creek is believed to occur through the unconsolidated sediments above the bedrock contact. The pit-lake elevation did not reach the lowest elevation of the bedrock contact until approximately July 2008. Stream flow has been monitored and water quality has been periodically measured at the downstream monitoring location, MNSW8 (Figure 1).

During the past several years, these outflows included:

1. Outflow from Area 1 pit (prior to July 2008),
2. Pumped discharge from Area 1 Pit (July 2008 to July 2010),
3. Shallow groundwater outflow from Area 6 Pit (July 2008 to present), and
4. Runoff and shallow groundwater flow from portions of Area 1 and Area 6 that are outside of the pit watersheds.

In addition to the outflows from Area 1 and Area 6 listed above, the following sources also contribute to the flow observed at MNSW8:

5. Seepage from a tailings basin located upstream of the site,
6. Runoff and shallow groundwater flow from the Stephens pit watershed,
7. First creek (including potential runoff and seepage from St. James pit waste rock), and
8. Runoff/shallow groundwater flow from largely undisturbed portions of Second Creek watershed.

Contributions from these sources (5 through 8) were assumed to be negligible, as outflows from Area 1 and Area 6 Pits account for the majority of the flow in Second Creek (evidenced by the fact that flow in Second Creek upstream of Area 6 Pit seepage dropped to below measurable levels when Area 1 Pit was not discharging) and concentrations associated with these flows are typically 10 to 20% of those from Area 1 and Area 6 Pits. Of these additional sources, the tailings basin is anticipated to provide the largest contribution. Estimates of the loading associated with the tailings basin indicate that this contribution does not affect the field-based rates at the reported precision (<2% of loading from Area 1 and Area 6 Pits).

The instantaneous sulfate loadings at MNSW8, were calculated for each of the dates that water-quality data were available. Sulfate loading rates were calculated as instantaneous rates, as shown in Equation 2.

$$L_i = \frac{C_i * Q * 8.937 * 10^5}{M_r * Py} \qquad \text{(Equation 2)}$$

Where:
L_i = instantaneous loading rates in the stream at the time of measurement, in g SO_4 per kg FeS_2 per year,
C_i = concentration at MNSW8 on the given day, in mg/L,
Q = average flow at MNSW8 on the given day, in ft^3 per second (cfs),

M_r = the mass of waste rock contributing solutes to the pit in kg,
Py = the calculated average pyrite fraction of the waste rock, and
$8.937*10^5$ = a combined unit conversion factor (g*L*s per mg per ft^3 per year).

For comparison to these observed loading rates, anticipated loads were also calculated as the product of the pit-lake sulfate concentrations and flow rates estimated (subsurface flow from Area 6 Pit) or measured (Area 1 Pit) for pit outflow.

Sulfate release to the Area 6 Pit
Field-based sulfate release rates for the Area 6 Pit were also calculated based on the rate of accumulation within the pit. The analysis presented below does not include sources other than waste rock (e.g., groundwater inflow, runoff, etc.), due to uncertainties regarding the respective flows and concentration from those sources. Estimates of the sulfate mass contributed to the pit by these other sources indicate that they are small relative to the contribution from waste rock. Extensive calculations (not provided here) indicate that sulfide oxidation associated with the waste rock in the Area 6 Pit watershed comprises 80 to >90% of the sulfate contributed to the pit.

An estimate of the sulfate mass in the Area 6 Pit (and associated in-pit waste rock pore water) was made for four different points in time (August 2008, September 2008, February 2009, and May 2009), when sufficient data regarding the stratification of the pit were available. On 18 May 2009, an extensive depth profile was conducted that included discrete sampling of the entire depth range of the Area 6 Pit at 5-m intervals. These data are anticipated to provide the best measure of sulfate mass in the lake. Other dates were limited to discrete sampling from three depth intervals. For these dates, continuous depth profiles of specific conductance were used to identify the approximate depths of the thermocline and monimolimnion. Based on these lake layer delineations, sulfate concentrations were estimated at a 1-ft discretization. Figure 2 illustrates the interpreted depth profiles for sulfate concentrations. The mass of sulfate in the lake was then estimated for each layer as the product of the volume of the layer and the concentration of the layer (as illustrated in Figure 2). The dissolved mass in the pore water of the waste rock stockpiles was estimated as the product of the total inundated volume occupied by the in-pit waste rock stockpiles, the upper end of the estimated range of porosity for the stockpiles (38%), and the average dissolved constituent concentration previously observed in pore water (Hanna 2010). The total sulfate mass was then calculated as the sum of the mass in the pore water and the mass in the lake.

These sulfate masses were used to calculate field-based sulfate release rates using Equation 3.

$$L_a = \frac{M_a}{M_r * Py * t} \qquad \text{(Equation 3)}$$

Where:
L_a = field-based loading rate calculated from sulfate accumulation in the pit in g SO_4 per kg FeS_2 per year,
M_a = the sulfate mass calculated in the pit after t years of infilling in g,
M_r = the mass of waste rock contributing sulfate to the pit in kg,
Py = the calculated average pyrite fraction of the waste rock, and
t = the amount of time the pit has been accumulating sulfate in years.

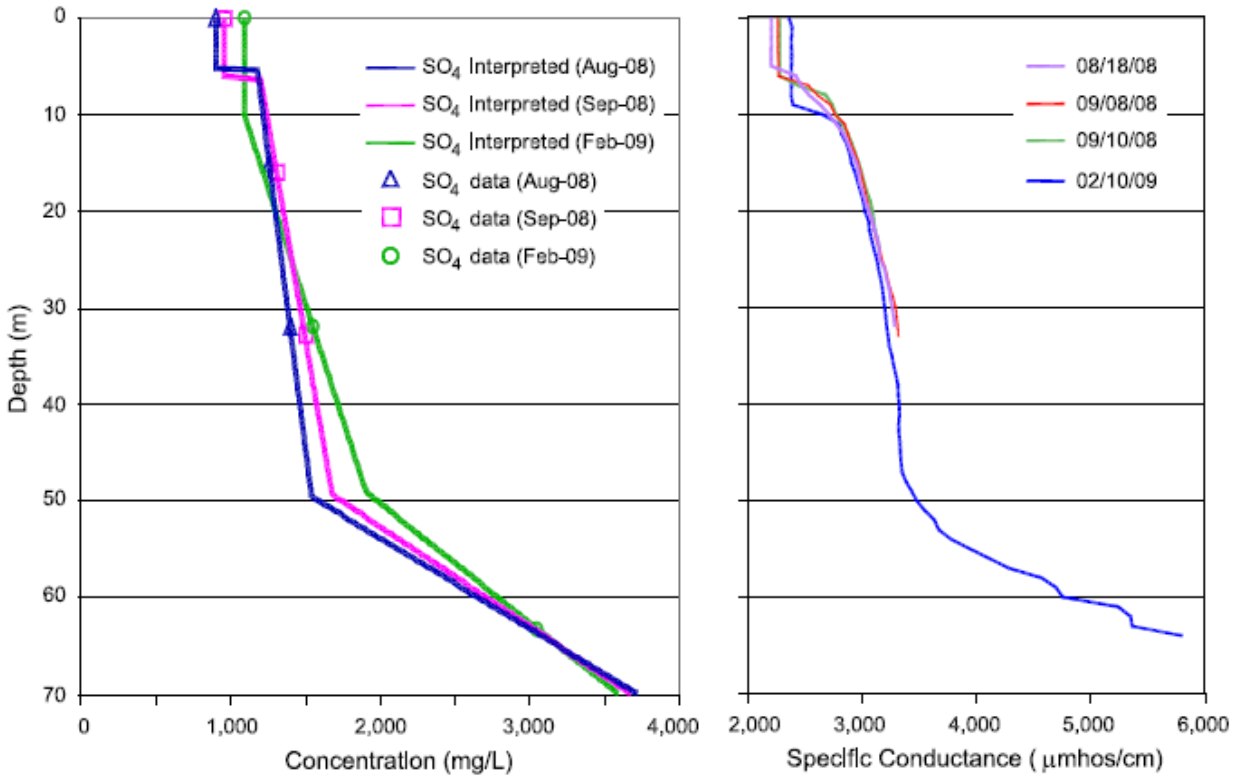

Figure 2. Continuous depth profiles of specific conductance and interpreted depth profile of SO_4.

Results and Discussion

Humidity cell tests and sample characterization

In general, the two drill holes in unweathered rock encountered 40 to 50 ft of overburden, 55 to 65 ft of the Upper Cherty member, 66 to 71 ft of the P submember, 11 to 13 ft of the Q submember, and 140 to 145 ft of the Lower Cherty member. These unit thicknesses are generally consistent with operational drilling logs throughout the site, although the P submember thins and pinches out in the vicinity of the Area 1 Pit due to an erosional unconformity.

Results of the detailed characterization of the Lower Slaty waste rock were described by Hanna (2010) and HCItasca (2010). In summary, unweathered samples of the Lower Slaty P submember were net neutralizing and Q submember samples were potentially acid generating; however, weathered samples apparently represented a mixture of P and Q submembers, with dominantly net-neutralizing properties (Hanna 2010). The ABA and mineralogical results from weathered samples were generally consistent with results from the unweathered rock samples, after accounting for exposure time and weathering rates (sulfide typically comprised >95% of total sulfur in unweathered samples and >75% in weathered samples). Leachates from short-term leach tests (e.g., Synthetic Precipitation Leaching Procedure) and humidity cells (for all humidity cells on the unweathered drill core and weathered waste rock) were circumneutral to mildly alkaline and were consistent with sulfide oxidation and neutralization by magnesian siderite and ankerite dissolution.

Pyrite occurred in a disseminated mode and as fine veinlets, with the former being dominant. Disseminated pyrite generally occurred as aggregates of euhedral grains finer than 20 µm or sieve-textured grains finer than 300 µm. Pyrite veinlets typically occurred as aggregates of individual grains 20 to 300 µm in diameter, and a tendency toward separation along these veins and bedding was noted (Johnson 2009). Both modes of occurrence were generally concurrent in the Lower Slaty (P and Q submembers),

with the disseminated variety comprising the majority of the pyrite in all cases. Disseminated idioblastic pyrite was observed to occur within granoblastic siderite and within a siderite-rich matrix. The primary difference in sulfides in the P and Q submembers was the sulfide content, which was much higher in the Q submember. Average sulfide content observed in the unweathered samples from the Lower Slaty P was 0.14% (0.02-0.33, n=8) and from the Lower Slaty Q was 2.68% (2.48-2.84%, n=6). The dominant carbonate mineral was magnesian siderite, with an average abundance of 24 wt % and a consistent total calcium and magnesium content of roughly 23 mole % relative to total cations. Siderite in the Lower Slaty is also disseminated and was finer in the Q submember than the P submember (Johnson 2009). Average carbonate-carbon content of the Lower Slaty P submember was 3.68% (2.70-4.30, n=8) and that of the Lower Slaty Q submember was 1.55% (0.80-2.10%, n=6). Pyrite in the Lower Cherty and Upper Cherty was much less abundant than in the Lower Slaty and, where present, was disseminated.

Laboratory sulfate release rates normalized for rock mass were observed to increase with sulfur content. Pyrite was essentially the only sulfide mineral observed to be present, and rates (Table 1) were normalized for pyrite content rather than rock mass (note that normalization of rates to pyrite content obscures the linear relationship between sulfate release and sulfur content). The rates ranged from 13.6 to 42.5 g SO_4 per kg pyrite per year. The sample with the lowest sulfide content (0.02% S^{2-}) yielded the highest calculated rate. The sulfur content of this sample suggests that the rate is subject to error because of analytical accuracy for low sulfur levels; e.g., if the sulfur content were 0.03 rather than 0.02 percent, the calculated rate would be two-thirds of that reported. Elimination of this rate yields an average of 21.9 g SO_4 per kg pyrite per year. By contrast, rates from the 25 humidity cells on weathered waste rock ranged from 53.1 to 698, with an average of 260 g SO_4 per kg pyrite per year.

Table 1. Laboratory-based sulfate release rates from humidity cells on unweathered drill core.

Sulfide Content (wt %)	0.02	0.24	0.32	2.39	2.47	2.72	2.73
Rate (g SO_4/year)	0.0085	0.068	0.059	0.33	0.74	0.76	0.37
Rate (g SO_4/kg pyrite per year)	42.5	28.3	18.3	13.6	29.8	27.9	13.6

Field rates

Rock mass

The estimates of waste rock mass based on mining records, the geologic block model and pit bathymetry data, and the aerial survey data are provided in Table 2. The overall waste rock volumes were concluded to be accurate to within approximately ±5%, based on agreement between the operational records and aerial survey data. Uncertainty was also associated with the porosities (or equivalently, bulking factors) used to estimate bulk density and convert volume to mass. Additional uncertainty was associated with a small mine beneath stockpiles 6017 and 6018 that may or may not have been filled with waste rock. Values are provided for the total mass of waste rock in each pit watershed (pit empty), as well as for the mass of waste rock exposed when the lakes have recovered to their quasi steady-state elevations of approximately 1,542 and 1,450 ft above mean sea level for Area 1 and Area 6, respectively (pit full). These two sets of bounding conditions (pit empty and pit full) represent the maximum and minimum mass of potentially exposed waste rock (and associated sulfate loading rates), respectively.

Table 2. Ranges of exposed waste rock mass calculated for pit-empty and pit-full scenarios.

Scenario	Pit Empty (kg)			Pit Full (kg)		
	Lower Bound	Best Estimate	Upper Bound	Lower Bound	Best Estimate	Upper Bound
A1 to Second Creek	4.19E+10	4.50E+10	5.41E+10	3.52E+10	3.78E+10	4.55E+10
A6 to Second Creek	6.65E+10	7.15E+10	8.98E+10	3.99E+10	4.29E+10	5.38E+10
A6 to Area 6 Pit	6.22E+10	6.69E+10	8.42E+10	3.56E+10	3.82E+10	4.82E+10

Pyrite content

Respective pyrite contents of 0.90 wt % and 0.62 wt % were calculated for Area 1 and Area 6 and were used in calculation of field-based rates. For comparison, Area 1 and Area 6 pyrite contents calculated from the unweathered core and relative abundance of waste rock units in each area (representative of conditions at the time of extraction) were 1.42% and 0.97%. Use of these latter values to calculate field-based rates would have resulted in rates that were approximately 60% lower.

Sulfate release to Second Creek

The sulfate loadings determined at MNSW8 are instantaneous values and are dependent on flow rates. If this approach were to be used to estimate the actual mass released over an extended period of time, it would be necessary to base those estimates on a range of flow rates over the period of interest. Changes in sulfate storage in the pits following release from waste rock stockpiles and prior to reaching the stream station could cause instantaneous rates in pits and Second Creek to differ; however, during the periods in the analysis below, the Area 1 and Area 6 Pits were near hydrologic steady-state conditions. Excepting small changes due to seasonal variation and lake turnover, sulfate concentrations during these periods have also been relatively constant for all but the Area 6 Pit, which has exhibited moderate increases in sulfate concentrations (although recent observations indicate that concentrations may be stabilizing as water levels reach hydraulic equilibrium, which reduces loading due to inundation of in-pit waste rock and increases sulfate loss from outflow of sulfate-bearing lake water). Due to the steady-state assumption inherent to this approach, exposed waste rock mass for the pit-full scenario was used for calculation of these rates. For these reasons, sulfate loading rates calculated from Second Creek data should provide a reasonable indication of sulfate release rates in the Area 1 Pit, whereas, for the Area 6 Pit they may underestimate sulfate release from stockpiles.

Sulfate release rates to Second Creek were grouped based on whether Pit 1, Pit 6, or both pits were contributing to creek flow. Sulfate loads in the creek could then be evaluated for input from Area 1 only, Area 6 only, and both Area 1 and Area 6 (Figure 3 and Table 3).

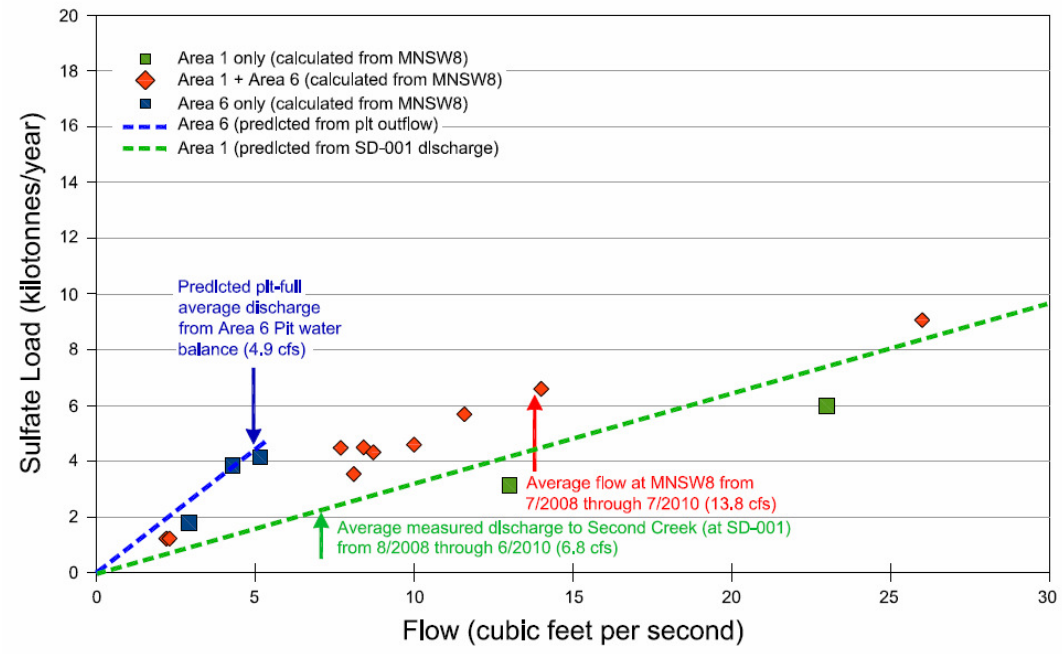

Figure 3. Sulfate load as a function of flow in Second Creek.

Instantaneous loading rates observed in Second Creek under each of the flow conditions described above were also compared to the loading rates anticipated based on outflow rates for each pit and the water quality of each pit (Figure 3). The average flow rates and sulfate fluxes for Second Creek (denoted with arrows in Figure 3) are within the range of flow conditions on which the field-based rates were calculated.

As is apparent from Figure 3, the loading rates calculated for pit discharge are in good general agreement with the ranges of instantaneous rates observed in Second Creek. There is reasonable agreement between loading calculated from Area 1 Pit discharge (green dashed line in Figure 3) and loading observed in Second Creek during times that Area 6 Pit was not experiencing outflow (green squares in Figure 3). Unfortunately, the MNSW8 observations from this period (28 May 2008 to 17 June 2008) precede the period when discharge from Area 1 was exclusively pumped (and measured), and it is therefore not possible to fully reconcile the difference between the outflow rate from Area 1 and the flow rate at MNSW8. The lower loading (or perhaps more appropriately, the higher flow rates and nearly equivalent loading) observed at MNSW8 may be attributed to additional flow contributions to Second Creek (e.g., items 5 through 8 identified in the Methods Section), which would be expected to have concentrations well below those of the Area 6 Pit and Area 1 Pit (and which would result in a nearly lateral shift to the right of the green dashed line in Figure 3). Nonetheless, the relationship supports the previously stated assumption that loadings from other sources to MNSW8 are relatively small, as well as supporting the conceptual model for flow in Second Creek (e.g., negligible bedrock outflow from Area 6 Pit to Second Creek). There is also good agreement between loading calculated from Area 6 Pit outflow (blue dashed line in Figure 3) and loading observed at MNSW8 during times where Second Creek was dry upstream from Area 6 (blue squares in Figure 3). This observation supports the Minnesota Department of Natural Resources (MN DNR) conclusion that flow in Second Creek during this period was derived largely from Area 6 Pit outflow (Pers comm, T. Bavin 2010).

Table 3. Flow conditions and sulfate release rates to Second Creek.

Date	Flow Conditions	Field-Based Rate (g SO_4/kg pyrite per year) from Sulfate Release to Second Creek		
		Upper Bound	Best Estimate	Lower Bound
5/28/2008	Area 1 Only	9.8	9.1	7.6
6/17/2008	Area 1 Only	19.0	17.7	14.7
7/15/2008	Area 1 and Area 6	11.7	10.9	8.9
8/19/2008	Area 1 and Area 6	6.2	5.8	4.7
9/9/2008	Area 1 and Area 6	2.1	2.0	1.6
10/8/2008	Area 1 and Area 6	2.1	2.0	1.6
11/10/2008	Area 1 and Area 6	16.2	15.1	12.3
2/23/2009	Area 1 and Area 6	8.2	7.6	6.2
5/4/2010	Area 1 and Area 6	8.0	7.4	6.1
5/25/2010	Area 1 and Area 6	10.1	9.4	7.7
6/8/2010	Area 1 and Area 6	8.0	7.4	6.1
6/22/2010	Area 1 and Area 6	7.6	7.1	5.8
7/7/2010	Area 6 Only	7.3	6.8	5.4
7/19/2010	Area 6 Only	17.1	15.9	12.6
8/12/2010	Area 6 Only	15.4	14.4	11.4
Average	Area 1 Only	14.4	13.4	11.1
	Area 1 and Area 6	8.0	7.5	6.1
	Area 6 Only	10.7	9.9	8.0
	All	9.9	9.2	7.5

Sulfate release to Area 6 Pit

Use of sulfate accumulation rates in Area 6 Pit offers several advantages. Firstly, the sulfate accumulation approach is independent of flow rates, unlike the Second Creek approach. Secondly, unlike the Second Creek approach, the sulfate accumulation approach does not depend on a near steady-state assumption. Finally, due to the limited outflow from Area 6 Pit during infilling, the sulfate accumulation approach facilitates comparison of laboratory-based rates to longer-duration, time-integrated release rates (i.e., the mass accumulated in the pit over approximately 8 to 10 years of infilling), rather than comparison to an instantaneous rate, such as that observed using the Second Creek data. Unfortunately, outflow from the Area 1 Pit preceded collection of sufficient geochemical data to estimate the cumulative sulfate release in the same manner as Area 6. Therefore, this approach is only applicable to the Area 6 Pit.

The sulfate release rates calculated from solute release to Area 6 Pit were very consistent for the four dates evaluated, with a relative percent difference of 9.0% between the maximum and minimum of these rates (Table 4). The rate calculated for the last date was lowest, and may be the result of increasing pit outflow as the lake level rose above the bedrock contact.

Table 4. Sulfate release rates calculated from solute release to Area 6 Pit.

Date	Field-Based Rate (g SO_4/kg pyrite per year) from Sulfate Loading to Area 6 Pit					
	Pit Empty			Pit Full		
	Upper Bound	Best Estimate	Lower Bound	Upper Bound	Best Estimate	Lower Bound
8/18/2008	20.9	19.5	15.5	36.6	34.0	27.0
9/10/2008	21.4	19.9	15.8	37.5	34.9	27.6
2/20/2009	20.6	19.2	15.2	36.0	33.5	26.6
5/19/2009	19.6	18.2	14.5	34.2	31.8	25.2

Comparison of laboratory and field-scale release rates

The average field-based rates calculated from sulfate loading in Second Creek are lower than those calculated from sulfate accumulation in the Area 6 Pit (Table 5). As discussed above, the time-integrated nature of the sulfate accumulation approach is anticipated to provide a more reliable field-based rate than the instantaneous rates calculated from Second Creek. The field:laboratory scaling factors for the sulfate accumulation approach were, surprisingly, greater than unity (1.2). That is, sulfate release rates per unit mass pyrite in the field were higher than those in the laboratory.

Table 5. Comparison of laboratory-based and field-based sulfate release rates and scaling factors.

Scenario	Laboratory-Based Rate	Sulfate Release to Second Creek		Sulfate Release to Area 6 Pit	
		Rate	Scaling Factor	Rate	Scaling Factor
Upper Bound	21.9	9.9	0.5	28.4	1.3
Best Estimate		9.2	0.4	26.4	1.2
Lower Bound		7.5	0.3	20.9	1.0

Although reliable estimates are not available for the particle-size distribution of waste rock in the field, the particle size used in the laboratory tests for unweathered rock was small (<2 mm), and is, in fact, smaller than the size recommended by the method; this should have resulted in higher rates in the laboratory, and driven the scaling factor further below unity. Sulfate-rinsing efficiency within the unsaturated portions of the waste rock stockpiles should be less than that of the humidity cells, which would tend to lower rates in the field. The field:laboratory scaling factors presented here are specific to the waste rock disposal practices at the site. Of particular importance is the fact that the sulfate release to the Area 6 pit included rock that was ultimately submerged (about 40% of the total). Consequently, the calculated field rate included sulfate released due to submersion, which would have been stored within a waste rock pile constructed subaerially. Thus, this sulfate release rate is higher than that expected from strictly subaerially

constructed piles. Correction for sulfate that was present in influent waters would have reduced the field-based rates, but pit infilling is predominantly from precipitation, runoff, and shallow groundwater inflow, which typically have concentrations much lower than those observed in the pit; it is estimated that correction for influent sulfate would have reduced calculated field-based rates by roughly 10%. Lower temperatures in the field should produce field rates that are about 10% of those in the lab, based on the Arrhenius equation; this variable alone would have resulted in a scaling factor of less than 0.1.

As mentioned above, the laboratory rates presented here are from testing of unweathered drill core samples (such as those typically used for pre-mining characterization), and are a factor of 10 lower than the rates observed in the humidity cells of weathered waste rock samples of the same lithology. The order of magnitude difference between release rates observed in the fresh and weathered samples indicates a temporal evolution of sulfide oxidation. Factors contributing to this process could include increased biological activity in the field (and sustained in the humidity cells for weathered samples), although the authors are not familiar with such acceleration reported for circumneutral pH environments. Additionally, the petrologic character of the Lower Slaty waste rock may contribute to acceleration of weathering. The geochemically induced physical evolution of sulfidic mine wastes can occur at several scales. Large-scale disaggregation of rock can occur, increasing the overall surface area of the rock. This has been observed previously in bedded pyrrhotite in the Virginia Formation (Figure 4). Similarly, this can occur at the mineral veinlet scale. Although direct evidence of this type of expansion and exposure of sulfides was not observed in the samples analyzed, the petrographic descriptions indicated "Pyrite occurs in thin (25 micron thick) foil-like veinlets that are parallel to and cross-cutting bedding. The rock separates easily along the pyrite veinlets" and other occurrences, such as "euhedral aggregates" might also increase sulfide mineral exposure with weathering. This may also occur as a result of liberation of pyrite resulting from dissolution of the pyrite-associated granoblastic siderite and siderite-rich matrix. Finally, intragrain exposures may increase as a function of weathering. This type of mechanism has been described by Jerz and Rimstidt (2004) with regard to pyrite oxidation in moist air: "Museum pyrites probably disaggregate due to the precipitation, in surface cracks, of ferrous sulfates, which have a much larger molar volume than pyrite". It is conceivable that the sieve-textured grains of pyrite would be particularly susceptible to this type of disaggregation mechanism.

Figure 4. Disaggregation due to oxidation of bedded pyrrhotite in the Virginia Formation.

Summary and Conclusions

Sulfate release rates were calculated for field piles of sedimentary iron formation waste rock excavated during open-pit mining, and, based on solute accumulation in Area 6 Pit, ranged from 14.5 to 37.5 g SO_4 per kg pyrite per year. These rates approximated those for unweathered drill core subjected to humidity cell testing. The high rate of release in the field was attributed to additional exposure of pyrite surface area during weathering. This exposure was attributed in part to the modes of pyrite occurrence in the waste rock which, in turn, suggests that field:laboratory scaling factors are dependent on lithology. In addition to the chemical characterization of waste rock, detailed petrographic analyses, including optical and electron microscopy, facilitated interpretation of the relationship between laboratory-based and field-based release

rates. It is anticipated that ongoing humidity cell testing and field monitoring will continue to add to the understanding of geochemical processes at the site. Commonly, the types of field-based data utilized in this study are not available for environmental characterization and prediction for mining projects. This study indicates that detailed chemical and petrological characterization can provide important insights when determining field:laboratory scaling factors for characterization and prediction and that, where possible, evaluation of weathered materials can be highly informative.

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Acronyms

American Society for Testing and Materials (ASTM)

Biwabik Iron Formation (BIF)

Cubic feet per second (CFS)

Hydrochloric acid (HCl)

Minnesota Department of Natural Resources (MN DNR)