NON-FERROUS MINE WASTE CHARACTERIZATION PROJECT

Project Extension Status

Minnesota Department of Natural Resources Division of Minerals Reclamation Section

June 1999

NON-FERROUS MINE WASTE CHARACTERIZATION PROJECT

Project Extension Status

Kim Lapakko Jennifer Engstrom David Antonson

Minnesota Department of Natural Resources Division of Minerals Reclamation Section

June 1999

Table of Contents

List	of Tables	iii
List	of Figures	vi
1.	EXECUTIVE SUM	MARY
2.	INTRODUCTION .	
3.	OBJECTIVES	
4.	BACKGROUND: N	1INE WASTE DISSOLUTION
5.	METHODS 5.1. Materials 5.2. Procedure 5.2.1. 5.2.2. 5.3. Calculation	12sAmbient Temperature Experiment12Elevated Temperature Experiment14ns16
б.	RESULTS AND DIS 6.1. Introduction 6.2. Solids Ann 6.3. Ambient 7 6.3.1 6.3.2 6.3.3	SCUSSION 16 on 16 alysis 18 Temperature Experiment 19 Introduction 19 Case 1 Samples: Low to High Acid Production Potential (AP), No 19 Case 1 Samples: Low to High Acid Production Potential (AP), No 19 Case 2 Samples (T9, T6): Moderate to High AP, Low to High NP 19
	6.3.4 6.3.5 6.3.6 6.3.7 6.3.8	 Case 3 Samples (T2, T10): High AP, High NP
	6.4.1 6.4.2 6.4.3	 Introduction

Table of Contents

·	6.4.4. 6.4.5. 6.4.6. 6.4.7.	Case 3 Samples (T1, T4, T8, T12): High AP, High NP
7.	ACKNOWLEDGEMEN	NTS
8.	REFERENCES	

.

.

List of Tables

Table 1.	Particle size distribution of tailings in weight percent
Table 2.	Chemical analysis for regulatory parameters in tailing samples
Table 3.	Mineralogic composition of tailings in weight percent
Table 4.	Major host rock composition (in weight percent) of non-ferrous tailings
Table 5.	Mineralogic acid potential (AP) and neutralization potential (NP[(Ca/Mg)CO ₃]) for tailings
Table 6.	Total sulfur, sulfate, and sulfide analyses conducted by three laboratories on the non-ferrous solids
Table 7.	Ambient Temperature Experiment summary of reactor sampling periods
Table 8.	Ambient Temperature Experiment sampling frequency
Table 9.	Pumping time, duration, and volume for T2 and 1.64% S Duluth Complex rock in the Short Rinse Interval Experiment
Table 10.	Elevated Temperature Experiment summary of reactor sampling periods
Table 11.	Elevated Temperature Experiment sampling frequency
Table 12.	Rates of release (in millimoles per week) for solids T9 and T6 of the Ambient Temperature Experiment for weeks 0-290
Table 13.	Percent depletion of acid potential and neutralization potential from the Ambient Temperature Experiment in 290 weeks
Table 14.	Selected mineral names and chemical compositions
Table 15.	Rates of release for solids T2 and T10 of the Ambient Temperature Experiment for weeks0-290
Table 16.	Oxidation rates for weeks 20 to 57 expressed in terms of pyrite mass and surface area

;

List of Tables

Table 17.	Total years of dissolution for depletion of neutralization potential and acid production potential based on the rates of release during the Ambient Temperature Experiment
Table 18.	Time at which sulfate release from the Elevated Temperature Experiment exceeded sulfate generated during sample storage, as determined from results of the Ambient Temperature Experiment
Table 19.	Temporal variation of sulfate, calcium, and magnesium concentrations in the Elevated Temperature Experiment
Table 20.	Comparison of rates of release for sulfate and calcium plus magnesium from the Ambient Temperature and Elevated Temperature Experiments
Table 21.	Case 2 Samples: Rates of release of sulfate, calcium plus magnesium, calcium, and magnesium for the Elevated Temperature Experiment for the solids that generated acidic drainage
Table 22.	Percent depletion of acid production potential and neutralization potential from the Elevated Temperature Experiment for the three solids that produced acidic drainage, at the point at which the drainage became acidic
Table 23.	Percent AP released during the Elevated Temperature Experiment
Table 24.	Case 3 Samples: Rates of release (millimoles per week) of sulfate, calcium plus magnesium, calcium, and magnesium in the Elevated Temperature Experiment from solids T1, T4, and T8
Table 25.	Initial sulfur, sulfate, sulfide, and iron sulfide minerals contents and sulfate release rates (mmol/wk) for the Wet-Dry Cycle and the Elevated Temperature Tests for the samples in the Environmental Protection Agency Project
Table 26.	Initial sulfur, sulfate, sulfide, pyrite, pyrrhotite contents, AP released, and ratio of AP released for the Wet-Dry Cycle (WD; 1-132 weeks) and the Elevated Temperature (ET; 1-130/131 weeks) Tests for the samples in the Environmental Protection Project73
Table 27.	Percent NP released during the Elevated Temperature Experiment
Table 28.	Total years of dissolution for depletion of neutralization potential and acid production potential based on the rates of release during the Elevated Temperature Experiment

List of Tables

- Table 30.Cumulative mass release during the one rinse per week versus two rinses per week during
the Elevated Temperature Experiment weeks 49-64 for solids T2 and T10.77

List of Figures

Figure 1.	Ambient Temperature Experiment reactor design
Figure 2.	Temperature and relative humidity versus time for the Ambient Temperature Experiment
Figure 3.	Water addition system and reactor design for the Short Rinse Interval Experiment
Figure 4.	Elevated Temperature Experiment reactor design
Figure 5.	pH, sulfate, calcium, and magnesium concentrations for the Ambient Temperature Experiment for solid T9, reactor 17: weeks 5-290
Figure 6.	Sulfate, calcium plus magnesium, calcium, and magnesium cumulative mass release for the Ambient Temperature Experiment, solid T9: weeks 0-290
Figure 7.	pH, sulfate, calcium, and magnesium concentrations for the Ambient Temperature Experiment for solid T6, reactor 11: weeks 5-290
Figure 8.	Sulfate, calcium plus magnesium, calcium, and magnesium cumulative mass release for the Ambient Temperature Experiment, solid T6: weeks 0-290
Figure 9.	pH, sulfate, calcium, and magnesium concentrations for the Ambient Temperature Experiment for solid T2, reactor 3: weeks 5-290
Figure 10	.pH, sulfate, calcium, and magnesium concentrations for the Ambient Temperature Experiment for solid T10, reactor 19: weeks 5-290
Figure 11	.Sulfate concentrations for T2 and T10 for the Ambient Temperature Experiment for weeks 5-290
Figure 12	.Initial and remaining AP[sulfide] and NP[(Ca/Mg)CO ₃] for the Ambient Temperature Experiment, weeks 0-290
Figure 13	.pH and net alkalinity for the Elevated Temperature Experiment for solid T9, reactor 9: weeks 2-232
Figure 14	Specific conductance, sulfate, calcium, and magnesium concentrations for the Elevated Temperature Experiment for solid T9, reactor 9: weeks 2-232

List of Figures

Figure 15. Sulfate, calcium plus magnesium, calcium, and magnesium cumulative mass release for the Elevated Temperature Experiment, solid T9, reactor 9: weeks 2-232
Figure 16.pH, sulfate, calcium, and magnesium concentrations for the Elevated Temperature Experiment for solid T2, reactor 15: weeks 2-256
Figure 17. Specific conductance and net alkalinity for the Elevated Temperature Experiment for solid T2, reactor 15: weeks 2-256
Figure 18. pH and net alkalinity for the Elevated Temperature Experiment for solid T10, reactor 11: weeks 2-232
Figure 19. Specific conductance, sulfate, calcium, and magnesium concentrations for the Elevated Temperature Experiment for solid T10, reactor 11: weeks 2-232
Figure 20. pH and net alkalinity for the Elevated Temperature Experiment for solid T1, reactor 3: weeks 2-232
Figure 21.pH and net alkalinity for the Elevated Temperature Experiment for solid T4, reactor 5: weeks 2-232
Figure 22. pH and net alkalinity for the Elevated Temperature Experiment for solid T8, reactor 7: weeks 2-256
Figure 23. Specific conductance, sulfate, calcium, and magnesium for the Elevated Temperature Experiment for solid T1, reactor 3: weeks 2-232
Figure 24. Specific conductance, sulfate, calcium, and magnesium for the Elevated Temperature Experiment for solid T4, reactor 5: weeks 2-232
Figure 25. Specific conductance, sulfate, calcium, and magnesium for the Elevated Temperature Experiment for solid T8, reactor 7: weeks 2-256
Figure 26.pH, sulfate, calcium, and magnesium concentrations for the Elevated Temperature Experiment for solid T12, reactor 1: weeks 2-232
Figure 27. Percent total sulfur remaining at weeks 6, 10, 20, 40, 100, and 200 for the odd numbered reactors of the Elevated Temperature Experiment

1. EXECUTIVE SUMMARY

This report describes the third phase of a study on potential future Minnesota mine wastes. The study was funded by the Minnesota Minerals Coordinating Committee and the Minnesota Department of Natural Resources, Division of Minerals. The general objective of the study is to determine the long term drainage quality from abandoned tailings which could be generated by gold and/or titanium mining in Minnesota. Implicit in this objective is determination of the relationship between the solid-phase characteristics of the tailings and their drainage quality.

In the first phase, ten tailings samples from active North American gold mines and two titanium tailings generated in pilot plant tests were characterized (particle size, chemistry, mineralogy, static tests) and subjected to dissolution testing at room temperature for 52 weeks (Lapakko 1991). Although the drainage from all of the tailings was in the neutral to basic range, static tests (Acid Base Accounting, Modified Acid Base Accounting, Alkaline Production Potential: Sulfur Ratio) indicated that, over a longer period of dissolution, two of the samples (T9, T2) had potential to produce acidic drainage and two others (T6, T10) had marginal potential for producing acidic drainage. However, mineralogic analyses indicated the static tests overestimated, by roughly 50 percent, the neutralization potential present as calcium and magnesium carbonate in T6. Consequently, T6 had a higher potential for producing acidic drainage than indicated by the static tests.

For the remaining six gold tailings samples (T1, T3, T4, T5, T7, T8), the amount of calcium and magnesium carbonate minerals was deemed adequate to neutralize the acid produced by oxidation of the iron sulfides present. This assessment was based on net mineralogic neutralization potentials $(NP[(Ca/Mg)CO_3] - AP(S^{2-}))$ of 47 to 220 mg/g CaCO₃ rock and NP/AP ratios of 2.0 to 12 (more recent data indicates a net NP range of 44 to 230 mg/g CaCO₃ and a ratio of 2.1 to 92). The assessment assumes that 1) all neutralization potential is available for neutralizing acid; 2) neutralizing minerals will dissolve to neutralize acid from iron sulfide mineral oxidation; 3) acid neutralizing minerals will dissolve only to neutralize acid from iron sulfide oxidation; and 4) neutralizing mineral dissolution will maintain pH at 6.0 or greater. Elevated concentrations of arsenic, antimony, and molybdenum were detected in drainage from some of the samples and present the greatest potential impact of non-acidic drainage.

In the second phase (Lapakko 1993), it was concluded that the tailings collected for the study provide the best available approximation of tailings which might be generated if a gold mine were developed at a greenstone belt exploration site in Minnesota. The titanium tailings also provided the similar best available approximation for tailings from future titanium mining in Minnesota. Dissolution tests at ambient temperature were continued from phase one, methods of removing trace metals from tailings drainage were investigated, dissolution testing at 100°C was initiated, and the effects of other predictive test design variables on results were investigated.

Dissolution testing at 25°C of four tailings samples examined in phase 1 (T2, T6, T9, T10) was extended to a total period of record of 151 weeks (Ambient Temperature Experiment). The pH of drainage from one tailings sample (T9) decreased below 6.0 after 122 weeks and reached 3.45 at 151

weeks. The neutralization potential present as calcium and magnesium carbonate (NP[Ca/Mg)CO₃]) was 14 mg/g CaCO₃ and was present entirely as calcite. At week 122 the observed releases of calcium and magnesium in drainage represented dissolution of 14.6 and 1.34 mg/g CaCO₃, respectively. The total of 16 mg/g CaCO₃ exceeded the NP[(Ca/Mg)CO₃]. Whereas it is likely that most, if not all, of this discrepancy is due to limitations in solid-phase and aqueous-phase analytical resolution, host rock mineral dissolution may have contributed to the difference. Drainage from T2, T6, and T10 remained neutral. Based on the mineralogy of these three samples and their observed rates of iron sulfide oxidation and calcium/magnesium carbonate dissolution, their drainage could become acidic after six to fourteen years of dissolution.

Specific surface area and scanning electron microscope analyses of the pyrite present in some of the samples indicated that the surface area of the pyrite was the critical variable controlling the rate of pyrite oxidation. Trace metal concentrations in the laboratory drainage during the previous phase provided a good indicator of potential for elevated concentrations of antimony, arsenic, copper, lead, molybdenum, nickel, and zinc in the field. If elevated metal concentrations did occur at an operation, standard lime treatment would be adequate for removal of most metals from drainage. However, addition of ferric sulfate in the treatment process would be required for removal of antimony, arsenic, and molybdenum, which tend to present in solution as oxyanions. Variations of this process are used at the Giant and Con Mines near Yellowknife, Northwest Territories (Legge 1993) and at the David Bell Mine near Marathon, Ontario (Meyer 1992).

The rates of sulfide mineral oxidation for individual periods at 100°C (48-week Elevated Temperature Experiment on T1, T2, T4, T8, T9, T10, T12) were generally 15 to 50 times the average rate for weeks 20 to 57 at room temperature. This accelerated dissolution indicates that tests at high temperatures may predict the quality of drainage from mine wastes in a shorter time frame than tests run at room temperature. For example, drainage from T9 acidified after eight weeks of testing at 100°C as compared with the 122 weeks elapsed at 25°C in the Ambient Temperature Experiment. Samples T1, T4, T8, and T12 produced drainage pH values which were continuously above 6.0, while the pH of drainages from T2 and T10 oscillated between circumneutral and acidic over time. Predictive implications of this oscillation are unclear and, consequently, caution is recommended before selecting elevated temperature dissolution for mine waste drainage quality prediction.

The effects of the mine waste sample mass (75 to 1500 g with a constant rinse volume) and rinse interval (time between rinses) on laboratory predictive test results were described. The acid neutralized by calcium and magnesium carbonate dissolution (moles H^+ neutralized/mole carbonate mineral dissolved) increased from less than one at the 75 g mine waste mass to a maximum of two at higher masses. From the perspective of the Law of Mass Action, the extent of acid neutralized per mole of carbonate mineral dissolved increased with the rate of acid generation. The apparent rate of iron sulfide oxidation decreased as the rinse interval duration increased beyond one week. Consequently, the use of rinse intervals longer than one week would increase the time required for drainage quality predictive tests. The apparent rate of iron sulfide oxidation did not increase at rinsing intervals shorter than one week.

In the third phase of the project, funded solely by the Minnesota Department of Natural Resources, Division of Minerals, the dissolution of the four tailings samples (T2, T6, T9, T10) in the Ambient Temperature Experiment was extended from 151 to 290 weeks, and dissolution of seven tailings samples (T1, T2, T4, T8, T9, T10, T12) in the Elevated Temperature Experiment was extended from 48 to 232 weeks.

The significant results of this project extension are as follows.

Ambient Temperature Experiment

- Additional data were collected which support the contention that the quality of drainage in short term dissolution experiments may not accurately simulate the long-term drainage quality of mine wastes after mine abandonment. In phase two, the pH of drainage from sample T9 decreased below 6.0 after 122 weeks of dissolution and, in phase 3, stabilized in the range of 3.0 to 3.2 from week 165 to 290. The drainage from sample T6 was in the typical range of 7.9 to 8.1 until week 235, at which time it began to gradually decrease. This drainage pH dropped below 6.0 at week 284 and reached 4.49 at week 290. At the time of acidification for solids T9 and T6, the remnant FeS₂ contents were 6.19% (or 3.31% S²⁻) and 2.49% (or 1.33% S²⁻), respectively. In both cases, such acidification would be expected during the long term after mine abandonment for tailings exposed to wet-dry cycling in the environment. Short term laboratory results would not have simulated this long term behavior, but rather would have provided a record of only neutral drainage.
- 2. Additional data were collected to compare the neutralization potential release observed empirically in dissolution experiments (empirical neutralization potential or ENP) with the neutralization potential determined based on the calcium and magnesium carbonate content of the solid (NP[(Ca/Mg)CO₃]). This comparison allows assessment of the extent to which calcium and magnesium carbonates present in mine waste react to neutralize acid. In phase two, the ENP of T9 was calculated as 16 mg/g CaCO₃ as compared with an NP[(Ca/Mg)CO₃] of 14 mg/g CaCO₃, all of which was reported as calcite. While this apparent discrepancy could have been the result of analytical limitations, dissolution of feldspar, clay, and amphibole minerals present in the tailings may have also contributed to acid neutralization.

In phase three, the ENP of sample T6 was calculated as 40 mg/g $CaCO_3$ as compared to an NP[(Ca/Mg)CO₃] of 45 mg/g CaCO₃. The lower neutralization observed in the dissolution tests may have been the result of limitations in analytical resolution (both solid and aqueous phases), the loss of solids during the experiment, and/or incomplete dissolution of the calcium and magnesium carbonates present (1.3 percent calcite, 3.6 percent ankerite). Incomplete dissolution could result from the lower inherent reactivity of ankerite or coating of calcium and magnesium carbonate minerals with iron oxyhydroxides during dissolution. Such coating would reduce the reactivity of the carbonate minerals and the consequent acid neutralization.

3. The pH of drainage from the remaining two samples, T2 and T10, typically ranged from 8.0 to 8.2, with alkalinities typically ranging from about 60 to 80 mg/L as CaCO₃. These values

indicate, along with the calcium and magnesium concentrations in solution, that calcium and/or magnesium carbonate minerals remained and were dissolving. This mineral dissolution was adequately rapid to neutralize the acid produced by the oxidation of iron sulfide minerals present. This oxidation rate at the end of the present period of record was within the range observed earlier in the experiment (i.e. oxidation had not slowed appreciably).

Using the solid-phase NP[(Ca/Mg)CO₃] values in conjunction with average rates of NP[(Ca/Mg)CO₃] depletion (average rate of calcium plus magnesium release) indicated that the calcium and magnesium carbonates would be depleted from T2 and T10 after a total of 12 and 10 years of dissolution, respectively. Iron sulfides would be present in both of the samples at the time of NP[(Ca/Mg)CO₃] depletion. Assuming these iron sulfides would continue to oxidize and produce acid, the drainage from these solids would be expected to acidify when the rate of calcium and magnesium carbonate mineral dissolution decreased below that of the associated iron sulfide oxidation. This would occur when the chemically available carbonate minerals were depleted or their reactivity was reduced due to mineral surface coating.

- 4. The results from the ten samples subjected to dissolution at 25°C support the reasonability of using the initial iron sulfide, calcium carbonate, and magnesium carbonate contents along with observed rates of sulfate, calcium, and magnesium release to estimate the depletion of carbonate minerals and consequent potential for future acidification of drainage. Such an approach would greatly reduce the time and cost of tailings drainage quality prediction. Additional verification is required before this approach could be applied with confidence to all tailings, as opposed to those from hydrothermal quartz-carbonate deposits.
- 5. Sulfide oxidation rates at rinse intervals of 6, 24, and 84 hours were equal to or less than those at a one week rinse interval. Therefore, tests at shorter rinse intervals would not reduce the time required for testing. In the second phase of the project, the rinse interval was extended beyond one week (Lapakko 1993). The apparent rate of sulfide mineral oxidation decreased as the rinse interval duration increased beyond one week. Consequently, the use of intervals longer than one week would increase the time required for mine waste drainage quality predictive tests.

Elevated Temperature Experiment

- 6. In general, release of sulfate, calcium, and magnesium was initially rapid, decreased over the initial 50 to 60 weeks, and then plateaued. During the first 57 weeks of biweekly rinses at elevated temperature, sulfate release was six to ten times that for 55 weekly rinses at ambient temperature. At elevated temperature, however, rates decreased over time, and the minimum rates observed were similar or lower (in the case of T10) than minimum rates observed at ambient temperature. In addition, sulfate release at elevated temperature did not increase as drainage became acidic. This was substantially different from the marked sulfate release increase observed at ambient temperature for acidic drainage.
- 7. Two general temporal trends were observed for drainage pH in the Elevated Temperature Experiment, which was extended from 48 to 232 weeks. First, the drainages from samples T9,

T2, and T10 acidified after initially producing some alkaline drainage. The pH of drainage from sample T9 decreased below 6.0 after eight weeks of dissolution, remained in the typical range of 2.5 to 2.8 through week 22, then gradually increased to values in the upper fours at week 191. At week 8, 61 percent of the NP had been depleted.

The pH of drainage from sample T2 (1.5 percent calcite, 16 percent dolomite) oscillated between neutral and acidic for the first 60 weeks of dissolution, permanently decreased below 6.0 after 61 weeks, declined until week 93, and then varied in the typical range of 3.8 to 4.3. The cumulative mass of calcium and magnesium released at this time, indicates that the calcite and dolomite initially present (189 mg/g $CaCO_3$) had been largely depleted, with only 17 percent remaining. It should be noted that drainage from this sample at ambient temperature had acidified after 290 weeks of dissolution.

The pH of drainage from T10 oscillated between neutral and acidic during weeks 0 to 50 and 130 to 210. Between these two periods the drainage pH was neutral. The sample had a total sulfur content of about 6.4% and an NP[(Ca/Mg)CO₃] of 200 mg/g CaCO₃, most of which was present as ankerite (19.7% versus 2.1% calcite). After 216 weeks of dissolution drainage pH decreased below 6.0, at which time about 80% of the NP[(Ca/Mg)CO₃] had been depleted. As was the case with samples T9 and T6, drainage acidified prior to depletion of calcium and magnesium carbonates. This suggests that these minerals are less available for neutralization, while maintaining pH above 6.0, in the Elevated Temperature Experiment than at ambient temperature.

Second, drainage from samples T1, T4, T8, and T12 remained neutral throughout the Elevated Temperature experiment. Drainage from the first three samples was neutral because calcium and magnesium carbonate minerals remained and were dissolving to neutralize acid produced by iron sulfide mineral oxidation. The time to drainage acidification for these samples was estimated as 5 to 16 years based on data over the entire period of record. The iron sulfides had been depleted from T12, thus no acid was being produced.

8. The results from samples T6 and T10 further indicate that results from experiments of short duration do not necessarily reflect the drainage quality, particularly pH, over a longer period of dissolution.

The extended experimentation provided additional empirical data on the generation of acidic drainage by hydrothermal quartz-carbonate gold mine tailings, data which are presently sparse. Mining of hydrothermal quartz-carbonate deposits in Minnesota would likely generate tailings similar to those examined in this study. When this occurs, empirical data on dissolution of such tailings will be necessary to assess the potential for drainage to adversely impact natural water quality.

In the **next phase** of this project, results of continued experimentation will be reported. A cursory examination of the Ambient Temperature Experiment data beyond the scope of this report (weeks 291 to 447) revealed that the drainage pH of solid T9 began to increase around week 360 reaching

about 5.8 by week 447. The sulfate concentrations in drainage from T9 exhibited a peak in release at week 322 of 1047 mg/L and then decreased to near 20 mg/L at week 447. Preliminary calculations to week 436 for T9 reveal that the FeS₂ had been depleted. (These calculations were not conducted for the other three solids.) The drainage pH of solid T6 continued to decrease to a low of 3.77 at week 358 and then increased to near 4.75 at week 447. The sulfate concentrations in drainage from T6 decreased from a maximum of about 200 mg/L at week 290 to near 20 mg/L at week 447. For solid T2, the drainage pH remained near 8.0, while the sulfate concentrations continued to decrease after week 290, reaching about 20 mg/L by week 447. At week 290, half of the NP initially present remained. Given the decrease in sulfate release, at least an additional 290 weeks would be required to deplete the NP. The drainage pH of T10, however, dropped below 6.0 at week 423, oscillated near 6.0, and then dropped and remained below 6.0 from week 441 to week 447. The sulfate concentrations in drainage from T10 increased to about 150 mg/L shortly before the drainage pH dropped below 6.0, and then decreased to about 40 mg/L.

Only two of the solids (T2 and T8) used in the Elevated Temperature Experiment were continued beyond the scope of this report and these two were discontinued at week 367. Data to week 360 were available at the time of this writing. The drainage pH of solid T2 remained near 4.0, with a short drop to just under 3 at week 212. The sulfate concentration in the drainage was typically less than or equal to 10 mg/L. The drainage pH from solid T8 decreased below 6.0 near week 310, then rose to remain above 6.0 until week 356. The sulfate concentration in the drainage remained below 5.0 mg/L during this time.

For the next phase of this project, the above described data will be analyzed in a manner similar to this report. The data presented in appendices F and G (leached sample analyses) will be examined and the implications addressed. Additional leached samples will probably be analyzed. Geochemical modeling is also being considered. There will be additional comparison of the observed NP with the NP determined on fresh solids.

2. INTRODUCTION

Exploration for gold, titanium, and other non-ferrous minerals is presently occurring in Minnesota. If an economic deposit is discovered, the mine wastes must be characterized and the mine waste drainage quality must be projected prior to mine development. This information will be used to identify the types of water quality control required to protect the water resources of the state. Since there is presently no mining of base or precious metals in Minnesota there is little information available on the characteristics of, or drainage quality from, such mining wastes. The lack of such information will inhibit the effectiveness and efficiency of drainage quality prediction, as well as the environmental review and permitting processes.

There is little debate that protection of water resources by pre-operational prediction of mine waste drainage quality is a sound concept. Such prediction is, however, a relatively new field of study. It is recognized that mine waste drainage quality can be strongly influenced by mine waste composition. Whether or not drainage from tailings exposed to the atmosphere will be acidic can

6

be predicted with a high degree of certainty if the tailings exhibit a large compositional imbalance of acid-producing minerals relative to acid-neutralizing minerals. For tailings in general, however, prediction of drainage quality based on their composition is more tenuous. Similarly, laboratory dissolution tests can readily simulate the acidic nature of drainage from tailings which contain an abundance of acid-producing minerals relative to acid-neutralizing minerals. In general, however, the relatively short duration typical of laboratory dissolution tests, and complications of simulating environmental conditions, introduce uncertainty into prediction of the quality of drainage from tailings over the long period after mine abandonment.

In the initial phase of this study twelve nonferrous tailings were collected, characterized (particle size, chemistry, mineralogy, static tests), and subjected to dissolution in a 52-week laboratory experiment (Lapakko 1991). Although the drainages from all of the tailings were in the neutral to basic range, static tests indicated two of the samples (T9, T2) had potential to produce acidic drainage and two others (T6, T10) had marginal potential for producing acidic. Mineralogic analyses indicated that the calcium and magnesium carbonate content of T6 was lower than the neutralization potential measured in static tests. Elevated concentrations of arsenic, antimony, and molybdenum (and to a lesser degree barium, copper, nickel, and zinc) were observed in drainage from some of the samples. The second study phase included

- description of the geology of the mines from which tailings were collected and comparison of this geology with that of potential Minnesota mines;
- additional analysis of the pyrite present in the tailings;
- additional dissolution testing (25°C) of the four tailings identified as potential acid-producers;
- determination of the effects of sample mass on the results of predictive dissolution tests (25°C);
- determination of the effects of rinse interval duration on the results of predictive dissolution tests (25°C);
- dissolution testing at elevated temperature;
- comparison of trace metal concentrations in the laboratory drainage during phase 1 (25°C) with those in the field; and
- compilation of methods of removing problematic metals from hydrothermal quartz-carbonate tailings drainage.

In the third and present phase of the experiment the two major dissolution experiments were continued. First, the ambient temperature dissolution of the four tailings samples (T2, T6, T9, T10) in the Ambient Temperature Experiment was extended from 151 to 290 weeks. Second, the dissolution of seven tailings samples (T1, T2, T4, T8, T9, T10, T12) at 100° C in the Elevated Temperature Experiment was extended from 48 to 232 weeks.

3. OBJECTIVES

The general objective of this project, the third phase of a study initiated in 1989, was to extend the ambient temperature and elevated temperature dissolution experiments in order to better describe the long term dissolution behavior of the nonferrous tailings examined in the earlier phases (Lapakko 1991, 1993). The information on the relationship between solid-phase characteristics of mine wastes and drainage quality is limited. In particular, there are few long-term drainage quality records for well-characterized tailings. Such long-term data is critical in predicting, prior to mineral resource development, the dissolution behavior of abandoned mine wastes. Increasing the available data on this relationship will improve the ability to predict the quality of drainage from mine wastes of similar composition.

More specifically, the objectives of this project were as follows.

For dissolution at ambient temperature (25°C, Ambient Temperature Experiment):

- 1. Over a period of 290 weeks, determine the quality of drainage from four quartz-carbonate gold tailings (T2, T6, T9, T10) that, based on solid-phase composition, have the potential to produce acidic drainage. More specifically, describe the temporal variation of pH, specific conductance, and concentrations of alkalinity or acidity, sulfate, calcium, and magnesium in drainage from these tailings.
- 2. For the four tailings, determine the extent of iron sulfide mineral oxidation and calcium carbonate and magnesium carbonate mineral dissolution over the period of record.
- 3. For the four tailings, determine the rates of iron sulfide oxidation and calcium carbonate and magnesium carbonate mineral dissolution.
- 4. For samples which produce acidic drainage, determine the mass of calcium carbonate and magnesium carbonate minerals dissolved prior to acidification (empirical neutralization potential or ENP) and compare this to the neutralization potential originally present as calcium carbonate and magnesium carbonate in the tailings (NP[(Ca/Mg)CO₃]).
- 5. Determine the influence of rinse intervals shorter than one week on drainage quality and the rates of iron sulfide mineral oxidation and carbonate mineral dissolution.

For dissolution of six quartz-carbonate gold tailings (T1, T2, T4, T8, T9, T10) and one titanium tailing (T12) at elevated temperature (100°C) over a period of 232 or 256 weeks (Elevated Temperature Experiment):

1. Determine the quality of drainage from the tailings. More specifically, describe the temporal variation of pH, specific conductance, and concentrations of alkalinity or acidity, sulfate, calcium, and magnesium in drainage from these tailings.

- 2. Determine the extent of iron sulfide mineral oxidation and calcium carbonate and magnesium carbonate mineral dissolution.
- 3. For samples which produce acidic drainage, determine the mass of calcium and magnesium carbonate minerals dissolved prior to acidification (empirical neutralization potential or ENP) and compare this to the neutralization potential originally present as calcium carbonate and magnesium carbonate in the tailings (NP[(Ca/Mg)CO₃]).
- 4. Determine the rates of iron sulfide oxidation and calcium carbonate and magnesium carbonate mineral dissolution.

4. BACKGROUND: MINE WASTE DISSOLUTION

Prior to developing a base or precious metal resource, it is necessary to predict the quality of drainage which will be generated by the mining wastes. The generation of acidic drainage by mine wastes is the primary water quality concern associated with base and precious metal mining. In addition to high acidity, these drainages typically have elevated concentrations of the leachable trace metals present in the mine waste. Trace metal release in neutral drainage is a secondary concern. There are a multitude of historical cases in which levels of acidity and/or trace metals in mine waste drainages have greatly exceeded water quality standards.

Iron sulfide and trace metal sulfide minerals, as well as calcium carbonate and magnesium carbonate minerals, play a dominant role in the release of acid and trace metals from mine wastes. Acid is produced as a result of the oxidation of iron sulfide minerals present in mine waste, as indicated by reaction 1 (Nelson 1978) and reaction 2 (Sung and Morgan 1980). Acid (H^+) and sulfate are released to solution in a molar ratio of 2:1.

$$FeS(s) + (3/2)H_2O + (9/4)O_2(g) = FeOOH(s) + 2H^+(aq) + SO_4^{-2}(aq)$$
[1]

$$FeS_{2}(s) + (5/2)H_{2}O + (15/4)O_{2}(g) = FeOOH(s) + 4H^{+}(aq) + 2SO_{4}^{2}(aq)$$
[2]

The rate of iron sulfide oxidation by oxygen is proportional to the available sulfide surface area (Nelson 1978) and dissolved oxygen concentration (McKay and Halpern 1958; Nelson 1978) with only a slight dependence on pH (Nelson 1978). However, research on pyrite indicates that "as pH decreases to 4.5, ferric iron becomes more soluble and begins to act as an oxidizing agent" (Nordstrom 1982). As pH decreases further, bacterial oxidation of ferrous iron becomes the rate limiting step in the oxidation of pyrite by ferric iron (Singer and Stumm 1970), which is the only significant oxidizing agent in this pH range (Nordstrom 1982; Singer and Stumm 1970; Kleinmann et al. 1981). It should be noted that with this mechanism, the rate of pyrite oxidation is independent of the pyrite surface morphology and available surface area (Stumm and Morgan 1981).

The oxidation of pyrite has also been reported to be dependent upon temperature and relative humidity. Morth and Smith (1966) reported the pyrite (Middle Kittanning No. 6 coal seam, Ohio)

oxidation rate doubled with a 10°C temperature increase and, at 25°C, doubled as relative humidity increased from 50 to 75 percent. They also noted that the rate increased as the oxygen content of the water vapor increased from 10 to 100 percent. The authors suggested that the oxidation rate limiting step was removal of reaction products from reactive sites on the pyrite surface, for which water was the medium.

Hammack (1987) used x-ray photoelectron spectrometry to determine that the conversion of pyritic sulfur to sulfate was linear with respect to time until 40 to 50 percent of the pyrite surface was oxidized. The oxidation rate at 45 to 88 percent relative humidity was virtually constant and was about half that at 98 percent relative humidity. The oxidation rate increased as gas phase oxygen content increased to 10 percent but, in contrast with the findings of Morth and Smith (1966), was independent of oxygen at higher concentrations.

Borek (1994) subjected seven replicates of six pyrite samples to oxidation at relative humidities of 34, 50, 70, and 79 percent. One replicate of each pyrite sample was removed after intervals of 30, 60, 90, 150, 200, and 250 days and was analyzed for reaction products using Mössbauer spectroscopy. Of the three hydrothermal pyrite samples, those from Iron Mountain and the Noranda Waite-Amulet mine produced no reaction products under any of the reaction conditions. The third sample, from the Waldo mine in New Mexico, produced hematite at all humidities. Two of the sedimentary pyrites (Kirby-R, Kirby-U) weathered substantially only at relative humidities of 70% and 79%, while the third (Pittsburgh pyrite) weathered at all humidities. The sedimentary pyrites produced only melanterite and rozenite. It was concluded that the product generated "seems dependent on the mode of pyrite formation" while the amount of product was a function of the relative humidity and reaction duration.

Dissolution of sulfate minerals such as melanterite and jarosite will also produce acid (reactions 3 and 4, respectively). It should be noted that the solubility of jarosite is slight, except at low pH. As was the case for the sulfide minerals, the dissolution of melanterite yields two moles of acid per mole of sulfate dissolved. In contrast, the dissolution of jarosite yields 1.5 moles of acid per mole of sulfate dissolved. The dissolution of sulfate minerals such as gypsum (reaction 5, Stumm and Morgan 1981), anhydrite (CaSO₄), or barite (BaSO₄) will not produce acid. Oxidation of trace metal sulfide minerals will lead to acid production if, and only if, the trace metal released from the sulfide mineral subsequently precipitates as a metal oxide, hydroxide, or carbonate (or some combination thereof). This oxidation will, however, release trace metals from the highly insoluble sulfide phase. FeSO₄.7H₂O(s) + (1/4)O₂(g) = FeOOH(s) + SO₄²⁻(aq) + 2H⁺(aq) + (11/2)H₂O [3]

$$KFe_{3}(SO_{4})_{2}(OH)_{6}(s) = K^{+}(aq) + 3FeOOH(s) + 2SO_{4}^{2-}(aq) + 3H^{+}(aq)$$
[4]

$$CaSO_4 \cdot 2H_2O(s) = Ca^{2+}(aq) + SO_4^{2-}(aq) + 2H_2O$$
[5]

The most effective minerals for neutralizing (consuming, buffering) acid are those containing calcium carbonate or magnesium carbonate, examples of which are calcite, magnesite, dolomite, and ankerite (CaCO₃, MgCO₃, CaMg(CO₃)₂, CaFe(CO₃)₂, respectively). Dissolution of calcium carbonate and magnesium carbonate components neutralizes acid (reactions 6-9) and the rate of

dissolution increases as the rate of acid production increases. Reactions 6 and 8 are dominant above approximately pH 6.3, while reactions 7 and 9 are dominant below this pH.

$$CaCO_{3}(s) + H^{+}(aq) = HCO_{3}(aq) + Ca^{2+}(aq)$$
 [6]

$$CaCO_3(s) + 2H^+(aq) = H_2CO_3(aq) + Ca^{2+}(aq)$$
 [7]

$$MgCO_3(s) + H^+(aq) = HCO_3(aq) + Mg^{2+}(aq)$$
 [8]

$$MgCO_{3}(s) + 2H^{+}(aq) = H_{2}CO_{3}(aq) + Mg^{2+}(aq)$$
[9]

Dissolution of minerals such as anorthite (reaction 10; Busenberg and Clemency 1976) and forsterite (reaction 11; Hem 1970) can also neutralize acid, but their dissolution rate (and associated rate of acid neutralization) is very slow in the neutral pH range. These minerals dissolve more rapidly as pH decreases and, therefore provide more acid neutralization under acidic conditions.

$$CaAl_{2}Si_{2}O_{8}(s) + 2H^{+}(aq) + H_{2}O = Ca^{2+}(aq) + Al_{2}Si_{2}O_{5}(OH)_{4}(s)$$
[10]

$$Mg_{2}SiO_{4}(s) + 4H^{+}(aq) = 2Mg^{2+}(aq) + H_{4}SiO_{4}(aq)$$
[11]

Iron carbonates will provide no net neutralization of acid for drainage in an oxidizing environment. The initial dissolution of one mole of iron carbonate will neutralize one or two moles of acid (reactions 12, 13). However, under oxidizing environmental conditions the one mole of ferrous iron released will oxidize to ferric iron (reaction 14) which will precipitate as ferric oxyhydroxide (reaction 15). The oxidation of ferrous iron is slower than the subsequent ferric oxyhydroxide precipitation, and is reported to be second-order with respect to OH⁻ concentration above approximately pH 5 (Sung and Morgan 1980; Eary and Schramke 1990). The oxidation and precipitation reactions will yield two moles of acid (reaction 16). Thus, iron carbonate will not contribute to acid neutralization (reaction 17).

$$FeCO_3(s) + H^+(aq) = HCO_3^-(aq) + Fe^{2+}(aq)$$
 [12]

$$FeCO_3(s) + 2H^+(aq) = H_2CO_3(aq) + Fe^{2+}(aq)$$
 [13]

$$Fe^{2+}(aq) + (1/4)O_2(g) + H^+(aq) = Fe^{3+}(aq) + (\frac{1}{2})H_2O$$
[14]

$$Fe^{3+}(aq) + 2H_2O = FeOOH(s) + 3H^+(aq)$$
 [15]

$$Fe^{2+}(aq) + (1/4)O_2(g) + (3/2)H_2O = FeOOH(s) + 2H^+(aq)$$
 [16]

$$FeCO_3(s) + (1/4)O_2(g) + (3/2)H_2O = FeOOH(s) + H_2CO_3(aq)$$
[17]

5. METHODS

5.1. Materials

The methods of sample collection and analysis are presented in Lapakko (1991). The data on particle size distribution, chemistry, mineralogy, and static results are presented in tables 1, 2, 3, 4, and 5. Additional compositional data collected in previous phases of this study are presented in appendix A.

Three laboratories (Bondar-Clegg, Ottawa, Ontario; Lerch Brothers, Hibbing, MN; and Midland Research, Nashwauk, MN) conducted total sulfur, sulfate, and sulfur-as-sulfide analyses. There was reasonable agreement among many of the solids. The mean was calculated for the parameters analyzed. The result determined by each laboratory was calculated as a percent of the mean. For 27 of the 33 total sulfur samples, the results were within 25% of the mean. For 23 of the 28 sulfur as sulfide samples the results were within 25% of the mean. For additional detail see table 6. For the purposes of this report and all subsequent data analyses, the results from Bondar-Clegg were used.

5.2. Procedures

5.2.1. Ambient Temperature Experiment

Duplicate samples of all twelve tailings (T1 through T12) were subjected to the Ambient Temperature Experiment, which began on 6 June 1990 (week 0). All samples in this experiment were discontinued after 57 weeks except for T2, T6, T9, and T10, for which single reactors were continued and remain in progress (table 7). The discontinued reactors were used in an experiment examining the influence of variable rinse intervals on rates of mineral dissolution, the data for which are presented in Lapakko 1993. The present report presents data through week 290 (27 December 1995) on the reactors yet in progress in the Ambient Temperature Experiment.

In this experiment, a 75 g sample of unmodified tailings (i.e. as received) was placed into the upper segment, or reactor, of a two-stage filter unit (figure 1). On week 0, all samples were rinsed with 200 mL of distilled-deionized water, to remove products which accumulated from oxidation during sample storage. The distilled water was added slowly with a burette, to minimize disturbance of the solids, and allowed to drain overnight through the mine waste sample. This rinsing was repeated weekly throughout the course of the experiment.

Between rinses the solids were retained in the reactors and stored for further oxidation within individual compartments of a wooden housing. A thermostatically controlled heating pad was placed beneath the housing to control temperature. The housing was stored in a small room equipped with an automatic humidifier and dehumidifier, to maintain a stable range of humidity. During the 290-week experiment, temperature and relative humidity were monitored a total of 1070 and 1061 times, respectively, typically three to four times a week, using a Taylor wet-bulb/dry-bulb hygrometer. The average weekly temperatures ranged from 21.7 to 29.0°C, with an average of

25.3°C and a standard deviation of 1.5°C (n=287). The average weekly relative humidities ranged from 42 to 80%, with an average of 55% and a standard deviation of 6.0% (n=287; figure 2; see also appendix B).

The volume of rinse water, or drainage, was determined by weighing the lower stage (receiving flask) of the reactor. pH and specific conductance were analyzed directly in the lower stage of the reactor, after which a 20 mL sample was taken for analysis of alkalinity (if pH exceeded 6.30) or acidity. The remaining sample was then filtered for subsequent analysis of metals and sulfate. Samples taken for metal analyses were acidified with 0.2 mL AR Select nitric acid (Mallinckrodt) per 50 mL sample.

An Orion SA 720 pH meter equipped with a Ross combination pH electrode (8165) was used for pH analysis, and a Myron L EP conductivity meter was used to determine specific conductance. Alkalinity and acidity were analyzed using standard titration techniques (APHA et al. 1992). Through week 200, sulfate was analyzed at the MN DNR laboratory in Hibbing using an HF Scientific DRT-100 nephelometer for the barium sulfate turbidimetric method (APHA et al. 1992). Subsequent analyses (starting 13 April 1994) were conducted at the Minnesota Department of Agriculture (MDA) laboratory using a Technicon AA2 automated colorimeter or, for concentrations below 5 mg/L, a Dionex ion chromatograph. Metals samples collected through week 51 were analyzed for calcium and magnesium only using a Perkin Elmer 603 atomic absorption spectrophotometer in the flame mode at the MN DNR Hibbing laboratory. Subsequently calcium and magnesium concentrations were determined using a Varian 400 SPECTRAA at the MDA (starting 13 April 1994). See table 8 for details of sampling frequency.

An alteration of the above procedure was designed to determine if the rate of iron sulfide oxidation increased with more frequent rinsing (**Short Rinse Interval Experiment**). Tailings sample T2 and a 1.64-percent sulfur Duluth Complex (DC) rock were subjected to dissolution with rinse intervals of 6, 24, and 84 hours at room temperature. Aliquots of T2 (319.3 g) and the Duluth Complex sample (297.1 g) were rinsed several times before the experiment to remove residual reaction products from the sample surfaces. The solids were placed into a 150-mm diameter filter funnel equipped with a GF/F 15.0-cm glass microfibre filter. During the first rinse of the Duluth Complex rock sample the water added to the funnel drained very rapidly, which resulted in poor rinsing. Consequently the solids were transferred to a 90-mm diameter funnel. The individual drainage volumes were determined and the solutions were analyzed for specific conductance and sulfate (appendix D, tables D1.2, D1.3). On 4 January 1993, the funnels were placed in a controlled temperature/humidity room to dry.

On 8 January, three 75-g masses were split from each sample using the four corners method (Scott 1942) and added to standard reactors (figure 3). Fixed volumes of distilled water were pumped to each reactor at specific time intervals using a Mityflex model 903 peristaltic pump in conjunction with a ChronTrol model XT four circuit programmable timer (table 9). The timer was equipped with a backup battery in case of power failure. The water was distributed within the reactor using a 1 mL Eppendorf pipet tip, which was attached with epoxy to the tygon tubing from the pump. The

opening at the end of the pipet tip was heat sealed and six holes were perforated around the circumference of the tip using a stick pin. This was done to create relatively fine sprays to distribute flow across the solids bed with a minimum of solids disturbance. Samples of the drainage through the solids bed were collected on Monday mornings, and the pump tubing was purged before the reactors were returned to receive water input.

An Orion SA 720 pH meter equipped with a Ross combination pH electrode (8165) was used for pH analysis, and a Myron L EP conductivity meter was used to determine specific conductance. Alkalinity and acidity were analyzed using standard titration techniques (APHA et al. 1992). Sulfate was analyzed using an HF Scientific DRT-100 nephelometer for the barium sulfate turbidimetric method (APHA et al. 1992). Samples were analyzed for calcium and magnesium using a Perkin Elmer 603 atomic absorption spectrophotometer in the flame mode.

5.2.2. Elevated Temperature Experiment

The Elevated Temperature Experiment was a modification of a procedure called the Soxhlet Extraction Test (Renton 1983; Renton et al. 1985, 1988) and was begun on 19 February 1992. Duplicate reactors were used for all tailings except for T2 and T10, for which triplicate reactors were used. 75 g samples of each tailing were placed onto a Whatman GF/A glass microfibre filter which rested on the perforated plate in the upper segment of a two-piece polypropylene Buchner funnel (figure 4). Prior to the inception of the experiment all samples were rinsed with three 200-mL volumes of distilled-deionized water, to remove products accumulated from oxidation during sample storage. The distilled water was added slowly from a graduated cylinder, to minimize disturbance of the solids. For each reactor, all preliminary rinse samples were analyzed for pH, alkalinity/acidity, and specific conductance. Two of the three preliminary rinse samples from each reactor were analyzed for sulfate, calcium, and magnesium (Lapakko 1993).

The solids were retained in the reactors and were stored between rinses in a Thelco Precision Scientific oven. During the 232 weeks of the experiment, the temperature was measured 758 times, averaging about three readings per week. Weekly average temperature in the oven ranged from 89.0 to 107.0° C, with an average of 97.2° C and a standard deviation of 2.5° C (n=204; appendix C, table C1.12). Prior to the first rinse, it was recognized that some of the solids had consolidated. This consolidation resulted in the formation of cracks in the solids bed, which was only about 1.5-cm deep. It was clear that these cracks would have resulted in preferential flow through the solids. To improve flow through the bed and the resultant removal of reaction products, the solids were gently mixed with a stainless steel spatula then leveled prior to rinsing. To maintain uniformity in the methods, this procedure was applied to all solids, regardless of observed cracks.

The solids were rinsed every two weeks through week 48 and weekly subsequently (table 10). The rinsing frequency was increased with the intention of further accelerating the weathering. To each reactor 200 mL of distilled-deionized water, heated to 85°C, was added from a graduated cylinder and allowed to drain overnight through the tailings sample into a 500-mL sample bottle. This procedure was repeated on the following day. The two samples were composited, weighed to determine sample volume, and pH and specific conductance were determined directly in the sample

bottle. A 20-mL sample was taken for analysis of alkalinity (if pH exceeded 6.30) or acidity. The remaining sample was then filtered for subsequent determinations of sulfate, calcium, and magnesium (table 11).

In an attempt to investigate possible changes to the methods used on the majority of the reactors, three small experiments were conducted alongside the Elevated Temperature Experiment. To determine if the second rinse was increasing the rate of dissolution, a third reactor was used for samples T2 and T10 (reactors 16 and 13, respectively). These reactors were rinsed once per week and sampled once per week from weeks 49-64, while the other 14 reactors were rinsed twice per week and sampled once per week for the same period. In both cases, the water was heated to 85°C.

The second procedure that was investigated was the heating of the water to 85°C. Again the triplicate reactors for solids T2 and T10 were used. These two reactors were sampled bi-weekly and rinsed with two volumes of 200 mL room temperature water for weeks 2 to 48. The other 14 reactors were also sampled bi-weekly, but were rinsed with two volumes of 85°C water over the same period.

The third alteration to the methods was to determine if the rinse interval (time between sampling) affected the dissolution of the solids. From weeks 2 to 48, the 14 duplicate reactors from solids T1, T2, T4, T8, T9, T10, and T12 were sampled bi-weekly after having been rinsed with two volumes of 85°C water. From weeks 49-64, these reactors were sampled weekly and were also rinsed with two volumes of 85°C water.

All of the reactors, except the triplicate reactors of T2 and T10, were rinsed twice bi-weekly with deionized water at 85°C and sampled for 48 weeks, and were rinsed twice (85°C deionized water) and sampled weekly from week 49 to the end of record. The third reactors for T2 and T10 were terminated after 64 weeks, as were the even numbered reactors of each duplicate pair. The reactors containing solids T1, T4, T9, T10, and T12 were discontinued after 232 weeks. The remaining two reactors (T2 and T8) were discontinued after 367 weeks, and data to week 256 are presented (table 10).

Samples for analysis of calcium and magnesium were acidified with 0.2 mL AR Select nitric acid (Mallinckrodt) per 50 mL sample. An Orion SA 720 pH meter equipped with a Ross combination pH electrode (8165) was used for pH analysis, and a Myron L EP conductivity meter was used to determine specific conductance. Alkalinity and acidity were analyzed using standard titration techniques (APHA et al. 1992). Through week 111 (30 March 1994), sulfate was analyzed at the MN DNR laboratory in Hibbing using an HF Scientific DRT-100 nephelometer for the barium sulfate turbidimetric method (APHA et al. 1992). Subsequent analyses were conducted at the Minnesota Department of Agriculture (MDA) laboratory using a Technicon AA2 automated colorimeter or, for concentrations below 5 mg/L, a Dionex ion chromatograph.

Metal samples through week 114 (13 March 1994) were analyzed for calcium and magnesium only using a Perkin Elmer 603 atomic absorption spectrophotometer in the flame mode at the MN DNR

Hibbing laboratory. Subsequently calcium and magnesium concentrations were determined using a Varian 400 SPECTRAA at the MDA.

5.3. Calculations

The masses of sulfate, calcium, and magnesium release were calculated as the product of the observed concentration in the drainage and the drainage volume. Missing concentrations were estimated as the average of the previous and subsequent analyzed values. Some values were reported as less than the detection limit (e.g. <0.1 mg/L). For purposes of mass release calculations in the Ambient Temperature Experiment, a value of zero was used for those values reported as less than detection limit. In the Elevated Temperature Experiment, a value of one half the detection limit (e.g. 0.05 mg/L) was used. There were no such values in the Short Rinse Interval Experiment. For each reactor sulfate, calcium, and magnesium release rates were calculated for numerous periods. Cumulative sulfate release over time was plotted for each reactor. Periods of linear sulfate release were selected based on visual examination of the plots, and the release rate for each period was determined by linear regression. Calcium and magnesium release rates were determined by conducting linear regression analyses over the same periods.

The neutralization potential present in the tailings as calcium carbonate and magnesium carbonate $(NP[(Ca/Mg)CO_3])$, expressed as mg/g CaCO₃, was calculated as indicated below (reaction 18).

$$NP[(Ca/Mg)CO_3] = 10 \times (\%CaCO_3) + 11.9 \times (\%MgCO_3)$$
[18]

Empirical neutralization potentials (ENP) were calculated to determine the acid-neutralizing mineral dissolution prior to drainage pH decreasing below 6 and remaining in this range. The acid-neutralizing mineral dissolution was calculated as the sum of the cumulative calcium and cumulative magnesium released (expressed as $mg/g CaCO_3$) prior to the point at which drainage pH decreased below pH 6. If the pH of drainage from a solid never decreased permanently below 6, the ENP was reported as greater than that calculated from the total calcium and magnesium release.

6. **RESULTS AND DISCUSSION**

6.1. Introduction

The generation of acid is the primary drainage quality concern associated with abandoned mine wastes, which include tailings, waste rock, and the mine itself. The extended time frame over which these wastes will generate drainage is difficult to simulate in the relatively short period over which predictive dissolution testing can be conducted. That is, it is difficult to simulate the dissolution of mine wastes over a period of decades and centuries in the course of weeks or even years of laboratory testing.

Mine wastes often contain iron sulfide minerals, which will oxidize in the presence of atmospheric oxygen and water. This oxidation leads to the production of acid. Dissolution of other minerals

present in the mine waste may neutralize some or all of this acid. Minerals containing calcium carbonate and magnesium carbonate are the most effective acid-neutralizers. If the rate of acid production exceeds that of acid neutralization, the mine waste drainage will become acidic.

The following three variations in the neutralizing mineral content of sulfide-bearing mine wastes produce three different temporal variations in drainage pH. In all three cases "sulfide-bearing waste" refers to a waste in which the iron sulfide content is above the threshold value required to generate acidic drainage. For example, a waste containing two percent reactive iron sulfides would fit this description.

Case 1: A sulfide-bearing mine waste which contains no neutralizing minerals will generate acidic drainage almost immediately. Iron sulfide oxidation, and the consequent acid production, will begin as soon as the iron sulfide minerals are removed from depth and exposed to atmospheric oxygen and water at the earth's surface.

Case 2: A sulfide-bearing mine waste which contains a small amount of reactive neutralizing minerals will initially produce a neutral drainage. The acid produced by sulfide oxidation will be neutralized initially by the dissolution of the acid-neutralizing minerals. The drainage will remain neutral until these minerals are depleted, at which time it will become acidic.

Case 3: A sulfide-bearing mine waste which contains a substantial amount of reactive neutralizing minerals will produce neutral drainage for an extended time. Over time the sulfide minerals may be depleted while neutralizing minerals are yet present, and the drainage will remain neutral. Conversely, the neutralizing minerals may be depleted while sulfide minerals remain and are oxidizing, and the drainage would acidify. During long time frames, precipitate coatings on surfaces of iron sulfide and/or acid neutralizing minerals may play a role in determining drainage quality. Such coatings may gradually accumulate and inhibit the reactivity of the minerals on which they form. If coatings form on the acid-neutralizing minerals and iron sulfide oxidation continues, drainage from the waste will become acidic. If substantial coatings form on the iron sulfide minerals and the rate of iron sulfide oxidation is adequately inhibited, the drainage will not acidify. At present it is not possible to quantitatively model the formation of coatings with the accuracy required to predict the effects on drainage quality.

The first case can be readily detected by dissolution testing, since the drainage will acidify within a few weeks. In the second case, the duration of the dissolution test must be fairly long. For example, laboratory dissolution tests were conducted on a mixture of 75 g rock (2.1 percent sulfur, mostly as pyrrhotite) and 0.79 g rotary kiln fines (a waste largely comprised of limestone and CaO generated in the production of lime from limestone). The drainage pH from this mixture, which had a neutralization potential of 8.4 mg/g CaCO₃, was above 7.0 for 75 weeks then decreased below pH 6.0 (Lapakko 1990). A mixture of 75 g of the same rock and 0.79 g – 10 mesh limestone yielded a neutralization potential of 11 mg/g CaCO₃. This mixture produced neutral drainage for 109 weeks, at which time the drainage pH decreased below 6.0 (Lapakko and Antonson 1991).

As is clear from the previous examples, a very long dissolution test would be required to identify the acid producing character of a sample containing a substantial fraction of calcium/magnesium carbonate minerals. Such a test would be conducted until the drainage acidified or until the iron sulfide minerals were depleted or became unreactive. This depletion or decrease in this reactivity would be indicated by a decrease in sulfate release.

6.2. Solids Analysis

In the initial phase of this study, sulfur species present in the tailings were determined by Bondar-Clegg and Lerch Brothers (Lapakko 1991). Although the agreement between the two sets of analyses was generally good, discrepancies were observed for total sulfur contents of T7, T9, and T10, as well as for sulfide contents of T9 and T10 (table 6). Samples were subsequently submitted for additional analyses. It was decided that the initial values from Bondar-Clegg would be used with the exception of sample T10.

The total sulfur and sulfide contents determined for T10 by Bondar-Clegg were 4.08 and 3.89 percent, respectively, and reanalysis indicated these values were most likely low. Three additional analyses yielded average total sulfur and sulfide contents 6.40 and 5.93 percent, respectively (table 6). It was assumed that the original values were in error, and the averages of the remaining three analyses were used. The 5.93% sulfide content was used to determine an AP value of 185 mg/g CaCO₃. Subsequent analyses by Newmont (Denver, CO) indicated total sulfur and sulfide contents of 6.5 and 6.2 percent (appendix A, table A3.5), supporting the use of the alternative values. Since the sulfide mineralogy of the sample was also based on the original sulfide content, the values presented should be increased by 52% (5.93/3.89 = 1.52), yielding a pyrite content of 11.1%. It should be noted that these values are different from those reported in earlier publications.

Except for T7, the original sulfide determinations for the remaining samples were in reasonable agreement with the subsequent analyses (table 6). Bondar-Clegg reported values of 0.10% total sulfur and 0.08% sulfide (table 6) while the averages of 0.32% total sulfur and 0.21% sulfide were determined for the three additional analyses conducted on solid T7. It is believed that these values are more accurate, and additional analyses conducted by Newmont support this contention (appendix A, table A3.5). Since the Bondar-Clegg values were within about 0.2% of the average of other analyses, the Bondar-Clegg values were retained as a matter of convenience.

It is worth noting that Bondar-Clegg used a sodium carbonate leach to determine the sulfide content of T9, and this protocol yielded more accurate values for sulfide content. The values determined by Newmont using this method were in agreement with those from Bondar-Clegg (3.87 versus 3.64 percent sulfide, respectively; table 6; appendix A, table A3.5). The method used by other laboratories was apparently less accurate since the presence of barite in the sample was not accounted for. This emphasizes the importance of familiarity with sample mineralogy when selecting protocols for sulfur determinations.

Na HCU3 length should not Dissible Burite OZ Sulfile

6.3. Ambient Temperature Experiment

6.3.1. Introduction

In the initial phase of this project, all twelve tailings samples generated drainage in the neutral pH range during the 52-week dissolution experiment (Lapakko 1991). Based on chemical and mineralogic analyses, the potentials of samples T2, T6, and T9 to produce acid exceeded their respective potentials to neutralize acid (table 5). This suggests that the neutralization potential of these samples would be depleted while acid was yet being generated, at which time drainage would acidify. The acid neutralization potential of sample T10 exceeded its acid production potential but this difference was small. Samples T2, T6, T9, and T10 were continued for an additional 99 weeks of dissolution in the Ambient Temperature Experiment (Lapakko 1993), and have been continued with attendant data compilation for a total of 290 weeks at the time of this report.

6.3.2. Case 1 Samples: Low to High Acid Production Potential (AP), No to Low Neutralization Potential (NP)

Since none of the samples produced acidic drainage during the initial 52-week phase, it is clear that none conformed to the Case 1 profile.

6.3.3. Case 2 Samples (T9, T6): Moderate to High AP, Low to High NP

Samples T9 and T6 conformed to the Case 2 profile. The samples contained significant amounts of NP and greater amounts of AP. They produced neutral drainage for 2.3 and 5.5 years, respectively, but the NP was ultimately depleted and drainage acidified within the 290-week period of record. Discussion on these two solids summarizes 1) solid-phase characteristics, 2) drainage pH, 3) sulfate concentrations, mass release, and rates of release, and 4) calcium and magnesium concentrations, mass release, and rates of release.

Sample T9 had an AP[S²⁻] (AP calculated based on 3.64% S²⁻) of 114 mg/g CaCO₃ and an NP[(Ca/Mg)CO₃] of 14 mg/g CaCO₃ (table 5). The AP was virtually all as pyrite (6.6%) and the NP was present as calcite (table 3). The major host rock minerals were quartz (27.5%), feldspar (27.6%), mica (16%), chlorite (2.1%), and amphibole (2.9%; table 4).

As discussed in the previous report covering weeks 0 to 151, sample T9 produced drainage pH values in the typical range of 7.8 to 8.1 prior to week 100, at which time drainage pH began to decrease rapidly, and fell below 6.0 at week 122 (Lapakko 1993). This trend continued, with pH dropping below 4.0 at week 136 and reaching a minimum of 2.94 at 220 and 272 weeks. Subsequent values fluctuated in the typical range of 3.0 to 3.2 (figure 5). Net alkalinity (alkalinity - acidity) concentrations followed a similar temporal trend (appendix B, figure B3.3). At the time of acidification, the remnant sulfide content was 3.31%, indicating the FeS₂ content was 6.19% (appendix B, table B6.3).

Five noteworthy temporal variations of sulfate concentrations were observed. First, sulfate concentrations were elevated at the start of the experiment (8.4 mmol/L at t = 0) and decreased during the first ten weeks to a relatively low range. This reflected the removal of products of sulfide oxidation which occurred between the time of sample collection and the week 0 rinse (figure 5). The values prior to week 5 were not included in the figure since they would limit the graphical resolution for the lower concentrations which occurred over the remainder of the experiment. Data for this period are presented in appendix B, table B2.11.

Second, between weeks 10 to 122 sulfate concentrations were relatively constant, with an average sulfate release of 0.035 mmol/wk. This represents a period of relatively constant and slow acid production, which resulted in the depletion of the calcite present. Third, after week 122, sulfate concentrations increased substantially subsequent to drainage acidification (figure 5). This represents an increase in the rate of sulfide mineral oxidation and consequent acid production and is, therefore, an important temporal variation in sulfate concentration. The average sulfate release for weeks 123 to 290, after drainage acidification, was 0.19 mmol/wk (appendix B, tables B4.12 - B4.16). Determination of rates over shorter intervals indicates that those prior to drainage acidification were often an order of magnitude lower than those subsequently (table 12).

The increase in sulfate release was related to pH, which decreased below 4.5 at week 130. Research on pyrite oxidation indicates that as "pH decreases to 4.5, ferric iron becomes more soluble and begins to act as an oxidizing agent" (Nordstrom 1982). As pH further decreases, bacterial oxidation of ferrous iron becomes the rate limiting step in the oxidation of pyrite by ferric iron (Singer and Stumm 1970), which is the only significant oxidizing agent in this pH range (Nordstrom 1982; Singer and Stumm 1970; Kleinmann et al. 1981). This indicates that the elevated sulfate concentrations near the end of the experiment were probably due to increased biologically mediated ferric iron oxidation of the sulfide minerals as pH decreased below 4.0. The rate of chemical oxidation may have increased also, although the extent of this increase was most likely slight relative to the increase in biological oxidation (Nordstrom 1982).

Fourth, concentrations cycled throughout the experiment, with peaks at approximately 60, 115, 167, 216, and 277 weeks (figure 5). These periods of elevated sulfate release were largely in July and August. During these summer months relative humidity and to a lesser extent, temperature, tended to be elevated in the room in which the solids were stored (figure 2). Thus, the experimental design was more successful in controlling temperature than relative humidity (see also methods).

Fifth, from about week 150 to 230 sulfate release averaged about 0.24 mmol/wk and decreased to 0.17 mmol/wk subsequently (table 12). This may be the initiation of a decrease in the rate of iron sulfide oxidation, although the data are not adequate to make this determination. Such a trend could result from the depletion of more reactive pyrite phases or from the coating of iron sulfide mineral surfaces with precipitates such as iron oxyhydroxides.

A total of 1.28 g of sulfur was released over the 290 weeks. This represents 31 percent of the total sulfur present in these tailings. Assuming all of the sulfur was released from pyrite (i.e. no barite dissolved), roughly 45 percent of the pyrite was oxidized and the AP was reduced by 45 percent

(table 13). The removal of such a substantial fraction of the pyrite could readily be responsible for the decline in sulfate concentrations observed around week 230 (figure 5).

Calcium concentrations were highest at week zero, measuring 7.5 mmol/L, and decreased to one tenth of this value by week 10. This decrease reflected the "rinsing off" of host rock minerals dissolved by acid produced as a result of iron sulfide mineral oxidation between the collection of the tailings and the start of the experiment (figure 5). The initial calcium concentrations were excluded from the figure in order to retain better graphical resolution for the subsequent lower values.

The calcium released to solution reflected the dissolution of calcite which, prior to week 122, was largely responsible for neutralizing the acid produced by iron sulfide oxidation. Indeed, throughout the experiment calcium concentrations tended to exhibit peaks coincident with sulfate peaks. Calcium concentrations generally decreased until the drainage acidified, and then remained within a fairly low range (figure 5). This suggested that the calcium carbonate initially present in the sample was being depleted or rendered unreactive. Subsequently, the acid produced by the iron sulfide oxidation, as indicated by the sulfate concentrations, was not neutralized and the drainage acidified.

The cumulative release calculations support the contention that the carbonate minerals initially present (table 3) in the sample had been depleted. The cumulative release of calcium from T9 was calculated as 11 millimoles at week 122 (figure 6; appendix B, tables B4.12 - B4.16). Using this value to represent the depletion of carbonate minerals from the solid indicates that 105% of the 10.5 millimoles initially present had been depleted. One mmol of magnesium had been released at this time, and the total calcium plus magnesium release represented 115% of the original carbonate content. The magnesium release was most likely from non-carbonate host rock minerals, since magnesium rarely, if ever, occurs in calcite from hydrothermal systems (Mattson 1999).

In contrast, less than thirty-one percent of the total sulfur initially present in the sample had been depleted (table 13). The remaining iron sulfides (mostly pyrite) continued to produce acid, of which only a fraction was neutralized, and the drainage pH decreased. The acid neutralized during this acidic phase was apparently due to dissolution of feldspar, mica, chlorite, and amphibole minerals present in the tailings (table 14; mineral compositions from Klein and Hurlbut Jr. 1985). This dissolution was reflected by continued low-level release of calcium and magnesium.

As was the case with sulfate and calcium, magnesium concentrations exhibited a relative high at week zero, reflecting the rinsing of host rock dissolution products generated prior to the experiment. Magnesium concentrations were relatively low throughout the experiment, with the exception of some elevated values from about week 100 to week 140, the period during which drainage pH declined and acidified. Magnesium concentrations in the latter stages were slightly higher than those in the early stages (figure 5). The slight increase in magnesium release was apparently the result of increased release from non-carbonate minerals (e.g. mica, chlorite, amphibole) at the lower pH. The rate of total calcium plus magnesium release was slower during the second half of the

experiment, measuring about 12 millimoles prior to week 122 and only 4 millimoles in the subsequent 170 weeks (figure 6).

Sample T6 had an AP[S²⁻] of 65 mg/g CaCO₃ and an NP[(Ca/Mg)CO₃] of 45 mg/g CaCO₃ (table 5). The AP was present as both pyrite (1.29%) and pyrrhotite (3.50%; table 3). The NP was present as calcite (1.3%) and ankerite (3.6%), which was assigned a "typical" composition of 53.6% CaCO₃, 31.4% MgCO₃, and 15% FeCO₃. Thus, of the 45 mg/g CaCO₃ NP, calcium carbonate contributed 32 mg/g and magnesium carbonate contributed 13 mg/g. (Note: The percent MgCO₃ must be multiplied by 1.19 to convert to percent as CaCO₃.) The major host rock minerals were quartz (40.6%), chlorite (16.8%), siderite (14%), mica (11.2%), amphibole (2.6%), stilpnomelane (2.3%), feldspar (1.4%), apatite (0.3%), and magnetite (0.1%; table 4).

The T6 drainage quality and mass release trends were similar to those observed for sample T9, although the time to drainage acidification was substantially longer. The pH of drainage from sample T6 was around 8.0 for the first 230 weeks of the experiment. At this time it began to decrease, dropping below 6.0 at week 284 and reaching 4.49 at week 290 (figure 7). Net alkalinity concentrations followed a similar trend. At the time of acidification (284 weeks) the remnant sulfide content was 1.33%, indicating a FeS₂ content of 2.49% (appendix B, table B6.3). (Drainage pH decreased below 4 at about week 310 and oscillated from 3.85 to 4.0 through week 321, the last data available at the time of this writing. Data beyond week 290 are not included in the tables and figures of this report.)

As was the case with T9, sulfate concentrations declined over the initial weeks of the experiment, reflecting the removal of oxidation products which accumulated after the tailings were collected. The subsequent concentrations were in a fairly stable range with a subtle cyclic variation. As was the case with T9, the peaks in these cycles were associated with summer months, and were probably due to elevated humidity and possibly temperature.

As was also the case with T9, sulfate concentrations increased when pH declined. An increase in sulfate concentrations was observed between weeks 200 and 230, as pH began to decrease below 8.0. A much larger increase was observed near week 270, as pH began to decline and drop below 6.0 at week 284. During the 290 weeks of dissolution, about 18 millimoles of sulfate were released to solution (figure 8). The sulfate release indicates a remnant sulfur content of 1.35 percent at the end of this phase of experimentation (table 13).

Calcium and magnesium concentrations were initially elevated, with week zero concentrations of 4 and 2 mmol/L, respectively. These concentrations decreased by about an order of magnitude over the first ten weeks, reflecting the removal of products of reactions occurring after the collection of the tailings (figure 7). In contrast to T9, there was no obvious response of calcium or magnesium concentrations to the subtle cyclic variation in sulfate concentrations. Concentrations of both parameters were fairly stable until about week 230, at which time they began to decline. At week 284, when pH dropped below 6.0, the total calcium and magnesium releases were 16.2 and 13.9 millimoles, respectively. The 30.1 mmol total represents about 90% of the 33.8 millimoles of NP[(Ca/Mg)CO₃] calculated as present based on the mineralogic data (table 3).

The calcium and magnesium release indicates that most, or all, of the calcium and magnesium carbonates (calcite and ankerite) had been depleted from the solid-phase. The difference between the mass of calcium and magnesium release in the drainage and that present as calcium carbonates and magnesium carbonates is quite small, equivalent to a calcite content of 0.5 percent. It is not unreasonable to conclude that the calcium carbonates and magnesium carbonates had been depleted given the a) potential for error in solid-phase measurements, b) potential for error in aqueous phase measurements, and c) loss of solids during the course of the experiment. The calculation of the solid-phase NP was complicated by the fact that it was necessary to partition calcium and magnesium among calcite, ankerite, and siderite as well as within the ankerite present in this sample. Secondly, it is possible that some calcium and/or magnesium carbonate remained but was less reactive than that dissolved initially. The peak in magnesium release after week 284 is consistent with this possibility.

It should be noted that the molar ratio of calcium to magnesium release was 1.2:1. In contrast the molar ratio of calcium to magnesium for the carbonates present in the solid-phase was 2.5:1. It seems most likely that the discrepancy was the result of error in the solid-phase speciation of the carbonate minerals. That is, a larger fraction of the solid-phase carbonate was associated with magnesium than indicated by the mineralogic analyses. The solid-phase composition would be consistent with the aqueous phase data if the ankerite content assumed (see first paragraph of T6 presentation) was 33% calcium carbonate and 47% magnesium carbonate.

Case 3 Samples (T2, T10): High AP, High NP 6.3.4.

Samples T2 and T10 fit the Case 3 profile. They had substantial amounts of both AP and NP and produced non-acidic drainage for the entire 290 weeks. Their drainage quality indicates that iron sulfides oxidized throughout the 290 week period, and the acid produced was neutralized by dissolution of the calcium and magnesium carbonates present. The net result was a slightly alkaline drainage with elevated concentrations of sulfate, calcium, and magnesium.

Sample T2 had an AP[S²⁻] of 228 mg/g CaCO₃ and an NP[(Ca/Mg)CO₃] of 189 mg/g CaCO₃ (table 5). The AP was supplied virtually entirely by pyrite (13.6%). The neutralization potential was present as calcite (1.5%) and dolomite (14.5%), which yielded total calcium carbonate and magnesium carbonate NP values of 101 and 88 mg/g CaCO₃, respectively (table 3).

Typical pH and alkalinity ranges for T2 drainage were 8.0 to 8.2 and 60 to 90 mg/L as CaCO₃, respectively. Drainage pH decreased slightly around week 230, concurrent with an increase in sulfate release, and oscillated subsequently (figure 9). Sulfate, calcium, and magnesium concentrations were highest at the beginning of the experiment, reflecting the removal of reaction products which accumulated between the time of samples collection and the beginning of the experiment. Subsequently concentrations remained within fairly narrow ranges, indicating fairly constant rates of sulfide mineral oxidation and carbonate mineral dissolution.

The most marked temporal variation in sulfate concentrations was a somewhat cyclic oscillation. As mentioned previously, relative peaks occurred during the summer months and the oscillation was attributed to seasonal variations in relative humidity and possibly temperature. These oscillations were relatively mild and, after the first 20 weeks, sulfate release rates generally exceeded half the maximum observed (table 15). Calcium and magnesium concentrations responded to this cyclic variation in acid production, and generally paralleled the temporal sulfate trends. Mass release calculations indicated that substantial amounts of both acid-producing and acid-neutralizing minerals remain in this sample (table 13).

Sample T10 had an AP[S²⁻] of 185 mg/g CaCO₃, which was supplied entirely by pyrite (11.1%). The NP[(Ca/Mg)CO₃] was 200 mg/g CaCO₃, and was supplied by both calcite (2.1%) and ankerite (19.7%). The total calcium carbonate and magnesium carbonate NP values were 127 and 74 mg/g CaCO₃, respectively (tables 3, 5).

The typical ranges of pH and alkalinity in the T10 drainage were 8.0 to 8.2 and 50 to 100 mg/L. The pH was above the typical range at the beginning of the experiment and dropped below it during the period from week 230 to 255. This is about the same period as the pH of drainage from T2 declined, although with T10 there was no concurrent increase in sulfate release. The pH decrease with no concurrent increase in acid production seems curious with no obvious explanation. Alkalinity generally increased through week 50 and gradually decreased from week 80 through week 290. There was no dip in the alkalinity values associated with the pH decrease between weeks 230 and 255 (figure 10).

Two temporal trends of sulfate, calcium, and magnesium concentrations were similar to those observed for other solids. First, concentrations were highest at the beginning of the experiment, reflecting the removal of reaction products generated after sample collection. The second trend common to all solids was the cyclic variation of sulfate concentrations during which peak values occurred during the summer months. Calcium and magnesium concentrations also followed this trend, as was the case for T2 and T9.

There were, however, two distinct and noteworthy points regarding the sulfate, calcium, and magnesium concentrations in drainage from sample T10. First, despite a lower sulfide content (5.9% versus 7.3%), T10 generated sulfate concentrations higher than those from T2 (figure 11). Over the 290-week duration the sulfate release rate for T10 was 2.2 times that from T2 (table 15). Part of this can be explained by the higher specific surface area of T10 (0.51 versus 0.32 m²/g; table 16). Taking this into account in conjunction with pyrite content, the pyrite surface areas of T10 and T2 can be estimated as 4.2 and 3.3 m², respectively. Thus, the rate per unit pyrite surface area for T10 was 1.7 times that for T2. Given that error was introduced in determination of specific surface areas (Lapakko 1993), the values suggest that pyrite present in T10 was oxidizing more rapidly than that in T2.

Second, rather than remaining in a relatively constant range in T10 drainage, concentrations of sulfate and calcium tended to increase, while magnesium concentrations tended to decrease over time. In some cases, such as T9, increasing sulfate concentrations have been a precursor of drainage acidification (figure 5). The increases may indicate the development of acidic microenvironments in which iron sulfide oxidation is accelerated. For example, the upper portion of the tailings bed

may generate acidic drainage which is neutralized by dissolution of calcium and magnesium carbonate minerals present in the underlying tailings. The oxidation of sulfide minerals in the upper portion of the bed would be more rapid due to the influence of iron oxidizing bacteria, as discussed above. It is also possible that acidic microenvironments could develop at other locations at which calcium and magnesium carbonate minerals have been depleted within the tailings bed.

6.3.5. Projected Drainage Quality from T2 and T10

Drainage from samples T2 and T10 may acidify in the future since both contain additional acid producing and acid neutralizing minerals. The cumulative mass release from these samples was calculated for sulfate, calcium, and magnesium (appendix B, tables B4.2-B4.6, B4.17-4.21). These values were then compared with the iron sulfide and calcium/magnesium carbonate content of the samples. The values determined indicated that for samples T2 and T10, 22 and 39 percent of iron sulfides initially present oxidized, and 48 and 59 percent of the total calcium carbonate and magnesium carbonate initially present dissolved, respectively, during the 290 week experiment (figure 12; table 13).

The rates of release during the experiment were also calculated (table 15). These rates, in conjunction with the initial AP and NP, were used to estimate the dissolution time required to deplete the AP (iron sulfide minerals) and NP (calcium and magnesium carbonate minerals) present in the samples. The time required for AP depletion was calculated by dividing the AP remaining (mmol/g $CaCO_3$) at week 290 by the rate of sulfate release at the end of the period of record (mmol/wk). This quotient was divided by 52 to convert time from weeks to years. The time required for NP depletion was calculated similarly (table 17).

This method was used previously to predict the time to acidification for samples T9 and T6. The time required to deplete the calcite from T9 was calculated based on the rate of calcium release over the initial 30 weeks of dissolution (Lapakko and Wessels 1995). The time required to deplete the calcium and magnesium carbonates from T6 was based on the rates of calcium and magnesium release over the initial 150 weeks of dissolution (Lapakko 1993). The predicted times of 112 and 321 weeks were in reasonable agreement with the observed lag times of 122 and 284 weeks, respectively.

Using the same calculation, the NP of T2 and T10 would be depleted before the AP (table 17). This implies that both samples would eventually produce acidic drainage. For example, sample T2 would produce neutral drainage for 12.5 years, at which time the NP would be depleted. Subsequently, the drainage would be acidic until the AP was depleted after an additional 18 years.

Despite the fairly accurate predictions observed for samples T9 and T6, this estimation provides only a "first-cut" guess on the variation of drainage pH over the long term. It does not account for the possible accumulation of coatings on sulfide and carbonate mineral surfaces. As previously discussed, these coatings will inhibit the dissolution of the minerals on which they formed, as will formation of leached layers at the mineral surface. These phenomena have been observed in other laboratory studies (Lapakko and Antonson 1991; Lapakko et al. 1997). Given the potential for

coating formation on the mineral surfaces over decades of reaction, a high degree of uncertainty is associated with this estimation.

The dissolution behavior of the samples over time can be accurately assessed only by extended dissolution studies. Although conducting such studies under field conditions would most closely approximate the conditions of actual mine waste disposal, and therefore the quality of drainage generated, laboratory tests may provide a more practical approach. Such studies would be difficult, at best, within the typical regulatory time frame. Consequently, projects must be conducted specifically to address the long term dissolution behavior of mine wastes in general, in anticipation of mineral resource development. In such studies the relationship between solid-phase composition and drainage quality must be established with as much accuracy as possible, so results can be more readily extrapolated to specific mine wastes when mineral development is proposed.

6.3.6. Rates of Sulfide Mineral Oxidation as a Function of Solid-Phase Sulfide Content

Rates of sulfate release were determined for numerous periods over the 290-week experiment (tables 12, 15). For pyrrhotite oxidation, the rate of mineral oxidation equals the rate of sulfate release, while for pyrite the rate of mineral oxidation is half the rate of sulfate release. Rates of calcium and magnesium release were determined for the same periods.

Sulfate release rates were also determined for weeks 20 to 57 in the first phase of this project when all drainages were slightly alkaline. Regression analysis conducted on these rates (mmol/wk) and solid-phase sulfide content yielded equation 19. The most recent rates from samples T2, T6, and T10 were within 25% of the values in the earlier phase. Sulfate release from T9 however was about five to ten times that in the earlier phase, due to acidification of its drainage (as discussed earlier). The sulfate release from T6, the drainage from which acidified at week 284, will most likely increase in the future for the same reason.

$$d(SO_4)/dt = 0.013 \ (\% \ S^2) - 0.000, \ n = 24, \ r^2 = 0.693$$
 [19]

The r^2 value indicates that the variation in percent sulfur accounts for 69 percent of the variation in the sulfate release rate. It is clear that other variables also influence these rates, and Lapakko (1993) concluded the following.

In conclusion, the rate of sulfate release (i.e. the apparent rate of iron sulfide oxidation) was apparently controlled by the iron sulfide mineral surface area present. Other factors such as iron sulfide chemistry, crystal structure (including lattice dislocations), and surface coating may also affect release rates. However, for the samples examined by the methods in this study, these effects were not discernible.

Lapakko (1993) plotted the rate of sulfate release versus the estimated pyrite surface area for five of the samples. Regression analysis of these data yielded a pyrite oxidation rate of 5.6×10^{-11} mol m⁻²(FeS₂)(s⁻¹). For comparison, Nicholson and Scharer (1994) determined a rate of 1.13×10^{-10} mol·m⁻²(FeS₂)(s⁻¹) for pure pyrite and an average rate of $5\pm 2.1 \times 10^{-10}$ mol·m⁻²(FeS₂)(s⁻¹) for five

literature values. Thus, the present rate is half that determined and about one-ninth of the average of literature values. This agreement appears to be reasonable, particularly in light of the fact that Nicholson and Scharer (1994), and possibly the literature sources they cited, used a geometric estimation to determine surface area. In contrast, surface area values were estimated based on BET analyses of the tailings samples. The BET (Brunauer et al. 1938) values exceed those determined by geometric estimation, even with roughness corrections, and would tend to yield lower rates per unit surface area.

6.3.7. Short Rinse Interval Experiment

To determine if the rate of iron sulfide oxidation increased with more frequent rinsing, an additional 26 week test was conducted on solid T2. Three reactors were rinsed at intervals of 6, 24, and 84 hours. These results were also compared with the results from the one week rinse interval. The drainage quality data are presented in appendix D, tables D1.7.-D1.9, with corresponding concentration versus time plots in appendix D, figures D2.1-2.3 and D2.7-2.9. All three produced neutral drainage. For the 26 week test, the sulfate, calcium, and magnesium mass releases for each of the three rinse intervals were within 2% of the mean for each parameter (appendix D, table D3.1).

The rates of release (weeks 1-26) for the three reactors were 0.060, 0.059, and 0.063 mmol/week for 6, 24, and 84 hour rinse intervals, respectively (appendix D, table D5.3). The average rate was slower than the overall rate for the same solid (0.078 mmol/wk) in the Ambient Temperature Experiment. For the weeks 5 to 18, the rate was 0.22 mmol/wk (table 15). This rate is 2.7 times the rate of the shorter rinse interval reactors. These rates imply that the early rate of release may be faster at a one week interval versus the shorter rinse intervals. (A 1.64 %S Duluth Complex rock sample was also subjected to these experimental conditions, with a similar result. The rate of release from each of the reactors was 60-75% of the rate of release from that same solid tested with one week rinse intervals (appendix D, table D5.3)).

6.3.8. Summary

- 1. Only two of the ten gold tailings samples examined in this study produced acidic drainage during the Ambient Temperature Experiment. Sample T9 produced circumneutral drainage for 120 weeks. Drainage pH dropped below 6.0 at week 122, reached a minimum of 2.94 at week 220, and subsequently fluctuated between 3.0 and 3.2. Sample T6 produced circumneutral drainage until week 284, at which time it dropped below 6.0. Drainage pH reached 4.49 at week 290, decreased below 4 at about week 310, and oscillated from 3.85 to 4.0 through week 321, the last data available at the time of this writing. This demonstrates that the quality of drainage generated in short term dissolution experiments may not accurately reflect the drainage quality generated by mine wastes over a longer time frame.
- 2. At the time drainage pH decreased below 6.0, the sum of calcium and magnesium release from T9 and T6 represented 114% and 90% of their respective NP[(Ca/Mg)CO₃] values. This suggests that the availability of calcium and magnesium carbonates for acid neutralization was high, and that other minerals did not contribute substantially to acid neutralization. At the time
of drainage acidification, the remnant sulfide contents for T9 and T6 were about 3.3% and 1.3%, respectively, implying remnant FeS₂ contents for T9 and T6 of 6.19% and 2.49%, respectively.

- 3. Based on earlier work, the rate of sulfide oxidation increased with solid-phase sulfide content. The oxidation rate for T9 and T6 also increased as drainage pH became acidic. On a molar basis, the total calcium plus magnesium release from carbonate minerals was about 1.6 to 1.9 times that of sulfate.
- 4. The time to deplete capacities for acid production and acid neutralization can be estimated based on solid-phase analyses and dissolution testing. First, the potentials for acid production and acid neutralization must be determined for samples subjected to dissolution testing. Second, the drainage volume generated in dissolution tests must be determined and the drainage must be analyzed for sulfate, calcium, and magnesium in addition to pH. Third, the rates of release for sulfate, calcium, and magnesium must be calculated from these values. Dividing the AP and NP remaining at the end of the period of record by the appropriate rates (AP by sulfate release rate; NP by the sum of calcium and magnesium release, in appropriate units) will yield a first-cut estimate of whether drainage will remain basic (i.e. acid producing capacity will be depleted before acid neutralizing capacity).

This approach predicted, with reasonable accuracy, the lag times prior to acidification of drainage from samples T9 (112 weeks predicted versus 122 weeks observed) and T6 (321 weeks predicted versus 284 weeks observed). However, this method of estimation ignores the formation of precipitate coatings on the surfaces of acid producing and acid neutralizing minerals. Although these coatings are known to form, knowledge of their formation in mine wastes is inadequate to quantify their influence on drainage quality.

- 5. Samples T2 and T10 continued to produce drainage of slightly basic pH for a total of 290 weeks. Even after 290 weeks of dissolution, these samples contain a substantial amount of calcium and magnesium carbonate minerals. The technique described above indicated that the drainages from these two samples would become acidic in twelve and ten years, respectively. However, over this duration the pH within the tailings will be neutral to basic, and coatings may form on the iron sulfide minerals present. Such coatings may effectively inhibit their oxidation, thereby precluding the generation of acidic drainage. Similarly, coatings may occur on acid-neutralizing minerals, in which case drainage would acidify earlier than predicted.
- 6. Long term dissolution tests can reduce the uncertainty associated with predicting precipitate coating formation on sulfide and carbonate mineral surfaces and the influence of these coatings on mine waste drainage quality. Conducting such tests with operational size waste under actual field conditions provides the best simulation of the environmental behavior of the mine waste. Long term laboratory testing provides the next best approximation.
- 7. The pyrite surface area was the predominant control on the rate of pyrite oxidation observed in this experiment.

- 8. In earlier studies, the release of arsenic, antimony, or molybdenum in slightly basic drainage was observed from three (T7, T8, and T9) of the samples. The potential for such trace metal release must be considered with tailings generated from hydrothermal gold deposits such as these.
- 9. Sulfide oxidation rates at rinse intervals of 6, 24, and 84 hours were equal to or less than those at a one week rinse interval. Therefore, tests at shorter rinse intervals would not reduce the time required for testing.
 - 6.4. Elevated Temperature Experiment
 - 6.4.1. Introduction

Duplicate samples T1, T2, T4, T8, T9, T10, and T12 were subjected to the Elevated Temperature Experiment. Sample T6 was not tested due to inadequate sample mass. The samples were rinsed every two weeks through week 48 and weekly subsequently. Between rinses, samples were stored in an oven with an average weekly temperature of about 97° C (table C1.12). At 64 weeks, the duplicate reactors were discontinued. Although their results are not discussed in the following section, they are presented in appendix C along with other experimental details. Samples T1, T4, T9, T10, and T12 were discontinued at 232 weeks. Testing of the remaining two samples (T2, T8) was discontinued after 367 weeks, and data to week 256 (31 December 1996) are presented.

The following discussion presents results from reactors with 232- and 256-week periods of record. Discussion of these solids summarizes 1) solid-phase characteristics; 2) drainage pH and alkalinity; 3) sulfate concentrations, mass release, and rates of release; 4) calcium and magnesium concentrations, mass release, and rates of release; and 5) the remnant solid-phase sulfide and calcium/magnesium carbonate content. The solids are categorized based on the three general relationships between solid-phase composition and drainage quality used for the Ambient Temperature Experiment.

6.4.2. Case 1 Samples: Low to High Acid Production Potential (AP), No to Low Neutralization Potential (NP)

As was the case at 25°C, there were no samples which produced acidic drainage immediately and, therefore, fit the Case 1 profile.

6.4.3. Case 2 Samples (T9, T2, T10): Moderate to High AP, Low to High NP

Samples T9, T2, and T10 conformed to the profile of Case 2 samples. The samples contained significant amounts of NP and AP. They produced some neutral drainage for 6, 60, and 216 weeks, respectively, but the NP was eventually depleted and drainage acidified.

Sample T9 had an AP[S²⁻] of 114 mg/g CaCO₃ and an NP[(Ca/Mg)CO₃] of 14 mg/g CaCO₃ (table 5). Virtually all of the AP was present as pyrite (6.6%) and the NP was present as calcite (1.4%,

table 3). The major host rock minerals were quartz (27.5%), feldspar (27.6%), mica (16%), chlorite (2.1%), and amphibole (2.9%); table 4).

The pH of T9 drainage generally ranged from 7 to 8 during the first six weeks of the experiment. At week 8 it dropped to about 2.7, reached a minimum of 2.55 at week 12, then increased to around 4.0 at week 52. Subsequent values remained in the typical range of 4.0 to 4.2, with the exception of an excursion into the upper fours between weeks 191 and 207. The temporal variation of net alkalinity (alkalinity - acidity) was consistent with that of pH (figure 13).

Sulfate concentrations of T9 drainage peaked near 20 mmol/L at about week 10, when the drainage was most acidic (figure 14). The sulfate peak reflected sulfide mineral oxidation, since any sulfate generated during sample storage would have been rinsed off by week 6 (table 18). Sulfate concentrations subsequently decreased to a fairly stable lower level (table 19, figure 14). From week 55 to 145 concentrations typically ranged from 0.10 to 0.16 mmol/L, and from 0.052 to 0.10 mmol/L subsequently. Sulfate mass releases indicate that at weeks 55 and 145 the respective remnant sulfide contents were 61% and 55% of that originally present in the sample (appendix C, tables C4.23, C4.24). It was assumed that the barite present in the sample did not contribute significantly to the sulfate release.

Whereas the maximum sulfate release rate at elevated temperature was more than six times that at ambient temperature, the overall rate at elevated temperature was lower (table 20). This was due to the short duration of the rapid sulfate release at elevated temperature (table 18) relative to the longer period of high sulfate release after acidification at ambient temperature (table 12). After residual oxidation products were rinsed from the solids and before week 20, the rate of sulfate release at elevated temperature (1.53 versus 0.018 mmol/wk; tables 21, 12, respectively). Thus, the elevated temperature accelerated sulfate release over the short term, but the release rate decreased to fairly low rates for the majority of the period of record. In contrast, sulfate release at ambient temperature remained fairly high throughout the period following drainage acidification.

The decrease in the oxidation rate may have been the result of the decrease in the amount of sulfide minerals or decreased pyrite reactivity. Given the remnant sulfur contents at weeks 55 and 145 (see previous paragraph), rates 61% and 55%, respectively, of that for weeks 8 through 20 (this excludes the removal of residual reaction products) would be expected if there were no change in the pyrite reactivity. Since the observed rates were only about 3% and 2% of the rate in the early stages (table 21), it is reasonable to conclude that the pyrite reactivity had decreased. Decreased reactivity may have resulted from development of a precipitate coating on the pyrite surface. Cementation of the pyrite grains by iron oxyhydroxides, with a consequent reduction in available surface area, may also have inhibited sulfate release.

Calcium concentrations peaked near 7.5 mmol/L in weeks six and eight then decreased. Magnesium concentrations peaked near 1.0 mmol/L during weeks eight and ten then decreased. Sample T9 contained 1.4 percent calcite, the lowest acid neutralizing carbonate mineral content of the gold mine tailings examined (T1 - T10; table 3). Mass release calculations indicate that by week eight 60 to

70 percent of the calcite was depleted (table 22), by week ten more than 80 percent was depleted, and that by week twenty virtually no calcite remained (figure 15).

The decreases in calcium concentrations and drainage pH at week 8, indicate that the solid-phase calcite was either depleted or rendered less reactive at this time. The mass release calculation indicates that calcite was not depleted. Thus, the calcite had apparently been passivated.

Before addressing potential mechanisms of calcite passivation, the potential for procedural and analytical error must be considered. Solids were lost from reactors during the experiment, but this loss and the attendant loss of calcite were most likely slight during the eight weeks prior to drainage acidification. Data from eight terminated reactors indicate mass losses of roughly 0.1 to 0.2 g/wk, with an average loss of 0.16 g/wk (appendix G, table G1). While some of this loss results from accidental solids loss, mineral dissolution also contributes.

Analytical error is an unlikely explanation. Calcite was the only carbonate detected in this solid (table 3) and, consequently, the determination of evolved carbon dioxide would quantify the calcite content within 10%. Furthermore, calcium release prior to drainage acidification at ambient temperature implied a calcite content within 5% of that reported for solid-phase analyses (section 6.2). In addition, it is highly unlikely that aqueous calcium determinations and drainage volume measurements could have underestimated calcite dissolution by 30 to 40%.

Six potential mechanisms, other than loss of solids, come to mind for the apparent reduction in the calcite dissolution rate. The first two involve a reduction in carbonate mineral reactivity, while three additional describe potential limitations of acid transport to reactive carbonate mineral surfaces. It is possible that one or more of these proposed mechanisms were active.

First, carbonate mineral dissolution may have been inhibited due to coating by precipitates such as iron oxyhydroxides. It is conceivable that ferrous iron released during pyrite oxidation would be transported to carbonate mineral surfaces in an acidic solution. The extent of transport would be particularly high during the initial stage of the experiment when sulfide oxidation was accelerated. Upon dissolution of the carbonate mineral, solution pH would rise, ferrous iron would oxidize, and a ferric precipitate would form on the mineral surface. If this coating were adequately extensive, dissolution of the carbonate mineral would be inhibited. Second, carbonate mineral dissolution may have been inhibited by cementation of carbonate mineral grains, with an attendant reduction in available surface area.

Third, transport of acid from iron sulfide minerals to carbonate mineral surfaces may have been limited by the development of preferential flow channels. Whereas such preferential flow was not observed for T9 at ambient temperature, cementation of particles or the relatively rapid generation of mineral dissolution products at elevated temperature may have enhanced channeling. Fourth, aqueous phase transport of acid to the calcium carbonate minerals may have been limited by rapid evaporation of the aqueous transport phase at elevated temperature. The time required for evaporation was determined to be less than three hours.

Fifth, when acid reacts with calcium and magnesium carbonate minerals, carbonic acid (reaction 7) is formed and yields carbon dioxide gas (reaction 20). This might create localized areas of elevated gas pressure in the neighborhood of carbonate minerals. This gas could become trapped in the pores near the calcium carbonate grains and limit the transport of acid to the carbonate mineral surface. This could also explain the erratic oscillation of pH observed for many of the solids at the beginning of the experiment, when sulfide oxidation rates were high (relative to both later experimental stages and to testing at ambient temperature) and the consequent carbon dioxide generation would likewise be high.

 $H_2CO_3(aq) = CO_2(g) + H_2O$

[20]

A sixth potential mechanism has been discounted. It has been suggested that "air locks" may form due to water accumulation in the pores among small tailings particles to inhibit flow in an experimental procedure different from the one employed in the present project (Bradham and Caruccio 1991). The air locks reportedly "had the effect of isolating the samples from oxygen infiltration, and thus pyrite oxidation." Such an occurrence could also inhibit water, and consequently acid, from contacting carbonate minerals. Since similar flow inhibition would be expected during dissolution at ambient temperature, in which carbonate minerals were totally available, it is probably not influential in this test. Furthermore, it is likely that virtually all water present in the solids evaporated during oxidation in the oven at temperatures near 100° C. All water present was evaporated after three hours in the oven in a trial conducted to determine drying time.

No magnesium carbonate was reported in this sample, and magnesium is unlikely to be present in calcite formed in hydrothermal deposits (Mattson 1999). It is possible that some of the early magnesium release was from the mica, chlorite, and amphibole present in the sample. The subsequent low-level release of calcium and magnesium was apparently due to dissolution of feldspar, mica, chlorite, and amphibole present.

The drainage quality in the Elevated Temperature Experiment indicates that sample T9 would produce acidic drainage if subjected to wet-dry cycling in the field, which is consistent with the relative amounts of pyrite and calcite in the solid and with results from testing at ambient temperature. The dissolution time required for drainage acidification, however, was 122 weeks at ambient temperature and only eight weeks at elevated temperature. This relatively rapid depletion of calcium carbonate was due to the accelerated iron sulfide oxidation, and consequent acid production, resulting from the higher reaction temperature.

Sample T2 had an AP[S²⁻] of 228 mg/g CaCO₃ and an NP[(Ca/Mg)CO₃] of 189 mg/g CaCO₃ (table 5). The AP was supplied virtually entirely by pyrite (13.6%, table 3). The neutralization potential was present as calcite (1.5%) and dolomite (16.1%), which yielded total calcium carbonate and magnesium carbonate NP values of 101 and 88 mg/g CaCO₃, respectively (table 5). The sample also contained 1.3% siderite, and the major host rock minerals were feldspar (22.1%), quartz (20.7%), chlorite (12.1%), and mica (9.1%; table 4).

For the first 60 weeks the pH of drainage from T2 oscillated between acidic and basic ranges, with typical durations of one to three weeks in each range. Then pH decreased below 6.0, declined fairly rapidly, and after week 120 typically ranged from 3.5 to 4.0 (figure 16). The temporal trends in net alkalinity were consistent with those observed for pH (figures 16, 17).

A maximum sulfate concentration of 41 mmol/L was observed at week 12 (figure 16). This represented oxidation of sulfide minerals present, since oxidation products generated during storage were removed by week 4 (table 18). After the sulfate peak, concentrations decreased continuously. This decline was very gradual at the end of the record, with values decreasing from 0.16 mmol/L at week 85 to 0.083 mmol/L at week 256 (figure 16).

Whereas the maximum rate at elevated temperature was 15 times that at ambient temperature, the overall elevated temperature rate was within a factor of two of that at ambient temperature (3.3 versus 0.22 mmol/wk; table 20). This was due to the relatively short duration of rapid release at elevated temperature (table 18). After residual oxidation products were rinsed from the solids and before week 32, the rate of sulfate release at elevated temperature was at least 15 times that at ambient temperature (tables 2, 15, respectively). The rate of sulfate release at elevated temperature, however, ultimately decreased to levels lower than the minimum observed at ambient temperature (table 20). In contrast, sulfate release rates at ambient temperature remained within a relatively constant range.

The decrease in the oxidation rate may have been due to the decrease in the amount of sulfide minerals or decreased pyrite reactivity. The sulfate release at week 85 was approximately 128 mmol, which represents about 75% of the sulfide initially present in the sample (7.3% sulfide). If the reactivity of the sulfides present had not changed, sulfate concentrations about 25% of the maximum, or around 10 mmol/L, would be expected at week 85 due to the decrease in available sulfides. Thus, it is reasonable to conclude that the pyrite reactivity had been reduced due to partial passivation of the surface or to reduction of reactive surface area. More specifically, the low sulfate release suggests development of an inhibitive layer at the mineral surface or cementing of pyrite grains, with a consequent reduction in available surface area.

Calcium and magnesium concentrations were highest during the initial 32 weeks, with typical ranges of 10 to 14 mmol/L and 4.1 to 10 mmol/L, respectively. Concentrations of both decreased over time and ultimately plateaued at less than 0.04 mmol/L. The most marked decrease occurred during weeks 40 to 60, immediately prior to drainage acidification (figure 16).

The concurrent decreases in drainage pH and calcium and magnesium concentrations at week 61 indicate that the calcium and magnesium carbonate minerals had been depleted or rendered relatively unreactive. The initial NP[(Ca/Mg)CO₃] of T2 was 189 mg/g as CaCO₃, most of which was present as dolomite. The cumulative calcium and magnesium released at week 61 represented the depletion of 158 mg/g as CaCO₃ of this NP (84%), and over the subsequent 142 weeks represented dissolution of only an additional 5 mg/g as CaCO₃. At week 61, the cumulative calcium and magnesium mass releases indicated respective dissolutions of 97 and 61 mg/g as CaCO₃,

representing 96 and 69 percent of the respective initial calcium carbonate and magnesium carbonate mineral contents.

The mass release calculations indicate that the calcium carbonate initially present was virtually entirely dissolved and that 31 percent of the magnesium carbonate content remained. This is conceptually consistent with effective dissolution of the calcium carbonate component and reduced reactivity of magnesium carbonate components. Potential causes of such a reduction are presented in the previous discussion of sample T9. Analysis of leached solid phases for carbonate mineral content and morphology would provide insight into the active mechanisms.

As mentioned in the discussion of T9, there are experimental and analytical explanations for drainage acidification prior to apparent depletion of calcium and magnesium carbonates. The loss of solids, and the attendant NP, from the T2 reactor over 61 weeks would tend to be greater than that for T9 over 8 weeks. At week 245 the solids mass remaining in the T2 reactor was 39.7 grams, which extrapolates to a loss of 8.8 grams in 61 weeks (appendix G, table G1). If solids loss were significant, similar losses in the calcium carbonate and magnesium carbonate phases might be expected. This was not the case, as virtually all of the calcium carbonate present in the solid was accounted for by the calcium released in the drainage.

Analytical error in the solid-phase analysis for carbon dioxide evolved would affect the total carbonate mineral content of the rock, but this measurement is within 10% of the carbonate level in T2. Error in the speciation of carbonate minerals would contribute more error in this sample than in T9. T2 was reported to contain 1.3% siderite, as well as calcite and dolomite (1.55 and 16.1%, respectively), which would complicate speciation. Nonetheless, the fraction of carbonate associated with iron is fairly small, and little error would be expected due to its presence.

In the Elevated Temperature Experiment, drainage from T2 acidified after 61 weeks of reaction, suggesting that these tailings would produce acidic drainage if exposed to oxidizing wet-dry cycle conditions in the field. At ambient temperature, however, this sample produced neutral drainage for 5.6 years. The rates of calcium and magnesium release, in conjunction with the solid-phase composition, indicate that an additional seven years of dissolution would be required before the calcium and magnesium carbonates were depleted and drainage acidified. This time frame is roughly 10 times that for acidification at elevated temperature. It should furthermore be noted that the drainage may not acidify at ambient temperature if sulfide minerals become extensively coated. Such coating could reduce the rate of sulfide mineral oxidation to the extent that dissolution of the feldspar, chlorite, and/or mica present would be adequately rapid to neutralize the acid produced.

Sample T10 had an AP[S²⁻] of 185 mg/g CaCO₃, which was supplied entirely by pyrite (11.1%). The NP[(Ca/Mg)CO₃] was 200 mg/g CaCO₃, and was supplied by both calcite (2.1%) and ankerite (19.7%; table 3). The total calcium carbonate and magnesium carbonate NP values were 127 and 74 mg/g CaCO₃, respectively (table 5). Both the AP and NP were among the highest of the samples examined. The major host rock minerals were siderite (31.4%), quartz (16.3%), feldspar (13.3%), mica (4.4%), and chlorite (4.2%; table 4).

The pH of drainage from T10 oscillated between neutral and acidic between weeks 0 to 50 and then remained in the neutral range until week 130, after which oscillations recurred until week 216 (figure 18). Drainage pH then decreased below 6.0, reaching a minimum of 3.6 at week 225, seven weeks before the reactor was terminated. Temporal variations in alkalinity paralleled those observed for pH.

Sulfate concentrations from T10 reached a maximum of 46 mmol/L at week 4. The sulfate peak reflected a rapid rate of sulfide oxidation, since the majority of residual reaction products were rinsed off at week 2 (table 19). Subsequently concentrations decreased steadily, falling below 0.02 mmol/L at week 200 (figure 19). The initial rate of oxidation (after removal of residual oxidation products) was roughly 15 times that at ambient temperature (tables 21, 15, respectively). However, the rate at elevated temperature decreased to values well below the minimum observed at ambient temperature (table 20). Consequently, the overall rates of release for the period of record were roughly equal for the two experiments (table 20).

The decrease in sulfate release at elevated temperature indicated that sulfide minerals available for reaction had been substantially depleted or rendered relatively unreactive. At week 200 the cumulative sulfate release was 110 mmol, indicating a remnant solid-phase sulfur content of 1.2% and an AP of 37 mg/g CaCO₃. Since 20% of the initial sulfur remained, sulfate concentrations of roughly 9 mmol/L ($0.20 \times$ maximum concentration of 46 mmol/L) would be expected, assuming no decrease in pyrite reactivity. Observed concentrations below 0.02 mmol/L imply a reduction in reactivity and/or available surface area, as discussed for T9 and T2. It is important to note, however, that despite the low rate of sulfide mineral oxidation and the consequent acid production, the drainage acidified after week 216. No increase in the rate of sulfide oxidation was observed after acidification.

Calcium and magnesium concentrations were highest at the beginning of the experiment, peaking at 18 and 9.9 mmol/L, respectively, within the first eight weeks. Concentrations subsequently declined and reached minimums of 0.005 and 0.02 mmol/L, respectively, at week 220. Temporal variations generally paralleled those for sulfate (figure 19). This similarity indicates that dissolution of the carbonate minerals was largely due to attack by acid released as a result of pyrite oxidation.

Calcium and magnesium mass release data indicated that roughly 80 percent (159 mg/g CaCO₃) of the calcium and magnesium carbonate minerals initially present (200 mg/g CaCO₃) had been dissolved after 216 weeks (table 22). The drainage acidification after week 216 indicates no remaining available NP. As has been previously stated, it is assumed that the "missing" NP is due to a combination of 1) solids loss during the experiment (which would tend to be highest for T10 since the time to acidification was the longest); 2) solid-phase and aqueous-phase analytical error (the potential error in carbonate mineral speciation would be higher since carbonate was associated with calcium, magnesium, and iron); 3) inhibition of calcium or magnesium carbonate reactivity due to precipitate coating of carbonates or mineral grain cementation; and 4) inhibition of acid transport to available reactive calcium or magnesium carbonate mineral surfaces due to a) development of preferential flow channels, b) rapid evaporation of water, or c) entrapment of carbon dioxide near carbonate mineral grains.

The reactor was terminated after 232 weeks and analysis of the leached solid indicated an evolved carbon dioxide content of 0.498% (appendix C, table C7.6). This implies a maximum remaining calcium carbonate content of 1.1% and an NP[(Ca/Mg)CO₃] of 11 mg/g CaCO₃. Unfortunately this sample also contained ankerite and siderite. Thus, it is not possible to conclude if the carbonate present was present as remnant NP with calcium and magnesium, or with iron. Even if the carbonate were present with calcium and magnesium, the sum of NP released and the NP remaining is 30 mg/g CaCO₃ less than that reported for the unleached solid (159 + 11 versus 200 mg/g CaCO₃). This reflects loss of solids during the experiment, nonrepresentative splitting of original or leached samples, analytical error in solid-phase carbon dioxide evolved or aqueous-phase calcium and magnesium analyses, or incorrect speciation of carbonate minerals in the unleached solids. The majority of error can be attributed to solids loss during experimentation, as the mass of solids remaining after 232 weeks was 24.2 grams as compared to an initial mass of 75 grams (appendix G, table G1.1). While some of this loss can be attributed to mineral dissolution, a substantial amount would be the result of accidental loss during the experiment.

In the Elevated Temperature Experiment, drainage from T10 acidified after 4.2 years (216 weeks) of reaction, suggesting that these tailings would produce acidic drainage if exposed to oxidizing wetdry cycle conditions in the field. At ambient temperature, however, this sample produced neutral drainage for 5.6 years. The rates of calcium and magnesium release, in conjunction with the solidphase composition, indicate that an additional 4.5 years of dissolution would be required before the calcium and magnesium carbonates were depleted and drainage acidified at ambient temperature (table 17). This time frame is roughly 2.4 times that for acidification at elevated temperature. It should furthermore be noted that the drainage may not acidify at ambient temperature if sulfide minerals become extensively coated. Such coating could reduce the rate of sulfide mineral oxidation to the extent that dissolution of the feldspar, chlorite, and/or mica present would be adequately rapid to neutralize the acid produced.

Data from the initial 64 weeks of T10 dissolution indicated that its drainage would not acidify. Drainage pH actually decreased below 6.0 after 4.2 years (217 weeks) of dissolution at elevated temperature. Much of the error in projection was due to the availability of only 80% of the NP[(Ca/Mg)CO₃], as opposed to the 100% availability assumed for the projection. In addition, the sulfur content may have been somewhat higher than the value used for projections, due to the variability in sulfur determinations on this sample (see section 6.2). It should be noted that rates of NP[(Ca/Mg)CO₃] release decreased with time as opposed to remaining constant as assumed for the projection. This would tend to underestimate the time to NP depletion.

The erratic oscillation of drainage pH and alkalinity earlier in the experiment presents some cause for concern. Such oscillation was also observed for sample T2, and to a minor extent for T9. The oscillation may have been due, in part, to the elevated contents of iron sulfides and calcium/magnesium carbonates. The high rate of acid production (a result of both the high iron sulfide content and the elevated temperature) accelerated calcium and magnesium carbonate dissolution which, in turn, would generated a relatively large amount of carbon dioxide. If acid transport were limited by elevated carbon dioxide pressure in pores near the carbonate minerals, the high carbon dioxide generation by this samples would tend to inhibit neutralization until the carbon dioxide escaped to the atmosphere. Since this behavior was not observed in dissolution tests at ambient temperature, it is assumed that similar limitation of acid transport to carbonate mineral surfaces would not occur in the field.

6.4.4. Case 3 Samples (T1, T4, T8, T12): High AP, High NP and Low AP, Low NP

This group consists of samples least likely to produce acidic drainage. The mineralogy of T12 was markedly different from the hydrothermal quartz-carbonate tailings (T1-T10) and its results are discussed at the end of this section. The mineralogy of T1, T4, and T8 was similar, as was their dissolution behavior. The AP values were moderate, ranging from 15 to 53 mg/g CaCO₃, while the NP range of 110 to 207 mg/g CaCO₃ was comparatively high (table 5). The AP was present largely as pyrite except for sample T8, which contained some pyrrhotite (table 4). Dolomite provided virtually all of the carbonate mineral NP. The samples contained 0.1 to 1.9% siderite and the major host rock minerals were quartz, feldspar, mica, and chlorite (table 4). Sample T12 was distinct from the other samples, with an AP less than 0.3 mg/g CaCO₃ and an NP of 4 mg/g CaCO₃. The sulfides in T12 were partially oxidized and poorly liberated (appendix A, table A5.1) and calcite was the only carbonate mineral detected (table 3). The host rock mineralogy was also distinct, with roughly half the sample consisting of serpentine and magnetite.

Samples T1, T4, and T8 produced drainage pH values in the typical range of 7.5 to 8.1 (figures 20, 21, 22, respectively). These drainage pH values are slightly lower than those observed for the 57-week dissolution of these solids at room temperature, which were typically between 8.0 and 8.2 (Lapakko 1991). (Testing of these solids at room temperature was terminated after 57 weeks. See section 5.2.1.) Alkalinity followed similar temporal trends for the three solids, decreasing for the first 50 to 60 weeks then becoming relatively stable in the range of 30 to 60 mg/L (figures 20, 21, 22). Alkalinities from T8 appeared to decline gradually over this last period.

Sulfate concentrations in the drainages from T1, T4, and T8 peaked from 4 to 12 weeks into the experiment at values ranging from 2.3 to 4.7 mmol/L (table 19). Concentrations subsequently declined consistently, reaching levels of 0.01 to 0.03 mmol/L after about week 210. The maximum rates of sulfate release at elevated temperature were roughly 15 to 20 times those observed at ambient temperature (table 20). The minimum rates for the two experiments were in closer agreement (table 20), although it must be noted that the ambient temperature period of record for these samples was only 57 weeks. Nonetheless, the results suggest that elevated temperature will produce elevated sulfide oxidation initially, but rates will eventually decline to levels at or below those at ambient temperature.

This decrease was influenced to some degree by the decrease in available iron sulfides. At week 232 (254 for solid T8), the sulfide content of the T1, T4, and T8 had been respectively reduced to 0, 22, and 60% of the original values (table 23). The sulfate release rates at this time were 6.3, 2.3, and 3.7% of their initial values, indicating an inhibited reactivity of the sulfide minerals present (table 24). As with the previous set of samples (section 6.3.3) formation of ferric oxyhydroxide coatings on pyrite surfaces and/or cementation of pyrite grains may have inhibited oxidation.

Of all samples examined, the fraction of sulfide oxidized was lowest from T8, in which 23 percent of the sulfide occurred with pyrrhotite (table 23). It should be noted, however, that the extent of sulfide oxidation was also relatively low for sample T9, in which pyrite was the predominant sulfide. Barite was also present in T9 and may have contributed to inhibition of pyrite oxidation. No sulfate minerals were detected in the other samples.

Results of previous work (Lapakko et al. 1995) indicated that elevated temperature accelerates pyrrhotite oxidation to a lesser degree than pyrite oxidation (tables 25 and 26). This may be related to differences in initial mechanisms of oxidation or ultimate rate inhibition for pyrite and pyrrhotite. Pyrite oxidation occurs by reaction of water and oxygen at the mineral surface, and its rate is limited by the reactions at the mineral surface (Kriegman-King and Reinhard 1994; Morse 1991; Nicholson et al. 1990; Hammack 1985, 1987). As oxidation continues, reaction has been reported to be limited by formation of precipitate coatings on the mineral surface. In contrast, pyrrhotite oxidation is ultimately limited by diffusion of ferric iron and electrons through a ferric oxyhydroxide leached layer at the mineral grain surface. As the layer thickens, diffusion is inhibited (Pratt et al. 1994a, 1994b).

The elevated temperatures may have enhanced development of the leached layer on pyrrhotite grains to a greater extent than precipitate layers on pyrite grains. It should also be noted that the leached layer which limits pyrrhotite oxidation may be a more effective oxidation retardant than the precipitate coating on pyrite surfaces. In particular, the leached layer may be more uniform and continuous, whereas precipitate coatings on pyrite are reported to be "poorly adhered" and "susceptible to dessication" (Yanful et al. 1997). Such coating may have been less effective in limiting the transport of oxygen and/or water to the mineral surface.

Calcium and magnesium concentrations generally paralleled those of sulfate. Concentration peaks occurred within the first 12 weeks for both calcium (approximately 2.7 - 4.2 mmol/L) and magnesium (0.8 - 1.6 mmol/L). The initial peak feature is more obvious for calcium and magnesium. These concentrations decreased to about 0.2 mmol/L (figures 23, 24, 25).

It should be noted that for T4 and T8 concentration peaks for calcium and magnesium occurred at week 130. Calcium and magnesium peaks, in the absence of sulfate peaks, also occurred at week 215 for T4 and at weeks 190 and 225 for T8. Corresponding peaks in alkalinity and specific conductance occurred at these times, indicating the elevated calcium and magnesium values were not the result of analytical error. The coincidence of these peaks suggests that dissolution of calcium and magnesium carbonates was accelerated by something other than the acid production which resulted from iron sulfide oxidation. This behavior is most puzzling, particularly as it occurred for two solids at the same time.

After 232 weeks of dissolution at elevated temperature, the AP was depleted from samples T1 and T12 (table 23). Substantial NP remained also remained in sample T1 (table 27). It was concluded that these samples would not generate acid in the long term. At this time the remnant AP and NP for T4 were 8 and 71 mg/g CaCO₃, suggesting that the excess NP would be adequate to neutralize the acid produced over the long term. However, the rate of NP depletion at the end of the

experiment was substantially higher than that of AP depletion. Consequently, projections based on these data suggested NP would be depleted prior to AP, and the drainage would acidify after about six years (table 28). If acidification did occur the rate of acid production would be quite small given the low rate at 232 weeks, the decreasing rate of acid production over time, and the projected sulfide content of 0.18% at the time of NP depletion. It is conceivable that dissolution of the feldspar, chlorite, and mica present in the rock (table 4) would be capable of neutralizing acid produced at such a slow rate. Due to their low potential for acid production, testing of these samples at elevated temperature was terminated after 232 weeks.

After 256 weeks of dissolution at elevated temperature, the NP of T8 only slightly exceeded the AP (39 versus 32 mg/g CaCO_3). Based on the rates of NP and AP depletion, drainage from this sample was projected to acidify after an additional 3.4 years of dissolution (table 28). As was discussed for T4, the projected rate of acid production would be relatively low, and dissolution of host rock minerals (mica, feldspar, chlorite; table 4) might be capable of neutralizing the acid produced. Dissolution testing of this sample was continued.

The pH of drainage from **sample T12** was typically between 6.5 and 7.0, although there were five periods during which excursions below pH 6 occurred (figure 26). The low pH values are difficult to explain. The iron sulfide content of this sample was low. It should be noted, however, that analyses of leached samples yielded a higher sulfur content than that reported for the unleached sample (0.026 versus <0.01; appendix G, table G1.2 and table 2, respectively), suggesting that the initial value may have been in error. In addition, the total sulfur released from the sample was more than seven times that indicated to be present by solid-phase analysis (table 23). Nonetheless, the sulfur content present in the leached sample plus that released to drainage during the experiment, indicate an initial sulfur content less than 0.1%. This would yield an AP of 3 mg/g CaCO₃ which is lower than the reported NP of 3.7 mg/g CaCO₃ (table 5).

Sulfate concentrations after week 12 were uniformly low throughout the experiment, from less than 0.02 to 0.08 mmol/L, indicating that the rate of iron sulfide oxidation and consequent acid production was consistently low. Consequently, it is difficult to identify the source of the acid release and resultant pH decrease at the end of the experiment. It is possible that some contamination, perhaps by air-phase transport, was the cause. It is concluded that the anomalously low pH values are not an indicator of any great potential to produce acid.

6.4.5. Rates of Sulfide Mineral Oxidation

Characteristic curves of the fraction of total sulfur present versus time are presented in figure 27. Due to the relatively high percentage of barite, which is unreactive under these conditions, the curve for T9 was calculated based on the initial sulfide content. The more rapid release during the first 40 weeks and subsequent slower release is reflected in this figure. The rates decreased over time due to the diminishing sulfide mineral mass and, possibly, the formation of coatings on the sulfide mineral surfaces.

The rates at the beginning of the experiment generally exceeded overall rates at room temperature by a factor of 40 (table 20). During the first 57 weeks of biweekly rinses at elevated temperature, sulfate release was six to ten times that for 57 weekly rinses at ambient temperature (table 29). However at elevated temperature rates decreased over time, and the minimum rates observed were similar or lower (T10) than minimum rates observed at ambient temperature (table 20). In addition, sulfate release at elevated temperature did not increase as drainage became acidic. This was substantially different than the marked sulfate release increase observed at ambient temperature for acidic drainage.

The extent of sulfide mineral oxidation from T1 was the greatest, with virtually all sulfides oxidized (figure 27). The extent of sulfide oxidation from samples T8 and T9 was lower than that for the samples in general, perhaps due to the sulfur-bearing minerals in these samples. T8 contained a substantial amount of pyrrhotite and T9 was the only sample containing barite (table 3). (T6 and T7 also contained pyrrhotite but were only tested at ambient temperature.) T8 also contained pyrite, and it is possible that the occurrence of both minerals reflected mineralizing conditions which produced a less reactive form of pyrite.

The rate of calcium and magnesium carbonate mineral dissolution was also accelerated in the Elevated Temperature Experiment, although to a lesser degree than the sulfide mineral oxidation. As a result of the preferential acceleration of the sulfide mineral oxidation, more acid was neutralized per mole of carbonate mineral dissolved (table 29). The dissolution of calcium or magnesium carbonate minerals will neutralize between zero and two moles of acid, as discussed in section 4. Tailings samples T1, T4, and T8 generated neutral drainage throughout the Elevated Temperature Experiment, as was the case in the Ambient Temperature Experiment. However, the molar ratio of acid produced to carbonate mineral dissolved at the high temperature was two to three times that at the lower temperature. The high acid neutralization at elevated temperature was most likely the result of the higher rate of acid production. A similar occurrence was observed at ambient temperature for rapid sulfide oxidation, and attendant acid production, resulting from a high mass of iron sulfide present (table 29; see also Lapakko 1993, figure 12).

6.4.6. Modification of Elevated Temperature Experiment Protocol

As described in section 5.2.2., testing was conducted to examine the effects of a) one versus two 200-mL rinse volumes of 85 °C deionized water, b) room temperature versus 85 °C rinse water temperature, and c) weekly versus bi-weekly rinsing. To compare one versus two 200-mL rinses, one reactor of T2 and T10 tailings were rinsed once per week from weeks 49 to 64. At the same time, a pair of duplicate reactors of each sample was rinsed with two 200-mL volumes. The mass releases of sulfate, calcium, and magnesium for the single rinses were not substantially different from the double rinses for either solid (table 30).

To determine if rinsing efficiency using deionized water at room temperature differed from that at 85 °C, one reactor of T2 and T10 were rinsed biweekly from weeks 2 to 48 with two 200-mL volumes of room temperature water. At the same time, a pair of duplicate reactors of each sample was rinsed with two 200-mL volumes of water heated to 85 °C. The mass releases of sulfate,

calcium, and magnesium for the ambient temperature rinses were not substantially different from the rinses with 85 °C water (table 31).

An experiment was not specifically designed to determine the relationship between one- and twoweek rinse intervals. To gain some insight on this relationship, the extent of oxidation with a oneweek rinse interval was compared to that with a two-week rinse interval using data from before and after a change in experimental design. The rinse interval for duplicate pairs of T1, T2, T4, T8, T9, T10, and T12 was changed from two weeks to one week after 48 weeks of reaction. The mass release of sulfate, calcium, and magnesium at the shorter interval was generally less than that at the longer interval. However, mass release was decreasing with time over the initial 48 weeks and this trend most likely continued (appendix E, figures E3.7, E3.8). It is likely that a rinse interval as short as one day would produce the same amount of sulfide oxidation as the two-week interval. The water retained by one tailings sample (T4) was found to evaporate entirely in less than three hours in the oven. Since water is a reactant in the oxidation of iron sulfide minerals (reactions 1, 2), little reaction would be expected after evaporation.

6.4.7. Summary

Duplicate samples T1, T2, T4, T8, T9, T10, and T12 were subjected to the Elevated Temperature Experiment. Samples T1, T4, T9, T10, and T12 were discontinued at 232 weeks. Testing of solids T2 and T8 was terminated at week 367, and data to week 256 (31 December 1996) are presented.

- 1. For all samples drainage pH was initially above 6.0, but for three samples permanently decreased below this value. Sulfate concentrations generally peaked within the first 12 weeks at values typically ranging from 3.1 to 52 mmol/L. They subsequently decreased and, after about 150 weeks (typically), plateaued at values of 0.01 to 0.1 mmol/L (table 19). The initial rates of sulfate release were typically 15 to 20 times maximum rates at ambient temperature. However, these rates decreased over time to levels similar to the minimum rates observed at ambient temperature (table 20). Whereas reduction in the sulfide mineral mass contributed to some of the decrease in rates, reduction in reactivity played a major role. It is also of interest to note that elevated temperature sulfate release rates did not increase after drainage acidification. Calcium and magnesium concentrations generally paralleled those of sulfate, although magnesium values tended to be less variable.
- 2. The pH of drainage from samples T9, T2, and T10 decreased below 6.0 after dissolution periods of 8, 61, and 217 weeks, respectively. Upon acidification, the remnant sulfur contents of T9, T2, and T10 were 5.2%, 2.3%, and 1.2%, respectively, indicating that all three have potential to generate acidic drainage for a substantial period. In testing at ambient temperature, drainage from T9 acidified after 122 weeks of dissolution, while T2 and T10 generated neutral drainage throughout the 290 week period of record.
- 3. The fractions of NP[(Ca/Mg)CO₃] available for acid neutralization prior to drainage acidification for T9, T2, and T10 were 67, 82, and 80 percent (table 22). These values are lower than the 105 and 90 percent values for available NP[(Ca/Mg)CO₃] determined for T9 and T6

at ambient temperature. Accidental solids loss during the elevated temperature tests accounts for some of the unavailable NP, and additional analysis on the extent of this contribution is warranted. Several other factors may have contributed to the reduction in carbonate reactivity at elevated temperature.

- 4. The pH of drainage from T2 and T10 at elevated temperature oscillated between circumneutral and acidic prior to permanently decreasing below pH 6. This oscillation was not observed for samples T1, T4, T8, and T12, which remained in the neutral range. The oscillation may be due to accelerated generation of carbon dioxide, and consequent elevation of gas pressure in the pores near carbonate minerals. Such conditions could inhibit acid transport to carbonate mineral surfaces for neutralization. The wide variation in drainage pH may serve as an early indicator of ultimate drainage acidification. Such oscillation has not been observed in ambient temperature dissolution tests in the present study or in previous studies. Furthermore, this behavior would not be expected under environmental conditions.
- 5. Samples T1, T4, T8, and T12 generated neutral drainage throughout the Elevated Temperature Experiment, as was the case in testing at ambient temperature for 57 weeks (Lapakko 1993).
- 6. The agreement between results at elevated temperature and ambient temperature testing of samples T1, T4, T8, T9, and T12 suggests that the two tests provide the same predictions with respect to potential for acid generation. Furthermore, data from sample T9 suggest that the Elevated Temperature Experiment may predict the quality of drainage from similar composition mine wastes (typically quartz-carbonate tailings) much more rapidly than the Ambient Temperature Experiment at lower temperature. The shorter test duration required is due to the accelerated sulfide oxidation at the higher temperature. Whereas samples T2 and T10 acidified at elevated temperature, they did not do so at room temperature. Based on the agreement between the two tests for T9, it might be concluded that T2 and T10 would also eventually acidify at room temperature.
- 7. There are other potential complications and reasons for caution in the extrapolation of results generated at elevated temperature. The elevated temperatures are not typical of the reaction environment in the field and, consequently, the drainage quality in this test may not simulate that in the field. Both the reduced availability of NP[(Ca/Mg)CO₃] and the pH oscillation described above deviate from observations in testing at ambient temperature.

A key characteristic of the test was the initial acceleration of iron sulfide oxidation, as indicated by sulfate release, followed by a decline to relatively low oxidation rates. Both the exceptionally high iron sulfide oxidation rates and very low rates, as well as enhanced evaporation, may have inhibited the effectiveness of carbonate minerals present.

First, the elevated sulfate release in the initial stage of the experiment reflected rapid oxidation of iron sulfide minerals present. Elevated iron concentrations would favor formation of coatings on the surfaces of both pyrite and acid-neutralizing minerals. Elevated iron concentrations transported in an acidic solution to the carbonate mineral surface, where neutralization occurred, could oxidize and precipitate as iron hydroxides or oxyhydroxides at the surface. If this precipitation were adequately extensive, calcite dissolution would be inhibited. Furthermore, the acidic conditions could also lead to cementation of carbonate minerals within a matrix of other particles, thus rendering them less available for contact with acid generated subsequently.

Second, when sulfide oxidation and the consequent acid production is low, dissolution of carbonate minerals without acid neutralization (e.g. $CaCO_3 = Ca^{2+} + CO_3^{2-}$) is enhanced. That is, the acid neutralized per mole of carbonate mineral dissolved decreases at the low rates of sulfide oxidation (table 29). Thus, the carbonate mineral dissolution neutralizes less acid during the extended periods of low acid production.

Third, the high temperatures also accelerate evaporation rates. Due to a limited availability of water, iron present in acidic solutions that are neutralized at the carbonate mineral surface is less likely to be transported from the site of neutralization. Thus, the lack of water enhances carbonate mineral coating by iron precipitates. The degree of formation of coatings on mineral surfaces and/or cementation at the high temperatures may not reflect behavior at environmental temperatures.

Thus, although T2 and T10 produced acidic drainage at elevated temperature, this may not be the case at ambient temperature, since the calcium and magnesium carbonates may be more available for neutralization. The incomplete availability of calcium and magnesium carbonate minerals, despite a very fine particle size, suggests that results at elevated temperature may deviate from those under conditions more closely approximating those in the environment. In contrast, the calcite dissolved prior to acidification of T9 at ambient temperature was calculated as slightly larger than the calcite present, indicating that all of the calcite dissolved prior to drainage pH decreasing below 6.0.

It must be noted that samples T1, T4, T8, and T12 produced neutral drainage throughout the test at elevated temperature, as was the case at ambient temperature. Thus, if there are deviations between the two tests they may be of consequence only for cases in which NP slightly exceeds AP. These cases are the most likely to yield incorrect results if the availability or acid-neutralizing efficiency of calcium and magnesium carbonates is limited.

Modifications recommended for future use of the Elevated Temperature Test are use of a) shorter intervals between rinses, b) one rather than two 200-mL water volumes for rinsing, and c) room temperature water for rinses rather than water heated to 85 °C. The first recommendation allows results to be generated more rapidly, and the remaining two reduce the personnel time required for testing.

7. ACKNOWLEDGEMENTS

Anne Jagunich, with assistance from Kate Willis, Katherine Dahlin, Cal Jokela, and Pat Geiselman conducted dissolution experiments and analyzed drainage samples for pH, specific conductance, alkalinity, and acidity. Over the first 200 weeks of the project, Albert Klaysmat and Jean Matthew analyzed drainage samples for metals (calcium and magnesium) and sulfate, respectively. Greg Walsh was responsible for data entry. Separation of the sulfide mineral fraction of the tailings and analysis of their chemistry and mineralogy were conducted by Louis Mattson of Midland Research, Nashwauk, MN. Specific surface area of the sulfide mineral fraction was analyzed by Eyasu Mekonnen of the Soil Science Department at the University of Minnesota, St. Paul, MN. Additional solid-phase analyses were conducted by Charles Bucknam at Newmont Metallurgical Services, Denver, CO. Helpful report review was provided by Anne Jagunich, Lyn Jakel, and Jon Wagner. Project funding during the first four years of the project was provided by the Minnesota Department of Natural Resources, Division of Minerals.

8. **REFERENCES**

American Public Health Association, American Water Works Association, Water Environment Federation. 1992. Standard Methods for the Examination of Water and Wastewater. 18th edition. American Public Health Association, Washington, DC.

Borek, S.L. 1994. Effect of humidity of pyrite oxidation. <u>In</u> Environmental Geochemistry of Sulfide Oxidation, ACS Symposium Series No. 550. C.N. Alpers and D.W. Blowes (eds.). American Chemical Society, Washington, DC. p. 31-44.

Bradham, W. S., Caruccio, F. T. 1991. A comparative study of tailings analysis using acid/base accounting, cells, columns, and soxhlets. <u>In Proc. of the Second International Conference on the Abatement of Acidic Drainage, V. 1, CANMET, Montreal, Quebec, Canada. p. 157-173.</u>

Brunauer, S., Emmett, P. H., Teller, E. 1938. Adsorption of gases in multimolecular layers. American Chemical Society, vol. 60. p. 309-319.

Busenberg, E., Clemency, C. 1976. The dissolution kinetics of feldspars at 25°C. Geochim. Cosmochim. Acta 40, 41-49.

Eary, E. L., Schramke, J. A. 1990. Rates of inorganic oxidation reactions involving dissolved oxygen. <u>In Chemical Modeling of Aqueous Systems II, Melchior, D. C. and Basset, R. L. eds. ACS</u> Symposium Series 416, American Chemical Society, Washington, D. C. p. 379-396.

Hammack, R.W. 1987. Pyrite oxidation under unsaturated conditions part I: Abiotic oxidation. In Proceeding: Billings Symposium on Surface Mining and Reclamation in the Great Plains and

American Society for Surface Mining and Reclamation. Billings, MT. Montana State University Reclamation Research Unit Report No. 8704. p. 289-295.

Hammack, R.W. 1985. The relationship between the thermal activity of pyrite and the rate of acid generation. <u>In</u> 1985 Symposium on Surface Mining, Hydrology, Sedimentology, and Reclamation. University of Kentucky, Lexington, KY, December 9-13. p. 139-144.

Hem, J. D. 1970. Study and interpretation of the chemical characteristics of natural water. Geological Survey Water-Supply Paper 1473, Washington, D.C. 363 p.

Klein, C., Hurlbut Jr., C. S. 1985. Manual of mineralogy. John Wiley and Sons, New York. 596 p.

Kleinmann, R. L. P., Crerar, D. A., Pacelli, R. R. 1981. Biogeochemistry of acid mine drainage and a method to control acid formation. Mining Eng. March 1981.

Kriegman-King, K.R., Reinhard, M. 1994. Transformation of carbon tetrachloride by pyrite in aqueous solution. Environ. Sci. Technol. 28. p. 692-700.

Lapakko, K. A. 1993. Nonferrous mine waste characterization Project: Final report. June 1993. MN DNR, Div. Minerals, St. Paul, MN. 98 p. plus appendices.

Lapakko, K. A. 1992. Characterization and static testing of ten gold mine tailings. <u>In</u> Achieving land use potential through reclamation. Proc. 9th National Meeting ASSMR, Duluth, MN, June 14-18, 1992. p. 370-384.

Lapakko, K. A. 1991. Non-ferrous mine waste project. Minnesota Department of Natural Resources, Division of Minerals, St. Paul, MN. 68 p. plus appendices.

Lapakko, K.A. 1990. Solid-phase characterization in conjunction with dissolution experiments for prediction of drainage quality. <u>In</u> Proc. Western Regional Symposium on Mining and Mineral Processing Wastes, F. Doyle (ed.), Soc. for Mining, Metallurgy, and Exploration, Inc., Littleton, CO. p. 81-86.

Lapakko, K. A., Antonson, D. A. 1991. The mixing of limestone with acid producing rock. Proc. Second International Conference on the Abatement of Acidic Drainage. Montreal, Canada, September 16-18, 1991. p. 343-358.

Lapakko, K. A., Antonson, D. A., Wagner, J. R. 1997. Mixing of limestone with finely-crushed acid-producing rock. <u>In Proceedings Fourth International Conference on Acid Rock Drainage</u>. Vol. 3, Vancouver, British Columbia, Canada, May 31 - June 6, 1997. p. 1345-1360.

Lapakko, K.A., Wessels, J. N. 1995. Release of acid from hydrothermal quartz-carbonate hosted gold-mine tailings. <u>In</u> Sudbury '95, Conference on Mining and the Environment, Sudbury, Ontario, May 28th - June 1st, 1995. p. 139-148.

Lapakko, K. A., Wessels, J. N., Antonson, D. A. 1995. Long term dissolution testing of mine waste. Report to the United States Environmental Protection Agency. Grant No. X-8200322-01-0. MN DNR Div. Minerals, St. Paul, MN. 85 p. plus appendices.

Legge, M. 1993. Personal communication with Mike Legge, Industrial Coordinator II, Water Resources Division, Yellowknife, Northwest Territories, (403) 920-8243.

Mattson, L.A. 1999. Personal communication with Louis Mattson, Mineralogical Consulting Service, Pengilly, MN.

McKay, D.R., Halpern, J. 1958. A kinetic study of the oxidation of pyrite in aqueous suspension. Trans. Of Metall. Soc. Of A.I.M.E., June.

Meyer, K. 1992. The David Bell Mine water quality management strategy. CIM Bull. Sept. 1992. p. 37-30.

Morse, J.W. 1991. Oxidation kinetics of sedimentary pyrite in seawater. Geochim. Cosmochim. Acta, v. 55. p. 3665-3667.

Morth, A.H., Smith, E.E. 1966. Kinetics of the sulfide-to-sulfate reaction. In Symposium on Fossil Fuels and Environmental Pollution, ACS Division, Fuel Chemistry Preprints, v. 10. p. 83-92.

Nelson, M. 1978. Kinetics and mechanisms of the oxidation of ferrous sulfide. Ph.D. Thesis, Stanford University, Palo Alto, CA.

Nicholson, R.V., Scharer, J.M. 1994. Laboratory studies of pyrrhotite oxidation kinetics. In Environmental Geochemistry of Sulfide Oxidation, C.N. Alpers and D.W. Blowes (eds.). ACS Symposium Series No. 550, American Chemical Society, Washington, DC. p. 14-30.

Nicholson, R.V., Gillham, R.W., Reardon, E.J. 1990. Pyrite oxidation in carbonate-buffered solution: 2. Rate control by oxide coatings. Geochim. Cosmochim. Acta, v. 54. p. 395-402.

Nordstrom, D. K. 1982. Aqueous pyrite oxidation and the consequent formation of secondary iron minerals. <u>In</u> Acid Sulfate Weathering. Chapter 3. J.R. Kittrick, D.S. Fanning, L.R. Hossner (eds.), Spec. Publ. 10, Soil Sci. Am. Madison, WI. p. 37-56.

Pratt, A.R., Muir, I.J., Nesbitt, H.W. 1994a. X-ray photoelectron and Auger electron spectroscopic studies of pyrrhotite and mechanism of air oxidation. Geochim. Cosmochim. Acta, v. 58. p. 827-841.

Pratt, A.R., Nesbitt, H.W., Muir, I.J. 1994b. Generation of acids from mine waste: Oxidative leaching of pyrrhotite in dilute H_2SO_4 solutions at pH 3.0. Geochim. Cosmochim. Acta, v. 58. p. 5147-5159.

Renton, J. J., Rhymer, T. E., Stiller, A.H. 1988. A laboratory procedure to evaluate the acid producing potential of coal associated rocks. Mining Science and Technology, 7. p. 227-235.

Renton, J. J., Stiller, A. H., Rhymer, T. E. 1985. Evaluation of the acid producing potential of toxic rock materials. <u>In</u> Stopping Acid Mine Drainage: A New Approach. West Virginia Geological and Economic Survey. p. 7-12.

Renton, J. J. 1983. Laboratory studies of acid generation from coal associated rocks. In Proceedings of Surface Mining and Water Quality, Clarksburg, W. Va. May 26, 1983.

Scott, W. W. 1942. Scott's standard methods of chemical analysis. D. Van Norstrand Co, Inc., New York, NY.

Singer, P. C., Stumm, W. 1970. Acid mine drainage: The rate determining step. Science, 167. p. 1121-1123.

Stumm, W., Morgan, J. J. 1981. Aquatic chemistry - an introduction emphasizing chemical equilibria in natural waters. John Wiley & Sons, Inc. p. 470.

Sung, W., Morgan, J. J. 1980. Kinetics and product of ferrous iron oxygenation in aqueous systems. Environ. Sci. Techno. 14. p. 561-568.

Yanful, E.K., Mycroft, J., Pratt, A.R. St-Arnaud, L.C. 1997. Factors controlling metal leaching from mine rock: The case of Stratmat and Selbaie waste rocks. <u>In</u> Proceedings of the Fourth International Conference on Acid Rock Drainage, May 31-June 6, 1997, Vancouver, B.C., v. 2. p. 663-679.

		Screet	n Size	
Solid	$+0.149 \text{ mm}^{1}$	$+0.053 \text{ mm}^2$	$+0.025 \text{ mm}^3$	-0.025 mm ⁴
T1	14.37	35.01	16.66	33.96
T2	0.27	2.48	6.24	91.01
Т3	4.04	22.77	19.06	54.13
T4	1.83	18.25	18.60	61.32
Т5	8.97	26.82	19.45	44.76
Т6	12.88	40.32	20.54	26.26
T7	13.72	27.77	15.87	42.64
Т8	7.99	24.49	17.19	50.33
Т9	1.42	28.90	28.05	41.63
T10	0.58	16.63	18.16	64.63
T11	83.75	14.28	1.22	0.75
T12	56.04	15.04	12.84	16.08

Table 1. Particle size distribution of tailings in weight percent (wet screening by Hanna Research Center).

Equal to +100 Mesh Equal to +270 Mesh Equal to +500 Mesh Equal to -500 Mesh

	Con	centrat	ions in p	ercent						Сс	oncentrat	ions in pa	arts per m	nillion					
Solid	S _{TOT}	SO4	S ²⁻	CO ₂	Ag	As	Ba	Be	Cd	Cr	Cu	Hg	Мо	Ni	Pb	Sb	Se	Tl	Zn
T1	0.51	0.06	0.49	9.86	<0.5	38	67	<0.5	1	146	26	0.23	<1	32	15	<5	<1	<1	339
T2	7.63	1.00	7.3	8.91	<0.5	429	36	<0.5	3	165	155	1.80	<1	125	122	<5	2	<1	931
T3	1.03	0.05	1.01	7.50	<0.5	151	22	<0.5	<1	209	117	0.05	<1	118	22	<5	7	3	114
T4	1.15	0.14	1.10	6.84	<0.5	115	25	<0.5	<1	212	149	0.03	<1	110	19	<5	<1	1	110
T5	0.67	0.04	0.66	2.94	<0.5	47	38	<0.5	1	64	39	0.02	2	27	55	<5	1	2	84
T6	2.12	0.16	2.07	7.54	<0.5	1240	42	<0.5	<1	104	67	0.03	<1	18	21	<5	3	4	66
T7	0.10	0.05	0.08	10.23	<0.5	1346	53	<0.5	<1	281	33	0.05	<1	126	14	18	2	1	60
T8	1.73	0.07	1.70	4.88	<0.5	>2000	102	<0.5	<1	213	124	1.38	<1	140	106	41	1	<1	85
Т9	5.58	5.83	3.64	0.61	1.0	234	402	<0.5	1	78	32	21.6	1130	19	26	288	<1	33	152
T10	4.08 ¹	0.57	3.89 ¹	21.85	<0.5	281	90	<0.5	2	52	23	0.06	<1	26	28	<5	2	4	61
T11	<0.02	0.02	< 0.01	0.17	<0.5	72	72	<0.5	5	2368	1098	0.04	<1.	463	40	<5	<1	<1	97
T12	<0.02	0.03	< 0.01	0.16	<0.5	17	42	<0.5	<1	156	1615	0.03	<1	620	19	<5	<1	1	103

Table 2. Chemical analysis for regulatory parameters in tailing samples (analysis by Bondar-Clegg).

¹ Sulfur analyses assumed to be in error. See section 6.3.3.

NOTE: Additional whole rock chemical analysis data in appendix A, table A3.2., A3.3.

Miner	al	T1	T2	T3	T4	Т5	T6	T7	T8	T9	T10	T11 ¹	T12 ¹
Carbonates													
Calcite Dolomite Ankerite Siderite CaCO ₃ +MgCO	O ₃ ²	0.2 18.9 - 1.9 20.7	1.5 16.1 - 1.3 18.9	0.5 14.5 0.9 16.3	0.6 13.0 - 1.1 14.7	6.0 - 0.5 0.2 6.5	1.3 - 3.6 14.0 4.5	0.2 20.9 - 0.2 22.9	_3 10.1 _ 0.1 11.0	1.4 - - 1.4	2.1 19.7 31.4 20.0	0.4 - - 0.4	0.4 - - 0.4
Regulatory El	ement-Bea	aring Mi	nerals					, ,					
Pyrite Pyrrhotite Barite ⁴ Arsenopyrite Chalcopyrite Molybdenite Galena Stibnite Sphalerite	S Ba, SO ₄ As Cu Mo Pb Sb Zn	0.86 0.04 - 0.01 0.01 - <0.01 - 0.05	13.58 0.02 - 0.09 0.04 - 0.01 - 0.14	1.82 0.10 - 0.03 0.03 - <0.01 - 0.02	1.99 0.05 - 0.03 0.04 - <0.01 - 0.02	1.09 0.22 - 0.01 0.01 - <0.01 - 0.01	1.29 3.50 - 0.27 0.02 - <0.01 - 0.01	0.04 0.54 - 0.29 0.01 - <0.01 <0.01 0.01	2.43 1.04 - 0.40 0.04 - 0.01 0.01 0.01	$\begin{array}{c} 6.57 \\ 0.13 \\ 14.22 \\ 0.05 \\ 0.01 \\ 0.19 \\ < 0.01 \\ 0.04 \\ 0.02 \end{array}$	7.32 ⁵ - 0.06 0.01 <0.01 - 0.01	- tr ⁶ - tr - - -	- tr - tr - - -

Table 3. Mineralogic composition of tailings in weight percent (analysis by Hanna Research Center).

¹ The trace amounts of the sulfides observed in this sample were partially oxidized and generally poorly liberated. Most of the nickel in T11 and T12 occurred in olivine and serpentine rather than in sulfide minerals.

² Total calcium carbonate and magnesium carbonate expressed as percent calcium carbonate, i.e. 10×CaCO₃ + 11.9×MgCO₃.

 3 - = not present

⁴ Barite was the only sulfate mineral detected. Sulfate in other samples is probably due to pyrite and/or pyrrhotite oxidation which often forms melanterite, FeSO₄·7H₂O.

⁵ Later analysis determined erroneous sulfur percentage in sample T10, therefore pyrite content is adjusted to 11.1%.

 6 tr = trace

Mineral	T1	T2	Т3	T4	T5	Т6	T7	Т8	Т9	T10	T11	T12
Quartz	43.7	20.7	32.0	31.1	26.6	40.6	37.3	36.3	27.5	16.3	_	4.4
Feldspar	14.1	22.1	18.1	22.0	36.9	1.4	15.9	13.4	27.6	13.3	-	15.7
Mica	9.3	9.1	8.6	8.5	7.5	11.2	10.6	24.3	16.2	4.4	-	-
Chlorite	7.9	12.1	21.2	19.8	17.4	16.8	13.6	8.6	2.1	4.2	4.4	6.5
Amphibole	-	-	-	-	-	2.6	-	1.4	2.9	-	-	8.3
Serpentine	-	-	-	-	-	-	-	-	-	-	10.3	36.2
Olivine	-	-	-	-	-	-	-	-	-	-	0.3	5.9
Stilpnomelane	-	-	-	-	-	2.3	-	-	-	-	-	-
Talc	-	-	-	-	-	-	-	-	-	-	2.2	2.4
Calcite	0.2	1.5	0.5	0.6	6.0	1.3	0.2	-	1.4	2.1	0.4	0.4
Dolomite	18.9	16.1	14.5	13.0	-	-	20.9	10.1	-	-	-	-
Ankerite	-	-	-	-	0.5	3.6	-	-	-	19.7	-	-
Siderite	1.9	1.3	0.9	1.1	0.2	14.0	0.2	0.1	-	31.4	-	-
Magnetite	0.1	< 0.1	0.3	-	-	0.1	0.2	0.8	< 0.1	-	43.5	13.5
Ilmenite	-	-	-	-	-	-	-	-	-	-	37.9	6.6
Tourmaline	1.6	1.4	-	-	2.2	-	-	_ ·	-	-	-	-
Apatite	0.3	0.3	0.4	0.4	0.4	0.3	<0.3	<0.3	<0.3	<0.3	0.3	< 0.3

Table 4. Major host rock composition (in weight percent) of non-ferrous tailings (analysis by Hanna Research Center).

Notes:

In addition to the minerals listed, the samples may contain accessory to trace amounts of one or more of the following minerals; rutile, sphene, garnet, sillimanite, epidote, diopside, fluorite, graphite, tetrahedrite, and scheelite.

"-" denotes not present "<" denotes present in amounts less than detection limit

Solid	% S ²⁻¹	AP ²	NP ³	Net NP ⁴	NP/AP ⁵
T1	0.49	15.3	207	191.7	13.5
T2	7.3	228.1	189	-39.1	0.83
T3	1.01	31.6	163	131.4	5.2
T4	1.10	34.4	147	112.6	4.3
T5	0.66	20.6	65	44.4	3.2
Т6	2.07	64.7	45	-19.7	0.70
T7	0.08	2.5	229	226.5	91.6
T8	1.70	53.1	110	56.9	2.1
Т9	3.64	113.8	14	-99.8	0.12
T10	5.93 ⁶	185.5	200	14.5	1.1
T11	< 0.01	<0.3	4	3.7	13.3
T12	<0.01	<0.3	4	3.7	13.3

Table 5. Mineralogic acid potential (AP) and neutralization potential (NP[(Ca/Mg)CO₃]) for tailings. Additional static test results in Lapakko 1991 (table 5) and Lapakko 1992.

¹ Sulfide analysis by Bondar-Clegg

² AP = Acid Potential, calculated as $31.25 \times \% S^{2-}$

³ NP = Neutralization Potential, calculated as $[(10 \times CaCO_3) + (11.9 \times MgCO_3)]$

⁴ Net NP = NP - AP

.

⁵ NP/AP = ratio of NP to AP

⁶ Calculated as (6.3+6.09+5.4)/3; original value in error, see text for details.

					Sulj	fur, sulfate, ai	nd sulfid	e analyses	and mean						
0.111	Bondar-Cl	egg (6-13	3-90)	Lerch I (1-14-91)		Midlar	Midland (6-25-93)			Lerch II (3-97)			mean		
Solia	total sulfur	sulfate	sulfide	total sulfur	sulfide	total sulfur	sulfate	sulfide	total sulfur	sulfate	sulfide	total sulfur	sulfate	sulfide	
T1	0.51	0.06	0.49	0.55	0.50	0.45	0.16	0.40		2 2		0.50	0.11	0.46	
T2	7.63	1.00	7.30	8.19	7.87	7.93	1.16	7.54				7.92	1.08	7.57	
T3	1.03	0.05	1.01	1.12	1.08							1.08	0.05	1.05	
T4	1.15	0.14	1.10	1.23	1.18	1.13	0.36	1.01				1.17	0.25	1.10	
T5	0.67	0.04	0.66	0.63	0.59	0.71	0.21	0.64				0.67	0.13	0.63	
T6	2.12	0.16	2.07	2.18	2.10	2.14	0.26	2.05				2.15	0.21	2.07	
T7	0.10	0.05	0.08	0.31	0.30	0.32	0.21	0.25	0.34	0.10	0.07	0.27	0.19	0.18	
T8	1.73	0.07	1.70	1.86	1.79	1.79	0.32	1.68				1.79	0.20	1.72	
Т9	5.58	5.83	3.64	5.40	5.03	5.33	0.61	5.13	5.60	0.22	3.00	5.48	2.37	4.20	
T10	4.08	0.57	3.89	6.51	6.30	6.31	0.65	6.09	6.38	0.19	5.40	5.82	1.41	5.42	
T11	0.02	0.02	0.01	0.04	0.01							0.03	0.02	0.01	
T12	0.02	0.03	0.01	0.04	0.00							0.03	0.03	0.01	

Table 6. Total sulfur, sulfate, and sulfide analyses conducted by three laboratories on the non-ferrous solids.

-

		Percent difference from the mean										-
Salid	Bondar-Clegg (6-13-90)		Lerch I (1-	-14-91)	Midlar	nd (6-25-	93)	Lero	ch II (3-97	7)	Notes: Sulfate values reported as	
Solia	total sulfur	sulfate	sulfide	total sulfur	sulfide	total sulfur	sulfate	sulfide	total sulfur	sulfate	sulfide	sulfate, except for Lerch results
T1	1.32	45.45	6.01	9.27	8.17	10.60	45.45	14.18				from 3-97 reported as sulfate as
T2	3.62	7.41	3.58	3.45	3.95	0.17	7.41	0.37				sulfate. Bondar-Clegg and
Т3	4.19	0.00	3.35	4.19	3.35							Midland sulfide values calculated
T4	1.71	44.00	0.30	5.13	7.60	3.42	44.00	7.90				by subtraction. For those values
T5	0.00	68.00	4.76	5.97	6.35	5.97	68.00	1.59				reported as less than detection
Т6	1.24	23.81	0.21	1.55	1.23	0.31	23.81	1.02				to detection. For T10 sulfide
T7	62.62	73.21	54.29	15.89	71.43	19.63	12.50	42.86	27.10	46.43	60.00	content use
T8	3.53	64.10	1.42	3.72	3.80	0.19	64.10	2.38				(6.30+6.09+5.40)/3=5.93% sulfide;
Т9	1.87	146.34	13.32	1.41	19.79	2.69	74.23	22.09	2.24	90.70	28.56	determined that Bondar-Clegg
T10	29.90	59.57	28.24	11.86	16.22	8.42	53.90	12.41	9.62	86.52	0.38	value out of fine.
T11	33.33	0.00	0.00	33.33	0.00							
T12	33.33	0.00	100.00	33.33	100.00							

Solid	Reactor(s)	Period of Record	$pH < 6.0^{1}$	Termination
		weeks	F	date
T1	1 and 2	57	remained above 6.0	7/10/91
TO	3	290	remains above 6.0	continuing ²
12	4	57	remained above 6.0	7/10/91
Т3	5 and 6	57	remained above 6.0	7/10/91
T4	7 and 8	57	remained above 6.0	7/10/91
T5	9 and 10	57	remained above 6.0	7/10/91
	11	290	week 284	continuing ²
16	12	57	remained above 6.0	7/10/91
T7	13 and 14	57	remained above 6.0	7/10/91
T8	15 and 16	57	remained above 6.0	7/10/91
 TO	17	290	week 122	continuing ²
19	18	57	remained above 6.0	7/10/91
70.1.0	19	290	remains above 6.0	continuing ²
110	20	57	remained above 6.0	7/10/91
T11	21 and 22	57	remained above 6.0	· 7/10/91
T12	23 and 24	57	remained above 6.0	7/10/91

Table 7. Ambient Temperature Experiment summary of reactor sampling periods.

Drainage pH drops below 6.0 and remains below (to week 290) These reactors remain in progress as of June 3, 1999. 1

2

;

Table 8. Ambient Temperature Experiment sampling frequency.

Parameter	Unit	Sampling Date (week)
drainage volume	mL	0, 2-14 (weekly) 19-79 (approx. every 4 th week) 82-290 (weekly)
specific conductance	μS	weekly
pH	standard	weekly
alkalinity	mg/L	0-10 (weekly) 12-257 (every 2 nd week) 261-288 (every 4 th week)
acidity	mg/L	same as alkalinity when pH<6.3
sulfate	mg/L	0-3 (weekly) 5-89 (every 2 nd week) 93-290 (approx. every 4 th week)
calcium	mg/L	0-3 (weekly) 5-13 (every 2 nd week) 17-290 (approx. every 4 th week)
magnesium	mg/L	same as calcium

Table 9. Pumping time, duration, and volume for T2 and 1.64% S Duluth Complex rock in the Short Rinse Interval Experiment.

Solid	Reactor	Rinse Interval		Pumping Duration	Pumping Volume	Pre-Test Rinse ¹
		hours	Pumping Times	seconds	mL	mL
1.64% S	1	(04.00 10.00 16.00 22.00 1-1-	ε	(35
T2	4	0	04:00, 10:00, 16:00, 22:00 daily	5	6	42
1.64% S	2	24	10.00 1.11	16	25	36
T2	5	24		16	25	42
1.64% S	3	0.4			07	35
T2	6	84	10:00 Monday; 22:00 Thursday	56	87	43

¹ Rinse volume added on January 11, 1993 to saturate the solid beds.

.

,

.

Solid	Reactor ¹	Rinse Water	Period of Record ²	pH<6.0 ³	Termination
		Temperature	weeks	L	date
	3	hot	232	remained above 6.0	7/16/96
11	4	hot	64	remained above 6.0	4/28/93
	14	hot	64	week 64	4/28/93
T2	15	hot	256	week 61	2/17/995
	16 ⁴	cold	64	week 62	4/28/93
	5	hot	232	remained above 6.0	7/16/96
14	6	hot	64	remained above 6.0	4/28/93
	7	hot	256	remained above 6.0	2/1/99 ⁵
18	8	hot	64	remained above 6.0	4/28/93
	9	hot	232	week 8	7/16/96
19	10	hot	64	week 8	4/28/93
	11	hot	232	week 217	7/16/96
T10	12	hot	64	remained above 6.0	4/28/93
	134	cold	64	remained above 6.0	4/28/93
	1	hot	232	remained above 6.0	7/16/96
T12	2	hot	64	remained above 6.0	4/28/93

 Table 10.
 Elevated Temperature Experiment summary of reactor sampling periods.

¹ All reactors rinsed biweekly through week 48 and weekly subsequently.

² As of December 29, 1996, week 256

.

³ Drainage pH drops below 6.0 and remains below (for indicated period of record)

⁴ Rinsed once per week with room temperature water ("cold") during weeks 2-48, 85°C rinse ("hot") twice per week during weeks 49-64

⁵ Discontinued after the period of this report, at week 367.

Parameter	Unit	Sampling Date (week)
drainage volume	mL	weekly (except for 144-148, 150, 171, 244)
specific conductance	μS	weekly
pH	standard	weekly
alkalinity	mg/L	2-10 (weekly) 14-158 (every 2 nd week) 162-255 (every 4 th week)
acidity	mg/L	same as alkalinity when pH<6.3
sulfate	mg/L	2-14 (weekly) 18-61 (skip every 3 rd week) 63-100 (weekly) 102-158 (every 2 nd week) 162-255 (every 4 th week)
calcium	mg/L	same as sulfate
magnesium	mg/L	same as sulfate

Table 11.Elevated Temperature Experiment sampling frequency.

	Reactor	Period (weeks)	Number of Analyzed Values ¹	Sulfate		Ca+Mg		Calcium		Magnesium	
Solia				rate ²	r ²	rate	r ²	rate	r ²	rate	r ²
		0-6 ³	5	0.287	0.833	0.340	0.863	0.340	0.863	_4	
		7-53	19	0.018	0.964	0.062	0.992	0.061	0.992	0.002	0.985
		54-69	5	0.071	0.996	0.106	0.997	0.102	0.996	0.005	0.998
-	1.7	70-97	11	0.021	0.994	0.048	0.996	0.044	0.996	0.004	0.985
19	17	98-142	9	0.063	0.993	0.063	0.940	0.041	0.937	0.023	0.943
	1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 19	143-229	23	0.245	0.998	0.028	0.997	0.019	0.997	0.009	0.994
		230-290	15	0.172	0.996	0.016	0.998	0.011	0.998	0.004	0.964
		0-290	87	0.135	0.901	0.043	0.928	0.034	0.889	0.009	0.962
		0-17 ³	11	0.126	0.991	0.153	0.994	0.097	0.995	0.056	0.992
	11	18-197	55	0.037	0.996	0.106	1.000	0.059	0.999	0.047	0.999
Τ6		198-220	5	0.084	0.998	0.104	0.999	0.055	1.000	0.049	0.998
		221-270	13	0.037	0.985	0.064	0.998	0.030	0.996	0.035	0.998
		271-290	5	0.196	0.987	0.108	0.989	0.032	0.959	0.076	0.995
		0-290	89	0.046	0.973	0.102	0.997	0.055	0.993	0.047	0.999

Table 12.Rates of release (in millimoles per week) for solids T9 and T6 of the Ambient
Temperature Experiment for weeks 0-290.

¹ based on sulfate analyses

² rate in millimoles/week

³ initial period includes removal of reaction products accumulated during sample storage

⁴ no variation in dependent variable; 6 of 7 values were below detection limit and were calculated as zero release

ì

Solid	Reactor	Initial Sulfide (S ²⁻) ¹	Initial AP (S ²⁻)	AP (S ²⁻) Released	AP (S ²⁻) Remaining	Initial AP (S ²⁻) Remaining	
		%	mg/g CaCO ₃	mg/g CaCO ₃	mg/g CaCO ₃	%	
T2	3	7.3	228.1	49.5	178.6	78.3	
T6	11	2.07	64.7	24.2	40.5	62.6	
T9	17	3.64	113.8	53.2	60.6	53.2	
T10	19	5.93	185.3	72.3	113.0	61.0	

Table 13.Percent depletion of acid potential and neutralization potential from the Ambient
Temperature Experiment in 290 weeks.

¹ Sulfur analyses by Bondar-Clegg.

Solid	Reactor	Initial NP	Calcium Released	Magnesium Released	NP Released	NP Remaining	Initial NP Remaining	
		mg/g CaCO ₃	%					
T2	3	189	55.9	35.7	91.6	97.4	51.5	
T6	11	45	21.8	19.1	40.9	4.1	9.1	
T9	17	14	18.2	3.0	21.2	-7.2	-51.4	
T10	19	200	71.9	46.5	118.4	81.6	40.8	

Selected mineral names and chemical compositions. Table 14.

Mineral Name	Chemical Composition						
Feldspar Group							
orthoclase-albite	KAlSi ₃ O ₈ -NaAlSi ₃ O ₈						
albite-anorthite	$NaAlSi_3O_8$ - $CaAl_2Si_2O_8$						
	Mica Group						
muscovite	$KAl_2(AlSi_3O_{10})(OH)_2$						
phlogopite	KMg ₃ (AlSi ₃ O ₁₀)(OH) ₂						
biotite	$K(Mg, Fe)_3(AlSi_3O_{10})(OH)_2$						
lepidolite	K(Li, Al) ₂₋₃ (AlSi ₃ O ₁₀)(O, OH, F) ₂						
margarite	$CaAl_2(Al_2Si_2O_{10})(OH)_2$						
	Chlorite Group						
chlorite	$(Mg, Fe)_3(Si, Al)_4O_{10}(OH)_2 \cdot (Mg, Fe)_3(OH)_6$						
apophyllite	KCa ₄ (Si ₄ O ₁₀) ₂ F· 8H ₂ O						
prehnite	$Ca_2Al(AlSi_3O_{10})(OH)_2$						
Amphibole Group							

 $W_{0-1}X_2Y_5Z_8O_{22}(OH, F)_2$ where W represents Na⁺ and K⁺, X represents Ca²⁺, Na⁺, Mn²⁺, Fe²⁺, Mg²⁺, and Li⁺ and Y represents Mn²⁺, Fe²⁺, Mg²⁺, Fe³⁺, Al³⁺, and Ti⁴⁺, and Z represents Si⁴⁺ and Al³⁺

	Reactor	Period (weeks)	Number of Analyzed Values ¹	Sulfate		Ca+Mg		Calcium		Magnesium	
Solid				rate ²	r ²	rate	r ²	rate	r ²	rate	r ²
		0-4	4	2.625	0.979	2.721	0.984	1.949	0.991	0.772	0.950
		5-18	7	0.220	0.991	0.323	0.995	0.160	0.997	0.163	0.992
		19-67	17	0.097	0.985	0.210	0.997	0.101	0.995	0.109	0.997
		68-212	40	0.064	0.998	0.177	0.999	0.105	1.000	0.073	0.996
12	3	213-237	7	0.133	0.998	0.210	0.999	0.141	0.998	0.069	0.999
		238-261	6	0.044	0.997	0.170	0.999	0.123	0.998	0.047	0.999
		262-290	7	0.107	0.998	0.202	0.999	0.138	0.999	0.064	0.999
		0-290	88	0.078	0.969	0.187	0.993	0.110	0.994	0.076	0.977
		0-9	7	0.468	0.796	0.519	0.863	0.341	0.778	0.178	0.979
		10-52	16	0.095	0.993	0.265	0.997	0.132	1.000	0.133	0.991
		53-68	5	0.203	0.999 0.332 1.000	1.000	0.143	1.000	0.188	1.000	
T10	19	69-151	24	0.138	0.989	0.277	0.999	0.151	0.992	0.126	0.998
		152-229	20	0.224	0.996	0.315	0.999	0.201	0.999	0.114	0.997
		230-290	15	0.172	0.996	0.265	1.000	0.195	0.999	0.071	0.998
•		0-290	87	0.174	0.987	0.296	0.999	0.175	0.992	0.121	0.989

Rates of release for solids T2 and T10 of the Ambient Temperature Experiment for Table 15. weeks 0-290.

based on sulfate analyses rate in millimoles/week 1

,

2

	FeS Content	A _s : Specific Surface Area ¹	Rate of Sulfate Release ²	Rate of Sulfate Release ³	Rate of Sulfate Release ⁴	
Solid		2.		mol/g (FeS)•s	mol/m ² (FeS)•s	
	g/75 g tailings	m²/g	mmol/week	x 10 -11	x 10 ⁻¹¹	
<u>T1</u>	0.68	1.18	0.004	0.97	0.82	
<u>T2</u>	10.2	0.323	0.084	1.4	4.2	
T4	1.53	0.450	0.014	1.5	3.4	
<u>T9</u>	5.03	0.174	0.016	0.52	3.0	
<u>T10</u>	5.49	0.511	0.098	3.0	5.8	
T3	1.44	NA ⁵	0.010	1.2	NA	
T5	0.98	NA	0.001	0.17	NA	
T6 ⁶	3.59	NA	0.036	1.7	NA	
T7 ⁶	0.44	NA	0.004	1.5	NA	
T86	2.6	NA	0.005	0.32	NA	

Table 16.Oxidation rates for weeks 20 to 57 expressed in terms of pyrite mass and surface area
(Lapakko 1993).

¹ Superpanner separation, untreated; sulfide mineral separation using superpanner followed by heavy liquid (3.75 specific gravity) separation. 3-point and 1-point BET measurements averaged as [2(3-point) + 1-point]/3. The 3-point and 1-point measurements were within four percent of their mean.

² For weeks 20-57, average of the two reactors.

³ Calculated as Rate (mmol/wk)/(86,400×7×g FeS×1000).

⁴ Calculated as Rate (mmol/wk)/(86,400×7×g FeS×A,×1000).

 5 NA = not analyzed

⁶ Pyrrhotite comprises 3.50%, 0.54%, and 1.04% of the iron sulfide in samples T6, T7, and T8, respectively.
Total years of dissolution for depletion of neutralization potential and acid production Table 17. potential based on the rates of release during the Ambient Temperature Experiment.

Sample		Com	position		Rate of I	Depletion ²	Total Years to	
	mmol/g	CaCO ₃	mmol/g CaCO ₃		mmo	l/g∙wk	Depletion ³	
	NPo	APo	NP ₂₉₀ ¹	AP ₂₉₀ ¹	NP ₂₉₀	AP ₂₉₀	NP	AP
T2	1.89	2.28	0.97	1.79	0.0027	0.0014	12.5	30.2
T10	2.00	1.85	0.82	1.09	0.0035	0.0023	10.1	14.7

1 NP or AP remaining at time = 290 weeks for each solid.

2

Rates from appendix B, table B6.4; represent rate of release for last period. Years_{NP}= [(NP₂₉₀/Rate of NP Depletion)/52 + 290/52] and Years_{AP}= [(AP₂₉₀/Rate of AP depletion)/52 + 290/52]. This assumes that the rates observed during the last rate period will remain constant over time. 3

Table 18.Time at which sulfate release from the Elevated Temperature Experiment exceeded
sulfate generated during sample storage, as determined from results of the Ambient
Temperature Experiment¹.

		Initial Rinse AT Release Weeks 0-5	ET Release Exceeded AT	ET Release to Week Noted
Solid	Reactor	sulfate	Release	sulfate
		mg	at week	mg
T1	3	82.48	6	133.8
T2	15	1230.22	4	1426.9
T4	5	92.43	4	117.6
T8	7	77.60	10	124.2
T9	9	330.51	6	307.3
T10	12	591.23	2	580.5

¹ For additional detail, including even numbered reactors and solid T12, see appendix C, table C2.34.

-										
Solid	T1	T2	T4	Т8	Т9	T10	T12			
Reactor	3	15	5	7	9	11	1	Average		
			S	Sulfate						
peak week	4	12	8	12	10	4	4	8		
peak conc.	224	3940	446	304	1860	4360	58	1599		
plateau weeks	156-232	142-232	152-232	176-256	146-232	150-232	142-232	na ¹		
plateau conc.	1.5-4	5-10	1-4	3-5	6-9	0.6-3	0.3-1	na		
Calcium										
peak week	4	18	8	10	6	8	4	8		
peak conc.	116	660	173	120	302	722	13	301		
plateau weeks	180-232	80-256	152-232	154-256	89-232	73-232	54-232	na		
plateau conc.	10-13	0.1-1	10-15	10-12	0.5-1.2	0.3-3	0.1-1	na		
			Ma	gnesium						
peak week	38	4	10	38	8	4	48	21		
peak conc.	18	348	38	19	27	242	26	103		
plateau weeks	176-232	96-256	145-232	146-256	134-232	176-232	180-232	na		
plateau conc.	4-5	0.5-1	3-5	3-5	0.1-0.4	1-3	3-5	na		

Table 19.Temporal variation of sulfate, calcium, and magnesium concentrations in the Elevated
Temperature Experiment (all values in mg/L).

na = not applicable

,

.

<u> </u>	Ambient T	emperature Ex	periment ²	Eleva	ated Temperatu	lire ³
Solid	minimum	maximum	overall	minimum	maximum	overall
		S	sulfate (mmol	/week)		
T1	0.004	0.012	0.005	0.010	0.164	0.044
T2	0.044	0.220	0.078	0.039	3.303	0.130
T4	0.014	0.024	0.015	0.011	0.471	0.044
Т8	0.005	0.022	0.008	0.016	0.414	0.041
Т9	0.021	0.245	0.135	0.027	1.533	0.068
T10	0.095	0.224	0.174	0.016	3.43	0.169
T12	0.001	0.005	0.003	0.004	0.015	0.006
		calcium p	lus magnesiu	m (mmol/week	x)	
T1	0.057	0.069	0.066	0.175	0.266	0.219
T2	0.170	0.323	0.187	0.019	2.948	0.124
T4	0.089	0.096	0.091	0.179	0.494	0.214
T8	0.071	0.076	0.071	0.163	0.509	0.187
Т9	0.016	0.106	0.043	0.009	0.263	0.018
T10	0.265 ⁴	0.332	0.296	0.067	3.010	0.257
T12	0.020	0.024	0.016	0.061	0.126	0.084

Table 20.Comparison of rates of release for sulfate and calcium plus magnesium from the
Ambient Temperature and Elevated Temperature Experiments¹.

¹ Initial rinse periods for both experiments not considered for this tabulation; weeks 0-5 for Ambient Temperature Experiment and see table 18 for initial rinse weeks for Elevated Temperature Experiment.

² Minimum and maximum rates for T1, T4, T8, and T12 from appendix B, table B6.6 and B6.7; overall rates for weeks 0-57. Minimum and maximum rates for T6 and T9 from table 12 and for T2 and T10 from table 15; overall rates for weeks 0-290.

³ Minimum and maximum rates from appendix C, tables C6.4, C6.5, and C6.6. Overall rates are for duration of the longest running reactor for each solid (weeks 0-232/254).

⁴ Rate observed over two periods, weeks 10-52 and weeks 230-290.

Table 21.Case 2 Samples: Rates of release of sulfate, calcium plus magnesium, calcium, and
magnesium for the Elevated Temperature Experiment for the solids that generated
acidic drainage (weeks 0-232 or 254). Italics indicate the regression analysis yielded
a relatively low r² value for the rate presented.

		Period	Number of	Sul	fate	Ca+	·Mg	Calc	ium	Magn	esium
Solid	Reactor	(weeks)	Analyzed Values ¹	slope ²	r ²	slope	r ²	slope	r ²	slope	r ²
		2-4	2	5.819	1.000	4.035	1.000	1.992	1.000	2.043	1.000
		6-32	11	3.303	0.990	2.948	0.996	1.923	0.999	1.025	0.981
тэ	15	34-42	3	1.217	1.000	1.641	0.993	1.022	0.985	0.618	1.000
12	15	44-53	5	0.379	0.970	0.485	0.986	0.192	0.991	0.293	0.979
		54-254	96	0.039	0.983	0.019	0.914	0.005	0.816	0.014	0.940
		2-254	117	0.130	0.163	0.124	0.155	0.070	0.133	0.054	0.195
		2-6	3	0.699	0.901	0.813	0.923	0.779	0.922	0.034	0.943
		8-20	6	1.533	0.908	0.263	0.728	0.208	0.715	0.055	0.775
		22-32	4	0.126	0.980	0.024	0.994	0.017	0.998	0.006	0.991
Т9	9	34-46	4	0.259	0.993	0.015	1.000	0.011	0.989	0.004	0.941
		48-122	59	0.049	0.998	0.017	0.989	0.013	0.987	0.004	0.987
		123-232	37	0.027	0.993	0.009	0.996	0.006	0.986	0.003	0.989
		2-232	113	0.068	0.535	0.018	0.559	0.014	0.495	0.005	0.782
		2 ³	1	2.35	1.000	2.64	1.000	2.27	1.000	0.37	1.000
		4-14	6	3.430	0.986	3.010	0.996	2.424	0.997	0.587	0.965
		16-38	8	1.621	0.989	1.592	0.994	1.068	0.991	0.524	0.987
T10	11	40-71	21	0.285	0.987	0.528	0.960	0.212	0.895	0.316	0.987
		72-119	37	0.108	0.969	0.197	0.995	0.014	0.991	0.182	0.995
		120-232	39	0.016	0.903	0.067	0.894	0.009	0.876	0.058	0.897
		2-232	112	0.169	0.436	0.257	0.622	0.099	0.341	0.158	0.837

based on sulfate analyses

.

² slope = millimoles/week release
 ³ Calculated as slope between wee

Calculated as slope between week 0 (0 mmol release) and release at week 2 (in mmol); rate in millimoles per week.

Table 22.Percent depletion of acid production potential and neutralization potential from the
Elevated Temperature Experiment for the three solids that produced acidic drainage,
at the point at which the drainage became acidic.

Solid	Reactor	Week	Initial Sulfide (S ²⁻)	Initial AP(S ²⁻)	AP(S ²⁻) Released	AP(S ²⁻) Remaining	Initial AP(S ²⁻) Remaining
		рн<6.0	%	mg/g CaCO ₃	mg/g CaCO ₃	mg/g CaCO ₃	%
	14	64	7.3	228	175	53	23
T2	15	61	7.3	228	168	60	26
	16	62	7.3	228	171	57	25
	9	8	3.64	114	10.5	103	91
19	10	8	3.64	114	14.9	99	87
T10	11	217	5.93	185	146	39	21

Solid	Reactor	Week	Initial NP	Calcium Released	Magnesium Released	NP Released	NP Remaining	Initial NP Remaining
		pH<6.0	mg/g CaCO ₃	%				
	14	64	189	98.0	57.9	155.9	33.1	17.5
T2	15	61	189	96.7	61.1	157.8	31.2	16.5
	16	62	189	91.1	60.5	151.6	37.4	19.8
	9	8	14.0	7.94	0.67	8.6	5.4	38.5
T9	10	8	14.0	9.20	0.83	10.0	4.0	28.4
T10	11	217	200	95.1	63.8	158.9	41.1	20.6

Solid	Reactor	Period of Record	Initial Sulfide	Initial AP	AP Released	Percent AP
		weeks	%	Initial AP AP Rele mg/g CaCO ₃ mg/g Ca 15.3 17.3 15.3 17.3 228.1 175 228.1 175 228.1 178 228.1 171 34.4 26.9 34.4 21.5 53.1 21.3 53.1 12.7 113.8 53.2 113.8 53.2 113.8 44.0 185.3 147 185.3 145 0.3 2.38	mg/g CaCO ₃	Released
	3 ¹	232	0.49	15.3	17.3	113
11	4	64	0.49	15.3	10.3	67
	14	64	7.3	228.1	175	77
T2	15	256	7.3	228.1	178	78
	16 ¹	64	7.3	228.1	171	75
Τ4	5	232	1.10	34.4	26.9	78
T4	6	64	1.10	34.4	21.5	63
TO	7	256	1.70	53.1	21.3	40
18	8	64	1.70	53.1	12.7	24
то	9	232	3.64	113.8	53.2	47
19	10	64	3.64	113.8	44.0	39
	11	232	5.93	185.3	147	79
T10	12	64	5.93	185.3	145	78
	13 ¹	64	5.93	185.3	139	75
T10	1	232	0.01	0.3	2.38	762
112	2	64	0.01	0.3	1.03	330

Table 23.Percent AP released during the Elevated Temperature Experiment.

¹ Reactors rinsed with room temperature water.

Table 24.Case 3 Samples: Rates of release (millimoles per week) of sulfate, calcium plus
magnesium, calcium, and magnesium in the Elevated Temperature Experiment from
solids T1, T4, and T8. Italics indicate the regression analysis yielded a relatively low
r² value for the rate presented.

		Period	Number of	Sul	fate	Ca+	Mg	Calc	ium	Magn	esium
Solid	Reactor	(weeks)	Number of Analyzed Values1 3 3 5 34 49 21 112 2 9 4 48 49 112 5 3 5 3 5 3 5 3 5 58 44 118	rate ²	r ²	rate	r ²	rate	r ²	rate	r ²
		2-6	3	0.324	0.995	0.502	0.996	0.401	0.994	0.101	1.000
		8-18	5	0.164	0.998	0.259	0.999	0.199	0.998	0.060	0.987
T1	2	20-78	34	0.089	0.996	0.266	0.999	0.166	0.999	0.100	0.998
11	.	79-155	49	0.043	0.977	0.221	0.999	0.133	1.000	0.089	0.999
	- 14	156-232	21	0.010	0.981	0.175	0.997	0.108	0.997	0.067	0.996
		2-232	112	0.044	0.847	0.219	0.994	0.134	0.993	0.085	0.995
		2-4	2	0.397	1.000	0.576	1.000	0.433	1.000	0.143	1.000
		6-28	9	0.471	0.993	0.494	0.990	0.365	0.991	0.129	0.977
Τ4	5	30-40	4	0.182	0.988	0.387	0.996	0.249	0.995	0.138	0.996
14	5	42-99	48	0.066	0.994	0.235	0.995	0.149	0.993	0.087	0.997
		100-232	49	0.011	0.901	0.179	0.993	0.109	0.994	0.071	0.992
		2-232	112	0.044	0.584	0.214	0.976	0.133	0.967	0.081	0.987
		2-10	5	0.127	0.781	0.239	0.908	0.199	0.890	0.039	0.976
		12-18	3	0.414	0.997	0.509	0.998	0.435	0.999	0.075	0.992
		20-26	3	0.075	0.989	0.171	0.999	0.119	0.999	0.052	0.993
T8	7	28-42	5	0.156	0.982	0.285	0.995	0.186	0.997	0.099	0.993
		44-119	58	0.072	0.993	0.232	0.993	0.152	0.993	0.080	0.992
		120-254	44	0.016	0.969	0.163	0.996	0.102	0.995	0.061	0.996
		2-254	118	0.041	0.626	0.187	0.859	0.120	0.847	0.067	0.893

based on sulfate analyses

² rate in millimoles/week

Table 25.Initial sulfur, sulfate, sulfide, and iron sulfide minerals contents and sulfate release rates (mmol/wk) for the Wet-Dry
Cycle and the Elevated Temperature Tests for the samples in the Environmental Protection Agency Project (Lapakko
et al. 1995).

Calid	Sulfur	Sulfate	Sulfide	Pyrite	Pyrrhotite	Wet-Di	ry Cycle	Elevated Te	emperature
50110	%	%	%	%	%	minimum	maximum	minimum	maximum
RK1	0.46	0.04	0.42	0.74	0.03	0.007 (60-132) ¹	0.086 (0-3)	0.008 (68-130)	0.227 (0-14)
RK2	0.64	0.01	0.63	_2	0.64	0.008 (84-132)	0.044 (0-24)	0.007 (84-130)	0.084 (0-4)
RK3	1.63	0.03	1.60	2.43	-	0.011 (26-105)	0.110 (0-6)	0.033 (56-130)	0.287 (0-8)
RK4	2.91	0.09	2.82	5.16	-	0.022 (5-40)	0.444 (0-4)	0.109 (90-130)	0.906 (0-18)
TL1	0.96	0.06	0.90	1.58	_	0.007 (33-132)	0.088 (0-1)	0.016 (4-8)	0.086 (0-2)
TL2	1.49	0.04	1.45	2.60	_	0.012 (2-109)	0.184 (0-1)	0.045 (65-131)	0.290 (14-30)
TL3	2.19	0.07	2.12	1.08	4.30	0.035 (21-132)	0.320 (0-1)	0.012 (65-131)	0.466 (0-4)
TL4	2.30	0.20	2.10	3.68	_	0.007 (86-103)	0.117 (0-4)	0.014 (22-77)	0.216 (0-2)
TL5	5.05	0.20	4.85	8.17	_	0.209 (86-132)	0.661 (0-21)	0.169 (49-131)	1.730 (10-22)
TL6	5.81	0.63	5.18	1.93	10.92	0.103 (60-132)	2.187 (0-4)	0.065 (65-131)	2.879 (0-2)

¹ Numbers in parentheses represent the weeks over which the rate was calculated.

 2 -= not detected by XRD

Table 26. Initial sulfur, sulfate, sulfide, pyrite, pyrrhotite contents, AP released, and ratio of AP released for the Wet-Dry Cycle (WD; 1-132 weeks) and the Elevated Temperature (ET; 1-130/131 weeks) Tests for the samples in the Environmental Protection Project after table 13 in Lapakko et al. 1995. Elevated temperature had little or no accelerative impact on samples in which substantial pyrrhotite was present. This was indicated by the low ET/WD ratios for solids RK2, TL3, and TL6.

Solid	Sulfur	Sulfate	Sulfide	Pyrite	Pyrrhotite	AP release from WD	AP release from ET	Ratio
	%	%	%	%	%	mg/g CaCO ₃	mg/g CaCO ₃	EI/WD
RK1	0.46	0.04	0.42	0.74	0.03	1.9	8.0	4.21
RK2	0.64	0.01	0.63	_1	0.64	3.3	2.2	0.67
RK3	1.63	0.03	1.60	2.43	. —	3.0	12	4.00
RK4	2.91	0.09	2.82	5.16	-	13	47	3.62
TL1	0.96	0.06	0.90	1.58	_	1.7	9.7	5.71
TL2	1.49	0.04	1.45	2.60	_	3.5	16	4.57
TL3	2.19	0.07	2.12	1.08	4.30	8.3	9.3	1.12
TL4	2.30	0.20	2.10	3.68	-	2.7	6.6	2.44
TL5	5.05	0.20	4.85	8.17	_	63	65	1.03
TL6	5.81	0.63	5.18	1.93	10.92	33	33	1.00

 1 -= not detected by XRD

Solid	Reactor	Period of	Initial NP	Calcium Released	Magnesium Released	NP Released	Percent
		Record	mg/g CaCO ₃	mg/g CaCO ₃	mg/g CaCO ₃	NP Released H mg/g CaCO ₃ 69.2 22.8 1 155.9 1 163.5 1 151.8 7 76.3 3 35.3 7 70.8 2 23.8 1 15.5 1 159.1 1 133.6 1 121.3 24.3	Released
	3	232	207	43.8	25.4	69.2	33
11	4	64	207	15.5	7.26	22.8	11
	14	64	189	98.0	57.9	155.9	82
T2	15	256	. 189	98.4	65.1	163.5	87
	16 ¹	64	189	91.2	60.6	151.8	80
	5	232	147	49.4	26.9	76.3	52
14	6	64	147	24.3	11.0	35.3	24
	7	256	110	47.2	23.6	70.8	64
18	8	64	110	17.2	6.62	23.8	22
	9	232	14	14.8	2.81	17.6	126
19	10	64	14	13.4	2.05	15.5	110
:	11	232	200	95.1	64.0	159.1	80
T10	12	64	200	93.9	39.7	133.6	67
	13 ¹	64	200	87.9	33.4	121.3	61
	1	232	4	2.44	21.9	· 24.3	609
112	2	64	4	1.25	5.38	6.6	166

Table 27.Percent NP released during the Elevated Temperature Experiment.

Reactors were rinsed with room temperature water.

1

;

Solid	Reactor	Period of Record (weeks)	Composition				Rate of D	epletion ²	Total Years	
			mmol/g CaCO ₃		mmol/g	CaCO ₃	mmol/g·wk		to Depletion ³	
			NPo	APo	$NP_{T=end}^{l}$	$AP_{T=end}$	$NP_{T=end}$	$AP_{T=end}$	NP	AP
T1	3	232	2.07	0.15	1.39	0.00	0.0023	0.0001	16.1	4.5
	4	64	2.07	0.15	1.84	0.05	0.0034	0.0010	11.6	2.2
T4	5	232	1.47	0.34	0.71	0.08	0.0024	0.0001	10.2	19.8
	6	64	1.47	0.34	1.12	0.13	0.0038	0.0011	6.9	3.5
Т8	7	256	1.1	0.53	0.39	0.32	0.0022	0.0002	8.3	35.7
	8	64	1.1	0.53	0.86	0.40	0.0037	0.0010	5.7	8.9
T10	12	64	2	1.85	0.67	0.40	0.0059	0.0043	3.4	3.0
	13	64	2	1.85	0.80	0.47	0.0069	0.0055	3.5	2.9
TI2	1	232	0.04	0.0	0.00	0.00	0.0008	0.0001	4.5	4.5
	2	64	0.04	0.0	0.00	0.00	0.0010	0.0001	1.2	1.2

Table 28.Total years of dissolution for depletion of neutralization potential and acid production
potential based on the rates of release during the Elevated Temperature Experiment.

¹ NP or AP remaining at T = end of period of record in weeks

² Rates from tables appendix C, tables C6.5, C6.6, C6.7; represent rate of release for last period.

³ Years_{NP}= [(NP_{T=end}/Rate of NP Depletion)/52 + (T = end/52)], and Years_{AP}= (AP_{T=end}/Rate of AP depletion)/52+(T=end/52)]. This assumes that the rates observed at the end of the experiment will remain constant over time (see appendix C, tables C6.4, C6.5, C6.6).

	Reactor	Elev	ated Temperat	ure	Ambient Temperature			
Solid		AP Released	NP Released	$\underline{\mathrm{H}^{+}\mathrm{prod.}^{2}}$	AP Released	NP Released	used $\underline{H^+ \text{ prod.}^2}$	
		mg/g CaCO ₃	mg/g CaCO ₃	dissolved	mg/g CaCO ₃	mg/g CaCO ₃	carbonate dissolved	
T1	odd	9.40	20.8	0.90	1.32	6.46	0.41	
	even	9.57	20.2	0.95	1.31	5.70	0.46	
-	odd	174	154	2.26	25.8	34.2	1.51	
T2	even	167	157	2.13	25.6	33.8	1.51	
T4	odd	21.3	31.8	1.34	2.20	8.26	0.53	
	even	20.9	32.8	1.27	2.34	7.75	0.60	
Т8	odd	12.5	21.4	1.17	1.57	6.22	0.50	
	even	12.0	21.1	1.14	1.49	5.95	0.50	
Т9	odd	44.5	14.6	6.10	6.14	9.60	1.28	
	even	43.4	15.2	5.71	6.64	9.15	1.45	
T10	odd	132	129	2.05	17.0	27.8	1.22	
	even	142	130	2.18	15.8	26.6	1.19	
T12	odd	1.10	7.02	0.31	0.550	1.46	0.75	
	even	0.96	6.09	0.32	0.610	1.38	0.88	

Table 29.Comparison of neutralization from the Elevated Temperature Experiment and the
Ambient Temperature Experiment¹ in 57 weeks of release.

.

¹ Ambient Temperature Experiment data from Lapakko 1993, table 18.

² H⁺ produced per mole of calcium and magnesium carbonate mineral dissolved. Calculated as (2 × AP Released)/NP Released.

Table 30.Cumulative mass release during the one rinse per week versus two rinses per week
during the Elevated Temperature Experiment weeks 49-64 for solids T2 and T10.

	Reactor	One Rinse or Two Rinse	Cumulative Mass Release			
Solid			Sulfate	Calcium	Magnesium	
			mg	mg	mg	
T2	14	two	301.1	85.0	59.1	
	15	two	355.6	72.4	63.3	
	16	one	290.5	75.8	60.5	
T10	11	two	428.7	153.3	126.2	
	12	two	657.7	82.0	142.8	
	13	one	619.5	163.7	96.6	

•

.

Table 31.Cumulative mass release during the "hot" rinse (85 °C water) versus "cold" rinse
(room temperature water) during the Elevated Temperature Experiment weeks 2-48
for solids T2 and T10 (excluding the initial rinse period release up to week 4 for T2 or
week 2 for T10).

Solid	Reactor	Hot Rinse or Cold Rinse	Cumulative Mass Release			
			Sulfate	Calcium	Magnesium	
			mg	mg	mg	
T2	14	hot	10581.2	2570.0	855.0	
	15	hot	10342.4	2573.0	938.2	
	16	cold	10395.4	2391.1	918.6	
T10	11	hot	7468.1	2243.9	518.7	
	12	hot	9219.3	2546.2	557.8	
	13	cold	8179.5	2120.5	474.1	

Figure 1. Ambient Temperature Experiment reactor design.



Figure 2. Temperature and relative humidity versus time for the Ambient Temperature Experiment (weeks 0 - 290).



Figure 3. Water addition system and reactor design for the Short Rinse Interval Experiment.

Peristaltic pump Timer Tygon tubing Tee Feed water Reactors Reactor Design Tygon tubing 5/32" vent holes Pipette tip Reactor top Flow distribution holes Perforated base with filter Solids -Reactor base

Water Addition System

Figure 4. Elevated Temperature Experiment reactor design.



Figure 5. pH, sulfate, calcium, and magnesium concentrations for the Ambient Temperature Experiment for solid T9, reactor 17: weeks 5-290.



Figure 6. Sulfate, calcium plus magnesium, calcium, and magnesium cumulative mass release for the Ambient Temperature Experiment, solid T9: weeks 0-290 (10.5 millimoles of calcium initially present).



Figure 7. pH, sulfate, calcium, and magnesium concentrations for the Ambient Temperature Experiment for solid T6, reactor 11: weeks 5-290.



Figure 8. Sulfate, calcium plus magnesium, calcium, and magnesium cumulative mass release for the Ambient Temperature Experiment, solid T6: weeks 0-290.

24 millimoles calcium initially present

9.8 millimoles magnesium initially present







Figure 10. pH, sulfate, calcium, and magnesium concentrations for the Ambient Temperature Experiment for solid T10, reactor 19: weeks 5-290.



Figure 11. Sulfate concentrations for T2 and T10 for the Ambient Temperature Experiment for weeks 5-290.



Figure 12. Initial and remaining AP[sulfide] and NP[(Ca/Mg)CO3] for the Ambient Temperature Experiment, weeks 0-290.



Figure 13. pH and net alkalinity for the Elevated Temperature Experiment for solid T9, reactor 9: weeks 2-232.



Figure 14. Specific conductance, sulfate, calcium, and magnesium concentrations for the Elevated Temperature Experiment for solid T9, reactor 9: weeks 2-232.



Figure 15. Sulfate, calcium plus magnesium, calcium, and magnesium cumulative mass release for the Elevated Temperature Experiment, solid T9, reactor 9: weeks 2-232.







Figure 17. Specific conductance and net alkalinity for the Elevated Temperature Experiment for solid T2, reactor 15: weeks 2-256.



Figure 18. pH and net alkalinity for the Elevated Temperature Experiment for solid T10, reactor 11: weeks 2-232.



Figure 19. Specific conductance, sulfate, calcium, and magnesium concentrations for the Elevated Temperature Experiment for solid T10, reactor 11: weeks 2-232.



Figure 20. pH and net alkalinity for the Elevated Temperature Experiment for solid T1, reactor 3: weeks 2-232.



Figure 21. pH and net alkalinity for the Elevated Temperature Experiment for solid T4, reactor 5: weeks 2-232.


Figure 22. pH and net alkalinity for the Elevated Temperature Experiment for solid T8, reactor 7: weeks 2-256.











Figure 25. Specific conductance, sulfate, calcium, and magnesium concentrations for the Elevated Temperature Experiment for solid T8, reactor 7: weeks 2-256.



103





Figure 27. Percent total sulfur remaining at weeks 6, 10, 20, 40, 100, and 200 from the odd numbered reactors of the Elevated Temperature Experiment (reactors of solids that ran for at least 232 weeks).

NOTE: Data for solid T9 (reactor 9) calculated based on initial sulfide content.

