

Short Term Sulfate Release Rates and Sulfide Oxidation Mechanisms for Taconite Tailings from the Minntac and Keetac Mining Facilities

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Table of Contents

1. Executive Summary.....	4
2. Introduction	5
3. Objectives	5
4. Methods	6
4.1 Tailings Description	6
4.2. Sample Collection	6
4.3. Tailings Preparation	7
4.4. Tailings Physical and Chemical Analyses	7
4.5. Kinetic Tests.....	7
4.5.1. Large Cells.....	8
4.5.2. Small Reactors.....	8
4.5.3. Shaker Flasks.....	9
4.6. Aqueous Chemistry	10
4.7. Stable Isotopes.....	10
4.8. SO ₄ Release Rate Calculations.....	11
5. Results	11
5.1. Sulfur and SO ₄ Content of the Tailings.....	11
5.2. Particle Size.....	12
5.3. Drainage and Water Retention	12
5.4. Chemistry	13
6. Discussion	15
6.1. SO ₄ Release.....	15
6.2. Carbonate Mineral Dissolution	15
6.3. Stable Isotopes.....	16
6.4 Methods Comparison	17
7. Conclusions	18
8. Acknowledgements	19
9. References	19
Appendix A.....	21
Appendix B.....	39

Appendix A

Table 1. S and SO ₄ content for Minntac and Keetac tailings.....	21
Table 2. Tailings particle size distributions (% passing).	21
Table 3. Chemical parameters for leachate, water balance, and environmental conditions for Minntac Oxidized Coarse (Humidity Cell # 1).....	22
Table 4. Chemical parameters for leachate, water balance, and environmental conditions for Minntac Oxidized Coarse (Humidity Cell # 2).....	23
Table 5. Chemical parameters for leachate, water balance, and environmental conditions for Minntac Fresh Coarse (Humidity Cell # 3).....	24
Table 6. Chemical parameters for leachate, water balance, and environmental conditions for Minntac Fresh Coarse (Humidity Cell # 4).....	25
Table 7. Chemical parameters for leachate, water balance, and environmental conditions for Keetac Fresh Coarse (Humidity Cell # 5).....	26
Table 8. Chemical parameters for leachate, water balance, and environmental conditions for Keetac Fresh Coarse (Humidity Cell # 6).....	27
Table 9. Chemical parameters for leachate, water balance, and environmental conditions for Minntac Fresh Fine (Humidity Cell # 7).....	28
Table 10. Chemical parameters for leachate, water balance, and environmental conditions for Minntac Oxidized Fine (Humidity Cell # 8).....	29
Table 11. Chemical parameters for leachate, water balance, and environmental conditions for Minntac Fresh Fine (Reactor # 9).	30
Table 12. Chemical parameters for leachate, water balance, and environmental conditions for Minntac Fresh Fine (Reactor # 10).	31
Table 13. Chemical parameters for leachate, water balance, and environmental conditions for Minntac Oxidized Fine (Reactor # 11).	32
Table 14. Chemical parameters for leachate, water balance, and environmental conditions for Minntac Oxidized Fine (Reactor # 12).	33
Table 15. Major cations and anions for humidity cells and reactors during week 10 and 12.....	34
Table 16. Chemical and physical parameters for Minntac Fresh Fine shaker flasks.....	35
Table 17. Chemical and physical parameters for Minntac Oxidized Fine shaker flasks.....	36
Table 18. Total S content (wt %) and SO ₄ release rates in μmol SO ₄ /kg tailings x week for each tailings sample.	36
Table 19. Average SO ₄ release rates in μmol SO ₄ /kg x week and statistics for each type of tailings (<i>n</i> = 2).	37
Table 20. δ ³⁴ S _{SO4} and δ ¹⁸ O _{SO4} values for the humidity cells and reactors, and δ ¹⁸ O _{H2O} and δD _{H2O} for the DI water used to rinse the samples.....	38

Appendix B

Figure 1. Average pH for the coarse tailings ($n=2$).....	39
Figure 2. Average pH for the fine tailings small reactors ($n=2$) and large humidity cells ($n=1$). ..	39
Figure 3. Average SO_4 concentration for the coarse tailings ($n=2$).	40
Figure 4. Average SO_4 concentrations for fine tailings small reactors ($n=2$) and large humidity cells ($n=1$).	40
Figure 5. Average SO_4 release rates for the coarse tailings ($n=2$).	41
Figure 6. Average SO_4 release rate for the fine tailings small reactors ($n=2$) and large humidity cells ($n=1$).	41
Figure 7. Ca concentrations for the coarse tailings ($n=2$).	42
Figure 8. Ca concentrations for the fine tailings small reactors ($n=2$) and large humidity cells ($n=1$).	42
Figure 9. Mg concentrations for the coarse tailings ($n=2$).	43
Figure 10. Mg concentrations for the fine tailings small reactors ($n=2$) and large humidity cells ($n=1$).	43
Figure 11. Alkalinity for the coarse tailings ($n=2$).	44
Figure 12. Alkalinity for the fine tailings small reactors ($n=2$) and large humidity cells ($n=1$). ..	44
Figure 13. $\delta^{34}\text{S}_{\text{SO}_4}$ and $\delta^{18}\text{O}_{\text{SO}_4}$ values for the large humidity cells and the small reactors.	45
Figure 14. Average SO_4 release rates (white bars) or average SO_4 release rates normalized to wt. % S content (black bars) for Minntac and Keetac tailings.....	46
Figure 15. SO_4 vs. alkalinity, Mg, and Ca for the Minntac and Keetac coarse tailings.	47
Figure 16. SO_4 vs. alkalinity, Mg, and Ca for the fine tailings samples in the small reactors and large humidity cells.....	48

1. Executive Summary

Coarse and fine tailings samples from the Minntac and Keetac mining facilities were subjected to three different types of kinetic testing over sixteen weeks to estimate short-term sulfate (SO_4) release rates for different types of taconite tailings and to test different methods for determining SO_4 release rates for fine grained waste rock. Average short-term SO_4 release rates for the coarse and fine tailings samples from Minntac and Keetac ranged between 39 and 125 $\mu\text{mol SO}_4/\text{kg tailings} \times \text{wk}$ (excluding the oxidized fine tailings from Minntac that released little to no SO_4). Release rates for the Minntac samples generally were correlated with tailings S content and particle size, however, the SO_4 release rate for the Keetac tailings sample was higher than expected based on the S content and the particle size distribution of the sample. During the experiment, Mg-rich carbonates neutralized any acid that was generated by the oxidation of sulfide minerals in the tailings which caused the pH of the rinse waters to remain alkaline over the ten to twelve week experimental period. Both Mg and alkalinity increased with increasing SO_4 concentrations in the rinse waters, however, Ca concentrations were generally similar over all SO_4 concentrations because the rinse waters became and remained at saturation with respect to calcium carbonate. More Mg and alkalinity were generated per mEq of SO_4 by the fine

tailings samples than by the coarse tailings samples. Stable isotope measurements suggest different sulfide oxidation mechanisms and different pyrite size fractions were responsible for sulfate generation during the experiment. $\delta^{18}\text{O}$ values for the dissolved SO_4 in the rinse waters indicates the oxygen in the SO_4 generated at the beginning of the study was derived from both water and atmospheric oxygen potentially due to the chemisorption of atmospheric oxygen onto pyrite surfaces when the tailings were dry. After multiple rinsing and drying cycles, the oxygen in the SO_4 that was generated appeared to be mostly sourced from the rinse water. $\delta^{34}\text{S}$ values for the dissolved SO_4 possibly indicates fine grained, secondary sulfide minerals were the primary source of SO_4 in the fresh tailings samples whereas larger, primary sulfides were the dominant source of SO_4 in the oxidized tailings sample. Lastly, it is recommended that a smaller mass of tailings be used (75 instead of 1000 g) and the rinse volume be reduced from 200 mL to 100 mL for kinetic tests performed on very fine grained waste rock samples.

2. Introduction

Ensuring compliance with current SO_4 standards is an important part of the review process for new mining permits and amendments to existing permits. The administration of new permits and permit amendments has been hampered by the current lack of information about sulfide oxidation mechanisms and SO_4 release rates for taconite rock. While field studies have provided important insights into sulfide oxidation mechanisms for taconite rock, specific sulfate release rates for taconite tailings have rarely, if ever, been measured. Ultimately, it will be important to have as much information as possible on SO_4 release from tailings to help ensure that future water quality predictions are accurate and that appropriate remedial actions are incorporated into permits. The main goal of this study is to generate an initial understanding of the geochemical mechanisms controlling SO_4 release from taconite tailings to provide at least a qualitative understanding of the most important release mechanisms.

3. Objectives

The three main objectives of this study are to:

- 1) Ascertain short-term SO_4 release rates for different types of taconite tailings.
- 2) Investigate sulfide oxidation mechanisms for taconite tailings using oxygen and sulfur isotopes of dissolved SO_4 .
- 3) Test different methods for obtaining SO_4 release rates from materials with very fine particles.

4. Methods

4.1 *Tailings Description*

Taconite tailings are the coarse and/or finely ground, nonmagnetic portions of taconite ore that are generated during the concentrating process. At Minntac, the tailings are primarily composed of the nonmagnetic portions of the Lower Cherty and Lower Slaty units of the Biwabik Iron Formation. The coarse tailings are generated from the classifier following the first stage of milling and magnetic separation of the taconite ore. The fine tailings are generated after several additional stages of crushing and magnetic separation from the crusher thickener overflow and the tailings thickener underflow (Minntac 2004 Draft EIS). At Keetac the tailings are primarily composed of the nonmagnetic portions of the Lower Cherty units of the Biwabik Iron Formation. After the magnetic iron oxide minerals are separated from the nonmagnetic tailings, the tailings are pumped from the concentrator to the tailings thickeners where excess water is removed by sedimentation. Unlike at Minntac, the coarse and fine tailings are not separated at the Keetac facility and instead the coarse and fine fractions are co-disposed in the tailings basin (Keetac 2010 Final EIS).

4.2 *Sample Collection*

Tailings samples were collected by the MN DNR at the Minntac and Keetac mining facilities on September 12th and 13th, 2012. At Minntac, samples of both fresh and oxidized, and fine and coarse tailings were collected. Only a fresh tailings sample was collected at the Keetac facility. The Minntac oxidized tailings samples were collected from the coarse and fine tailings that comprise the outer tailings basin dike of the Minntac basin. A shovel was used to remove approximately a two-and-a-half gallon sample of both coarse and fine tailings from the dike at one location on the western side of the basin. After sample collection, the tailings samples were stored in sealed, five gallon plastic buckets for later use. The exact age of the tailings could not be discerned because while construction of the outer dike began in the mid-1960s, the dikes continually undergo construction and maintenance. Therefore, the tailings could have been deposited anywhere between initial construction and present time. A similar sized fresh coarse tailings sample was obtained near the coarse tailings load out pocket at Minntac using the same sampling technique. The Minntac fresh fine tailings slurry sample, which is composed of both fine tailings solids and plant process water, was obtained from the fine tailings stream leaving the concentrator. Approximately two-and-a-half gallons of fine tailings slurry was collected directly from the stream using a plastic bailer. The fine tailings slurry was stored in a sealed, plastic bucket and the solids were allowed to settle out prior to analysis. At Keetac, approximately two-and-a-half gallons of tailings slurry (both coarse and fine) were collected from the end of the tailings pipeline at the tailings basin using a Teflon sampling cup and were stored in a sealed, plastic bucket after collection.

4.3. Tailings Preparation

In November, 2012 the process water that separated from the Minntac fresh fine and Keetac tailings after settling was siphoned off the top of the tailings using a large syringe. All of the tailings samples were then spread thinly on plastic sheets and were allowed to air dry prior to processing. Dried tailings were rolled by hand using a 1L plastic bottle filled with water to break up any clumps that formed during drying. Extensive rolling was needed to break up the large clods that formed in the Minntac fresh fine tailings. Some rolling was needed to break down the smaller clods that formed in the Keetac tailings after drying. Rolling was also performed on the Minntac oxidized coarse and Minntac fresh coarse samples, but the tailings were generally well aggregated. Samples were homogenized using the four corners method after rolling (Scott 1942). Each homogenized sample was divided in half and one of the halves was further divided into quarters. The sub-samples were then stored in plastic bags and archived for future use. One of the quarters was split in half and was further split using a riffle splitter for the experiments. Each sample being split was sent through the riffle splitter three times to obtain two homogenous splits. Riffle splitting was continued until the mass needed for analyses was obtained (75-1000 g depending on the analysis).

4.4. Tailings Physical and Chemical Analyses

One sample from each tailings type was analyzed for sulfur and SO₄ content at ACT Labs in Ancaster, Ont, CA by combustion followed by infrared detection. The particle size distribution was also determined for each tailings sample using ASTM test method 276 and nine different mesh sizes.

4.5. Kinetic Tests

All of the tailings samples were subjected to humidity cell testing using a modified version of the standard ASTM method D 5744 – 13e1 (see Lapakko and White 2000, and Lapakko and Antonson 2002). Instead of using humidity cells with the dimensions specified in the ASTM method, humidity cells with interior dimensions of 27 or 29 cm height by 16 cm diameter were used. The cells were stored in a humidity/temperature controlled room, rather than receiving alternating humid and dry air flow (option B in the ASTM method). In addition to the larger humidity cells, the fine tailings samples were also run in smaller units referred to here as “reactors” (Nalgene filter units) with interior dimensions of 10.5 cm height by 12 cm diameter. This was done because there were questions as to whether the fine tailings would drain adequately and oxidize properly between rinses in the larger volume humidity cells. SO₄ release rates for the fine tailings were also determined using oxidation data collected from 500 mL flasks containing the fine tailings and deionized (DI) water. The flasks were stored on a shaker table during the experiment (referred to here after as the “shaker method”) to promote the oxidation of the tailings and to prevent them from settling during the test.

4.5.1. Large Cells

A 1000 g mass of air dried tailings was subjected to repeated cycles of oxidation and leaching in the large humidity cell experiments. Two cells were set up for each of the coarse tailing samples, yielding two duplicates for Minntac Oxidized Coarse (humidity cell ID # 1 and 2), Minntac Fresh Coarse (ID # 3 and 4), and Keetac Fresh Coarse (ID # 5 and 6). No duplicates were run for the fine tailings samples, yielding a single replicate for Minntac Fresh Fine Large (ID # 7), and Minntac Oxidized Fine Large (ID # 8). Prior to adding the tailings to the large humidity cells, the cells were washed with a 10% HNO₃ solution to remove any residues from prior tests. A 0.7 μM polypropylene filter (National Filter Media Corporation, Polymax B, Style 225-075-2) was placed on top of the perforated plate on the bottom of the cells before the tailings were added to prevent any fines from washing out of the reactors during rinsing.

The tailings in each cell were rinsed three times with 500 ml of DI water prior to the initiation of the tests to remove any oxidation products that had accumulated on the tailings. Following the initial rinses, the reactors were each rinsed once a week with 500 ml of DI water and were allowed to drain overnight. During each rinse, water was allowed to sit in the reactor for ten minutes prior to draining (a one hour period was used for the first week). When rinsing the reactors, the DI water was added slowly around the side to prevent the filter from becoming unseated and to keep any fines from sticking to the edge of the reactors. Any water remaining on top of the fine tailings was removed with a syringe after the drainage period. In between rinses, the reactors were covered to prevent evaporation and were stored in a temperature and humidity controlled chamber.

Each humidity cell was weighed before and after rinsing to determine the amount of evaporation from and the amount of water retained in the tailings after free drainage had ceased. The receiving flask containing the leachate was also weighed after each rinse and the total rinse volume was calculated by dividing the weight of the water in the flask by a density of 1 g cm⁻³. Chemical analyses (alkalinity, pH, conductivity, major cations (Ca, K, Mg, Na), and SO₄) were carried out on each of the rinse water samples using methodologies outlined in sections 4.6 and 4.7. The water samples collected from the week ten rinses were also analyzed for other major cations and anions in addition to the parameters listed above. Dissolved SO₄ was collected via BaCl₂ precipitation for stable isotope analysis (see isotope methodology in section 4.7) during weeks zero, ten, and sixteen. The large humidity cells were allowed to oxidize for a three week period prior to collecting isotope samples in week sixteen.

4.5.2. Small Reactors

Smaller masses of fine tailings were subjected to the same rinsing and oxidation cycles in small reactors because it was hypothesized that the fine tailings might not drain properly in the large humidity cells. Instead of 1000 g samples, 75 g samples of air-dried fine tailings were placed in 250 ml reactors containing 1.6-micron Whatman GF/A glass fiber filter papers (5.5 cm

diameter). Duplicates were created for each of the two treatments: Minntac Oxidized Fine Small (reactor ID # 9 and 10) and Minntac Fresh Fine Small (reactor ID # 11 and 12). The small reactors were initially rinsed with 200 ml of DI water three times to remove any oxidation products that may have collected on the tailings during drying and were rinsed with 200 ml of DI water each week after the initial rinses. The small cells did not have a plug, so were allowed to drain immediately upon filling. The small reactors were initially allowed to drain in the temperature/humidity controlled chamber, but starting at week seven they were rinsed in the lab with the large humidity cells. The small reactors usually drained completely, but occasionally a small amount of water was left on top of the tailings after two days of draining and was removed using a syringe. The rinse volume was changed to 100 mL in week twelve to try and prevent water from ponding on top of the tailings. The entire filter unit was weighed before and after rinsing to determine the amount of evaporation from the reactors and the amount of water retained in the fine tailings after rinsing. The total rinse volume was determined by dividing the mass of water in the bottom half of the filter unit after rinsing by a density of 1 g cm^{-3} .

Chemical analyses (alkalinity, pH, conductivity, major cations (Ca, K, Mg, Na), and SO_4) were carried out on each of the rinse samples using the methodologies outlined in sections 4.6 and 4.7. The water samples collected from the week ten rinses were also analyzed for other major cations and anions in addition to the parameters listed above. Dissolved SO_4 was collected via BaCl_2 precipitation for stable isotope analysis (see isotope methodology in section 3.7) during week zero, week ten, and week sixteen. The small reactors were allowed to oxidize for a three week period prior to collecting isotope samples in week sixteen.

4.5.3. Shaker Flasks

Fine tailings samples were also allowed to oxidize in flasks containing oxygenated DI water to test a third method for determining SO_4 release rates for fine tailings. For the shaker flask method, 150 grams of fine tailings were placed in 500 ml, Pyrex Erlenmeyer flasks. Six replicates were constructed for each sample type (Minntac Oxidized Fine Shaker, and Minntac Fresh Fine Shaker). 400 ml of DI water was added to each of the flasks containing the tailings samples and each flask was covered with a perforated plastic cup to prevent water from splashing out. The flasks were then placed on an Eberbach shaker table on the highest setting to try and promote aeration of the tailings and to prevent the fine tailings from settling out on the bottom of the flasks. Each week (except for the second week), an aliquot of water was removed from one random flask from each treatment and the conductivity and pH were determined for the water sample. The water removed for the measurements was returned to the flasks after analysis. During weeks three, six, and nine, two random flasks were removed from the shaker table and the water in the flasks were analyzed for alkalinity, Ca, K, Mg, Na, and SO_4 using methods listed in sections 4.6 and 4.7 in addition to pH and conductivity. Dissolved SO_4 was collected via BaCl_2 precipitation for stable isotope analysis (see section 3.7) during week nine.

4.6. *Aqueous Chemistry*

The pH of the water samples was measured using an Orion 720 A+ pH meter with a Ross Sure-Flow pH electrode. Conductivity was measured using a Myron L conductivity meter Model EP-10. The calcium carbonate equivalent alkalinity of the samples was determined by titrating them with 0.02 N sulfuric acid to an endpoint of pH 4.5 (American Public Health Association 1992).

The water samples collected for cation and anion analysis were filtered through a 0.45 μm , PES membrane filter prior to analysis and the cation samples were preserved with 200 μl of ultra-pure nitric acid after filtration. The Minnesota Department of Agriculture environmental laboratory analyzed the cation samples for: Ca, Na, Mg, K using inductively coupled plasma mass spectrometry (ICP-MS, Hewlett Packard HP4500 Series, model #G1820A), and the anion samples were analyzed for SO_4 using a Lachat QuickChem 8000. Anion samples with SO_4 concentrations less than 5 mg L^{-1} were analyzed using a Dionex ion chromatograph. Cation and anion samples from week ten were analyzed by the University of Minnesota Aqueous Geochemistry Laboratory in Minneapolis, MN. The major cations were measured using inductively coupled plasma optical emission spectrometry (Thermo Scientific iCAP 6500 duo optical emission spectrometer) and anions were measured using anion chromatography (Dionex Ion Chromatography System 2000).

4.7. *Stable Isotopes*

Approximately 100-500 ml of the rinse water samples was collected for sulfur and oxygen isotope analysis of SO_4 . SO_4 was extracted as solid BaSO_4 using procedures modified from Carmody et al. (1998). Water samples were first filtered through a 0.45 μm PES membrane filter; and the filtrate was acidified to pH 3-4 using 1M HCl and heated at 90°C for one hour so that any carbonate present would be degassed as CO_2 . Though dissolved organic material is likely very low in these samples, 6 ml of 6% H_2O_2 was also added to each sample prior to heating to oxidize and degas any organics present. These measures reduce contamination of the BaSO_4 precipitate. After heating, ~5 ml of 20% BaCl_2 was added (in excess) and the samples were allowed to cool for at least three hours. The cooled samples were filtered through pre-weighed 0.45 μm PES membrane filters to collect the BaSO_4 precipitate, and were dried overnight at 90°C. Once dry, the BaSO_4 powder was weighed, scraped into glass vials, and stored for analysis. Vials containing the BaSO_4 precipitate were shipped to the University of Waterloo Environmental Isotope Laboratory in Ontario, CA where they were analyzed for $\delta^{34}\text{S}_{\text{SO}_4}$ and $\delta^{18}\text{O}_{\text{SO}_4}$. Relative ^{34}S and ^{32}S abundances for the precipitates were determined using an Isochrom Continuous Flow Stable Isotope Ratio Mass Spectrometer (GV Instruments, Micromass, UK) coupled to a Costech Elemental Analyzer (CNSO 2010, UK). $^{34}\text{S}/^{32}\text{S}$ results are reported in δ -notation ($\delta^{34}\text{S}$) relative to the international standard Canyon Diablo Troilite (CDT). Relative ^{18}O and ^{16}O abundances for the precipitate were determined using a GVI Isoprime Mass Spectrometer coupled to a Hekatech High Temperature Furnace and a Euro

Vector Elemental Analyzer, and reported as $\delta^{18}\text{O}$ relative to the international standard Vienna Standard Mean Ocean Water (VSMOW).

Rinse water samples were collected from the DI water system in Hibbing laboratory for $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ and $\delta^2\text{H}_{\text{H}_2\text{O}}$ ($\delta\text{D}_{\text{H}_2\text{O}}$) analysis during week ten of the experiment. Duplicate 30 ml samples were stored unpreserved and unfiltered in tightly sealed HDPE bottles with limited headspace until shipped to University of Waterloo Environmental Isotope Lab for analysis. $^{18}\text{O}/^{16}\text{O}$ was analyzed via gas equilibration and head space injection into an IsoPrime Continuous Flow Isotope Ratio Mass Spectrometer (CF-IRMS). $^2\text{H}/^1\text{H}$ was analyzed via chromium reduction on a EuroVector Elemental analyzer coupled with an IsoPrime CF-IRMS. Internal laboratory standards are calibrated and tested against international standards from the International Atomic Energy Agency (IAEA). All $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ and $\delta^2\text{H}_{\text{H}_2\text{O}}$ results are reported relative to VSMOW.

4.8. *SO₄ Release Rate Calculations*

Weekly SO₄ release rates were calculated using the following equation:

$$R_T = \frac{C_w \times V_w}{M_T \times T} \times 10.417$$

Where:

R_T = SO₄ release rate in $\mu\text{mol SO}_4/\text{kg tailings} \times \text{week}$

C_w = SO₄ concentration in mg/L in the rinse water or in the shaker flask

V_w = volume of water captured after rinsing in mL or the volume of water in the shaker flask

M_T = mass of tailings in g

T = total oxidation time in weeks

10.417 = conversion factor ($\mu\text{mols SO}_4 \times \text{L} \times \text{g} / \text{mg} \times \text{mL} \times \text{kg}$)

The volume of water collected in the flask after rinsing and not the original rinse volume was used for V_w because capillarity caused some of the rinse water to be retained in the tailings after free drainage had ceased. The time elapsed between rinses was used to calculate the oxidation period. Some of the samples took one to two days to drain after rinsing, however, it was assumed that the tailings were oxidizing during this period. Lastly, since the tailings in the shaker flasks were not rinsed prior to the initiation of the test, C_w for the shaker flask SO₄ release rates were determined by subtracting the average SO₄ concentration for week three from the week six concentrations.

5. Results

5.1. *Sulfur and SO₄ Content of the Tailings*

The amount of sulfur in the tailings samples ranged from 0.02 to 0.24 wt. % (Table 1). The Minntac Oxidized Fine and Keetac Fresh Coarse samples had the lowest wt. % S (0.02 % and

0.03 %, respectively), followed by the Minntac Fresh Fine (0.09 %), and the Minntac Fresh Coarse and Minntac Oxidized Coarse samples (0.22 % and 0.24 %, respectively). The amount of SO_4 in the tailings was below the detection limit of 0.3 wt. % for all samples except Minntac Fresh Coarse and Minntac Oxidized Coarse, which both had 0.5 wt. % SO_4 (Table 1).

5.2. *Particle Size*

Between 52 to 72 % of the particles in the Minntac fine tailings sample were smaller than 0.04 mm (Table 2), and the majority of the remaining tailings particles were between 0.04 and 0.18 mm. In contrast, 75% of the coarse tailings particles from Minntac and 69% of the Keetac tailings particles were between 0.42 and 4.75 mm, with the Keetac tailings having nearly double the percentage of particles in the largest size fraction compared to the Minntac coarse tailings.

5.3. *Drainage and Water Retention*

The coarse tailings humidity cells usually drained relatively quickly. The Minntac Oxidized Coarse and Minntac Fresh Coarse samples drained in approximately five minutes, and the Keetac Fresh Coarse samples drained in approximately forty-five minutes. In contrast, the fine tailings humidity cells and reactors took approximately one to two days. Occasionally, small, surficial cracks were observed in the fine tailings reactors after the oxidation period. The cracks disappeared when the reactors were rinsed, and were considered too small to cause preferential drainage in the samples. The Minntac Fresh Fine sample run in the large humidity cell typically took more than two days to drain. After the two day drainage period any remaining overlying water was removed from the humidity cell containing the fine tailings using a syringe (between 58 to 225ml of water was typically removed from Minntac Fresh Fine). In week one, 199 ml of the overlying water was removed from the Minntac Oxidized Fine Large sample, however, the humidity cell drained completely in two days during the remaining weeks.

Approximately 32% of the rinse water was retained in the Minntac coarse tailings post rinse, ranging between 135-206 mL with an average of 160 ml (tables 3-6). A similar amount of water (26%) was retained in the Keetac tailings, ranging between 115-143 mL with an average of 128 ml (Tables 7 and 8). A much larger percentage of the rinse water was retained in the humidity cells with the fine tailings: the amount of water retained was approximately 85% of the total rinse volume ranging between 263-423 mL with an average of 343 ml (Tables 9-14). Less water was retained in the fine tailings when a smaller mass of tailings was used: the water retention was between 24-37 ml and averaged 27 ml (~15% of the rinse water).

The temperature and humidity controlled chamber that the humidity cells and reactors were stored in between rinses had an average temperature of 21.5 °C and an average relative humidity of 55.6% over the course of the experiment. On average, evaporative water loss from the humidity cells and reactors was minor with the large humidity cells losing between 1 and 36 mL of water with an average water loss of 6 mL. A larger percentage of tailings pore water was lost

via evaporation from the smaller reactors. The total amount of water lost from the small reactors ranged between 0 and 27 mL and averaged 5 ml for all of the reactors.

5.4. Chemistry

The pH of the water in the reactors, humidity cells, and shaker flasks remained alkaline throughout the experiment. Keetac samples had a pH between 7.9-8.3, and an average pH of 8.1, the lowest of all the samples (Figure 1). The pH for the Minntac coarse tailings was between 8.1-8.6, and averaged 8.3, and gradually declined over the course of the experiment. The range in pH for the fine tailings was similar to the coarse tailings, between 8.0-8.7 (Figure 2, Tables 16-17). However, the three different fine tailings methods had slightly different pH: the shaker method had the highest average pH of 8.5, followed by the large cells with an average pH of 8.4, and the small cells, with an average pH of 8.3.

SO₄ concentrations for Minntac Fresh Coarse tailings samples were between 14.0-23.4 mg/L, with an average of 17.1 mg/L (Figure 3). SO₄ concentrations were lower in the oxidized coarse tailings, ranging between 7.69-13.7 mg/L, and averaging 11.5 mg/L. Keetac Fresh Coarse had the lowest SO₄ concentrations for the coarse tailings, with a range between 5.89-11.3 mg/L, and an average of 7.84 mg/L. SO₄ concentrations were between 0-24.0 mg/L for the fine tailings large cells, with average SO₄ concentrations of 14.3 mg/L and 4.04 mg/L in the fresh and oxidized tailings, respectively (Figure 4). SO₄ concentrations were usually below detection for Minntac Oxidized Fine Small, but were between 1.76-13.4 mg/L and averaged 5.34 mg/L for Minntac Fresh Fine Small. The SO₄ concentrations gradually declined in small reactors containing the Minntac Fresh Fine samples until week eight; then increased for the remainder of the experiment. SO₄ concentrations were between 14.6-14.8 mg/L for Minntac Oxidized Fine Shaker, but were much higher for Minntac Fresh Fine Shaker: between 142-169 mg/L with an average of 152 mg/L (Tables 16 and 17).

The short-term SO₄ release rates and related statistics for all of the tailings samples are summarized in tables 18 and 19. Release rates calculated for the fine tailings run in the humidity cells were excluded from the averages due to drainage problems that could have affected the release rate estimates. For the coarse tailings, the SO₄ release rates were highest for the Minntac fresh tailings, ranging from 70.4-118 μmol SO₄/kg/week and averaging 84.6 μmol SO₄/kg/week (Figure 5). SO₄ release rates were between 37.2-69.6 μmol SO₄/kg/week and averaged 56.1 μmol SO₄/kg/week for Minntac Oxidized Coarse. The Keetac tailings had the lowest SO₄ release rates of the coarse tailings, with a range of 25.6-57.0 μmol SO₄/kg/week and an average of 38.6 μmol SO₄/kg/week. Minntac Fresh Fine Large had SO₄ release rates between 2.15-92.1 μmol SO₄/kg/week (Figure 6). The highest SO₄ release rates for the experiment occurred in the fresh fine tailings reactors, with rates between 47.3-278 μmol SO₄/kg/week. The release rates for Minntac Fresh Fine Small decreased rapidly until week 5, followed by a rapid increase until week ten. The average SO₄ release rates for the fresh fine tailings were similar in the reactor and shaker flasks, 125 μmol SO₄/kg/week and 121 μmol SO₄/kg/week, respectively, but were almost

double the average release rate of 52.6 $\mu\text{mol SO}_4/\text{kg}/\text{week}$ for the fine tailings run in the humidity cell. The oxidized fine tailings had the lowest SO_4 release rates in the experiment, with near zero release rates for the reactors and shaker flasks, and rates between 0-102 $\mu\text{mol SO}_4/\text{kg}/\text{week}$ and an average of 19.8 $\mu\text{mol SO}_4/\text{kg}/\text{week}$ for the humidity cell.

Average short-term SO_4 release rates normalized by wt. % S were: 139 $\mu\text{mol SO}_4/\text{mg S}/\text{week}$ for Minntac Fresh Fine Small, 129 $\mu\text{mol SO}_4/\text{mg S}/\text{week}$ for Keetac Fresh Coarse, 38.5 $\mu\text{mol SO}_4/\text{mg S}/\text{week}$ for Minntac Fresh Coarse, and 23.4 $\mu\text{mol SO}_4/\text{mg S}/\text{week}$ for Minntac Oxidized Coarse.

Ca concentrations were relatively similar for the Minntac and Keetac coarse tailings samples, and were between 5.78-13.7 mg/L, with an average of 10.2 mg/L (Figure 7). Ca concentrations were between 11.7-21.7 mg/L for the fine tailings humidity cells, with averages of 18.0 mg/L for Minntac Fresh Fine Large, and 13.4 mg/L for Minntac Oxidized Fine Large. Ca concentrations ranged between 8.75 mg/L and 27.9 mg/L for the reactors, with slightly higher average Ca concentrations in the fresh tailings than the oxidized tailings: 18.0 mg/L and 14.0 mg/L, respectively (Figure 8). For the shaker flasks, the average Ca concentrations in the fresh tailings were approximately double those of the oxidized tailings: 34.7 mg/L and 16.9 mg/L, respectively (Table 16 and 17). Calcium concentrations increased in most of the samples throughout the experiment (Figures 7 and 8).

Mg concentrations were between 7.31-11.8 mg/L and averaged 9.43 mg/L for the Minntac coarse tailings (Figure 9). Mg concentrations were comparable in Keetac Fresh Coarse, ranging from 4.63-8.93 mg/L and averaging 7.22 mg/L. The fine tailings humidity cells had a range in Mg concentrations of 14.6-34.6 mg/L, and averages of 29.0 mg/L and 17.9 mg/L for the fresh and oxidized cells, respectively. Mg concentrations declined throughout the experiment for the Minntac Oxidized Fine Large sample. For the reactors, Mg concentrations ranged from 5.90-12.2 mg/L, and averaged 8.83 mg/L, with similar concentrations between fresh and oxidized samples (Figure 10). The shaker flasks had Mg concentrations between 27.6-43.5 mg/L, and the fresh fine tailings had higher Mg concentrations than the oxidized tailings: 38.1 mg/L and 29.5 mg/L, respectively (Tables 16 and 17).

A significant amount of alkalinity was generated for all tailings samples. Minntac Fresh Coarse had the highest alkalinity of the coarse tailings, with alkalinity values between 54-68 and an average alkalinity of 65 mg/L. Alkalinity was between 30-49 mg/L in the Keetac tailings and in Minntac Oxidized Coarse, with an average alkalinity of approximately 40 mg/L for both samples (Figure 11). For the fine tailings large cells, alkalinity was between 105-133 and averaged 119 mg/L for Minntac Fresh Fine Large, and was between 130-165 and averaged 146 mg/L for Minntac Oxidized Fine Large (Figure 12). Alkalinity was between 56-101 mg/L in the reactors, and was comparable between the fresh and oxidized tailings, with averages of 67 and 73 mg/L, respectively. For the shaker flasks, alkalinity was highest in the oxidized tailings, ranging from

120-155 mg/L and averaging 137 mg/L, and lowest in the fresh tailings, between 98-120 mg/L and with an average of 114 mg/L (Tables 16 and 17).

The $\delta^{18}\text{O}$ values for the dissolved SO_4 in the humidity cells and reactors during week zero ranged from -4.0 to +2.8 ‰, and were higher than the average $\delta^{18}\text{O}$ value for the rinse water (-11.6‰) (Figure 13, Table 20). During weeks ten and sixteen the $\delta^{18}\text{O}$ values for the dissolved SO_4 in different samples were between -13.5 and -8.8‰, which bracketed the average $\delta^{18}\text{O}$ value for the rinse water. The $\delta^{34}\text{S}$ values for the dissolved SO_4 in the large humidity cells and reactors ranged between +3.6 and +9.2‰ during week zero. $\delta^{34}\text{S}$ values for the dissolved SO_4 in the shaker flasks and in the Minntac oxidized coarse humidity cells in weeks nine, ten, and sixteen were similar to the values from weeks zero and one, however, $\delta^{34}\text{S}$ values for the dissolved SO_4 in the Minntac fresh fine humidity cells and reactors and in the Minntac fresh coarse reactors decreased to between -8.3 to -1.0‰ during the same time period. $\delta^{34}\text{S}$ values for the dissolved SO_4 in the Keetac humidity cells increased to between +16.9 to +18.8‰ in weeks sixteen and ten, respectively.

6. Discussion

6.1. SO_4 Release

It is well known that sulfate release rates for waste rock and tailings typically are positively correlated with waste rock S content and negatively correlated with particle size for waste rock with similar mineralogy and petrology (Lapakko et al. 2004, MN DNR 2004, Lapakko et al. 2006). Thus, it is not surprising that the Minntac Oxidized Fine sample, which had little S, produced little to no SO_4 , nor that the fresh fine tailings had higher release rates than the fresh coarse tailings (Figure 14). However, the Keetac tailings sample, which, in general, had a larger percentage of coarse particles than the Minntac coarse tailings samples, had a higher S-normalized release rate than the Minntac samples suggesting that other factors such as the size and distribution of sulfide minerals in the different tailings samples, sulfide liberation, and mineral reactivity also likely affected short-term SO_4 release rates from the samples.

6.2. Carbonate Mineral Dissolution

The oxidation of sulfide minerals in waste rock can produce alkaline, neutral, or acidic leachate depending on the balance between acid production and the neutralization potential of the waste rock, with the dissolution of Ca and Mg carbonates being the main mechanism that usually neutralizes acid generation (Lapakko et al. 2004). All of the tailings samples tested in this study produced alkaline leachate that contained high levels of Ca, Mg, and alkalinity. Mg was positively correlated with SO_4 when all of the coarse tailings ($R^2 = 0.30$) and fresh fine tailings samples ($R^2=0.67$) were grouped together (Figure 15 and 16). Alkalinity was also positively correlated with SO_4 for the coarse ($R^2=0.28$) and fine grained ($R^2=0.72$) tailings samples.

However Ca concentrations were not correlated with SO_4 levels for the coarse ($R^2=0.002$) or fine ($R^2=0.06$) tailings samples and generally remained in a constant range across all SO_4 concentrations, ranging from 0.4 to 0.7 mEq/L for the coarse tailings sample and 0.4 to 1.5 mEq/L for the fine tailings samples. The oxidized fine tailings samples were excluded from the analyses because they produced little to no SO_4 .

The high Mg concentrations in the leachate and positive correlations between Mg and SO_4 for the different samples indicates Mg-rich carbonate minerals in the tailings were responsible for neutralizing the acid that was generated during the oxidation of sulfide minerals in the tailings. In contrast, the lack of a correlation between Ca and SO_4 and relatively constant Ca concentrations indicates that, while Ca was released from the waste rock, the rinse waters quickly became and then remained saturated with respect to calcium carbonate.

For the fine tailings samples, approximately 2.55 mEq of Mg and 1.74 mEq of alkalinity were generated per mEq of SO_4 that was released by the tailings. In contrast, less Mg and alkalinity were generated by the coarse tailings samples per mEq of SO_4 that was released with approximately 0.81 mEq Mg and 0.70 mEq of alkalinity generated per mEq SO_4 that was released. Currently, no chemical or mineralogical data is available for the carbonate minerals in the tailings, therefore, we cannot speculate on what factor(s) controlled the amount of Mg, Ca, and alkalinity that was released by the different tailings samples at this time.

6.3. Stable Isotopes

Electrochemical studies have concluded the oxygen incorporated into SO_4 during pyrite oxidation is wholly sourced from water molecules (Holmes and Crundwell, 2000). However, studies that have examined pyrite oxidation mechanisms using stable isotopes have suggested that, under certain conditions, atmospheric oxygen can also be incorporated into SO_4 during pyrite oxidation (Tichomirowa and Junghans, 2009). If the SO_4 produced during the oxidation of sulfide minerals in the tailings samples was generated by the first mechanism then the $\delta^{18}\text{O}$ value for the oxygen in the dissolved SO_4 for all samples should have been similar to the average $\delta^{18}\text{O}$ value for the rinse water. However, during the initial stage of the experiment, the $\delta^{18}\text{O}_{\text{SO}_4}$ values for all tailings samples were much higher than the average $\delta^{18}\text{O}$ value for the rinse water oxygen (the average $\delta^{18}\text{O}$ value for the rinse water was -11.5‰ whereas the $\delta^{18}\text{O}$ values for the dissolved SO_4 in the tailings samples were between -6 and $+4\text{‰}$ in week zero). The heavier $\delta^{18}\text{O}_{\text{SO}_4}$ values relative to rinse water $\delta^{18}\text{O}$ values likely indicates that a significant percentage of the oxygen in the SO_4 that was produced during the early stages of the experiment came from the atmosphere ($\delta^{18}\text{O} = +23.5\text{‰}$). In contrast, the $\delta^{18}\text{O}$ values for the SO_4 produced at the end of the experiment generally bracketed the rinse water $\delta^{18}\text{O}$ values. Shaker flask SO_4 $\delta^{18}\text{O}$ values however, were about $+5.5\text{‰}$ higher than those for the rinse water, indicating that at least some of the oxygen in the dissolved SO_4 was derived from the oxygen in the rinse water in those experiments.

Tichomirowa and Junghans (2009) attributed the increased incorporation of atmospheric oxygen into SO_4 during the early stages of pyrite oxidation to the chemisorption of atmospheric oxygen

onto pyrite surfaces. The authors' hypothesized highly reactive, broken S-S bonds on the surfaces of the fine grained pyrite particles were responsible for the phenomena. It is possible that a similar mechanism was also responsible for the higher percentage of atmospheric oxygen being incorporated into the SO_4 produced at the beginning of the present experiments and throughout the shaker flask experiments. But, once that fraction was removed, normal sulfide oxidation mechanisms dominated SO_4 generation in the tailings samples.

Surprisingly, $\delta^{34}\text{S}$ values for the dissolved SO_4 produced by the tailings samples also generally differed between the beginning and end of the experiments. At the beginning of the experiments, most of the $\delta^{34}\text{S}$ values for the sulfate produced by all tailings types clustered around the average $\delta^{34}\text{S}$ value for primary sulfides in the Biwabik Iron Formation ($\sim +7.0\text{‰}$) (Theriault, 2011). However, while the $\delta^{34}\text{S}$ values for the SO_4 generated by the Minntac coarse samples remained around $+7.0\text{‰}$ at the end of the experiment, the $\delta^{34}\text{S}$ values for SO_4 in the Minntac fresh tailings samples decreased to between -10 and 0‰ and the $\delta^{34}\text{S}_{\text{SO}_4}$ values for the Keetac samples increased to between $+15$ to $+20\text{‰}$. The shift in $\delta^{34}\text{S}_{\text{SO}_4}$ values for the fresh tailings samples possibly indicates fine grained, secondary sulfide minerals were preferentially oxidized in the latter stages of at least some of the experiments, whereas, primary sulfides contributed to SO_4 generation during the initial stages of all experiments. In contrast, the lack of a shift in $\delta^{34}\text{S}$ values for the SO_4 produced by the oxidized tailings from Minntac suggests that all of the finer grained, secondary sulfide minerals had been completely oxidized in the older samples, and primary sulfides were the only sulfides left in the tailings to generate SO_4 .

6.4 Methods Comparison

Fine tailings kinetic experiments were invariably plagued by variable and slow drainage rates. For example, it often took one to two full days for the reactors containing the 75 g tailings samples to drain when 200 mL rinse volumes were used. The large humidity cells containing one kg samples did not always completely drain after two days, and so excess water had to be removed via a syringe. For the shaker flask experiments, the tailings failed to remain suspended even with the shaker table on its highest setting.

Over all, it was determined that the small reactors with 75 g tailings samples produced the best results for the fine tailings samples. Incomplete drainage of water from the large humidity cells containing the fine tailings could have inhibited oxygen ingression at depth and also could have indicated the entire mass of tailings were not being rinsed during each rinse cycle.

Sedimentation problems in the shaker flask experiments also could have limited the mass of tailings that were exposed to oxygen in the flasks. These factors would have resulted in an underestimate of SO_4 release rates. Thus, in future studies of this type, it recommended that sulfate release rates be determined using 75 g rock masses and 100 mL rinse volumes to try and prevent the aforementioned problems.

7. Conclusions

- 1) Average short-term SO_4 release rates and S normalized release rates for the different taconite tailings samples ranged between 39-125 $\mu\text{mol SO}_4/\text{kg}/\text{week}$ and 24-139 $\mu\text{mol SO}_4/\text{mg S}/\text{week}$, respectively. Of the samples tested, the fine tailings sample from Minntac had the highest short-term SO_4 release rate and Keetac had the lowest. When normalized to tailings sulfur (S) content, the fine tailings had the highest short-term SO_4 release rate followed by the Keetac tailings. The coarse tailings samples from Minntac had the lowest normalized SO_4 release rates. The discrepancies in short-term SO_4 release rates and normalized release rates for the different tailings samples were likely due to multiple factors including particle size, the size and distribution of sulfide minerals, and the liberation and reactivity of mineral sulfide.
- 2) All tailings samples had high, short-term acid neutralization capacity. Acid neutralization generated considerable Mg and Ca hardness and alkalinity in all samples; however, the fine tailings generated more Mg and alkalinity per mEq of SO_4 than the coarse tailings. Ca levels in the rinse waters were generally constant over all SO_4 concentrations because the rinse waters were at saturation with respect to calcium carbonate.
- 3) $\delta^{18}\text{O}$ values suggest the oxygen in the SO_4 generated at the beginning of the study was derived from both water and atmospheric oxygen and all of the oxygen in the SO_4 generated at the end of the study was sourced from the rinse water. $\delta^{34}\text{S}$ values suggest that the main source of SO_4 in the fresh tailings was fine grained, secondary sulfides, while the main source of SO_4 in the oxidized tailings were larger, primary sulfides.
- 4) Results from the study indicate fine grained tailings samples should probably be run in smaller reactors with 75 g tailings masses and 100 mL rinse volumes for the best results. Drainage problems in the large humidity cells and settling problems in the shaker flasks reduced the confidence in the SO_4 release rates calculated using those methods.

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Appendix A

	Sulfur (wt %)	SO ₄ (wt %)
Minntac Oxidized Coarse	0.24	0.5
Minntac Fresh Coarse	0.22	0.5
Minntac Oxidized Fine	0.02	< 0.3
Keetac Fresh Coarse	0.03	< 0.3
Minntac Fresh Fine	0.09	< 0.3

Table 1. S and SO₄ content for Minntac and Keetac tailings.

	<i>Particle Size</i>								
	> 4.75 mm	4.75-2.00 mm	2.00-0.84 mm	0.84-0.42 mm	0.42-0.18 mm	0.18-0.07 mm	0.07-0.04 mm	< 0.07 mm	< 0.04 mm
Minntac Oxidized Coarse	5.03	33.9	24.4	17.3	10.3	7.75		1.35	
Minntac Fresh Coarse	2.02	28.0	24.8	20.6	13.7	9.24		1.60	
Keetac Fresh Coarse	10.7	36.7	21.4	10.6	5.49	8.15	6.97		
Minntac Fresh Fine	0.00	0.00	0.00	0.00	3.18	28.27	16.1		52.4
Minntac Oxidized Fine	0.00	0.899	0.00	0.478	0.507	8.36	17.9		71.9

Table 2. Tailings particle size distributions (% passing).

	Week												
	0	1	2	3	4	5	6	7	8	9	10	16	
Date	12/10/12	12/17/12	12/24/12	12/31/12	1/7/13	1/14/13	1/22/13	1/28/13	2/4/13	2/11/13	2/19/13	4/3/13	
Sample Size (g)	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	
Oxidation Time (days)		7	7	7	7	7	8	6	7	7	8	21	
Rinse Volume (ml)	490.2	484.2	460.2	477.2	488.2	479.2	413.2	487.7	485.2	483.2	475.2	509.0	
Moisture Post Rinse (ml)	149.4	144.4	147.4	148.4	136.4	137.4	140.4	142.4	143.4	141.4	138.4	144.4	
Moisture Post Oxidation (ml)		137.4	137.4	140.4	139.4	131.4	133.4	136.4	137.4	134.4	134.4	127.4	
Evaporation (ml)		12.0	7.0	7.0	9.0	5.0	4.0	4.0	5.0	9.0	7.0	21.0	
Temperature (°C)	21.4	21.7	21.7	21.4	21.4	21.1	21.1	21.4	21.4	21.7	21.4		
Relative Humidity (%)	55.5	56.0	56.0	55.5	55.5	55.0	55.0	55.5	55.5	56.0	55.5		
Conductivity (µS/cm)	70	120	110	100	100	120	110	130	120	100	110		
pH	8.8	8.4	8.3	8.3	8.2	8.3	8.2	8.3	8.2	8.2	8.1		
Alkalinity (mg/L CaCO₃)	30	40	48	45	33	28	40	40	30	25	35		
Ca	4.35	6.99	7.22	8.48	9.05	10.3	9.44	10.2	10.2	10.5	10.8		
K	0.280	0.270	0.320	0.350	0.370	0.330	0.330	0.320	0.350	0.350	0.378		
Mg	5.22	9.23	8.82	9.91	9.86	9.30	7.94	7.86	8.04	7.31	8.40		
Na	< 0.1	0.140	0.140	0.200	0.170	0.150	0.150	0.150	0.150	0.140	0.139		
SO₄	2.88	12.2	8.45	10.3	12.6	13.2	10.0	10.8	11.6	11.4	12.6		
δ¹⁸O_{SO4}	-2.0											-13.5	-11.6
δ³⁴S_{SO4}	8.2											8.5	8.3
δ¹⁸O_{H2O}												-11.5	
δD_{H2O}												-79.5	

Table 3. Chemical parameters for leachate, water balance, and environmental conditions for Minntac Oxidized Coarse (Humidity Cell # 1). Cations and SO₄ are in mg/L and the isotope values are in ‰.

	Week											
	0	1	2	3	4	5	6	7	8	9	10	16
Date	12/10/12	12/17/12	12/24/12	12/31/12	1/7/13	1/14/13	1/22/13	1/28/13	2/4/13	2/11/13	2/19/13	4/3/13
Sample Size (g)	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000
Oxidation Time (days)		7	7	7	7	7	8	6	7	7	8	21
Rinse Volume (ml)	461.9	474.9	469.9	480.9	486.9	476.9	484.9	494.8	487.9	488.9	477.9	479.9
Moisture Post Rinse (ml)	189.8	172.8	165.8	162.8	152.8	158.8	159.8	160.8	160.8	159.8	158.8	160.8
Moisture Post Oxidation (ml)		170.8	164.8	157.8	154.8	148.8	155.8	157.8	157.8	157.8	154.8	149.8
Evaporation (ml)		19.0	8.0	8.0	8.0	4.0	3.0	2.0	3.0	3.0	5.0	10.0
Temperature (°C)	21.4	21.7	21.7	21.4	21.4	21.1	21.1	21.4	21.4	21.7	21.4	
Relative Humidity (%)	55.5	56.0	56.0	55.5	55.5	55.0	55.0	55.5	55.5	56.0	55.5	
Conductivity (µS/cm)	70	120	108	100	105	120	125	130	110	105	110	
pH	8.7	8.4	8.5	8.4	8.3	8.3	8.3	8.4	8.3	8.3	8.1	
Alkalinity (mg/L CaCO₃)	33	55	50	45	45	48	48	45	40	40	40	
Ca	4.87	7.66	7.79	8.64	9.04	9.94	10.0	10.5	9.60		10.5	
K	0.200	0.290	0.340	0.350	0.360	0.320	0.350	0.320	0.330		0.352	
Mg	5.58	9.66	8.44	9.87	9.87	8.61	9.04	8.14	7.94		8.11	
Na	< 0.1	0.150	0.140	0.150	0.160	0.140	0.150	0.130	0.130		0.112	
SO₄	3.19	11.1	6.93	9.49	14.8	13.0	14.4	11.5	11.8		12.7	
δ¹⁸O_{SO4}	-0.3										-13.5	-13.9
δ³⁴S_{SO4}	8.6										8.5	8.1
δ¹⁸O_{H2O}											-11.5	
δD_{H2O}											-79.5	

Table 4. Chemical parameters for leachate, water balance, and environmental conditions for Minntac Oxidized Coarse (Humidity Cell # 2). Cations and SO₄ are in mg/L and the isotope values are in ‰.

	Week											
	0	1	2	3	4	5	6	7	8	9	10	16
Date	12/10/12	12/17/12	12/24/12	12/31/12	1/7/13	1/14/13	1/22/13	1/28/13	2/4/13	2/11/13	2/19/13	4/3/13
Sample Size (g)	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000
Oxidation Time (days)		7	7	7	7	7	8	6	7	7	8	21
Rinse Volume (ml)	489.8	480.8	467.8	482.8	481.8	485.8	466.8	488.5	483.8	491.8	474.8	472.8
Moisture Post Rinse (ml)	207.7	205.7	200.7	193.7	190.7	187.7	205.7	199.7	200.7	195.7	199.7	204.7
Moisture Post Oxidation (ml)		197.7	201.7	191.7	186.7	187.7	183.7	202.7	195.7	196.7	192.7	191.7
Evaporation (ml)		10.0	4.0	9.0	7.0	3.0	4.0	3.0	4.0	4.0	3.0	9.0
Temperature (°C)	21.4	21.7	21.7	21.4	21.4	21.1	21.1	21.4	21.4	21.7	21.4	
Relative Humidity (%)	55.5	56.0	56.0	55.5	55.5	55.0	55.0	55.5	55.5	56.0	55.5	
Conductivity (µS/cm)	100	200	205	190	170	190	200	200	185	170	180	
pH	9.3	8.5	8.4	8.4	8.3	8.4	8.4	8.3	8.2	8.2	8.2	
Alkalinity (mg/L CaCO₃)	20	53	65	65	65	65	68	68	75	75	70	
Ca	4.02	9.03	8.67	10.9	10.3	11.6	13.4	12.9	12.8		14.9	
K	1.22	3.35	3.54	3.47	3.22	2.66	2.70	2.40	2.34		2.37	
Mg	3.68	9.07	9.02	10.8	10.0	9.86	11.1	9.83	10.5		12.0	
Na	6.21	18.6	17.7	14.3	11.6	9.92	9.12	7.43	6.72		5.87	
SO₄	10.6	22.1	14.5	13.9	20.1	15.2	17.6	13.5	14.5		15.7	
δ¹⁸O_{SO4}	-3.2										-12.2	-12.0
δ³⁴S_{SO4}	3.5										-7.8	-7.4
δ¹⁸O_{H2O}											-11.5	
δD_{H2O}											-79.5	

Table 5. Chemical parameters for leachate, water balance, and environmental conditions for Minntac Fresh Coarse (Humidity Cell # 3). Cations and SO₄ are in mg/L and the isotope values are in ‰.

	Week											
	0	1	2	3	4	5	6	7	8	9	10	16
Date	12/10/12	12/17/12	12/24/12	12/31/12	1/7/13	1/14/13	1/22/13	1/28/13	2/4/13	2/11/13	2/19/13	4/3/13
Sample Size (g)	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000
Oxidation Time (days)		7	7	7	7	7	8	6	7	7	8	21
Rinse Volume (ml)	492.6	485.6	461.6	472.6	481.6	483.6	486.6	489.9	489.6	490.6	476.6	487.6
Moisture Post Rinse (ml)	134.0	137.0	135.0	135.0	136.0	137.0	140.0	138.0	138.0	138.0	142.0	139.0
Moisture Post Oxidation (ml)		132.0	132.0	125.0	130.0	133.0	135.0	137.0	137.0	137.0	136.0	135.0
Evaporation (ml)		2.0	5.0	10.0	5.0	3.0	2.0	3.0	1.0	1.0	2.0	4.0
Temperature (°C)	21.4	21.7	21.7	21.4	21.4	21.1	21.1	21.4	21.4	21.7	21.4	
Relative Humidity (%)	55.5	56.0	56.0	55.5	55.5	55.0	55.0	55.5	55.5	56.0	55.5	
Conductivity (µS/cm)	80	190	182	190	180	220	215	200	180	175	175	
pH	9.3	8.7	8.5	8.5	8.5	8.4	8.4	8.4	8.3	8.2	8.2	
Alkalinity (mg/L CaCO₃)	27	55	68	70	70	65	63	58	60	60	63	
Ca	3.33	6.31	5.92	7.98	9.39	12.1	12.8	11.6	12.5		12.4	
K	1.18	3.63	4.11	4.50	4.12	3.09	2.60	2.21	2.09		2.06	
Mg	3.37	7.55	7.39	10.2	11.2	12.0	12.2	10.0	10.4		11.7	
Na	5.75	19.3	19.6	17.8	14.5	11.0	8.53	6.70	5.99		5.16	
SO₄	9.22	24.7	17.7	18.8	7.96	19.8	20.8	16.1	17.1		18.5	
δ¹⁸O_{SO4}	-0.6										-13.6	-11.8
δ³⁴S_{SO4}	3.7										-8.7	-9.3
δ¹⁸O_{H2O}											-11.5	
δD_{H2O}											-79.5	

Table 6. Chemical parameters for leachate, water balance, and environmental conditions for Minntac Fresh Coarse (Humidity Cell # 4). Cations and SO₄ are in mg/L and the isotope values are in ‰.

	Week											
	0	1	2	3	4	5	6	7	8	9	10	16
Date	12/10/12	12/17/12	12/24/12	12/31/12	1/7/13	1/14/13	1/22/13	1/28/13	2/4/13	2/11/13	2/19/13	4/3/13
Sample Size (g)	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000
Oxidation Time (days)		7	7	7	7	7	8	6	7	7	8	21
Rinse Volume (ml)	491.5	479.5	458.5	475.5	481.5	482.5	484.5	491.2	488.5	487.5	481.5	485.5
Moisture Post Rinse (ml)	113.4	120.4	117.4	119.4	116.4	116.4	117.4	116.4	116.4	116.4	115.4	117.4
Moisture Post Oxidation (ml)		110.4	115.4	109.4	112.4	113.4	115.4	115.4	114.4	114.4	114.4	111.4
Evaporation (ml)		3.0	5.0	8.0	7.0	3.0	1.0	2.0	2.0	2.0	2.0	6.0
Temperature (°C)	21.4	21.7	21.7	21.4	21.4	21.1	21.1	21.4	21.4	21.7	21.4	
Relative Humidity (%)	55.5	56.0	56.0	55.5	55.5	55.0	55.0	55.5	55.5	56.0	55.5	
Conductivity (µS/cm)	70	120	112	90	155	150	140	130	110	100	100	
pH	9.1	8.3	8.2	7.9	7.9	8.1	8.1	8.2	8.0	8.1	8.1	
Alkalinity (mg/L CaCO₃)	25	45	40	28	35	38	38	45	40	45	43	
Ca	2.89	5.30	5.22	11.1	13.6	11.2	11.6	10.5	10.4		9.75	
K	2.10	3.89	3.35	2.43	1.46	1.06	0.940	0.820	0.750		0.745	
Mg	2.10	4.39	4.70	8.14	9.57	7.84	7.66	6.52	6.25		6.97	
Na	4.49	7.46	5.10	3.76	2.23	1.67	1.43	1.14	0.990		0.951	
SO₄	6.08	10.6	7.61	8.42	8.41	7.99	8.51	5.75	5.57		5.28	
δ¹⁸O_{SO4}	2.4										-10.2	-9.4
δ³⁴S_{SO4}	9.2										18.8	16.5
δ¹⁸O_{H2O}											-11.5	
δD_{H2O}											-79.5	

Table 7. Chemical parameters for leachate, water balance, and environmental conditions for Keetac Fresh Coarse (Humidity Cell # 5). Cations and SO₄ are in mg/L and the isotope values are in ‰.

	Week											
	0	1	2	3	4	5	6	7	8	9	10	16
Date	12/10/12	12/17/12	12/24/12	12/31/12	1/7/13	1/14/13	1/22/13	1/28/13	2/4/13	2/11/13	2/19/13	4/3/13
Sample Size (g)	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000
Oxidation Time (days)		7	7	7	7	7	8	6	7	7	8	21
Rinse Volume (ml)	486.0	480.0	467.0	475.0	486.0	475.0	478.0	480.0	479.0	476.0	472.0	470.0
Moisture Post Rinse (ml)	146.6	142.6	139.6	142.6	136.6	138.6	138.6	137.6	134.6	136.6	135.6	136.6
Moisture Post Oxidation (ml)		138.6	136.6	132.6	135.6	131.6	130.6	131.6	128.6	127.6	126.6	114.6
Evaporation (ml)		8.0	6.0	7.0	7.0	5.0	8.0	7.0	9.0	7.0	10.0	22.0
Temperature (°C)	21.4	21.7	21.7	21.4	21.4	21.1	21.1	21.4	21.4	21.7	21.4	
Relative Humidity (%)	55.5	56.0	56.0	55.5	55.5	55.0	55.0	55.5	55.5	56.0	55.5	
Conductivity (µS/cm)	60	120	158	160	120	140	140	135	120	120	120	
pH	9.1	8.2	8.0	8.0	8.0	8.1	8.1	8.1	8.0	8.1	8.1	
Alkalinity (mg/L CaCO₃)	25	45	38	33	40	45	50	45	50	50	55	
Ca	2.70	6.25	12.0	13.3	11.1	11.6	12.1	10.6	11.4		12.1	
K	2.14	3.72	2.48	1.75	1.60	1.38	1.41	1.16	1.17		1.15	
Mg	1.98	4.87	8.35	9.72	7.66	8.02	7.42	6.40	7.13		8.29	
Na	4.66	7.24	4.10	2.74	2.25	1.98	1.75	1.31	1.26		1.18	
SO₄	4.58	7.38	6.17	8.95	14.2	8.11	8.60	6.28	6.73		6.50	
δ¹⁸O_{SO4}	3.2										-10.2	-10.9
δ³⁴S_{SO4}	9.1										18.8	17.3
δ¹⁸O_{H2O}											-11.5	
δD_{H2O}											-79.5	

Table 8. Chemical parameters for leachate, water balance, and environmental conditions for Keetac Fresh Coarse (Humidity Cell # 6). Cations and SO₄ are in mg/L and the isotope values are in ‰.

	Week											
	0	1	2	3	4	5	6	7	8	9	10	16
Date	12/12/12	12/18/12	12/24/12	12/31/12	1/7/13	1/14/13	1/22/13	1/28/13	2/4/13	2/11/13	2/19/13	4/3/13
Sample Size (g)	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000
Oxidation Time (days)		6	6	7	7	7	8	6	7	7	8	21
Rinse Volume (ml)	482.8	255.7	315.8	336.8	374.8	345.8	358.8	418.8	361.8	422.8	416.8	268.3
Moisture Post Rinse (ml)	328.0	290.0	272.0	263.0	266.0	268.0	269.0	269.0	270.0	273.0	275.0	266.0
Moisture Post Oxidation (ml)		292.0	260.0	261.0	262.0	264.0	266.0	268.0	268.0	269.0	271.0	260.0
Evaporation (ml)		36.0	30.0	11.0	1.0	2.0	2.0	1.0	1.0	1.0	2.0	20.0
Temperature (°C)	21.4	21.7	21.7	21.4	21.4	21.1	21.1	21.4	21.4	21.7	21.4	
Relative Humidity (%)	55.5	56.0	56.0	55.5	55.5	55.0	55.0	55.5	55.5	56.0	55.5	
Conductivity (µS/cm)	260	300	320	300	260	290	290	260	230	210	210	
pH	8.7	8.5	8.6	8.5	8.4	8.4	8.4	8.5	8.2	8.5	8.3	
Alkalinity (mg/L CaCO₃)	105	130	130	133	120	125	120	105	110	105	110	
Ca	7.65	11.7	14.6	19.1	18.7	21.7	21.3	17.8	18.4		18.8	
K	6.76	5.14	4.87	3.04	2.35	2.21	2.01	1.69	1.66		2.06	
Mg	13.1	18.2	20.2	20.6	18.4	18.4	17.7	14.6	14.8		18.0	
Na	26.6	20.6	15.6	11.2	8.69	6.92	6.93	5.38	4.83		5.69	
SO₄	25.1	21.1	24.0	19.4	0.550	13.5	14.2	10.4	13.2		12.5	
δ¹⁸O_{SO4}	-0.3										-12.7	-12.1
δ³⁴S_{SO4}	7.0										-1.6	-3.7
δ¹⁸O_{H2O}											-11.5	
δD_{H2O}											-79.5	

Table 9. Chemical parameters for leachate, water balance, and environmental conditions for Minntac Fresh Fine (Humidity Cell # 7). Cations and SO₄ are in mg/L and the isotope values are in ‰.

	Week											
	0	1	2	3	4	5	6	7	8	9	10	16
Date	12/12/12	12/18/12	12/24/12	12/31/12	1/7/13	1/14/13	1/22/13	1/28/13	2/4/13	2/11/13	2/19/13	4/3/13
Sample Size (g)	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000
Oxidation Time (days)		6	6	7	7	7	8	6	7	7	8	21
Rinse Volume (ml)	469.7	268.1	474.7	493.7	472.7	472.7	477.7	471.6	469.7	480.7	467.7	230.7
Moisture Post Rinse (ml)	448.0	422.0	419.0	404.0	409.0	412.0	408.0	409.0	415.0	413.0	420.0	423.0
Moisture Post Oxidation (ml)		428.0	419.0	414.0	400.0	405.0	407.0	405.0	405.0	411.0	408.0	410.0
Evaporation (ml)		20.0	3.0	5.0	4.0	4.0	5.0	3.0	4.0	4.0	5.0	11.0
Temperature (°C)	21.4	21.7	21.7	21.4	21.4	21.1	21.1	21.4	21.4	21.7	21.4	
Relative Humidity (%)	55.5	56.0	56.0	55.5	55.5	55.0	55.0	55.5	55.5	56.0	55.5	
Conductivity (µS/cm)	270	290	290	255	280	230	265	190	215	200	215	
pH	8.5	8.5	8.6	8.6	8.5	8.5	8.5	8.4	8.3	8.5	8.4	
Alkalinity (mg/L CaCO₃)	145	165	165	158	145	145	145	138	138	130	130	
Ca	14.0	12.8	13.5	12.6	12.5	13.7	13.6	13.6	14.4		14.1	
K	0.440	0.490	0.620	0.580	0.560	0.510	0.510	0.470	0.480		0.531	
Mg	32.9	34.2	34.6	32.3	30.0	27.6	26.1	25.2	25.3		25.5	
Na	0.790	0.840	0.970	0.930	0.880	0.820	0.780	0.710	0.710		0.822	
SO₄	1.04	1.09	1.21	0.660	11.8	20.8	0.510	<0.02	<0.02		0.315	
δ¹⁸O_{SO4}	-4.0											
δ³⁴S_{SO4}	7.4											
δ¹⁸O_{H2O}												-11.5
δD_{H2O}												-79.5

Table 10. Chemical parameters for leachate, water balance, and environmental conditions for Minntac Oxidized Fine (Humidity Cell # 8). Cations and SO₄ are in mg/L and the isotope values are in ‰.

	Week												
	0	1	2	3	4	5	6	7	8	9	10	12	16
Date	12/13/12	12/18/12	12/24/12	12/31/12	1/7/13	1/14/13	1/22/13	1/28/13	2/4/13	2/11/13	2/19/13	3/6/13	4/3/13
Sample Size (g)	75	75	75	75	75	75	75	75	75	75	75	75	75
Oxidation Time (days)		5	6	7	7	7	8	6	7	7	8	7	21
Rinse Volume (ml)	198.1	192.0	193.9	196.2	195.0	194.4	195.4	196.8	193.6	180.1	188.7	90.8	97.1
Moisture Post Rinse (ml)	28.9	26.4	26.5	26.2	26.6	26.9	27.0	27.3	26.7	30.9	29.9	28.2	25.3
Moisture Post Oxidation (ml)		20.2	24.8	22.5	22.8	23.9	23.8	23.7	23.7	12.9	26.6	23.3	24.2
Evaporation (ml)		8.7	1.7	3.9	3.4	2.7	3.1	3.3	3.6	13.9	4.2	6.6	3.7
Temperature (°C)	21.4	21.7	21.7	21.4	21.4	21.1	21.1	21.4	21.4	21.7	21.4	21.7	
Relative Humidity (%)	55.5	56.0	56.0	55.5	55.5	55.0	55.0	55.5	55.5	56.0	55.5	55.3	
Conductivity (µS/cm)	100	150	140	135	140	130	145	180	170	150	190	225	
pH	8.4	8.4	8.5	8.2	8.2	8.2	8.2	8.3	8.2	8.3	8.1	8.3	
Alkalinity (mg/L CaCO ₃)	45	65	65	60	60	60	58	65	78	65	85	113	
Ca	5.55	9.26	12.6	13.9	15.0	17.2	18.1	20.2	25.2		26.2	30.8	
K	1.20	2.15	1.78	1.29	0.980	0.700	0.670	0.730	0.870		0.956	1.03	
Mg	5.20	8.10	8.39	7.67	6.75	6.02	5.91	6.36	8.27		10.8	13.2	
Na	3.02	4.26	2.97	1.98	1.42	1.02	0.900	0.880	0.910		0.883	0.768	
SO ₄	1.86	7.39	4.58	2.61	1.88	1.79	2.85	3.78	7.49		12.1	15.1	
δ ¹⁸ O _{SO4}	1.0												-8.2
δ ³⁴ S _{SO4}	6.9												-0.4
δ ¹⁸ O _{H2O}												-11.5	
δD _{H2O}												-79.5	

Table 11. Chemical parameters for leachate, water balance, and environmental conditions for Minntac Fresh Fine (Reactor # 9). Cations and SO₄ are in mg/L and the isotope values are in ‰.

	Week												
	0	1	2	3	4	5	6	7	8	9	10	12	16
Date	12/13/12	12/18/12	12/24/12	12/31/12	1/7/13	1/14/13	1/22/13	1/28/13	2/4/13	2/11/13	2/19/13	3/6/13	4/3/2013
Sample Size (g)	75	75	75	75	75	75	75	75	75	75	75	75	75
Oxidation Time (days)		5	6	7	7	7	8	6	7	7	8	7	21
Rinse Volume (ml)	199.9	196.1	155.2	196.7	195.3	192.6	190.7	196.1	191.5	191.8	188.6	92.7	95.1
Moisture Post Rinse (ml)	23.6	23.8	26.8	25.3	25.2	25.2	25.2	25.8	25.1	24.0	24.2	24.5	24.4
Moisture Post Oxidation (ml)		21.3	28.0	23.5	22.8	22.8	20.6	23.2	19.5	19.1	16.4	19.3	20.2
Evaporation (ml)		2.3	-4.2	3.3	2.5	2.4	4.6	2.0	6.3	6.0	7.6	4.9	4.1
Temperature (°C)	21.4	21.7	21.7	21.4	21.4	21.1	21.1	21.4	21.4	21.7	21.4	21.7	
Relative Humidity (%)	55.5	56.0	56.0	55.5	55.5	55.0	55.0	55.5	55.5	56.0	55.5	55.3	
Conductivity (µS/cm)	120	135	143	130	130	120	145	120	150	115	120	190	
pH	8.3	8.3	8.5	8.2	8.1	8.2	8.2	8.1	8.1	8.2	7.9	8.3	
Alkalinity (mg/L CaCO ₃)	40	58	65	60	58	55	58	58	70	48		90	
Ca	6.87	8.69	12.9	12.6	13.8	15.8	17.4	16.9	21.4			24.9	
K	1.79	1.54	1.78	1.36	1.09	0.790	0.770	0.710	0.840			0.937	
Mg	6.54	6.95	8.52	7.19	6.41	5.94	5.88	5.47	6.69			11.2	
Na	3.83	3.36	3.24	2.20	1.55	1.11	0.96	0.810	0.820			0.655	
SO ₄	3.65	3.95	5.40	2.72	1.92	1.73	2.27	1.90	3.49			11.7	
δ ¹⁸ O _{SO4}	1.0												-9.5
δ ³⁴ S _{SO4}	6.9												-1.5
δ ¹⁸ O _{H2O}												-11.5	
δD _{H2O}												-79.5	

Table 12. Chemical parameters for leachate, water balance, and environmental conditions for Minntac Fresh Fine (Reactor # 10). Cations and SO₄ are in mg/L and the isotope values are in ‰.

	Week											
	0	1	2	3	4	5	6	7	8	9	10	16
Date	12/13/12	12/18/12	12/24/12	12/31/12	1/7/13	1/14/13	1/22/13	1/28/13	2/4/13	2/11/13	2/19/13	4/3/2013
Sample Size (g)	75	75	75	75	75	75	75	75	75	75	75	75
Oxidation Time (days)		5	6	7	7	7	8	6	7	7	8	21
Rinse Volume (ml)	199.5	194.1	193.4	196.7	196.2	191.9	193.4	195.0	193.7	193.5	192.8	94.2
Moisture Post Rinse (ml)	36.4	35.2	35.4	34.9	34.8	35.1	35.2	36.0	35.9	36.4	36.5	35.5
Moisture Post Oxidation (ml)		33.1	10.0	33.1	32.0	33.3	29.6	32.5	33.2	33.9	32.3	31.9
Evaporation (ml)		3.3	25.2	2.3	2.9	1.5	5.5	2.7	2.8	2.1	4.1	4.7
Temperature (°C)	21.4	21.7	21.7	21.4	21.4	21.1	21.1	21.4	21.4	21.7	21.4	
Relative Humidity (%)	55.5	56.0	56.0	55.5	55.5	55.0	55.0	55.5	55.5	56.0	55.5	
Conductivity (µS/cm)	120	130	132	130	130	140	150	120	130	130	150	
pH	8.3	8.3	8.5	8.5	8.3	8.3	8.3	8.2	8.1	8.1	8.2	
Alkalinity (mg/L CaCO₃)	55	68	68	70	70	73	73	70	75	78	80	
Ca	6.54	8.37	11.1	11.7	12.7	14.2	14.9	15.5	17.4		18.1	
K	0.230	0.270	0.330	0.350	0.350	0.280	0.290	0.290	0.310		0.361	
Mg	9.85	10.3	12.0	11.0	10.6	9.66	9.18	8.63	8.83		9.44	
Na	0.390	0.500	0.480	0.490	0.460	0.390	0.390	0.380	0.370		0.472	
SO₄	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02		0.140	
δ¹⁸O_{SO4}												
δ³⁴S_{SO4}												
δ¹⁸O_{H2O}												-11.5
δD_{H2O}												-79.5

Table 13. Chemical parameters for leachate, water balance, and environmental conditions for Minntac Oxidized Fine (Reactor # 11). Cations and SO₄ are in mg/L and the isotope values are in ‰.

	Week											
	0	1	2	3	4	5	6	7	8	9	10	16
Date	12/13/12	12/18/12	12/24/12	12/31/12	1/7/13	1/14/13	1/22/13	1/28/13	2/4/13	2/11/13	2/19/13	4/3/2013
Sample Size (g)	75	75	75	75	75	75	75	75	75	75	75	75
Oxidation Time (days)		5	6	7	7	7	8	6	7	7	8	21
Rinse Volume (ml)	200.0	195.4	191.0	197.1	194.2	158.2	193.6	187.5	193.5	192.8	189.7	95.9
Moisture Post Rinse (ml)	35.7	35.3	35.4	35.1	34.7	35.5	36.2	36.2	35.8	35.6	36.1	34.2
Moisture Post Oxidation (ml)		32.7	8.3	32.9	30.3	31.2	31.7	31.5	31.8	30.0	29.6	30.2
Evaporation (ml)		3.0	27.1	2.5	4.9	3.5	3.8	4.7	4.5	5.8	6.0	-7.8
Temperature (°C)	21.4	21.7	21.7	21.4	21.4	21.1	21.1	21.4	21.4	21.7	21.4	
Relative Humidity (%)	55.5	56.0	56.0	55.5	55.5	55.0	55.0	55.5	55.5	56.0	55.5	
Conductivity (µS/cm)	120	140	132	140	150	150	150	120	140	130	120	
pH	8.3	8.3	8.4	8.4	8.3	8.3	8.3	8.3	8.2	8.4	8.1	
Alkalinity (mg/L CaCO₃)	70	68	68	63	73	80	75	70	78	78		
Ca	6.90	9.13	11.2	12.2	13.2	15.5	15.8	15.6	17.7			
K	0.230	0.320	0.340	0.320	0.330	0.290	0.300	0.310	0.310			
Mg	10.1	10.7	11.2	11.0	10.5	9.92	9.32	8.86	8.60			
Na	0.340	0.450	0.430	0.420	0.430	0.410	0.390	0.510	0.370			
SO₄	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02			
δ¹⁸O_{SO4}												
δ³⁴S_{SO4}												
δ¹⁸O_{H2O}												-11.5
δD_{H2O}												-79.5

Table 14. Chemical parameters for leachate, water balance, and environmental conditions for Minntac Oxidized Fine (Reactor # 12). Cations and SO₄ are in mg/L and the isotope values are in ‰.

	Week 10										Week 12	
	Minntac Oxidized Coarse 1	Minntac Oxidized Coarse 2	Minntac Fresh Coarse 3	Minntac Fresh Coarse 4	Keetac Fresh Coarse 5	Keetac Fresh Coarse 6	Minntac Fresh Fine 7	Minntac Oxidized Fine 8	Minntac Fresh Fine 9	Minntac Oxidized Fine 11	Minntac Fresh Fine 9	Minntac Fresh Fine 10
	Sample Mass (g)	1000	1000	1000	1000	1000	1000	1000	1000	75	75	75
Rinse Volume (mL)	475.2	477.9	474.8	476.6	481.5	472.5	416.8	467.7	188.7	192.8	90.8	92.7
Alkalinity (mg/L CaCO ₃)	35	40	70	63	43	55	110	130	85	80	113	90
Al	0.00	0.00	0.01	0.01	0.00	0.00	0.01	0.00	0.02	0.02	0.05	0.02
Ba	0.00	0.00	0.07	0.05	0.01	0.01	0.07	0.00	0.08	0.04	0.10	0.08
Ca	10.8	10.5	14.9	12.4	9.75	12.1	18.8	14.1	26.2	18.1	30.8	24.9
Fe	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00
K	0.378	0.400	2.37	2.10	0.700	1.10	2.10	0.500	1.00	0.400	1.00	0.900
Mg	8.40	8.10	12.0	11.7	7.00	8.30	18.0	25.5	10.8	9.40	13.2	11.2
Mn	0.000	0.000	0.018	0.004	0.000	0.000	0.000	0.000	0.011	0.000	0.004	0.001
Na	0.100	0.100	5.90	5.20	1.00	1.20	5.70	0.800	0.900	0.500	0.800	0.700
P	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005
Si	1.7	1.0	1.1	1.1	1.6	1.6	7.2	3.2	2.9	3.2	2.9	2.3
Sr	0.007	0.007	0.052	0.045	0.027	0.033	0.115	0.008	0.050	0.011	0.054	0.047
Flouride	0.019	0.020	0.027	0.030	0.039	0.038	0.119	0.090	0.036	0.025	0.044	0.048
Acetate	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Formate	0.03	<0.01	0.03	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.08
Chloride	0.032	0.036	0.098	0.081	0.049	0.034	0.055	0.104	0.038	0.044	0.076	0.056
Nitrite - N	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002
Bromide	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Nitrate - N	0.432	0.416	1.40	2.12	1.40	1.08	1.00	0.466	1.83	0.517	1.06	2.40
Oxalate	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Thiosulfate	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Sulfate	12.6	12.7	15.7	18.5	5.30	6.50	12.5	0.300	12.1	0.140	15.1	11.7

Table 15. Major cations and anions for humidity cells and reactors during week 10 and 12. Reactors 10 and 12 were saved for isotope analysis during week 10, so were not analyzed. Cations, and anions are in mg/L.

	Week											
	1	3	3	4	5	6	6	7	8	9	9	
Date	12/18/12	12/31/12	12/31/12	1/9/2013	1/15/13	1/22/12	1/22/12	1/30/13	2/6/13	2/13/13	2/13/13	
Sample Size (g)	150	150	150	150	150	150	150	150	150	150	150	
Water Volume (ml)		391.5	392.5			388.0	385.7			371.2	381.3	
Conductivity (µS/cm)	420	500	500	600	600	650	700	800	700	700	700	
pH	8.5	8.5	8.6	8.4	8.4	8.4	8.5	8.5	8.3	8.5	8.5	
Alkalinity (mg/L CaCO₃)		105	98			120	120			120	120	
Ca		29.7	30.2			38.6	40.4					
K		10.8	10.8			9.30	9.72					
Mg		33.8	34.5			40.4	43.5					
Na		33.0	32.9			30.6	32.2					
SO₄		142	148			148	169					
Sulfate Release Rate						26.9	214					
δ¹⁸O_{SO4}										-5.8	-5.8	
δ³⁴S_{SO4}										4.8	4.8	
δ¹⁸O_{H2O}										-11.5	-11.5	
δD_{H2O}										-79.5	-79.5	

Table 16. Chemical and physical parameters for Minntac Fresh Fine shaker flasks. Two flasks were collected for measurements during weeks 3,6, and 9. Cation and SO₄ concentrations are in mg/L, the isotope values are in ‰, and SO₄ release rates are in µmol SO₄/kg tailings x week.

	<i>Week</i>											
	1	3	3	4	5	6	6	7	8	9	9	
Date	12/18/12	12/31/12	12/31/12	1/9/13	1/15/13	1/22/12	1/22/12	1/30/13	2/6/13	2/13/12	2/13/12	
Sample Size (g)	150	150	150	150	150	150	150	150	150	150	150	
Water Volume (ml)		383.0	382.8			384.4	386.9			379.6	381.6	
Conductivity (µS/cm)	190	235	215	270	270	310	315	345	290	330	315	
pH	8.5	8.6	8.6	8.5	8.5	8.6	8.6	8.6	8.5	8.7	8.7	
Alkalinity (mg/L CaCO₃)		120	125			125	145			153	155	
Ca		16.1	16.4			17.2	17.8					
K		0.550	0.550			0.490	0.500					
Mg		27.6	28.0			30.8	31.5					
Na		0.770	0.790			0.810	0.820					
SO₄		14.6	14.8			14.8	14.6					
Sulfate Release Rate						0.890	0.00					
δ¹⁸O_{SO4}										-5.4	-5.4	
δ³⁴S_{SO4}										7.4	7.4	
δ¹⁸O_{H2O}										-11.5	-11.5	
δD_{H2O}										-79.5	-79.5	

Table 17. Chemical and physical parameters for Minntac Oxidized Fine shaker flasks. Two flasks were collected for measurements during weeks 3,6, and 9. Cation and SO₄ concentrations are in mg/L, isotope values are in ‰, and SO₄ release rates are in µmol SO₄/kg tailings x week.

	Sulfur (wt %)	<i>Week</i>											
		1	2	3	4	5	6	7	8	9	10	12	
Minntac Oxidized Coarse 1	0.24	61.5	40.5	51.2	64.1	65.9	37.7	64.0	58.6	57.4	54.4		
Minntac Oxidized Coarse 2	0.24	54.9	33.9	47.5	75.1	64.6	63.6	69.2	60.0		55.5		
Minntac Fresh Coarse 3	0.22	111	70.7	69.9	101	76.9	74.9	80.2	73.1		68.0		
Minntac Fresh Coarse 4	0.22	125	85.1	92.6	39.9	99.7	92.3	95.9	87.2		80.3		
Keetac Fresh Coarse 5	0.03	52.9	36.3	41.7	42.2	40.2	37.6	34.3	28.3		23.2		
Keetac Fresh Coarse 6	0.03	36.9	30.0	44.3	71.9	40.1	37.5	36.6	33.6		28.0		
Minntac Fresh Fine Large 7	0.09	65.6	92.1	68.1	2.1	48.6	46.4	52.9	49.8		47.6		
Minntac Oxidized Fine Large 8	0.02	3.55	6.98	3.39	58.1	102	2.22	0.00	0.00		1.34		
Minntac Fresh Fine Small 9	0.09	276	144	71.1	50.9	48.3	67.7	121	201		278	166	
Minntac Fresh Fine Small 10	0.09	151	136	74.3	52.1	46.3	52.6	60.4	92.8			132	
Minntac Oxidized Fine Small 11	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00		3.28		
Minntac Oxidized Fine Small 12	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00				

Table 18. Total S content (wt %) and SO₄ release rates in µmol SO₄/kg tailings x week for each tailings sample.

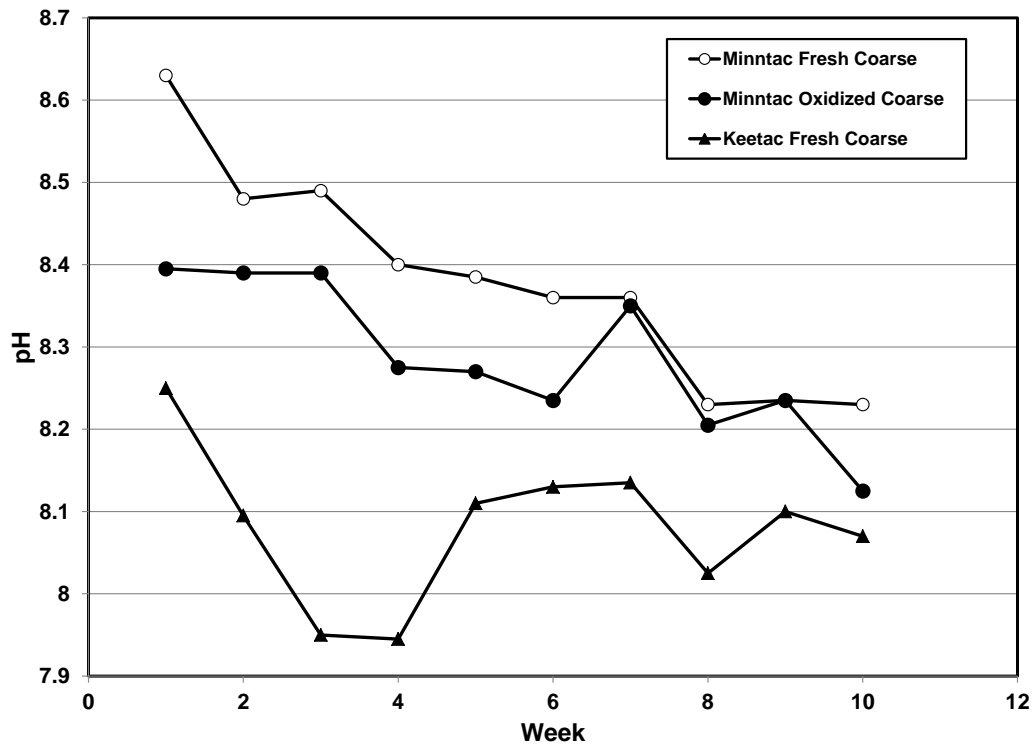
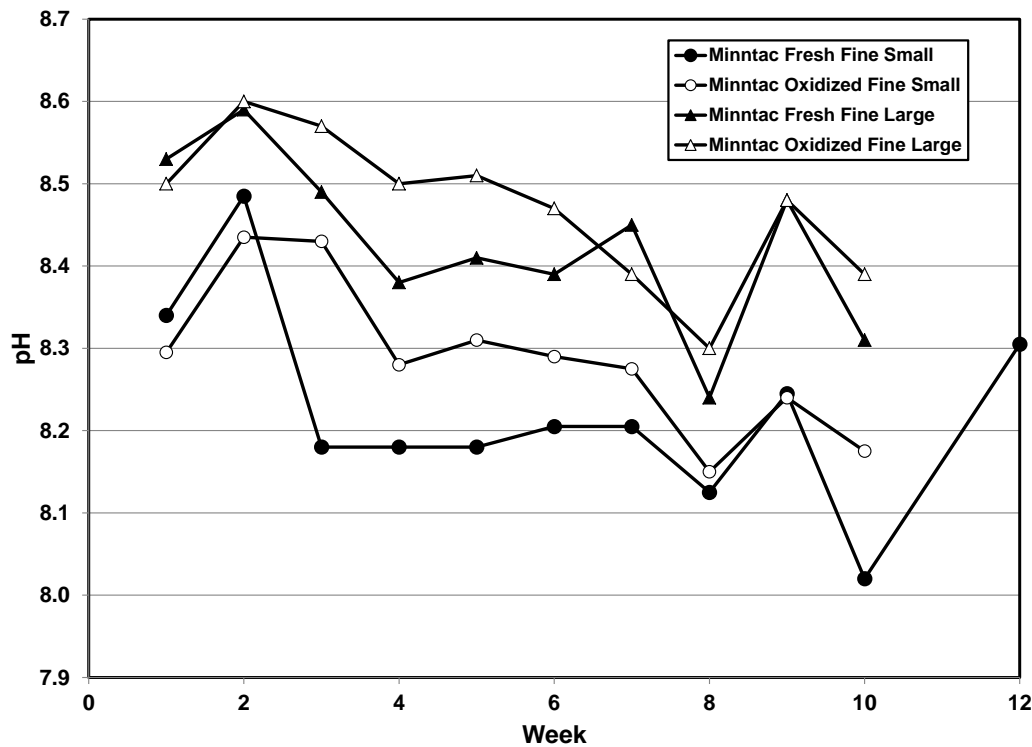
		Week										All Weeks		
		1	2	3	4	5	6	7	8	9	10	12	Mean	Median
Minntac Oxidized Coarse	Mean	58.2	37.2	49.4	69.6	65.2	50.7	66.6	59.3	50.2	55.0		56.1	56.6
	Stdev	4.68	4.65	2.58	7.78	0.919	18.4	3.63	0.955		0.728		4.92	3.63
	<i>Sulfur (wt %) 0.24</i>	% RPD	11.4	17.7	7.40	15.8	1.99	51.3	7.72	2.28		1.87		13.0
Minntac Fresh Coarse	Mean	118	77.9	81.2	70.4	88.3	83.6	88.0	80.1		74.2		84.6	81.2
	Stdev	10.1	10.2	16.0	43.1	16.1	12.3	11.1	10.0		8.67		15.3	11.1
	<i>Sulfur (wt %) 0.22</i>	% RPD	12.1	18.6	27.9	86.6	25.8	20.8	17.8	17.6		16.5		27.1
Keetac Fresh Coarse	Mean	44.9	33.2	43.0	57.0	40.1	37.5	35.5	31.0		25.6		38.6	37.5
	Stdev	11.3	4.48	1.82	21.0	0.022	0.079	1.64	3.70		3.39		5.28	3.39
	<i>Sulfur (wt %) 0.03</i>	% RPD	35.7	19.1	6.00	52.1	0.076	0.299	6.52	16.9		18.8		17.3
Minntac Fresh Fine	Mean	213	140	72.7	51.5	47.3	60.1	90.4	147		278	149	125	115
	Stdev	88.6	5.72	2.25	0.813	1.45	10.7	42.6	76.8			24.2	28.1	10.7
	<i>Sulfur (wt %) 0.09</i>	% RPD	58.8	5.79	4.38	2.23	4.33	25.1	66.5	73.8		23.0	29.3	23.0
Minntac Oxidized Fine	Mean	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0		3.28		0.365	0.0
	Stdev	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0				0.0	0.0
	<i>Sulfur (wt %) 0.02</i>	% RPD	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0			0.0	0.0

Table 19. Average SO₄ release rates in $\mu\text{mol SO}_4/\text{kg} \times \text{week}$ and statistics for each type of tailings ($n = 2$). The mean and median for each sample over the entire experiment was also calculated. Release rates calculated for the fine tailings run in the large humidity cells were not included in the fine tailings averages due to drainage issues that could have affected the release rate estimates.

		Minntac Oxidized Coarse 1	Minntac Oxidized Coarse 2	Minntac Fresh Coarse 3	Minntac Fresh Coarse 4	Keetac Fresh Coarse 5	Keetac Fresh Coarse 6	Minntac Fresh Fine 7	Minntac Oxidized Fine 8	Minntac Fresh Fine 9	Minntac Fresh Fine 10	Minntac Oxidized Fine 11	Minntac Oxidized Fine 12
$\delta^{18}\text{O}_{\text{SO}_4}$	<i>Week 0</i>	-2.0	-0.3	-3.2	-0.6	2.4	3.2	-0.3	-4.0	1.0	1.0		
	<i>Week 10</i>	-13.5	-13.5	-12.2	-13.6	-10.2	-10.2	-12.7					
	<i>Week 16</i>	-11.6	-13.9	-12.0	-11.8	-9.4	-10.9	-12.1		-8.2	-9.5		
$\delta^{34}\text{S}_{\text{SO}_4}$	<i>Week 0</i>	8.2	8.6	3.5	3.7	9.2	9.1	7.0	7.4	6.9	6.9		
	<i>Week 10</i>	8.5	8.5	-7.8	-8.7	18.8	18.8	-1.6					
	<i>Week 16</i>	8.3	8.1	-7.4	-9.3	16.5	17.3	-3.7		-0.4	-1.5		
$\delta^{18}\text{O}_{\text{H}_2\text{O}}$	<i>Week 10</i>	-11.5	-11.5	-11.5	-11.5	-11.5	-11.5	-11.5	-11.5	-11.5	-11.5	-11.5	-11.5
$\delta\text{D}_{\text{H}_2\text{O}}$	<i>Week 10</i>	-79.5	-79.5	-79.5	-79.5	-79.5	-79.5	-79.5	-79.5	-79.5	-79.5	-79.5	-79.5

Table 20. $\delta^{34}\text{S}_{\text{SO}_4}$ and $\delta^{18}\text{O}_{\text{SO}_4}$ values for the humidity cells and reactors, and $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ and $\delta\text{D}_{\text{H}_2\text{O}}$ for the DI water used to rinse the samples.

Appendix B

Figure 1. Average pH for the coarse tailings ($n=2$).Figure 2. Average pH for the fine tailings small reactors ($n=2$) and large humidity cells ($n=1$).

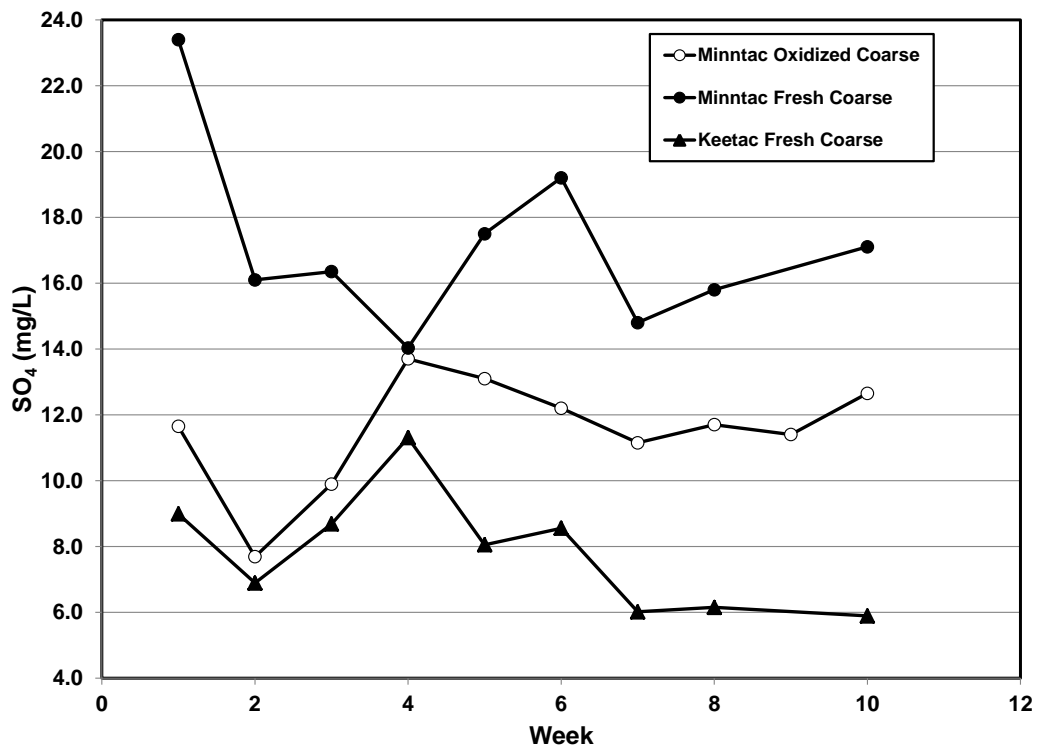


Figure 3. Average SO_4 concentration for the coarse tailings ($n=2$).

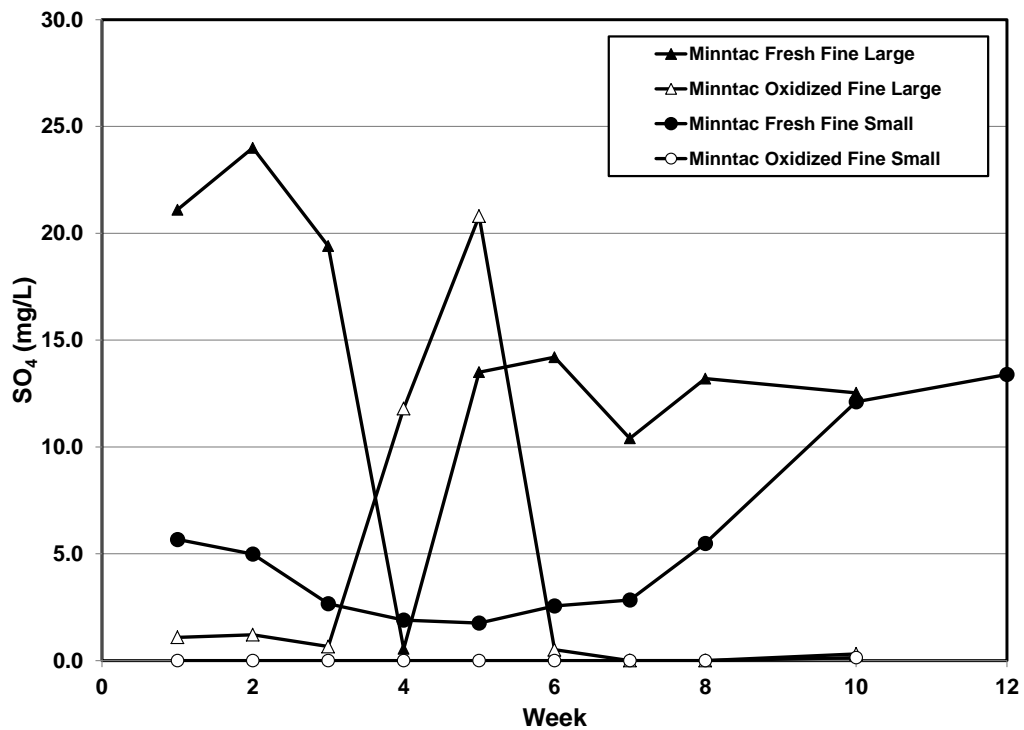


Figure 4. Average SO_4 concentrations for fine tailings small reactors ($n=2$) and large humidity cells ($n=1$).

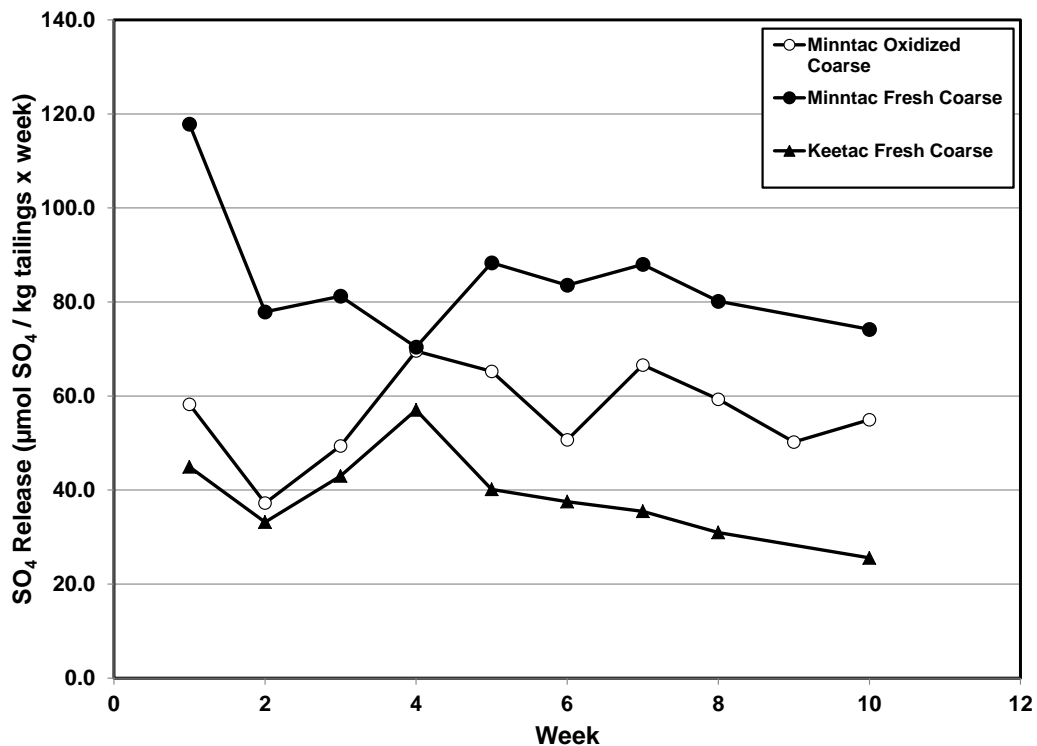


Figure 5. Average SO_4 release rates for the coarse tailings ($n=2$).

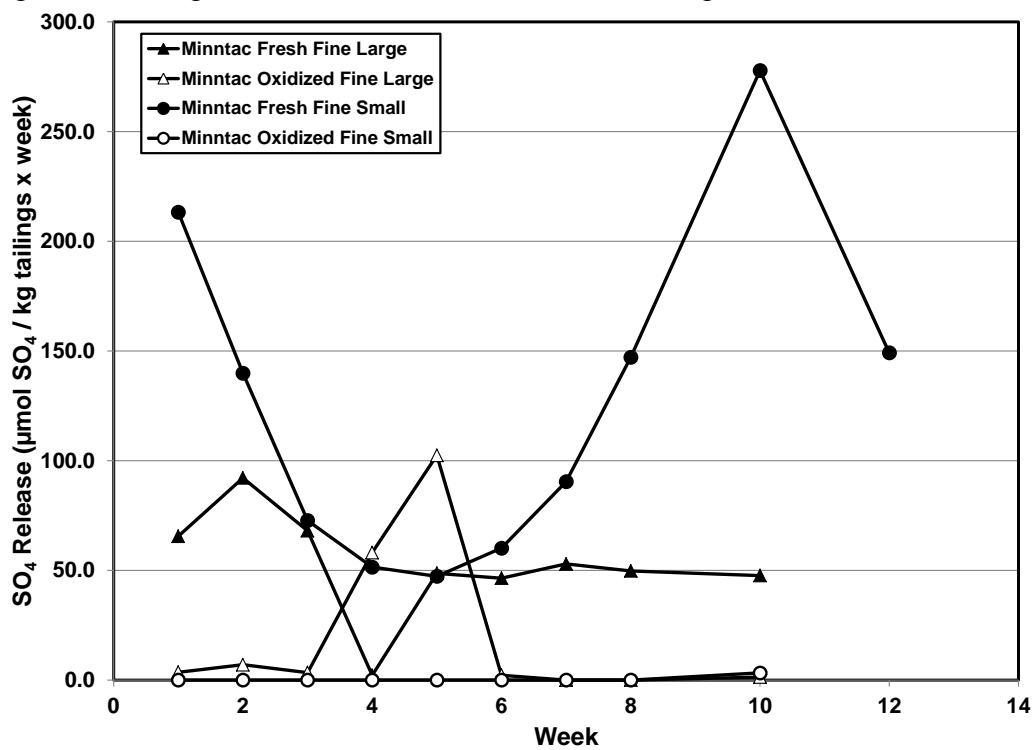


Figure 6. Average SO_4 release rate for the fine tailings small reactors ($n=2$) and large humidity cells ($n=1$).

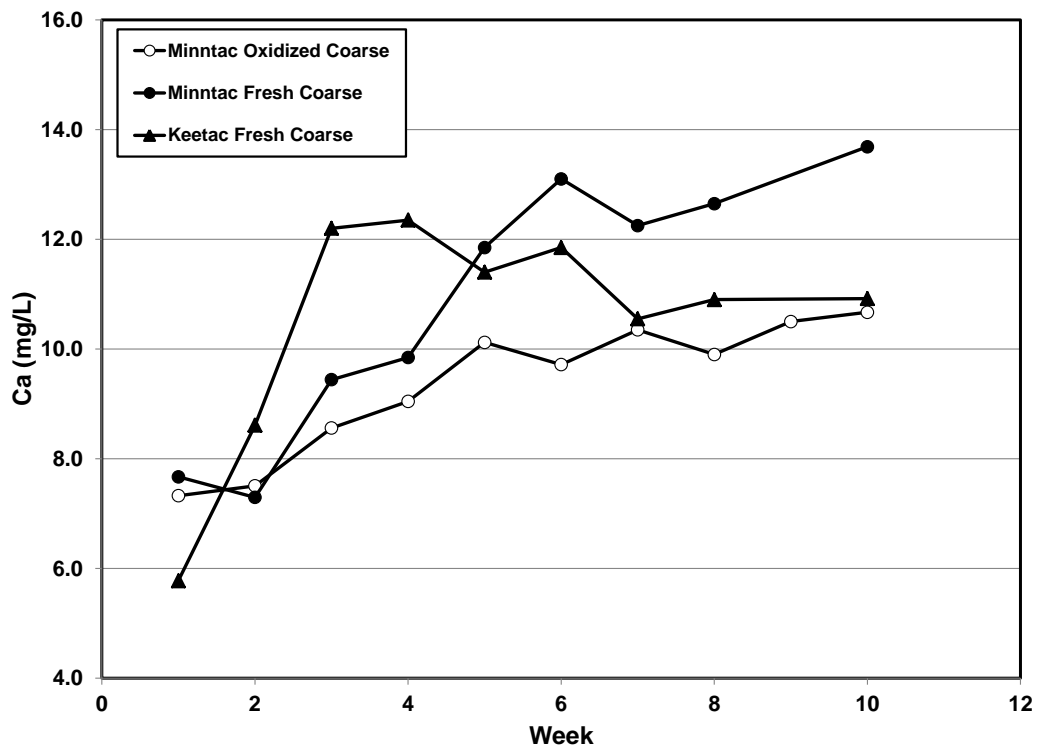


Figure 7. Ca concentrations for the coarse tailings ($n=2$).

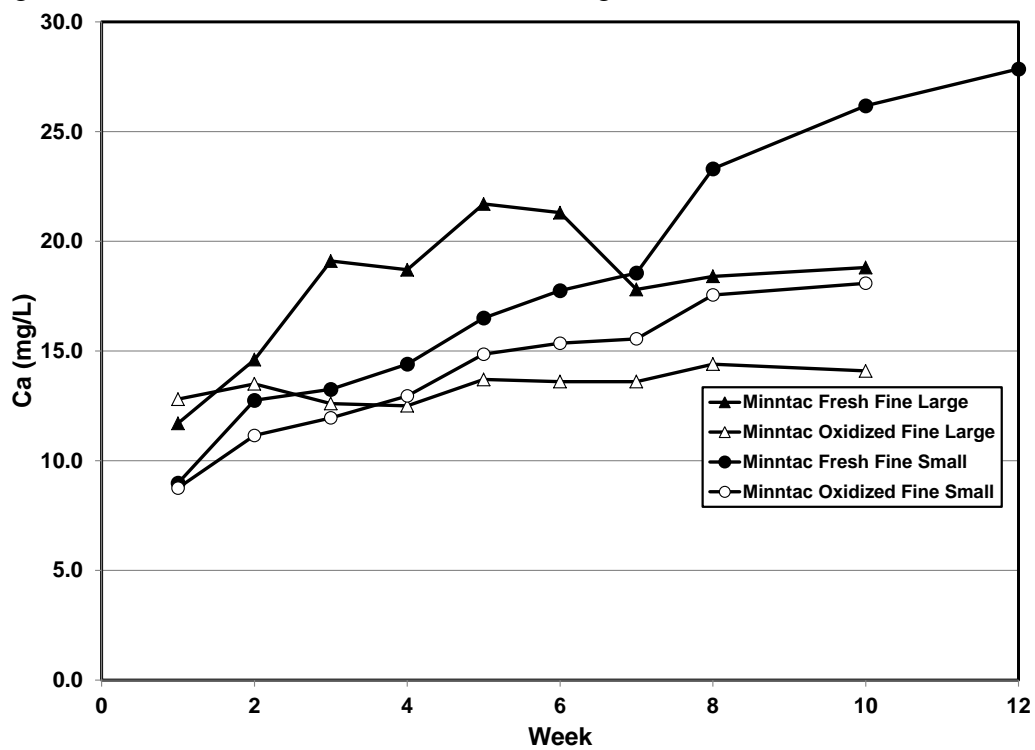


Figure 8. Ca concentrations for the fine tailings small reactors ($n=2$) and large humidity cells ($n=1$).

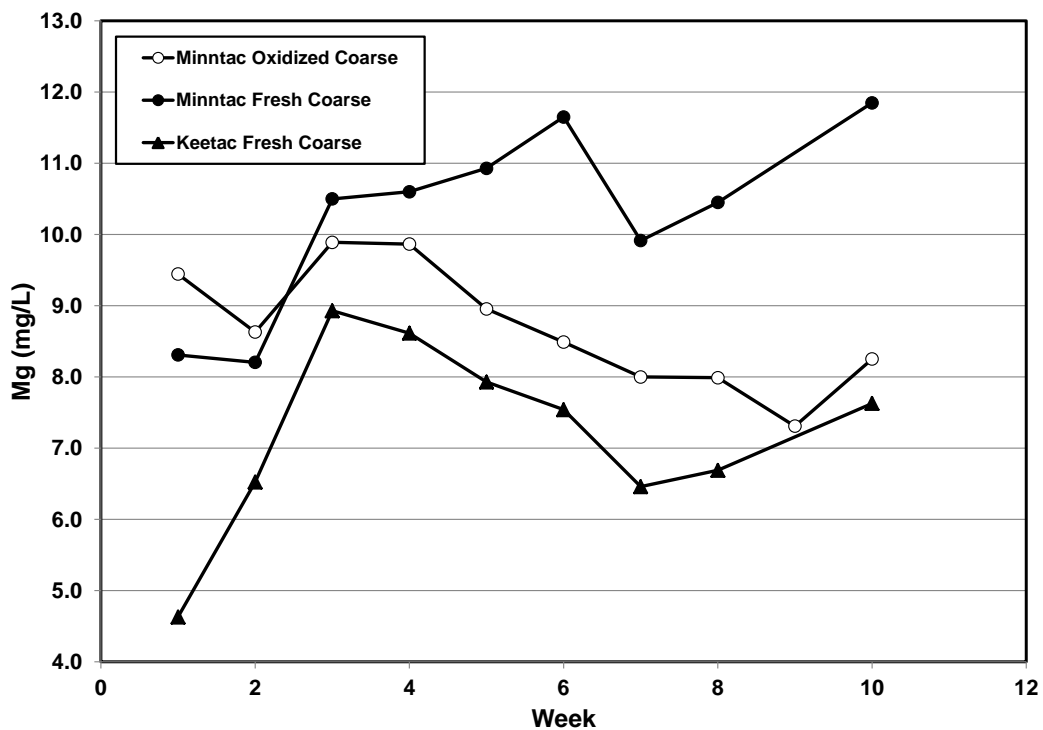


Figure 9. Mg concentrations for the coarse tailings ($n=2$).

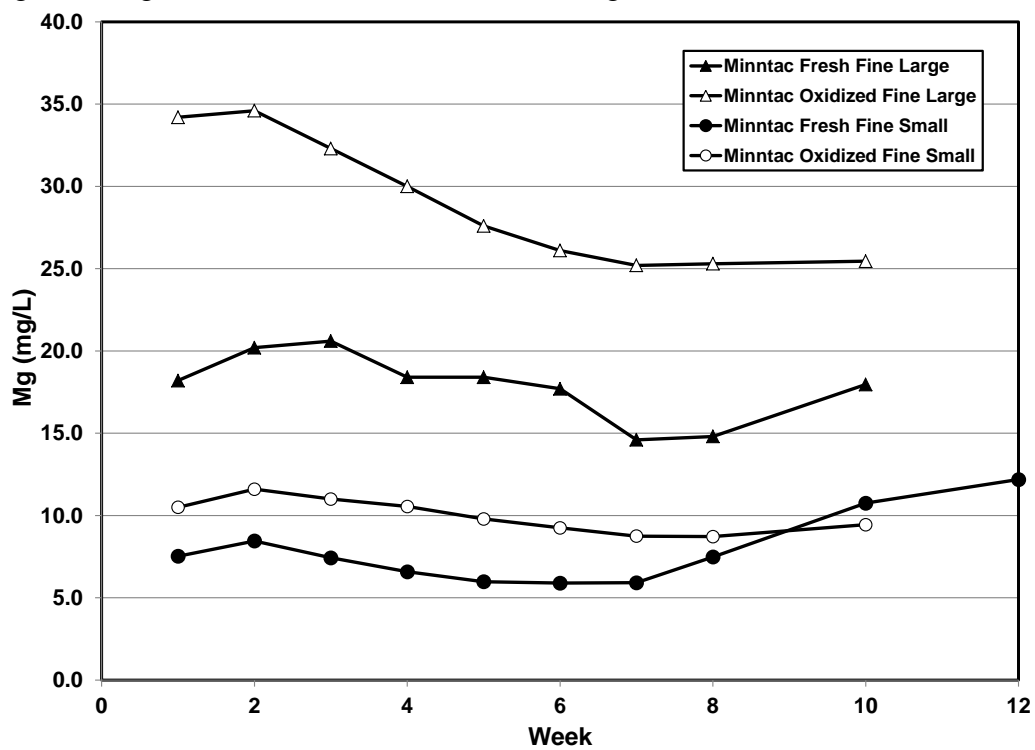


Figure 10. Mg concentrations for the fine tailings small reactors ($n=2$) and large humidity cells ($n=1$).

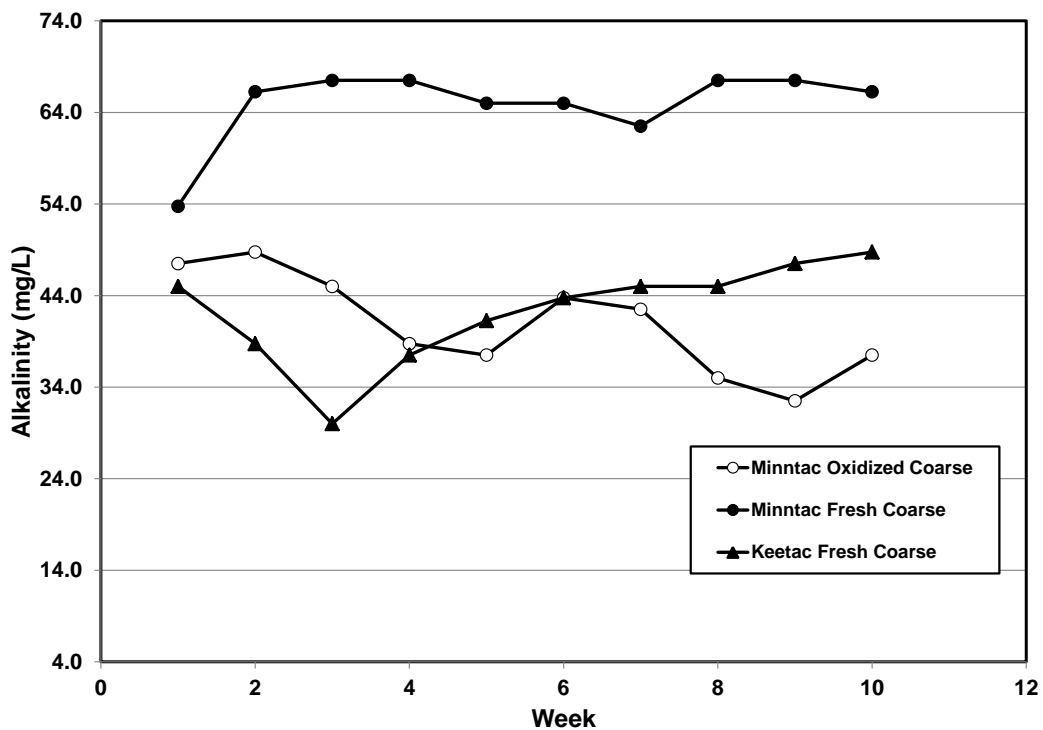


Figure 11. Alkalinity for the coarse tailings ($n=2$).

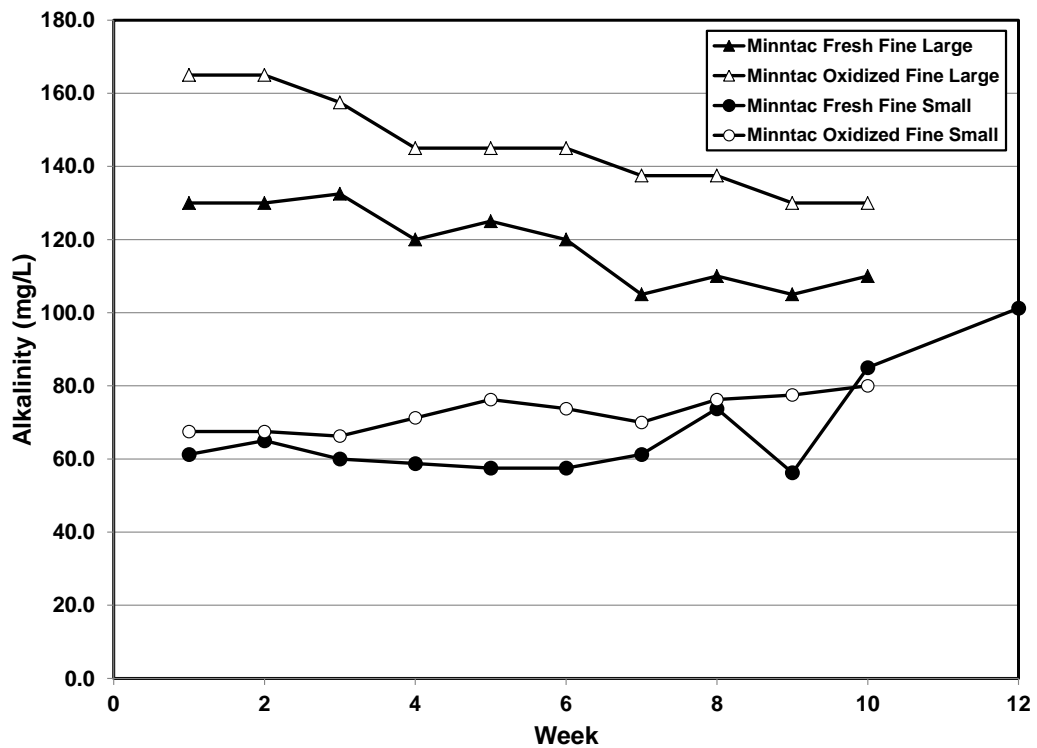


Figure 12. Alkalinity for the fine tailings small reactors ($n=2$) and large humidity cells ($n=1$).

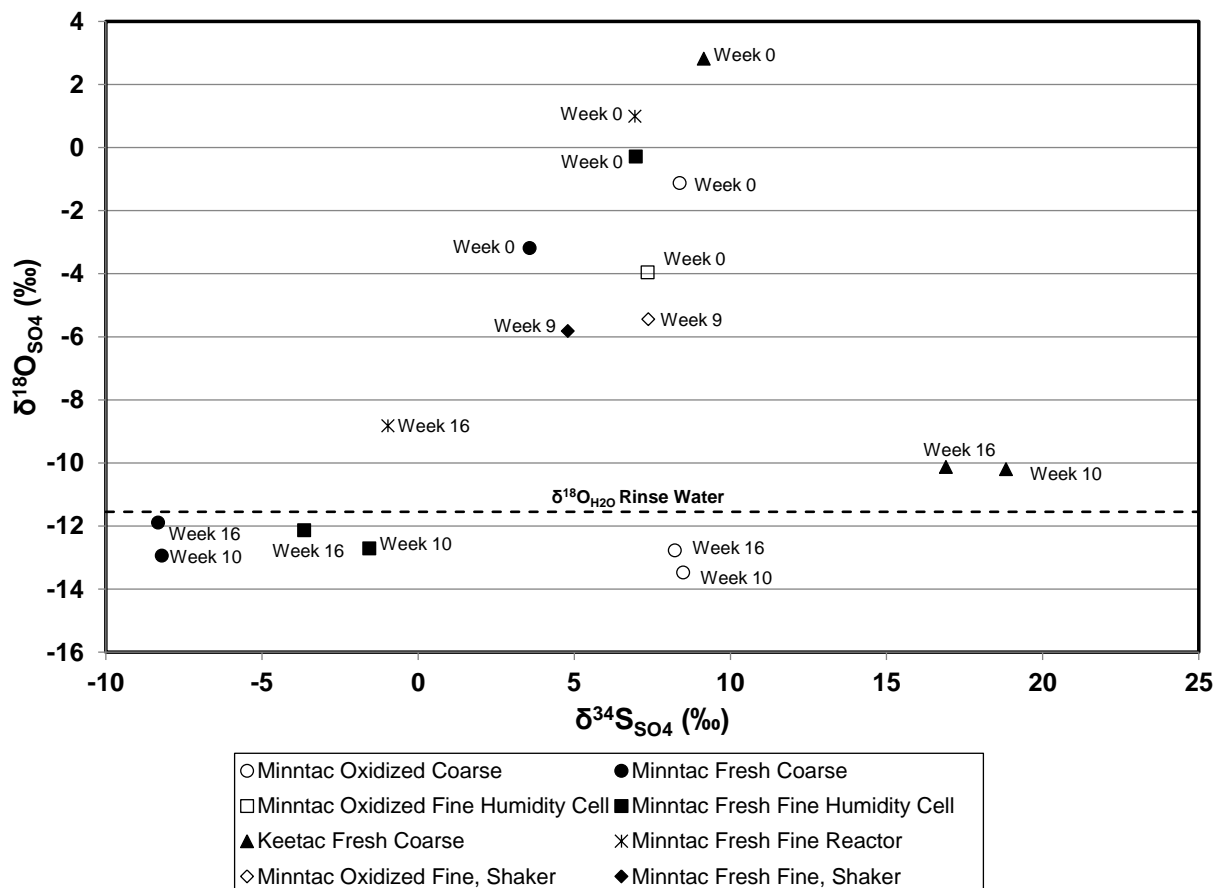


Figure 13. $\delta^{34}\text{S}_{\text{SO}_4}$ and $\delta^{18}\text{O}_{\text{SO}_4}$ values for the large humidity cells and the small reactors. When data was available for duplicate cells and reactors, the results were averaged between the duplicates. The dashed line shows the $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ of the DI water used to rinse the samples.

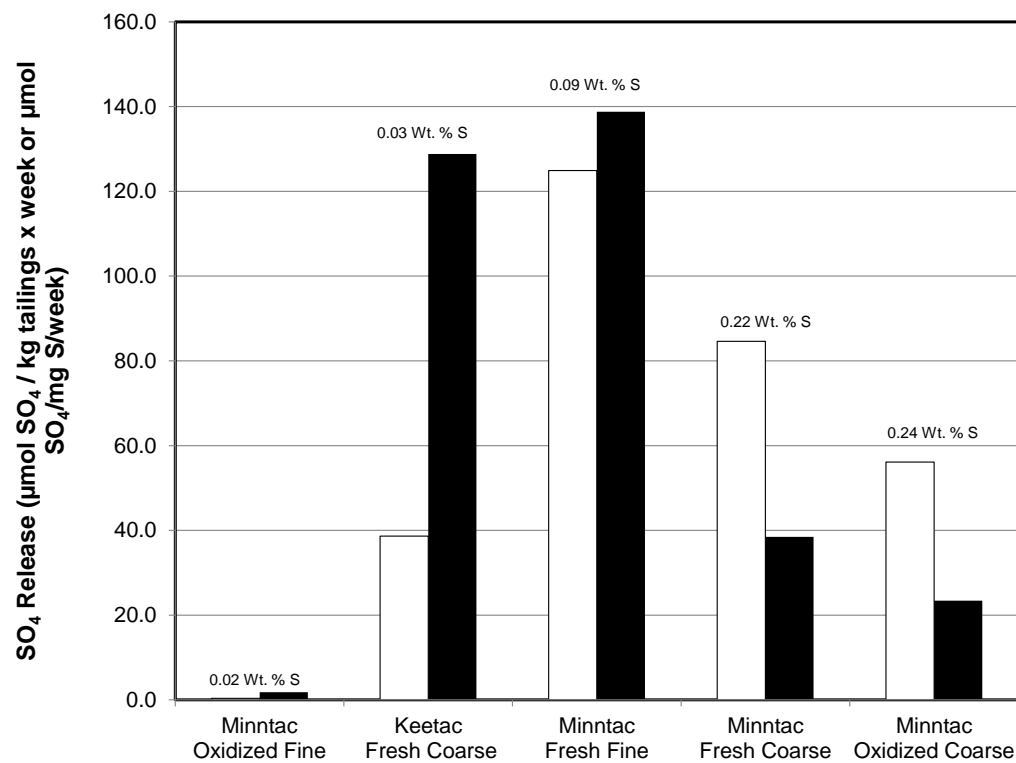
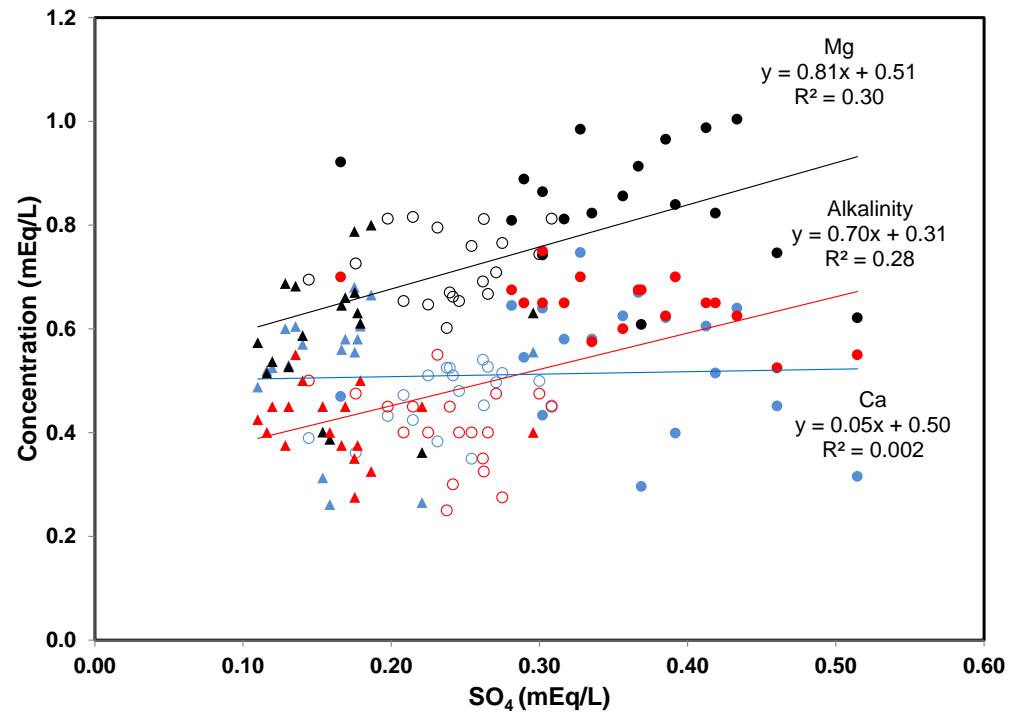
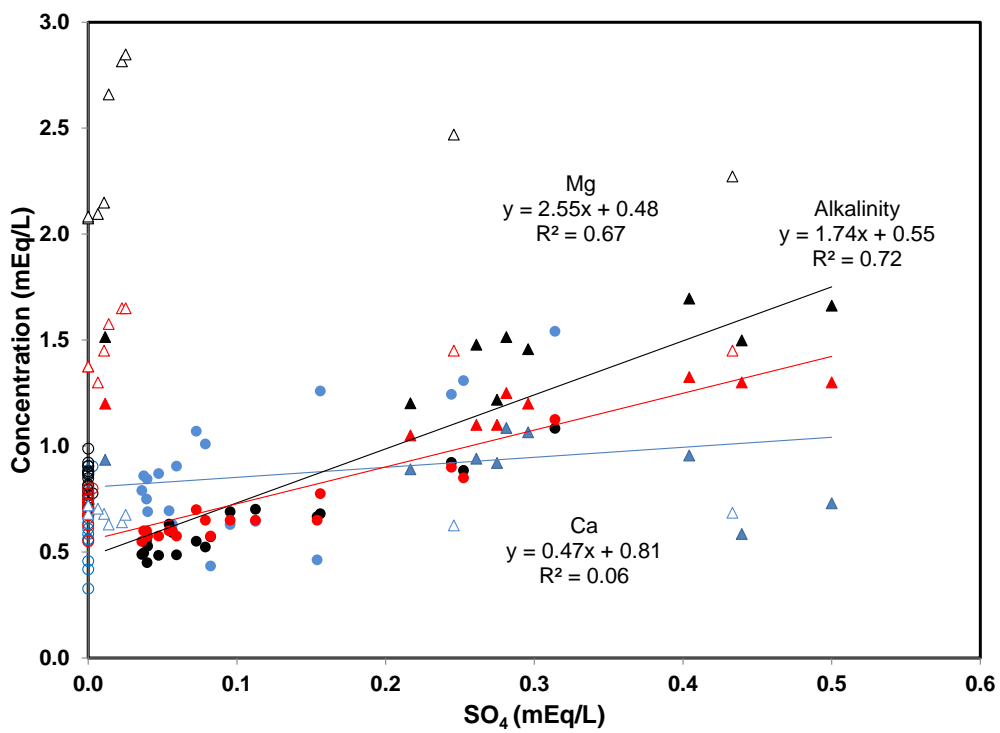


Figure 14. Average SO₄ release rates (white bars) or average SO₄ release rates normalized to wt. % S content (black bars) for Minntac and Keetac tailings. Both rates are represented on the y-axis. Average SO₄ release rates are short term rates, and are averaged across weekly measurements for a 10 to 12 week oxidation period. The average release rates for the fine tailings exclude the rates calculated for the fine tailings run in the large humidity cells.



Key	Ca	Mg	Alkalinity
Minntac Fresh Coarse	●	●	●
Minntac Oxidized Coarse	○	○	○
Keetac Fresh Coarse	▲	▲	▲

Figure 15. SO₄ vs. alkalinity, Mg, and Ca for the Minntac and Keetac coarse tailings.



Key	Ca	Mg	Alkalinity
Minntac Fresh Fine Small	●	●	●
Minntac Oxidized Fine Small	○	○	○
Minntac Fresh Fine Large	▲	▲	▲
Minntac Oxidized Fine Large	△	△	△

Figure 16. SO_4 vs. alkalinity, Mg, and Ca for the fine tailings samples in the small reactors and large humidity cells.