# Geochemical Tracer Based (GTB) Sulfate Balance Models for Active Tailing Basins on Minnesota's Iron Range (II) Field-Based Sulfate Release Rates for Coarse and Fine Tailings

Michael Berndt<sup>1</sup>, Travis Bavin<sup>1</sup>, Steven Koski<sup>2</sup>, Cheyanne Jacobs<sup>2</sup>, and Megan Kelly<sup>1</sup>

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<sup>1</sup>Minnesota Department of Natural Resources Lands and Minerals Division 500 Lafayette Rd., St. Paul, MN 55155

<sup>2</sup>Minnesota Department of Natural Resources Lands and Minerals Division 1525 3rd Ave E, Hibbing, MN 55746



### Abstract

This study is the second in a three part series documenting sulfate release and cycling in taconite tailing basins and quantifies release rates for sulfate to pore waters in tailings. Part one of this series presents and evaluates sulfate sources for process waters while part three focuses on waters sampled in seeps, wells, and surface waters outside the basin.

Thirty-nine 3- to 8-foot tailings cores were collected from four taconite tailings basins in 2014 and 2015 and sectioned for chemical and physical analysis. The cored tailings ranged in age from about 1 to 30 years. Water samples were isolated from selected depths in each core by centrifugation and the samples were analyzed for dissolved sulfate, chloride, and bromide. A selected set of pore water samples were also analyzed for hydrogen and oxygen isotope ratios in pore water ( $\delta^2 H_{H20}$  and  $\delta^{18} O_{H20}$ ). Bromide and chloride concentrations were used for identifying and quantifying residual process waters in the pore fluids. The seasonal variation in  $\delta^2 H_{H20}$  and  $\delta^{18} O_{H20}$  was used along with a HYDRUS 1D model to demonstrate that infiltration depth could be reasonably used as a proxy for pore water residence time.

Sulfate release rates for tailings in each core section were calculated using:

$$R = (V_{H2O}/M_{rock}) \times (m_{SO4}) / t \qquad (Equation 1)$$

where  $V_{H2O}/M_{rock}$  is the water to rock mass ratio (L/kg),  $m_{SO4}$  is the sulfate released into pore water (umol/L), and t is the contact time for water reacting with tailings. A weighted water to rock volume/mass ratio was computed for material above each core interval. Time, *t*, was estimated either by comparing the volume of water present in the core to an infiltration curve or from the time since tailings deposition, depending on whether substantial amounts of process water were present in the core. The amount of "new sulfate" formed from pyrite oxidation was computed by subtracting out the sulfate derived from residual process water (calculated by ratio with chloride) from the total sulfate. Rates were calculated in terms of umol/kg tailings/week and converted to sulfate flux, F, in units of metric tons/mile<sup>2</sup>/week.

Rate calculations were highly variable and site specific depending on drainage characteristics, age of tailings, plant cover, and tailings type. More work is still required for a full understanding of sulfate release rates from tailing basins, but the data tables for release rates and fluxes provide a starting point for providing better quantification of the relative impacts of tailings on sulfate in waters that penetrate tailings on Minnesota's Iron Range.

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### Introduction

A common method for predicting sulfate generation and release from mined rocks, including tailings, involves making measurements in a laboratory setting followed by extrapolation to the field (Lapakko, 2015). However, climate and hydrology of the field site must be taken into account when extrapolating laboratory rates to the setting where the mined materials are to be placed (Amos et al., 2015). The frequency and duration of drying and rinsing cycles, which are carefully controlled in laboratory settings, are highly variable in the field. Moreover, the degree of saturation in tailings can vary over time, and this also impacts the rate at which tailings weather in field versus laboratory settings. Temperature variation in the field can be extreme. Microbial processes may vary from laboratory to field and are often involved in sulfur oxidation processes. Still, when predictions are needed before a mine exists, there is little choice but to conduct experiments and extrapolate laboratory rates to the field. When a mining feature does exist, however, then the alternative approach is to measure rates directly in the field.

The goal in this study is to measure sulfate release rates directly in the field for taconite tailings that have already been deposited in tailings basins. The method involves calculating the mass of sulfate added from tailings to coexisting pore waters, and determining contact time and appropriate water volume to rock mass ratios for that time period. Weathering in the field is a complicated process owing to variability in the timing and duration of precipitation and the potential occurrence of drying events. The drainage characteristics for tailings deposited in the field also depends on particle size, tailings density, antecedent moisture conditions, location with respect to local water tables, and other factors. Moreover, while sulfate may be generated by pyrite oxidation, some sulfate may be present in process water still contained in the tailings or can be concentrated by evaporation in the core's upper layers or diluted by fresh precipitation falling on the tailings. Thus a geochemical tracer based (GTB) method was developed here to quantify rates under a variety of settings. If sulfate from residual process water is abundant in pore waters, so too should chloride which is also elevated in process waters. Residual sulfate can be computed by ratio with dissolved chloride and any additional sulfate present in pore fluids can be assumed to have been added by oxidation of pyrite since the time the tailings were deposited. In older well-drained tailings, however, process waters are largely replaced by dilute waters infiltrating from the surface. In these cases, rinsing is confirmed using dissolved chloride, and the time over which any sulfate was added is determined by comparing estimated infiltration rates prior to core collection with the pore-water's sampling depth.

The aim of this study is to provide a series of empirically determined sulfate release rates that can be compared with operation-scale sulfate mass balances conducted for five taconite processing plants in Part 1 of this series (Berndt et al., 2016) and also with estimates of sulfate release that occurs when waters migrate through dikes composed of tailings into nearby surface and groundwater in Part 3 (Kelly et al., 2016). Release rates are calculated for freshly deposited tailings and also for tailings deposited from 1 to 30 years ago. This facilitates the prediction of changes in release rates that might be expected in the following decades as fresh tailings are deposited and as sulfide minerals in older tailings are either oxidized and weathered away, or become buried and are no longer well exposed to oxygen. A parallel study was conducted on the tailings collected in this study to determine the reduction in pyrite surface areas and development of weathering rinds (Jacobs et al., 2016). The combined studies provide data needed for the

potential application of shrinking core models to predict long term release of sulfate to taconite tailing basins (Rimstidt, 2014).

### Methods

#### Sampling and Processing

A total of 39 cores ranging from approximately 3 to 8 feet in length were collected from four tailing basins: Hibbing Taconite, U. S. Steel Minntac, United Taconite, and the ArcelorMittal Minorca Mine. A truckmounted Giddings Soil Probe (Giddings Machine Company, Windsor, Colorado) was used to collect the cores. After initial testing, it was found that collection of cores in approximately 6 to 18 inch segments provided virtually high retrieval for most core sections and minimized compression. Most core sections were collected into 3.5-inch PETG plastic tubes, although a few sections were collected in 2-inch core tubes when more directed force was needed to penetrate the tailings. Core sections were sealed in the field and brought back to the Minnesota Department of Natural Resources Lab in Hibbing, Minnesota for further processing, which typically took place over the next several days to week.

Moisture content and dry and wet density were determined for all core sections.. Particle size distributions and sulfur concentrations were determined for a subset of cores. The moisture content  $(V_{H2O})$  or volume of water in a known volume of core and bulk density (the mass of solid rock material in a volume of core) was determined by first measuring the core volume geometrically, and then weighing composited wet and dry samples obtained from the core. Pore-water samples were extracted from selected depth intervals using centrifugation and centrifuge tubes that contained 0.45 micron filters. In some cases a small amount of water appeared to bypass the filter, as evidenced by the presence of a cloudy particulate phase. When this happened, the sampled water was refiltered using a syringe and 0.45 micron cartridge filter. More detailed coring, sampling, and processing methods are provided by Bavin et al. (2016).

#### **Chemical Methods**

Approximately 0.2 to 2 ml-sized samples were shipped cold (on ice) to the University of Minnesota Aqueous Geochemical Laboratory where they were diluted and analyzed for dissolved bromide, chloride, and sulfate by ion-chromatography (Dionex ICS 2000). Detection limits for bromide, chloride, and sulfate on undiluted samples are approximately 0.01, 0.01, and 0.02 mg/L. The small samples were diluted by as much as 100x, resulting in higher detection limits for smaller samples. Bromide levels in many of the samples were below detection in highly diluted samples, but all samples contained measureable chloride and sulfate concentrations needed for calculation of sulfate release rates.

A few samples were selected for water isotope analyses to confirm that infiltration depth can be used as a proxy for the time it takes for precipitation to infiltrate deeply into tailings. Small aliquots of approximately 1 to 5 ml of undiluted porewater were sealed tightly into small glass vials and shipped to the University of Waterloo Environmental Isotope Lab for analysis. Vials were tightly sealed with limited headspace to minimize evaporative loss. Values for <sup>18</sup>O/<sup>16</sup>O ratios were determined via gas equilibration and head space injection into an IsoPrime Continuous Flow Isotope Ratio Mass Spectrometer (CF-IRMS).

Values for <sup>2</sup>H/<sup>1</sup>H ratios were determined using chromium reduction on a EuroVector Elemental Analyzer coupled with an IsoPrime CF-IRMS. Internal laboratory standards were calibrated and tested against international standards from the International Atomic Energy Agency (IAEA), including Standard Light Antarctic Precipitation (SLAP), Greenland Ice Sheet Precipitation (GISP), and Vienna Standard Mean Ocean Water (VSMOW). Values for  $\delta^{18}O_{H2O}$  and  $\delta^{2}H_{H2O}$  are reported in ‰ relative to the international standard Vienna Standard Mean Ocean. Sample replicates were run approximately every 8 samples. Analytical uncertainties are ±0.2‰ and ±0.8‰ for  $\delta^{18}O$  and  $\delta^{2}H$ , respectively.

#### **Computation of Field-Based Sulfate Release Rates**

Sulfate release rate calculations for each core interval were determined using the following equation:

$$R_{SO4} = (V_{H2O}/M_{rock}) \times (m_{SO4}) / t. \qquad (Equation 1)$$

where  $R_{SO4}$  is the sulfate release rate (commonly reported in units of umol/kg/week for the mining industry),  $V_{H2O}$  is the volume of water (L),  $M_{rock}$  is the mass of rock (kg),  $m_{SO4}$  is the sulfate concentration (umol/L), and *t* is the pore water residence time (time since the water infiltrated the tailings in weeks). For standard humidity cells (e.g., ASTM, 2009)  $V_{H2O}$  is 0.5 liters,  $M_{rock}$  is 1.0 kg, *t* is one week, and sulfate concentration is measured in the 0.5 liters of water that are used to rinse the cell each week. Calculating rates from pore fluid data is similar to the laboratory method except that all of the parameters must be estimated.

Time, *t*, was estimated by comparing modeled infiltration amounts (in inches) (Bavin et al., 2016; included in the appendix) to the total inches of water that were stored in each core at or above the core interval. In simplest terms, *t* is number of weeks required to infiltrate the volume of water found in and above the core interval in the specific time period before the core was collected in the field. It is recognized that this method ignores many aspects of infiltration. For example, moisture contents are not static, becoming elevated near the surface immediately following rain events and then decreasing again as water percolates to deeper levels. Moreover, infiltration of water near the surface can be reversed by evaporation from the surface during dry periods. Water also infiltrates through selected pathways (e.g., Kapetas et al, 2014). Although this effect is partly mitigated by chemical exchange processes during the lulls between rain events, it introduces uncertainty in evaluating reactive transport processes in unsaturated materials. As will be discussed later, however, using infiltration depth as a proxy for time was evaluated using water isotope distributions.

Water to rock ratios ( $V_{H2O}/M_{rock}$ ) sometimes varied down core, and thus a length-weighted water volumeto-rock mass ratio (wtd W/R) was used for rate calculations. The release rates and fluxes reported in the data tables are integrated values that apply to the entire column of tailings in and above the section from which the pore fluids were collected. In effect, each core section can be considered to have behaved like a humidity cell, where the sample drawn at some depth, D, is from water that reacted for time, t, with tailings and  $V_{H2O}/M_{rock}$  = "wtd W/R". Some of the uncertainty in the method could be reduced by comparing rates calculated from adjacent core sections, which might be expected to provide reasonably similar release rates to each other. In a few cases where rates for adjacent cells were highly disparate, the inspection of the calculated results for all core intervals together provided a means to determine which values were likely more representative of rates for the entire core.

Many of the pore fluids contained sulfate that was sourced from process water still trapped in the cores. Therefore, it was necessary to subtract any "old sulfate" not generated by reaction from the sulfate concentration measured in the core section. The "old sulfate" was calculated by assuming that its values relative to chloride were directly proportional to those in averaged process water (Berndt et al., 2016). In most cases, subtracting this "old sulfate" from the total sulfate resulted in a concentration for "new sulfate". If chloride concentrations were low, as was generally the case in unsaturated old tailings, then the new sulfate value was similar to the measured sulfate value because little or no process water was present. If chloride concentrations were high, however, then "new sulfate" values could be considerably lower than total measured sulfate values. This was most commonly the case for relatively fresh tailings which had experienced limited drainage since deposition. In a few cases, the calculated "new sulfate" was negative. When this happened, it was suspected that either some sulfate reduction occurred, or that the process water deposited with the tailings had a lower sulfate to chloride ratio than the average process water measured in the study by Berndt et al. (2016). If the chloride levels in the sample were similar to process water values, then it was assumed that none of the water initially entrained in the tailings had been displaced by precipitation and t in Equation 1 was set equal to the time difference between tailings deposition and collection of the core.

It should be noted that if actual infiltration rates are lower than those calculated, then *t* will be underestimated and release rates will be overestimated. In this respect, the calculated rates represent maximum values for heavily vegetated sites, where transpiration inhibits infiltration of some of the water. Conversely, assuming an infiltration rate slower than actual would lead to underestimations of sulfate release rates. This could lead to some uncertainty in the maximum release rates for coarse tailings, since it was assumed infiltration in coarse tailings is similar to that in moderately fine tailings.

Because  $R_{SO4}$  values computed for each core section are integrated for the thickness of the column, they can be used directly to compute the sulfate flux for a layer that is as thick as the column is tall. Flux is equal to the mass of tailings in the layer (e.g., kg/unit area) multiplied by  $R_{SO4}$ . In this document flux (F) is computed in units of metric tons per square mile to facilitate direct comparison with tailings deposited at the scale of a tailings basin. It is important to note that the flux values calculated for a layer of a given thickness will likely not be one half that of a layer twice the thickness. Actual fluxes should vary non-systematically with depth owing to oxygen depletion and development of weathering profiles over time.

### **Results and Discussion**

#### **General Statement**

As noted previously, a primary assumption made when measuring field-based release rates include the notion that infiltrating water moves downward through tailings in a relatively systematic manner, displacing old pore-fluids with fresh pore water. At the scale of a single infiltration event, however, it is

known that flow can be characterized by the relatively rapid downward movement of water through macropores, typically bypassing residual water stored in micropores. Macropore-micropore exchange occurs during intermittent periods, however, leading to the transport of newly formed sulfate down to deeper levels.

To test the validity of the applied method, water isotopic composition was measured for an entire core into which infiltration had occurred for more than a year (Figure 1). In that section,  $\delta^{18}O_{H20}$  and  $\delta^{2}H_{H20}$ values were found to increase and decrease together along values that fall on the local meteoric line. The variations that were observed are similar to those expected for summer and spring or fall precipitation events. The seasonal variation present in pore fluids would be muted if there was a lot of mixing of different age pore waters in the cores. This provides some degree of confidence that the method used to calculate *t* for unsaturated tailings is reasonable and that water movement downward is relatively systematic at the scale of this core's length (8 feet).

Another matter relates to the reasonability of calculating "new sulfate" concentrations by subtracting "old sulfate" derived from residual or evaporated process water using a chloride-based adjustment. This method is only appropriate if the chloride was introduced from process water and not from some other unknown sources that lacked sulfate. A comparison of bromide versus chloride for samples where bromide concentrations were above detection limits (Figures 2 and 3) provide support for this approach. If the bromide to chloride ratios for process waters were clearly different for pore waters and process waters, then it would indicate the presence of another chloride source within pore fluids. Bromide to chloride ratios for most of the pore water samples were close to those measured for process waters at all of the operations, with the possible exception of Hibbing Taconite. These may have had small contributions of chloride from biosolids that are applied to the tailings for reclamation purposes or that bromide/chloride ratios in 2009 process waters (when the tailings were deposed) were different from those measured during the study period (Berndt et al., 2016). The impact of this on the measurements values will be discussed below, in the Hibbing Taconite section.

Several samples containing elevated bromide concentrations without elevated chloride were reported by the analytical laboratory in samples from a few cores collected at U. S. Steel – Minntac in 2014. Those areas were cored again in 2015, and this time there were no anomalous bromide values observed. Thus, the elevated bromide concentrations observed in several of the 2014 samples from Minntac are attributed to laboratory error and are not shown in Figure 2.

### Hibbing Taconite (Hibtac)

Tailings samples ranging in age from approximately 1 month to 9 years old were cored on July 14, 2015, at eight locations in Hibbing Taconite's tailings basin (Figure 4). The basin is located north of the city of Hibbing, Minnesota in the Mississippi and Rainy River Watersheds.

Six cores were collected on a north-south trending transect in the East Area cell of the basin (Cores 1-6 in Figure 4) down to depths ranging from 40 to 90 inches. The southern part of the transect was located near the main tailings discharge to the East Area tailings cell and the northern part was located near the northern edge of the cell. The transect location was chosen to account for fluvial deposition processes

that cause particle size sorting and layering during tailings deposition. Larger tailings particles are typically deposited near to the main discharge point while finer particles typically settle out farther down gradient from the discharge location.

Tailings were last deposited in the East Area cell between 2006 and 2009 when Hibbing taconite did not segregate tailings into coarse and fine fractions. Extensive reclamation had been conducted in the cell prior to core collection, including application of biosolids and addition of other amendments to the tailings surface. Most of the cell was well covered with grasses ranging in height from 2 to 4 feet at the time of coring.

An approximately 4-foot long coarse tailings core was also collected on the north facing slope of the cell dike for West 3 Area cell dike. The section of the dike that the sample was collected from was recently raised in June 2015 (Core 7 in Figure 4). Finally, a fresh fine-tailings sample was collected from a small beach area in the southwest corner of the West Area 1 cell (Core 8 in Figure 4). Only a grab sample was collected at that location because the tailings were not solid enough to support the truck with the Giddings Probe.

Pore-water sulfate concentrations ranged from approximately 130 mg/L to 2474 mg/L in the cores collected from the Hibtac tailings basin (Figure 5; Table 1). In general, sulfate levels were elevated with respect to the average sulfate concentration in the fine tailings slurry (178 mg/L; Berndt et al., 2016). In contrast, chloride levels in the core pore waters generally bracketed the average chloride concentration in the fine tailings slurry (55 mg/L) ranging from approximately 4 to 350 mg/L, respectively.

Pore-water chloride concentrations (Figure 5) were close to background levels near the surface in cores 1 and 2, indicating those sections of the core were rinsed by infiltrating precipitation. However, chloride concentrations were elevated deeper in the cores and were also elevated in Cores 3 to 7 throughout their entire lengths. The high chloride values indicate that some or all of the cores contained some of the residual process water initially entrained during deposition. The upper portions of Cores 1 and 2, based on low chloride values and low moisture contents, were well drained and could be interpreted as containing infiltration from precipitation during the months prior to coring. Under these circumstances, the rate estimates calculated by the method used here could be high due to incomplete rinsing of sulfate. The remaining core sections in the East Basin, with high chloride, were interpreted as containing mostly old residual water from 2009. Pore waters in those sections were therefore considered to have reacted with tailings under nearly saturated conditions for 312 weeks, the time since they were originally deposited.

Upper end release rates in the unsaturated portions of tailings that contained little process water appeared to be about 20 to 45 umol sulfate/kg/wk (Table 1, Figure 6). Additional new sulfate appeared to be present in pore waters sampled from the top of the process water zone (e.g., total sulfate >2000 mg/L). The high sulfate concentrations in those cases may relate to long residence times for process waters at or near the atmospheric interface. The estimated sulfate release rates at the top of the process-water zone, assuming the same waters were present since 2009 is 10 umol/kg/week. Below this zone, the calculated release rates are much less and even negative.

Biosolids, which were applied to the East Cell, have been known to release both chloride and sulfate when applied to tailings (Eger and Antonson, 2005; Eger et al., 2004; MN DNR, 2000). The impact of this application event was not evaluated here because the time dependent sulfate release rates for samples containing large amounts of process water at this site are low anyway - or even negative (for parts of Cores 2 and 3). Thus, sulfate release from poorly drained fine tailings amended with biosolids would also be expected to be low. It is possible that oxygen is not penetrating through into the tailings in this case.

Core 7 contained freshly deposited tailings from the West Area 1 (Table 1, Figure 6, top). Release rates of up to 18 umol/kg/wk were found near the surface, but averaged about 4.5 umol/kg/wk for the top 4 feet. These rates suggest a flux of about 2.0 metric tons of sulfate/week applies to a 4 foot by 1 square mile layer of freshly deposited taconite tailings (Figure 6, bottom).

In part 1 of this study, it was found that tailings oxidation in the basin is not a major source of sulfate for Hibbing Taconite's process waters (Berndt et al., 2016) while in Part 3 (Kelly et al., 2016) it was found that much of the sulfate in process waters is removed by sulfate reduction beneath the basin prior to leaking into the environment. Thus, even though these tailings were capable of producing elevated sulfate, the existing basin does not appear to be a large source of sulfate to the Iron Range and may actually behave as a net sulfate sink.

#### **U. S. Steel Minntac**

A total of 15 fine and coarse tailings samples ranging in age from fresh to approximately 29 years were collected from the Minntac tailings basin (Figure 7) in 2014 and 2015. The basin is located near the City of Mt. Iron, Minnesota in the Rainy River Watershed. On September 17, 2014, two cores were collected from fine tailings deposited in Cell A1-E in 1986 or before (Cores 1 and 2, Figure 7). The cell was sparsely covered with vegetation, including tall grasses and small trees and shrubs. Three cores of relatively freshly deposited fine tailings were also collected on the same day from Cell M2. These cores were collected along a transect extending from southwest to northeast (Cores 6-8, Figure 7) outward from the cell's discharge point. Tailings were last deposited in the cell in 2013. Reclamation conducted prior to sampling had covered the cell with a patchy layer of medium to tall grasses. Shrinkage cracks covered much of the tailings surface. Core sections were only collected down to a maximum depth of 24.5 inches.

Two coarse tailings cores were collected from the Minntac basin in 2014, one from Section 11 of the outer dike on the east side of the basin, deposited between 1985 and 1990 (Core 12), and the other from fresh tailings deposited in 2014 between Cells A1-E and A2 (Core 14). A 2-inch diameter soil coring tube was used in conjunction with the 3.5-inch diameter tube to collect the older coarse tails core sections due to difficulty penetrating the coarse tailings with the larger diameter tube.

Nine additional cores were collected from Minntac's tailings basin on June 17, 2015. Three fine tailings cores were collected from Cell A2, located near Cell A1-E (Cores 3-5, Figure 7). Tailings had last been deposited in Cell A2 in 1986 and the tailings surface was covered with a patchy layer of tall grasses and small trees/bushes. Cores were collected along a transect extending from the southern part of the cell to the northern dike, once again on a transect extending outward from the discharge point to the cell. All

cores were collected on the east side of the cell near the coarse tailings dike because small trees prevented access to much of the cell area.

Three cores were also collected from relatively fresh tailings on a transect extending from the east side of Cell K near the tailings discharge point to the west side where the tailings water is decanted into Cell 2 (Cores 9-11, Figure 7). Tailings had last been deposited in Cell K in 2012 and reclamation work had covered the cell with a patchy layer of medium to tall grasses. Much of the tailings surface was covered with a network of shrinkage cracks.

Two additional coarse tailings cores were collected from Section 11 of the outer coarse tailings, just north of where Core 12 was collected in 2014 (Cores 13 and 13Dup, Figure 7). A grab sample of freshly produced coarse tailings was also collected from within the plant in 2015.

Pore-water sulfate concentrations generally increased with depth in the fine tailings cores collected in Cell A1-E in the Minntac tailings basin, ranging from approximately 10 to 775 mg/L, respectively (Figure 8, Table 2). The maximum sulfate concentration measured in both cores was lower than the average sulfate concentration in typical tailings slurry (Berndt et al., 2016). In contrast to the Hibtac cores, pore water chloride levels in Cores 1 and 2 were low indicating the water in them was sourced from precipitation and not process water. The increasing pore-water sulfate concentrations with increasing depths are likely the result of sulfate accumulating in precipitation as it percolates downward through the tailings profile and comes into contact with oxidizing sulfide mineral surfaces in the tailings.

Similar to the fine tailings cores collected in Cell A1-E, sulfate concentrations generally increased with depth in the tailings cores collected in Cell A2, ranging from approximately 40 to 1200 mg mg/L, respectively, with the highest concentrations measured in Core 3Dup (Figure 9, Table 3). Like the cores collected in Cell A1-E, pore water chloride levels were low, indicating the water in them was sourced almost entirely from precipitation. Therefore, the dissolved sulfate in the pore water was almost certainly sourced from the oxidation of sulfide minerals in the tailings and accumulated as the waters percolated downward through the tailings profile.

In contrast to the cores collected in Cells A1-E and A2, pore-water chloride concentrations were elevated in the tailings collected from Cell M2, indicating that large amounts of residual process water remained in the cores (Figure 10, Table 4). Chloride levels in Cores 6 and 8 ranged from approximately 200 to 275 mg/L, which are even higher than amounts typically found in process waters. This indicates that the dissolved salts in the tailings pore waters had likely been concentrated by evaporation. In contrast, the average chloride concentration in the pore water in Core 7 was approximately 75 percent lower than the concentration in process waters. This indicates that, although residual salts were present from process waters, a significant percentage of the pore water was sourced from precipitation.

Pore-water sulfate concentrations in Cores 6 and 8 were elevated compared to the average sulfate concentration in the fine tailings slurry, ranging from 1000 to 2800 mg/L, respectively. The pore water sulfate concentrations in Core 7 were lower than the tailings slurry, averaging 637 mg/L for all intervals, respectively. Pore-water chloride concentrations in Cores 9-11 (Figure 11, Table 5) ranged from approximately 2 to 340 mg/L, respectively, indicating variable evaporation and drainage of the process

water had occurred since 2013. Pore-water sulfate concentrations were often quite elevated, ranging up to 3350 mg/L.

Sulfate concentrations in pore waters from coarse tailing ranged from approximately 60 to 1500 mg/L in the cores that were collected from Section 11 of the outer dike on the east side of the Minntac tailings basin (Figure 12, Table 6). Chloride levels in those cores were also elevated compared to background levels, ranging from 9 to 140 mg/L, and are assumed to have been derived from process water. Elevated chloride levels are difficult to understand for coarse tailings, since they are expected to be well rinsed in the 25 to 30 years since they were deposited. We assume that the elevated sulfate relates to the spraying of roads with process water during dry periods, based on the general bromide and chloride trends for Minntac (Figure 2, bottom).

In contrast to the cores collected from Section 11 of the outer dike, the chloride in the pore water in Core 14 is most likely sourced from the process water that was deposited directly with the tailings when the dike was raised in 2014 (Table 6). The average chloride concentration in the pore waters for this core is approximately 157 mg/L, which is similar to the average concentration in process waters. In contrast, the average pore-water sulfate concentration is approximately 2450 mg/L, which is approximately three times greater than the concentration in process waters.

Sulfate release rates calculated for the upper few feet of Minntac's Cores 4 and 5 (Table 3, Figure 13) are among the highest in the study, ranging from 69 to 146 umol/kg/wk. These cores were collected in older tailing samples from points located distally from the cell's tailing discharge site. It is unlikely that very fine tailings would provide sulfate release rates this elevated 26 years after deposition. In fact, there was likely not sufficient sulfide in the tailings to provide this much sulfate to water for a 26 year period. Either they were not altering this fast for the entire period of time or the high values are an artifact of the method used to estimate the rates. Comparison of rates with those for adjacent sections suggests that the latter may be true. The highest computed rates correspond to samples having relatively moderate sulfate values that are not greatly different from values measured in the sections immediately below, where computed rates are much lower (7 to 23 umol/kg/wk).

A possible explanation for high estimated rates is that water penetrated the upper sections of core immediately following a relatively long dry period. The water that penetrated the core during this period may have rinsed sulfate that formed over the much longer dry period immediately before sampling. A better approach in this instance might be to set *t* as the amount of time that passed between the beginning of the dry period and the time that the core was collected, approximately 53 weeks in this case. Assigning these values would, however, potentially underestimate the actual release rates because some sulfate formed during the dry period probably was rinsed into the sections below. Rates calculated for the sections immediately below range

from 7 to 23 umol/kg/wk are probably more representative of the actual overall release rates since they are less impacted by recent dry periods and provide averaged values for the entire core section to those depths.

Outside of those results, the release rates for each tailings type appear to be relatively consistent with expected values based on lab data from Von Korff and Bavin (2014), which should be elevated compared to field values. Fresh fine tailings collected from locations closer to the discharge point (Cores 9 and 10) yielded modeled results that are variable but averaged between about 25 and 40 umol/kg/wk (Figure 13 top) corresponding to a flux of about 15 metric ton/mile<sup>2</sup>/wk (Cell K, Table 5, cores 9 and 10, 25 and 32 inches, respectively). Computed rates and fluxes appear to be lower than this at the more distal location where tailings are finer (Core 11). During the early stages of drying out when the tailings are closer to saturation immediately following deposition (Cell M2, Table 4) there may be less penetration of oxygen. As the tailings age the release rates for fine tailings also appear to be generally lower (excepting the spuriously high results in the top two sections of Cores 4 and 5). The calculations indicate that after approximately 25 years of alteration, the sulfate flux for an approximately 100 inch or thicker layer of fine tailings ranges between about 10 and 15 metric tons/mile<sup>2</sup>/wk (Figure 13).

Release rates estimated for the two sections of fresh coarse tailings from the inner dike (Core 14) were 30 and 41 umol/kg/wk. Flux rates for a 34-inch layer of fresh coarse tailings, corresponding to the deepest core section sampled at this site is 7.7 metric tons/mile<sup>2</sup>/wk. This value would increase for tailings of greater thickness since the bottom of the oxidation zone was likely not sampled in our study. The sulfate concentrations measured in pore fluids from deeper sections of the inner dike measured close to 4000 mg/l at depths of 40 to 100 feet (Kelly et al., 2016b) supporting the likelihood of continued release to depths greater than 34 inches.

Estimated release rates for the old coarse tailings (Cores 12, 13, and 13-Dup) from the outer dike appeared to be low near the surface, but reached values of 9 to 20 umol/kg/wk when calculated using deeper core intervals (4 to 6 feet). This suggests that sulfide depletion in the shallow zones was allowing oxidation to proceed to deeper levels in the deposited tailings. Sulfate flux at 80 inches depth average 15 metric tons/mile<sup>2</sup>/week for cores 12 and 13, but was only 7 metric tons/mile<sup>2</sup>/week in Core 13 Dup, values that are similar to those computed for the older fine tailings sampled in this study. The similarity suggests a possible external limitation (e.g., oxidation rate limited to diffusion rates for O<sub>2</sub> into the tailings).

The field-based rates measured for fresh fine tailings and for fresh or old coarse tailings in this study are lower than those measured in the laboratory by Von Korff and Bavin (2014) using standardized humidity cell tests which ranged from about 39 to 125 umol/kg/week. However, the field-based release rates measured in this study are higher than those measured in the laboratory for old fine tailings. Von Korff and Bavin sampled old fine tailings from the surface of the outer dike, which was constructed in the late 1980s. The sample used in those experiments had probably oxidized to the point that little pyrite remained. The present study measured the averaged rate for thick sections of old tailings that still contained sulfide minerals that continue to oxidize when oxygen diffuses into the tailings.

#### United Taconite (Utac)

Eight tailings samples were collected on July 16, 2015 at United Taconite's tailings basin (Figure 14) in Forbes, Minnesota, ranging in age from approximately 7 months to 15 years. Three fine tailings cores were collected from Basin 1 along a transect extending inward from the coarse tailings dike on the north

side to a small wetland in the center (Cores 1-3, Figure 3). During operation, the fine tailings for this mine are discharged into the basin near the outer edge of the dike and the tailings settle out as water flows to a reclaim pump in the center of the basin. The discharge location is regularly rotated around the perimeter of the basin to keep the water pool in the center from encroaching on the outer dike. As a result, a beach area is deposited containing a higher proportion of relatively coarse particles around the periphery of the basin and transitions to finer particles near the center of the basin.

The DNR Lands and Minerals Division conducted several studies examining the viability of using biosolids and other organic substrates to improve vegetation establishment on taconite tailings in the past (Eger et al., 2000; Eger and Antonson, 2005; MN DNR Lands and Minerals, 2002). Biosoilds were applied to most of the cored fine tailings area in 2002. Utac's 2014 annual operating report indicates the Western Lake Superior Sanitary District (WLSSD) also applied biosolids to approximately 252.97 acres on Tailings Basin 1 in 2014 and that biosolids will continue to be used on the basin in 2015. Currently, most of the fine tailings area in Basin 1 is covered with alfalfa, with the exception of the wetland and a small area with test plots covered by trees. This vegetation would be expected to increase evapotranspiration and lead to lower infiltration rates than for bare tailings. This means that using infiltration rates estimated for non-vegetated fine tailings in the Minntac basin will likely overestimate actual infiltration rates.

Three coarse tailings cores were also collected from the top crest of the coarse tailings dike on the north side of Basin 1 (Cores 5-7, Figure 3). The tailings had undergone reclamation and regrading since closure and had also been amended with biosolids around 2000–2002. They were covered with patchy grasses that were a few feet in height. The coarse tailings core sections were collected down to depths of approximately 68 to 79 inches, respectively.

Finally, one fine and one coarse tailings core were collected from Basin 2, which is the currently active tailings basin at for United Taconite. The fine tailings core (Core 4, Figure 3) was collected from a small beach area on the east side of the basin that last had active tailings deposition in January, 2015. Core sections were only collected down to a depth of 48 inches at that location. The coarse tailings core was collected from the crest of the Basin 2 dike near the beach area where the fine tailings core was collected (Core 8, Figure 3). The dike had last been raised in June, 2014.

Pore-water sulfate concentrations in the fine tailings cores collected from Basin 1 at Utac ranged from approximately 200 to 1350 mg/L (Cores 1 to 3 in Figure 15 and Table 7), which is substantially higher than the average sulfate concentration in present day fine tailings slurry (223 mg/L; see Berndt et al., 2016). In contrast, pore-water chloride concentrations were low in Cores 1 to 3, with the exception of a couple of deeper intervals in Core 1. The elevated chloride in the deep interval from Core 1 indicates possible residual process water.

Unlike the older fine tailings cores collected at Minntac, the pore water sulfate concentrations in the older fine tailings cores collected at Utac generally did not increase with depth. Rather, sulfate concentrations varied across all depths, possibly because water uptake by the alfalfa growing on Basin 1 was limiting the downward percolation of water and organic carbon degradation was limiting O2 penetration through the tailings.

Pore-water sulfate concentrations were also elevated in Core 4 from Basin 2, reaching 1100 mg/L at 3 ft depth. Pore-water chloride concentrations in Core 4 were low near the surface but were elevated to 160 mg/L in the deeper/high sulfate interval, meaning that residual salts from process water were present in the pore fluids. However, the 160 mg/L value is approximately three times higher than the average chloride concentration in the current tailing slurry, indicating likely impact from evaporation.

Pore-water sulfate concentrations in the coarse tailings cores collected from Basin 1 at Utac (Cores 5 to 7 in Figure 16 and Table 8) were lower than the concentrations in the fine tailings cores and range from approximately 120 to 470 mg/L, respectively. Chloride levels in the coarse tailings cores were slightly elevated, ranging from approximately 18 to 34 mg/L, suggesting that some residual process water was present.

Pore-water sulfate concentrations in Core 8 reached 630 mg/L in the 26 to 40-inch interval. Pore-water chloride concentration was only 10.7 mg/L. Thus, most of the sulfate in the pore water for Core 8 was likely sourced from the oxidation of sulfide minerals in the freshly deposited coarse tailings.

As was the case for Minntac, sulfate concentrations in shallow pore fluids from old fine tailings (Cores 1 to 3, Table 7, values greater than 100 excluded from Figure 17) resulted in sulfate release rates that appeared to be unrealistically high (81 to 359 umol/kg/wk). Calculations suggest that sustaining these rates since deposition in 2000 would deplete or more than consume available sulfide minerals. It is possible, if not likely, that the topmost section from Cores 1 to 3 contained excess sulfate generated during previous dry periods and this sulfate was rinsed into the waters from more recent rain events. A similar process appears to have impacted the sulfate release rates for upper sections of Minntac Cores 3 Dup and 4.

Core 1, located closest to the access road, appeared to have much more dissolved chloride than Cores 2 and 3, and the source of this Cl is not known. This additional chloride appears to have confounded the calculation since rates in the bottom of Core 1 are near zero. For cores 2 and 3, containing less Cl in pore waters and located further from the access, rates increase to values of values of 9 to 16 for intervals below four feet in Core 2 and to 29 and 22 for similarly deep intervals in Core 3. These rates are similar to those calculated for old tailings at Minntac.

It is important to note that the overall infiltration rates used to calculate *t* are for bare tailings, even though the fine tailings at United Taconite are covered with relatively dense vegetation in Basin 1. The added transpiration associated with plant growth would decrease infiltration compared to those used in the rate calculations, meaning that actual *t* values might be greater than estimated in Table 7. Because *t* is in the denominator of Equation 1, the computed rates of sulfate release would be expected to be higher than the actual rates. Differences in plant cover and differences in evaporation could also be leading to some of the variability found in the rate calculations at this site.

For fresh fine tailings in Basin 2, the pore water collected from the 28 to 48 inch interval was assumed to have been present in the tailing environment since deposition, leading to a sulfate release rate of 10 umol/kg/wk and a flux of 3.8 metric tons/sq mi/wk.

Coarse tailings that had aged in the field for approximately 16 years (Cores 5 to 7) provided release rates that averaged about 10 umol/kg/wk for the top 6 feet of material. This corresponds to an average flux of approximately 7.5 metric tons/mile<sup>2</sup>/wk. Fresh coarse tailings were only sampled down to 40 inches depth. The integrated rate for the top 40 inches was 42.7 umol/kg/wk, corresponding to a flux (for the same tailing thickness) of 8.9 metric tons/mile<sup>2</sup>/wk.

#### **ArcelorMittal Minorca**

Tailings ranging in age from approximately one month to 15 years were cored from ArcelorMittal's Upland Tailings Basin and Minorca In-pit Basin on July 23<sup>rd</sup>, 2015 (Figure 18). Six of the cores were collected from the Upland Tailings Basin, located northeast of the city of Virginia, Minnesota in the Rainy River Watershed. The seventh core was collected from the Minorca In-pit Tailings Basin, located east of the city of Virginia in the St. Louis River Watershed.

Three fine tailings cores were collected along a north-south trending transect on the west side of Cell 2A in the Upland Tailing Basin (Cores 1-3, Figure 18). Tailings were last deposited into the cell between 2000 and 2001 and the cell had been reclaimed since closure. At the time of sampling, the cell was covered with small bushes or trees and patchy grasses that were a few feet in height. Relatively fresh fine tailings (Core 4, Figure 18) were collected from the Minorca tailings disposal site which was last active in 2014, although periodic discharges of lesser amounts still occur. The tailings surface in the part of the basin that was sampled was completely devoid of vegetation and contained a network of shrinkage cracks.

Three cores of old coarse tailings were collected from the northern crest of Cell 2A's dike (Core 5-7, Figure 18). The section of the dike had last been raised between 1999 and 2000. A fresh coarse tailings core was collected from a recently raised section of dike on the eastern edge of Cell 2 in the Upland Basin (Core 8, Figure 18). The dike was raised in June 2014.

Pore-water sulfate and chloride concentrations were relatively low in all cores collected from fine tailings in Cell A2 (Cores 1 to 3, Figure 19, Table 9). Sulfate concentrations ranged from approximately 5 to 85 mg/L while chloride concentrations ranged from approximate 1 to 5 mg/L. The low chloride concentrations indicate that the dissolved sulfate in the pore waters was sourced from the oxidation of sulfide minerals in the tailings and not from old process water. In contrast, pore water sulfate concentrations in Core 4 collected in the Minorca In-Pit Basin reached as high as 1820 mg/L, which is much higher than the average recent value for fine tailings slurry sulfate concentration (82 mg/L from Berndt et al., 2016). Pore-water chloride levels were also high in Core 4, reaching up to 280 mg/L. This compared to an average chloride concentration of 95 mg/L for recent fine tailings slurry (Berndt et al, 2016), and indicates that evaporation has concentrated the dissolved chloride and sulfate concentrations.

Sulfate concentrations in pore waters from Cores 5 to 7 (old coarse tailings), were somewhat higher than found in Cores 1 to 3 (old fine tailings) and ranged up to 96 mg/L. Chloride concentrations, meanwhile, were elevated, suggesting that at least some of the sulfate was derived from residual process water.

Core 8, composed of fresh coarse tailings, had higher sulfate concentrations (336 mg/L; Figure 20, Table 10) than were found in Cores 5 to 7. Chloride concentrations in the cores were also relatively high,

however, indicating some of the sulfate was sourced from process water that was either still entrained in the tailings or sprayed on for dust control. For Core 6, the chloride concentrations were higher than expected for process waters. Subtracting the associated sulfate from process water often resulted in a negative release rate (not shown in Table 10).

Computed sulfate release rates were almost always less than 3 umol/kg/L for the older tailings collected in this study, whether fine or coarse. For land covered with greater than about 60 inches of relatively old coarse or fine tailings, the calculates suggest that the sulfate flux is less than about 2 metric ton/mile<sup>2</sup>/ week (Figure 21).

The elevated sulfate levels found in pore fluids from relatively fresh tailings sampled from the Minorca Pit, meanwhile, indicated a release rate of about 18.3 umol/kg/wk, which would correspond to a sulfate flux of 6 metric tons/mile<sup>2</sup>/wk for a 40 inch covering (See Figure 21). Release rates from fresh coarse tailings, meanwhile, were similar to those for freshly deposited fine tailings, capable of producing a flux of approximately 8 metric tons/mile<sup>2</sup>/wk from an approximately 3 foot layer (Also, Figure 21).

It is unknown why values calculated for fresh tailings are elevated compared to those for older tailings in this basin but it suggests that there may be a differences in sulfur concentrations. This could be due to changes in the ore that is being processes or to the complete weathering out of sulfur from the older tailings that were collected.

### **Summary and Conclusions**

A method was developed to measure empirical "field-based" sulfate release rates for taconite tailings and corresponding pore water samples collected from four taconite tailings basins. The method takes measured sulfate and chloride values from pore fluids in tailings and calculated the total amount of new sulfate introduced to the pore fluids since they were entrained into the tailings. The residence time for the pore water is estimated by comparing the moisture content and depth of the pore waters samples to infiltration tables that were constructed using Hydrus-1D and the mass of rock is calculated from the tailings bulk densities.

As expected most of the porewaters sampled from the basins had elevated sulfate levels that could be used for release rate calculations. However, the application of the technique became site specific owning to complications from the simplified model that was used to convert sulfate concentrations to rates.

At Hibbing Taconite, many of the sampled cores appeared to have elevated chloride and sulfate/chloride ratios that were, in turn, similar to present day process waters. Moreover, there was an extensive plant cover over part of the basin. The results suggest that for most of the cores that were sampled, there was very little infiltration of either water or oxygen. For a relatively few cores, rates were calculated, but the significance of the calculated values is not clear.

For U. S. Steel Minntac, sulfate in pore waters generally increased with depth and generally low chloride concentrations for most of the samples (except in some freshly deposited tailings) there was much less interference from residual process waters. Still, the application to fine tailings resulted in highly varied

rates for sections collected within approximately four feet from the surface. Some of the rates were higher than reasonable, and were thought to represent periods where relatively fresh waters penetrated tailings that had been relatively dry. This variability decreased in cores sections collected at depths greater than four feet from the surface and the calculated rates and flux values appeared to be more systematic. Both coarse and fresh tailings calculated from these intervals generated release rates that were in the 7 to 23 umol/kg/wk range. This basin has sulfate concentrations that are considerably higher than those found in other basins and much of the reason appears to relate to sulfate released from tailings (Berndt et al., 2016a). The data from this study may help to interpret the relatively importance of coarse and fine tailings to the overall sulfate balance in the basin.

At United Taconite, the older tailings were covered with dense vegetation and this provided an additional complication since the impact of the thick vegetative cover on infiltration rates were not well known. The plants should generate a decrease in infiltration rates, though, meaning that the rates calculated with the simple model are over estimates of actual release rates. Application of the method to fresh coarse and fine tailings sampled from Basin 2, which is not covered by vegetation, yielded rates of approximately 10 umol/kg/wk for both tailing types. These values are considerably less that those calculated for freshly deposited tailings at Minntac.

Use of the technique to measure field-based sulfate release rates at ArcelorMittal resulted in low rates for relatively old coarse and fresh tailings (<2 ug/kg/wk). The corresponding values for fresh tailings were considerably higher, but the reason for this is not known. The basin currently has low sulfate concentrations compared to those measured at other operations. However, it will be important to consider the possibility of these sulfate concentration becoming elevated if the tailings from newly mined ores begin generating sulfate at increased levels compared to those from past tailings.

Prior to conducting this study, very little specific information was available to help understand where sulfate was being generated and released in basins. While the results of this and the other linked studies shed some light on this issue, our understanding is still incomplete owing to a lack of precise understanding of the linkage between sulfate release to pore waters and the corresponding transport of those pore waters either into the process waters or from the basin into the surrounding ground and surface waters. Additionally, the residence times for pore waters in fine grained tailings may be very high owing to a lack in groundwater gradient and to low underlying permeability. It is hoped that as hydrologic understanding of the tailings basin increases that the results of this study can at least be used as a starting point to convert models based on hydrology into realistic, data-based models for transport of sulfate.

### Tables

**Table 1.** Physical and chemical data for cores collected from Hibbing Taconite. Red text marksinterpolated values. Cores 1-6 are from East Basin (2009) and Core 7 is from the West Basin (2015).

			Bulk	Vol	Wtd			New	Cum			
	Тор	Bot	Dens	H₂O	W/R	SO4	Cl	SO4	inf	t	R	F
	•		gm c	cm <u>³</u>	-						umol	met ton
	in	in	m <sup>3</sup>	cm <sup>3</sup>	L/kg	mg/L	mg/L	mg/L	in	wks	kg wk	mile <sup>2</sup> wk
Core 1	0.0	18.0	1.55	0.05	0.030	0.	0.	0.	0.8		0	
	18.0	30.0	1.5	0.06	0.033	230	8.7	202	1.5	3	26.1	6.1
	30.0	44.0	1.48	0.11	0.045	251	4.1	238	3	5.5	26.1	9.2
	44.0	55.0	1.54	0.06	0.043				3.6			
	55.0	61.0	1.24	0.29	0.059	2474	9.3	2444		312	9.4	5.2
	61.0	74.0	1.45	0.11	0.062	1770	26	1686		312	3.5	2.2
	74.0	88.1	1.46	0.14	0.067	1396	38.7	1270		312	2.8	2.1
Core 2	0.0	18.0	1.44	0.06	0.043	296	7.2	272	1.1	2.7	45.3	3.7
	18.0	30.0	1.45	0.14	0.064	146	7.5	121	2.8	5.5	19.7	4.3
	30.0	35.0	1.27	0.29	0.084							
	35.0	45.5	1.39	0.39	0.130	676	54.1	500		312	2.2	0.8
	45.5	60.0	1.55	0.32	0.150	2338	80	2077		312	10.4	5.0
	60.0	68.8	1.58	0.26	0.152	122	87	-160		312	-0.8	-0.5
	68.8	74.0	1.58	0.29	0.154	195	83	-73		312	-0.4	-0.2
	74.0	80.9	1.84	0.31	0.156	163	83	-108		312	-0.6	-0.4
Core 3	0	6	1.41	0.4	0.283	472	141	13		312	0.1	0.0
	6	12	1.43	0.395	0.279							
	12	20	1.45	0.39	0.275	130	71	-101		312	-0.9	-0.1
	20	30	1.21	0.31	0.269	142	76	-104		312	-0.9	-0.2
	29.5	46	1.34	0.3	0.253	145	79	-111		312	-0.9	-0.3
	46	53	1.52	0.34	0.249	193	72	-42		312	-0.4	-0.1
	52.5	65	1.34	0.32	0.247	556	76	310		312	2.6	1.3
Core 4	0.0	11.0	1.54	0.45	0.291	847	325	-209		312		
	11.0	21.0	1.23	0.26	0.258	584	154	84		312	0.7	0.1
	21.0	28.0	1.41	0.335	0.311							
	28.0	44.0	1.58	0.41	0.292	612	134	178		312	1.7	0.6
	44.0	55.3	1.45	0.47	0.298	581	140	127		312	1.3	0.6
	55.3	64.5	1.46	0.38	0.292	671	137	226		312	2.2	1.2
Core 5	0.0	20.0	1.23	0.32	0.256	/18	113	352		312	3.0	0.2
	20.0	27.0	1.41	0.47	0.277	432	67.6	212		312	2.0	0.4
	27.0	36.0	1.46	0.47	0.287	220	F7 0	4.45		24.2		0.5
<b>6 6</b>	36.0	43.3	1.5	0.47	0.292	330	57.2	145		312	1.4	0.5
Core 6	0.0	9.5	1.07	0.34	0.320	369	48.4	212		312	2.3	0.1
	9.5	23.0	1.18	0.5	0.381	336	39.8	207		312	2.6	0.3
	23.0	34.0	1.25	0.51	0.391	410	52	241		212	2.0	1 1
	34.0	57.0	1.51	0.47	0.356	410	52	241		312	2.9	1.1
	57.0	04.U	1.43	0.38	0.345	344	50.5 55 7	100		31Z	1.ð	0.9
Core 7	04.U	79.0	1.03	0.47	0.333	250	55./ 16.0	69 70	1	312 2 r	U.8	0.5
core /	0.0	20.0	1.09	0.05	0.030	142	70.8	õ/	ד סיב	2.5	19.0	1.9
	20.0	30.U 40.0	1.55 1.6 <b>7</b>	0.09	0.042	270	70	40	2.5 2 E	4	A E	1 7
	30.0	49.9	1.02	0.08	0.044	2/8	13	40	3.5	4	4.5	1.2

		Bulk	Vol	Wtd			New	Cum			
Тор	Bot	Dens	H <sub>2</sub> O	W/R	SO4	Cl	SO4	inf	t	R	F
		<u>gm</u>	<u>cm<sup>3</sup></u>							<u>umol</u>	<u>met ton</u>
in	in	cm <sup>3</sup>	cm <sup>3</sup>	L/kg	mg/L	mg/L	mg/L	in	wks	kg wk	mile <sup>2</sup> wk
Core 1											
0	6.5	1.18	0.16	0.133				1	13.5		
6.5	13	1.28	0.06	0.088	81	8.7	35	1.4	13.5	2.4	0.2
13	29	1.13	0.2	0.133	49	2.9	34	4.5	15.5	3.2	0.5
28.5	39	1.2	0.21	0.145	249	5	222	6.7	16	21.3	5.4
39	52	1.33	0.17	0.139	216	6.9	180	8.8	18	15.3	5.4
51.6	62	1.33	0.21	0.143	240	8.4	196	11	19	15.8	7.0
62	76	1.32	0.26	0.153	450	6	419	14.5	42	21.9	12.0
75.5	92	1.39	0.08	0.135	573	8.2	529	15.8	55	15.3	10.3
91.5	104	1.42	0.12	0.128	622	7	586	17.3	64	13.1	10.5
Core 2											
0	5	1.22	0.11	0.090				0.5	4		
5	10	1.22	0.11	0.090	8	3	-8	1.1	13.3	-0.8	0.0
10	24	1.21	0.2	0.133	104	11.4	44	3.9	15.2	4.2	0.5
24	40	1.19	0.29	0.175				8.4	17		
40	52	1.22	0.22	0.176	130	11	72	11	19	7.3	2.6
52	64	1.33	0.1	0.155	251	12.3	186	12.2	24	14	6.3
64	71	1	0.21	0.159				13.6	25		
70.5	74	1.36	0.43	0.166	366	9.6	316	14.9	49.5	14.7	8.1
73.5	83	1.55	0.41	0.180				18.7	65		
83	86	1.33	0.17	0.178				19.3	63.5		
86	99	1.41	0.08	0.160	777	14.1	703	20.3	67.5	17.9	13.4

**Table 2.** Physical and chemical data for fine tailing cores collected from US Steel Minntac's Cell A1-E.Tailings were last deposited in this cell in 1986. Red text marks interpolated values.

		Bulk	Vol	Wtd			New	Cum			
Top Bot		Dens	H <sub>2</sub> O	W/R	SO4	CI	SO4	inf	t	R	F
		gm	cm <u>3</u>	,		•			•	umol	met ton
in	in	cm <sup>3</sup>	cm <sup>3</sup>	L/kg	mg/L	mg/L	mg/L	in	wks	kg wk	mile <sup>2</sup> wk
Core 3					0.	0.	0,			0	
0	15	1.11	0.18	0.159	42	6.8	6	2.6	3.5	5.5	0.3
15	31	1.24	0.24	0.180	89	5.4	61	6.5	6	23.9	4.1
31	40	1.26	0.38	0.208	169	5.3	141	9.9	53	10.4	2.8
40	58	1.31	0.25	0.202	295	9	248	14.4	54.5	9.7	3.7
58	70	1.37	0.17	0.187	415	11.3	356	16.4	57.5	12.4	6.3
70	81	1.29	0.27	0.191	522	9.1	475	19.4	60	16	9.6
81	93	1.27	0.35	0.201	512	9.1	464	23.5	102	12	8.3
Core 3 d	up										
0	15	1.07	0.18	0.171	48	6.2	15	2.7	3.7	14.6	0.7
15	29	1.26	0.20	0.165	199	6.9	163	5.6	5.3	62	10.0
29	44	1.32	0.31	0.190	594	9.7	542	10.2	53.5	36.4	10.2
44	55	1.33	0.28	0.194	697	9.1	649	13.2	54.5	24.3	9.4
55	74	1.39	0.30	0.199	822	9.1	775	18.8	59	28.4	14.7
74	94	1.26	0.32	0.211	956	6.9	920	25.3	103.5	24.9	16.8
94	106	1.15	0.24	0.211	1211	6.4	1178	28.1	107	24.5	19.5
106	120	1.06	0.26	0.214	909	5.6	880	31.8	155.5	14.9	13.2
120	132	1.37	0.33	0.217	822	5.1	795	35.8	157	11.5	11.4
132	144	1.47	0.39	0.222	870	4.7	845	40.3	160	12.3	13.6
Core 4											
0	18	1.31	0.06	0.046	85	5.2	58	1.1	0.8	69.4	5.2
18	30	1.25	0.15	0.074	304	8.7	259	2.9	3	105.7	20.6
30	48	1.42	0.14	0.085	330	10.1	276	5.4	4	69.9	23.0
48	68	1.37	0.31	0.128	288	6.2	255	11.7	53.5	11.9	5.8
68	87	1.39	0.25	0.140	305	5.8	274	16.5	56.5	7.3	4.8
Core 5											
0	20	1.13	0.31	0.273	69	3.1	53	6.2	3	99.7	7.0
20	34	1.32	0.25	0.237	251	5.4	222	9.7	4.5	146.3	30.1
34	44	1.41	0.44	0.256	271	3.8	251	14.1	53	23.2	7.2
44	54	1.53	0.36	0.251	317	4.1	295	17.7	53.5	14.5	5.8
54	69	1.41	0.39	0.257	275	4.4	252	23.5	58	12.1	6.2

**Table 3**. Physical and chemical data for cores collected from US Steel – Minntac's Cell A2. Lastdeposition date for this cell was in 1989.

		Bulk	Vol	Wtd			New			
Тор	Bot	Dens	H <sub>2</sub> O	W/R	SO4	Cl	SO4	t	R	F
		gm	<u>cm<sup>3</sup></u>						<u>umol</u>	<u>met ton</u>
in	in	cm <sup>3</sup>	cm <sup>3</sup>	L/kg	mg/L	mg/L	mg/L	wks	kg wk	mile² wk
Core 6										
0	4.4	1.25	0.11					52		
4.4	13	1.09	0.16	0.129	2701	274.6	1257.1	52	32.5	2.0
13	17	1.24	0.01	0.097				52		
17.3	22	1.42	0.1	0.090				52		
Core 7										
0	7	1.37	0.14	0.100				52		
7	14	1.25	0.35	0.188	792	24.2	664.6	52	25.0	2.2
14	25	1.46	0.48	0.251	905	56.2	609.8	52	30.7	5.1
Core 8										
0	5	0.91	0.27	0.300				52		
5	10	1.08	0.35	0.315	1444	194.8	419.7	52	26.5	1.2
10	15	1.4	0.38	0.298	1096	197.5	57.4	52	3.4	0.3

**Table 4.** Physical and chemical properties for cores collected from US Steel Minntac's Cell M2, where tailings were deposited in 2013.

**Table 5.** Physical and chemical properties for cores collected from US Steel Minntac's Cell K, where finetailings were last deposited in 2013.

		Bulk	Vol	Wtd			New			
Тор	Bot	Dens	H <sub>2</sub> O	W/R	SO4	Cl	SO4	t	R	F
		gm	<u>cm<sup>3</sup></u>						<u>Umol</u>	<u>met ton</u>
in	in	cm <sup>3</sup>	cm <sup>3</sup>	L/kg	mg/L	mg/L	mg/L	wks	kg wk	mile <sup>2</sup> wk
Core 9										
0	16	1.32	0.15	0.112	376	2.4	363	3.5	121	8.0
16	35	1.38	0.22	0.138	2477	8.7	2432	90	38.7	16.2
35	59	1.41	0.32	0.174	2790	196.3	1757	90	35.4	14.4
Core 10										
0	16	1.33	0.24	0.183	551	22.4	434	4.5	184	12.3
16	28	1.43	0.13	0.142	1280	130.6	594	90	9.8	3.5
28	32	1.69	0.18	0.137	2767	186.9	1784	90	28.3	7.6
32	36	1.43	0.36	0.150	3358	66.9	3007	90	52.3	15.8
Core 11										
0	14	1.57	0.41	0.264	2591	339.4	806	90	24.6	1.7
14	32	1.44	0.44	0.287	1578	149.3	793	90	26.3	5.7
32	47	1.47	0.46	0.295	551	60.7	232	90	7.9	2.9

				Wtd							
Тор	Bot	<b>Bulk Dens</b>	Vol H <sub>2</sub> O	W/R	SO4	Cl	New SO4	Cum inf	t	R	F
		<u>gm</u>								<u>umol</u>	<u>met ton</u>
in	in	cm <sup>3</sup>	<u>cm<sup>3</sup> cm<sup>3</sup></u>	L/kg	mg/L	mg/L	mg/L	in	wks	kg wk	mile <sup>2</sup> wk
Core 12											
0	5.5	1.12	0.04	0.040				0.2	13.5		
5.5	11	1.63	0.02	0.022	63	10.5	7.6	0.3	13.5	0.1	0.0
11	24	1.72	0.06	0.029	117	9.3	67.8	1.1	13.5	1.5	0.3
24	38	1.72	0.06	0.031	224	23.7	99.2	1.9	13.5	2.4	0.7
38	51	1.64	0.06	0.032	370	18.4	273.	2.7	14.5	6.5	3.0
50.6	66	1.88	0.08	0.035	897	26.9	756	3.9	15.5	18.5	11.4
65.5	78	1.95	0.07	0.036	1530	146.6	759	4.8	15.5	18	14.3
Core 13											
0	12	1.83	0.05	0.027				0.6	1.5		
12	18	1.71	0.05	0.028				0.9	1.5		
18	22	2.34	0.07	0.029				1.2	1.7		
22	32	1.7	0.06	0.030	194	28.9	42.7	1.8	3.5	5.2	1.6
32	48	1.76	0.06	0.031	257	38.8	52.5	2.7	4	4.5	2.1
48	64	1.74	0.07	0.033	362	32.4	191	3.8	4.5	15.5	9.8
64	83	1.7	0.08	0.036	367	22.4	250	5.3	5	19.6	16.1
Core 13 I	Dup										
0	16	1.84	0.05	0.028				0.8	1.5		
16	28	1.89	0.05	0.028	264	41	48.7	1.5	2	8.1	2.1
28	44	1.78	0.06	0.031	230	27.6	85	2.5	3.7	9.6	4.0
44	62	1.75	0.06	0.032	296	31.2	132	3.6	4.3	11	6.7
62	80	1.74	0.07	0.034	269	29.8	113	4.8	5	8.5	6.8
Core 14											
0	8.1	1.52	0.05	0.031				0.4	13.5		
8.1	16	1.5	0.04	0.028	2269	73.6	1882	0.7	13.5	41	4.7
16	34	1.73	0.05	0.029	2636	239.6	1376	1.6	13.5	30	7.7

**Table 6.** Physical and chemical properties for cores of coarse tailings collected from U. S. Steel Minntac. These cores 12, 13, and 13 Dup are from Section 11 of the outer dike, which was last added on to in 1990. Core 14 is from the inner dike which had been added to in 2014.

		Bulk	Vol	Wtd			New	Cum			
Тор	Bot	Dens	H₂O	W/R	SO4	CI	SO4	inf	t	R	F
		gm	<u>cm³</u>							umol	met ton
in	in	cm <sup>3</sup>	cm <sup>3</sup>	L/kg	mg/L	mg/L	mg/L	in	wks	kg wk	mile <sup>2</sup> wk
Core 1											
0	17	1.47	0.07	0.047	630	10.7	589	1.2	2.8	104	8.2
17	27	1.48	0.12	0.060				2.4	5.3		
27	40	1.59	0.08	0.056	669	5	649	3.4	5.7	66	21.1
40	53	1.55	0.08	0.054				4.4	7.5		
53	65	1.57	0.06	0.051	222	25.3	125	5.1	7.5	9	5.0
65	78	1.57	0.06	0.049				5.9	8.5		
78	83	1.43	0.05	0.048	202	51	7	6.1	8.5	0.0	0.3
Core 2											
0	15	1.24	0.1	0.079	321	6.5	296	1.5	3	81	4.8
15	27	1.28	0.22	0.121				4.1	7.5		
27	38	1.28	0.18	0.128	261	1.5	255	6.2	8.5	40	10.4
38	59	1.35	0.15	0.123				9.4	56		
59	74	1.38	0.17	0.123	727	5.4	706	11.9	57	16	8.7
74	89	1.35	0.24	0.133	397	5.2	377	15.6	58.5	9	6.0
Core 3											
0	20	1.09	0.29	0.263	1121	2.2	1113	5.7	8.5	359	24.7
20	32	1.31	0.31	0.251				9.4	15.5		
32	42	1.33	0.31	0.246	1347	1	1343	12.5	58.5	59	16.6
42	54	1.32	0.05	0.198				13.2	58.5		
54	64	1.32	0.37	0.211	1065	1.8	1058	16.8	59	39	18.3
64	76	1.24	0.18	0.200				18.9	61.5		
76	85	1.28	0.31	0.204	678	4.6	660	21.6	64	22	13.9
Core 4											
0	15	1.58	0.05	0.031	266	5.6	244	0.75	2.5	32	2.4
15	28	1.68	0.04	0.029				1.3			
28	48	1.52	0.12	0.049	1105	160	494	3.7	25	10	3.8

**Table 7.** Physical and chemical properties of fine tailings collected from United Taconite. Cores 1-3were from Basin 1 which was abandoned in 2000. Core 4 is from Basin 1, which is still active.

			Vol	Wtd			New	Cum			
Тор	Bot	<b>Bulk Dens</b>	H <sub>2</sub> O	W/R	SO4	Cl	SO4	inf	t	R	F
		<u>gm</u>	<u>cm<sup>3</sup></u>							<u>umol</u>	<u>met ton</u>
in	in	cm <sup>3</sup>	cm <sup>3</sup>	L/kg	mg/L	mg/L	mg/L	in	wks	kg wk	mile <sup>2</sup> wk
Core 5											
0	14	1.71	0.03	0.019				0.5	2.3		
14	24	1.73	0.04	0.02				0.8	2.5		
24	34	1.68	0.03	0.02				1.2	2.7		
34	45	1.69	0.04	0.021				1.6	3.5		
45	55	1.73	0.06	0.023	265.2	33.5	137.2	2.2	5.3	6.2	3.3
55	66	1.69	0.05	0.024	257.2	17.4	190.6	2.7	5.5	8.7	5.7
66	79	1.7	0.04	0.024	468.6	29.9	354.3	3.3	5.5	16.3	12.7
Core 6											
0	11	1.68	0.03	0.019				0.4	2.5		
11	22	1.76	0.04	0.02				0.8	2.5		
22	34	1.74	0.04	0.021	121.3	18.1	52.2	1.3	2.5	4.6	1.4
34	43	1.72	0.05	0.023				1.7	3.7		
43	52	1.7	0.05	0.024	226.1	16.8	161.9	2.1	4.3	9.4	4.8
52	63	1.72	0.05	0.025				2.7	5.5		
63	74	1.69	0.08	0.028	307.2	27.9	200.8	3.6	6	9.8	7.2
Core 7											
0	8	1.69	0.02	0.014				0.2	2		
8	19	1.86	0.03	0.017				0.6	2.5		
19	29	1.8	0.04	0.018				1	2.5		
29	37	1.74	0.04	0.019				1.3	2.7		
36.5	48	1.78	0.04	0.02	234.5	29.7	121.1	1.7	4	6.4	3.1
48	56	1.75	0.04	0.021				2.1	5		
56	68	1.77	0.04	0.022	212.9	18.7	141.4	2.6	5.5	5.8	4.0
Core 8											
0	15	1.62	0.04	0.025				0.6	2.5		
15	26	1.63	0.04	0.025	208.3	11.8	163.4	1.1	2.5	17	3.6
26	40	1.63	0.04	0.024	629.9	10.7	589.2	1.6	3.5	42.7	14.5

**Table 8.** Physical and chemical properties of coarse tailings collected at United Taconite.

**Table 9.** Physical and chemical properties of fine tailings collected at ArcelorMittal. Cores 1 to 3 are from Basin 2A, which last received tailings in 2001. Core 4 is from the Minorca Pit which had last received tailings in 2014.

		Bulk	Vol	Wtd			New	Cum			
Тор	Bot	Dens	H₂O	W/R	SO4	Cl	SO4	inf	t	R	F
		<u>gm</u>	<u>cm<sup>3</sup></u>							<u>umol</u>	<u>met ton</u>
in	in	cm <sup>3</sup>	cm <sup>3</sup>	L/kg	mg/L	mg/L	mg/L	in	wks	kg wk	mile <sup>2</sup> wk
Core 1											
0	15	1.25	0.17	0.137	4.9	5	4.9	2.56	6.5	.009	0.0
15	30	1.37	0.11	0.109				4.27	8.5		
30	42	1.39	0.07	0.092	27	5.3	27	5.16	9.3	2.4	0.7
42	51	1.37	0.14	0.094				6.42	9.7		
51	67	1.48	0.27	0.116	85	3.3	85	10.7	57.5	3.0	1.5
67	82	1.49	0.23	0.124				14.2	59.5		
82	85	1.57	0.18	0.124	80.7	3.9	80.7	14.8	59.5	1.7	1.2
Core 2											
0	16	1.25	0.14	0.114	13.7	3.6	13.7	2.29	5.3	6.2	0.3
16	29	1.32	0.2	0.132				4.9	8		<u> </u>
29	40	1.33	0.27	0.152	11.9	2	11.9	7.85	9.5	2.2	0.5
40	48	1.48	0.37	0.1/1	42.0		42.0	10.9	56.5	0.5	0.0
48	62 70	1.4	0.31	0.183	13.8	1.6	13.8	15.2	58.5	0.5	0.2
62	/6	1.37	0.4	0.203	107	F 4	107	20.8	63 104 F	0.4	0.2
/0	87	1.41	0.3	0.204	16.7	5.4	16.7	24	104.5	0.4	0.2
core 3	17	1 7	0.22	0 1 9 2	<b>7</b> 0	17	<b>n</b> 0	2 72	7 2	1 5	0.0
17	20	1.2	0.22	0.105	2.0	1.7	2.0	9.72	125	1.5	0.0
30	12	1.31	0.37	0.229	17 5	1 2	17 5	13.50	58.5	13	0.4
42	46	1.54	0.42	0.254	17.5	1.2	17.5	15.0	58.5	1.5	0.4
46	57	1 23	0.41	0.200	24 9	14	24 9	19.5	61 5	12	05
56.8	60	1.11	0.35	0.274	20.8	1.6	20.8	20.7	62.5	1.0	0.4
60	69	1.7	0.49	0.277	45	1.3	45	24.9	105	1.5	0.8
68.5	77	1.35	0.32	0.273	25.9	1.1	25.9	27.6	108	0.7	0.4
Core 4										••••	••••
0	16	1.49	0.17	0.116	1816	282	1540.2		52	35.8	2.7
16	29	1.47	0.1	0.094					52		
29	40	1.6	0.19	0.101	1030	127	906.1		52	18.3	6.0

**Table 10.** Physical and chemical properties of coarse tailing collect from ArcelorMittal. Cores 5 to 7 are from Basin 1 in tailings believed to have been deposited in 1999. Core 8 is from Basin 2 from tailings believed to have been deposited in 2014.

		Bulk	Vol	Wtd			New	Cum			
Тор	Bot	Dens	H <sub>2</sub> O	W/R	SO4	Cl	SO4	inf	t	R	F
		gm	cm <sup>3</sup>	-						umol	met ton
in	in	cm <sup>3</sup>	cm <sup>3</sup>	L/kg	mg/L	mg/L	mg/L	in	wks	kg wk	mile <sup>2</sup> wk
Core 5											
0	12	1.73	0.03	0.015				0.32	2.5		
12	20	1.62	0.04	0.018	50.3	18.7	32	0.60	2.5	2.4	0.4
20	33	1.58	0.04	0.021	45	14.6	30.6	1.15	3.5	2.2	0.6
33	44	1.58	0.05	0.024				1.70	3.7		
44	55	1.58	0.05	0.026	60.3	16.9	43.8	2.28	5.5	2.5	1.3
55	67	1.57	0.05	0.027				2.90	5.7		
67	78	1.62	0.05	0.028	44.4	14	30.7	3.48	6	1.5	1.1
Core 6											
0	9	1.86	0.03	0.016				0.27	2.3		
9	17	1.78	0.04	0.018	56.5	135	-75.6	0.55	2.5		
17	28	1.75	0.04	0.019	70.9	204	-128.8	0.94	2.5		
28	34	1.69	0.04	0.02				1.19	2.7		
34	42	1.72	0.05	0.021	72.7	125	-49.7	1.56	3.5		
42	50	1.66	0.04	0.022				1.90	4.5		
50	62	1.71	0.05	0.024	83.3	118	-31.9	2.55	5.5		
Core 7											
0	15	1.74	0.03	0.016				0.41	2.2		
15	27	1.73	0.04	0.019	52.6	40.8	12.6	0.88	2.5	1.1	0.2
27	39	1.65	0.05	0.022	46.7	29.3	18.1	1.47	3	1.5	0.5
39	56	1.66	0.06	0.025				2.41	5.3		
56	69	1.65	0.06	0.027	96	43.1	53.8	3.13	5.5	2.8	1.9
69	80	1.7	0.06	0.028				3.76	7.3		
80	90	1.73	0.05	0.028	91.9	86.9	6.8	4.28	7.5	0.3	0.2
Core 8											
0	15	1.69	0.04	0.023	340.	28.5	312	0.59	2.5	30.2	2.4
15	26	1.66	0.05	0.025				1.09	2.5		
26	41	1.68	0.05	0.028	333	55.2	279	1.90	4.5	22.9	8.1

### **Figures**



**Figure 1.** Measured pore water  $\delta^{18}O_{H2O}$  profile in Minntac core 3Dup (left panel). The vertical show the depth intervals over which pore waters were extracted to generate the samples. The dashed lines in the right panel denote the estimated boundaries between different aged pore waters in the core and the dates denote the pore water age estimated by HYDRUS-1D for that section of the core. The pore water isotope ratios in the right panel were estimated using the pore water age estimates and the average montly  $\delta^{18}O_{H2O}$  values for preciptation in Northeastern Minnesota. Figure is from Bavin et al. (2016).



**Figure 2.** Bromide versus chloride for tailings slurry and pore waters from Hibbing Taconite (upper panel) and U. S. Steel Minntac (Lower Panel). Process water is from Berndt et al. (2016). Only 2015 water samples are shown for U. S. Steel Minntac.



**Figure 3.** Bromide versus chloride for tailings slurry and pore waters from United Taconite (upper panel) and ArcelorMittal (Lower Panel). Process water is from Berndt et al. (2016).



Figure 4. Tailings sampling locations at the Hibtac tailings basin.



**Figure 5.** Pore water sulfate and Cl concentrations in tailings cores collected from the Hibtac tailings basin on 7/14/15. The tailings in Cores 1 through 6 were unsegregated and were collected from the East Area cell at the Hibtac basin. Core 7 was a coarse tailings core collected from the northern crest of the West Area 3 dike. The tailings in Cores 1 through 6 were deposited between 2006 and 2009 and the tailings in Core 7 were deposited in June of 2015. The bars in the figures represent the depth intervals over which the pore water samples were collected.



**Figure 6.** Field based sulfate release rates and fluxes for Hibbing Taconite cores. "2009 pw" indicates samples from East Basin cores still filled with process water as indicated by high Br and Cl concentration. "2009 inf" represents cores where precipitation was actively infiltrating as indicated by low Vol H<sub>2</sub>O

contents and low Br and Cl concentrations. East Basin pore waters with negative field release rates and values were not plotted.



Figure 7. Coarse and fine tailings sampling locations at the Minntac tailings basin.



**Figure 8.** Pore water sulfate and Cl concentrations in fine tailings cores collected from Cell A1-E in the Minntac tailings basin on 9/17/14. Fine tailings were last deposited in Cell A1-E in 1986. The bars in the figures represent the depth intervals over which the pore water samples were collected.



**Figure 9**. Pore water sulfate and Cl concentrations in fine tailings cores collected from Cell A2 in the Minntac tailings basin on 6/17/15. Fine tailings were last deposited in Cell A2 in 1989. The bars in the figures represent the depth intervals over which the pore water samples were collected.



**Figure 10**. Pore water sulfate and Cl concentrations in fine tailings cores collected from Cell M2 in the Minntac tailings basin on 9/17/14. Fine tailings were last deposited in Cell M2 in 2013. The bars in the figures represent the depth intervals over which the pore water samples were collected.



**Figure 11**. Pore water sulfate and Cl concentrations in fine tailings cores collected from Cell K in the Minntac tailings basin on 6/17/15. Fine tailings were last deposited in Cell K in 2013. The bars in the figures represent the depth intervals over which the pore water samples were collected.



**Figure 12.** Pore water sulfate and Cl concentrations in coarse tailings cores collected from the outer and inner coarse tailings dikes at the Minntac tailings basin. Cores 12 and 14 were collected on 9/17/14 and cores 13 and 13Dup were collected on 6/17/15/ Cores 12, 13, and 13Dup were all collected from Section 11 of the outer coarse tailings dike which was last raised between 1985 and 1990. Core 14 was collected from a section of the inner coarse tailings dike that was raised in 2014. The bars in the figures represent the depth intervals over which the pore water samples were collected.



Figure 13. Field based sulfate release and fluxes for core samples collected at U. S. Steel Minntac.



Figure 14. Coarse and fine tailings sampling locations at the Utac tailings basin.



**Figure 15.** Pore water sulfate and Cl concentrations in fine tailings cores collected from the Utac tailings basin on 7/16/15. Cores 1 through 3 were collected from Basin 1 which last had tailings deposited in it around May, 2000. Core 4 was collected from Basin 2, which is still active. The beach area from where the Core 4 was collected last had tailings deposited on it in January, 2015. The bars in the figures represent the depth intervals over which the pore water samples were collected.



**Figure 16.** Pore water sulfate and CI concentrations in coarse tailings cores collected from the Utac tailings basin on 7/16/15. Cores 5 through 7 were collected from the northern crest of the Basin 1 dike. The Basin 1 dike was last raised around August, 1999 and had been re-graded prior to sampling. Core 8 was collected from a section of the Basin 2 dike that was raised in June 2014. The bars in the figures represent the depth intervals over which the pore water samples were collected.



Figure 17. Field-based sulfate release rates and fluxes for tailing cores collected at United Taconite.



**Figure 18.** Coarse and fine tailings coring locations at the ArcelorMittal Upland Tailings Basin (top panel) and Minorca In-Pit Basin (bottom panel).



**Figure 19**. Pore water sulfate and Cl concentrations in fine tailings cores collected from Cell 2A of the ArcelorMittal Upland Tailings Basin (Cores 1 - 3) and the from Minorca In-Pit Tailings Basin (Core 4) on 7/23/15. Tailings were last deposited in Cell 2A of the Upland Basin between 2000 and 2001. Most tailings are pumped to the Upland Basin; however, the Minorca In-Pit Basin still receives intermittent discharges when pumping to the Upland Basin is down. Tailings were last pumped to the Minorca Basin in 2014. The bars in the figures represent the depth intervals over which the pore water samples were collected.



**Figure 20**. Pore water sulfate and Cl concentrations in coarse tailings cores collected from the northern crest of the Cell 2A dike (Core 5 - 7) and from the Cell 2 dike (Core 8) at ArcelorMittal's Upland Tailings Basin on 7/23/15. The Cell 2A dike was last raised between 1999 and 2000. The section of the Cell 2 dike where Core 8 collected was raised in June/July of 2015. The bars in the figures represent the depth intervals over which the pore water samples were collected.



Figure 21. Field based sulfate release rates and fluxes for tailing cores collected at ArcelorMittal.

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Appendix 1: Net Infiltration/Time Approximation Table

I		Time	Net		Time	Net Inf.		Time	Net			Time	Net
ļ	Date	Wks	(in)	Date	Wks	(in)	Date	Wks	(in)		Date	Wks	(in)
	5/1/12	0	0.00	5/7/13	53	13.67	5/6/14	105	24.89		5/5/15	157	36.86
	5/8/12	1	0.51	5/14/13	54	13.70	5/13/14	106	27.38		5/12/15	158	38.18
	5/15/12	2	0.72	5/21/13	55	14.70	5/20/14	107	27.60		5/19/15	159	40.30
	5/29/12	4	6.13	5/28/13	56	15.17	5/27/14	108	28.12		5/26/15	160	41.48
	6/5/12	5	6.30	6/4/13	57	16.02	6/3/14	109	32.89		6/2/15	161	41.61
	6/12/12	6	7.37	6/11/13	58	16.69	6/10/14	110	33.55		6/9/15	162	43.14
	6/19/12	7	9.13	6/18/13	59	17.33	6/17/14	111	35.87		6/16/15	163	43.33
	6/26/12	8	12.02	6/25/13	60	18.65	6/24/14	112	36.31		6/23/15	164	43.70
	7/3/12	9	12.30	7/2/13	61	19.91	7/1/14	113	36.66		6/30/15	165	44.97
	7/10/12	10	12.82	7/9/13	62	20.31	7/8/14	114	36.44		7/7/15	166	45.19
	7/17/12	11	12.56	7/16/13	63	21.45	7/15/14	115	36.66		7/14/15	167	45.13
	7/24/12	12	12.61	7/23/13	64	21.27	7/22/14	116	36.09		7/21/15	168	44.66
	7/31/12	13	13.70	7/30/13	65	21.16	7/29/14	117	36.48		7/28/15	169	44.33
	8/7/12	14	13.69	8/6/13	66	21.19	8/5/14	118	35.87		8/4/15	170	43.63
	8/14/12	15	13.29	8/13/13	67	20.71	8/12/14	119	35.74		8/11/15	171	43.69
	8/21/12	16	13.05	8/20/13	68	19.97	8/19/14	120	35.34		8/18/15	172	42.97
	8/28/12	17	12.57	8/27/13	69	20.13	8/26/14	121	35.16		8/25/15	173	44.83
	9/4/12	18	11.81	9/3/13	70	21.38	9/2/14	122	35.45		9/1/15	174	44.15
	9/11/12	19	11.41	9/10/13	71	21.21	9/9/14	123	35.22				
	9/18/12	20	11.08	9/17/13	72	20.65	9/16/14	124	35.92				
	9/25/12	21	10.97	9/24/13	73	20.31	9/23/14	125	36.06				
	10/2/12	22	10.65	10/1/13	74	20.05	9/30/14	126	35.64				
	10/9/12	23	10.67	10/8/13	75	21.49	10/7/14	127	35.88				
	10/16/12	24	10.44	10/15/13	76	21.70	10/14/14	128	35.93				
	10/23/12	25	10.51	10/22/13	77	22.09	10/21/14	129	35.53				
	10/30/12	26	10.92	10/29/13	78	22.04	10/28/14	130	35.36				
	11/6/12	27	10.68	11/5/13	79	22.08	11/4/14	131	35.25				
	11/13/12	28	11.23	11/12/13	80	22.08	11/11/14	132	35.25				
	11/20/12	29	10.97	11/19/13	81	22.07	11/18/14	133	35.20				
	11/27/12	30	10.87	11/26/13	82	21.89	11/25/14	134	35.20				
	12/4/12	31	10.86	12/3/13	83	21.88	12/2/14	135	35.12				
	12/11/12	32	10.78	12/10/13	84	21.88	12/9/14	136	35.11				
	12/18/12	33	10.89	12/17/13	85	21.86	12/16/14	137	35.19				
	12/25/12	34	10.89	12/24/13	86	21.85	12/23/14	138	35.45				
	1/1/13	35	10.89	12/31/13	87	21.84	12/30/14	139	35.39				
	1/8/13	36	10.89	1///14	88	21.84	1/6/15	140	35.33				
	1/15/13	37	11.00	1/14/14	89	21.84	1/13/15	141	35.32				
	1/22/13	38	11.00	1/21/14	90	21.84	1/20/15	142	35.31				
	1/29/13	39	11.00	1/28/14	91	21.83	1/2//15	143	35.30				
	2/5/13	40	11.00	2/4/14	92	21.83	2/3/15	144	35.30				
	2/12/13	41	11.00	2/11/14	93	21.82	2/10/15	145	35.29				
	2/19/13	42	11.00	2/18/14	94	21.82	2/1//15	146	35.29				
	2/26/13	43	11.00	2/25/14	95	21.82	2/24/15	147	35.29				
	3/5/13	44	11.00	3/4/14	96	21.82	3/3/15	148	35.28				
	3/12/13	45	11.00	3/11/14	97	22.16	3/10/15	149	35.28				
	3/19/13	46	11.00	3/18/14	98	22.13	3/1//15	150	35.45				
	3/20/13	4/	12.45	3/25/14	99 100	22.13	3/24/15	151	35.57				
	4/2/13	48	12.45	4/1/14	100	22.70	3/31/15	152	35.93				
	4/9/13	49	13.09	4/8/14	101	22.99	4///15	153	35.94				
	4/16/13	50	13.20	4/15/14	102	23.15	4/14/15	154	36.09				
	4/23/13	51	13.32	4/22/14	103	23.45	4/21/15	155	30.80				
I	4/30/13	52	13.4b	4/29/14	104	24.23	1 4/28/15	120	30.80	1			