Duluth Complex Tailings Dissolution:
Ten-year laboratory experiment

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0. EXECUTIVE SUMMARY

Environmental review of proposed mining operations in Duluth Complex rock requires evaluation of potential impacts of tailings on water quality. Sulfide minerals present in such mine tailings can react with oxygen and water to release acid and heavy metals. This reaction is affected by the water content of the tailings and the depth within the tailings. Laboratory dissolution tests are typically conducted by mining companies to aid in predicting the water quality resulting from tailings dissolution. The effectiveness of predictions based on such tests is dependent on their design and the extrapolation of the laboratory results to field conditions. Both of these aspects require an understanding of reactions occurring in tailings basins and the variables that affect these reactions. The present study contributes to this understanding and provides an extensive dissolution test data set for comparison with, and to inform interpretation of, test results submitted for environmental review.

In the present project laboratory dissolution tests were conducted on tailings produced by pilot-plant processing of Duluth Complex rock from the Babbitt prospect (also known as AMAX or Mesaba prospect) of the Partridge River Intrusion. Reaction of these tailings affects water quality, and the effects of 1) tailings water content and 2) bed depth on reactions were examined. Of particular interest were reactions affecting pH and release of copper, nickel, cobalt, and zinc. The present report addresses the characterization of tailings (bulk density, particle size distribution, chemistry, mineralogy, static tests) and 10 years of laboratory dissolution testing. Dissolution tests were conducted on 75-g samples in unsaturated (uncovered) and saturated (covered) reactors (both in triplicate) and in duplicate 1000-g humidity cells.

Key dissolution tests results are as follows.

1. All test produced circumneutral drainage pH, with the minimum of all values near 6.4.
2. During the first three years of testing, sulfide oxidation in saturated (non-evaporating) reactors was more rapid than that in unsaturated (evaporating) reactors, apparently due to the greater water retention.
3. The aforementioned accelerated oxidation yielded slightly lower drainage pH values in the saturated reactors.
4. The slightly lower pH values resulted in nickel concentrations in saturated reactor drainage that were roughly 25 times those in drainage from the unsaturated reactors.
5. Sulfide mineral oxidation rates (normalized for tailings mass) for the humidity cells were limited by oxygen diffusion, resulting in drainage pH values higher and trace metal concentrations lower than those for the smaller reactors.

Thus, although similar Partridge River intrusion tailings are unlikely to produce acidic drainage, nickel release will increase with pH decreasing into the sixes. Results further indicated that such decreases are more likely in areas of the basin in which tailings are saturated (but not submerged). The data generated also provide a basis for evaluating the variation of oxidation reactions with tailings depth and 10 years of drainage quality data for comparison with, and to aid interpretation of, future results.

1. INTRODUCTION

Teck-Cominco Inc. (Vancouver, B.C. Canada) processed a bulk sample of Duluth Complex rock collected in April 2001 from approximately the center of Section 29, T60N, R12W. The company sent 280 kg of the tailings generated from their pilot plant test to the Minnesota Department of Natural Resources Division of Lands and Minerals (MN DNR) in the late summer of 2001. These tailings were characterized (bulk density, particle size distribution, chemistry, mineralogy) and subjected to dissolution tests that began 19 February 2002. This is the second progress report on the project, and it presents drainage quality data through 7 February 2012, a total of 520 weeks of dissolution testing. Previously a 2003 report addressed the first 30 weeks of the experiment, and a 2009 paper compared results from the three different test methods over a period of about four years (Lapakko et al. 2003, Lapakko and Berndt 2009).

2. OBJECTIVES

In general, the present project intends to investigate the quality of drainage that would be generated by tailings produced by processing of Duluth Complex rock for recovery of base metals. Of particular interest are the potentials for release of acid, copper, nickel, cobalt, and zinc. In addition, comparison of laboratory dissolution methods for prediction of mine waste drainage quality was of interest. More specifically, the objectives of the study are as follows.

1. Describe the temporal variation of drainage pH and concentrations of alkalinity, sulfate, calcium and magnesium.
2. Determine the rates of sulfate, calcium, magnesium, sodium, and potassium release from tailings.
3. Determine concentrations of copper, nickel, cobalt and zinc in laboratory drainage from tailings.
4. Compare results from saturated and unsaturated small reactors containing 75 g tailings.
5. Compare results from small reactors with those from humidity cells containing 1000 g tailings.

3. METHODS

3.1. Materials

A tailings sample of approximately 280 kg was received by the MN DNR. The tailing sample was from the processing of a bulk sample of mineralized gabbro taken in 2001 from the Babbitt (Mesaba) prospect of the Partridge River Intrusion (PRI) near Babbitt, MN (see Figure 1 for flow chart). Three randomly selected samples were taken and analyzed at Lerch Brothers Inc. (Hibbing, MN) for total sulfur and CO_2 to determine the variability in tailings composition.

Total sulfur contents of the triplicate samples were 0.20, 0.19, and 0.20 percent, and the corresponding values for CO_2 were 0.28, 0.23, and 0.29 percent. The results indicated the tailings were reasonably homogeneous, but the CO_2 measurements were suspect based on previous experience with Duluth Complex rock. (As indicated in Results, subsequent analyses yielded considerably lower values.)

From the original bulk sample, a subsample weighing approximately 30 kg was randomly selected for additional testing. The sample was spread out on a table lined with paper to air dry. After drying a metal rolling pin was used to crush the tailings that were clumped together. The sample was then split using the Four Corners method (Scott 1942). Approximately one half (15 kg) of the sample was removed. The sample was then split again using the Four Corners method. Again approximately one half (7 kg) of the sample was removed. These two samples were archived for possible future testing.

The remainder of the sample (8 kg) was split using a Jones Splitter containing 0.75-inch chutes. After passing the sample through the splitter 3 times, one half (4 kg) of the sample was removed and archived. The remainder of the sample was split into aliquots of approximately 0.25 kg. Four of these aliquots were randomly selected to make up two 1 kg humidity-cell charges. Six aliquots were split one additional time to make up six 75-gram reactor charges. The remaining sample for each of the eight aliquots was archived for future analyses.

Dry and wet bulk densities of the tailing were determined at the MN DNR laboratory in Hibbing, MN. The dry density was determined by weighing 200 cm^3 of tailings. The wet bulk density was determined by weighing the same sample of tailings after saturating the sample with deionized water.

3.2. Apparatus

Small Reactors (75 g charge): The samples were placed onto a 1.6-micron Whatman GF/A glass fiber filter (5.5 cm diameter) resting on a perforated plastic plate in the upper section of a two-stage filter unit or reactor (Figure 2). The internal diameter was 7.0 cm at the top of the unit and 5.7 cm at the bottom (the top of the perforated plate). On 15 February 2002 the reactors were filled. A plastic weighing boat was placed on a scale and 75 grams was weighed out and added to the top section of the small reactors. The bed depth and volume were approximately 1.7 cm and 47.5 cm^3, respectively.

Humidity Cells (1 kg charge): Cylindrical cells (I.D. = 10.2 cm, h = 19.0 cm) constructed of acrylic plastic were used in the experiment. A 0.64-cm high acrylic sleeve was glued into the bottom of the cell to support a 0.16-cm thick PVC plate, which was perforated with 0.32-cm holes spaced 0.48 cm on center. The plate was covered with a polypropylene filter (National Filter Media Corporation, Polymax B, Style 226-075-2) which supported the solids. The bottom was sealed with an acrylic plate with a 0.85-cm outlet port in the center and a removable cover, with a 0.85-cm vent hole, was place on top of the cell (Figure 3). Prior to filling, the cells were acid washed with 10% HNO_3 and then rinsed three times with deionized water. The cells were weighed and the weight was recorded on the cell.

On 15 February 2002 the cells were each filled with 1000 g tailings, which were added in increments of approximately 250 grams. A plastic pan was placed on a scale and four of the

250-gram splits were added. The weight was generally about 50 grams over the desired 1000-gram sample size. A plastic spoon was used to randomly remove the excess and add it to the remaining 250-gram split. The 1000-gram sample was then poured into the cell. The samples were very dry and some of the very fine dust-like particles were lost due to suction from the exhaust hood. The plastic pan and spoon were rinsed with deionized water after each reactor was filled. The cells with dry solids were weighed and the tare weight recorded. The tailings bed depth was approximately 7.5 cm.

3.3. Experimental Procedure

A total of six small reactors and two humidity cells were used (Table 1). The small reactors were used to allow direct correlation of data with those generated using these reactors to examine the dissolution of Duluth Complex rock samples. To examine the effects of moisture content on dissolution, three small reactors were covered and three were uncovered. Two covered and two uncovered reactors were used to analyze drainage quality at a fairly high frequency. The third reactor in each set was to be analyzed less frequently and was intended to provide leached tailings for analysis prior to termination of the other reactors. The duplicate humidity cells were intended to provide a comparison of the small reactors and the ASTM D5744-96 method that uses these cells and to investigate the effect of tailings bed depth on drainage quality.

The solids in all units were rinsed three times at week zero to remove oxidation products that accumulated from the time they were processed until the beginning of the experiment. Deionized water (200 mLs) was slowly dripped into the small reactor from a buret and was allowed to drain freely from the cell. The reactors were subsequently rinsed weekly with one 200 mL volume of deionized water. Reactors 1-3 remained uncovered, and covers were placed on reactors 4-6 immediately after the water addition to inhibit evaporation of pore fluid.

The rinsing procedure for the humidity cells was to place a rubber cap on the outlet port and add 500 mLs of deionized water to each cell. After the week zero rinse with three 500-mL volumes of deionized water, humidity cells samples were rinsed weekly with a single 500 mL volume. The water was slowly dripped into the cell, with the outlet capped, from a separatory funnel. Covers were placed onto the cells immediately after the water addition. The water remained in the cell for ten minutes after the last one was filled, and then the cells were uncapped and allowed to drain into a collection vessel.

Effluent (or drainage) samples were weighed and analyzed for pH and specific conductance at the MN DNR laboratory. From the remaining drainage, samples were collected and filtered for subsequent determinations of sulfate and metal concentrations. After filtration, samples to be analyzed for metals were preserved with 0.2 mLs Baker Instr-Analyzed nitric acid per 50 mL sample. Samples were rinsed three times at the initiation of the dissolution experiment (week 0). The first rinse and a volume-weighted composite of rinses two and three were analyzed for SO_4, Ca, Mg, Na, K, Cu, Ni, Co, and Zn at the Minnesota Department of Agriculture (MDA, St. Paul, MN). Data for the initial rinses in the drainage quality tables represent a volume weighted composite of rinse 1 and the composite results of rinses 2 and 3 (see Appendix 3, Tables A3.2, A3.3 for initial rinse data).

3.4. Reaction Conditions

Between rinses the samples were retained in the cells to oxidize. The cells were stored in a room (8.5 x 10.5 x 9.5 ft) in which temperature and humidity were controlled by commercially available equipment. Temperature was maintained by a thermostatically controlled heater

(Lakewood 750) and humidity was maintained by a Holmes HM 3500 humidifier and a Sears Kenmore dehumidifier, both of which were controlled by Honeywell humidistats. Over the 520-week period of record temperature and relative humidity were measured three to four times a week with a Taylor wet-bulb, dry-bulb hygrometer, and readings were used to determine average weekly values. Each apparatus sat in the laboratory for the first 24 hours after the rinse water was added each week, after which they were returned to the constant temperature room.

Water retention in the small reactors and large cells was determined by weighing. During the first seven weeks of the experiment the units were weighed four to five times a week (Appendix 2, Table A2.3). Subsequently, weights were determined immediately before and one day after rinsing.

3.5. Analyses

3.5.1. Solid Phase Analyses

Particle size distribution (Table 2) was determined by Lerch Brothers Inc. using method ASTM E 276-93 (ASTM 2000). Triplicate samples were analyzed for sulfur, sulfate (sulfide was determined by difference), and evolved carbon dioxide by ACTLABS in Tucson, AZ using ASTM E-1915-97 (ASTM 2000). A 10% hydrochloric acid solution was used to solubilize the carbonate minerals, and the carbonate present was quantified as the difference between total carbon in the initial sample and that in the residue. The remaining solid-phase constituents were determined by ACTLABS in Ancaster, ON (Tables 3 and 4). Whole rock constituents were determined using a lithium tetraborate fusion modified from ASTM E886-94 (ASTM 2000) and analysis by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) using a Thermo Jarrell-Ash ENVIRO II ICP. Concentrations of Ag, Cd, Cu, Ni, Pb, Zn, and Bi were determined using a total digestion modified from Crock et al. (1983), with analysis by ICP-AES. Other trace elements were determined using instrumental neutron activation analysis (Hoffman 1992).

Peter McSwiggen (McSwiggen & Associates, Minneapolis, MN) determined mineral content and chemistries. Tailings grains were mounted into a one-inch epoxy mount, which was then polished and carbon coated. One hundred twenty-three grains were randomly selected for analysis. Each grain was analyzed using a JEOL 8600 Electron Probe Microanalyzer (15 kV accelerating voltage, 20 namp beam current, 5 second dwell time, 5 μm beam diameter). Seven hundred sixty five tailings grains (nonsulfides) and seven sulfide mineral grains were also examined using the microprobe to estimate grain size distribution of these particles.

Paste pH and neutralization potential using the Sobek method (Sobek et al. 1978) were determined at the MN DNR lab on the three unleached tailings samples, and these samples were also analyzed by Lerch Brothers for sulfur and CO_2 (Appendix 2). For paste pH, 20 mLs of deionized water was added to 10 g of solids in a beaker. The slurry was stirred twice during the course of an hour. The pH of the slurry was then measured using an Orion model 720A meter with a Ross combination electrode (model 8165).

For NP determinations, modifications of the standard Sobek et al. (1978) procedure were used. A water bath was used in the digestion step rather than heating the sample with a flame. Three 2.0 g samples were weighed and placed into three 250 mL flasks. Based on a fizz rating of “none”, 20 mLs of 0.1N HCL was added to each flask. The flasks were placed into a hot water bath of 90-95 ^{o}C and heated until the reaction was nearly complete**,** indicated when no further gas evolution was visible and particles settled evenly over the bottom of the flask. Deionized water was added to make a total volume of 125 mLs and the contents were boiled for 1 minute. The contents were covered and cooled to room temperature and then titrated with 0.1N NaOH to the endpoints of pH 7.0 and pH 8.3.

3.5.2. Drainage Quality Analyses

Water samples were analyzed for specific conductance, pH, and alkalinity at the MN DNR laboratory. Specific conductance was analyzed using a Myron L conductivity meter, and an Orion SA720 meter, equipped with a Ross combination pH electrode (8165), was used for pH analyses. Alkalinity (for pH $\geq$ 6.3) and acidity were determined using standard titration techniques for endpoints of 4.5 and 8.3, respectively (APHA et al. 1992). The remaining sample was filtered for metals and sulfate analyses.

Metals and sulfate samples were analyzed at MDA. Ca, Mg, Na, and K were determined with a Varian 400 SPECTRAA; inductively coupled plasma mass spectrometry (ICP-MS, Hewlett Packard HP4500 Series, model #G1820A) was used for the remaining metals analyses. Sulfate concentrations were determined using a Lachat QuickChem 8000 or, for $[SO_4] < 5$ mg/L, a Dionex ion chromatograph.

3.6. Calculations

Weekly chemical mass release for each solute was calculated as the product of drainage volume and solute concentration. Cumulative release was calculated as the sum of weekly release values. For weeks that solute concentrations were not determined, the concentration was estimated as the average of previous and subsequent measured values.

Rates of solute release were calculated for every week drainage quality samples were analyzed for a specified solute. For each solute, the weekly rate of release was calculated as the product of the volume and solute concentration divided by the rock mass originally present. The weekly release rates were averaged over annual (52 week) periods. Standard deviations were calculated to provide a measure of rate variability during the periods. Annual average sulfate release per grams of sulfur remaining was calculated by dividing the weekly sulfate release by the calculated grams of sulfur for each reactor and humidity cell. The grams of sulfur remaining were calculated using the cumulative sulfate concentration (converted to grams of sulfur) and subtracted from the initial sulfur present based on solid-phase analysis.

4. RESULTS

4.1. Introduction

Tailings generated by processing of anorthositic gabbro bulk sample (Duluth Complex, Partridge River intrusion, Babbitt prospect) were characterized and subjected to dissolution testing in the laboratory. Characterization consisted of density determinations, particle size analysis, bulk chemistry, mineral content and chemistry, acid base accounting, and paste pH. Laboratory dissolution tests were conducted on the tailings under each of three conditions: triplicate unsaturated (uncovered) reactors containing 75 g of tailings, triplicate saturated (covered) reactors containing 75 g tailings (Figure 2), and duplicate 1000 g tailings in a covered humidity cell (Figure 3). Drainages from the third 75-g unsaturated reactor and third saturated reactor were analyzed less frequently than those from the other reactors. They will be used for analysis of leached solids prior to termination of the first two reactors in each set (Table 1). Dissolution tests are discussed in terms of temporal variation of drainage quality (pH, alkalinity, SO_4, Ca, Mg, Na, K, Cu, Ni, Co, Zn), rates of solute release, and total solute release. The period of record presented in this report is 520 weeks, but replicated units for all three dissolution conditions remain in progress.

4.2. Solid-Phase Analyses

The dry and wet bulk densities of the tailings were 1.65 and 2.04 g/cm^3, respectively (Appendix 2, Attachment A2.1). Water content at saturation was determined to be 0.24 g water/g tailings. Based on the water content at saturation and associated tailings volume (80 and 200 cm^3), the tailings porosity was calculated as 40 percent. Sieve analysis of the tailings indicated approximately 80 % were finer than 100 mesh, 29 % finer than 270 mesh, and 16 % finer than 500 mesh (Table 2).

Analysis of images generated by electron microprobe was also used to describe particle size distribution. Mineral grain cross-sectional area was used as a surrogate for mass and calculated circular diameter ($d_{circ} = (4A/\pi)^{0.5}$) was used for particle diameter. Results using this approach agreed well with the sieve analysis for the larger fractions, yielding 84 % finer than 100 mesh, 28 % finer than 270 mesh (Appendix 1, Attachment A1.4). The mass in the -500 mesh fraction was only 7.5 %, or about half the value determined by sieving.

The tailings contained 0.2% sulfur, at least 90% of which was present as sulfide (Table 3). The carbon dioxide content was less than 0.05%, indicating an NP(CO_2) less than 1.1 g $CaCO_3$ equivalent (kg tailing)$^{-1}$. The major whole rock components were SiO_2 (47.5%), Al_2O_3 (15.6%), and Fe_2O_3 (15.2%). Calcium and magnesium contents as oxides were 7.8% and 7.0% (Table 3). Copper, nickel, cobalt and zinc contents were determined as 510, 360, 59 and 120 ppm (Table 4).

The mineral contents and chemistries were 57% labradorite ($Ca_{0.57}Na_{0.43}Si_{2.42}O_8$), 11% augite ($Ca_{0.83}Mg_{0.77}Fe_{0.35}Si_{1.92}O_{6.00}$), 9.8% olivine ($Mg_{1.10}Fe_{0.89}Si_{0.99}O_{4.00}$), 9.8% quartz (anomalous, apparently contamination), and 5.7% biotite ($K_{1.78}(Mg_{3.27}Fe_{1.79})(Al_{2.39}Si_{5.55}O_{17})(OH)_{1.72}$). Ilmenite, potassium feldspar, and orthopyroxene were also reported present at near 1% (Appendix 1, Attachment A1.3).

Chalcopyrite (approximately $CuFeS_2$) was the only sulfide mineral detected during the microprobe analysis. The chemical analyses (assuming 0.2 %S^{2-}) in conjunction with the chalcopyrite chemistry indicated that the sulfur content associated with chalcopyrite was roughly 0.05%. The NiO content of the olivine was 0.15 % which, considering the bulk nickel content of 360 ppm and olivine content of 9.8 %, implies that the nickel content associated with sulfur was 239 ppm. This yields an estimated sulfur content associated with pentlandite of 0.02 %. It is assumed that the remaining 0.13 %S (0.2 %S_{bulk} – 0.05 %S($CuFeS_2$) – 0.02 %S (($Fe_{4.5}Ni_{4.5})S_8$) = 0.13% S) is largely associated with pyrrhotite. Microprobe analysis indicated that 87 % of the sulfide minerals were liberated and, therefore, readily available for oxidation.

The 0.2 %S content indicated an acid production potential (AP) of 6.2 g $CaCO_3$ equivalent (kg tailing)$^{-1}$, assuming all sulfur were associated with iron. Accounting for the sulfur associated with copper and nickel yields 0.16 %S associated with iron and a refined AP of 5.0 g $CaCO_3$ equivalent (kg tailing)$^{-1}$, Neutralization potentials (Sobek et al. 1978) determined in triplicate averaged 19 g $CaCO_3$ equivalent (kg tailing)$^{-1}$. Using a backtitration endpoint of 8.3 for two of the three samples (rather than the 7.0 endpoint used in the technique of Sobek et al. 1978) yielded an average NP of 14 g $CaCO_3$ equivalent (kg tailing)$^{-1}$ for duplicate samples (Appendix

2, Table A1.4). These values were considerably higher than the NP(CO_2) of less than 1.1 g $CaCO_3$ equivalent (kg tailing)$^{-1}$. The paste pH of the tailings was 8.29.

4.3. Reaction Conditions

4.3.1. Temperature and Relative Humidity

Over the 520-week period of record, average weekly temperature ranged from 20.3 to 27.9 ^{o}C. Temperature averaged 23.7 ^{o}C with a standard deviation of 1.4 ^{o}C. Relative humidity ranged from 42 % to 75 %, averaging 58 % with a standard deviation of 4.3 % (Appendix 2, Table A2.2).

4.3.2. Water Retention

Water retention was determined the morning after the reactors were rinsed, roughly a 24-hour period. Retention in the duplicate unsaturated reactors was initially in close agreement, but values began to diverge after about three years. The discrepancy decreased through year 8, when the volume retained in reactor 1 was consistently about 5 mL less than that in reactor 2 (Appendix 2, Figure A2.1). Subsequently replication improved markedly, and for the period of record water retention in Reactors 1 and 2 averaged 14.5 and 16.8 mL, respectively. The reasons for these variations are not understood. In contrast, replication was consistently good for the duplicated saturated reactors and humidity cells (Appendix 2, Figures A2.2, A2.3).

Retention in all reactors during the initial 40 weeks typically ranged from 20-25 mL, somewhat higher than the 18 mL inferred by the saturated moisture content determination (see previous section). Subsequently retention in the unsaturated reactors declined to a typical range of 10-15 mL after week 300. Retention in the saturated reactors declined to a lesser degree, with values after week 400 reporting in the typical range of 18 to 25 mL. For the entire period of record retention in the unsaturated reactors was about 7 mL less than that in the three saturated reactors (Appendix 2, Table A2.5). The lower retention in the unsaturated reactors was the result of evaporation between the rinse and measurement of water retention approximately 24 hours later; the covers on the remaining reactors effectively inhibited evaporation during this period (and throughout the weekly cycle). Water retention in the unsaturated reactors varied seasonally, with values tending to be greater during summer months, when less evaporation would be expected due to humid conditions in the laboratory (section 3.4). Retention in all reactors tended to decrease slightly over the period of record (Appendix 2, Figures A2.1, A2.2).

Water retention in the duplicate humidity cells was highly reproducible (Appendix 2, Table A2.5, Figure A2.3). The average retention in the duplicate cells over the period of record was 240.1 and 243.3 mL, in excellent agreement with the 24 % saturated moisture content (section 4.2). The measured retention was about 20 % lower than the average retention per unit mass in the smaller saturated cells. The average evaporation during the weekly cycle was about 5.5 mL for the larger cells, slightly higher than that for the saturated reactors (Appendix 2, Table A2.5).

4.3.3. Leachate Volume

The drainage volume from the duplicate unsaturated reactors reflected, at least qualitatively, differences in moisture retention. Replication was initially very good but, over time, volumes from Reactor 2 tended to be slightly lower than those from Reactor 1 (Appendix 2, Figure A2.4). The difference averaged about 3.4 mL over the period of record (Appendix 2, Table A2.7). The unsaturated reactors, R1 and R2, averaged 169.3±2.87 mL and 165.9±3.76 mL respectively. The saturated reactors, R4 and R5, averaged 191.0±4.08 mL and 186.8±7.77 mL respectively (Appendix 2, Figures A2.5, A2.6).

4.4. Drainage Quality and Solute Release

4.4.1. 75-g Reactors

Drainage quality for both unsaturated and saturated reactors replicated reasonably well (Figures 4-5, Tables 5-6), but some discrepancies were apparent. For the unsaturated reactors, reactor 1 sulfate concentrations tended to be lower than those from reactor 2 in year 1 and this ordering was reversed in year 2. Subsequently agreement was good (Figures 4 and 5). Concentrations of calcium, magnesium, and sodium from reactor 1 tended to be lower than those from reactor 2 after year 1. The net effect of these differences led to 5th percentile annual pH values from Reactor 1 that tended to be 0.05 to 0.1 units lower than those from Reactor 2. Similar differences were observed for the saturated reactors (Figures 4 and 5).

The initial rinse at week zero was consisted of three 200-mL additions of deionized water as opposed to the single 200 mL volume in subsequent weeks. The initial rinse typically contained the highest concentrations of solutes. This reflected the removal of reaction products accumulated between the time of sample collection and the beginning of the experiment. Subsequent rinses reflected reaction products generated during the previous week.

Drainage pH from the reactors was initially near 7.9 and reached minimums in the range of 6.4 to 6.6. Drainage pH from the saturated reactors reached the minimum range between weeks 50 to 150, as opposed to weeks 400 and 450 for the unsaturated reactors (Figure 6). Alkalinity concentrations from all reactors were initially elevated, with concentrations as high as 25 – 30 mg/L as $CaCO_3$ in the first weeks. The saturated reactors yielded higher concentrations in the initial weeks and declined to levels below detection (5 mg/L as $CaCO_3$) after 40 weeks. The decline for the unsaturated reactors was slightly slower, reaching the detection limit after 48 weeks (Figure 6, Appendix 3, Tables A3.4 – A3.9).

Sulfate concentrations decreased rapidly initially and tended to plateau or decrease slightly after year 6 (Figure 7). Concentrations from the unsaturated reactors were higher than those from the saturated reactors during the first 10 weeks. However, sulfate release from the unsaturated reactors decreased more rapidly, yielding second year sulfate release rates that were roughly 20 to 35 percent of first year rates as opposed to a corresponding range of roughly 50 to 70 percent for the saturated reactors (Figure 7). Sulfate release rates for all reactors after year 6 were around five percent of those in year 1 (Table 5). The fraction of solid-phase sulfur depleted during the 10-year period was roughly 46 % for the unsaturated reactors and 66 % for the saturated reactors (Table 8). In all reactors about two-thirds of the sulfur depletion occurred during the first two years.

Molar concentrations of major cations initially decreased in the order Ca > Mg > K > Na and the ordering subsequently evolved to Mg > Ca > Na > K. Concentrations of calcium and potassium tended to parallel those of sulfate (Figure 7; Appendix 3, Tables A3.4 - A3.9). Calcium and potassium release rates in year 10 were, respectively, roughly 5 and 10 % of those in year 1 (Table 5). In contrast, magnesium and sodium concentrations were less variable over the period of record (Figure 7), with release rates at year 10 averaging 18 and 60%, respectively, of year 1 rates (Table 5). Total molar release of calcium was the highest, measuring about 1.15 times that of magnesium and roughly 2.5 times that of sodium and potassium. Total release of sodium was around 1.1 times that of potassium (Table 7).

It should be noted that unsaturated reactors 1 and 2 displayed unusual behavior with respect to potassium release (Figure 7). Potassium concentrations decreased to the detection limit (0.1 mg/L) by week 140 and remained below the detection limit through week 250, at which point concentrations increased to approximately 0.4 mg/L. Concentration decreased to 0.2 mg/L by Year 10, but always remained above the detection limit. A subset of the samples after week 250 was sent back to Minnesota Department of Agriculture (MDA) for re-analyses, and the initial results were confirmed.

Further examination of the drainage quality revealed that the Mg/K ratio for the unsaturated reactors was approximately 2 after week 250, and this approximates the corresponding stoichiometric ratio for biotite present in the tailings (Mg/K = 3.27/1.78 = 1.84, Appendix 1, Attachment A1.3). Based on this analysis, it appeared that the potassium concentrations determined at MDA was erroneous for weeks 100-250. A subset of these samples was sent to Pace Analytical laboratory and they confirmed potassium concentrations below the detection limit (0.2 mg/L).

It should be noted that this behavior in potassium was isolated to these two unsaturated reactors in this experiment and did not occur in any other experimental results conducted in the MNDNR Hibbing laboratory during this time frame. This, in conjunction with the confirmatory analyses described above, suggests that the anomalous behavior of potassium could not be readily attributed to analytical error or experimental methods. Furthermore, there is no obvious geochemical explanation for the relatively sudden decrease in potassium concentrations to levels below detection with a subsequent increase to previous levels (Appendix 3, Figures A3.17-18). Perhaps the wet-dry cycling (variation from saturation to essentially dry on a weekly basis) in these reactors physically affected biotite present in the samples and, consequently, potassium release in some unusual fashion. However, the authors are presently unaware of any publications on biotite dissolution that might suggest such a possibility.

Nickel contributed the majority of trace metal release, followed by zinc. Cobalt concentrations from all reactors and copper concentrations from the saturated reactors were typically near or below detection limits (Figure 8). Trace metal release tended to increase with the subtle decreases in drainage pH. As mentioned above, periods of relatively low pH occurred from the saturated reactors during years 2 and 3 and from the unsaturated reactors during years 8-10. Although the extent of pH depression was not large, with minimum values near 6.5, trace metal concentrations generally responded to these subtle changes.

Nickel and other heavy metal concentrations increased substantially over relatively small pH changes. From year 1 to year 2, drainage pH from the saturated reactors decreased from about 7 to 6.6, and, consequently, the rate of nickel release from the saturated reactors in year 2 was about eight times that in year 1 (Figure 9, Table 6). Nickel release rates from the saturated reactors averaged 20 and 6 times those from the unsaturated reactors in years 2 and 3, respectively, in response to pH differences of roughly 0.1 to 0.5 units (Figure 9, Table 6). Nickel release from the saturated reactors decreased to levels typically near or below detection after year 4. Cobalt concentrations from the saturated reactors paralleled these trends (Figure 10) and were only above detection during the period of pH depression. Drainage pH from the unsaturated reactors decreased from 7.1 to 6.7 after year 6, and nickel release rates increased correspondingly. Zinc release responded to the pH declined for the saturated reactors at year 2 and for the unsaturated reactors after year 6 (Table 6).

Copper concentrations from the saturated reactors were typically near or below detection limits. Copper release rates from the unsaturated reactors during years 8-10, when drainage pH from these reactors was lowest, tended to be higher than the corresponding average rates (Table 6). Total release of copper was less than 0.5 % of that present initially and, correspondingly, zinc was less than 4 %. The fractions of nickel and cobalt depletion were intermediate to these values (Table 7).

4.4.2. 1000-g Humidity Cells

Drainage quality from the duplicate 1000 g humidity cells was in good agreement (Figure 11; Appendix 3, Tables A3.10-A3.11). Drainage pH was initially near 8, slowly decreased below 7 near week 200 and then, with the exceptions of occasional excursions into the lower sevens, typically ranged between 6.8 and 7 (Figure 6). These values were generally 0.1 to 0.3 units higher than those observed from the small reactors. Similarly, alkalinities from the humidity cells were higher than those from reactors. Concentrations were 50 mg/L as $CaCO_3$ at week 1 and declined over time, falling below 20 mg/L as $CaCO_3$ at week 40, below 10 mg/L as $CaCO_3$ at week 115, and typically below detection (5 mg/L as $CaCO_3$) after week 240 (Figure 6; Appendix 3, Tables A3.10-A3.11).

The initial rinses contained the highest concentrations of solutes. Sulfate concentrations ranged from 20 – 40 mg/L through week 5, decreased below 20 mg/L at week 40, and stabilized near 10 mg/L after week 100 (Figure 11). Although sulfate release decreased over time, the extent was mild relative to that for the reactors. The sulfate release rate in year 1 was about 115 μmol•(kg rock•wk)$^{-1}$ in year 1, decreased through year 4, and then stabilized near 50 μmol•(kg rock•wk)$^{-1}$ (Table 5). Total release during the 10-year period represented about 53 % of that originally present. After year 3 the depletion was relatively constant, annually averaging about 4.2 % of that originally present (Table 8).

Major cation molar release rates from all units, reflecting rates of acid neutralization, initially decreased in the order Ca > Mg > K > Na and subsequently evolved to Mg > Ca > K > Na. Major cation concentrations followed two distinct temporal trends. Calcium and potassium concentrations followed a trend similar to that of sulfate concentrations, with markedly elevated values during the initial weeks, declining exponentially, and then becoming relatively stable (Figure 12). The dissolution time prior to stabilization, however, was considerably longer than that for sulfate concentrations, on the order of 250 to 300 weeks (Figure 12). Year 10 release rates for calcium and potassium were roughly 10 and 20 percent of the respective year 1 rates (Table 5). The calcium and potassium releases observed represented about 2 and 4 %, respectively, of the amounts originally present in the tailings.

Releases of magnesium and sodium were more stable over time than those of sulfate, calcium, and potassium. Magnesium concentrations were slightly elevated initially, decreased through roughly week 60, and then increased through about week 400 and plateaued (Figure 12). Sodium concentrations were slightly elevated initially, then declined and stabilized near 0.3 mg/L after about 40 weeks of dissolution. For both solutes, release rates in year 10 were near 70 % of those in year 1.

Of the trace metals, nickel release was typically the highest. The magnitudes of copper, cobalt and zinc release did not vary greatly. Nickel concentrations at week 1 were near 0.05 mg/L, and then remained around 0.01 mg/L through week 30. Concentrations were near or below the detection limit from about week 60 through 200. Concentrations tended to increase slowly at this time, coincident with pH declining below 7, reaching values in the approximate range of 0.006 to 0.008 mg/L after about week 350. Zinc concentrations were typically below detection but displayed occasional excursions as high as 0.007 mg/L. However, even the occasional excursions yield values typically below 0.004 mg/L (Figure 13). Copper concentrations were 0.006 – 0.009 mg/L at week 0 then decreased and remained below detection after week 6. Cobalt concentrations were typically below detection throughout the test. Release rates and total metal release generally reflected these trends, although it should be noted calculations were affected by concentrations reported below detection (Table 6).

5. DISCUSSION

5.1. Introduction

This section presents a brief description of the mineral dissolution reactions that occur during chemical weathering of Duluth Complex tailings. This summary is intended to provide a conceptual structure to frame the discussion of results. It should be noted that detailed analysis of mineral dissolution reactions, such as calculation of mineral dissolution rates, is beyond the scope of this report.

Duluth Complex tailings were characterized (bulk density, particle size distribution, chemistry, mineralogy, static tests) and subjected to laboratory dissolution testing. Although the dissolution tests remain in progress, the following discussion presents the first 10 years of data. The dissolution tests conducted to examine the influence of moisture content and tailings depth on reactions rather than to simulate field drainage quality. Laboratory dissolution tests were conducted on 75-g samples in unsaturated and saturated reactors (both in triplicate) and in duplicate 1000-g humidity cells. Measurements of bed volume and water retention after the rinse were consistent with respective determinations of tailings density and saturated water content.

The three reaction conditions produced two general similarities in drainage quality. First, drainage pH from all tests initially ranged from 7.8 to 8 and declined for 100 (saturated reactors) to 400 weeks, reaching minimums of 6.4 to 6.6. Second, solute concentrations were highest at the beginning of the experiment and tended to decline and plateau over time. Concentrations of sulfate, calcium, and magnesium from the thin beds (~1.5 cm deep) generally decreased and plateaued after about six to eight years of dissolution. Similar behavior was observed in the deeper beds (~ 7.5 cm deep) after five to six years of dissolution.

Repeatability for all replicates was good for the period of record but was variable over time. Replication was generally better for saturated reactors and humidity cells than for the unsaturated reactors. Drainage pH values for all replicate pairs were virtually always within 0.1 units. Although discrepancies in concentrations were observed over time, the difference from the mean total mass release of sulfate, calcium, magnesium, sodium, and potassium for duplicates was less than four percent in 80 % of the cases (Table 7). The three instances in which the percent difference from the mean exceeded four percent were for magnesium, sodium, and potassium mass release from the unsaturated reactors (6.2, 6.0, and 14 %, respectively).

The unsaturated and saturated reactors provided respective reaction environments in which pore water evaporated and remained near saturation. This allowed assessment of the effects of moisture content on geochemical reactions. The tailings in the humidity cells also remained near saturation, and comparison with the saturated reactors allowed assessment of the influence of bed depth on reactions. In addition to differences in reaction environment, the solid-phase characterization aided interpretation of drainage quality data and solute release rates.

5.2. Solid-Phase Characteristics

Approximately 80 percent of the tailings mass was finer than 100 mesh, 29 percent finer than 270 mesh, and 16 percent finer than 500 mesh. Analysis of electron microprobe images yielded similar results for the -100 and -270 mesh fractions. However, the -270 fraction was approximately partitioned as 20 % coarser than 500 mesh and 8 % finer than 500 mesh. Thus, the sieving yielded a larger percentage in the finest fraction. This is somewhat puzzling because it seems that sieving would be more likely to under represent the fines due to adherence of these particles to coarser grains. Nonetheless, it is noteworthy that the agreement between the sieving and image analysis for the -100 and -270 mesh fractions was quite good.

The tailings contained 0.2% sulfur, at least 90% of which was present as sulfide, and less than 0.05% carbon dioxide. Assuming all sulfur is present as iron sulfide yields an acid potential (AP) of 6.2 g $CaCO_3$ equivalent (kg tailing)$^{-1}$. Accounting for the sulfur associated with copper and nickel (see below) yields 0.16 %S associated with iron and a refined AP of 5.0 g $CaCO_3$ equivalent (kg tailing)$^{-1}$. The CO_2 content of the sample (<0.05 %) implies a maximum neutralization potential of 1.1 g $CaCO_3$ equivalent (kg tailing)$^{-1}$, assuming all CO_2 is associated with calcium or magnesium. This is considerably lower than the 19 and 14 g $CaCO_3$ equivalent (kg tailing)$^{-1}$ neutralization potential determined using variants of the method of Sobek et al. (1978). This suggests that silicate mineral dissolution contributed to the latter determinations.

Dissolution of the silicate mineral present plagioclase (57 wt. %) and lesser amounts of augite and olivine (both ~10 wt. %)) can neutralize acid after (and before) the trace amounts of carbonate minerals are depleted. The silicate mineral neutralization potential is kinetically limited and will not be effective in maintaining pH 6 drainage if the rate of acid production is too high (White et al. 1999, Lapakko 1994). The fine particle size of the tailings suggests that the minerals present largely occur as individual grains and are, therefore, exposed and available for reaction. That is, the fraction of minerals included within other minerals or interstitial to other minerals is small. This was generally supported by electron microprobe images, although multimineralic aggregates of very fine particles were observed (Appendix 1, Attachment A1.5). Although these aggregates were assumed to be artifacts of sample preparation, such aggregation might also occur under natural conditions.

Copper, nickel, cobalt and zinc contents were determined as 510, 360, 59 and 120 ppm. The chemical analyses (assuming 0.2 %S^{2-}) in conjunction with the chalcopyrite chemistry indicated that the sulfur content associated with chalcopyrite was roughly 0.05%. The NiO content of the olivine was 0.15 % which, considering the bulk nickel content of 360 ppm and olivine content of 9.8 %, implies that the nickel content associated with sulfur was 239 ppm. This yields an estimated sulfur content associated with pentlandite of 0.02 %. It is assumed that the remaining 0.13 %S (0.2 %S_{bulk} – 0.05 %S as ($CuFeS_2$) – 0.02 %S as (($Fe_{4.5}Ni_{4.5})S_8$) = 0.13% S) is largely associated with pyrrhotite. Microprobe analysis indicated that 87 % of the sulfide minerals were liberated and, therefore, readily available for oxidation. This estimate, however, was based on a

median sulfide mineral diameter of 53 μm determined by examination of seven sulfide grains. In contrast, the median silicate mineral diameter of 83 μm included examination of 765 grains.
The mass of tailings calculated based on bed dimensions in the reactors and humidity cells were in excellent agreement with the measured mass. The tailings mass calculated for the reactors was within four percent of the measured mass. The corresponding value for the humidity cells was less than one percent (Appendix 2, Attachment A2.2).

5.3. Effect of Moisture Retention on pH

The water retention anticipated based on moisture content measurements was somewhat lower than that in the reactors about 24 hours after rinsing but in good agreement with that correspondingly retained in the humidity cells. Subsequently, all but about 2 mL of pore water in the unsaturated reactors evaporated in three days, and essentially all pore water had evaporated by four days after rinsing. The average rate of drying in the unsaturated reactors between the three weekly weights performed was 6.2±2.3 mL (Appendix 2, Table A2.4). In contrast, water retained in the saturated reactors and humidity cells declined only slightly during the one-week cycle.

The effect of moisture content on reactions was assessed based on comparison of unsaturated and saturated reactors. It is assumed that the entire tailings mass present in the thin beds (~1.7 cm deep) was subjected to oxidizing conditions. That is, oxygen diffusion did not limit oxidation rates. Sulfate release from these reactors decreased over time, due largely to the depletion of sulfide minerals by oxidation.

Minimum pH values from thin beds in the reactors were in the neighborhood of 6.4-6.5. Drainage pH from the saturated reactors reached the minimum range between weeks 50 to 150, as opposed to weeks 400 and 450 for the unsaturated reactors. The more rapid pH decline for the saturated reactors is attributed to sulfate release rates during the first three years that were about 1.6 times those from the unsaturated reactors. Apparently the greater water retention in these units (section 4.3.2) was more conducive to sulfide oxidation.

The rate of acid production (as indicated by sulfate release) was higher under water-saturated conditions (covered reactors) than in an environment in which pore water was allowed to evaporate (uncovered reactors). The ratio of average annual rates from the saturated reactors to corresponding rates from the unsaturated reactors reached a maximum of 2.7 in year two and declined to 1.1 for years seven and eight (Table 5; Appendix 4, Figure A4.9). In subsequent years the sulfate release rates for the saturated reactors was roughly 80 to 90 % of that from the unsaturated reactors. However, it should be noted that the sulfur content of rock in the saturated reactors was less than two-thirds that in the unsaturated reactors, due to the more rapid oxidation during years one through eight (Table 8). Thus, normalizing based on mass sulfur present would yield higher rates for the saturated reactors in the final two years (Figure 14).

Lapakko and Berndt (2009) discussed the faster pyrrhotite oxidation under saturated conditions based on the initial 202 weeks of dissolution. During this period oxidation rates under saturated conditions averaged 1.7 times those under unsaturated condition. They recognized that the data did not allow confident presentation of a mechanistic foundation for the difference, but they did present a plausible explanation based on previous studies of pyrite oxidation. The following paragraphs are excerpted from Lapakko and Berndt (2009).

> The pore water in the uncovered reactors evaporated over roughly 3.5 days and the covered reactors were near field saturation throughout the weekly oxidation cycle. The difference in sulfate release rates observed might be due to different mechanisms of pyrrhotite oxidation under conditions close to field saturation and in humid air. Lapakko and Antonson (2006) reported oxidation rates for pyrite in waste rock at near field saturation (with respect to water) were consistent with those presented by Williamson and Rimstidt (1994). However, rates presented by Jerz and Rimstidt (2004) appear more appropriate for reaction under the drier conditions observed in the uncovered reactors.
>
> Recognizing that the mechanism of pyrrhotite oxidation might differ from that of pyrite, pyrite oxidation rates under the two test conditions were calculated to provide a comparison with observed sulfate release rates. For the uncovered reactors, conditions close to saturation were assumed for 3.5 days of the weekly cycle and sulfate release for this period was calculated using data from Williamson and Rimstidt (1994). Dry conditions (in moist air) were assumed for the remainder of the week and sulfate release was calculated using data from Jerz and Rimstidt (2004). The sulfate release calculated using Williamson and Rimstidt (1994) rates for the entire week was 1.7 times that using the Williamson and Rimstidt (1994) rates for 3.5 days and rates from Jerz and Rimstidt (2004) for 3.5 days. Thus, the ratio of uncovered: covered rates agrees well with this ratio. It is also possible, however, that rates were affected by differences in the activity of neutrophilic bacteria such as *Thiobacillus thioparus* (Gould and Kapoor, 2003). However, bacterial populations were not determined.

It is also interesting to note that sulfate release from the unsaturated reactors generally exceeded that from the saturated reactors during the first 10 weeks of dissolution (Figure 15). Subsequently, sulfate release rates (normalized for tailings mass) from the saturated reactors was greater through at least year 8 (Table 5; Appendix 4, Figure A4.9). It is conceivable that a ferric oxyhydroxide coating developed more rapidly on pyrrhotite in the unsaturated reaction environment. The lesser amount of water available for transporting reaction products from the mineral surface might accelerate this development. Analysis of sulfide coatings for leached samples from the two reaction environments will lend insight into this possibility.

The potential effect of drainage pH on sulfide mineral oxidation and the resultant sulfate release rate must be considered. For example, drainage pH from the saturated reactors was markedly lower than that from the unsaturated reactors during years two through five (Figure 6). It is conceivable that the lower pH during this period enhanced biological mediation of sulfide mineral oxidation. In particular the largest difference in drainage pH between unsaturated (unsaturated tailings) and saturated reactors (saturated tailings) occurred during year two (Figure 6). This is also the time when the ratio of sulfate release rate from the saturated tailings to that of the unsaturated tailings was highest (Table 5). However, drainage pH values from saturated and unsaturated tailings were similar after year five (week 260). Nonetheless, sulfate release from the saturated tailings remained higher during years six through eight, reflecting the dependence of sulfate release on water content. As noted above, even in years nine and ten the release from the saturated tailings was higher when normalized for sulfur mass present (Figure 14, Table 9).

5.4. Acid Neutralization

Acid neutralization occurred by silicate mineral dissolution throughout the experiment and was apparently augmented by dissolution of trace amounts of calcite in the initial phase of the experiment. Although the CO_2 content of the tailings was reported as less than 0.05 %, dissolution of trace amounts of carbonate mineral likely contributed to elevated calcium and alkalinity release at the beginning of the experiment.

It should be noted that the trace carbonate mineral present, assumed to be calcite, was depleted more rapidly from the saturated reactors. This is evidenced by the more rapid release of both alkalinity and calcium under saturated conditions (Figure 15). It should be further noted that the sulfate release from the saturated reactors during this period was slightly less than that from the unsaturated reactors. Thus the more rapid calcite dissolution was apparently the result of the saturated conditions rather than accelerated acid production resulting from sulfide mineral oxidation. A similar observation for silicate minerals was reported by Lapakko and White (2000).

The cumulative calcium release during the first 40 to 50 weeks was roughly 1.2 and 1.4 millimoles under unsaturated and saturated conditions, respectively (Figure 16). The maximum calcite content inferred from the reported CO_2 content of the tailings ($CO_2 < 0.05$ %) is 0.85 millimoles. This indicates that some of the calcium release during this period was from silicate minerals such as plagioclase and augite.

Once calcite was depleted, acid generated resulting from iron sulfide oxidation was neutralized by dissolution of silicate minerals, including labradorite. In the saturated reactors, calcium release was significantly higher than sodium release until approximately week 104, at which point the ratio of calcium to sodium approached the stoichiometric ratio of plagioclase in the solids (1.425) and remained constant (see section 4.2; Tables 5, 10; Appendix 4, Figures A4.20, A4.21). Future analysis should examine rates of silicate mineral dissolution (i.e. labradorite, augite, olivine, biotite) to quantify the neutralization rates by dissolution of the various components.

5.5. Effect of pH on trace metal release

A major consequence of the accelerated sulfide mineral oxidation and consequent pH depression was a large increase in nickel and cobalt concentrations. As pH decreased from 6.8 to 6.4 in the saturated reactors, nickel and cobalt concentrations increased by 35 and 8 times respectively. Increases in nickel and zinc release were also observed, to a lesser extent, in the unsaturated reactors when pH decreased to 6.4 by week 400. Release rates increased 2-3 times as a result of this small decrease in pH.

5.6. Comparison of tailings and waste rock release rates

A sample of 0.2% S waste rock from the Babbitt Prospect of the Partridge River Intrusion was subjected to dissolution under the same conditions to which the unsaturated tailings were exposed. The rock particles ranged from 0.053 to 0.149 mm in diameter and were coarser than the tailings, for which 29 percent were finer than 0.053 mm (Table 2). The plagioclase contents of the waste rock and tailings were similar (50 and 57 percent, respectively), as were the calcium contents of the plagioclase present (Appendix 1, Table A1.7). Augite and biotite contents of the waste rock were reported to be slightly lower than those of the tailings (11 vs. 7.8% and 5.7 vs. 2.3%, respectively). In contrast, the olivine content of the waste rock was considerably higher than that in the tailings (26 vs. 9%). Respective concentrations of copper, nickel, and cobalt in the waste rock were 2.0, 1.2, and 1.2 times those in the tailings (Appendix 1, Table A1.6).

The pH of drainage from the waste rock sample was typically 0.8 to 1 unit lower than that of the tailings, with respective minimum values of 5.7 and 6.5. Both higher sulfide mineral oxidation rates and lower silicate mineral dissolution rates contributed to the lower pH values from the waste rock. The rates of sulfate release from unsaturated tailings reactors averaged about 60 μmol (kg rock·wk)$^{-1}$ over the first eight years of the experiment (Table 5), 80 percent of the 75 μmol (kg rock·wk)$^{-1}$ reported for the 0.20 %S waste rock over the same period (Lapakko et al. 2013). Sulfate release rates for the tailings and rock were very close in year 1 (260 vs 240 μmol (kg rock·wk)$^{-1}$) and year 8 (16 vs 15 μmol (kg rock·wk)$^{-1}$). Rates for the rock tended to be somewhat higher in the intermediate years.

Sulfate release rates area influenced by the sulfide mineral surface area exposed, the sulfide mineral chemistry, and the availability of oxygen. Considering the finer particle size of the tailings, and associated higher specific surface area, it would be expected that they would exhibit higher sulfate release rates. The lower observed sulfate release rates observed for the tailings are apparently the result of removal of “liberated” sulfide minerals during mineral processing. Consequently, relative to unprocessed waste rock, a greater fraction of sulfide minerals present in the tailings are included within other rock particles and, therefore, less available for reaction. This supported by mineralogical analyses that reported respective liberation probabilities of 100 and 87 percent for the rock and tailings (Appendix 1, Attachment A1.5).

It should be noted that there were also sulfide mineral content differences between the two samples. Respective copper contents of 0.1 and 0.051 percent for the waste rock and tailings were used to estimate the fraction of sulfur present with chalcopyrite. Assuming all copper was present as chalcopyrite indicated an estimated 50 percent of the sulfur in the waste rock and 25 percent of the sulfur in the tailings was associated with chalcopyrite. This infers that the pyrrhotite content of the tailings was about 1.5 times that of the waste rock. Pyrrhotite is reported to oxidize more rapidly than chalcopyrite, so this would tend to accelerate sulfate release from the tailings relative to the waste rock.

Finally, the finer grained tailings might have limited oxygen diffusion to sulfide mineral surfaces and thereby inhibited sulfide mineral oxidation. Both the finer grain size itself and increased water retention with finer grain size would tend to reduce diffusion. However the influence of oxygen diffusion might not be substantial due to the thin tailings beds used in the experiment.

Average rates of calcium and magnesium release from the tailings were on the order of twice those from the rock. This was apparently largely due to the finer size of the tailings, resulting in a greater surface area of silicate minerals. Plagioclase was the major calcium-bearing mineral in both the waste rock and tailings. There was little difference between the waste rock and tailings in plagioclase contents (50 vs. 57%) or the atom fractions of calcium in the plagioclase (0.54 vs. 0.57; Appendix 1, Table A1.7). Thus, mineralogical differences between the samples were small and any associated influences on calcium release would likely be minimal.

There were differences in magnesium-bearing contents of the waste rock and tailings. Relative to the tailings, the waste rock had less augite and biotite (7.8 vs. 11%, 2.3 vs. 5.7%, respectively) and more olivine (26% vs. 9.8%). The rates of calcium and magnesium release from the tailings were roughly twice the corresponding rates from the waste rock. The difference in calcium release rates was attributed to differences in particle size, given the similarity in plagioclase contents and chemistries between the two samples. Particle size, and its associated influence on silicate mineral surface area, would be expected to have a similar effect on magnesium release. If this is so, mineralogical differences between the tailings and rock had little influence on magnesium release. This further suggests, given that the olivine content of the waste rock was more than 2.5 times that of the tailings, that magnesium release was dominated by dissolution of augite and biotite rather than olivine.

Respective annual rates of copper and nickel from the waste rock, on average, were 40 and 150 times greater than those from the tailings. Similarly annual rates of zinc and cobalt release from the waste rock averaged 4 and 8 times those from than the tailings, respectively. These rates tended to be highest during years 2 and 3. The differences are attributed to pH values from the waste rock that was near 1 unit lower than those from the tailings. Concentrations of copper, nickel, and cobalt in the waste rock were 2.0, 1.2, and 1.2 times those in the tailings, respectively (Appendix 1, Table A1.6). These differences probably contributed to a lesser degree.

5.7. Sulfide oxidation as function of tailings bed depth

In the deeper tailings beds in humidity cells, sulfide oxidation was limited by oxygen diffusion through the water saturated tailings. Consequently, the humidity cell tailings bed consisted of, in a simplified sense, an upper zone of oxidation and a lower zone that was essentially devoid of oxygen. Consequently, sulfide oxidation was limited to the upper zone of the bed. Preliminary calculations indicated that roughly one third of the tailings, representing an approximate depth of 2.5 cm, were in the oxidation zone in the initial stage of the experiment. Sulfate release rates from the humidity cells were relatively constant after year 2, reflecting the progression of the oxidation zone downwards into zones of unoxidized tailings. Thus, sulfide oxidation in the humidity cells during the 10-year experiment was limited by oxygen diffusion rather than the amount of reactant (sulfide minerals) present. Drainage pH levels from the deeper beds (~7.5 cm deep) were about 0.3 units higher in all cases. The experiments indicated both water content of thin tailings beds and tailings bed depth affected the quality of drainage from the tailings.

In the lower half of the humidity cells, acid neutralization reactions may have occurred. Release rates of calcium decreased significantly in the first 200 weeks and began to level off at the stoichiometric ratio of plagioclase in the solids by week 360 (Appendix 4, Figures A4.22, A4.23). Rates of potassium release also decreased significantly over the first 200 weeks and began to level off in a similar manner as calcium. Magnesium release rates reached a minimum by 100 weeks, but subsequently have increased in concentration by a factor of two.

Trends in trace metal release rates were much more erratic in the humidity cells. Nickel release rates tended to stay near the detection limit until pH went below 7 after 200 weeks, at which point nickel release approximately doubled. The majority of drainage quality for copper, cobalt, and zinc were at or below the detection limit and too sporadic, therefore no clear trend was observed over the period of record.

5.8. Comparison of saturated reactors and humidity cells

Rates of cation release from the saturated reactors were generally higher than those from the humidity cells. For example, rates of sodium and potassium release from the saturated reactors were typically about 3 and 1.5 times, respectively, those from humidity cells (Figure 12, Table 5). Cation release from the humidity cells was, however, higher in two cases. First, calcium release rates from the humidity cells in years 2 and 3 were 1.3 to 1.5 times that from the saturated reactors. This occurred despite the fact that sulfate release rates from the humidity cells were 0.3 to 0.7 times those from the saturated reactors during this period. The elevated calcium release from the humidity cells is attributed to calcite dissolution and this is supported by alkalinity data. Alkalinity from the saturated reactors decreased below detection after week 40, while concentrations in drainage from the humidity cells remained above detection until at least week 162 (Appendix 3, Tables A3.4-A3.11). The low alkalinity release from the saturated reactors after week 40 suggests that calcite content had been substantially reduced, perhaps near depletion. This is consistent with the elevated calcium release during year 1 (Table 5), when calcium release per gram tailing from the reactors was almost 2.5 times that from the humidity cells (see discussion on calcite depletion in section 5.4). The calcite dissolution from the humidity cells during years 2 and 3 was not driven entirely by sulfide mineral oxidation. This is supported by humidity cell sulfate release rates during years 2 and 3 that were 0.4 and 0.7 times, respectively, corresponding rates from the saturated reactors (Table 5). That is, some of the calcium release was due to calcite solubility.

Second, magnesium release rates from the humidity cells roughly equaled that from the saturated reactors in years 6 and 7 and clearly exceeded the latter rates in years 8-10. This was possibly influenced by higher sulfate release from the humidity cells during this period (Table 5).

A charge balance was calculated to determine the acid neutralization potential of the cation release. The annual average cation-anion ratio for the unsaturated and saturated reactors was 1.01±0.43 and 0.81±0.18, respectively, whereas the ratio for the humidity cells was 1.01±0.1 (Table 11). These differences between cations and anions can be attributed to the resolution in measured alkalinity. For the reactors, alkalinity reached values below the detection limit by the first year. Since half the detection limit value was used in the charge balance for alkalinity (0.05 meq/L), the difference between cations–anions should be ± 0.05, which it is in most cases. Better analytical resolution of alkalinity would allow for a more in-depth examination of the charge balance in the future. Alternatively, alkalinity could be calculated as the difference between measured cation and anion concentrations

Trace metal release rates from the saturated reactors were almost always higher than the humidity cells. The one exception being nickel release in the humidity cells was 10% higher during years 9 and 10, when pH levels were close to one another. Copper release on average was typically five times higher in the saturated reactors. Release of nickel, zinc, and cobalt were 25, 19, and 7 times higher in the reactors, respectively. Differences in trace metal release were highest between the saturated reactors and the humidity cells during year 2, when pH decreased from pH 6.8 to 6.4 in the saturated reactors (Figure 13).

6. SUMMARY

In the present project laboratory dissolution tests were conducted on tailings produced by processing of Duluth Complex rock from the Babbitt prospect (also known as AMAX and Mesaba prospect) of the Partridge River Intrusion for recovery of base metals. Reaction of these tailings affects water quality, and the effects of 1) tailings water content and 2) bed depth on reactions were examined. Of particular interest were reactions affecting pH and release of copper, nickel, cobalt, and zinc. This report describes the characterization of tailings (bulk density, particle size distribution, chemistry, mineralogy, static tests) and 10 years of laboratory dissolution testing. Dissolution tests were conducted on 75-g samples in unsaturated (uncovered) and saturated (covered) reactors (both in triplicate) and in duplicate 1000-g humidity cells.

The dry bulk density of the tailings was determined as 1.65 g cm-3. Approximately 80 percent were finer than 100 mesh, 29 percent finer than 270 mesh, and 16 percent finer than 500 mesh. The tailings contained 0.2% sulfur, at least 90% of which was present as sulfide, and less than 0.05% carbon dioxide. The major whole rock components were SiO_2 (47.5%), Al_2O_3 (15.6%), and Fe_2O_3 (15.2%). Calcium and magnesium contents as oxides were 7.8% and 7.0%. Copper, nickel, cobalt and zinc contents were determined as 510, 360, 59 and 120 ppm. Plagioclase (~An60Ab40) was the dominant mineral (57%), with augite, olivine, and quartz each comprising roughly 10 percent.

The 0.2% S content indicated an acid production potential of 6.2 g $CaCO_3$ equivalent (kg tailing)$^{-1}$. A digestion modified from Sobek et al. (1978) and backtitration endpoints of 7.0 and 8.3 yielded respective neutralization potentials (NP) of 19 and 14 g $CaCO_3$ equivalent (kg tailing)$^{-1}$, considerably higher than the NP(CO_2), which was determined as less than 1.1 g $CaCO_3$ equivalent (kg tailing)$^{-1}$. The paste pH of the tailings was 8.29.

Drainage quality from all replicates was in good agreement and differences were observed among the three methods. Drainage pH from all units was initially near 8 and tended to decline subsequently. Minimum pH values for the reactors were near 6.5 as opposed to roughly 6.8 for the humidity cells. Drainage pH from the saturated reactors declined most rapidly, reaching minimum values after about 50 weeks, as opposed to 400 weeks for the unsaturated reactors and humidity cells.

The comparatively low pH for the saturated reactors persisted from roughly week 50 to week 150. The pH depression was due largely to sulfide mineral oxidation rates in the saturated reactors that were 2.7 and 1.7 times those from unsaturated reactors during years two and three, respectively. The increased rates were apparently influenced by greater water retention in the saturated cells (i.e. less evaporation). Sulfate release from all reactors decreased over time and the magnitude of decrease declined over time. This suggested that sulfide oxidation was a first order reaction with respect to solid-phase sulfur content and oxygen transport was not rate limiting. In contrast, sulfate release rates from the humidity cells was virtually constant after year 2, suggesting that oxygen transport limited the rate of sulfide mineral oxidation. Major cation molar release rates from all units, reflecting rates of acid neutralization, initially decreased in the order Ca > Mg > K > Na and subsequently evolved to Mg > Ca > Na ≥ K.

Trace metal concentrations in drainage from the reactors exhibited a dependence on the minor variations of pH within the circumneutral region. Concurrent with the relatively small pH decrease in the saturated reactors at week 50, nickel concentrations increased to near 0.1 mg L^{-1}, roughly 25 times those in the unsaturated reactors. Similar but less pronounced trends were observed for cobalt and zinc. Nickel, copper, and zinc concentrations also increased as drainage pH from the unsaturated reactors declined slightly after about five years of reaction. Slight increases in nickel concentrations were also observed as pH of drainage from the humidity cells decreased in the upper sixes after year 4.

Key results are as follows.

1. Under all test conditions the tailings produced circumneutral pH, with the minimum of all values near 6.4.
2. During the first three years of testing, sulfide oxidation in saturated (non-evaporating) reactors was more rapid than that in unsaturated (evaporating) reactors, apparently due to the greater water retention.
3. The aforementioned accelerated oxidation yielded slightly lower drainage pH values in the saturated reactors.
4. The slightly lower pH values produced nickel concentrations in drainage from the saturated reactors that were roughly 25 times those in drainage from the unsaturated reactors.
5. Sulfide mineral oxidation rates (normalized for tailings mass) for the humidity cells were limited by oxygen diffusion, resulting in drainage pH values higher and trace metal concentrations lower than those for the smaller reactors.

These results provide valuable insight for assessing the geochemical behavior of tailings during environmental review. They also provide an empirical benchmark for comparison with results of future dissolution tests on fairly low-sulfur Duluth Complex tailings.

7. ADDITIONAL WORK

The present studies should be continued to provide a long-term empirical data base for informing environmental review of proposed copper-nickel mining operations. Analysis of the present data should be continued to estimate dissolution rates of individual minerals present in the tailings. This is particularly important for the silicate minerals present because it would allow better prediction of the long-term acid-neutralizing potential of the solids. Sulfide mineral oxidation in tailings beds should also be modeled as a function of moisture content and tailings depth, using the experimental data for calibration. Analysis of leached solids and geochemical equilibrium modeling should be conducted to examine possible phases controlling trace metal concentrations.

8. ACKNOWLEDGMENTS

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Table 1. Description and numbering of reactors and humidity cells.

Reactor / Cell Number	Mass of Tailing (g)	Reactor / Cell Description
1	75	Uncovered small reactor[1]
2	75	Uncovered small reactor (duplicate)[1]
3	75	Uncovered small reactor (sampled on a limited basis)[2]
4	75	Covered small reactor[1]
5	75	Covered small reactor (duplicate)[1]
6	75	Covered small reactor (sampled on a limited basis)[2]
7	1000	Humidity cell[3]
8	1000	Humidity cell (duplicate)[3]

1 - Duplicate covered and uncovered small reactors designed to monitor drainage quality and the effect of different moisture conditions. These reactors will also enable us to tie into data from previous work with the Duluth Complex.

2 - Small reactors setup to analyze leached tailing at some point in time during the experiment. These reactors are sampled on a limited basis.

3 - Duplicate humidity cells to serve as a comparison using the DNR version of the ASTM method.

Table 2. Particle size distribution. Analysis by Lerch Brothers, Inc..

MESH SIZE	PERCENT
+100	19.70
-100 / +270	51.50
-270 / +500	12.85
-500	15.95

Table 3. Whole rock chemistry (percent). Analysis by ACTLABS, Inc.

Parameter	Duplicate 1	Duplicate 2	Duplicate 3
S	0.20	0.20	0.20
S^{2-} [1]	0.18	0.18	0.18
SO_4^{2-} as S	<0.016	0.020	<0.016
CO_2	<0.05	<0.05	<0.05
$A1_2O_3$	15.64	15.52	15.68
CaO	7.77	7.75	7.79
Fe_2O_3	15.22	15.84	15.60
K_2O	0.77	0.87	0.83
MgO	6.97	7.35	7.20
MnO	0.163	0.172	0.168
Na_2O	2.48	2.48	2.49
P_2O_5	0.18	0.17	0.18
SiO_2	47.51	48.10	48.28
TiO_2	1.521	1.672	1.591
LOI	0.67	0.48	0.66
TOTAL[2]	98.88	100.31	100.48

[1] Determined by difference.

[2] For parameters from Al_2O_3 through LOI2.

Table 4. Trace metal chemistry for concentrations >50 ppm. Analysis by ACTLABS, Inc.

Parameter	Duplicate 1	Duplicate 2	Duplicate 3
Ba	215	213	218
Co	59	61	64
Cr	152	160	162
Cu	511	516	508
Ni	355	363	366
Pb	106	81	79
Sr	264	261	264
V	137	148	146
Zn	116	114	115
Zr	83	109	99

Note: See Table A1.3 for complete trace metal analyses

Table 5. Page 1 of 3. Minimum pH and average annual rates of release for sulfate, calcium, magnesium, sodium, and potassium in umol*(kg rock*week)$^{-1}$. Period of record is 6 - 520 weeks for R1, R2, R4, R5, HC7, HC8. Period of record is 6 – 232 weeks for R3 and R6. During the first year, 11-16 concentrations were sampled for each parameter. Sampling frequency for subsequent years decreased to approximately 6-8 per year.

ID	Year	min pH[1]	Sulfate		Calcium		Magnesium		Sodium		Potassium	
			rate	s.d.	rate	s.d.	rate	s.d.	rate	s.d.	rate	s.d.
Reactor 1 75 grams -100/+270 unsaturated	1	7.04	294	135	313	129	114	20.5	22.5	7.27	120	50.2
	2	6.87	62.4	15.3	76.4	15.2	80.1	9.5	14.5	2.11	35.5	17.1
	3	6.72	45.4	10.5	42.4	7.07	60.8	10.8	17.1	5.03	16.9	20.2
	4	6.78	31	3.99	26.9	3.93	44.8	4.98	13.4	1.68	2.85*	0.023
	5	6.88	25.1	2.58	24.1	3.03	40.7	3.34	13.8	2.1	6.85	10.5
	6	6.65	19.5	2.71	19.9	1.98	37.4	5.14	13.4	1.44	11.9	8.07
	7	6.59	16.6	2.16	18.9	3.12	30.9	2.44	15.3	3	21.4	5.49
	8	6.50	15.3	1.82	19.1	2.96	28.5	3.08	17.1	3.18	18.7	2.97
	9	6.41	13.9	5.68	15.3	2.36	18.1	9.68	17.5	2.07	12.9	8.05
	10	6.64	13.9	4.12	13.8	5.22	20.8	4.04	12.8	7.69	12	3.22
	Total[2]	6.52	53.7	86	57	91.9	47.6	29.8	15.7	2.94	25.9	34.3
Reactor 2 75 grams -100/+270 unsaturated	1	7.20	232	77.4	300	109	107	14.3	22	7.49	84.8	38.4
	2	6.92	81.4	19.9	84.1	20	93.8	14.4	16	2.74	13.3	6.08
	3	6.84	48.4	10.6	45.8	5.49	67.6	8.39	19	4.32	2.79*	0.0255
	4	6.88	33.4	4.79	32.7	4.93	56.2	5.33	16	1.57	2.77*	0.0267
	5	6.88	23.9	2.26	29	2.14	48.8	3.37	16.5	2.35	5.06	4.07
	6	6.74	19	2.75	23.2	2.84	40.4	3.68	15.5	1.98	21.8	1.9
	7	6.71	16.9	3.42	24.6	3.22	38.6	4.74	21.2	5.11	18	2.54
	8	6.57	16.7	1.28	23.2	2.51	33.5	2.55	17.4	1.62	14.2	0.838
	9	6.45	22.4	10.1	21.9	2.63	30.8	3.34	18.7	2.49	11.7	1.51
	10	6.64	16.3	2.55	19.9	5.19	28.2	3.43	16.2	3.91	9.64	1.34
	Total[2]	6.60	51	66.6	60.4	86.3	54.4	27.1	17.9	2.31	18.4	24.1
Reactor 3 75 grams -100/+270 unsaturated	1	7.24	240	68.4	290	70.7	106	11.2	21.1	2.92	98.5	20
	2	6.99	89.9	28.1	96.5	27.8	98.8	13	14	1.71	16.2	8.64
	3	6.81	55.8	6.17	53.1	4.23	78.6	12.5	21.7	3.6	4.6	3.03
	4	6.90	34.1	6.25	32	4.69	53.6	6.28	15.5	2.63	2.84*	0.0247
	5	7.00	26.4	2.39	29.7	1.39	51	1.9	16.6	2.74	3.97	4.29
	6	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
	7	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
	8	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
	9	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
	10	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
	Total[2]	6.93	89.3	87.8	100	110	77.7	25.3	17.8	3.42	25.2	41.3

[1] 5th percentile value

[2] Average and standard deviation for annual average release rates

* Majority of concentrations during this time interval were below detection limit. One half the detection limit was used to calculate the annual average release rate.

Table 5. Page 2 of 3. Minimum pH and average annual rates of release for sulfate, calcium, magnesium, sodium, and potassium in umol*(kg rock*week)$^{-1}$. Period of record is 6 - 520 weeks for R1, R2, R4, R5, HC7, HC8. Period of record is 6 – 232 weeks for R3 and R6. During the first year, 11-16 concentrations were sampled for each parameter. Sampling frequency for subsequent years decreased to approximately 6-8 per year.

ID	Year	min pH[1]	Sulfate		Calcium		Magnesium		Sodium		Potassium	
			rate	s.d.	rate	s.d.	rate	s.d.	rate	s.d.	rate	s.d.
Reactor 4 75 grams -100/+270 saturated	1	6.81	371	161	385	192	158	29.8	27.7	4.59	91.5	38.7
	2	6.48	180	61.6	75.7	19.6	105	30.2	33.3	4.72	41.3	11.2
	3	6.59	74.7	16.3	39.6	4.64	51.1	5.14	26.8	5.48	20.2	5.2
	4	6.60	66.5	15.5	32.3	4.12	49	6.64	21.2	2.31	19.6	2.23
	5	6.82	38.3	3.87	27	2.62	39.4	2.08	21.6	4.17	17.3	3.26
	6	6.72	25.9	3.83	20.5	1.97	32.9	2.02	17.7	4.6	12.6	1.76
	7	6.80	18.9	1.25	21.6	2.54	33.3	2.72	19.5	4.6	14.2	2.43
	8	6.61	18.1	1.93	22.6	2.3	30.6	2.12	21.6	3.25	13.5	0.757
	9	6.65	12.1	4.74	18.4	3.91	23.2	4.99	20.3	2.41	10.4	1.19
	10	6.67	13.2	4.95	18.7	5.27	23.8	2.6	18.7	6.11	9.86	1.59
	Total[2]	6.59	81.9	114	66.1	113	54.7	43.5	22.8	4.9	25	25
Reactor 5 75 grams -100/+270 saturated	1	6.79	311	108	372	160	163	31.1	32.3	5.47	85.4	31.4
	2	6.41	212	78.3	84.9	25.9	115	37.8	38.1	5.02	38.3	11.1
	3	6.55	89.2	16.4	41.4	3.06	54.3	6.69	29.8	5.17	24.5	9.32
	4	6.52	54.2	11.2	29.2	4.1	41.2	3.79	22.2	2.61	17.1	1.78
	5	6.78	33.9	4.88	25	2.31	36.2	1.74	20.3	3.04	16.9	5.38
	6	6.64	24.1	3.43	18.5	1.93	29.6	3	17.1	1.61	12.4	1.14
	7	6.79	19.2	1.17	21.7	3.26	31.3	3.08	21.3	6.51	13.9	3.22
	8	6.67	18.4	2.77	22.4	2.2	28.9	1.49	20.7	2.1	13.9	1.29
	9	6.51	15.2	12.7	17.8	2.08	20.1	3.61	20.8	2.35	9.4	1.29
	10	6.59	15.8	2.88	16.1	4.47	22.2	3.71	19.2	8.9	8.84	1.01
	Total[2]	6.50	79.3	101	64.9	110	54.2	47.1	24.2	6.8	24.1	23.2
Reactor 6 75 grams -100/+270 saturated	1	6.86	306	135	358	149	157	21.4	26.6	3.93	80.5	21.4
	2	6.55	187	71.8	85.7	23.7	113	27	34.3	3.4	39.8	7.86
	3	6.49	108	10	52.8	9	69.8	5.53	34.1	2.74	30	8.57
	4	6.44	62.9	22.9	29	6.57	41.1	7.06	28.3	9.48	16.6	3.09
	5	6.76	34.4	4.29	24.3	1.04	34.2	1.07	25.4	6.23	15.4	3.47
	6	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
	7	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
	8	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
	9	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
	10	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
	Total[2]	6.51	140	109	110	141	83	51.7	29.7	4.18	36.5	26.6

[1] 5th percentile value

[2] Average and standard deviation for annual average release rates

* Majority of concentrations during this time interval were below detection limit. One half the detection limit was used to calculate the annual average release rate.

Table 5. Page 3 of 3. Minimum pH and average annual rates of release for sulfate, calcium, magnesium, sodium, and potassium in umol*(kg rock*week)$^{-1}$. Period of record is 6 - 520 weeks for R1, R2, R4, R5, HC7, HC8. Period of record is 6 – 232 weeks for R3 and R6. During the first year, 11-16 concentrations were sampled for each parameter. Sampling frequency for subsequent years decreased to approximately 6-8 per year.

ID	Year	min pH[1]	Sulfate		Calcium		Magnesium		Sodium		Potassium	
			rate	s.d.	rate	s.d.	rate	s.d.	rate	s.d.	rate	s.d.
Humidity cell 7 1000 grams -1/4 inch	1	7.30	115	25.5	157	28.6	47.8	22	10.3	3.44	35.2	9.52
	2	7.38	71.8	13.3	103	18.6	17.9	1.16	6.81	0.691	23.2	4.36
	3	7.15	55.6	6.61	59.8	12.6	25.9	2.84	6.71	1.21	16.1	3.32
	4	6.87	49.2	4.59	34.6	4.11	30.2	2.56	6.63	0.503	12.8	1.22
	5	6.88	49.5	5.63	26.5	2.64	34.8	3.11	7.13	0.998	11.7	1.43
	6	6.82	51.8	5.69	19.2	1.74	35.1	3.72	6.27	0.427	9.4	0.751
	7	6.79	49.6	3.43	16.1	1.13	35.1	3.47	7.24	1.47	9.37	0.479
	8	6.74	51.6	3.72	17.2	0.999	40.3	3.25	7.89	0.705	10.5	2.51
	9	6.69	51	2.81	15.9	1.87	39.6	3.37	8.03	0.491	8.8	0.765
	10	6.82	50.9	5.23	14.5	2.69	38.9	4.93	7.18	1.57	8.57	1.52
	Total[2]	6.78	59.7	20.7	46.4	47.9	34.6	8.34	7.42	1.15	14.6	8.53
Humidity cell 8 1000 grams -1/4 inch	1	7.48	116	23.5	154	23.5	45.6	21.7	11.6	3.89	40.4	7.56
	2	7.39	76.5	13	109	16.5	16.2	1.01	6.79	0.635	23	3.7
	3	7.24	61.8	6.5	64.9	14.6	26.2	3.47	6.78	0.727	15	1.41
	4	6.97	53.2	5.97	35.3	5.82	30.7	2.47	6.71	0.703	12.9	1.66
	5	6.87	48.4	5.94	25.1	3.59	32	2.71	7.04	0.763	11.4	1.46
	6	6.87	50.2	4.88	18.8	2.47	32.7	3.22	6.34	0.416	9.25	0.724
	7	6.76	49.4	4.96	16.1	0.927	33.5	3	7.85	1.67	9.48	0.684
	8	6.64	51	4.62	17	1.06	36.4	2.75	8.21	0.583	10.1	1.73
	9	6.69	50.9	2.56	16.1	0.845	37.8	2.2	8.44	0.387	8.78	0.279
	10	6.74	48	6.39	14.4	2.95	33.7	5.1	7.56	2	7.9	1.25
	Total[2]	6.74	60.6	21.4	47.1	48.3	32.5	7.64	7.73	1.53	14.8	10

[1] 5th percentile value

[2] Average and standard deviation for annual average release rates

* Majority of concentrations during this time interval were below detection limit. One half the detection limit was used to calculate the annual average release rate.

Table 6. Page 1 of 3. Minimum pH and average annual rates of release for sulfate, copper, nickel, cobalt, and zinc in umol*(kg rock*week)$^{-1}$. Period of record is 6 - 520 weeks for R1, R2, R4, R5, HC7, HC8. Period of record is 6 – 232 weeks for R3 and R6. During the first year, 11-16 concentrations were sampled for each parameter. Sampling frequency for subsequent years decreased to approximately 6-8 per year.

ID	Year	min pH[1]	Sulfate		Copper		Nickel		Cobalt		Zinc	
			rate	s.d.	rate	s.d.	rate	s.d.	rate	s.d.	rate	s.d.
Reactor 1 75 grams -100/+270 unsaturated	1	7.04	294	135	0.0543	0.0443	0.0883	0.0504	0.0381*	0.000469	0.12	0.0506
	2	6.87	62.4	15.3	0.0582	0.0282	0.132	0.0377	0.0378*	0.000219	0.0771	0.0404
	3	6.72	45.4	10.5	0.0351*	0.000336	0.0794	0.0362	0.0378*	0.000362	0.0593	0.0275
	4	6.78	31	3.99	0.064	0.0432	0.0802	0.0226	0.0378*	0.000296	0.0911	0.0489
	5	6.88	25.1	2.58	0.0441	0.0266	0.082	0.0269	0.0379*	0.000216	0.0596	0.0326
	6	6.65	19.5	2.71	0.0428*	0.0186	0.165	0.0373	0.0385*	0.000309	0.0476*	0.0341
	7	6.59	16.6	2.16	0.0666	0.0262	0.284	0.024	0.0386*	0.000555	0.191	0.109
	8	6.50	15.3	1.82	0.115[3]	0.0629	0.289	0.0621	0.0388*	0.000163	0.142	0.0965
	9	6.41	13.9	5.68	0.0557	0.0241	0.369	0.0603	0.0389*	0.000426	0.369	0.0711
	10	6.64	13.9	4.12	0.0706	0.0287	0.337	0.0715	0.0387*	0.000585	0.262	0.0815
	Total[2]	6.52	53.7	86	0.0606	0.0221	0.191	0.117	0.0383	0.000462	0.142	0.104
Reactor 2 75 grams -100/+270 unsaturated	1	7.20	232	77.4	0.0415	0.0174	0.0679	0.0371	0.0377*	0.00113	0.0943	0.0386
	2	6.92	81.4	19.9	0.0459	0.0218	0.147	0.025	0.0378*	0.000239	0.112	0.0228
	3	6.84	48.4	10.6	0.0345*	0.000476	0.104	0.053	0.0372*	0.000514	0.0788	0.0503
	4	6.88	33.4	4.79	0.0469	0.0222	0.125	0.0317	0.0368*	0.000355	0.109	0.0243
	5	6.88	23.9	2.26	0.0392	0.0148	0.0937	0.0149	0.0368*	0.000956	0.0559	0.0299
	6	6.74	19	2.75	0.0348*	0.000321	0.113	0.0148	0.0375*	0.000346	0.0662	0.045
	7	6.71	16.9	3.42	0.0342*	0.00212	0.178	0.0401	0.0369*	0.00229	0.178	0.0484
	8	6.57	16.7	1.28	0.0661	0.0399	0.183	0.047	0.0379*	0.000206	0.135	0.12
	9	6.45	22.4	10.1	0.0633	0.0389	0.359	0.0916	0.044	0.0153	0.293	0.0992
	10	6.64	16.3	2.55	0.0843	0.0408	0.453	0.0816	0.0469	0.0217	0.313	0.0778
	Total[2]	6.60	51	66.6	0.0491	0.0168	0.182	0.125	0.039	0.00351	0.144	0.091
Reactor 3 75 grams -100/+270 unsaturated	1	7.24	240	68.4	0.0429	0.0205	0.0442	0.016	0.038*	0.000833	0.126	0.0233
	2	6.99	89.9	28.1	0.035*	0.000509	0.123	0.0153	0.0378*	0.000549	0.107	0.0537
	3	6.81	55.8	6.17	0.0353*	0.000291	0.0787	0.0483	0.038*	0.000314	0.0801	0.0613
	4	6.90	34.1	6.25	0.0467	0.0189	0.0803	0.0169	0.0415*	0.0121	0.11	0.0722
	5	7.00	26.4	2.39	0.035*	0.000123	0.0577	0.0229	0.0377*	0.000132	0.137	0.0619
	6	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
	7	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
	8	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
	9	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
	10	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
	Total[2]	6.93	89.3	87.8	0.039	0.00546	0.0767	0.0299	0.0386	0.00164	0.112	0.0215

[1] 5th percentile value

[2] Average and standard deviation for annual average release rates

[3] Two of the highest copper values in the period of record occurred during year 8, along with few values below the detection limit.

* Majority of concentrations during this time interval were below detection limit. One half the detection limit was used to calculate the annual average release rate.

Table 6. Page 2 of 3. Minimum pH and average annual rates of release for sulfate, copper, nickel, cobalt, and zinc in umol*(kg rock*week)$^{-1}$. Period of record is 6 - 520 weeks for R1, R2, R4, R5, HC7, HC8. Period of record is 6 – 232 weeks for R3 and R6. During the first year, 11-16 concentrations were sampled for each parameter. Sampling frequency for subsequent years decreased to approximately 6-8 per year.

ID	Year	min pH[1]	Sulfate		Copper		Nickel		Cobalt		Zinc	
			rate	s.d.	rate	s.d.	rate	s.d.	rate	s.d.	rate	s.d.
Reactor 4 75 grams -100/+270 saturated	1	6.81	371	161	0.0468*	0.0242	0.234	0.494	0.0506	0.0231	0.223	0.163
	2	6.48	180	61.6	0.0404*	0.000536	2.16	0.5	0.149	0.0312	0.283	0.04
	3	6.59	74.7	16.3	0.0403*	0.00103	0.534	0.371	0.0533	0.0242	0.134	0.105
	4	6.60	66.5	15.5	0.0403*	0.000445	0.135	0.0393	0.0434*	0.000479	0.177	0.0641
	5	6.82	38.3	3.87	0.0402*	0.000362	0.0595	0.0315	0.0434*	0.000379	0.19	0.0745
	6	6.72	25.9	3.83	0.0405*	0.000817	0.0438*	0.000885	0.0436*	0.000881	0.131	0.0508
	7	6.80	18.9	1.25	0.0398*	0.00744	0.0433*	0.000669	0.0429*	0.000802	0.197	0.0563
	8	6.61	18.1	1.93	0.0451*	0.0144	0.0433*	0.00115	0.0432*	0.00115	0.12	0.096
	9	6.65	12.1	4.74	0.0398*	0.000937	0.0431*	0.00101	0.0429*	0.00101	0.248	0.0229
	10	6.67	13.2	4.95	0.0395*	0.000446	0.0428*	0.000483	0.0426*	0.000481	0.246	0.0482
	Total[2]	6.59	81.9	114	0.0413	0.0025	0.334	0.659	0.0555	0.0331	0.195	0.0556
Reactor 5 75 grams -100/+270 saturated	1	6.79	311	108	0.0397*	0.00286	0.45	0.743	0.0597	0.0402	0.17	0.0805
	2	6.41	212	78.3	0.0497	0.0199	3.5	1.26	0.237	0.0903	0.41	0.106
	3	6.55	89.2	16.4	0.0402*	0.000731	0.516	0.294	0.0516*	0.0197	0.139	0.11
	4	6.52	54.2	11.2	0.0489*	0.0295	0.114	0.074	0.0538*	0.0352	0.218	0.0896
	5	6.78	33.9	4.88	0.0399*	0.000729	0.0432*	0.000789	0.043*	0.000786	0.176	0.0954
	6	6.64	24.1	3.43	0.0379*	0.00269	0.0411*	0.00291	0.0409*	0.0029	0.154	0.0473
	7	6.79	19.2	1.17	0.0391*	0.00115	0.0592*	0.0472	0.0422*	0.00124	0.251	0.103
	8	6.67	18.4	2.77	0.039*	0.000672	0.0474*	0.0144	0.042*	0.000725	0.313	0.0917
	9	6.51	15.2	12.7	0.0385*	0.00134	0.0418*	0.00138	0.0416*	0.00137	0.22	0.111
	10	6.59	15.8	2.88	0.0381*	0.00116	0.0412*	0.00125	0.041*	0.00125	0.158	0.0427
	Total[2]	6.50	79.3	101	0.0411	0.0044	79.3	101	0.0653	0.0606	0.221	0.0851
Reactor 6 75 grams -100/+270 saturated	1	6.86	306	135	0.0406*	0.000512	0.0728	0.0269	0.0436*	0.000487	0.143	0.106
	2	6.55	187	71.8	0.0401*	0.000859	1.71	0.595	0.084	0.0493	0.306	0.0608
	3	6.49	108	10	0.0404*	0.00068	0.784	0.211	0.0678	0.0283	0.34	0.0856
	4	6.44	62.9	22.9	0.04*	0.000826	0.229	0.106	0.0431*	0.000891	0.21	0.0787
	5	6.76	34.4	4.29	0.04*	0.00275	0.0716	0.0331	0.0431*	0.000296	0.154	0.0232
	6	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
	7	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
	8	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
	9	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
	10	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
	Total[2]	6.51	140	109	0.0402	0.000291	0.573	0.698	0.0563	0.0188	0.23	0.0887

[1] 5th percentile value

[2] Average and standard deviation for annual average release rates

* Majority of concentrations during this time interval were below detection limit. One half the detection limit was used to calculate the annual average release rate.

Table 6. Page 3 of 3. Minimum pH and average annual rates of release for sulfate, copper, nickel, cobalt, and zinc in umol*(kg rock*week)$^{-1}$. Period of record is 6 - 520 weeks for R1, R2, R4, R5, HC7, HC8. Period of record is 6 – 232 weeks for R3 and R6. During the first year, 11-16 concentrations were sampled for each parameter. Sampling frequency for subsequent years decreased to approximately 6-8 per year.

ID	Year	min pH[1]	Sulfate		Copper		Nickel		Cobalt		Zinc	
			rate	s.d.	rate	s.d.	rate	s.d.	rate	s.d.	rate	s.d.
Humidity cell 7 1000 grams -1/4 inch	1	7.30	115	25.5	0.00907	0.0038	0.0592	0.0301	0.00805*	0.000329	0.011	0.00959
	2	7.38	71.8	13.3	0.0111	0.00715	0.0228	0.0104	0.00822*	0.000145	0.00966	0.00441
	3	7.15	55.6	6.61	0.00763*	0.0000549	0.0121	0.00604	0.00823*	0.0000592	0.0119	0.011
	4	6.87	49.2	4.59	0.00771*	0.0000996	0.0225	0.0058	0.00831*	0.000107	0.0148	0.0162
	5	6.88	49.5	5.63	0.00764*	0.0000995	0.0308	0.00392	0.00824*	0.000107	0.0108	0.00693
	6	6.82	51.8	5.69	0.00763*	0.000126	0.0292	0.0131	0.00823*	0.000136	0.0111	0.00634
	7	6.79	49.6	3.43	0.0104	0.00708	0.0414	0.00957	0.00826*	0.00012	0.0214	0.0165
	8	6.74	51.6	3.72	0.0102	0.00495	0.0417	0.00445	0.0082*	0.0000863	0.0116	0.0118
	9	6.69	51	2.81	0.00764*	0.0000493	0.0428	0.00624	0.00824*	0.0000531	0.012	0.00597
	10	6.82	50.9	5.23	0.00765*	0.000111	0.038	0.00622	0.00825*	0.00012	0.0171	0.0177
	Total[2]	6.78	59.7	20.7	0.00866	0.00139	0.034	0.0134	0.00822	0.0000669	0.0131	0.00364
Humidity cell 8 1000 grams -1/4 inch	1	7.48	116	23.5	0.00906	0.00399	0.058	0.036	0.00814*	0.000188	0.0085*	0.00389
	2	7.39	76.5	13	0.00765*	0.000116	0.00954*	0.00368	0.00825*	0.000125	0.00743*	0.000113
	3	7.24	61.8	6.5	0.00771*	0.0000558	0.00835*	0.0000604	0.00831*	0.0000602	0.0119	0.0107
	4	6.97	53.2	5.97	0.0077*	0.0000508	0.00924*	0.00298	0.0083*	0.0000548	0.0101	0.00644
	5	6.87	48.4	5.94	0.00764*	0.0000556	0.0192	0.00481	0.00824*	0.00006	0.00841	0.00295
	6	6.87	50.2	4.88	0.00765*	0.0000826	0.0248	0.00465	0.00825*	0.0000891	0.00742*	0.0000808
	7	6.76	49.4	4.96	0.00765*	0.0000616	0.0404	0.00994	0.00825*	0.0000664	0.013	0.00715
	8	6.64	51	4.62	0.00762*	0.0000432	0.042	0.0134	0.00822*	0.0000466	0.0075*	0.000264
	9	6.69	50.9	2.56	0.00767*	0.0000793	0.0613	0.00381	0.00827*	0.0000855	0.0135	0.00692
	10	6.74	48	6.39	0.00764*	0.0000533	0.0557	0.0133	0.00824*	0.0000575	0.0111	0.00888
	Total[2]	6.74	60.6	21.4	0.0078	0.000446	0.0329	0.0212	0.00825	0.0000474	0.00987	0.00236

[1] 5th percentile value

[2] Average and standard deviation for annual average release rates

* Majority of concentrations during this time interval were below detection limit. One half the detection limit was used to calculate the annual average release rate.

Table 7. Total mass release percent depletion for weeks 0-520.

Reactor /HC	Total mass release after 520 weeks, mmol/kg rock									Trace metals, % remaining after 520 weeks			
	SO_4	Ca	Mg	Na	K	Cu	Ni	Co	Zn	Cu	Ni	Co	Zn
Unsaturated 75-g Reactors													
1	28.3	30.1	26.4	9.7	14.7	0.032	0.0994	0.02	0.0746	99.6%	98.4%	98.0%	95.9%
2	28.2	32.4	29.9	10.9	11.1	0.0251	0.094	0.0201	0.0737	99.7%	98.5%	98.0%	96.0%
3[1]	23.7	26.1	20.3	5.8	7.51	0.00954	0.0204	0.00914	0.0256	NA	NA	NA	NA
Saturated 75-g Reactors													
4	41.9	33.8	29.7	13.4	14	0.0217	0.172	0.0289	0.0992	99.7%	97.2%	97.1%	94.6%
5	40.9	33.4	29.4	13.7	13.6	0.0213	0.237	0.0326	0.112	99.7%	96.1%	96.7%	93.9%
6[1]	35.9	28.2	21.4	8.82	10.2	0.00940	0.151	0.0134	0.0565	NA	NA	NA	NA
1000-g Humidity Cells													
7[2]	34.3	25.5	19.5	5.38	8.07	0.00464	0.0184	0.00432	0.0066	99.9%	99.7%	99.6%	99.6%
8[2]	31.9	25.8	18.4	5.5	8.27	0.00418	0.0175	0.00433	0.0049	99.9%	99.7%	99.6%	99.7%

[1] Reactors 3 and 6 were terminated after 232 weeks

[2] Incorrect values have been updated for humidity cell total mass release, 6/17/2014

Table 8. Annual percent sulfur remaining for reactors and humidity cells.

Year	Unsaturated 75-g Reactors			Saturated 75-g Reactors			1000-g Humidity Cells	
	R1	R2	R3[1]	R4	R5	R6[1]	HC7	HC8
1	74.6%	77.7%	76.8%	68.1%	72.0%	71.0%	84.7%	89.3%
2	69.8%	71.2%	70.4%	54.9%	56.9%	57.8%	79.1%	83.3%
3	66.1%	67.3%	65.9%	49.0%	49.7%	49.6%	74.6%	78.2%
4	63.5%	64.5%	63.0%	43.3%	45.1%	43.8%	70.5%	73.8%
5	61.4%	62.5%	NA	40.1%	42.3%	NA	66.3%	69.8%
6	59.8%	60.9%	NA	38.0%	40.3%	NA	62.0%	65.5%
7	58.4%	59.5%	NA	36.4%	38.7%	NA	57.8%	61.4%
8	57.1%	58.1%	NA	34.9%	37.2%	NA	53.5%	57.2%
9	55.9%	56.2%	NA	33.9%	35.7%	NA	49.2%	52.9%
10	54.7%	54.8%	NA	32.8%	34.5%	NA	45.0%	48.9%

[1] Reactors 3 and 6 were terminated after 232 weeks

Table 9. Annual median pH, average sulfate release, and average sulfate release as a function of mass of sulfur remaining for 75 gram reactors.

Year	Unsaturated	Saturated	Unsaturated	Saturated	Unsaturated	Saturated
	Median pH		Avg SO_4 release rate (µmol/kg*wk)		Avg SO_4 release/g S remaining (µmol/g S*wk)	
1	7.48	7.55	262.9	341.2	152.6	202.3
2	7.12	6.64	71.9	195.9	48.6	152.6
3	7.02	6.70	46.9	81.9	34.1	77.6
4	6.95	6.75	32.2	60.4	24.6	64.8
5	7.07	6.92	24.5	36.1	19.4	42.3
6	6.92	6.90	19.2	25.0	15.7	31.1
7	6.81	6.92	16.7	18.9	14.0	24.8
8	6.76	6.83	16.0	18.2	13.7	24.8
9	6.57	6.70	18.2	13.6	16.0	19.2
10	6.74	6.82	15.1	14.5	13.6	21.1

Table 10. Estimated calcium release from plagioclase, $CaCO_3$ and other silicates. Release in mmol.

ID	Duration[1]	Total Ca[2]	Total Na[3]	Ca (plag)[4]	Ca w/ $CaCO_3$[5]	Ca from silicates[6]
Unsaturated, 75 gram reactors						
R1	275	1.949	0.442	0.63	0.83	0.49
R2	266	2.001	0.474	0.68	0.83	0.50
Saturated, 75 gram reactors						
R4	107	1.772	0.362	0.52	0.83	0.43
R5	101	1.754	0.363	0.52	0.83	0.41
1000 gram humidity cells						
HC7	362	23.03	4.18	5.96	11.00	6.07
HC8	367	23.36	4.30	6.13	11.00	6.23

[1] Time at which Ca to Na ratio equals the stoichiometric ratio for plagioclase (57/40=1.425)

[2, 3] Total Ca, Na mass release by the designated time period

[4] Estimated mass release of calcium associated with plagioclase, based the stoichiometric ratio

[5] Maximum amount of Ca with $CaCO_3$, (assumes 1.1 g $CaCO_3$/kg based on the maximum possible CO_2 content and assumption that all CO_2 is associated with $CaCO_3$)

[6] Remaining Ca that is associated with dissolution of other silicates (e.g. augite)

Table 11. Charge balance using average annual concentrations. Values reported in meq/L. For concentrations measured below the detection limit, half the detection limit was used.

Reactor/HC	Year	Ca	Mg	Na	K	SO4	Alk	Cations	Anions	Cations-Anions	Cations/Anions
Avg R1&R2 unsaturated reactors	1	0.273	0.098	0.010	0.046	0.234	0.148	0.427	0.382	0.045	1.12
	2	0.072	0.078	0.007	0.011	0.065	0.053	0.168	0.118	0.050	1.44
	3	0.040	0.058	0.008	0.004	0.042	0.050	0.110	0.092	0.018	1.20
	4	0.027	0.046	0.007	0.001	0.029	0.050	0.081	0.079	0.002	1.02
	5	0.024	0.041	0.007	0.003	0.022	0.061	0.074	0.083	-0.009	0.90
	6	0.019	0.035	0.006	0.008	0.017	0.055	0.068	0.072	-0.004	0.94
	7	0.020	0.031	0.008	0.009	0.015	0.050	0.068	0.065	0.003	1.05
	8	0.019	0.027	0.008	0.007	0.014	0.053	0.061	0.067	-0.006	0.91
	9	0.016	0.022	0.008	0.005	0.016	0.053	0.051	0.069	-0.018	0.74
	10	0.015	0.022	0.006	0.005	0.013	0.050	0.048	0.063	-0.015	0.76
Avg R4&R5 saturated reactors	1	0.295	0.127	0.012	0.035	0.269	0.204	0.468	0.473	-0.004	0.99
	2	0.063	0.087	0.014	0.016	0.155	0.050	0.180	0.205	-0.025	0.88
	3	0.032	0.041	0.011	0.009	0.064	0.050	0.093	0.114	-0.021	0.81
	4	0.024	0.035	0.009	0.007	0.047	0.050	0.075	0.097	-0.022	0.77
	5	0.020	0.030	0.008	0.007	0.028	0.053	0.065	0.081	-0.016	0.80
	6	0.016	0.025	0.007	0.005	0.020	0.055	0.053	0.075	-0.023	0.70
	7	0.017	0.026	0.008	0.006	0.015	0.054	0.057	0.069	-0.012	0.83
	8	0.018	0.024	0.008	0.005	0.015	0.050	0.055	0.065	-0.009	0.86
	9	0.015	0.017	0.008	0.004	0.011	0.050	0.044	0.061	-0.017	0.72
	10	0.014	0.019	0.008	0.004	0.012	0.050	0.044	0.062	-0.017	0.72
Avg HC7&HC8 humidity cells	1	0.648	0.194	0.023	0.079	0.483	0.490	0.944	0.973	-0.029	0.97
	2	0.437	0.070	0.014	0.048	0.307	0.212	0.569	0.519	0.050	1.10
	3	0.256	0.107	0.014	0.032	0.241	0.155	0.408	0.396	0.012	1.03
	4	0.143	0.124	0.014	0.026	0.210	0.067	0.307	0.276	0.031	1.11
	5	0.106	0.138	0.015	0.024	0.202	0.065	0.282	0.267	0.015	1.06
	6	0.078	0.140	0.013	0.019	0.210	0.060	0.250	0.271	-0.021	0.92
	7	0.066	0.141	0.016	0.019	0.204	0.053	0.242	0.257	-0.015	0.94
	8	0.071	0.159	0.017	0.021	0.212	0.050	0.267	0.262	0.005	1.02
	9	0.066	0.159	0.017	0.018	0.210	0.050	0.260	0.260	0.000	1.00
	10	0.060	0.149	0.015	0.017	0.203	0.050	0.241	0.253	-0.012	0.95

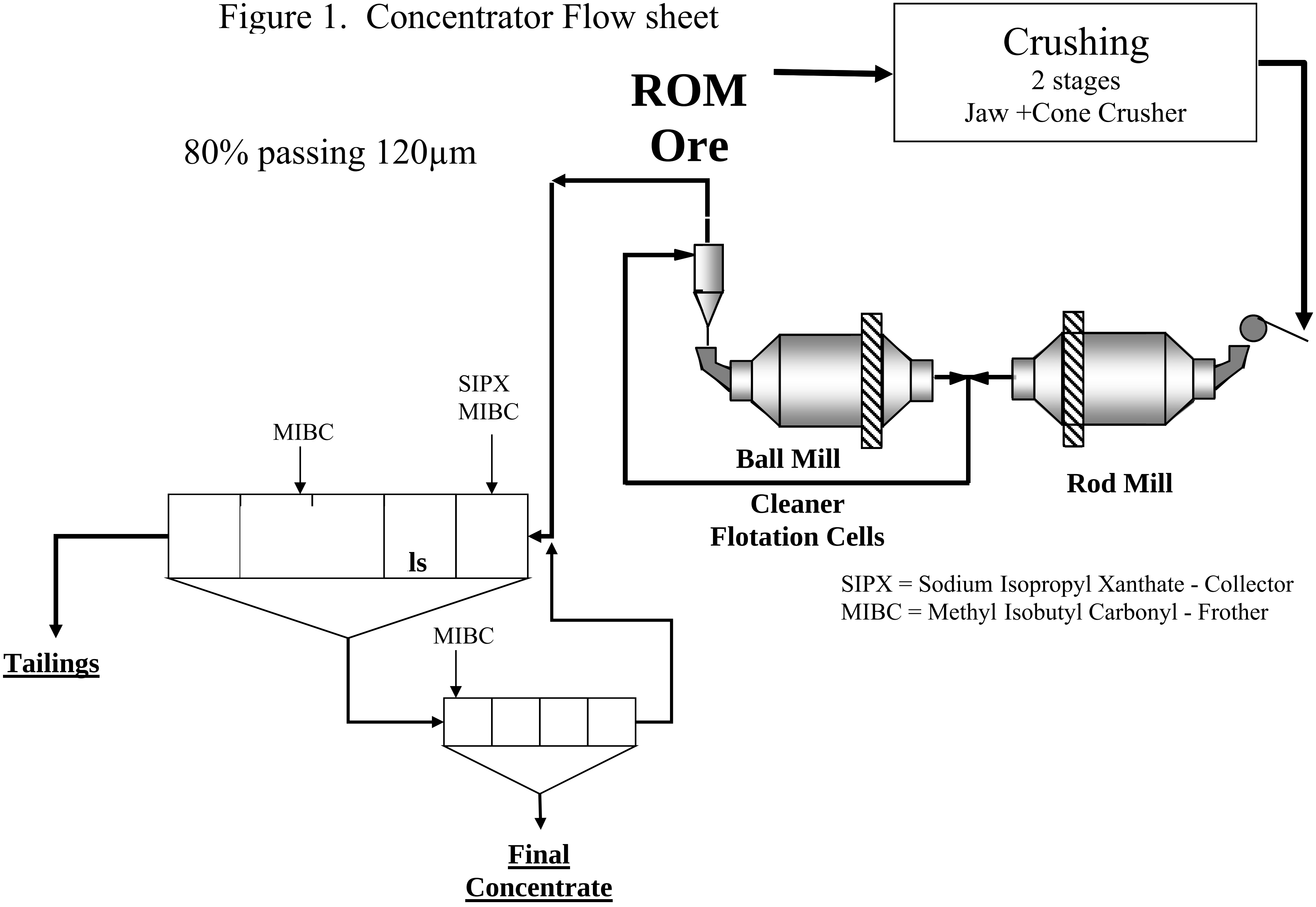


Figure 1. Concentrator Flow sheet

Figure 2. Schematic of small reactor.

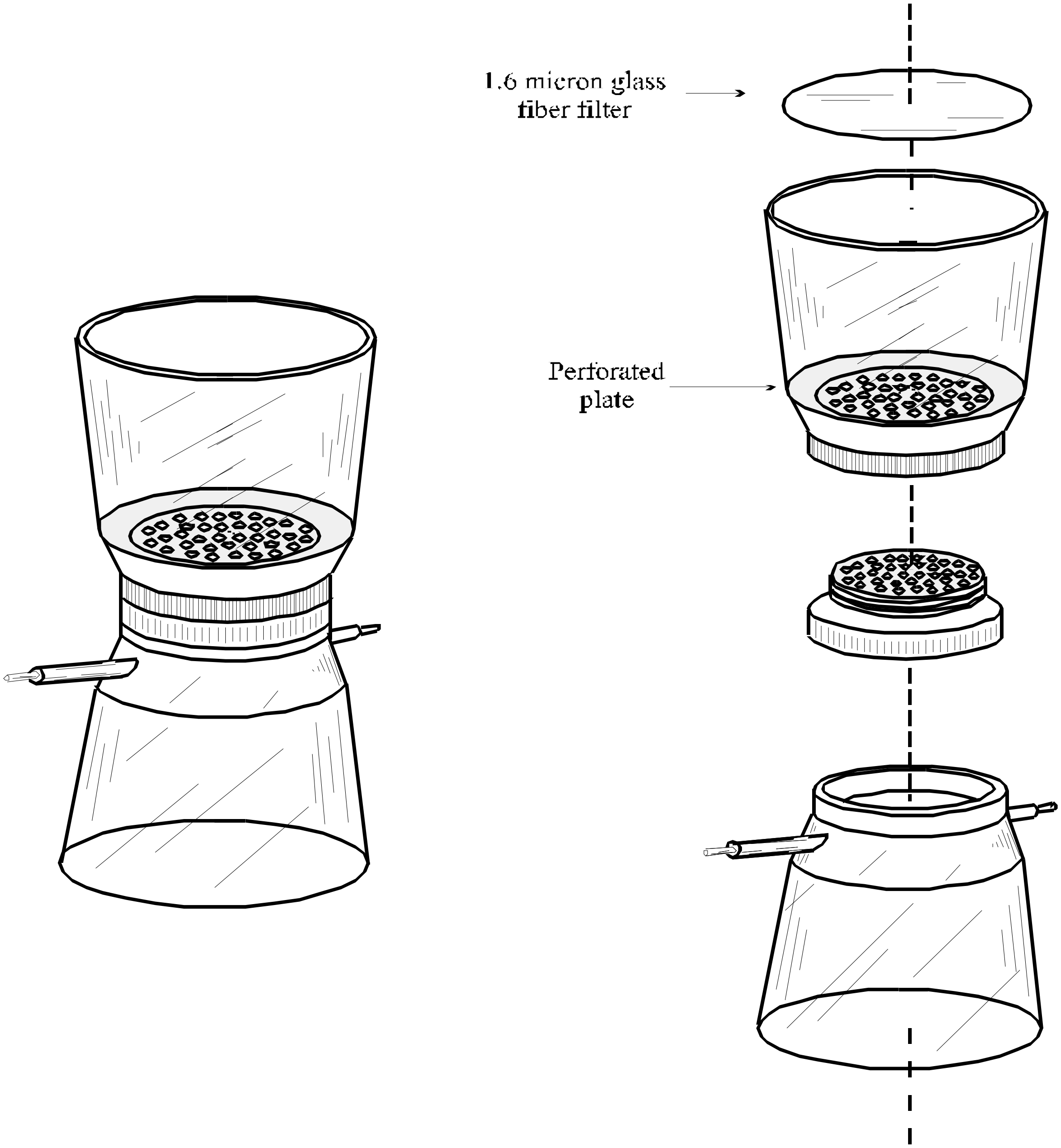


Figure 3. Schematic of humidity cell. All humidity cell materials are acrylic except the perforated plate (polyvinyl chloride) and the outlet pipe (high density polyethylene).

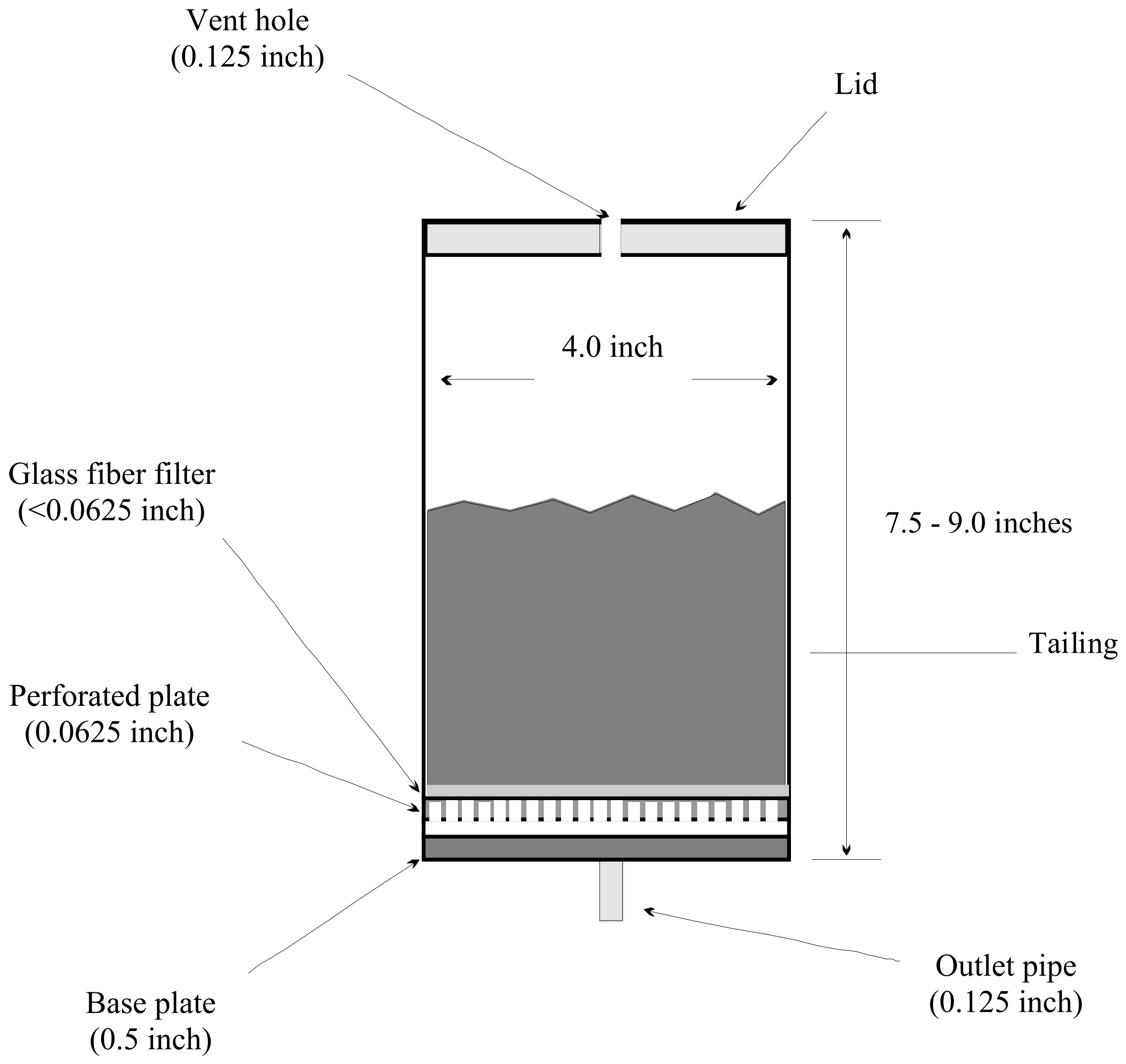


Figure 4. Drainage quality from the 75 g unsaturated tailings reactors (1, 2) replicated well.
Weeks 0-5 were excluded to improve resolution.
Red = reactor 1, Blue = reactor 2

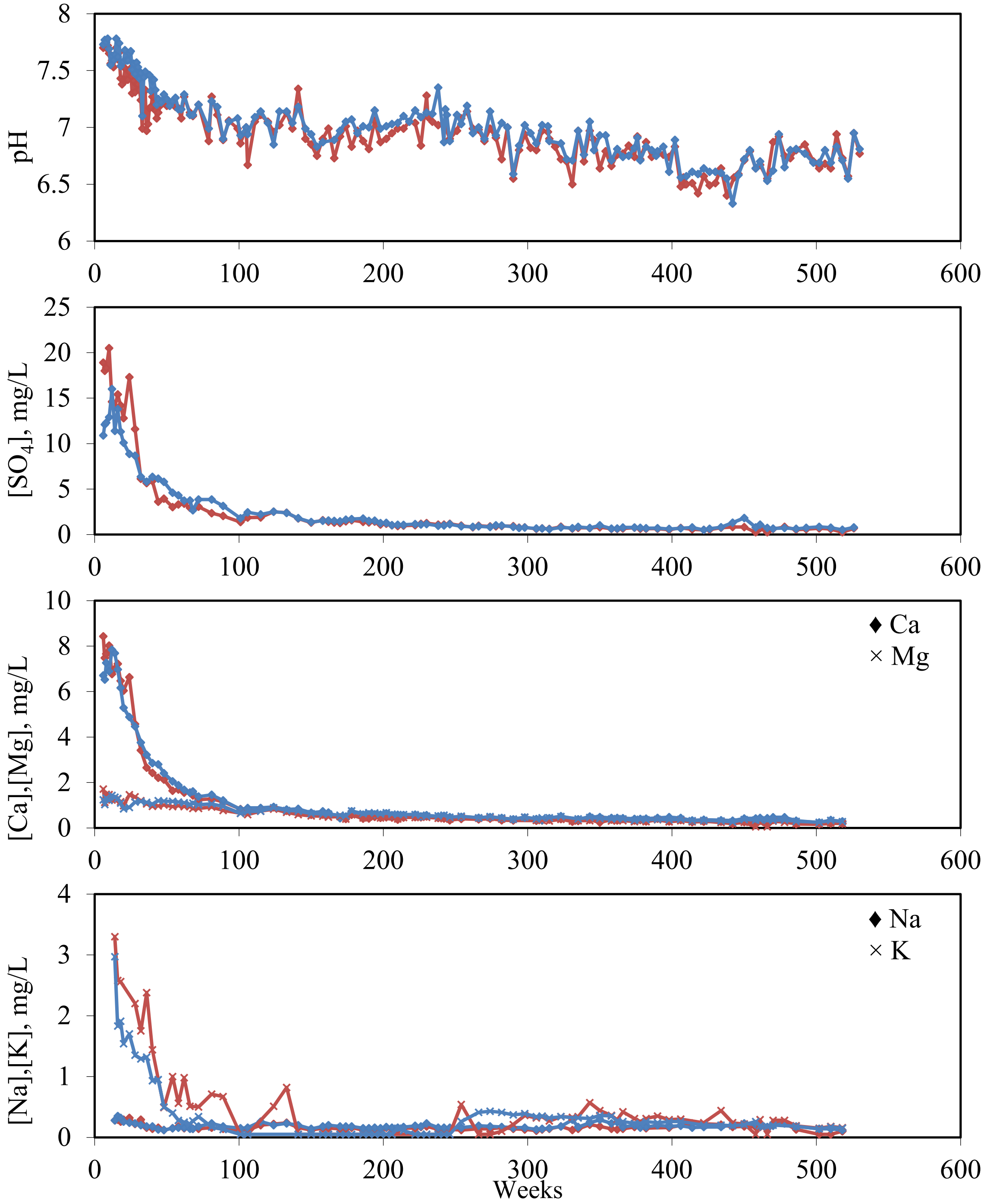


Figure 5. Drainage quality from the 75 g saturated tailings reactors (4, 5) replicated well.
Weeks 0-5 were excluded to improve resolution.
Red = reactor 4, Blue = reactor 5

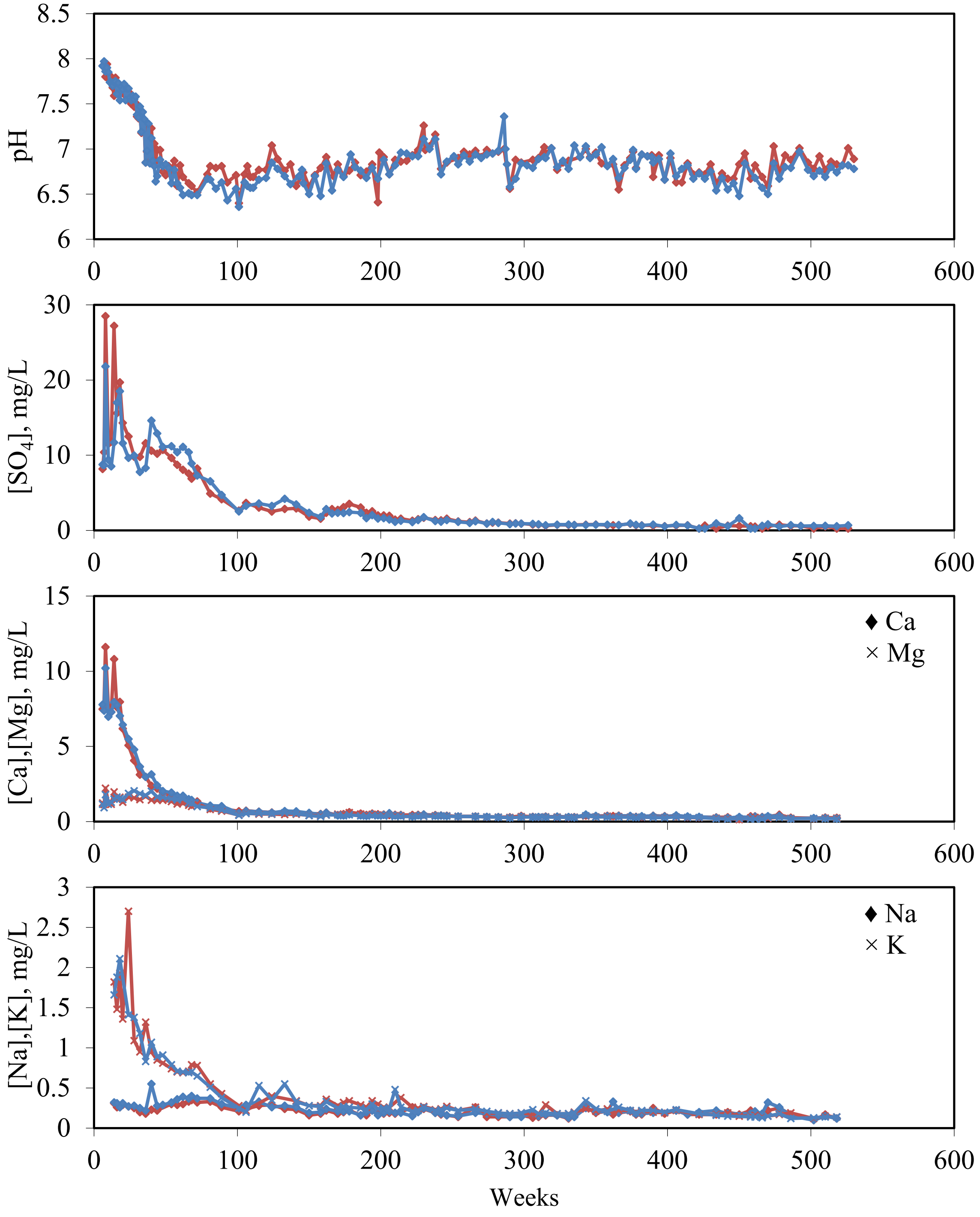


Figure 6. pH, alkalinity vs. time for 75 g reactors and 1000 g humidity cells. Weeks 0-5 were excluded to improve resolution.

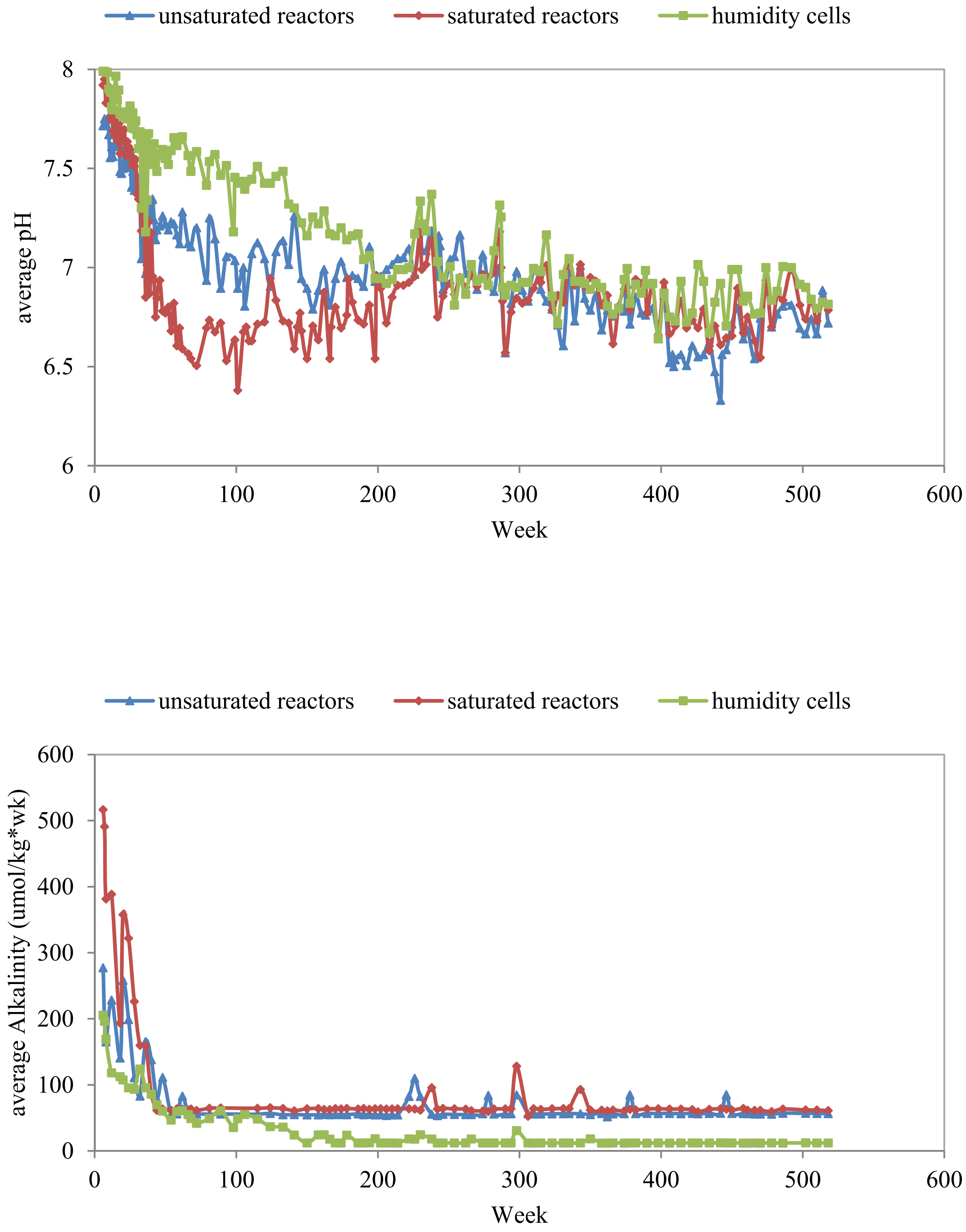
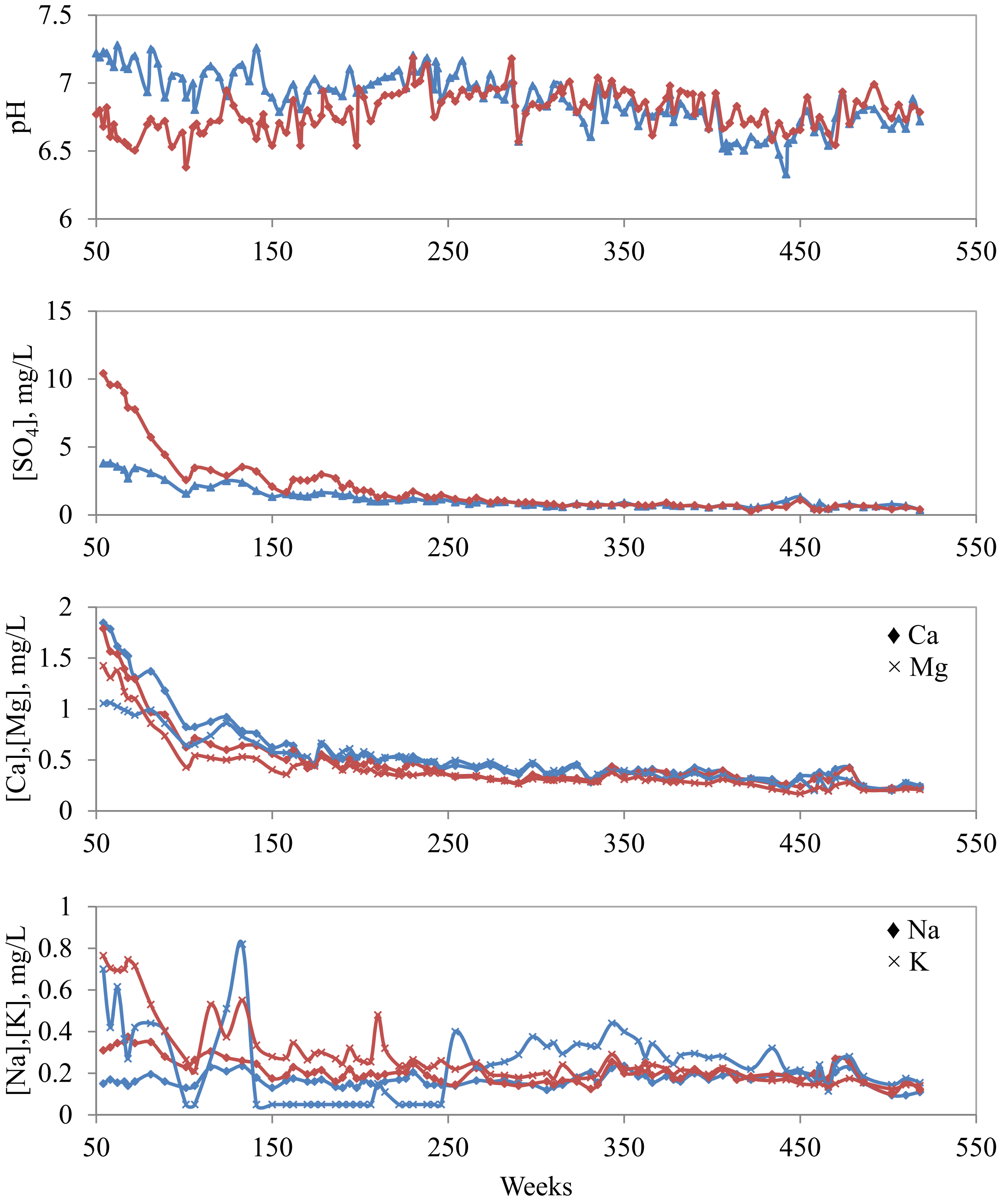


Figure 7. Average pH and SO_4, Ca, Mg, Na, K concentrations for unsaturated and saturated reactors. Weeks 0-50 were excluded to improve resolution. Similar comparison graphs for weeks 6-520 are located in Appendix 3 (Figure A3.33).

Red = saturated reactors, Blue = unsaturated reactors



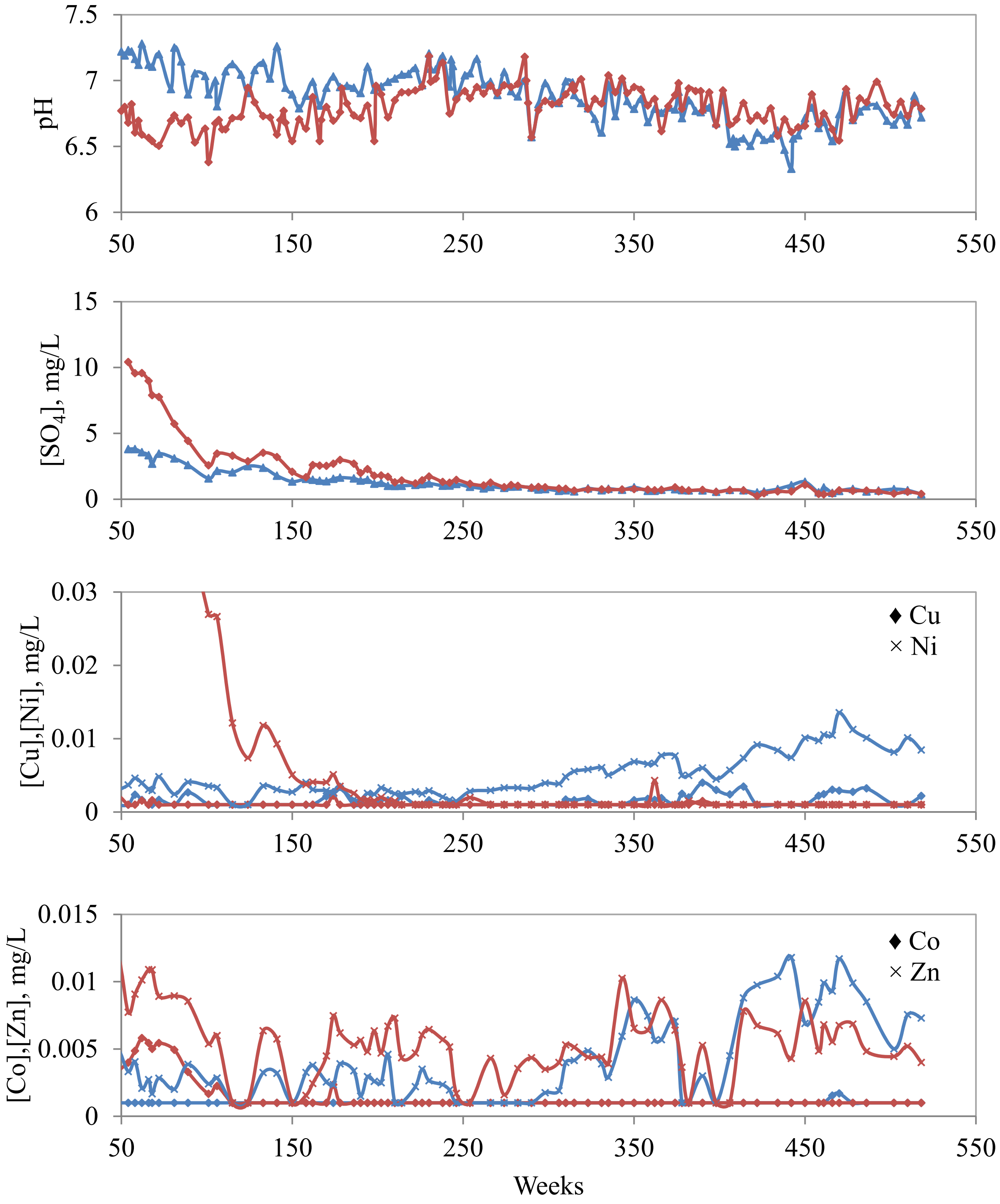


Figure 8. Average pH and SO_4, Cu, Ni, Co, Zn concentrations for unsaturated and saturated reactors. Weeks 0-50 were excluded to improve resolution. Similar comparison graphs for weeks 6-520 are located in Appendix 3 (Figure A3.34).

Red = saturated reactors, Blue = unsaturated reactors

Figure 9. Nickel and pH vs. time for the 75 g unsaturated reactor 1 and saturated reactor 4.
Weeks 0-5 were excluded to improve resolution.
Red = reactor 1 unsaturated, Blue = reactor 4 saturated

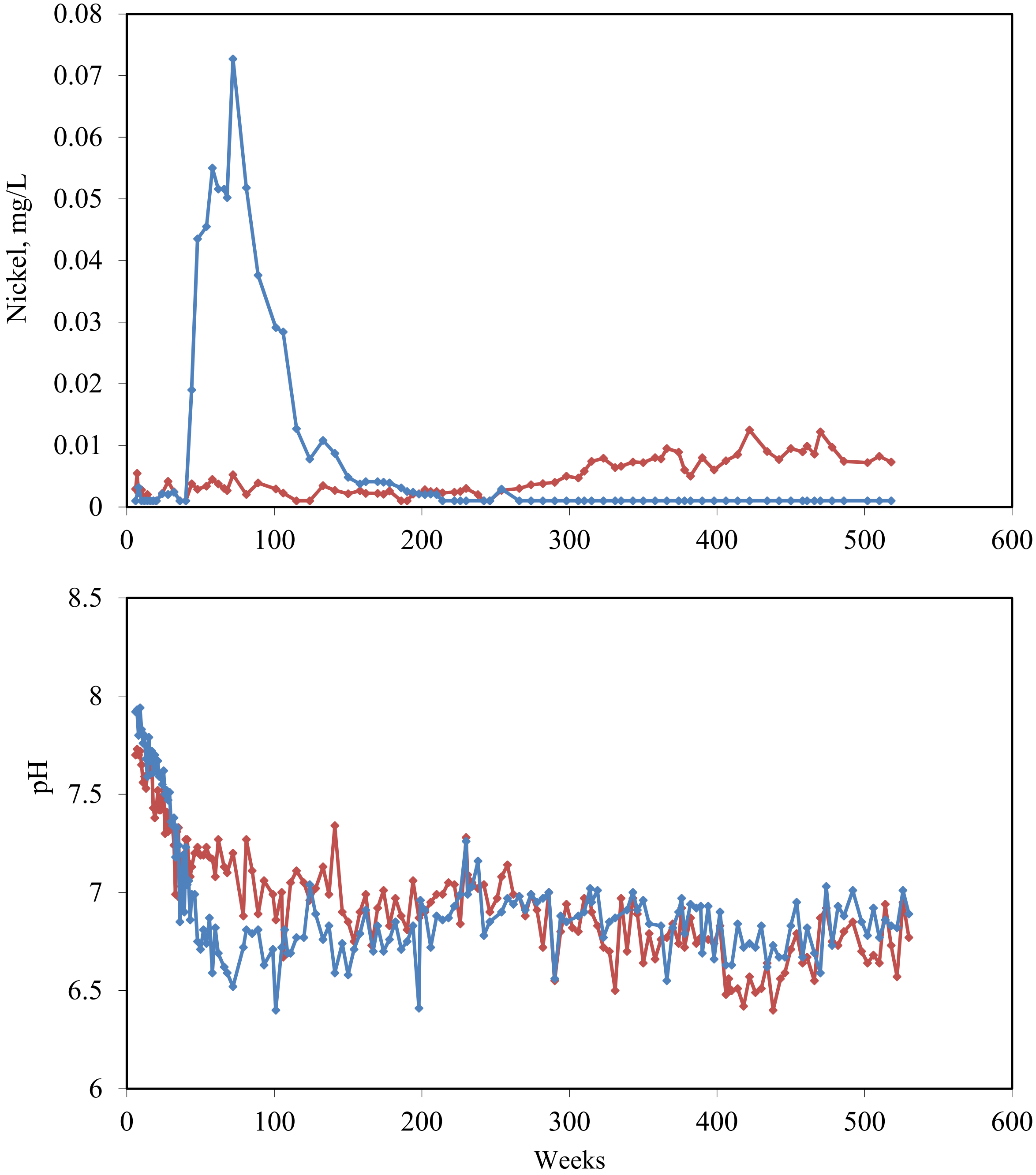


Figure 10. Cobalt and pH vs. time for the 75 g tailings unsaturated reactor 1 and saturated reactor 4. Weeks 0-5 were excluded to improve resolution.
Red = reactor 1 unsaturated, Blue = reactor 4 saturated

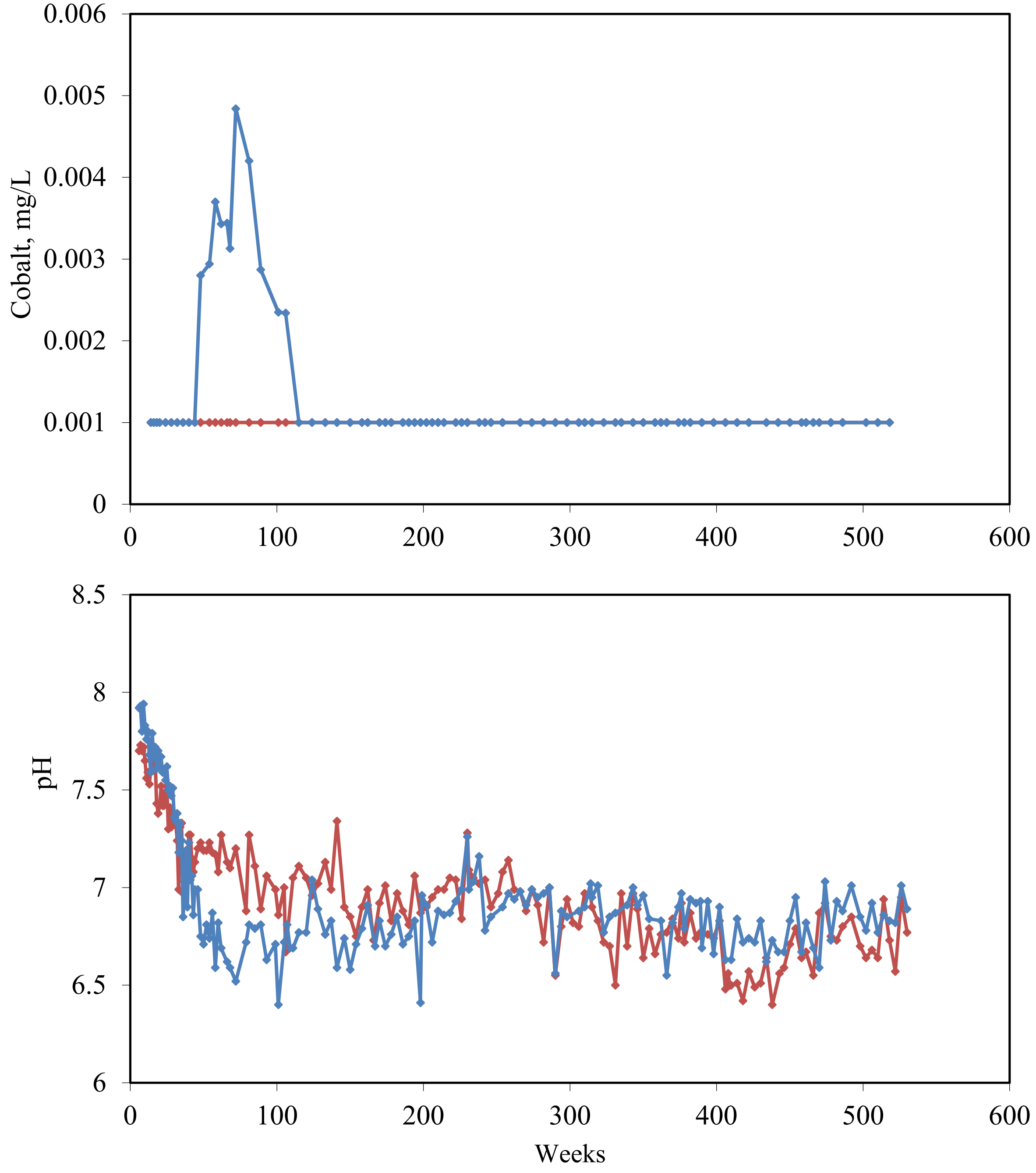


Figure 11. Drainage quality from the 1000 g tailings humidity cells (7, 8) replicated well.
Weeks 0-5 were excluded to improve resolution.
Red = humidity cell 7, Blue = humidity cell 8

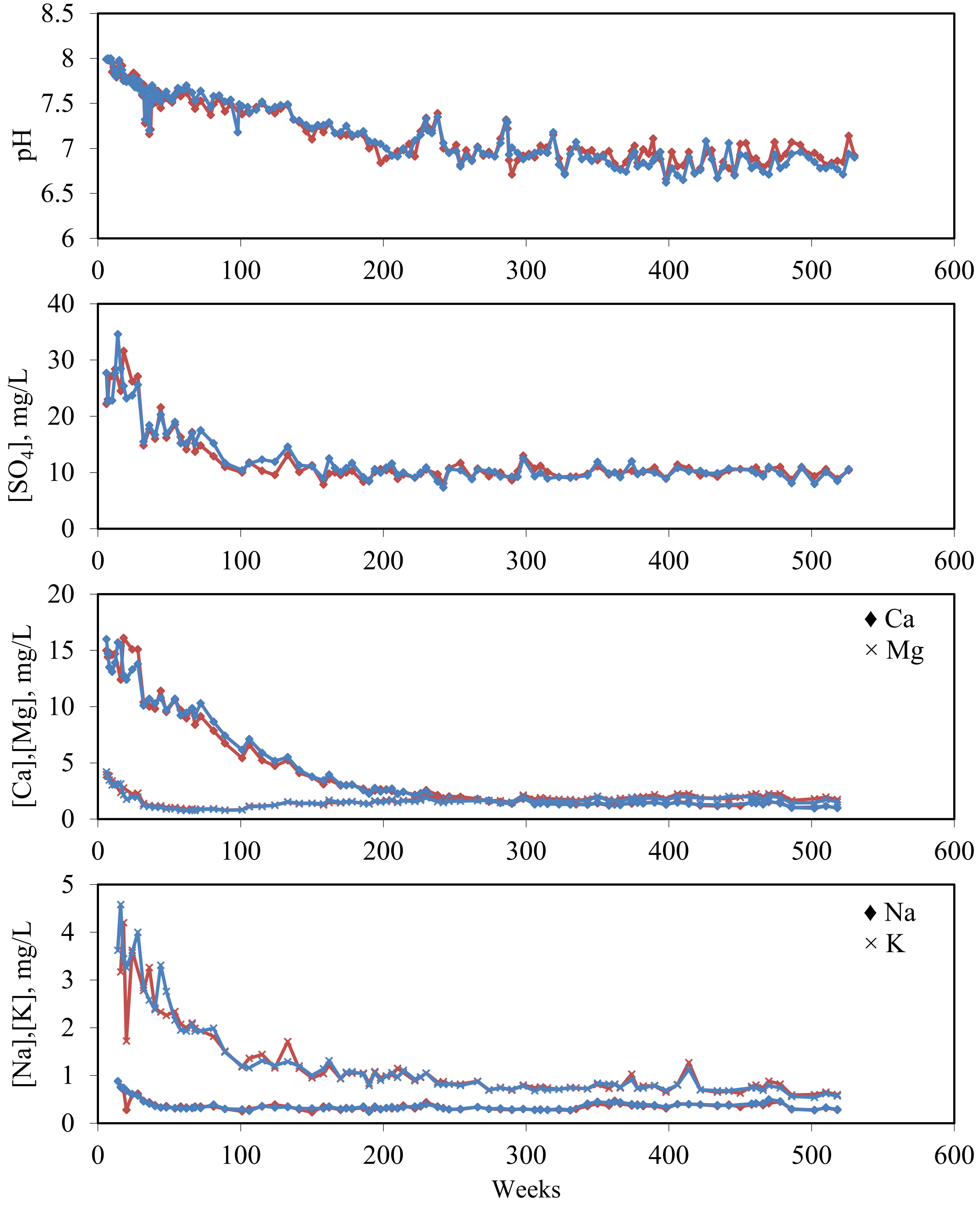


Figure 12. Average pH, SO_4, Ca, Mg, Na, K vs. time for saturated reactors and humidity cells. Weeks 0-50 were excluded to improve resolution. Similar comparison graphs for weeks 6-520 are located in Appendix 3 (Figure A3.35).

Red = saturated reactors, Blue = humidity cells

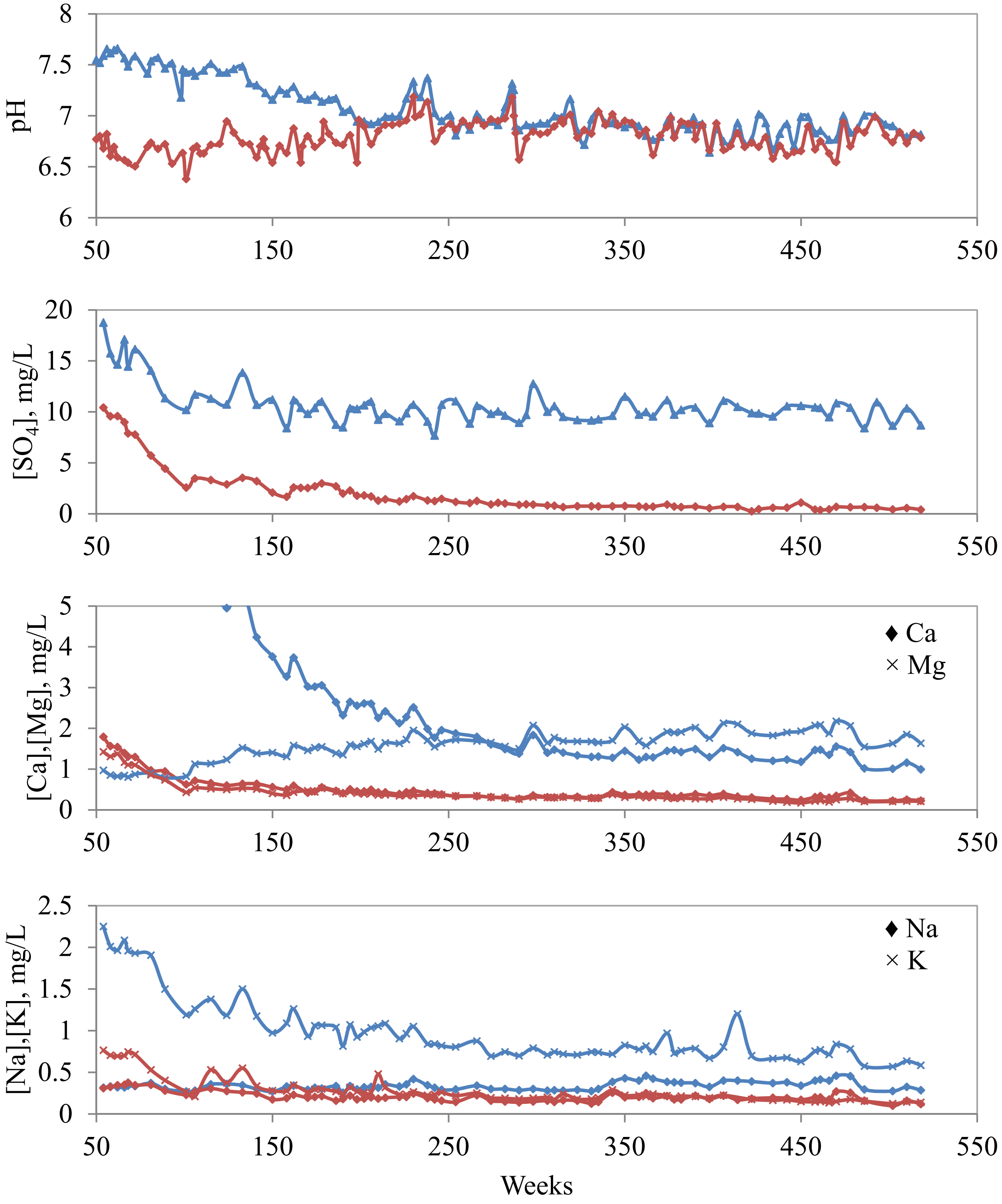


Figure 13. Average pH, SO_4, Cu, Ni, Co, Zn vs. time for saturated reactors and humidity cells. Weeks 0-50 were excluded to improve resolution. Similar comparison graphs for weeks 6-520 are located in Appendix 3 (Figure A3.36).

Red = saturated reactors, Blue = humidity cells

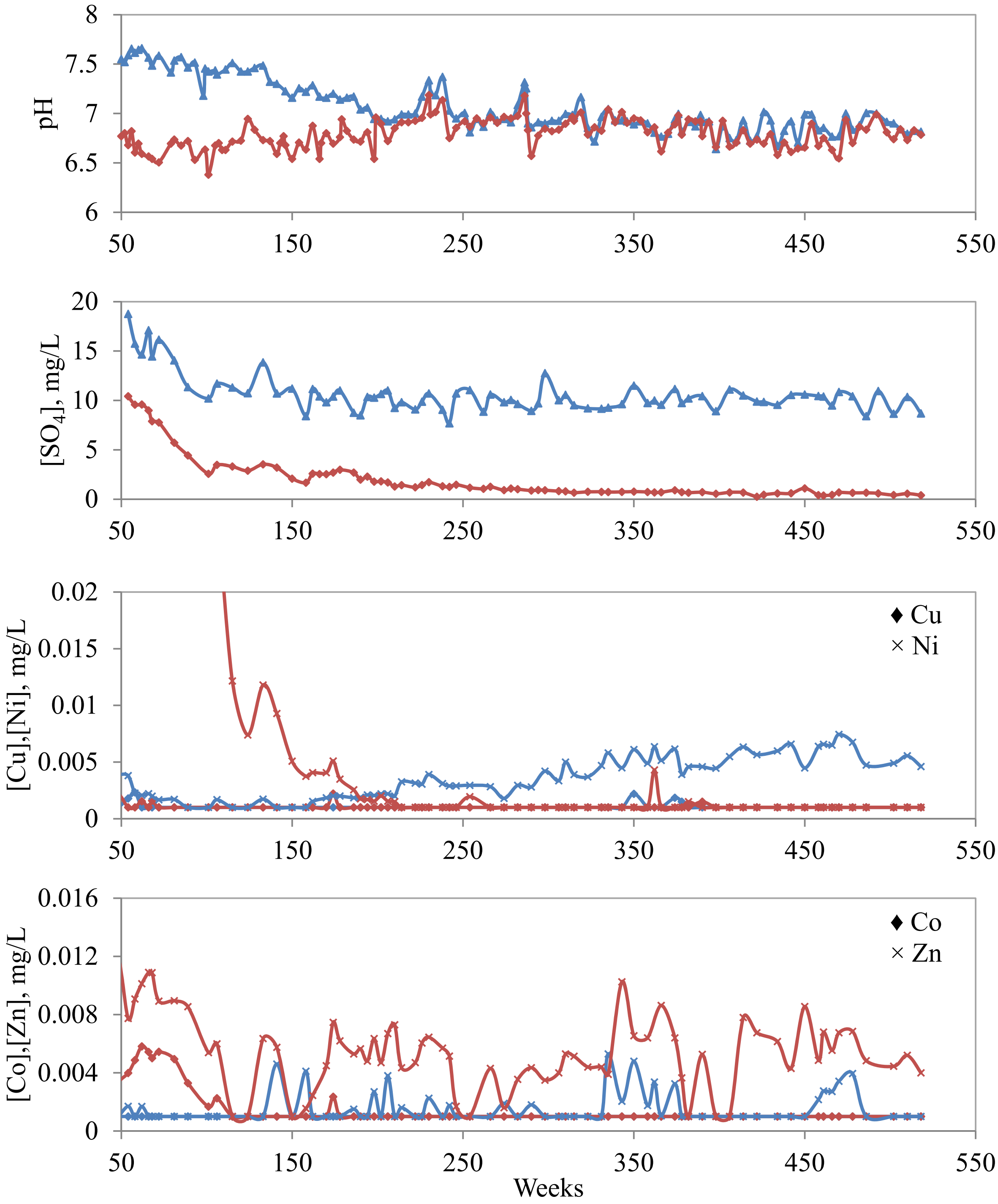


Figure 14. Sulfate release rates per gram sulfur remaining vs. time for reactors and humidity cells. Weeks 0-5 were excluded to improve resolution.

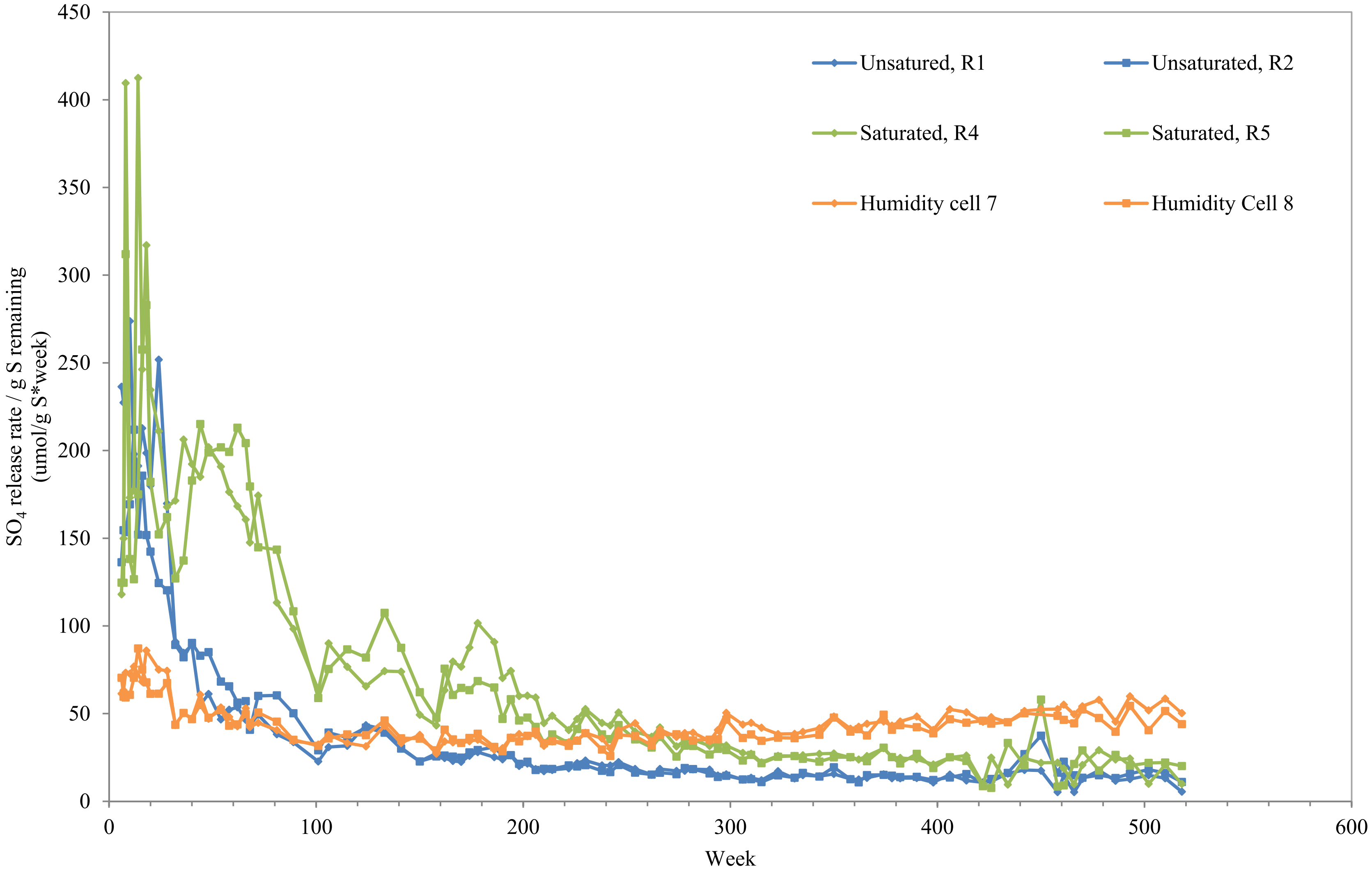


Figure 15. Calcium, alkalinity, and sulfate release rates vs. time for reactors, weeks 0-50.

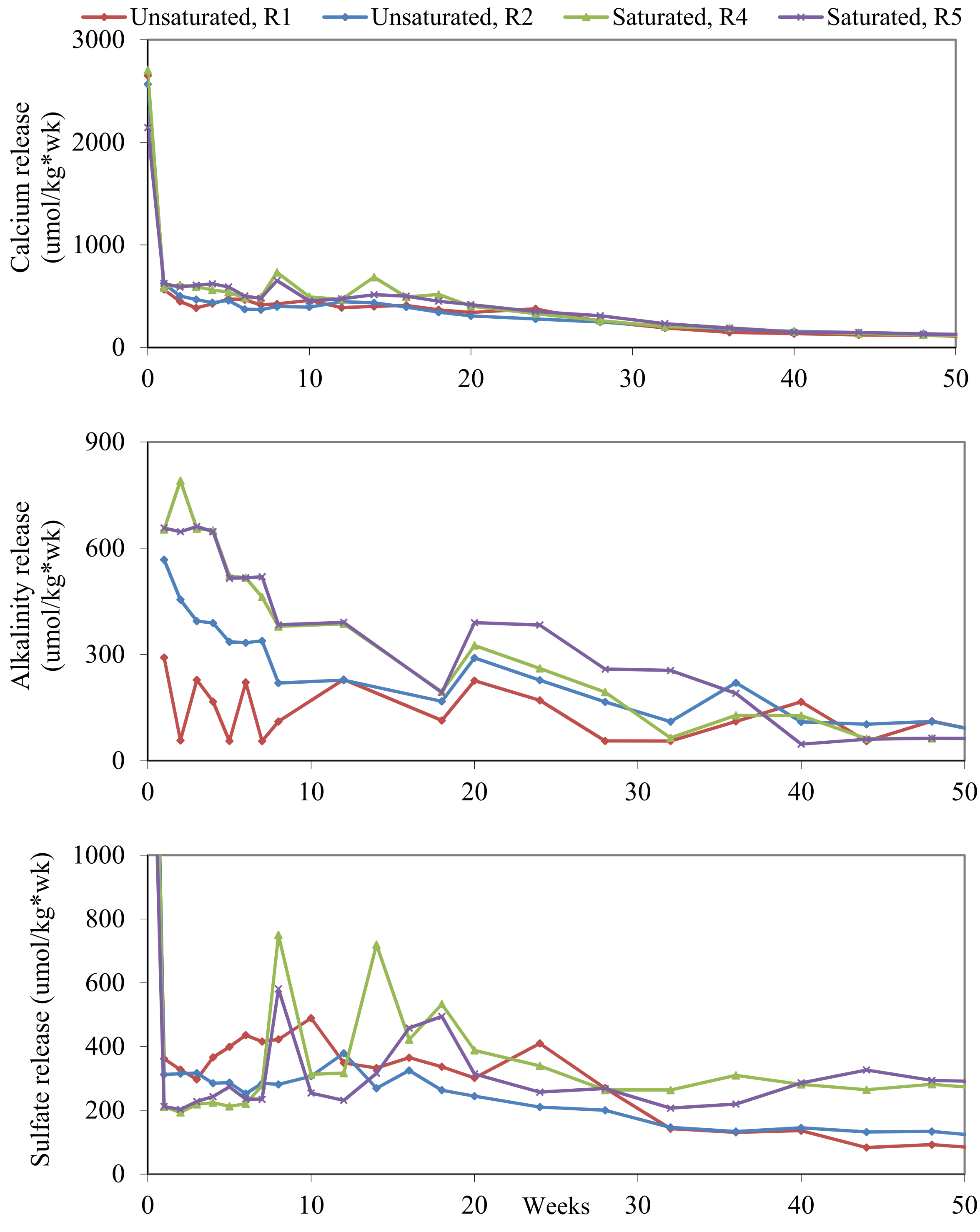


Figure 16. Calcium, alkalinity, and sulfate cumulative mass release vs. time for the 75 gram reactors, weeks 0-50. Assumed alkalinity equaled zero once it reached detection limit between weeks 40-50.