24-1388

LABORATORY DRAINAGE QUALITY FROM DULUTH COMPLEX ROCK AND ASSESSMENT OF TEST METHODS FOR WASTE ROCK DISSOLUTION

#6012

0

0

0

0

0

0

0

 \bigcirc

Final Report on Contract J910P82018 to the U. S. Bueau of Land Management Salt Lake City Office

31 October 2000

Kim A. Lapakko David A. Antonson Minnesota Department of Natural Resources Division of Lands and Minerals 500 Lafayette Road St. Paul, MN 55155-4045

Page
st of Tables iii
st of Figuresv
st of Attachments
st of Appendices vi
XECUTIVE SUMMARY vii
INTRODUCTION1
1.1.Kinetic Test Protocols11.1.1.Introduction11.1.2.ASTM D 5744-96 Method21.1.2.1.Introduction21.1.2.2.General Description of ASTM D 5744-9621.1.2.3.ASTM Method Approval Process31.1.3.Modification of ASTM D 5744-96 (MN DNR Method)31.2.Testing Waste Rock Lithologies41.3.Previous Work41.3.1.Assessment of ASTM D 5744-96 Replication41.3.2.Assessment of a Simplified Test Method (MN DNR Method)51.3.3.Dissolution of Waste Rock Lithologies51.4.Present Study51.5.Terminology6
OBJECTIVES
METHODS
3.1. Materials 7 3.2. ASTM Method D 5744-96 7 3.3. MN DNR Method 8 3.4. ASTM and MN DNR Rinse Alternatives 8 3.5. Approach 9 3.6. Analyses 9
RESULTS
4.1. Solids Analysis

 \mathbb{C}

TABLE OF CONTENTS

i

	4.2.	Assessment of ASTM Method D 5744-96 10
		4.2.1. Repeatability of ASTM Method D 5744-96 Drip Leach Alternative 10
		4.2.2. Reproducibility of ASTM Method D 5744-96 Drip Leach Alternative . 12
		4.2.3. Repeatability of ASTM Method D 5744-96 Flood Leach Alternative13
		4.2.4. Reproducibility of ASTM Method D 5744-96 Flood Leach Alternative 14
		4.2.5. Comparison of ASTM Method Drip and Flood Leach Alternatives 15
	4.3.	Assessment of MN DNR Protocol 15
		4.3.1. Repeatability of MN DNR Method Drip Leach Alternative
		4.3.2. Comparison of MN DNR Method Drip and Flood Leach Alternatives 16
	4.4.	Comparison of ASTM and MN DNR Methods, Drip Rinse Alternative 17
	4.5.	Comparison of ASTM and MN DNR Drip Leach Water Retention
	4.6.	Duluth Complex Gabbro Dissolution
5.	CONC	CLUSIONS
6.	ACKN	NOWLEDGMENTS
7.	REFE	RENCES

LIST OF TABLES

	Page
1.	Repeatability (intralaboratory replication) of the ASTM D 5744-96 Method 500-mL drip leach alternative for eight gabbro samples and one siltite-argillite sample at the US Bureau of Mines Salt Lake Research Center
2.	Reproducibility of ASTM 5744-96 500-mL drip-trickle leach method for 1.39% S gabbro at USBM, AAL (average of three cells) and MN DNR
3.	Protocol replication and comparison
4.	Particle size distributions
5.	Whole rock chemical composition of waste rock samples
6.	Abbreviated mineralogy
7.	Repeatability (intralaboratory replication) of the ASTM D5744-96 Method 500-mL drip leach alternative for 1.39%S gabbro sample at MN DNR and AAL 34
8.	Repeatability (intralaboratory replication) of the ASTM D5744-96 Method 500-mL drip leach alternative for one gabbro and five siltite-argillite samples at the MN DNR
9.	Reproducibility (Interlaboratory Replication) of ASTM Method D5744-96 drip leach alternative testing of gabbro sample MN 6.1. MN DNR cell 12 vs American Assay Laboratories cells C0, C1, C2
10.	Repeatability and reproducibility of the ASTM D5744-96 500-mL flood leach alternative for Duluth Complex gabbro
11.	Comparison of ASTM D 5744-96 drip-trickle and flood leach alternatives for 1.39% gabbro
12.	Repeatability (intralaboratory replication) of MN DNR Method drip rinse alternative for siltite-argillite, gabbro, mafic-intrusive, and tuffaceous- sedimentary rock
13.	Comparison of and drainage pH and release rates for MN DNR Method drip- and flood-rinse alternatives for 1.39% S_T gabbro sample

14.	Comparison of ASTM Method D5744-96 and MN DNR Method drip-trickle leach testing of siltite-argillite rock, gabbro, mafic-intrusive, tuffaceous- sedimentary and USGS AML weathered waste rock samples
15.	Release rate ratios for calcium to sulfate and magnesium to sulfate for ASTM Method D5744-96 and MN DNR Method
16.	Comparison of sulfate, calcium, and magnesium release rates (millimoles/kg·wk) and drainage pH for siltite-argillite samples subjected to ASTM Standard Method 5744-96 and changed to MN DNR method
17.	Comparison of ASTM and MN DNR protocol average water retention (grams) 47
18.	Comparison of water retention for ASTM and MNDNR methods (weights in grams $20 \le n \le 133$)
19.	Summary of drainage pH and release rates for Duluth Complex gabbro

LIST OF FIGURES

1.	Schematic of humidity cell for ASTM and MN DNR method
2.	Sulfate concentrations in drainage from ASTM drip leach cells at AAL cycled over time with a period of about 50 weeks
3.	Sulfate concentrations in drainage from ASTM flood leach cells at AAL cycled over time with a period of about 50 weeks

LIST OF ATTACHMENTS

1	Additions or corrections to appendices	55
1.	ruditions of confections to appendices	

\$

LIST OF APPENDICES

- 1. Solids composition
- 2. Laboratory methods (temperature, humidity, air flow, water retention weights)
- 3. Drainage quality and mass release for ASTM Standard Method.
- 4. American Assay Lab ASTM drainage quality and mass release from Duluth Complex rock
- 5. Drainage quality and mass release for ASTM flood rinse alternative.
- 6. Drainage quality and mass release for MN DNR Method.
- 7. Drainage quality and mass release for MN DNR flood rinse alternative.
- 8. ASTM and MN DNR methods drainage quality and cumulative mass release Comparison.
- 9. Calculation of rates of sulfate, calcium, and magnesium release for periods of linear sulfate release.

EXECUTIVE SUMMARY

Kinetic tests are a tool used in the prediction of mining waste rock drainage quality. Well-defined and reproducible kinetic test protocols will improve the integrity of test data and allow more reliable comparison of results from various test programs. With such protocols, data on the drainage quality and relative rates of acid production and neutralization for individual rock types can be generated. These data will provide a technical foundation which will improve design, interpretation, and accuracy of premine predictive testing. These improvements will lead to more effective and efficient mine waste management, with the ultimate benefit of reducing adverse impacts on water resources.

This kinetic test study assessed replication of results for the ASTM D 5744-96 Method for accelerated weathering of solid materials, including mining waste rock. Drainage pH, sulfate release rate and, in some cases, rates of calcium and magnesium release, were used to assess this replication. Replication for the ASTM D 5744-96 drip-trickle and flood alternatives was similar. Intralaboratory replication (repeatability) was excellent for both drainage pH and rates of sulfate release. Interlaboratory replication (reproducibility) was excellent for 145 weeks, but from week 145 to 172 results diverged. The divergence was attributed to differences in reaction environment temperatures between laboratories. Results for the drip-trickle leach alternative were not substantially different from those for the flood leach alternative. The replication of this test would be improved if temperature constraints were prescribed. Increased control of air flow rates during wet-air and dry-air cycles may also improve replication, particularly with regard to dissolution rates of magnesium carbonate minerals.

Repeatability was also assessed for the MN DNR (Minnesota Department of Natural Resources) Method drip leach alternative, a simplified method with lower equipment and operating costs. The repeatability of this test was similar to that of the ASTM D 5744-96. Results for the MN DNR Method drip leach alternative were similar to those for the flood leach alternative for this method. There was no substantial difference between results from the MN DNR Method and the ASTM Method, based on tests conducted within the same laboratory. Differences between the MN DNR Method and ASTM Method conducted in different laboratories were likely influenced by variations in reaction environment temperatures.

Duluth Complex gabbro rock was subjected to nine dissolution tests, five at American Assay Laboratories (AAL) and four at the MN DNR, each for a period of record of 172 weeks. Drainage pH decreased from circumneutral at week 10 to the range of 3.9 to 5.1 at week 172. Sulfate release rates also tended to decrease over time. A notable exception occurred in tests conducted at AAL, in which sulfate release rates for weeks 145 to 172 were roughly three times those from week 100 to 145. This increase, which was accompanied by a sharp decrease in pH, was attributed to elevated temperatures during the summer months at AAL.

1. INTRODUCTION

In order to develop effective, efficient, and economical pre-development waste rock management plans, it is necessary to estimate the quality of drainage generated by the lithologies excavated in order to access the ore. Water which contacts this waste rock will exit the rock with a quality which ranges from environmentally benign to that which is highly acidic, with elevated concentrations of trace metals. In the first case mitigation measures need not be extensive, while in the second remediation must be adequate to protect water quality. Prediction of waste rock drainage quality allows for mitigation measures to be scaled to the potential for adverse impact.

Existing data on a waste rock of similar composition, generated by similar mining methods, and exposed to environmental conditions for an extended time provide the best indicator of drainage quality. Since these data are rarely available, compositional characterization and dissolution testing (kinetic testing) are tools commonly applied to predict waste rock drainage. Whereas many tools have been developed and applied to characterize the physical, chemical, and mineralogical aspects of geologic materials, development and application of dissolution testing tools is less evolved.

Well-defined and reproducible kinetic test protocols will improve the integrity of test data and allow more reliable comparison of results from various test programs. With such protocols, data on the drainage quality and relative rates of acid production and neutralization for individual rock types can be generated. These data will provide a technical foundation which will improve design, interpretation, and accuracy of premine predictive testing. These improvements will lead to more effective and efficient mine waste management, with the ultimate benefit of reducing adverse impacts on water resources.

1.1. Kinetic Test Protocols

1.1.1. Introduction

A number of kinetic tests have been used for dissolution testing of mine wastes (e.g. Caruccio 1968; Lapakko 1988; Lawrence 1990; Ferguson and Morin 1991). These tests generally accelerate weathering beyond that observed in the field. It has been noted that some natural conditions, such as those typical of tropical areas (e.g., surface temperatures that exceed 40°C, compounded by tropical rainfall), are more conducive to weathering than those commonly employed in kinetic tests. Under such extreme temperatures, the rate of iron-sulfide mineral oxidation would increase (e.g. Nicholson and Scharer 1994). Critical components of accelerated-weathering tests include an abundant supply of oxygen, and a sufficient volume of water to help flush a large percentage of the reaction products from the sample being tested. Effects of weathering in the kinetic tests can be observed more quickly than in the natural environment, even under extreme conditions, due to factors such as the relatively large fraction of rock mass exposed to oxygen and the large volume of water (per unit mass of rock) available for transport of reaction products. Acceleration of weathering is desirable to reduce the time ordinarily required to generate empirical dissolution data for evaluating the potential of mine waste to produce problematic drainage.

1

1.1.2. ASTM D 5744-96 Method

1.1.2.1. Introduction

A "modified humidity cell" kinetic-test protocol, incorporating the humidity cell design and weekly protocol by Lawrence (1990), was augmented by the U.S. Bureau of Mines (USBM) at its Salt Lake City Research Center. The USBM-augmented protocol was used in modified humidity-cell tests conducted on mine-waste samples (siltite-argillite rock and gabbro) from 1991 through 1995. This protocol was designed to assess the relative potentials of mine waste samples to produce acidic drainage, rather than to simulate field drainage quality (White and Jeffers, 1994). Further, the augmented protocol was intended to accelerate the natural weathering of materials under controlled reaction conditions which, in theory, increase the reproducibility of results.

Based on this protocol and using data from long-term USBM humidity-cell tests, a draft standard test method for the modified humidity cell was initiated in 1992 by USBM and the American Society for Testing and Materials (ASTM). The intent of the method's authors was to provide in one readily accessible document (i.e., the Annual Book of ASTM Standards, v. 11.04) a more detailed description of the modified humidity cell protocol than was previously available in the literature. The ultimate goal of the authors was to promote method consistency and provide a helpful guide to new users of the modified humidity-cell protocol, not to impose a prescriptive protocol upon the acid-mine drainage research and practitioner community. Subjecting various rock types to a well-defined standard test makes results more useful, since data can be more readily compared, interpreted and extrapolated. One effort on compiling kinetic test data is presently in progress (Morin and Hutt 1999; Morin et al. 1996).

1.1.2.2. General Description of ASTM D 5744-96

The ASTM D 5744-96 method (ASTM method) suggests leaching cell dimensions and a method of cell loading. A type of non-contaminating filter medium that has been successfully used to support solids is identified. The method also describes maximum mine waste particle size; sample mass; dry-and wet-air cycle duration; flow rates, temperatures, and relative humidities of dry and wet air; water mass retained in the cell after the weekly leach and the dry- and wet-air portions of the weekly cycles; and the quality of water added for rinsing reaction products from the mine waste. Alternatives are presented for both the volume of water used in the leach procedure (500 or 1000 mL) and the method of application of the leach water ("drip-trickle" or "flood"). All products of dissolution may not be removed during the leach because of secondary product precipitation, and/or incomplete rinsing of soluble products. One approach to increasing the transport of soluble products is to use the 1000-mL leach alternative which is presented in the method.

1.1.2.3. ASTM Method Approval Process

Creating a standard method through ASTM is a consensus process that involves multiple steps. Eight drafts of the modified humidity cell protocol were peer reviewed by ASTM task group, subcommittee, main committee, Society, and editorial staff members during a four year period. Also during this period, more advanced versions of the draft method were reviewed by several members of the U.S. state and federal regulatory agencies, as well as selected Canadian and U.S. researchers of contaminated drainage from metal-mine wastes. The ASTM consensus process designated the augmented protocol as ASTM Method D 5744-96 in March 1996 (ASTM 2000).

An ASTM requirement for standardizing test methods includes the determination of intralaboratory (repeatability) and interlaboratory (reproducibility) replication of test results. This determination of precision is best accomplished through an interlaboratory study (ILS). At the time D 5744-96 was accepted as an ASTM standard method, it contained a preliminary precision statement based on intralaboratory replication from two different samples tested by USBM in duplicate humidity cells. To make the D 5744-96 precision statement more robust, an ILS was initiated in 1996 by the Bureau of Land Management (BLM continued the USBM's metal-mine waste studies after the 1996 closure of USBM).

An ILS is usually conducted by no fewer than six laboratories, and performed on at least three materials representing different test levels. After closure of USBM, only two laboratories (American Assay Labs - AAL, and Minnesota Department of Natural Resources - MN DNR) were available to participate in a long-term study of the method (i.e. test duration ≥ 20 weeks). Therefore, a comparison of humidity-cell data generated from waste-rock samples duplicated by these two laboratories will be used to present preliminary indications of the method's repeatability and reproducibility. Whereas this study does not meet the rigor prescribed by a formal ILS it does provide a substantial amount of information on kinetic test replication, an area which has been recognized as lacking quantitative description (Mills 1999).

1.1.3. Modification of ASTM D 5744-96 (MN DNR Method)

The ASTM D 5744-96 Method has demonstrated a high degree of intralaboratory and interlaboratory replication of results (White and Lapakko 2000) and requires moderate capital and personnel costs. A protocol referred to as the MN DNR method, with lower capital and personnel costs, was proposed as an alternative and subjected to testing to determine its repeatability and compare its results to those of the ASTM D 5744-06. The sample rinse alternatives (drip and flood) are the same as those for the ASTM D 5744-96. In contrast to the ASTM Method the MN DNR method does not include dry air or wet air introduction to the cells, but requires maintenance temperature and relative humidity ranges between sample rinses.

1.2. Testing Waste Rock Lithologies

Whereas literature values can provide dissolution rates for modeling individual isolated minerals present in a given lithology, empirical data are needed to provide rates describing their dissolution within the specific rock matrix. Distinct to each lithology is the grain size, surface morphology, and extent of liberation of the individual minerals. Within each rock type the interaction with other minerals and their dissolution products will also be unique. Thus, dissolution testing on individual lithologies is a necessary step in developing models for predicting the quality of drainage from individual lithologies. This testing will also provide, on a primary level, empirical data on drainage quality and dissolution rates for the lithologies tested. As the number of lithologies subjected to dissolution testing increases, the integrity of output will increase, as will the catalogue of empirical data available to assist prediction of drainage quality from similar lithologies.

To extend the benefit of humidity cell data, the Chemical and Fuels Engineering Department, University of Utah (U of U) has developed a model to describe weathering effects of mine waste subjected to humidity cell testing (White and Jeffers 1994, White et al. 1994, Lin 1996, Guard 1997). The cell configuration used in the D 5744-96 also provided conditions under which the data generated were used in the development of a three-dimensional waste rock kinetic model for field piles (Lin et al. 1997). The humidity cell design permitted modeling variations in interstitial water and the consequent variations in chemical reactions. Since all reaction products were not transported from the cell, modeling of secondary reactions was possible. Furthermore, recent efforts at the U of U suggest that the cell design may also lead to modeling of colloidal transport with waste rock drainage (Trujillo 1999).

1.3. Previous Work

1.3.1. Assessment of ASTM D 5744-96 Replication

Testing of the ASTM D 5744-96 method was initiated at the USBM, Salt Lake Research Center (SLRC) (White and Lapakko 2000). This project examined **repeatability (intralaboratory replication) of the drip-trickle alternative** using duplicate cells of eight Duluth Complex gabbro samples ($0.56\% \le S_T \le 1.39\%$, 59-week period of record) and one siltite-argillite sample ($S_T = 1.60\%$, 31-week period of record). For the drip-trickle alternative, drainage pH values at the end of the tests were within 0.2 units for seven of the nine paired tests and within 0.1 units for five pairs. Sulfate release rates also replicated well, with the difference from the mean value not exceeding 13 percent for the 21 comparisons. The replication for calcium and magnesium release rates was similar (Table 1). At the end of the test on the siltite-argillite sample, drainage pH values varied by almost one unit (5.34 vs 4.36). Data on release rates suggested that the pH difference was the result of different rates of acid neutralization by magnesium-bearing minerals, most likely magnesite.

Reproducibility (intralaboratory replication) of the drip-trickle leach alternative was examined over a 125-week period for a single Duluth Complex gabbro sample at three laboratories, one of which used triplicate cells (White and Lapakko 2000). The maximum difference from the mean pH

was reported as 0.5 units (Table 2). The percent difference from the mean for sulfate and calcium release rates was typically within 10%, although differences as high as 30% were observed (White and Lapakko 2000). Although data on **repeatability and reproducibility of the flood leach alternative** were limited, replication on the sample tested was comparable to or better than that observed for the drip-trickle alternative testing of the same sample.

1.3.2. Assessment of a Simplified Test Method (MN DNR Method)

To provide an indication of **repeatability of a simplified test method (MN DNR Method)**, six samples from three different rock types were subjected to dissolution testing for periods of 20 to 68 weeks (Lapakko and White 2000). Drainage pH values at the end of tests were within 0.5 units in all cases and within 0.05 units in four cases. The percent difference from the mean for overall sulfate rates from paired cells ranged from 0.04 to 17%, with a median of 6.3%.

Comparison of the MN DNR and ASTM D 5744-96 methods was based on testing of nine samples from four rock types for periods of 20 to 132 weeks. The difference in final drainage pH values for six of the samples was less than 0.1 unit, and these pH values were less than pH 3.65 or greater than pH 8.0. The final drainage pH difference for the last three samples ranged from 0.15 to 0.4 units, and these values were in the pH range of 6.2 to 7.2. Sulfate release rates for the periods of record for the MN DNR method were 70% to 150% of those for the ASTM method, with a median of 110%. Sulfate release rates for the two methods were not substantially different, as was the case for calcium release rates. The MN DNR method typically produced higher magnesium release rates.

1.3.3. Dissolution of Waste Rock Lithologies

The Duluth Complex gabbro is one lithology which has been subjected to several dissolution studies in both laboratory and field (Lapakko 1988, 1994; Lapakko and Antonson 1994). In this rock type virtually all of the sulfur-bearing minerals occur as sulfides. The present report is part of a larger project which examined the dissolution of siltite-argillite, mafic-intrusive, tuffaceous-sedimentary and weathered rocks as a function of solid-phase composition. The results of these phases of the project are presented in Lapakko (1996, 1998a, 1998c, 1999) and Lapakko and Antonson (2000a, 2000b) and are not discussed in the present report.

1.4. Present Study

The present study examines the 1) repeatability and reproducibility of the ASTM Standard Method D 5744-96; 2) repeatability of the MN DNR method; 3) compares results from "flood" rinse alternatives to the standard "drip" rinse approach for the two methods; and 4) compares results from the ASTM Method and the MN DNR method; and 5) dissolution of Duluth Complex gabbro. It was recognized that replication of results for a given kinetic test method and comparative results between methods could vary with rock type. Consequently, a testing program was initiated using five waste rock types, although not all lithologies were used for every evaluation. Comparisons were usually

based on drainage pH and rates of sulfate, calcium, and magnesium release over time, although in some cases were limited to drainage pH and sulfate release rate. Progress was previously reported in Lapakko (1998b).

1.5. Terminology

Previous publications have used the terms "drip-trickle leach" and "flood leach" to describe the addition of water to the cells to remove reaction products. For this report "drip" is used in place of "drip-trickle." This term describes the water addition and eliminates any presumption of describing, perhaps erroneously, the subsequent flow through the rock in the cell. Furthermore, the term "rinse" is used interchangeably with "leach."

2. **OBJECTIVES**

The objectives addressed in the present report are as follows.

- 1. Assess the repeatability (intralaboratory replication) of the ASTM drip and flood leach alternatives with respect to drainage pH and release rates for sulfate, calcium, and magnesium.
- 2. Assess the reproducibility (interlaboratory replication) of the ASTM drip and flood leach alternatives with respect to drainage pH and rates of sulfate release.
- 3. Compare results from the ASTM method drip rinse with a flood rinse alternatives with respect to drainage pH and release rates for sulfate, calcium, and magnesium.
- 4. Assess the reproducibility of an ASTM method modification (MN DNR method) with respect to drainage pH and release rates for sulfate, calcium, and magnesium.
- 5. Compare results from the MN DNR method drip and flood leach alternatives with respect to drainage pH and release rates for sulfate, calcium, and magnesium.
- 6. Compare results from the ASTM and MN DNR methods with respect to drainage pH and release rates of sulfate, calcium, and magnesium. In addition to tests specifically designed for this purpose, discuss results from five siltite-argillite cells switched from the ASTM method after 72 or 93 weeks to the MN DNR method for an additional 89 weeks.
- 7. Describe the drainage pH and release rates of sulfate, calcium, and magnesium from a Duluth Complex gabbro sample subjected to the ASTM Standard Method D 5744-96 and the MN DNR method for 172 weeks.

3. METHODS

3.1. Materials

The current study includes sixteen waste-rock samples, twelve of which were siltite-argillite rock. The sulfur was predominantly present as sulfate in six of the siltite-argillite samples and as sulfide in the remaining six. The remaining four rock samples were Duluth Complex gabbro, mafic-intrusive, tuffaceous-sedimentary, and a weathered carbonate-hosted, base-metal-sulfide bearing waste rock from a 75- to 100-year old oxidized metal-mine waste-rock dump.

The siltite-argillite samples were collected from blast-hole drill-cuttings, bulk samples, and from a bench surface at an open pit mine (Lapakko 1998a). The Duluth Complex gabbro rock was collected from a test pile which had been exposed to weathering for 15 years (Lapakko 1994, Eger and Lapakko 1985). The mafic-intrusive and tuffaceous-sedimentary rocks, were segregated from a "sulfide-carbonate mixed waste" bulk sample from an open-pit metal mine. The final sample is a carbonate-hosted, base-metal-sulfide bearing waste rock from a 75- to 100-year old oxidized metal-mine waste-rock dump, and was provided by Kathleen Smith of the U.S. Geological Survey (USGS). This sample is referred to as the USGS abandoned mine land waste rock sample (USGS AML sample) or simply the USGS sample.

3.2 ASTM Method D 5744-96 (Accelerated Weathering "Modified-Humidity Cell" Protocol)

A 16-cell array identical to that illustrated by figure 1 in the standard method was used (ASTM 2000). Four 0.25-kg aliquots (each in "zip-lock bags) comprising each sample were used to load individual humidity cells; this "4-bag" loading method was used to minimize sample stratification and consequent fluid "channeling" in the cell. Because of the limited number of samples being subjected to the ASTM method in this study, the full complement of cell positions in the array were not used.

The only departure from the standard-method protocol was the volume of de-ionized water used for the initial rinse (week 0) to remove residual reaction products generated prior to sample collection and during sample storage. Instead of a single 500-mL rinse, three 500-mL rinses totaling 1.5 L were performed on each sample. The 3-rinse procedure consisted of an initial 500-mL drip-trickle rinse to wet the 1-kg sample, a 500-mL flood rinse to saturate the sample (after sample was flooded, leachant was in contact with sample for 5 minutes prior to being drained), and a final 500-mL drip-trickle rinse. Recovered volumes from each of the three rinses were weighed, and composited. Samples (approximately 60 mL) from the composite were preserved and submitted for analyses so that selected cation/anion loads could be calculated.

The subsequent weekly cycles consisted of the following:

• Tuesday - previous week's leachant collected and weighed; each humidity cell weighed to determine amount of interstitial water present in the waste-rock sample after the rinse

(Appendix 2); three-day dry-air period initiated (same time each cycle) - NOTE: start of dryair period begins the new week (i.e., week 1).

- Friday dry-air period ends; each humidity cell weighed to determine evaporation rate of interstitial water (Appendix 2); three-day wet-air period initiated (same time each cycle).
- Monday wet-air period ends; each humidity cell weighed to determine gain/loss of interstitial water (Appendix 2); 500-mL drip-trickle rinse initiated.
- Tuesday previous week's leachant collected and weighed; each humidity cell weighed to determine amount of interstitial water present in the waste-rock sample after the rinse (Appendix 2); three-day dry-air period initiated; start of new week (i.e., week 2).

Initially air-flow rates (L/min) and relative-humidity readings were taken once daily for each cell during the three-day dry-air period; these readings were also taken once daily for each cell on Friday and the following Monday during the wet-air period. Subsequently, air flow rates and relative humidity were measured at the beginning and end of both the dry-air and wet-air cycles (Appendix 2).

3.3 MN DNR Method

A kinetic test method similar to ASTM Method D 5744-96 was designated as the MN DNR method. The MN DNR protocol uses the same humidity-cell diameter (Figure 1), waste-rock charge, and leachant volume and application method as described in ASTM D 5744-96 (section 3.2). The MN DNR cell was about 3 cm shorter than the ASTM cell. The latter had a thicker base plate; a larger space, to accommodate a fitting for introducing air flow, between the base plate and perforated plastic support; and a thicker cover. As was the case for the ASTM method used in this project, a week-0 rinse volume of 1.5 L is used rather than the 0.5 L volume described in the standard method. However, instead of subjecting the humidity cell apparatus to the humid or dry air flow into the cell, the cells were simply stored in a controlled temperature and humidity room between weekly rinses.

The cells were weighed to determine the water retained after the rinse (Tuesday), on the fourth day of the cycle (Friday, concurrent with the switch of ASTM cells from wet to dry air cycle), and before the rinse (Monday, Appendix 2). It should be noted that the relative humidity readings were from the room itself. The humidity within the cells was probably near 100%, since the water retained in the cells was fairly constant during the weekly cycles (i.e. water did not evaporate).

3.4. ASTM and MN DNR Rinse Alternatives

Two cells, one ASTM and one MN DNR, containing Duluth Complex gabbro were also run to examine the effect of using a "flood" rinse rather than the "drip-trickle" rinse described in the standard method. During the flood rinse, the outlet port was capped and water was dripped into the cell (to avoid disturbing the solids) from the separatory funnel until about two cm of water

accumulated above the rock. Water was then added in a steady stream. The flood duration was one hour, after which the cap was removed and the cell allowed to drain. This method of water addition was less time consuming than the drip-trickle rinse. The 500-mL rinse volume was used in all tests.

3.5 Approach

Samples used for the evaluations and the periods of record for testing are presented in Table 3.

3.6. Analyses

Particle size distributions of the mine waste samples were determined by Lerch Brothers, Inc., Hibbing, MN (Appendix 1). The mine waste samples were analyzed for sulfur, sulfide, sulfate, evolved carbon dioxide, as well as whole rock and trace constituent concentrations by ACTLABS, Inc., Wheat Ridge, CO (Appendix 1). Analyses to determine mineralogic composition and degree of liberation of sulfide and carbonate minerals were conducted on selected siltite-argillite samples (Lapakko 1998a) and the mafic-intrusive, tuffaceous-sedimentary, and USGS samples (Lapakko 1999). These analyses were conducted using x-ray diffraction, optical microscopy, and SEM by Barry Frey of Midland Research (Nashwauk, MN) and Louis Mattson (Pengilly, MN).

Water samples were analyzed for specific conductance, pH, alkalinity, acidity, and Eh at the MN DNR in Hibbing. Specific conductance was analyzed using a Myron L conductivity meter, and an Orion SA720 meter, equipped with a Ross combination pH electrode (8165), was used for pH analyses. Alkalinity (for pH \ge 6.3) and acidity were determined using standard titration techniques for endpoints of 4.5 and 8.3, respectively (APHA et al. 1992). Eh readings were taken using a Beckman model 11 meter with an Orion electrode (9678BN).

Metals and sulfate were analyzed by the Minnesota Department of Agriculture, St. Paul, MN. Prior to 23 August 1999, metals were determined with a Varian 400 SPECTRAA; a Zeeman GFAA furnace was attached for low concentrations. Subsequent analyses were conducted using inductively coupled plasma mass spectrometry (ICP-MS, Hewlett Packard HP4500 Series, model #G1820A). Sulfate concentrations exceeding five mg/L were determined using a Technicon AA2 automated colorimeter. Lower concentrations were determined using a Dionex ion chromatograph and, after 10 November 1998, a Lachat QuickChem 8000.

4. **RESULTS**

4.1. Solids Analysis

The rock samples were crushed and sieved to obtain particle diameters less than 6.35 mm. Particle size analysis of the 12 siltite-argillite samples revealed that 60% to 76% of the particles were coarser than 2.0 mm (10 mesh) and 1.1% to 3.7% finer than 0.074 mm (200 mesh, Table 4). Chemical analysis of the siltite-argillite revealed both a range in sulfur content ($0.12\% \le S_T \le 3.24\%$) and sulfur speciation (Table 5). In six samples sulfur occurred largely as sulfate, which was present

predominantly as alunite-jarosite (indistinguishable with the methods used) and barite, with lesser amounts of gypsum. In the remaining six samples sulfur occurred largely as sulfide in the form of pyrite. The samples in which sulfur was present largely as sulfate, magnesite was the only acidneutralizing carbonate mineral detected, with contents reported as less than 0.1% (Table 6). The major host rock minerals were quartz, K-feldspar, Na-feldspar, and illite-sericite, the sum of which comprised 78% to 95% of the mineral content.

The Duluth Complex **gabbro sample** particle size distribution was similar to that of the siltite-argillite rocks, with about 70% coarser than 2.0 mm and 4.5% finer than 0.074 mm (Table 4). The sulfur content was 1.4%, and was present largely as pyrrhotite, with some chalcopyrite/cubanite and pentlandite. The sample contained 0.5% calcite and the predominant host rock minerals were plagioclase, olivine, and pyroxene.

The **mafic-intrusive rock** was the finest of the samples, with about 20% coarser than 2.0 mm and 11% finer than 0.074 mm. The sulfur content was 7.05% and was present largely as sulfide in the form of pyrite. Dolomite (9%) was the only carbonate mineral present in other than trace quantities. The major host rock minerals were illite and quartz (Table 6).

The **tuffaceous-sedimentary sample** was the second finest of the rocks, with 34% coarser than 2.0 mm and 9% finer than 0.074 mm (Table 4). As was the case with the mafic-intrusive sample, the sulfur was present as pyrite, and dolomite (8.6%) was the only carbonate present in other than trace quantities. The major host rock minerals were quartz and illite (Table 6).

Of the rock particles in the **USGS AML weathered waste rock** sample, 62% were coarser than 2.0 mm and 6.4% were finer than 0.074 mm. The sulfur content was 13.7%, highest of the samples examined, and was present largely as pyrite and sphalerite (17.3% and 9.6%, respectively; Table 6). In addition, the sample contained about 52% siderite and 8% goethite. A content of mixed iron sulfates was reported as 4.6%.

4.2. Assessment of ASTM Method D 5744-96

A series of tests were conducted to examine replication of protocols and to compare different protocols. A summary of the tests conducted is presented in Table 3.

4.2.1. Repeatability (Intralaboratory Replication) of ASTM Method D 5744-96 Drip Leach Alternative (ASTM 2000)

In the present study, one sample of Duluth Complex gabbro was subjected to ASTM method protocol replication at the MN DNR (duplicate tests for 20 weeks) and at American Assay Laboratories (AAL, triplicate tests for 172 weeks). Calcium and magnesium concentrations in drainages at AAL were not determined. Five samples of siltite-argillite rock were also tested in duplicate at the MN DNR for periods of 20 or 24 weeks. Additional drainage quality data generated using the ASTM Method at the MN DNR and AAL are presented in Appendices 3 and 4, respectively.

For the Duluth Complex gabbro sample run for 20 weeks at the MN DNR, the replication of drainage pH, as well as sulfate, calcium and magnesium release, was excellent (Table 7). For the triplicate cells tested at AAL, the degree of replication tended to decrease over time (ignoring the first 10 weeks during which preexisting reaction products were removed). At week 59, drainage pH values were within 0.04 units of the mean of the three replicates, and sulfate release rates were within nine percent of the mean value. At week 172 the corresponding difference from the mean drainage pH was 0.16 units, and the maximum difference from the mean sulfate release rate was 20 percent. Nonetheless, over the course of the entire 172 weeks the three rates of sulfate release were within six percent of the mean value, indicating a high degree of replication for the overall period of record (Table 7).

It should be noted that sulfate concentrations for all three cells at AAL tended to oscillate over time with a period of about 50 weeks (Figure 2), suggesting an effect of seasonal variations. Drainage pH oscillated with a similar period, although in the opposite direction. The peak sulfate concentrations and low pH values were observed to occur during July and August, when temperatures were highest. (Tests began 25 September 1996.) According to McCrea (2000), typical temperature ranges for summer months were 21°C at night to 31°C during the day. Typical corresponding ranges for spring and fall were 17°C at night to 22°C in the day, and winter temperatures typically ranged from 15°C at night to 22°C in the day. Thus, summer temperatures were roughly 6°C to 8°C higher than those during the remainder of the year. This temperature elevation was apparently adequate to produce summer sulfate release rates roughly 50% to 100% higher than those during the remainder of the year.

Similar cyclic behaviors for sulfate release and pH have been observed in Duluth Compex dissolution experiments for which temperature was not controlled (Lapakko and Antonson 1994). It is possible that elevated temperatures in summer months enhanced iron sulfide oxidation by either increases in abiotic oxidation rate or by enhancing biological catalysis. Data reported by Nicholson and Scharer (1994) indicate that the pyrrhotite oxidation rate at pH 6 roughly quadrupled with a temperature increase of 10°C.

A second notable temporal variation occurred between weeks 145 and 172, when drainage pH decreased below 4.5 and the rate of sulfate release increased by almost a factor of three (Table 7). Seasonal temperature elevations may have contributed in part to the accelerated sulfide mineral oxidation rates. However, the threefold increase in the sulfate release rate was larger than the less than twofold increases associated with seasonal variations (see above). Furthermore, prior to week 145, sulfate release decreased over time (Table 7).

It is likely that increased bacterial catalysis contributed to an increase in iron sulfide oxidation as pH decreased below 4.5. Similar accelerations have been observed previously at the MN DNR in experiments on Duluth Complex gabbro rock and were attributed to enhanced bacterial catalysis of the iron sulfide mineral oxidation (Lapakko and Antonson 1994). Although bacterial populations were not determined for tests at the MN DNR, 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 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).

For the siltite-argillite samples (tests at MN DNR), the difference in drainage pH between duplicate cells did not exceed 0.11 units for four of the five pairs. For 11 of the 15 overall rates (sulfate, calcium, magnesium from week five to the end of record for five samples), the percent difference from the mean for duplicates was less than 10 percent (Table 8). The sample with the largest pH difference was 100.4 (5.95 vs 6.45), which had been subjected to dissolution testing for 31 weeks at the USBM SLRC prior to testing at the MN DNR. The pH difference was apparently due to variability in magnesite dissolution rate, as suggested by the higher rate of magnesium release from the higher pH cell (Table 8).

4.2.2. Reproducibility (Interlaboratory Replication) of ASTM Method Drip Leach Alternative

ASTM method testing of the Duluth Complex gabbro sample at the MN DNR (one cell) and AAL (three cells) was conducted for 172 weeks. The USBM previously tested this sample for 125 weeks (Table 2). The following discussion addresses only testing at the MN DNR and AAL. Detailed data are presented in Appendices 3 and 4, respectively.

As discussed in the previous section, drainage pH values from the three AAL cells were generally within about 0.2 units and sulfate release rates were generally in close agreement (Table 9). Drainage pH values from all cells tended to decrease over time. However, the rate of decrease was more rapid for the AAL cells, and after 172 weeks the average drainage pH for the three AAL cells was 4.04, as compared to 4.79 for the cell at the MN DNR. It should be noted, however, that the drainage pH at AAL tended to oscillate over time (see section 4.2.1), consequently the relative magnitude of values was dependent on the point in the oscillation at which comparisons were made. Nonetheless, it is clear that the AAL drainage pH values were substantially lower than those observed at the MN DNR.

The rates of sulfate release from week 10 through week 145 were good agreement, and the overall rates were very close (Table 9). Calcium and magnesium concentrations were not determined for drainage from the AAL cells. The calcium and/or magnesium release rates at AAL may have been slightly lower than those at the MN DNR. Since there was good interlaboratory agreement for sulfate release (reflecting acid production), calcium or magnesium release (reflecting acid neutralization) at AAL may have been lower to obtain the lower pH values observed.

As observed for the drip rinse alternative, between weeks 145 and 172 drainage pH decreased below 4.5 and the rate of sulfate release at AAL increased by almost a factor of three. In contrast, the sulfate release rate at the MN DNR changed little during these periods (Table 9). It is possible, if not likely, that the elevated temperature experienced by the AAL cells in the summer months contributed to accelerated sulfate release rates and, consequently, depressed pH. Temperatures at AAL reached

31°C in the summer. In contrast, temperatures at the MN DNR were fairly constant, averaging 23.5°C with a standard deviation of 2.43°C (Appendix 2, Table A2.2). Temperatures exceeded 28°C on only nine days of the entire period of record (Appendix 2, Table A2.1). Elevated temperatures apparently enhanced pyrrhotite oxidation, and the attendant acid production, to an extent which drove pH levels below 4.5. In this pH range, bacterial catalysis enhanced sulfide mineral oxidation to produce the elevated sulfate release rates observed in the final period (see section 4.2.1).

It must be noted, that due to the cyclic variation of rates of sulfate release and drainage pH from the AAL cells, intralaboratory comparisons were dependent on the time of year covered by the measurements. During the fall, winter and spring, temperatures at the MN DNR were generally higher than those at AAL. However, summer temperatures at the MN DNR were lower than those at AAL, and apparently played an important role in accelerating iron sulfide oxidation and the attendant acid production.

In summary, drainage pH produced at AAL was lower than that at the MN DNR. Sulfate release rates at the two laboratories were similar until drainage pH at AAL decreased below 4.5, at which time rates at AAL increased by almost a factor of three. The lower pH observed at AAL prior to the final rate period occurred despite lower rates of sulfate release, suggesting lower dissolution rates for acid neutralizing minerals. Given the elevated sulfate release observed at AAL during summer months, it is likely that sulfide oxidation rates were accelerated by elevated reaction environment temperatures. Thus, it is not unlikely that differences in results between the two laboratories were the result of variations in temperature, a variable which is not controlled in the standard method.

4.2.3. Repeatability (Intralaboratory Replication) of ASTM D 5744-96 Method Flood Rinse Alternative

The present study examines testing of the Duluth Complex gabbro sample in duplicate cells for 172 weeks at AAL. Repeatabilities of both drainage pH and sulfate release rates at AAL were excellent. Through week 145 the maximum difference in pH values at the end of rate periods was 0.12 units (excluding the initial 10 weeks). At week 172, however, pH values of 4.30 and 4.46 were observed for the duplicate cells (Table 10). While this difference was the greatest observed for the individual intervals, the discrepancy was still reasonably small and would not lead to a difference in classifying the reactivity of the rock. Nonetheless, it does suggest that the degree of replication may decrease over time, as was observed for the drip rinse method.

Similarly, the difference in sulfate release rates was the greatest for the interval from week 145 to 172. Nonetheless, the difference represented a difference from the mean value of only 10 percent. Over the entire period of record the sulfate release rates differed from the mean value by only 3.1 percent. Thus, the duplicate flood rinse alternative cells continue to generate highly reproducible drainage pH and sulfate release rates over the extended period of record. The repeatability appeared to be slightly better than that for the drip rinse alternative (Table 7).

It should be noted that sulfate concentrations for the duplicate cells at AAL tended to cycle over time with a period of about 50 weeks (Figure 3), suggesting an effect of seasonal variations. Drainage pH

oscillated with a similar period, although in the opposite direction. The peak sulfate concentrations and low pH values occurred during the summer months, as was the case with the drip leach alternative (Figure 2). This was apparently due to acceleration of sulfide mineral oxidation by the elevated temperatures during the summer. (See section 4.2.1.)

4.2.4. Reproducibility (Interlaboratory Replication) of ASTM D 5744-96 Method Flood Rinse Alternative

Reproducibility of the flood rinse alternative was assessed by comparison of tests on Duluth Complex gabbro for 172 weeks at AAL (two cells) and the MN DNR (one cell). Drainage pH values were within about 0.1 units over the initial 100 weeks, but at week 125 the drainage pH for the test at the MN DNR was about 0.6 units lower than the values at AAL (White and Lapakko 2000). At week 145 the drainage pH at the MN DNR was 0.23 units lower than the values observed at AAL, which was in closer agreement. By week 172 the discrepancy between the two laboratories was similar, but the drainage pH values for AAL were *lower* than that for the test at the MN DNR (4.30 and 4.46 vs 4.62, Table 10).

The replication of sulfate release rates generally decreased over the experiment also. The rates of sulfate release were within about eight percent of the mean value from week 10 to 100, but this disparity grew to 16 percent for the interval from week 100 to 145 and to 41 percent for the final rate period. Over the first 145 weeks of testing, the sulfate release rates for the cell at the MN DNR were higher than those observed for either of the cells at AAL. However, the AAL rates for the final period (weeks 145-172) were roughly three times those for the previous rate period, similar to the increase observed for the drip rinse alternative (Table 7). As a result the AAL rates for the final period, rates over the entire experiment were in close agreement, with a total range of 188 to 200 μ moles (kg rock)⁻¹ week⁻¹ (Table 10).

The large difference observed for the final period may have been influenced by accelerated sulfide oxidation resulting from higher summer temperatures. Drainage pH in both laboratories decreased over time, despite decreasing sulfate release rates. As pH of drainage from the AAL cells decreased below five, elevated summer temperatures may have accelerated iron sulfide oxidation to the extent that pH was driven below 4.5. Below this pH bacterial catalysis began to accelerate the iron sulfide oxidation and resultant acid production. This was manifested in the elevated rates of sulfate release and marked decrease of drainage pH. Thus the differences observed between the two laboratories was likely influenced by differences in temperature, a variable not controlled in the standard method.

Despite the complications introduced by cyclic variation in the apparent rate of sulfide mineral oxidation, the drainage pH and sulfate release rates replicated reasonable well between the two laboratories. The maximum drainage pH variation between the two laboratories at week 172 was 0.32 units and the overall rates of sulfate release were within 3.1 percent of the mean value.

4.2.5. Comparison of ASTM Method Drip and Flood Rinse Alternatives

The Duluth Complex gabbro sample was subjected to the ASTM test using both drip and flood methods of rinsing at AAL and the MN DNR. The present report addresses data for 172 weeks of testing. Data generated at AAL are presented in Appendix 4, while those generated at the MN DNR are presented in Appendices 3 (drip rinse) and 4 (flood rinse).

At AAL pH values at the end of rate periods for the drip rinse were consistently lower than those for the flood rinse, with a maximum difference of 0.33 units (Table 11). The sulfate release rates for the two rinse alternatives were also in close agreement, with the maximum percent difference from the mean only 5.4 percent. The sulfate release rates for the drip rinse were generally slightly less than or essentially equal to those for the flood rinse (Table 11). This is curious since the lower sulfate release rates for the drip rinse suggest a lower rate of acid production, and lower pH values were observed for this method of rinsing. This suggests that the neutralizing mineral dissolution rate in the drip rinse was slower than that in the flood rinse.

At the MN DNR, drainage pH values at the end of rate periods for the flood rinse were consistently lower than those for the drip rinse, with a maximum difference of 0.26 units after week 10 (Table 11). Consistent with this observation, sulfate release rates for the flood rinse were continuously greater than those for the drip rinse, although the maximum difference from the mean of the two rinse methods was only 9.2 percent. It is possible that the flood rinse alternative provided slightly more efficient removal of reaction products, the consequences of which must be considered in extrapolation of results. In particular, the flood technique may tend to accelerate weathering by limiting the accumulation of precipitates on reactive surfaces or within pathways for the transport of oxygen and/or water to reactive surfaces.

Rates of calcium release for the two rinse alternatives were in close agreement, while magnesium release rates for the flood rinse alternative exceed those for the drip rinse. Higher rates of sulfide oxidation for the flood rinse may have contributed to the elevated magnesium release.

The results from the two laboratories indicate that there is little difference in results from the drip rinse and flood leach alternatives. Drainage pH values for the end of rate periods up to 172 weeks for the two rinse methods were within 0.3 units and sulfate release rates were within 9.2 percent of the mean value for all rate periods at both laboratories. At both laboratories, sulfate release rates for the flood leach were slightly greater than or essentially equal to those for the drip leach.

4.3. Assessment of MN DNR Method

4.3.1. Repeatability (Interlaboratory Replication) of MN DNR Method Drip Rinse Alternative

Repeatability of the MN DNR method drip-trickle rinse alternative was assessed based on duplicates of six rock samples: four siltite-argillite (in three of which sulfur was present largely as sulfate and one in which sulfur was present largely as sulfide), one mafic-intrusive, and one tuffaceous-sedimentary (Table 3). The periods of record for the siltite-argillite samples ranged from 20 to 68

weeks. The mafic-intrusive and tuffaceous-sedimentary samples had a 72 week period of record. Detailed data generated for these samples using the MN DNR method are presented in Appendix 6.

For the siltite-argillite samples replication of drainage pH was poorest for the two samples with the lowest sulfur contents (0.12%, 0.29%), virtually all of which was present as sulfate. Drainage pH for the duplicate cells containing these samples varied by 0.5 units after the 20-week period of record (Table 12). It should be noted there were mitigating circumstances for the pH deviations. For the 0.12% S siltite-argillite sample, the drainage pH for the duplicate cells were in good agreement at week 16; over the next four weeks one increased by 0.2 units and the other decreased by 0.3 units. For the 0.29% S sample the drainage pH value for cell 21 at week 20 was inconsistent with readings for the previous three weeks, which were in the neighborhood of 6.6. Thus, despite the variations reported at week 20 for these two samples, the drainage pH values between duplicate cells were generally not highly disparate. For the remaining two pairs of siltite-argillite samples (0.38% S_T, 1.69% S_T), drainage pH values ranged from 2.4 to 3.6 and replicate drainage pH values were within 0.06 units.

For the two low sulfur samples the percent difference from the mean for duplicated sulfate release rates was typically less than 12%, and for the remaining two samples, sulfate release rates were within 6% of the mean value (Table 12). The agreement for calcium and magnesium release was not as close, with values for the percent difference from the mean often in the range of 10% to 20%. The rates of calcium and magnesium release were often low (usually less than 10 μ mol (kg rock)⁻¹ week⁻¹) and, although percent differences were occasionally high, the magnitude of difference between rates for duplicate cells was not large.

Three of the siltite-argillite samples were also duplicated using the ASTM method (0.12%, 0.29%, 1.69% S_T), and the reproducibility of release rates was similar for the two tests. The ASTM method, however, had a higher degree of reproducibility for drainage pH values, with maximum differences of 0.07 units as opposed to 0.5 units for the MN DNR method.

Replication for paired cells of both mafic-intrusive and tuffaceous-sedimentary rock samples over the 72-week period of record was excellent. Drainage pH values for the paired cells were within 0.1 units for all rate periods. The differences from the mean for sulfate, calcium and magnesium release rates were typically within 10 percent. The only exceptions were for the mafic-intrusive duplicates during the first 24 weeks of testing (Table 12). For the entire period of record the differences from the mean for all three parameters was less than seven percent.

4.3.2. Comparison of MN DNR Method Drip and Flood Rinse Alternatives

Drip and flood leach alternatives for the MN DNR method were conducted on a Duluth Complex gabbro sample for 172 weeks. Detailed data on the MN DNR drip and flood rinse alternatives are respectively presented in Appendices 6 and 7.

The flood cell produced lower drainage pH throughout the experiment. The pH difference between

the two methods generally decreased during the test, with a disparity of roughly 0.2 units at week 172. Overall rates of sulfate and calcium release (weeks 10-172) for the flood rinse were roughly 10 percent higher than those for the drip rinse, while magnesium release rates for the two rinses were comparable (Table 13). As was postulated for the ASTM method, the slightly higher rates for the flood rinse may have been due to more efficient rinsing by this method.

As mentioned previously, the influence of the increased rinsing efficiency must be considered when extrapolating test results to the field. The flood rinse scenario does not simulate typical waste rock hydrology in the field, and the enhanced removal of reaction products may tend to accelerate leaching processes in a manner inconsistent with field behavior. On the other hand, such acceleration may be beneficial, particularly since there is the added benefit that the weekly flooding procedure requires less time than the drip rinse.

4.4.⁷ Comparison of ASTM and MN DNR Methods, Drip Rinse Alternative

The ASTM method and the MN DNR method drip leach alternatives were both conducted on ten samples: six siltite-argillite (20 to 68 weeks), and one each of the Duluth Complex gabbro (172 weeks), mafic-intrusive (72 weeks), tuffaceous-sedimentary (72 weeks) and USGS abandoned mine land weathered waste rock (62 weeks) samples. In addition, five siltite-argillite samples were run for 72 or 93 weeks then changed to the MN DNR method for an additional 88 weeks (Table 3). Although this was done largely to save personnel time, the data provide incidental information for comparing the methods.

For the **six siltite-argillite samples** rates of sulfate, calcium and magnesium release were calculated for a total of 14 periods. Agreement between the two methods was very good for both drainage pH at the end of the rate periods and release rates. At the end of 11 rate periods the pH values for the two methods were within 0.15 units. Whereas the pH differences for the remaining three periods ranged from 0.32 to 0.67 units, examination of the conditions of their occurrence suggests that the discrepancies were not of severe consequence. Two of the more disparate values occurred for the sample with the lowest sulfur content (0.12% S). All pH values for these two cases were in the sixes and, consequently, the difference in H⁺ concentrations indicated by the pH difference was small. The third disparate value (0.47% S sample) occurred at week 12 and by week 36 the discrepancy had decreased to 0.15 units. At the end of the tests, the ASTM method yielded lower drainage pH values for three samples and higher values for the remaining three (Table 14).

For 12 of the 14 rate periods the difference from the mean sulfate release rates for the two methods was less than 10 percent. The two exceptions (17% and 29% difference from the mean) occurred for relatively low rates observed for the two samples with the lowest sulfur contents, in which virtually all of the sulfur occurred as sulfate. The magnitude of the maximum difference from the mean for these two samples was 8 μ moles (kg rock)⁻¹ week⁻¹. Over the entire periods of record, the ASTM method yielded higher sulfate release rates for three samples and lower values for the remaining three (Table 14).

Rates of calcium and magnesium release were also in good agreement. For 12 of the 14 rate periods, rates of calcium release were within 10 percent of the mean value. In contrast, magnesium release rates reached this level of agreement for only 7 of the rate periods, with values for percent difference from the mean as high as 50 percent. However, for cases in which the percent difference from the mean exceeded 10 percent, the magnitude of this difference was less than 4 μ moles (kg rock)⁻¹ week⁻¹. Over the entire periods of record, calcium release rates for the ASTM method were greater than or equal to those for the MN DNR method in four of the six cases. In contrast, magnesium release rates for the ASTM method were greater than those for the MN DNR method in only one of the six cases. As is clear from the previous discussion, however, the magnitude of differences in release rates was small (Table 14).

For the **Duluth Complex** gabbro, the ASTM method yielded drainage pH values at the end of rate periods which were 0.2 to 0.34 units lower than those for the MN DNR method. Sulfate release rates for the ASTM method were consistently lower than those for the MN DNR method, with the percent difference from the mean ranging from 9% to 18% for the four rate periods (Table 14). The ASTM method also yielded lower calcium and magnesium release rates, with the percent difference from the mean ranging from 9.1 to 21 percent. The difference between sulfate release rates and the sum of calcium and magnesium release rates was generally greater for the ASTM method. Thus the lower drainage pH values for this method were the result of slower dissolution of acid neutralizing minerals as opposed to more rapid oxidation of pyrrhotite.

One sample of the **mafic-intrusive** (7.05% S) rock was subjected to dissolution by both ASTM and MN DNR (duplicate cells) methods for a period of 72 weeks. For the three periods of rate determinations the maximum pH difference between the two methods was 0.18 units, and the difference at the end of the period of record was negligible (Table 14). The percent difference from the mean for the sulfate release rate ranged from 7.1% to 24%, with the rate of sulfate release for the ASTM method consistently lower than that for the MN DNR method. The best agreement between the two methods was observed at the end of the period of record. The percent difference from the mean for calcium and magnesium release rates ranged from 18% to 30%, with the rates for the ASTM method consistently lower than those for the MN DNR method. As was the case for sulfate release, the best agreement was observed at the end of the period of record.

One sample of **tuffaceous-sedimentary** (3.75% S) rock, was subjected to dissolution by both ASTM and MN DNR (duplicate cells) methods for 72 weeks. For the three periods of rate determinations the maximum pH difference between the two methods was 0.14 units, and at the end of the period of record the pH for the ASTM method was between the values for the MN DNR duplicate cells. The percent difference from the mean for the sulfate release rate ranged from 0.5% to 12%, with the greatest disparity between the two methods observed for the initial rate period (Table 14). The percent difference from the mean for calcium and magnesium release rates ranged from roughly 5% to 15%. As with the rate of sulfate release, agreement between the two methods was poorest in the initial rate period.

The USGS AML weathered waste rock sample was subjected to dissolution by both ASTM and

MN DNR methods for 62 weeks. For the first two rate periods the drainage pH values for the two methods were within 0.08 units but, after the third and final period the MN DNR method pH was 0.28 units lower than that for the ASTM method. The percent difference from the mean sulfate release rate was 7.3% for the first rate period and increased to 13 percent for the final period. The percent difference from the mean for calcium and magnesium release rates decreased from 22% after the first rate period to about 13% for the final period (Table 14). Sulfate, calcium and magnesium release rates for the ASTM method.

In summary, there were differences in the drainage pH and sulfate release rates produced by the two methods, but no consistent trends. For the siltite-argillite samples the two methods were in close agreement with respect to both drainage pH and release rates. For 172 weeks of testing the Duluth Complex gabbro sample, the ASTM method produced drainage pH which was 0.3 units lower than that of the MN DNR method. However, the difference was the result of slower dissolution of acid-neutralizing minerals rather than accelerated sulfide mineral oxidation.

For the mafic-intrusive sample, the ASTM method sulfate release rate was 20 percent lower than the rate for the MN DNR method, for the tuffaceous-sedimentary sample the rates were not substantially different, and for the USGS sample the ASTM method sulfate release rate was 20 percent higher (Table 14). Based on these data, it cannot be concluded that the ASTM method enhanced acid production relative to the MN DNR method. It should be noted that for the mafic-intrusive, tuffaceous-sedimentary, and USGS AML samples the MN DNR method produced higher alkalinities (Appendices 3 and 6). This suggests that dissolution of calcium and magnesium carbonate minerals may be favored in the MN DNR method. This is consistent with elevated (relative to the ASTM method) calcium and magnesium release from the mafic-intrusive and tuffaceous-sedimentary samples, but inconsistent with the opposite trend observed for the USGS AML sample.

The dissolution of calcium and magnesium carbonate minerals is driven, in part, by the acid produced as a result of iron sulfide mineral oxidation. Consequently, the dissolution rate of calcium and magnesium carbonates tends to increase as the rate of iron sulfide oxidation increases. To partially account for this influence, the ratios of calcium to sulfate release rates and magnesium to sulfate release rates were calculated (Table 15). The data indicate that the amount of calcium and magnesium carbonate dissolved per mole of sulfate released in the ASTM method was less than or equal to that in the MN DNR method. This suggests that the MN DNR method enhanced dissolution of calcium and magnesium carbonates.

The methods can also be compared, although less rigorously, for five siltite-argillite samples which were switched from the ASTM to the MN DNR method after 72 or 92 weeks. Two substantial increases in drainage pH were observed after the change in methods, with increases of 0.3 and 2 units for samples 99.4 and 99.1 (Table 16). Increases in the rates of calcium and magnesium release after switching to the MN DNR method suggest the pH increase is due to an increase in dissolution of calcium and magnesium carbonates.

4.5. Comparison of ASTM Standard and MN DNR Drip-Rinse Water Retention

Difference in water retained in the rock may affect dissolution of certain mineral components of rock. For the two methods, about 90 to 140 mL of water were typically retained after the weekly rinse, with considerably higher values for the mafic-intrusive and tuffaceous-sedimentary samples (Table 17). Changes in water retention over the one-week cycle were fairly small for the MN DNR method, with a water loss typically less than 10 mL. In contrast, the ASTM typically experienced average water losses of 50 to 70 mL during the dry-air cycle (on occasions the cells dried completely), while water addition during the wet-air cycle was typically less than 3 mL. As a result, the water retention in the MN DNR method was roughly 50 to 70 mL greater than that in the ASTM method for most of the weekly cycle period.

The additional water retention did not inhibit the rate of sulfate release for the MN DNR method, as indicated by the comparison of release rates (Table 14). It is conceivable that the higher water content of the MN DNR cells favored dissolution of calcium and magnesium minerals by facilitating the transport of acidic reaction products from the surfaces of iron sulfides to calcium/magnesium carbonates.

It should also be noted that the water retention for the ASTM method was more variable than that for the MN DNR method (Lapakko and White 2000). As would be expected, water retention after the leach was highly consistent for both methods. However, after the dry cycle in the ASTM method, the standard deviations from mean water retention generally ranged from 20% to 60% of the mean value. The comparable values for the MN DNR method were less than 9%, indicating a very high degree of consistency (Table 18). The variability for the ASTM method was likely related to variations in the flow rate for the dry air cycle.

Difference in water retained in the rock may affect dissolution of certain mineral components of rock. Previous data analysis indicated no significant effect of variations in water retention on sulfate concentrations in drainage for the ASTM method (White and Lapakko 2000). However, it is conceivable that the higher water content of the MN DNR cells favored dissolution of calcium and magnesium carbonates by facilitating the transport of acidic reaction products from the surfaces of iron sulfides to calcium/magnesium carbonates.

4.6. Duluth Complex Gabbro Dissolution

Duluth Complex gabbro was subjected to a total of nine tests, each with a 172 week period of record. AAL used both the ASTM Method drip leach alternative (three cells) and the flood leach alternative (two cells). At the MN DNR single cells were used for each of the ASTM Method drip leach alternative, ASTM Method flood leach alternative, MN DNR Method drip leach alternative, and MN DNR Method flood leach alternative.

In all cases drainage pH generally decreased, although seasonal oscillations were observed for the AAL cells. (See section 4.2.1.) Drainage pH at week 10 ranged from 6.3 to 7.2 and from 4.6 to 5.2

at week 145. Drainage pH from the cells at AAL decreased rapidly between weeks 145 and 172, reaching levels of 3.9 to 4.5 at the end of the period of record (Table 19). In contrast, the cells at the MN DNR reached pH levels of 4.6 to 4.9 at week 172. The rapid decrease at AAL is likely associated with elevated temperatures in the reaction environment during the summer months. The elevated temperatures apparently accelerated sulfide oxidation rates and, as pH decreased below 4.5, the oxidation rates were further accelerated by bacterial catalysis. (See section 4.2.1.)

The rates of sulfate release also tended to decrease over time. These rates were elevated during the first 10 weeks of testing due to removal of reaction products generated prior to testing. For the period from week 10 to 59, sulfate release rates ranged from 190 to 350 μ mol (kg rock)⁻¹ week⁻¹. For the period from week 100 to 145 these rates had decreased to a range of 110 to 180 μ mol (kg rock)⁻¹ week⁻¹. Sulfate release from the cells at AAL increased rapidly between weeks 145 and 172, reaching levels roughly three times those of the previous rate period. As mentioned above, and discussed in detail in section 4.2.1, this increase was attributed to elevated temperatures during the summer months. In contrast, the sulfate release from all cells at the MN DNR remained fairly constant over this period (Table 19).

Rates of calcium and magnesium release were also determined for cells run at the MN DNR. For all four cells rates of both calcium and magnesium release decreased over time (Appendix 9). The decrease in calcium release rates was more pronounced, with rates at the end of the period of record roughly 30 percent of those initially (ignoring weeks 0-10). This decrease suggests a decrease of a soluble calcium solid phase, possibly calcite present in trace amounts or a highly soluble silicate phase. The latter phase could be present in extremely fine grains. In contrast, the rates of magnesium release at week 172 were typically around 82 percent of those observed initially. It should be noted, however, that the decrease for the MN DNR flood alternative was greater, with final values less than 60 percent of the initial rates. It is interesting to note that the rates of calcium and magnesium release decreased over time despite the corresponding decrease in drainage pH.

Quantitatively, the ratio of the sum of calcium and magnesium release rates to the sulfate release rate was initially close to one. Over time this ratio decreased to about 0.8, indicating that the rate of acid neutralization (as indicated by the release of magnesium and calcium) decreased to a greater degree than the rate of acid production (as indicated by the release of sulfate). This is consistent with the decrease in drainage pH. The excess acid production in conjunction with the slowly declining drainage pH, suggest that the pH may continue to decrease slowly.

The maximum nickel and copper concentrations were 1.7 and 0.3 mg/L, respectively, while maximum cobalt and zinc concentrations were 0.12 mg/L (Appendix 3). Trace metal concentrations tended to increase as pH decreased.

5. CONCLUSIONS

- 1. The repeatability of the ASTM Method drip leach alternative with respect to drainage pH and sulfate release rate was excellent for one Duluth Complex gabbro sample (triplicate cells at AAL for 172 weeks) and, with respect to drainage pH and release rates of sulfate, calcium, and magnesium, very good for five siltite-argillite samples (Tables 7, 8).
- The reproducibility of the ASTM Method drip leach alternative with respect to drainage pH
 and sulfate release was generally good for one Duluth Complex gabbro sample tested at American Assay Laboratories (triplicate cells) and the MN DNR (one cell). Reproducibility was excellent over the first 145 weeks of testing, then results diverged by week 172 (Table 9). This was apparently due to differences in temperatures in the reaction environments. Given this possibility, it seems prudent to prescribe acceptable temperature ranges for testing.
- 3. The repeatability of the ASTM flood leach alternative (duplicate cells of Duluth Complex gabbro tested for 172 weeks at AAL) was excellent, with pH values within 0.16 units and sulfate release rates within 10 percent of the mean (Table 10).
- 4. The reproducibility of the ASTM flood leach alternative (172 weeks of testing of Duluth Complex gabbro in duplicate cells at AAL and one cell at the MN DNR) was good for the first 145 weeks of testing, then results diverged by week 172 (Table 10). This was apparently due to differences in temperatures in the reaction environments. Given this possibility, it seems prudent to prescribe acceptable temperature ranges for testing.
- 5. For 172 weeks of testing of Duluth Complex gabbro, drainage pH and sulfate release rates for the ASTM Standard Method flood leach alternative were not substantially different than those for the drip leach alternative (Table 11). This conclusion was based on comparison of duplicate flood leach alternative cells and triplicate drip leach alternative cells at AAL, as well as comparison of single cells for each alternative at the MN DNR. At AAL the drip leach produced lower pH values while the opposite was true at the MN DNR. At both laboratories, sulfate release rates for the two alternatives were within nine percent of the mean value.
- 6. The repeatabilities of the MN DNR Method drip leach alternative for drainage pH and sulfate, calcium and magnesium release rates were very good for four siltite-argillite samples (20 to 68 weeks), one mafic-intrusive sample (72 weeks), and one tuffaceous-sedimentary sample (72 weeks; Table 12). The agreement was generally better for samples which produced lower drainage pH and higher release rates.
- 7. Based on a 172 week test of Duluth Complex gabbro using the MN DNR Method, the flood rinse alternative produced slightly lower drainage pH and slightly higher release rates than the drip leach alternative (Table 13).
- 8. Relative to the ASTM Method (drip rinse) on a Duluth Complex gabbro sample, the MN

DNR Method (drip rinse) produced virtually the same drainage pH and release rates (SO₄, Ca, Mg) which were roughly 20 to 50 percent higher (Table 14). For six siltite-argillite samples, and one each of mafic-intrusive, tuffaceous-sedimentary, and weathered waste rock samples, drainage pH and rates of sulfate and calcium release for the two methods were in good agreement (Table 14). Magnesium release tended to be slightly higher with the MN DNR method, perhaps due to a higher degree of water retention.

- 9. With regard to the ASTM Method, temperature apparently affected rates of sulfide mineral oxidation (Figures 2, 3), and establishment of acceptable ranges for tests should be considered to increase test repeatability and reproducibility. The possible effects of variable and excess drying during the dry air cycle should also be considered (Tables 17, 18).
- 10. Duluth Complex gabbro rock was subjected to nine dissolution tests, five at AAL and four at the MN DNR, each for a period of record of 172 weeks. Drainage pH decreased from circumneutral at week 10 to the range of 3.9 to 5.1 at week 172. Sulfate release rates also tended to decrease over time. A notable exception occurred in tests conducted at AAL, in which sulfate release rates for weeks 145 to 172 were roughly three times those from week 100 to 145 (Table 19). This increase, which was accompanied by a sharp decrease in pH, was attributed to elevated temperatures during the summer months at AAL. As pH decreased below 4.5, bacterial catalysis of sulfide mineral oxidation further increased rates of iron sulfide mineral oxidation and the attendant acid production. In testing at the MN DNR, calcium release rates at the end of the period of record were roughly 30 percent of those near the beginning of the test. In contrast, magnesium release rates at the end of the tests were typically around 80 percent of those in the initial stages (excluding the first 10 weeks).

6. ACKNOWLEDGMENTS

Bill White of the US BLM Salt Lake City Office was largely responsible for obtaining and splitting samples, loading cells and providing report review. John Folman conducted laboratory dissolution tests and was responsible for data management. Sue Backe was responsible for formatting the final report.

7. **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.

ASTM. 2000. D 5744-96, Standard test method for accelerated weathering of solid materials using a modified humidity cell. Annual Book of ASTM Standards, 11.04. American Society for Testing and Materials, West Conschohocken, PA. p. 257-269.

Caruccio, F. T. 1968. An evaluation of factors affecting acid mine drainage and ground water interactions in selected areas of Western Pennsylvania. <u>In Proceedings of the Second Symposium on Coal Mine Drainage Research</u>; Bituminous Coal Research: Monroeville, PA. 107-151.

Eger, A.P., Lapakko, K.A. 1985. Heavy metals study. Progress report on the field leaching and reclamation program: 1977-1983. Minnesota Department of Natural Resources, Division of Minerals, St. Paul, MN. 53 p. plus appendices.

Ferguson, K. D. Morin, K.A. 1991. The prediction of acid rock drainage - Lessons from the database. <u>In Proceedings</u>, Second International Conference on the Abatement of Acidic Drainage, Montreal, Quebec, September 16-18, Volume 3, p. 85-106.

Guard, F. 1977. Humidity cell testing - an experimental and theoretical approach. U of UT Dept. of Chemical and Fuels Engineering, unpublished Master of Science Thesis, June 1997. 105.

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.

Lapakko, K.A. 1988. Prediction of acid mine drainage from Duluth Complex mining wastes in northeastern Minnesota. In Mine Drainage and Surface Mine Reclamation. V.1. Mine Water and Mine Waste. Proceedings of the 1988 Mine Drainage and Surface Mine Reclamation Conference. BuMines IC9183. p. 180-190.

Lapakko, K.A. 1994. Comparison of Duluth Complex rock dissolution in the laboratory and field. In Proceedings of the International Land Reclamation and Mine Drainage Conference on the Abatement of Acidic Drainage, Pittsburgh, PA, April 24-29, 1994. p. 419-428.

Lapakko, K.A. 1996. Laboratory drainage quality from siltite-argillite and Duluth Complex rock. Progress Report on Contract BLM J910P62009 to the U.S. Bureau of Land Management Salt Lake City Office, 27 November 1996. 12 p. plus appendices.

Lapakko, K.A. 1998a. Laboratory drainage quality from siltite-argillite and Duluth Complex rock. Progress Report on Contract BLM J910P72015 to the U.S. Bureau of Land Management Salt Lake

City Office, 11 February 1998. 41 p. plus appendices.

Lapakko, K.A. 1998b. Laboratory drainage quality from Duluth Complex rock and assessment of test methods for waste rock dissolution. Final Report on Contract BLM JP910P72015 to the U.S. Bureau of Land Management Salt Lake City Office, 30 April 1998. 18 p. plus appendices.

Lapakko, K.A. 1998c. Laboratory drainage quality from mafic-intrusive, tuffaceous-sedimentary, and weathered waste rocks. Progress Report on Contract J910C82009 to the U.S. Bureau of Land Management Salt Lake City Office, 30 November 1998. 20 p. plus appendices.

Lapakko, K.A. 1999. Laboratory drainage quality from mafic-intrusive, tuffaceous-sedimentary, and weathered waste rocks. Progress Report on Contract J910C82009 to the U.S. Bureau of Land Management Salt Lake City Office, 30 June 1999. 34 p. plus appendices.

Lapakko, K.A., Antonson, D.A. 1994. Oxidation of sulfide minerals present in Duluth Complex rock: A laboratory study. <u>In Environmental Geochemistry of Sulfide Oxidation; ACS Symposium</u> Series 550; American Chemical Society: Washington, DC, 1993. p. 593-607.

Lapakko, K.A., Antonson, D.A. 2000. Laboratory drainage quality from mafic-intrusive, tuffaceous-sedimentary, and weathered waste rocks. Final Report on Contract J910P82018 to the U.S. Bureau of Land Management Salt Lake City Office, 31 October 2000. 60 p. plus appendices.

Lapakko, K.A., White, W.W. III. 2000. Modification of the ASTM D 5744-96 kinetic test. In Proceedings from the Fifth International Conference on Acid Rock Drainage. SME, Littleton, CO. p. 631-639.

Lawrence, R. W. 1990. Prediction of the behavior of mining and processing wastes in the environment. <u>In</u> Mining and Mineral Processing Wastes, Doyle, F. M., (ed.), Proc. Western Regional Symposium on Mining and Mineral Processing Wastes, Berkeley, CA. Soc. Min. Eng. AIME: Littleton, CO. 115-121.

Lin, C. K. 1996. Modeling acid mine drainage. University of Utah, Department of Chemical and Fuels Engineering, unpublished Ph.D. dissertation, June 1996. 264.

Lin, C., E.M. Truijillo, White III, W.W. 1997. A three-dimensional, three-phase geochemical kinetic model for acid rock drainage. <u>In</u> Proceedings of the Fourth International Conference on Acid Rock Drainage, May 30 - June 6, 1997, Vancouver, British Columbia, Canada (in press). 14.

McCrea, K. 2000. Email communication from Karl McCrea of American Assay Laboratories, 19 October 2000.

Mills, C. 1999. Variables and uncertainties in the geochemical characterization of mineral samples by kinetic methods. <u>In</u> Summary Notes 5th Annual BC MEM - MEND 2000 Metal Leaching and ARD Workshop. MEND Program, Vancouver, BC, Dec. 9-10, 1998. Section C.2, p. 1-12.

Morin, K.A., Hutt, N.M. 1999. Humidity Cells: How Many? How Long? In Proceedings of Sudbury '99, Mining and the Environment II. September 12-15, 1999, Sudbury, Ontario, Canada. p. 109-117.

Morin, K.A., N.M. Hutt, Ferguson, K.D. 1996. The International Kinetic Database: Rates of acid generation, neutralization, and metal leaching from mines around the world. <u>In Proceedings of the</u> 3rd International and 21st Annual Minerals Council of Australia Environmental Workshop, October 14-18, Newcastle, New South Wales, Australia, 1132:148.

Nicholson, R.V., Scharer, J.M. 1994. Laboratory studies of pyrrhotite oxidation kinetics. In Environmental Geochemistry of Sulfide Oxidation; ACS Symposium Series 550; American Chemical Society: Washington, DC, 1994. p. 14-30.

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. 470 p.

Trujillo, Edward. 1999. Personal communication with Edward Trujillo, Chemical and Fuels Engineering Department, University of Utah. August 1999.

White, W.W. III, Jeffers, T.H. 1994. Chemical predictive modeling of acid mine drainage from metallic sulfide-bearing waste rock. 608-630. In Proceedings of American Chemical Society Symposium Series 550.

White III, W.W., Lapakko, K.A. 2000. Preliminary indications of repeatability and reproducibility of the ASTM D 5744-96 kinetic test for drainage pH and sulfate release rate. In Proceedings from the Fifth International Conference on Acid Rock Drainage. SME, Littleton, CO. p. 621-630.

White, W.W. III, Trujillo, E.M., Lin, C. 1994. Chemical predictive modeling of acid mine drainage from waste rock: Model development and comparison of modeled output to experimental data. 157-166. In Proceedings of the International Land Reclamation and Mine Drainage Conference and the Third International Conference on the Abatement of Acid Drainage, Pittsburgh, PA.

Table 1. Repeatability (intralaboratory replication) of the ASTM D 5744-96 Method 500mL drip leach alternative for eight gabbro samples and one siltite-argillite sample at the US Bureau of Mines Salt Lake Research Center (White and Lapakko 2000).

% S	Period	d pH ¹			Sulf	ate Rele	ase ²	Calc	ium Rele	ease ²	Magnesium Release ²		
	weeks	_1	2	Δ^3	1 2 % Δ^4			1	2	% ∆ ⁴	1	2	% Δ ⁴
					D	uluth Co	mplex G	abbro					
0.56	0-20	6.40	6.22	0.18	207	168	10	111	96	7.2	94	79	8.5
	20-39	5.41	5.84	0.43	146	119	10	75	73	1.0	60	47	12
	39-59	5.27	5.42	0.15	102	95	3.7	47	47	0.6	44	42	2.2
0.59	0-20	6.24	5.93	0.31	208	199	2.4	120	122	0.54	44	45	1.2
	20-59	4.94	4.58	0.36	124	134	3.9	62	64	2.2	25	30	8.6
0.63	0-20	6.70	6.34	0.36	144	158	4.7	114	124	3.9	35	29	10
	20-39	5.86	5.35	0.51	99	98	0.6	85	85	0.04	14	13	1.9
	39-59	5.45	5.42	0.03	71	58	9.9	61	_ 52	8.0	13	7.2	28
0.68	0-20	5.98	6.08	0.10	203	192	2.7	124	122	0.85	41	37	5.2
	20-59	4.72	4.78	0.06	119	126	2.7	63	69	4.30	23	24	2.2
0.71	0-10	5.44	5.56	0.12	284	367	13	168	212	12	61	79	13
	10-39	4.60	4.59	0.01	139	157	6.1	85	96	5.6	27	28	2.1
	39-59	4.61	4.71	0.10	154	165	3.7	82	95	7.6	25	28	5.5
0.84	0-20	7.21	7.11	0.10	185	182	0.9	193	181	. 3.1	38	38	0.9
	20-39	6.88	6.95	0.07	89	95	3.7	92	86	3.4	13	13	0.2
	39-59	6.03	6.08	0.05	90	100	5.5	99	98	0.8	9	13	19
0.99	0-10	5.12	5.10	0.02	366	395	3.8	178	196	4.7	80	84	2.3
	10-39	4.27	4.05	0.22	175	174	0.21	75	67	5.0	34	31	5.2
	39-59	4.15	3.96	0.19	198	210	2.9	61	62	0.4	44	46	2.6
1.39	0-10	6.81	7.06	0.25	482	410	8.1	327	258	12	162	136	8.7
	10-59	5.03	5.01	0.02	234	251	3.4	125	134	3.6	93	97	2.3
						Siltite	e-Argillit	e					
1.60	5-31	4.36	5.34	0.96	515	611	8.5	55	58	2.2	477	624	13

¹ pH at end of period ² μ mole (kg rock)⁻¹ week⁻¹ ³ $_{\Delta} = |pH_1 - pH_2|$ ⁴ % Δ = percent difference from mean = 100 |x₁ - x₂|/(x₁ + x₂)

Reproducibility of ASTM 5744-96 500-mL drip-trickle leach method for 1.39% S Table 2. gabbro at USBM, AAL (average of three cells) and MN DNR (White and Lapakko 2000).

Period	pH	I at end	l of per	riod	Sulfate Release ¹				Calcium Release ¹			Magnesium Release ¹		
weeks	US BM	AAL	MN DNR	Δmax^2	US BM	AAL	MN DNR	%∆ max ³	US BM	MN DNR	%∆ max ³	US BM	MN DNR	%∆ max ³
0-10	6.81	6.85	6.73	0.06	482	245	378	33	327	262	11	162	123	14
10-59	5.03	5.23	5.51	0.30	234	209	214	6.8	125	124	0.4	93	86	3.9
59-100	4.91	4.83	5.30	0.33	184	159	172	7.6	84	73	7.0	86	69	11
100-125	5.01	5.70	5.13	0.52	214	139	152	27	71	63	6.0	101	75	15
10-125	5.01	<u>5.70</u>	5.13	0.52	205	184	183	7.3	94	89	2.7	94	77	9.9

¹ μmole (kg rock)⁻¹ week⁻¹
² Maximum value for |pH - pH_{ave}|
³ Maximum value for 100|rate - rate_{ave}|/ rate_{ave}
Sample	St	S ⁻²	Cells	Weeks
		ASTM Drip Le	ach Repeatability (Intralaborato	ry)
			Duluth Complex	
6.1	1.39	1.32	12, 14	20
6.1	1.39	1.32	C0, C1, C2 ¹	172 ²
			Siltite-argillite	
10696	0.12	< 0.01	7, 8	20
30696	0.19	0.01	$3(2)^3, 5$	24
40696	0.26	< 0.01	3, 4	20
100.4	1.60	1.53	15, 16	20
11196	1.69	1.37	$14(2)^3, 16(2)^3$	24
	A	STM Drip Lea	ch Reproducibility (Interlaborat	ory)
			Duluth Complex	
6.1	1.39	1.32	$12 \text{ vs C0}, \text{C1}, \text{C2}^{1}$	172 ²
	I	ASTM Flood Le	each Repeatability (Intralaborate	ory)
			Duluth Complex	
6.1	1.39	1.32	$C3, C4^{1}$	172 ²
	Α	STM Flood Lea	ch Reproducibility (Interlabora	tory)
			Duluth Complex	
6.1	1.39	1.32	13 vs C3, C4 ¹	172
		AS	STM Drip vs Flood	
			Duluth Complex	
6.1	1.39	1.32	12 vs 13	172
6.1	1.39	1.32	C0, C1, C2 vs C3, C4 ¹	172 ²
	Ν	IN DNR Drip L	each Repeatability (Intralaborat	ory)
			Siltite-argillite	
10696	0.12	< 0.01	17, 20	20
40696	0.26	< 0.01	18, 21	20
71196	0.38	0	23, 25	70
11196	1.69	1.37	24, 26	70
			Mafic-intrusive	
MS-2	7.05	6.90	m-36, m-37	72
		Tu	iffaceous-sedimentary	
MS-8	3 90	3 75	m-31 m-32	72

Table 3. Protocol replication and comparison (Page 1 of 2).

Sample	St	S ⁻²	Cells	Weeks
		Μ	N DNR Drip vs Flood	
6.1	1.39	1.32	Duluth Complex 19 vs 22	172 ²
			ASTM vs MN DNR	
			Duluth Complex	
6.1	1.39	1.32	12 vs 19	172 ²
			Siltite-argillite	
10696	0.12	< 0.01	7, 8 vs 17, 20	28, 20
40696	0.29	0.10	3, 4 vs 18, 21	20
71196	0.38	0	$4(2)^3$ vs 23, 25	68
80597	0.47	0.44	$7(2)^3$ vs 28	36
10597	0.99	0.76	$14(3)^3$ vs 27	36
11196	1.69	1.37	14(2) ³ , 16(2) ³ vs 24, 26	68
	÷		Mafic-intrusive	
MS-2	7.05	6.90	m-36 ,m-37 vs n-2	72
		Τι	uffaceous-sedimentary	
MS-8	3.90	3.75	m-31, m-32 vs n-1	72
		USGS A	AML weathered waste rock	
USGS	13.70	12.99	m-41 vs n-3	62
		AST	FM switch to MN DNR	
			Siltite-argillite	
20696	0.96	0.02	6	0-93 vs 94-182
100.4	1.60	1.53	15	0-93 vs 94-182
81196	1.93	0.08	$11(2)^{3}$	0-72 vs 73-161
99.4	2.30	2.25	9	0-93 vs 94-182
99.1	3.24	3.16	10	0-93 vs 94-182

Table 3. Protocol replication and comparison program (Page 2 of 2).

 ¹ Cells C0, C1, C2, C3, C4 run at American Assay Laboratories, Sparks, Nevada.
 ² Although periods of record were longer for some cells, 172-week period was used for Duluth Complex rate calculations to allow comparison among all cells.

³ Number in parentheses after cell number indicates repeated use of a given cell.

		Sulfu	Siltite-A r present l	Argillite argely as s	ulfate			Sulfur	Siltite-A is present	Argillite largely as	sulfide		Gabbro	Mafic- Intrusive	Tuffaceous- Sedimentary	USGS AML
SAMPLE NUMBER	10696	30696	40696	71196	20696	81196	80597	10597	11196	100.4	99.4	99.1	6.1	MS-2	MS-8	
S _T	0.12	0.19	0.26	0.38	0.96	1.93	0.47	0.99	1.69	1.60	2.30	3.24	1.39	7.05	3.90	13.70
S ²⁻	<0.01	0.01	<0.01	0	0.02	0.08	0.44	0.76	1.37	1.53	2.25	3.16	1.32	6.90	3.75	12.99
1/4"	99.6	97.9	98.5	96.5	99.3	91.2	96.0	98.2	88.1	99.3	100.0	100.0	100.0	100.0	100.0	100.0
4M	92.3	89.5	90.7	86.1	92.8	67.3	82.2	86.3	62.5	72.4	85.5	88.4	79.4	100.0	99.9	80.8
10 M	31.7	26.6	29.8	52.6	31.5	24.4	32.8	29.8	23.8	26.9	37.5	39.6	32.1	82.5	65.5	38.2
20M	17.0	11.8	15.0	31.0	16.5	12.3	18.7	15.9	12.4	14.1	20.6	21.8	21.2	49.1	37.2	24.1
28M	12.8	8.3	11.0	23.4	12.3	9.0	14.3	12.0	9.3	10.6	15.7	16.9	18.9	41.2	30.2	19.8
35M	9.8	6.1	8.4	17.7	9.4	6.8	11.2	9.5	7.2	8.3	12.5	13.6	17.7	34.8	25.2	16.7
48M	7.2	4.3	6.2	12.7	6.9	4.9	8.4	7.3	5.3	6.4	9.8	11.0	15.5	26.4	20.5	13.8
65M	7.1	4.1	5.6	0.6	6.9	4.5	6.5	5.0	5.1	6.4	9.0	10.8	13.3	23.5	18.6	11.7
100M	4.0	2.3	3.5	6.9	3.6	2.6	4.8	4.4	2.9	3.9	5.8	7.7	9.8	17.6	13.7	9.7
150M	2.8	1.6	2.5	4.9	2.6	1.8	3.5	3.3	2.0	3.0	4.6	6.2	5.6	13.8	10.6	6.4
200M	2.0	1.1	1.8	3.6	1.8	1.2	2.6	2.5	1.4	2.3	3.7	5.0	4.5	1Ó.8	8.8	-

 Table 4. Particle size distributions. Values presented as percent passing.

		Sulfu	Siltite-A r present l	Argillite argely as s	sulfate			Sulfu	Siltite-A present la	Argillite argely as s	ulfide		Gabbro	Mafic- Intrusive	Tuffaceous- Sedimentary	USGS AML
SAMPLE NUMBER	10696	30696	40696	71196	20696	81196	80597	10597	11196	100.4	99.4	99.1	MN6.17	MS-2	MS-8	
S _T	0.12 ¹	0.161	0.29 ¹	.038 ²	0.96 ¹	1.93 ²	0.47 ¹	0.99 ¹	1.69 ²	1.606	2.30 ²	3.24 ²	1.30	7.05	3.90	13.70
S ²⁻	< 0.011	0.041	0.01 ¹	0 ^{2,3}	0.021	0.08 ³	0.44 ¹	0.76 ¹	1.37 ³	1.536	2.25 ³	3.16 ³	1.24	6.90	3.75	13.46
SO4 ²⁻ -S	0.12 ¹	0.121	0.28 ¹	0.441	0.94 ¹	1.85 ²	0.10 ¹	0.26 ¹	0.32 ²	0.206	0.05 ²	0.08 ²	0.17	0.45	0.45	0.72
CO ₂	0.03 ²	0.02 ²	0.02 ²	<0.01	<0.01	0.02	1.45	-0.01	<0.01	1.11	1.15	2.52	0.21	4.10	4.05	20.90
A1 ₂ O ₃	12.94	10.66	12.32	11.11	12.86	8.89	13.16	12.29	12.73	12.03	12.42	11.86	16.04	14.50	3.97	0.84
CaO	0.16	0.13	0.10	0.17	0.16	0.13	0.22	0.07	0.11	0.09	0.19	0.48	7.71	4.29	3.34	0.45
Cr ₂ O ₃	0.02	0.01	0.02	0.01	0.01	NA	NA	NA	0.03	NA	0.02	0.02	NA	NA	NA	NA
Fe ₂ O ₃	2.03	5.01	2.18	10.48	4.00	9.44	2.76	2.36	2.14	3.69	4.48	9.53	16.34	11.95	4.52	43.68
K ₂ O	6.92	7.14	9.51	6.45	6.85	6.59	4.36	6.00	5.51	5.76	5.88	4.53	0.92	4.52	1.56	0.04
MgO	0.72	0.50	0.42	0.59	0.86	0.45	1.13	0.55	0.64	1.24	1.55	1.54	8.99	1.40	1.68	2.12
MnO	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.04	-0.01	<0.01	0.01	0.01	0.04	0.16	0.15	0.08	9.53
Na ₂ O	0.89	0.41	0.39	0.38	0.25	0.3	3.22	1.44	1.50	1.81	2.04	1.99	2.02	0.07	0.05	<0.01
P ₂ O ₅	0.09	0.16	0.12	0.16	0.17	0.08	0.13	0.23	0.20	<0.01	0.14	0.21	0.16	1.38	0.49	0.05
SiO ₂	71.14	69.86	72.23	65.79	69.55	65.95	70.56	73.71	72.10	71.31	68.96	62.96	46.29	47.08	76.16	3.45
TiO ₂	0.51	0.53	0.53	0.46	0.57	0.37	0.47	0.52	0.44	0.50	0.44	0.50	1.53	3.08	0.60	0.04
LOI	3.09	5.08	1.94	4.23	3.70	NA	NA	NA	3.47	NA	3.67	6.43	NA	NA	NA	NA
TOTAL ⁴	95.81	94.83	98.69	96.93	98.12	97.84	98.21	98.71	97.73	99.69	99.68	99.58	102.12	100.77	101.60	96.72

Whole rock chemical composition of waste rock samples. Values presented as weight percent. Table 5.

Good agreement between Lerch and Chemex analyses; average of two values used.

¹ Good agreement between Lerch and Chemex analyses; average of two values used.
² Analysis by Lerch.
³ Determined by difference.
⁴ Total is the sum for the column excluding S and LOI and multiplying SO₄-S by three.
⁵ Sample was leached for 31 weeks at USBM and 20 weeks at MN DNR prior to analysis
⁶ Analyses by USBM Salt Lake City Research Center.
⁷ Sample was leached for 20 weeks at MN DNR prior to analysis

						Siltite-A	Argillite		Gabbro ¹	Mafic-	Tuffaceous-	USGS				
		Sulfur p	resent la	argely a	s sulfate	:		Sulfur p	resent la	argely as	s sulfide	:		Intrusive	Sedimentary	AML
Sample	10696	30696	40696	71196	20696	81196	80597	10597	100.4	11196	99.4	99.1	MN6.1	MS-2	MS-8	
S	0.12 ²	0.19	0.29 ²	0.38	0.96	1.93	0.47 ²	0.99 ²	1.60	1.69	2.30	3.24	1.42	7.05	3.90	13.70
S ²⁻	< 0.01 ²	0.04	0.01 ²	0 ³	0.02	0.08	0.44 ²	0.76 ²	1.06	1.37 ³	2.25	3.16	1.39 ³	6.90 ³	3.75 ³	13.46
CO ₂	0.03	0.02	0.02	<0.01	<0.01	0.02	1.45	<0.01	1.11	<0.01	1.15	2.52	0.12	4.10	4.05	20.90
Pyrite	0.1	0.1	<0.1	<0.1	<0.01	0.2	0.8	1.0	2.9	2.6	4.2	5.9		13	7.0	17.3
Sphalerite													<0.1			9.6
Galena													<0.1			1.9
Alunite-jarosite	0.4	0.7	1.5	2.8	6.2	12.4	0.5	0.7	1.0	1.2	0.1	0.2				
Melanterite																4.64
Gypsum	0.1	<0.1	<0.1	<0.1	<0.1	0.1	0.1	<0.1	0.1	<0.1	<0.1	0.1	0.9			0.9
Barite	0.3	0.2	0.5	0.2	0.3	0.2	0.1	0.1	0.2	1.1	0.2	0.2				
Dolomite														9.0	8.6	0.9
Magnesite	<0.1	<0.1	<0.1			<0.1	1.4	1.1	1.7		1.9	2.1				
Calcite							<0.1		0.1		<0.1	0.3	0.5			0.2
Siderite	0.1	<0.1	<0.1			<0.1	1.8	0.9	0.5		0.4	3.4				52.1
Quartz	35	38	32	36	39	44	31	34	36	37	31	29	<0.1	18	67	2.4
K-feldspar	30	36	52	28	24	31	17	8	25	20	27	18 [°]		<0.1	2.8	
Na-feldspar	8	3	3	3	2	3	27	24	15	13	17	17				
Illite-sericite	23	13	8	18	24	<1	18	28	16	24	16	20		50	12	
Fe oxides	2	5.2	2	10.8	3.2	7.9	0.9	1.5	1.4	0.3	1.5	3.5	2.8	2.2	<0.1	8.0
Kaolinite					0.1	0.2					<0.1	<0.1				2.1

Table 6. Abbreviated mineralogy. Values presented as weight percent. Additional detail in Appendix 1.

 Itemple
 Itemple

 \mathfrak{L}

					Testi	ng at MN	IDNR					
Period		$\mathbf{p}\mathbf{H}^{1}$					Re	lease Ra	tes ²			
Weeks					Sulfate			Calcium	l	N	A agnesiu	m
	C12	C14	max △	C12	C14	‰∆ ⁴	C12	C14	‰∆ ⁴	C12	C14	‰∆⁴
0-5	6.94	6.98	0.02	507	453	5.6	364	320	6.4	175	160	4.5
5-20	6.23	6.27	0.02	250	253	0.6	158	165	2.2	80	80	0

Table 7. Repeatability (intralaboratory replication) of the ASTM D5744-96 Method 500-mL drip leach alternative for 1.39%S gabbro sample at MN DNR and AAL.

					Te	esting at A	AL			
Period			рН¹					Sulfa	te Release	e Rate ²
weeks	CQ	C1	C2	Ave	\triangle max ³	C0	C1	C2	Ave	%∆ max ⁴
0-10	6.84	6.84	6.87	6.85	0.02	296	206	233	245	21
10-59	5.21	5.22	5.27	5.23	0.04	225	191	211	209	8.6
59-100	4.78	4.84	4.87	4.83	0.05	155	143	179	159	11
100-145	4.67	4.60	4.75	4.67	0.08	109	128	142	126	13
145-172	4.20	3.91	4.06	4.04	0.16	288	425	362	358	20
10-172	4.20	3.91	4.06	4.04	0.16	176	184	196	185	5.9

¹ At end of period.
² μmole (kg rock)⁻¹ week⁻¹
³ maximum value for |pH - pH_{ave}|, pH_{ave} calculate using average H⁺ concentration.
⁴ maximum value for |rate - rate_{ave}| x 100

% S	Period		pH		Sulf	ate Relea	ase ¹	Calc	cium Rele	ease ¹	Magn	esium Re	elease ¹
	weeks	1	2	∆² max	1	2	% Δ ³	1	2	% Δ3	1	2	% Δ ³
						Gab	bro						
1.39	5-20	6.23	6.27	0.02	250	253	0.6	158	165	2.2	80	80	0
	·				Argillite								
0.12	5-12	6.67	6.74	0.04	32	30	3.2	19	18	5.4	5.5	4.7	7.8
	12-20	6.46	6.53	0.04	44	31	17	31	18	27	3.9	6.5	25
0.19	5-10	4.12	4.14	0.01	119	118	0.8	67	65	1.5	19	16	8.6
	10-24	4.20	4.16	0.02	71	78	4.7	38	38	0	10	11	4.8
0.29	5-12	6.70	6.66	0.02	34	28	9.7	20	21	4.9	4.1	5.1	. 11
	12-20	6.64	6.53	0.02	32	30	3.2	17	17	0	5.2	4.9	3.0
1.60⁴	5-31	4.36	5.34	0.72	515	611	8.5	55	58	2.2	477	624	13
1.605	5-12	5.48	6.07	0.39	308	312	0.6	15	12	11	287	295	1.4
	12-20	5.95	6.45	0.32	278	300	3.8	18	12	20	256	292	6.6
1.69	5-10	2.35	2.32	0.02	3020	3150	2.1	13	13	0	37	35	2.8
	10-24	2.22	2.18	0.02	2690	2950	4.6	6.7	6.6	0.8	19	15	12

Table 8. Repeatability of ASTM 5744-96 500-mL drip-trickle leach method for gabbro and siltite-argillite rock.

¹ μ mole (kg rock)⁻¹ week⁻¹ ² maximum value for |pH - pH_{ave}|, pH_{ave} calculate using average H⁺ concentration. ³ maximum value for |rate - rate_{ave}| x 100 ⁴ Test run at USBM Salt Lake Research Center

⁵ Testing at MN DNR was continued using same cells used at USBM Salt Lake City Research Center.

Table 9.	Reproducibility (Interlaboratory Replication) of ASTM Method D5744-96 drip leach alternative testing of gabbro
	sample MN 6.1. MN DNR cell 12 vs American Assay Laboratories cells C0, C1, C2.

Period				р	\mathbf{H}^{1}				Sulf	ate Relea	ise Rate,	μ mol (kg ro	ock) ⁻¹ week	-1
(weeks)	MN		А	.AL ²		Ave ³	∆max ⁴	MN		А	AL ²		Ave	%Diff ⁵
	DNR	C0	C1	C2	Ave _{AAL}			DŅR	C0	C1	C2	Ave _{AAL}		
0-10	6.73	6.84	6.84	6.87	6.85	6.79	0.06	378	296	206	233	245	312	21
10-59	5.51	5.21	5.22	5.27	5.23	5.35	0.16	214	225	191	211	209	212	- 1.2
59-100	5.30	4.78	4.84	4.87	4.83	5.00	0.30	172	155	143	179	159	165	3.9
100-145	5.02	4.67	4.60	4.75	4.67	4.81	0.21	139	109	128	142	126	132	4.9
145-172	4.79	4.20	3.91	4.06	4.04	4.27	0.52	151	288	425	362	358	254	41
10-172	4.79	4.20	3.91	4.06	4.04	4.27	0.52	166	176	184	196	185	176	5.4

36

¹ pH at the end of the period.
 ² American Assay Laboratories
 ³ Average of MN DNR and AAL average; pH values calculated using [H⁺].

⁴ Maximum difference from average pH.

⁵ Percent difference from the mean of the two laboratories, calculated as the difference between the MN DNR value and the average of the AAL values, divided by the sum of these two values: %Diff = $[X_{MN DNR} - (X_{AAL1} + X_{AAL2})/2]/[X_{MN DNR} + (X_{AAL1} + X_{AAL2})/2].$

Period weeks				AAI	[MN	DNR	A	AL vs	MN DI	√R
		pH	[1		Sul	fate Re	elease F	Rate ²	pH ¹	Sulfate	pl	H	Sulfa	te Rate
	<u>C3</u>	<u>C4</u>	Ave	\max_{Δ^3}	C3	<u>C4_</u>	Ave_	max %∆⁴		Rate ²	Ave	\max_{Δ^3}	Ave	max %∆⁴
0-10	6.82	6.57	6.68	0.14	273	235	254	7.5	6.45	406	6.55	0.13	330	23
10-59	5.38	5.50	5.43	0.07	189	221	205	7.8	5.49	241	5.46	0.03	223	8.1
59-100	5.13	5.13	5.13	0	173	181	177	2.3	5.16	199	5.14	0.02	188	5.9
100-145	5.00	4.99	4.99	0.01	118	127	122	4.1	4.76	167	4.86	0.13	144	. 16
145-172	4.30	4.46	4.37	0.09	416	340	378	10	4.62	157	4.48	0.14	268	41
10-172	4.30	4.46	4.37	0.09	188	200	194	3.1	4.62	199	4.48	0.14	196	1.3

Table 10. Repeatability and reproducibility of the ASTM D5744-96 500-mL flood leach alternative for Duluth Complex gabbro.

¹ At end of period. ² μ mole (kg rock)⁻¹ week⁻¹ ³ maximum value for |pH - pH_{ave}| ⁴ absolute value of difference from mean, percent = 100 |x₁, -x₂| / (x₁ + x₂)

Period			A	AL								MN	DNR					
weeks		pН		Su	ulfate rat	te ¹		pН		Su	lfate ra	te ¹	Cal	lcium Ra	ate ¹	Mag	nesium	Rate ¹
	drip ²	flood ³	\max_{Δ^4}	drip ²	flood ³	%∆⁵	drip	flood	\max_{Δ^4}	drip	flood	%∆⁵	Drip	Flood	%∆⁵	Drip	Flood	$\%\Delta^5$
0-10	6.85	6.68	0.09	245	254	1.8	6.73	6.45	0.16	378	406	3.6	262	257	1.0	123	142	7.2
10-59	5.23	5.43	0.11	209	205	0.97	5.51	5.49	0.01	214	241	5.9	124	132	3.1	86	108	11
59-100	4.83	5.13	0.18	159	177	5.4	5.30	5.16	0.08	172	199	7.3	73	84	5.8	69	76	4.8
100-145	4.67	4.99	0.19	126	122	1.6	5.02	4.76	0.15	139	167	9.2	55	63	6.8	65	90	10
145-172	4.04	4.37	0.20	358	378	2.7	4.79	4.62	0.09	151	157	1.9	. 49	53	3.9	67	77	6.9
10-172	4.04	4.37	0.20	185	194	2.4	4.79	4.62	0.09	166	199	9.0	75	72	2.0	72	90	11

Table 11. Comparison of ASTM D 5744-96 drip-trickle and flood leach alternatives for 1.39% Duluth Complex gabbro.

38

¹ Rates in μmole (kg rock)⁻¹ week ⁻¹
² Average of triplicate cells; see Table 7.
³ Average of duplicate cells; see Table 10.
⁴ maximum value for |pH - pH_{ave}|, pH_{ave}
⁵ 100 |rate - rate_{ave}|/rate_{ave}

	l –							Siltite-Ar	gillite						
	0.12%	S _T , <0.01	%S ²⁻	0.29%	S _T , 0.01%	5S ²⁻			0.38%S _T	, 0.0%S ²⁻			1.69	9%S _T , 1.37	7%S ²⁻
	cell 17	cell 20	$\%\Delta^1$	cell 18	cell 21	$\%\Delta^1$	cell 23	cell 25	$\%\Delta^1$	cell 23	cell 25	$\%\Delta^1$	cell 24	cell 26	$\%\Delta^1$
Weeks		5-12			5-16			5-12			24-46			5-50	
SO₄	32	31	1.6	27	24	12	503	498	0.5	259	285	4.8	2930	2880	0.9
Ca	23	21	4.5	21	17	11	83	50	25	6.5	6.7	1.5	7.8	7.2	0.04
Mg	6.2	4.9	12	5.7	4.7	9.6	39	42	3.7	15	11	15	17	11	21
Final pH	6.96	6.56	0.24 ²	6.66	6.59	0.04 ²	3.08	3.09	0.01 ²	3.47	3.46	0.01 ²	2.41	2.39	0.01 ²
Weeks		12-20			16-20			12-24			46-68			50-68	
SO₄	25	17	19	24	23	2.1	336	328	1.2	248	238	2.1	1620	1820	5.8
Ca	22	14	22	20	18	5.3	19	14	15	3.4	3.5	1.4	1.8	2.1	7.7
Mg	3.7	4.4	8.6	6.1	0.59	82	21	17	11	3.7	2.5	19	0.47	1.4	50
Final pH	6.82	6.33	0.31 ²	6.75	6.25	0.322	3.21	3.20	0.01 ²	3.53	3.49	0.02 ²	2.56	2.62	0.03 ²
Weeks		5-20			5-20						5-68			5-68	
SO₄	29	23	12	26	23	6.1				284	290	1.0	2660	2680	0.4
Ca	22	16	16	20	16	11				12	8.9	15	5.4	5.1	2.9
Mg	4.9	4.5	4.3	5.5	4.0	7.9	9			13	10	13	11	7.6	18
Final pH	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$				0.32 ²				3.53	3.49	0.02 ²	2.56	2.62	0.03 ²	

Repeatability (intralaboratory replication) of MN DNR Method drip rinse alternative for siltite-argillite, mafic-intrusive, and tuffaceous-sedimentary rock. Release rates in μ mole (kg rock)⁻¹ wk⁻¹. (Page 1 of 2). Table 12.

¹ Percent difference from the mean = $100 |X_1 - X_2|/(X_1 + X_2)$ ² maximum pH difference from mean = maximum value for $|pH_1 - pH_{ave}|$

		Mafic-I	ntrusive			Tuffaceous-	Sedimentary	
		7.05% S _T ,	6.90% S ²⁻			3.90% S _T ,	3.75% S ²⁻	
	cell 36	cell 37	Ave	$\%\Delta^1$	cell 31	cell 32	Ave	$\%\Delta^1$
Weeks				5-	12			
SO ₄	1350	900	1125	20	740	820	780	5.1
Ca	1120	820	970	15	610	660	635	3.9
Mg	670	480	575	17	410	440	425	3.5
Final pH	8.02	7.98	8.00	0.02 ²	7.97	8.04	8.00	0.04 ²
Weeks				12	-24			
SO ₄	1340	960	1150	17	510	550	530	3.8
Са	1090	900	995	9.5	450	500	475	5.3
Mg	590	490	540	9.3	300	330	315	4.8
Final pH	8.08	8.13	8.10	0.03 ²	8.04	8.04	8.04	0 ²
Weeks				24	-72			
SO ₄	698	655	676	3.2	429	411	420	2.1
Са	700	695	698	0.4	375	408	392	4.2
Mg	418	449	434	3.6	264	291	278	4.9
Final pH	8.04	8.00	8.02	0.02	8.02	8.11	8.06	0.05
Weeks				5-	-72			
SO ₄	851	742	796	6.8	456	450	453	0.7
Ca	801	763	782	2.4	399	434	416	4.2
Mg	464	462	463	0.2	275	302	288	4.7
Final pH	8.04	8.00	8.02	0.02	8.02	8.11	8.06	0.05

Repeatability (intralaboratory replication) of MN DNR Method drip rinse alternative for siltite-argillite, mafic-intrusive, and Table 12. tuffaceous-sedimentary rocks. Release rates in μ mole (kg rock)⁻¹ wk⁻¹. (Page 2 of 2).

¹ Percent difference from the mean = 100 $|X_1 - X_2|/(X_1 + X_2)$ ² maximum pH difference from mean = maximum value for $|pH_1 - pH_{ave}|$

	Drip	Flood	Ave	%∆¹	Drip	Flood	Ave	<i>‰</i> ∆¹
Weeks		0-	10			1	00-145	
SO4	470	640	555	15	180	180	180	0
Ca	330	440	385	14	67	76	72	6.3
Mg	160	200	180	11	97	86	92	4.9
Final pH	7.18	6.30	6.55	0.63 ²	5.22	4.98	5.08	0.14 ²
Weeks		10	-59			1	45-172	
SO4	300	350	325	7.7	180	180	180	0
Ca	160	170	165	3.0	63	63	63	0
Mg	130	150	140	7.1	97	81	89	9.0
Final pH	5.71	5.29	5.45	0.26 ²	5.13	4.92	5.01	0.12
Weeks		59-	100			1	0-172	
SO ₄	210	250	230	8.7	220	240	230	4.3
Ca	84	92	88	4.5	90	98	94	4.3
Mg	100	100	100	0	110	110	110	0
Final pH	5.63	5.16	5.33	0.30 ²	5.13	4.92	5.01	0.12 ²

Table 13. Comparison of and drainage pH and release rates for MN DNR Method drip- and floodrinse alternatives for 1.39% S_T gabbro sample. Release rates in μ mole (kg rock)⁻¹ week⁻¹.

¹ Percent difference from the mean = $100|X_1 - X_2|/(X_1 + X_2)$ ² Maximum pH difference = maximum value for |pH - pH_{ave}|

								Siltite	e-Argilli	te								
	().12%S	T	().29%S	T	0).38%S-	2 Г	().47%S	Ţ	().99%S	Ţ		69%S ₁	2 [
	<u> <(</u>	<u>).01% S</u>	52-	().01%S	2-		$0\%S^{2-}$).44%S ⁻		0	.76% S	2-		<u>.37% S</u>	
Cell	<u> </u>	<u> </u>	$\%\Delta^2$	A^1	<u>M¹</u>	$\%\Delta^2$	A	<u>M¹</u>	$\%\Delta^2$	A	M	$\%\Delta^2$	A	<u>M</u>	$\%\Delta^2$	A	<u>M¹</u>	$\%\Delta^2$
Weeks		5-12			5-12			5-12			5-15			5-15			5-10	
SO ₄	32	32	0	31	27	6.9	531	500	3.0	236	223	2.8	4750	5332	5.8	3148	3149	0
Ca	19	23	9.5	20	22	4.8	56	62	5.5	21	20	2.4	18	18	0	13	11	8.3
Mg	5.5	6.2	6.0	4.4	6.0	15	50	40	10	146	168	3.9	60	60	0	35	27	13
pH _f	6.67	6.96	0.17 ³	6.68	6.55	0.07 ³	3.01	3.08	0.04 ³	5.40	6.07	0.45 ³	2.30	2.28	0.01 ³	2.32	2.27	0.033
Weeks		12-28			12-20		12-24				15-36			15-36			10-48	
SO ₄	36	20	29	31	22	17	311	332	3.3	125	107	7.8	3395	3344	0.8	2741	2907	2.9
Ca	21	20	2.4	17	16	3.0	15	16	4.8	12	9.8	10	5.2	5.6	3.7	7.4	7.5	0.7
Mg	2.4	5.8	41	5.0	4.2	8.7	17	19	5.6	115	123	3.4	27	20	15	6.4	14	37
pH _f	6.34	6.74	0.24 ³	6.58	6.43	0.08 ³	3.20	3.20	0 ³	7.05	7.20	0.08 ³	2.45	2.50	0.03 ³	2.60	2.48	0.06 ³
Weeks					_			24-68									48-68	
SO ₄							234	266	6.3							1602	1782	5.3
Ca							3.2	4.7	15							3.0	2.0	21
Mg							3.3	7.6	42							2.6	1.2	50
pH _f							3.54	3.51	0.02							2.58	2.55	0.02 ³
Weeks		5-28			5-20			5-68			5-36			5-36			5-68	
SO ₄	38	27	20	30	24	11	258	288	5.4	152	137	5.2	3746	3950	2.7	2457	2672	4.2
Ca	23	21	4.5	18	18	0	8.0	10.4	14	14	12	7.7	8.3	8.9	3.5	5.9	5.3	5.3
Mg	3.1	5.7	30	4.6	4.8	2.1	8.0	11.5	18	122	133	4.3	35	30	7.7	7.0	9.8	17
pH _f	6.34	6.74	0.24 ³	6.58	6.43	0.08 ³	3.54	3.51	0.02^{3}	7.05	7.20	0.08 ³	2.45	2.50	0.03 ³	2.58	2.55	0.02

Table 14. Comparison of ASTM Method D5744-96 and MN DNR Method drip-trickle leach testing of siltite-argillite rock, gabbro, maficintrusive, tuffaceous-sedimentary and USGS AML weathered waste rock samples. "A" and "M" ispresent ASTM and MN DNR, respectively. Release rates in μ mole (kg rock)⁻¹ week⁻¹. (Page 1 of 2).

¹ Average of duplicate cells. ² Percent difference from the mean = 100 $|X_1 - X_2|/(X_1 + X_2)|$ ³ Maximum difference from the mean = maximum of $|pH - pH_{ave}|$

pH_f: pH at end of period.

Table 14. Comparison of ASTM Method D5744-96 and MN DNR Method drip-trickle leach testing of siltite-argillite rock, gabbro, maficintrusive, tuffaceous-sedimentary and USGS AML weathered waste rock samples. "A" and "M" represent ASTM and MN DNR, respectively. Release rates in μ mole (kg rock)⁻¹ week⁻¹. (Page 2 of 2)

		Gabbro		•	Mafic-I	ntrusive		Tu	ffaceous-	Sediment	ary		USGS	
	1.309	%S _T , 1.24	% S ²⁻	7	7.05%S _T ,	6.90% S ²	-		3.90%S _T ,	3.75% S ²	-	13.704	%S _T , 13.4	6% S ²⁻
Cell	A12	M19	$\%\Delta^1$	A2	M36	M37	$\%\Delta^1$	A1	M32	M31	$\%\Delta^1$	A3	M41	$\%\Delta$
Weeks		10-59					5-	-12					5-14	
SO ₄	214	305	18	880	1350	890	12	610	810	740	12	1470	1270	7.3
Ca	124	156	11	620	1120	820	22	460	660	610	16	860	550	22
Mg	86	133	21	360	670	480	23	340	440	410	11	830	530	22
Final pH	5,51	5.71	0.11 ²	7.80	7.98	7.98	0.10 ²	7.90	8.04	7.97	0.05 ²	7.06	7.14	0.04
Weeks		59-100					12	-24					14-30	
SO ₄	172	207	9.2	710	1340	960	24	530	550	500	0.5	1030	871	8.4
Ca	73	84	7.0	580	1090	900	26	350	490	450	15	224	162	16
Mg	69	102	19	310	590	480	30	260	330	300	9.6	880	678	13
Final pH	5.30	5.63	0.20 ²	<u>8.09</u> 8.08 8.13 0.01 ²				7.99	8.04	8.08	0.04 ²	7.48	7.51	0.02
Weeks	1	00-145					24	-72					30-62	
SO ₄	140	180	13	590	700	660	7.1	440	410	430	2.3	878	672	13
Ca	55	67	9.8	450	700	700	22	330	410	380	9.0	92	69	14
Mg	65	97	20	300	420	450	18	250	290	260	4.8	927	729	12
Final pH	5.02	5.22	0.11 ²	8.00	804	8.00	0.01 ²	8.04	8.11	8.02	0.01 ²	8.01	7.73	0.16
Weeks		145-172												
SO_4	150	180	9.1											
Ca	49	63	12											
Mg	67	97	18											
Final pH	4.79	5.13	0.20 ²											
Weeks		10-172		5				72					5-62	
SO ₄	170	220	13	620	850	740	12	460	450	460	0.5	939	777	9.4
Ca	75	90	9.1	480	800	760	24	340	430	400	9.9	180	131	16
Mg	72	110	21	290	460	460	23	250	300	280	7.4	865	698	11
Final pH	4.79	5.13	0.20^{2}	8.00	8.04	8.00	0.01 ²	8.04	8.11	8.02	0.01 ²	8.01	7.73	0.16

Principal princ

² Maximum difference from the mean = maximum of $|pH - pH_{ave}|$

						Siltite-A	Argillite					
	0.12 <0.01	%S _T % S ²⁻	0.29 0.01	%S _T %S ²⁻	0.38 0%	$%S_{T}^{2}$	0.47 0.44	%S _T %S ²⁻	0.99 0.769	%S _T % S ²⁻	1.69 1.37	%S _T ² %S ²⁻
Cell	Α	M	A^1	\dot{M}^1	Α	M ¹	A	М	Α	М	Α	M ¹
Weeks	5-	12	5-	12	5-	12	5-	15	5-	15	5-	10
Ca/SO ₄	0.59	0.72	0.65	0.81	0.11	0.12	0.089	0.090	0.004	0.003	0.004	0.003
Mg/SO ₄	0.17	0.19	0.14	0.22	0.094	0.08	0.62	0.75	0.013	0.011	0.011	0.009
Final pH	6.67	6.96	6.68	6.55	3.01	3.08	5.40	6.07	2.30	2.28	2.32	2.27
Weeks	12-	-28	12-	12-20		-24	15-	-36	15-	-36	10-	-48
Ca/SO ₄	0.58	1.0	0.55	0.73	0.048	0.048	0.096	0.092	0.002	0.002	0.003	0.003
Mg/SO ₄	0.067	0.29	0.16	0.19	0.055	0.057	0.92	1.15	0.008	0.006	0.002	0.005
Final pH	6.34	6.74	6.58	6.43	3.20	3.20	7.05	7.20	2.45	2.50	2.60	2.48
Weeks					24	-68					48-	-68
Ca/SO ₄					0.014	0.018					0.002	0.001
Mg/SO ₄					0.014	0.029					0.002	0.001
Final pH					3.54	3.51					2.58	2.55
Weeks	5-:	28	5-	20	5-	68	5-	36	5-	36	5-	68
Ca/SO ₄	0.061	0.78	0.60	0.75	0.031	0.036	0.092	0.088	0.002	0.002	0.002	0.002
Mg/SO ₄	0.082	0.21	0.15	0.20	0.031	0.040	0.80	0.97	0.009	0.008	0.003	0.004
Final pH	6.34	6.74	6.58	6.43	3.54	3.51	7.05	7.20	2.45	2.50	2.58	2.55

Table 15. Release rate ratios for calcium to sulfate and magnesium to sulfate for ASTM Method D5744-96 and MN DNR Method. "A" and "M" represent ASTM and MN, respectively. (Page 1 of 2).

	Gat	obro	N	lafic-Intrusiv	/e	Tuffa	ceous-Sedim	entary	US	GS
	1.30%S _T ,	1.24% S ²⁻	7.0	5%S _T , 6.90%	5 S ²⁻	3.9	0%S _T , 3.75%	2- S ²⁻	13.70%S _T ,	13.46% S ²⁻
Cell	A12	M19	A2	M36	M37	A1	M32	M31	A3	M41
Weeks	10	-59			5-	12			5-	14
Ca/SO ₄	0.58	0.51	0.70	0.83	0.92	0.75	0.81	0.82	0.59	0.43
Mg/SO ₄	0.40	0.44	0.41	0.50	0.54	0.56	0.54	0.55	0.56	0.42
Final pH	5.51	5.71	7.80	7.98	7.98	7.90	8.04	7.97	7.06	7.14
Weeks	59-	100			12	-24			14	-30
Ca/SO ₄	0.42	0.41	0.82	0.81	0.94	0.66	0.89	0.90	0.22	0.19
Mg/SO ₄	0.40	0.49	0.44	0.44	0.50	0.49	0.60	0.60	0.85	0.78
Final pH	5.30	5.63	8.09	8.08	8.13	7.99	8.04	8.08	7.48	7.51
Weeks	100-	145			24	-72	······································		30	-62
Ca/SO ₄	0.39	0.37	0.76	1.00	1.06	0.75	1.00	0.88	0.10	0.10
Mg/SO ₄	0.46	0.54	0.51	0.60	0.68	0.57	0.71	0.60	1.06	1.08
Final pH	5.02	5.22	8.00	8.04	8.00	8.04	8.11	8.02	8.01	7.73
Weeks	145	-172								
Ca/SO ₄	0.33	0.35		· · ·						
Mg/SO ₄	0.45	0.54			•					
Final pH	4.79	5.13								
Weeks	10-	172		_	5-	72			5-	62
Ca/SO ₄	0.44	0.41	0.77 0.94 1.03			0.74	0.96	0.87	0.19	0.17
Mg/SO ₄	0.42	0.50	0.47 0.54 0.62			0.54	0.67	0.61	0.92	0.90
Final pH	4.79	5.13	8.00	8.04	8.00	8.04	8.11	8.02	8.01	7.73

Table 15. Release rate ratios for calcium to sulfate and magnesium to sulfate for ASTM Method D5744-96 and MN DNR Method. "A" and "M" represent ASTM and MN, respectively. (Page 2 of 2).

Table 16.Comparison of sulfate, calcium, and magnesium release rates (millimoles/kg·wk) and
drainage pH for siltite-argillite samples subjected to ASTM Standard Method 5744-96 and
changed to MN DNR method.

		· · · · · · · · · · · · · · · · · · ·		(· · · · · · · · · · · · · · · · · · ·
	0.96% S _{T,} 0.02% S ⁻² (20696)	1.93% S _{T,} 0.08% S ⁻² (81196)	1.60% S _T 1.53% S ⁻² (100.4)	2.30% S _{T,} 2.25% S ⁻² (99.4)	3.24% S _{T,} 3.16% S ⁻² (99.1)
	cell 6	cell 11 (2)	cell 15	cell 9	cell 10
		Final Period for	· ASTM Method		
Weeks	68-93	20-72	68-93	52-93	72-93
SO ₄	0.037	0.154	0.176	0.107	0.821
Ca	0.022	0.016	0.007	0.009	0.126
Mg	0.004	0.004	0.188	0.130	0.668
Final pH	4.88	3.70	7.09	7.24	4.27
		Periods for MN	N DNR Method		
Weeks	94-132	73-112	94-132	94-132	94-132
SO ₄	0.052	0.080	0.192	0.118	0.907
Ca	0.029	0.004	0.007	0.011	0.155
Mg	0.007	0.002	0.256	0.218	0.676
Final pH	4.74	3.78	7.03	7.55	6.26
Weeks	132-182	112-161	132-182	132-182	132-182
SO ₄	0.061	0.080	0.163	0.098	0.616
Ca	0.029	0.003	0.006	0.008	0.125
Mg	0.007	0.001	0.208	0.248	0.476
Final pH	4.36	3.71	7.19	7.83	4.45
Weeks	5-182	5-161	5-182	5-182	5-182
SO ₄	0.046	0.116	0.192	0.117	0.967
Ca	0.025	0.011	0.008	0.011	0.160
Mg	0.005	0.004	0.226	0.235	0.788
Final pH	4.36	3.71	7.19	7.83	4.45

					Silti	te-Argillite						
Sample		n	After]	Leach	Day	/ 41	Day	y 7 ¹	Day 4 After I	minus Leach ²	Day 7 min	us Day 4 ³
	ASTM	DNR	ASTM	DNR	ASTM	DNR	ASTM	DNR	ASTM	DNR	ASTM	DNR
10696	30	20	132	117	66	109	67	107	-66	-8	1	-2
	20	28	122	105	54	100	54	99	-68	-5	0	-1
40696	20	30	137	118	66	112	67	110	-71	-6	1	-2
	20	20	137	113	77	106	78	103	-60	-7	1	-3
100.4	93	48	83	88	17	87	19	86	-66	-1	2	-1
	20		93		25		28		-68		3	
71196	71	71	162	184	103	178	104	175	-59	-6	1	-3
		71		179		177		175		-2		-2
11196	27	71	111	104	58	97	58	93	-53	-7	0	-4
	71	71	107	111	51	105	51	102	-56	-6	0	-3
80597	37	37	104	131	44	126	44	124	-60	-5	0	-2
10597	37	37	121	129	69	122	70	119	-52	-7	1	-3

Table 17. Comparison of ASTM and MN DNR protocol average water retention (grams). (Page 1 of 3.)

¹ For the ASTM method Day 4 and Day 7 correspond to the end of the dry air and wet air cycles, respectively.
 ² Represents change in water retention during dry air cycle.
 ³ Represents change in water retention during wet air cycle.

				Siltite-A	Argillite Sw	itched fron	n ASTM to	DNR				
Sample	I	1	After	Leach	Day	4 ¹	Day	7 ¹	Day 4 After I	minus Leach ²	Day 7 min	nus Day 4 ³
	ASTM	DNR	ASTM	DNR	ASTM	DNR	ASTM	DNR	ASTM	DNR	ASTM	DNR
20696	93	89	150	115	97	114	98	114	-53	-1	1	0
99.4	93	89	84	70	22	69	22	68	-62	-1	0	-1
99.1	93	89	99	102	46	100	46	100	-53	-2	0	0
81196	72	89	138	114	80	110	80	109	-58	-4	0	-1
100.4	93	89	83	90	17	89	19	87	-66	-1	2	-2

Table 17. Comparison of ASTM and MN DNR protocol water retention (grams). (Page 2 of 3).

48

¹ For the ASTM method Day 4 and Day 7 correspond to the end of the dry air and wet air cycles, respectively. ² Represents change in water retention during dry air cycle. ³ Represents change in water retention during wet air cycle.

Sample	I	n	After I	Leach	Day	' 4 ¹	D	ay 7 ¹	Day 4 After J	minus Leach ²	Day 7 min	us Day 4 ³		
	ASTM	DNR	ASTM	DNR	ASTM	DNR	ASTM	DNR	ASTM	DNR	ASTM	DNR		
						Duluth C	Complex C	labbro						
MN-6.1	182	182	93	92	34	89	36	87	-59	-3	2	-2		
	182	172	98	106	30	103	34	102	-68	-3	4	-1		
	20		85		30		31		-55		1			
	Mafic-Intrusive													
MS-8	72	72	156	190	61	185	65	180	-95	-5	4	-5		
		72		192.		188		187		-4		-1		
			-			Tuffaceo	ous-Sedim	entary						
MS-2	72	72	184	234	110	231	109	227	-74	-3	-1	-4		
		72		232		229		226		-3		-3		
						US	SGS AML	,						
USGS	62	62	91	109	21	105	23	102	-70	-4	2	-3		

Table 17. Comparison of ASTM and MN DNR protocol water retention (grams). (Page 3 of 3)

¹ For the ASTM method Day 4 and Day 7 correspond to the end of the dry air and wet air cycles, respectively.
 ² Represents change in water retention during dry air cycle.
 ³ Represents change in water retention during wet air cycle.

		(One day a	after lead	h		A	fter dry	air	Four o	lays afte	r leach
S _T %	AS	ΓM me	thod	DN	VR metl	nod	AS	TM me	thod	DN	VR met	hod
	mean	S.D.	range	mean	S.D.	range	mean	S.D.	range	mean	S.D.	range
					Siltit	e-Argill	ite					
0.12	132	13.2	42	117	4.7	18	66	28.0	131	109	4.5	18
0.12	122	12.9	47	105	9.0	35	54	34.1	157	100	8.6	51
0.29	137	13.9	45	118	5.8	24	66	22.0	90	112	6.3	34
0.29	137	10.2	36	113	2.4	10	77	18.7	84	106	2.3	8
0.38	162	10.9	46	185	8.7	49	103	24.2	154	179	7.9	45
0.38				179	8.1	42				177	7.8	40
0.47	104	4.8	31	131	6.3	27	44	8.7	43	126	3.6	17
0.99	121	4.5	20	129	5.3	20	69	9.4	38	122	4.2	22
1.69	111	4.6	18	104	7.8	31	58	15.8	65	97	6.5	28
1.69	107	8.0	39	111	4.6	22	51	16.0	78	105	4.5	20
		•			C	Jabbro						
1.39	85	7.6	29	103	5.4	30	30	17.2	66	100	4.8	24
1.39	91	8.6	34	91	3.0	19	36	16.4	99	87	3.0	17
1.39	96	7.4	36				30	19.3	102			
	<u></u>	· · · · · · · · · · · · · · · · · · ·			Mafi	c-Intrusi	ve					
7.05	194	11.2	45	241	5.6	25	123	28.8	53	238	5.6	26
7.05				238	5.8	27				234	7.2	3
				Τι	nentary							
3.90	165	12.8	66	196	10.9	34	72	39.2	168	194	9.9	33
3.90				198	5.6	25				194	5.6	28

Table 18.Comparison of water retention for ASTM and MNDNR methods (weights in grams $20 \le n \le 133$) from Lapakko and White 2000.

	AAL					MN DNR					
	ASTM Method					ASTM	Method	MN DNI	NR MN DNR Method Drip Flood 7.18 6.30 5.71 5.29 5.63 5.16 5.22 4.98 5.13 4.92 470 640 300 350 210 250 180 180 180 70 100 180 70 100 180 70 100 180 70 76		
Weeks		Drip			bod	Drip Flood		Drip	Flood		
Drainage pH											
10	6.84	6.84	6.87	6.82	6.57	6.73	6.45	7.18	6.30		
59	5.21	5.22	5.27	5.38	5.50	5.51	5.49	5.71	5.29		
100	4.78	4.84	4.87	5.13	5.13	5.30	5.16	5.63	5.16		
145	4.67	4.60	4.75	5.00	4.99	5.02	4.76	5.22	4.98		
172	4.20	3.91	4.06	4.30	4.46	4.74	4.62	5.13	4.92		
Sulfate Release Rate, μ mole (kg rock) ⁻¹ week ⁻¹											
0-10	396	206	233	273	235	378	406	470	640		
10-59	225	191	211	189	221	214	241	300	350		
59-100	155	143	179	173	181	172	199	210	250		
100-145	109	128	142	118	127	139	167	180	180		
145-172	288	425	362	416	340	151	157	180	180		
		Ca	alcium Rel	lease Rate,	μ mole (kg	g rock) ⁻¹ we	ek				
0-10	NA	NA	NA	NA	NA	262	257	330	440		
10-59	NA	NA	NA	NA	NA	124	132	160	170		
59-100	NA	NA	NA	NA	NA	73	84	84	92		
100-145	NA	NA	NA	NA	NA	55	63	67	76		
145-172	NA	NA	NA	NA	NA	49	53	63	63		
Magnesium Release Rate, μ mole (kg rock) ⁻¹ week											
0-10	NA	NA	NA	NA	NA	123	142	160	200		
10-59	NA	NA	NA	NA	NA	86	108	130	150		
59-100	NA	NA	NA	NA	NA	69	76	100	100		
100-145	NA	NA	NA	NA	NA	65	90	97	86		
145-172	NA	NA	NA	NA	NA	67	77	97	81		

Table 19. Summary of drainage pH and release rates for Duluth Complex gabbro.

Figure 1. Schematic of humidity cell for ASTM and MN DNR method.

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





Figure 2. Sulfate concentrations in drainage from ASTM drip leach cells at AAL cycled over time, with a period of about 50 weeks.

σ ω



Figure 3. Sulfate concentrations in drainage from ASTM flood leach cells at AAL cycked iver time with a period of about 50 weeks.

Attachment 1

- Table A1.12.
 Whole rock chemistry of Duluth Complex rock sample which was inadvertently omitted from appendix 1.
- Table A1.13.
 Trace metal analysis of Duluth Complex rock sample which was inadvertently omitted from appendix 1.

Mineralogy of mafic-intrusive and tuffaceous-sedimentary rock (samples MS2 and MS8 are the only samples that are pertinent to this report) was inadvertently omitted from appendix 1.

Table A6.1 page 6 of 6 was omitted from appendix 6 and page 5 of 6 was inadvertently presented twice.

Parameter	MN6.1 original	MN6.1 leached ¹
S	0.78	1.30
S ²⁻	0.74	1.24
SO ₄ ²⁻ S	0.11	0.17
CO ₂	0.12	0.21
Al ₂ O ₃	15.12	16.04
CaO	8.27	7.71
Fe ₂ O ₃	14.79	16.34
K ₂	0.75	0.92
MgO	8.64	8.99
MnO	0.16	0.16
Na ₂ O	1.78	2.02
P ₂ O ₅	0.16	0.16
SiO	45.59	46.29
TiO	1.41	1.53

.

Table A1.12. Whole rock chemistry (percent) of Duluth Complex sample (MN6.1), original and leached. Analyses by ACTLABS in Wheat Ridge, CO.

1- Sample was leached for 20 weeks at MDNR

Parameter	MN6.1 original	MN6.1 leached
Ag	0.9	0.8
As	3	6
Au	<5	9
Ba	400	365
Be	2	2
Ві	<5	<5
Br	<1	1
Cd	0.9	0.7
Co	71	82
Cr	240	254
Cs	1.3	<5
Cu	2341	3526
Hf	1.8	2.5
Ir	<5	<5
Мо	<5	<5
Ni	451	621
РЬ	6	10
Rb	25	43
Sb	0.2	0.4
Se	<3	<3
Sr	271	278
Ta	<1	<1
V	232	242
w	3	3

Table A1.13. Page 1 of 2. Trace metal analysis of Duluth Complex sample (MN6.1), original and leached. Analyses by ACTLABS.

Parameter	MN6.1 original	MN6.1 leached			
Y	18	17			
Zn	174	268			
Zr	71	87			
Ce	29	35			
Eu	1.4	1.4			
La	14.6	15.5			
Lu	0.25	0.30			
Nd	15	18			
Sc	29	31			
Sm	3.1	3.5			
Тъ	<0.5	<0.5			
Th	1.4	1.2			
U	0.6	<0.5			
Yb	1.5	1.7			

Table A1.13. Page 2 of 2. Trace metal analysis of Duluth Complex sample (MN6.1), original and leached. Analyses by ACTLABS.

r

.

.

MINERALOGICAL CONSULTING SERVICE

29022 West Shore Lane ~ Pengilly, MN 55775-2222 Phone 218/885-2358 ~ Email cygnus@the-bridge.net

MINERALS DIVISION HIBBING

Attachment A1.1. Mineralogy

April 9, 1999

Mr. Kim Lapakko Minnesota DNR-Minerals Box 45 500 Lafayette Road St. Paul, MN 55155-4045

RE: BLM/USGS SAMPLES-MINERALOGY

Dear Mr. Lapakko:

The ten(10) BLM samples (M-1 thru M-10) and one (1) USGS sample received have been evaluated to identify minerals and determine percentages of those minerals in each sample. The liberation characteristics of the major carbonate and sulfide minerals were also determined. For each sample, the materials received consisted of crushed -1/4" head samples, pulverized (80%-150M) assay pulps and dry sieved size fractions from -1/4" to -200M (10-11 fractions per sample).

This evaluation was a joint study conducted by Mr. Barry Frey at the Midland Research Center and myself. X-ray diffraction (XRD) studies of both the whole rock and heavy mineral concentrates, the recovery of heavy mineral concentrates by superpanner, scanning electron microscopy (SEM/EDS) and all photos in this report were conducted by Mr. Barry Frey. I assisted with mineral identification, determined the mineral percentages and conducted the carbonate and sulfide liberation studies.

BLM Sample Mineralogy

The BLM samples are identified as "Mafic-Intrusive" (M-1 thru M-7) and "Tuffaceous-Sedimentary" (M-8 thru M-10). The seven (7) <u>Mafic-Intrusive</u> samples are generally similar and consist of fine to medium grained highly altered rock containing fine grained disseminated sulfides with additional sulfides in quartz and carbonate veinlets. The alteration and replacement is primarily of the host rock minerals and is probably associated with the mineralizing events. Except for tarnished pyrite and minor iron oxides, there is little direct evidence of surficial alteration. See photos M-1 thru M-7.

The three(3) <u>Tuffaceous-Sedimentary</u> samples are generally similar and consist of very fine grained, highly siliceous, black rock with numerous quartz and lesser carbonate veins. Sulfides tend to occur mostly in the veins, but are also disseminated in the rock.All three(3) of these samples contain carbonaceous material and it is most common inM-9. There is very little evidence of surficial alteration. See photos M-8 thru M-10.

NOTE: All samples in this mineralogical report are referenced by M-#, and are equivalent to the MS-#'s referenced in the remainder of the report.

Mr. Kim Lapakko April 9, 1999 Page 2

The Mafic-Intrusive and the Tuffaceous Sedimentary samples contain essentially the same mineral suite, only the relative amounts of each mineral differ. BLM sample minerals are listed in Table I. The mineral percentages (Table II) are based on minerals identified and the assay data that you provided for each sample. The following comments relate to BLM minerals and mineral percentages.

- Dolomite (ferroan) is the dominant carbonate in all samples. Typical dolomite composition used to determine mineral percentages is about 18.5% MgO, 24.5% CaO, 0.1% SrO, 1.2% MnO, and 9.0% FeO. Trace (Tr.) amounts of calcite are included in the dolomite percentage.
- Samples M-1 thru M-7 are very illite (sericite?)-rich and samples M-8 thru M-10 are very quartz-rich.
- Pyrite is essentially the only sulfide mineral positively identified and contains the arsenic (As) in the samples. Arsenic substitutes for Fe or S in the pyrite and was calculated as As₂S₃/AsS and included in the pyrite percentage. Arsenopyrite and marcasite may be present in trace (Tr.) amounts.
- Iron oxides are minor and due to surficial oxidization. Only hematite and goethite were observed.
- The minerals listing (Table I) includes a number of minerals not positively identified in this study, but suggested by the chemistry and overall mineralogy. These may help explain the distribution of some trace elements.
- Rare, cinnabar-red, grains were observed in samples M-2, M-4, and M-5. These grains generally yield Ca,Zn,S+/-CI SEM/EDS spectra and it's unknown if they represent a mineral or are other contamination.

USGS Sample Mineralogy

The USGS sample minerals and mineral percentages are listed in Table III. The sample is composed of relatively coarse grained siderite, pyrite, sphalerite, and galena plus a number of secondary sulfates, iron oxides, carbonates, and silicates(?). The crushed mineral grains available are surprisingly fresh looking considering that this material has reportedly been in stockpile for about eighty (80) years. The secondary minerals tend to be soft/friable materials that break-up easily on crushing and are relatively concentrated in the finer grained size fractions. Numerous small grains were picked for SEM/EDS examination to clarify the nature of secondary minerals. The

Mr. Kim Lapakko April 9, 1999 Page 3

mineral percentages (Table III) are based on minerals identified and the assay data provided. The following comments relate to the minerals and mineral percentages in Table III.

- Kaolinite appears to be largely a secondary mineral filling voids and coating primary minerals. Some of the SEM/EDS data suggests a K-AI-silicate may also be present, but only at trace levels as the sample contains only 0.04% K₂O.
- The siderite has a high Mn content (manganosiderite). Calcite (aragonite?) was detected only by SEM/EDS and occurs as slender crystals associated with secondary sulfates or intimately intergrown with other alteration materials.
- Pyrite appears to be normal pyrite. Sphalerite is a high Fe, high Mn variety and galena appears normal.
- The Fe-sulfates are calculated as melanterite, however more than one hydrated Fe-sulfate may be present. Anglesite was observed as coatings on galena and gypsum crystals are scattered through-out.
- Iron oxides consist of primary magnetite and secondary, mostly after pyrite, goethite>>>>hematite>>akaganeite. The primary magnetite by SEM/EDS contains minor Ti,Cr, and Co. The goethite contains a number of elements, most probably due to finely intergrown Mn-oxides, calcite/aragonite, pyrite, and kaolinite.
- Argentite and chalcopyrite were not positively identified in this sample, but are commonly associated with this chemistry and mineralogy. The 20 ppm silver and 460 ppm copper in the sample probably occur in these minerals.

Liberation

The liberation of the dominant carbonate and sulfide minerals in each sample is indicated in Table IV. This includes liberation of dolomite and pyrite for the BLM samples (M-1 thru M-10) and siderite, pyrite, sphalerite, galena plus total sulfide for the USGS sample. Liberation is based on observations from each of the 10-11 dry sieve fractions (-1/4" thru -200M) received for each sample. All dry sieve fractions were wet sieved prior to study to remove a coating of fines on all size particles and facilitate microscopic observations. Liberation characteristics were determined for the coarser sized particles by microscopic observation of loose grains and for the finer sized particles mounted in oil and examined with a petrographic microscope. Overall liberation is a weighted value based on the particle size distributions and liberation

Mr. Kim Lapakko April 9, 1999 Page 4

characteristics within each size fraction. Liberation is based on grain surface characteristics only and assumes that all size fractions for a given sample contain equal amounts of each mineral.

Overall liberation of both carbonates and sulfides in these samples is relatively poor (see Table IV). The dolomite and pyrite in the BLM samples is generally fine grained while the sample particle sizes are relatively coarse grained. The Mafic-Intrusive samples (M-1 thru M-7) are 50-60%+20M while the dolomite and pyrite, respectively. are reasonably well liberated in the total -100M and -150M size fractions. The Tuffaceous-Sedimentary samples (M-8 thru M-10) are 60-70%+20M while the dolomite and respectively. are reasonably well liberated in the pyrite. total -65M(M-8)/-100M(M-9/10) and -100M(M-8)/-150M(M-9/10) size fractions. The total -100M for the BLM samples ranges from about 8-15 Wt.% and the total -150M ranges from about 6-12Wt.%.

The USGS sample contains significantly coarser grained carbonate and sulfides than the BLM samples, but is also over 75%+20M. The siderite and the total mixed sulfides are reasonably well liberated in the total -35M size fractions that constitute about 14Wt.% of the USGS sample. The individual sulfides (pyrite, sphalerite, and galena) are all reasonably well liberated in the total -48M size fractions that represent about 12 Wt.% of the sample.

In both the BLM and USGS samples, the carbonate and sulfide(s) while poorly liberated, are well exposed on the surfaces of the coarser sized particles. Undoubtedly, both carbonates and sulfides are also included within the coarser sized particles.

Thank you for using my services for this study. Please phone or e-mail if you have any questions.

Sincerely,

Louis A. Mattson, Geologist/Process Mineralogist

Table I: MINERALS - BLM Samples M-1 thru M-10

<u>Mineral</u>	Formula	<u>Other Metals</u>			
Quartz	SiO ₂				
Dolomite	Ca(Ӣ҄g,Fe)(CO ₃) ₂	Mn, Si			
Calcite	CaCO ₃				
Illite	KAl ₃ Si ₃ O ₁₀ (OH) ₂	Cs, Rb, Ti			
K-feldspar	KAIŠi ₃ Ŏ ₈ Č				
Pyrite	FeS2	As, native/combined Au			
Apatite	Ca ₅ (PO₄) ₃	As,CO ₃ ?,F,REE,Th,U,V			
Arsenopyrite	FeĂsS	-			
Barite	BaSO₄	Ca,Sr			
Carbon	C				
Chalcopyrite*	CuFeS ₂				
Cinnabar*	HgS [–]				
Fe-Oxides	Fe ₃ O ₄ /Fe ₂ O ₃				
Gold	Au	Ag			
Gypsum	CaSO ₄ -2H ₂ O	Ba,Sr			
Kaolinite	Al ₂ Si ₂ Ô ₅ (ÕH) ₄				
Marcasite	FeS2				
Monazite*	REE(PO ₄)	Th,Y			
Orpiment*	As ₂ S ₃				
Realgar*	AsS				
Rutile	TiO ₂				
Scheelite*	CaWO ₄				
Sphalerite*	ZnS	Cd			
Stibnite	Sb ₂ S ₃				
Zircon	ZrSiO ₄	Hf,REE			

*Minerals not positively identified in this study, but suggested by chemistry and overall mineralogy.

TABLE II: BLM Samples - Mineral Weight Percentages

Minerals	M-1	M-2	M-3	M-4	M-5	M-6	M-7	M-8	M-9	M-10
Quartz	15.7	18.0	16.4	27.5	19.8	10.7	14.0	67.4	79.6	83.9
Dolomite	10.5	9.0	4.4	9.7	12.7	5.6	6.0	8.6	7.1	4.1
Calcite	Tr.	Tr	Tr.							
Illite	50.2	50.1	54.7	41.4	43.2	53.2	54.2	11.8	7.8	6.4
K-feldspar	<0.1	<0.1	<0.1	0.8	3.8	4.0	2.3	2.8	1.8	1.5
Pyrite	13.7	13.0	15.1	12.1	11.7	16.1	13.9	7.0	2.6	2.5
Apatite	3.8	3.5	4.2	3.4	3.7	4.3	4.4	1.2	0.4	0.9
Arsenopyrite	Tr.									
Barite	<0.1	<0.1	0.1	<0.1	0.1	0.1	0.1	<0.1	<0.1	<0.1
Carbon	?	?	?	?	?	?	?	<1?	1+/-	<1?
Fe-oxides	1.9	2.2	1.6	0.8	1.6	1.6	1.4	<0.1	0.4	0.5
Gold	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Gypsum	<0.1	0.2	0.1	1.6	0.5	0.9	<0.1	0.3	<0.1	<0.1
Kaolinite	1.1	0.8	<0.1	<0.1	<0.1	<0.1	0.2	0.3	0.2	0.1
Marcasite	Tr.									
Rutile	3.0	3.1	3.3	2.6	2.8	3.4	3.4	0.6	0.1	0.1
Stibnite	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Zircon	0.1	0.1	0.1	0.1	0.1	0.1	0.1	<0.1	<0.1	<0.1
		Other	Weight							
-----------------	--------------------------------------	----------------	---------	--	--	--				
Mineral	Formula	<u>Metals</u>	Percent							
Quartz	SiO2		2.4							
Kaolinite	Al₂Ši₂O₅(OH)₄		2.1							
Siderite	(Fe,Mn)ČO ₃	Mg,Ca	52.1							
Calcite	CaCO3	Fe,Mn	0.2							
Cerussite	PbCO3		<0.1							
Pyrite	FeS2		17.3							
Sphalerite	ZnS	Fe,Mn,Cd	9.6							
Galena	PbS	Sb, As, Bi, Ag	1.9							
Argentite(1)	Ag ₂ S		<0.1							
Chalcopyrite(1)	CuFeS ₂		<0.1							
Gypsum	CaSO		0.9							
Melanterite(2)	FeSO ₄ .7H ₂ O		4.6							
Anglesite	PbSO		<0.1							
Magnetite	Fe ₃ O ₄	Ti,Cr,Co	0.7							
Hematite(3)	Fe ₂ O ₃	 .								
Goethite(3)	FeÕOH	Mn	8.0							
Akaganeite(3)	B FeOOH									

Table III: USGS Sample; Minerals and Weight Percentages

(1)Not positively identified but probably present,
(2)May be mixed Fe-sulfates, exact compositions not determined
(3)Secondary iron oxides=goethite>>>>hematite>>akaganeite

Table IV: BLM/USGS Samples; Carbonate and Sulfide Liberation

Weight Percent Liberated

Sample	<u>Carbonate</u>	<u>Pyrite</u>	<u>Sphalerite</u>	Galena	Total <u>Sulfide</u>
M -1	16	15			
M-2	20	17			
M-3	20	17			
M-4	22	18			·
M -5	22	18		<u> </u>	
M- 6	20	19			
M-7	16	14			
M-8	22	17			
M-9	13	12			
M-10	14	14			
USGS	24	18	18	16	34

	Blank indicates no analysis																
	Page 6 of	f 6															
			Net														
week	Eh(mv)	pH	Alkalinity	Cond(uS)	SO4	Ca	Mg	Na	K	Al	Si	Fe	Mn	Cu	Ni	Co	Zn
151	227.7	5.22	_	115													
152	246	5.22	-5	92	28.5	5.2	4.3										
153	213.4	5.19		110													
154	NA	5.22		110													
155	242.7	5.13		110													
156	277.9	5.16	-5	105	27	4.9	4.8										
157	244.6	5.12		100													
158	234.8	5.19		110													
159	208.9	5,19		110													
160	214.5	5.18	-5	120	45.1	5.8	5.7										
161	243.8	5.24		105													
162	210.7	5.24		105													
163	234.3	5.19		120													
164	212.8	5.12	-7.5	110	38.9	4.9	4.8										
165	216.6	5.21		105													
166	214.7	5.19		102													
167	194.9	5.18		110													
168	266.9	5.17	-5	100	38.8	5	4.9										
169		5.20		90													
170		5.07	-2.5	90	36.2	5	4.6										
171						-											
172																	
173																	
174		5 18	-75	95	38	46	48				78						
175		2.10	7.5	20	50	4.0	4.0				7.0						
176																	
177																	
178		5 10	75	05	26.0	4.4	17										
170		5.19	-7.5	22	30.0	4.4	4./										
180																	
181																	
182		5 1 3	5	80	20.7	20	20										
104 West-4		J.15	-3	80	30.7	3.8	3.8										
week	J was a 110W	weignied	composite from	i 5 rinses.													

Table A6.1. Mn DNR(drip) method drainage quality from Duluth Complex sample(1.39% total sulfur Mn-6.1, cell 19).

Concentrations are in mg/L unless otherwise noted. pH is in standard units, alkalinity(values <0 indicates acidity) in mg/L as CaCO3.