Duluth Complex Rock Dissolution and

Mitigation Techniques:

A summary of 35 years of DNR research

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1. INTRODUCTION

Minnesota has an extensive taconite mining industry. The mines, tailings, and waste rock produced during this mining cover more than 135 square miles. Despite the vast amount of these wastes, drainage quality problems have been largely limited to recent concerns regarding sulfate release. Studies have been conducted to quantify the sulfate released with drainage from a tailings basin (Lapakko and Jagunich 1991) and to evaluate ground water quality impacts of disposing taconite tailings in existing open pits (e.g. Berndt et al. 1999, Lapakko and Jakel 1999).

Minnesota has potential for mining of nonferrous minerals, particularly within the Duluth Complex, a layered mafic intrusion in the northeastern part of the state. It is a large gabbroic body that contains low-grade copper and nickel sulfides, titanium oxides, and platinum group elements, and it has also been developed as a source of dimension stone. The Complex contains one of the largest known copper and nickel resources in the U.S. (Minnesota Environmental Quality Board 1979; Kingston et al. 1970).

Miller et al. (2002) reported on the mineral occurrences and geology of the Duluth Complex, from which Ruhanen (2006) summarized the following information on the Partridge River and South Kawishiwi intrusions. Dissolution of rocks from these two intrusions is the focus of the studies discussed in the present report.

The Partridge River intrusion hosts at least four copper-nickel prospects (Babbitt, Dunka Road, Wetlegs, Wyman Creek) and at least seven potential iron-titanium prospects (Miller et. al., 2002) (Section 17, Longear, Longnose, Wyman Creek, Section 22, Skibo, Water Hen) (Figure 1). The Section 22, Skibo, and Water Hen prospects all lie south, and within 12 miles, of the Wyman Creek prospect and are not depicted in Figure 1.

The Partridge River intrusion consists mainly of troctolitic rocks that form an arc-shaped exposure (Figure 1). It is estimated to be 2.5 km thick, and is underlain by the Virginia Formation slates and greywackes and the Biwabik Iron Formation. The basal 900 meters of the intrusion has been subdivided into seven stratigraphic units (Severson and Hauck 1990, 1997; Geerts 1991; Severson 1991, 1994) that can be correlated over a strike length of 24 km. These units dip 10 to 20 degrees to the southeast and have been described in detail due to the presence of copper-nickel (Cu-Ni) mineralization. Rocks overlying the Partridge River intrusion include other Duluth Complex rocks and metamorphosed basalts (probably North Shore Volcanic Group). These rocks are also present in the interior of the intrusion as large inclusions.

The contact zone between the Partridge River and South Kawishiwi intrusions is poorly exposed and sparsely drilled. The seven basal units become unrecognizable in the contact zone. This contact is complicated by the presence of a fault (Grano fault of Severson 1994) that was repeatedly activated during and after the emplacement of the two intrusions.

Figure 1. Map of Duluth Complex mineral prospects.
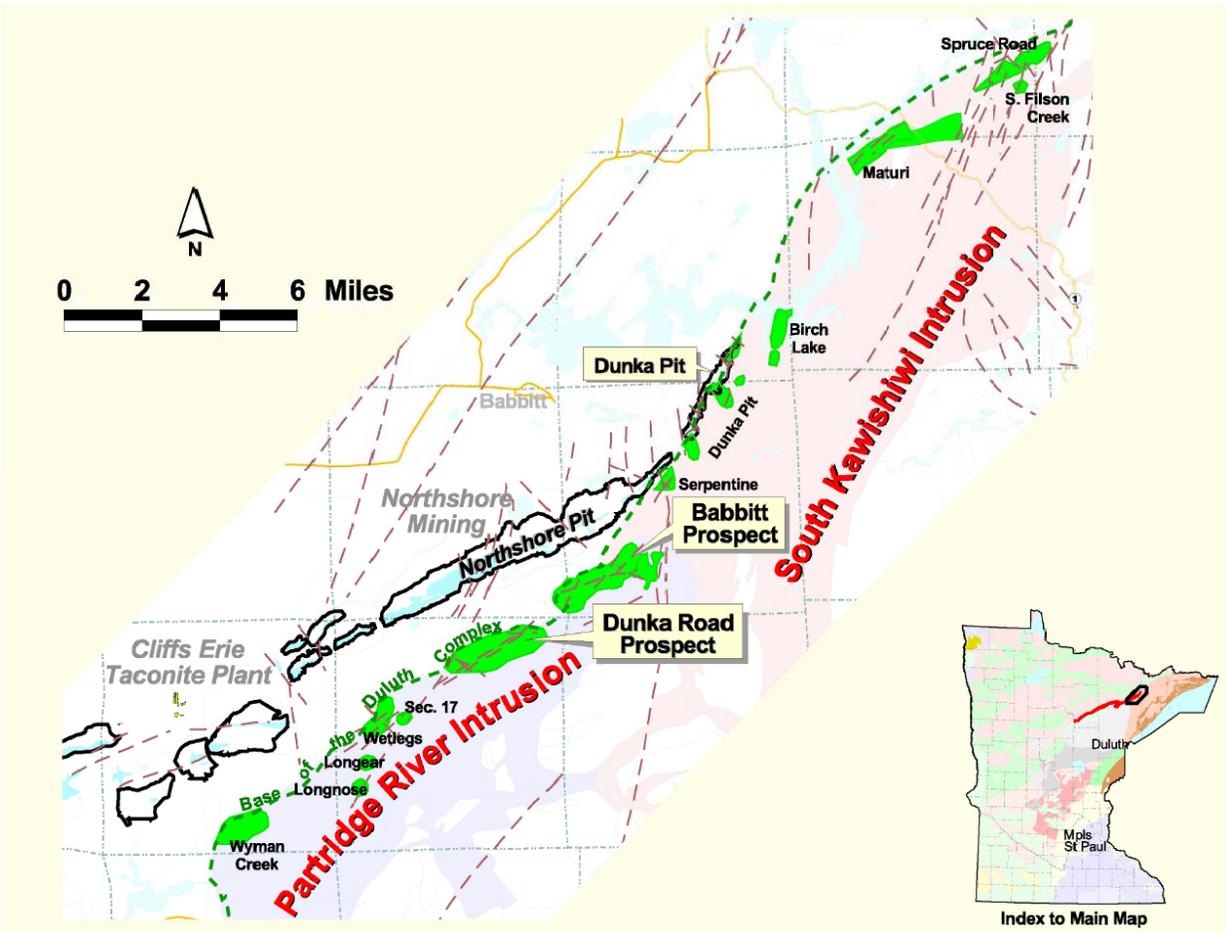
The South Kawishiwi intrusion hosts at least five copper-nickel prospects (Spruce Road, South Filson Creek, Maturi, Dunka Pit, Serpentine) and a potential platinum group element copper-nickel prospect (Birch Lake) (Figure 1). The intrusion is composed of troctolitic rocks exposed in an 8-by-32 kilometer arc-shaped band (Figure 1). The Giant's Range batholith is the dominant footwall rock, although Virginia Formation and Biwabik Iron Formation underlie the intrusion in some areas. Five major map units in the South Kawishiwi intrusion have been identified, although some geologists have further subdivided these units (e.g. Severson 1994). The units are not continuous throughout the intrusion. Major sulfide mineralization occurs at the base of the intrusion. Virginia Formation and Biwabik Iron Formation inclusions occur throughout the intrusion. Inclusions of basaltic hornfels (probably from the North Shore Volcanic Group) and quartz sandstone hornfels (probably from the Puckwunge and Nopeming sandstones) occur near some of the copper-nickel prospects. The lower ultramafic unit contains the majority of the high platinum group element values.

The presence of sulfide minerals in Duluth Complex rock also represents an environmental concern. When exposed to oxygen and water, iron sulfides such as pyrrhotite will oxidize and produce acid. At relatively low iron sulfide concentrations, the rate of acid generation will be low and dissolution of other minerals present in the rock can neutralize the acid produced. At higher iron sulfide concentrations, the rate of acid production will exceed the rate of neutralization, resulting in acidic drainage. Sulfide minerals containing copper, nickel, cobalt, or zinc will also oxidize to release the associated trace metal. Drainage that is acidic and/or containing elevated concentrations of trace metals is an environmental concern.

Mine wastes that produce problematic drainage must be managed such that the quality of waters of the state is not adversely impacted. Mine waste management strategies directed at this objective include preoperational mine waste characterization and drainage quality prediction and prevention, control, and treatment of problematic drainage. The Reclamation Section within the Division of Lands and Minerals of the Minnesota Department of Natural Resources (MN DNR) has conducted numerous studies on mine waste characterization, drainage quality prediction, and mitigation of mine waste drainage, as well as field studies on the release and aqueous transport of mining related contaminants.

Mine waste drainage quality and the mitigation of problematic drainage have been studied in Minnesota since the mid-1970s. Studies were initiated in 1976 under the auspices of the Regional Copper-Nickel Study and, in 1978, were continued by the MN DNR. Many of the studies were conducted in cooperation with industry or other governmental agencies (Lapakko and Brice 1998).

A process for characterizing potential mine wastes prior to nonferrous mine development was developed. The characterization process includes determining the mass and composition of wastes to be generated and conducting dissolution tests on representative samples of mine waste to predict the drainage quality from mine wastes. Studies have been conducted to examine the design of dissolution tests and interpretation of their results. Drainage from operational scale stockpiles of Duluth Complex has been monitored, and field studies on Duluth Complex test

piles were conducted. Laboratory studies have been conducted to describe the quality of drainage from Duluth Complex waste rock. Laboratory and field studies have been conducted on tailings generated from copper-nickel deposits in the Duluth Complex.

The strategies using alkaline solids and subaqueous disposal have been examined for their potential in the environmental management of mine wastes. Laboratory and field experiments are in progress to examine the mitigative potential of mixing alkaline solids with acid-producing mine waste. Laboratory and field tests were conducted to determine the effectiveness of limestone beds for treating mine waste drainage. Operational scale mitigation measures implemented at the Dunka mine have been summarized (Eger et al. 1999). Finally, disposal of sulfidic rock in a subaqueous setting, with and without various amendments, is under investigation in both the laboratory and field.

The following provides a brief overview of monitoring and research activities regarding the environmentally sound management of Duluth Complex mine wastes. In particular, this report summarizes research on prediction of drainage quality from Duluth Complex mining wastes and mitigation of Duluth Complex mine waste drainage using alkaline solids and subaqueous disposal. Many of these projects remain in progress. More detailed information is available in the publications cited. A brief discussion of mine waste dissolution chemistry is presented in Appendix 1. Information on other MN DNR research on environmentally sound management of mine wastes from other lithologies is presented in previous research summaries (Lapakko et al. 1998a, 2001).

The MN DNR has also conducted research on capping mine wastes to reduce precipitation input, joint disposal of waste rock and tailings, and treatment of mine waste using wetlands and sulfate reduction. These studies are not described in the present report. The Mineral Resources Research Center at the University of Minnesota, Minneapolis conducted mineral processing studies and, to a far lesser degree, environmental research on Duluth Complex rock. Extensive research on the geology of the Duluth Complex has also been conducted by the Natural Resources Research Institute, University of Minnesota, Duluth, and the Minnesota Geological Survey. This research is also excluded from the present report.

2. MINE WASTE CHARACTERIZATION

2.1. Conceptual Approach

The quality of mine waste drainage is variable, largely due to the variability in mine waste composition. By characterizing mine wastes and predicting mine waste drainage quality prior to mineral resource development, waste disposal facilities can be designed, sited, constructed, and reclaimed in a manner that will most effectively reduce contaminant release and the associated drainage treatment cost. Mitigation can be tailored to the predicted drainage quality and directed toward meeting water quality objectives. Wastes with mitigative capacity (e.g. limestone) can be identified during the characterization process. Finally, the cost of reclamation can be considered along with other mining costs in the assessment of resource development economics. Mine development can then progress with consideration of both metal recovery and the environmentally sound management of mine wastes.

A mine waste characterization process was designed for application on a site-specific basis (Lapakko 1990b, 1988b). The approach and many of the analytical techniques used are similar to those employed for evaluation of potential for resource recovery. The extent of rock units potentially contributing to mine waste is delineated and pertinent compositional aspects of these units are quantified. The quality of drainage from the potential wastes is then projected. Existing data on a mine waste of similar composition, generated by similar mining methods, and exposed to similar environmental conditions for an extended time provide the best indicator of drainage quality. A directory of contacts was compiled to facilitate collection of information on mine waste composition and drainage quality across the United States (Wessels et al. 1991).

Since data on the drainage quality from a mine waste of specific composition are often not available, it is commonly necessary to conduct laboratory dissolution tests to predict drainage quality. These tests could be conducted on a variety of representative samples from individual rock units to determine the relationship between mine waste composition and drainage quality. Additional sampling, analysis, and dissolution testing may be required based on the information compiled. The relationship between solid composition and chemical behavior is then extrapolated to the waste as a whole. A mine waste management program would be designed based on the projected drainage quality and quantity.

The mine waste composition and predicted drainage quality would be subject to verification during operation if mine development proceeded. Small-scale field tests on well-characterized waste allow more accurate extrapolation to operational scale drainage quality and drainage volume, and also allow assessment of mitigation design. Initiating such verification tests as soon as resource development begins maximizes the benefit of these tests for drainage quality prediction and mine waste management. These concepts were integrated into Minnesota's Nonferrous Mining Rules (Chapter 6132).

2.2.   Assessment of Tests for Predicting Mine Waste Drainage Quality

Several static and kinetic tests have been developed for predicting mine waste drainage quality. Static tests base predictions on solid phase analyses, while kinetic tests use data from dissolution tests on mine waste samples. Static tests attempt to quantify the capacity of a mine waste to produce acid (Acid Production Potential or AP) and to neutralize acid (Neutralization Potential or NP). The difference between these values or their ratio is used to estimate the potential of the mine waste to produce acidic drainage. They do not account for the availability of the acid-producing or acid-neutralizing minerals or the rate at which they dissolve. They are typically used as a tool for initial screening of mine wastes for their potential to produce acid.

AP is based on the quantities of sulfur present as acid-producing sulfide and sulfate minerals. Since techniques for determining these quantities have been developed and applied for geological assessment over many years, they are fairly accurate as long as the acid-producing phases present are known. NP is typically determined by subjecting the sample to partial digestion in an acidic solution, and then titrating the solution to determine the amount of acid neutralized during digestion.

Kinetic tests involve dissolution of mine waste samples and analysis of the resultant water quality. Tests such as these permit identification of some acid-producing mine wastes based on the laboratory drainage pH. However, if the mine waste contains a moderate amount of neutralization potential, it may not be depleted during the course of the test and drainage will remain neutral. Based on such data it might be concluded that the solids were not acid producing. However, over a longer duration the NP may be depleted while iron sulfides remain and continue to oxidize. In such a case the drainage would acidify upon depletion of the neutralizing minerals. Thus, to determine the degree to which laboratory tests model long-term field behavior, it is necessary to determine the extent to which acid producing and acid neutralizing minerals have been depleted in kinetic tests.

To evaluate several static and kinetic tests on a compositional range of mine wastes, the U.S. Environmental Protection Agency provided funding to the MN DNR for a project that was administered by the Western Governors' Association (WGA). A literature review was produced and followed by empirical evaluation of the ability of tests to predict mine waste drainage pH (Lapakko 1991b, 1992a). Insight into the accuracy of NP determinations has been gained as part of MN DNR testing of Duluth Complex rock and hydrothermal quartz-carbonate gold tailings. The influence of static test protocol variables on NP was also examined as part of the latter research, which was funded by the Minnesota Minerals Coordinating Committee and MN DNR Division of Minerals (Lapakko 1991a, 1992b). Much of the information from these and other studies is presented in White et al. (1997, 1999).

The EPA funded a continuation of the kinetic testing phase of the WGA project. In this continuation two dissolution tests were continued for a total duration of 132 weeks and the effect of particle size on mine waste drainage quality was examined (Lapakko et al. 1995). The U.S. Army Corps of Engineers provided funding for the final stage of this project, in which as much as 618 weeks of dissolution testing data were reported (Lapakko et al. 2004a).

2.3.   Static Testing of Duluth Complex Rock

As mentioned above, the objective of static tests is to determine the potentials of a mine waste to produce and neutralize acid. To accurately quantify the potential for acid production, the content of acid-producing minerals must be determined. In Duluth Complex mine wastes, iron sulfide phases are the dominant acid producers, and the predominant mineral phases are pyrrhotite and the iron sulfide fractions of chalcopyrite, cubanite, and pentlandite (respectively $Fe_{1-x}S$, $CuFeS_2$, $CuFe_2S_3$, $(Fe, Ni)_9S_8$). Because sulfide is commonly associated with copper and nickel (and to a lesser degree with cobalt and zinc), quantification of acid production by determination of total sulfur or sulfide-sulfur tend to overestimate the potential for acid production. That is, oxidation of the trace metal sulfide fraction of these minerals will not lead to substantial acid production unless the trace metals released precipitate as hydroxides or oxides.

Standard ABA NP values overestimate the capacity for Duluth Complex rock to neutralize acid while maintaining an environmentally acceptable drainage pH. Although carbonate minerals are generally present at very low concentrations in Duluth Complex rock (Stevenson et al. 1979, Lapakko 1988a), Standard Acid Base Accounting (Standard ABA) NP values in the typical range of 10 to 20 kg $CaCO_3$ eq t^{-1} (inferring 1-2% $CaCO_3$; Lapakko 1993a, White et al. 1999) and as high as 33 kg $CaCO_3$ eq t^{-1} (Lapakko 1993d, 1994b) have been reported. Laboratory empirical NP values ranged from 0 to 2.0 kg $CaCO_3$ eq t^{-1} (Lapakko 1990a, 1993a, Lapakko and Antonson 1991, White et al. 1997), confirming that the Standard ABA NP values overestimated by (5 to 21 kg $CaCO_3$ eq t^{-1}) the capacity of this rock to neutralize acid while maintaining drainage pH $\geq$ 6.0.

Furthermore, even after the pH of effluent from the rock samples had decreased below pH 6, Standard ABA tests conducted on the leached solids indicated a residual NP, typically in the range of 8 to 14 kg t^{-1} $CaCO_3$ (White et al. 1999). Based on data from field test piles of Duluth Complex rock, the Empirical Neutralization Potential (ENP_6, the neutralization occurring prior to drainage pH decreasing below 6) observed in the field was determined to range from 0.04 to 1.3 kg $CaCO_3$ eq t^{-1} and, as was the case for laboratory values, tended to decrease as sulfur content increased (Lapakko 1994b).

Because there are limitations in the accuracy of ABA analyses for Duluth Complex waste, other analytical tools might be more appropriate for determination of the potentials for acid generation and acid neutralization. Some of these tools are identified and their applications are described in two publications (Lapakko 2001b, Lapakko 2003a).

2.4.   Kinetic Testing of Duluth Complex Rock

To assess the accuracy of kinetic test results they must be compared, perhaps after modeling, to long-term field results for the same mine waste. While laboratory drainage pH from Duluth Complex rock agreed fairly well with field data (Lapakko 1994a, see also section 3.3.2.4), data for such comparisons are rarely available. Consequently, it is rarely possible to assess kinetic test accuracy based on field verification, and the extent to which the laboratory tests model field behavior must be addressed conceptually. Results of Duluth Complex dissolution in laboratory kinetic tests and in the field are presented in the following section.

3.   DRAINAGE QUALITY FROM DULUTH COMPLEX MINE WASTES

3.1.   Introduction

In 1976, The Regional Copper-Nickel Study was formed in response to public concerns regarding the environmental impact of copper-nickel mining. The final summary report was completed in 1979 (Minnesota Environmental Quality Board 1979). The investigations conducted included operational scale field studies at the Dunka Mine (an active iron ore operation), pilot scale field studies at the AMAX exploration site, monitoring of a bulk sample site, as well as laboratory experiments.

The earliest reports on the Duluth Complex focused on the impact of potential copper-nickel mining (Thingvold et al. 1979), and addressed the hydrology (Hewett 1980) and chemistry of stockpiles. The early laboratory studies (Lapakko 1980; Eisenreich et al. 1977a, 1977b) investigated the kinetics and mechanisms of gabbro dissolution as well as trace metal equilibria. The findings of the early field monitoring, the laboratory experiments, and the chemical equilibrium computer models were compiled in a comprehensive report (Eger and Lapakko 1980c), and summarized in shorter papers presenting the chemical mechanisms of leaching (Lapakko and Eger 1980a, 1980b).

3.2.   Field Data

3.2.1.   Operational Scale South Kawishiwi Intrusion Waste Rock

Field water quality data were collected at an operational taconite mine where Duluth Complex rock had been stripped and stockpiled, at six test piles, and at dimension stone quarries. Operational scale Duluth Complex rock stockpiles are present at the Dunka Mine near Babbitt, a full-scale open pit taconite operation now closed. The Dunka open pit intersects the geological contact between the South Kawishiwi intrusion of Duluth Complex and the Biwabik Iron Formation, and removal of Duluth Complex rock was required to mine the underlying taconite. More than 50 million tons of the sulfide-mineral-bearing rock is stored at the site, in stockpiles that cover 320 acres.

Since 1976, data have been collected on the drainage quality, quantity, and chemical mass release associated with stockpile drainages at the site. The Regional Copper-Nickel Study began data collection (Thingvold et al. 1979), and after 1980 monitoring was conducted by Erie Mining Company and LTV Steel Mining Company. Cleveland Cliffs has conducted monitoring since 2001. The most recent report (MN DNR 1996, unpublished) presented the results of monitoring from 1976 to 1993, and earlier reports are available (MN DNR 1987, 1994; Eger et al. 1981a; Eger and Lapakko 1980a; Eger et al. 1977). Other studies at the Dunka site have focused on the transport of trace metals leached from the stockpiles through a white cedar swamp (Eger et al. 1980a, 1981a; Eger and Lapakko 1988, 1989), Unnamed Creek (Eger and Lapakko 1980b), a second small drainage at the site (Strudell 1986), and Bob Bay (Lapakko and Eger 1981b; Strudell et al. 1984; MN DNR unpublished data 1990). Information on the kinetics, mechanisms, and capacities of metal sequestration by peat has been compiled in the form of

literature reviews (Lapakko et al. 1986b; Otterson 1978) and laboratory experiments on metal removal by peat have been conducted (Lapakko et al. 1986a).

The most recent report indicates total flow from the watershed is about one billion gallons per year, of which drainage associated with stockpiles has contributed roughly 5 to 20 percent (MN DNR 1996, table 5). During the period from 1976 through 1993, the majority of leachate samples had pH values between 6.0 and 8.5, but values as low as 4.2 were reported (MN DNR 1996, Figure 4). Particularly notable was the Seep 1 pH decrease from roughly 7.3 to near 5 during the period 1976-1991. There also were a number of pH values below 6 at Seep 3 in 1989. Sulfate concentrations from these two seeps were also elevated above the typical range of 1000 to 3000 mg L^{-1} for the seeps.

Concentrations of trace metals (Cu, Ni, Co, Zn) exceeded ambient levels by 10 to 10,000 times. Nickel contributed more than 90 percent of the trace metal load from the stockpiles, and its subsequent removal by natural processes in the Unnamed Creek system was less than 40 percent. Chemical mass release of trace metals from the stockpiles reached a maximum in 1988, when nickel concentrations were as high as 80 mg L^{-1} at Seep 3. Nickel concentrations at Seep 3 were notably elevated in the periods 1976-78 and 1988-90, with medians typically in the range of 20 to 50 mg L^{-1}, and decreased to roughly 10 to 20 mg L^{-1} by 1993. Nickel concentrations at Seep 1 were also elevated relative to other seeps, with median values often in the range of 15 to 20 mg L^{-1}. When nickel concentrations were elevated, concentrations of copper, cobalt, and zinc were often elevated as well.

A summary of the monitoring requirements for the current Dunka NPDES permit are presented in Attachment 1. Monitoring requirements are likely to change upon reissuance of the permit in 2012.

3.2.2. Duluth Complex Quarry Sites in the South Kawishiwi Intrusion

In late 1991, rock and water quality samples were taken from two abandoned dimension stone quarry sites in the Ely-Isabella area of northeastern Minnesota. Rock samples were also collected from three potential quarry sites. The abandoned sites and two of the potential quarry sites are located in Duluth Complex rock. The third potential site is in the Vermilion Granitic Complex.

Total sulfur content of the rocks was less than 0.05 percent and trace metal levels were low. Consequently, the pH of water in the abandoned pits ranged from 6.5 to 6.8, and sulfate concentrations were low. Sulfate concentrations in the three of the four water samples collected were below detection (2 mg L^{-1}) and the fourth sample had a sulfate concentration of 3.2 mg L^{-1}. Copper (0.002-0.004 mg L^{-1}) and zinc (0.008-0.017 mg L^{-1}) concentrations were higher than background levels in the area, but were well within water quality standards (Lapakko and Oberhelman 1993). It should be noted that the fraction of fine particles associated with rock at these sites may have been considerably less than that at a metal mine. That is, the surface area per unit mass at the quarry sites was probably less than that for metal mine waste rock. Consequently, the quarry rock would tend to react less rapidly than a similar mass of waste rock from a metal mine.

3.2.3. Test Piles of Rock from the Babbitt Deposit, Partridge River Intrusion

3.2.3.1.   Introduction

Six small test piles containing 820 to 1300 metric tons of low-grade copper-nickel Duluth Complex rock, taken from an exploration shaft, were constructed next to the MINNAMAX test shaft near Babbitt, Minnesota. For runoff collection, a Hypalon liner was placed at the base of each pile. Both drainage flow and quality were determined. In 1982, approximately 40 percent of test pile FL4 was removed for use in another study of stockpile reclamation techniques. In 1994, the piles were dismantled and the rock was incorporated into one concrete/rock monolith as a final reclamation measure for site closure (Barr Engineering 1995).

Drainage quality, quantity, and effects of soil covers are addressed in a series of reports (Eger and Lapakko 1985; Eger et al. 1981b, 1980b, 1979; Lapakko 1993b) and symposium publications (Eger and Lapakko 1981; Lapakko 1994a). During dismantling of three of the piles (FL1, FL5, FL6), rock samples were collected for physical, chemical, and mineralogical characterization. The most recent report on this project focused on the characterization of leached rock samples (Lapakko et al. 2004b).

3.2.3.2.   Drainage Quality

Sulfur contents of the test piles were 0.6 (four piles), 0.8 and 1.4 percent, copper contents were 0.35, 0.34, and 0.31 percent, and nickel contents were 0.08, 0.09, and 0.09 percent. The copper contents of the rock were relatively high, perhaps more representative of ore than waste rock. Consequently, a fairly large fraction of the sulfur was associated with copper rather than iron, and this would tend to reduce the potential for acid production at a specific sulfur content. The sulfur contents associated with iron (including that in chalcopyrite, cubanite, pentlandite, etc.) in the 0.6, 0.8, and 1.4 percent sulfur piles were 0.35, 0.51, and 1.19 percent (corresponding to FeS contents of roughly 0.6, 0.9, and 2.1 percent), and the corresponding sulfur contents associated with pyrrhotite were 0.13, 0.28, and 0.98 percent.

The minimum annual median drainage pH values produced by rock 0.6, 0.8, and 1.4 percent sulfur piles were approximately 4.8, 4.0 and 3.4, respectively. Drainage pH from the 0.6% S piles was still decreasing at the end of the tests. During the last year of operation, typical concentration ranges for copper, nickel, cobalt and zinc in drainage from pile FL1 (0.6% S) were 20-30, 50-70, 2-3, and 1-2 mg L^{-1}. Drainage pH values during this period typically ranged from 5.0-5.2. Maximum nickel concentrations for the 0.6% S piles ranged from roughly 70 to 200 mg L^{-1}, and those for the 0.8 and 1.4% S piles were roughly 220 and 700 mg L^{-1}, respectively.

The following general conclusions on Duluth Complex rock drainage quality from 1978 through 1993 were drawn based on this small-scale field program.

1.   Trace metal concentrations in drainage from test piles containing low-grade sulfide mineralization exceeded concentrations in undisturbed streams of the area by as much as five orders of magnitude.

2.   Drainage pH decreased while trace metal concentrations and mass release rates increased with the iron sulfide content of the stockpile.

3.   For the 16-year period of record, a critical iron sulfide content appears to occur at roughly 0.6 weight percent FeS (0.6 % total S) in the bulk rock. Rock of similar mineralogy and particle size distribution containing more than this critical amount would generate acidic leachate.

4.   The early drainage quality was not an accurate indicator of longer-term drainage quality. For the test piles that contained 0.6% S (FL1, FL2, and FL3), acid producing conditions did not occur for 5 to 6 years. Even after the 16 years of this study, less than 12% of the total sulfur was released from the piles as sulfate. Predictions based on data from the first years of this study would have underestimated trace metal release rates and acid production.

3.2.3.3.   Geochemical Modeling

Lapakko et al. (2004b) provided a brief description of the mineral dissolution reactions influencing drainage quality. Acid release was the balance of acid producing and acid neutralizing reactions. Oxidation of pyrrhotite was the dominant source of acid production. Acid neutralization was dominated by dissolution of calcium-bearing minerals above roughly pH 5.0 and by dissolution of magnesium-bearing minerals below this value. The dominant calcium minerals were plagioclase and augite, and the dominant magnesium minerals were augite and olivine.

Copper release resulted from oxidation of chalcopyrite and cubanite, and pentlandite oxidation provided most of the nickel release. These metals were mobile in solution under most conditions observed in the drainages. The rates of trace metal sulfide oxidation, therefore, controlled trace metal release and were apparently accelerated under acidic conditions.

Geochemical modeling was used to predict the mineralogic and hydrologic controls on test pile FL1. Nine samples from test pile FL1 were subjected to a sequential extraction procedure that indicated that trace metals released during the oxidation of sulfides were adsorbed to amorphous ferric oxyhydroxides (Kelsey et al. 1996). Predictions, using the geochemical modeling programs NETPATH and MINTEQAK, generally agreed with the sequential extraction results, but predicted a lesser degree of nickel adsorption on amorphous ferric oxyhydroxides (Kelsey et al. 1996).

3.2.3.4.   Post-Mortem Solid-Phase Analyses

About 40 percent of one of the 0.6% S piles (FL4) was partially removed in 1982 and sample were collected (Eger and Lapakko 1985, Lapakko et al. 1986a). Particle size distribution analysis indicated that 19 percent of the mass was finer than 6.4 mm (0.25 inches). Seven fractions finer than 2 mm were analyzed. Paste pH and sulfur, sulfide, copper, nickel, cobalt, and

zinc concentrations were determined. As particle size decreased, paste pH decreased and concentrations of the aforementioned components typically increased by factors of two to five.

In 1994, the piles were dismantled, and bulk and spatially distributed samples were collected from FL1 (0.63% S), FL6 (0.8% S), and FL5 (1.4% S) (Lapakko et al. 2004a). Samples were analyzed for particle size distribution, chemistry (including acid content), and semi-quantitative mineralogy. The major objective of this characterization was to identify physical, chemical, mineralogical, and hydrologic controls on the transport of acid and trace metals from the piles. Visual inspection of the piles found elemental sulfur, elemental copper, and a blue green precipitate (possibly a trace metal solid phase), in addition to the expected iron oxyhydroxides and gypsum. Substantial cementation was also observed in the higher sulfur piles, with agglomerates varying in size (1cm to 1m) and cohesiveness.

Particles finer than 0.5 mm constituted roughly five to six of the rock pile mass but were responsible for an estimated 25 to more than 50 percent of the pyrrhotite oxidation. An estimated 70 percent of the rock finer than 0.5 mm contributed to pyrrhotite oxidation. Rock at the surface of the piles oxidized to a greater degree than that at depth. Oxidation at depth may have been limited by different conditions that may have been present in different areas. For example, sulfide mineral oxidation may have been limited due to water-saturated conditions or cementation that limited oxygen transport, lack of contact with water, or limited oxygen transport in specific areas. Cementation was observed during the dismantling of the rock piles.

3.3. Laboratory Dissolution Studies

3.3.1. Test Methods

3.3.1.1. MN DNR Reactors

Laboratory studies on the dissolution of Duluth Complex rock were initially conducted at the University of Minnesota in batch reactor and column tests (Lapakko 1980). Subsequently, the MN DNR developed an experimental method based on the principle that sulfide minerals oxidize in the presence of atmospheric oxygen and water (Gottschalk and Buehler 1912; Caruccio et al. 1980). Samples were quite fine, ranging from 0.053 to 0.149 mm in diameter (-100/+270 mesh). Experiments were conducted on 75-g samples in units designed to permit the rinsing of solids and filtration of the rinse solution in one step (U.S. Patent No. 4,783,318). The solids (and reactors) were stored in a controlled temperature and humidity environment, and rinsed weekly with 200-mL volumes of distilled deionized water. This method was used for initial testing at the MN DNR and several subsequent experiments.

3.3.1.2. ASTM 5744

In 1992 US Bureau of Mines (USBM) initiated assessment of a laboratory test for weathering mine wastes, and in 1996 the American Society of Testing and Materials (ASTM) designated this test as ASTM D 5744-96 (ASTM 1996). This method uses a 1000 g sample of waste rock finer than 0.25 inches and recommends a cell with an internal diameter of 10.2 cm and height of 20.3 cm. The weekly rinse volume is either 500 or 1000 mL and can be added by either of two

methods ("drip" or "flood"). The day after the sample is rinsed a three-day cycle begins during which dry air is passed through the cell. This cycle is followed by a three-day cycle during which humidified air flows through the cell. On the seventh day the cell is rinsed, and the drainage is collected for analysis. The cells are weighed to determine the water retained after the rinse, on the fourth day of the cycle (concurrent with the switch of ASTM cells from wet to dry air cycle), and before the rinse. The method is described in detail in ASTM (2000), and assessments of the method are provided by White and Lapakko (2000), Lapakko et al. 2002a, and Lapakko (2003b). In general, the intralaboratory and interlaboratory replication were good. The major variable affecting results appeared to be temperature, with elevated temperatures yielding lower pH values and higher rates of sulfate release. (Variations in temperature were reported for the commercial laboratory.)

A kinetic test method similar to ASTM Method D 5744-96, described by Lapakko and White (2000) was designated as the MN DNR method. The MN DNR protocol uses the same humidity-cell diameter, waste-rock charge, and rinse volume and application method as described in ASTM D 5744-96. The MN DNR cell was about three centimeters 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. Three 0.5-L rinses were used at week-0 rinse rather than the single 0.5-L volume described in the standard method. Furthermore, 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. Experiments were conducted to assess replication of test options and compare their results (Lapakko 1998b, 1999a; Lapakko and White 2000; White and Lapakko 2000; Lapakko and Antonson 2000a; Lapakko et al. 2002a). Because there was little difference between the two methods, the MN DNR approach was incorporated into the ASTM method as Option B in 2007. The most recent developments in the method are presented by Bucknam et al. (2009). Additional modifications are in progress as of December 2011.

3.3.2. Waste Rock

3.3.2.1.   South Kawishiwi Intrusion (SKI)

In February 1989 an experiment using the small MN DNR reactors was initiated that ultimately examined the longer-term drainage quality from 17 South Kawishiwi Intrusion (SKI) Duluth Complex samples of variable sulfur content. The samples were collected from blast holes at the Dunka site in the SKI of the Duluth Complex. Dissolution testing was initiated on 15 of the samples in 1989 and 1990, and on two additional samples in August 1997. (Four Virginia formation hornfels samples also were tested from February 1989 to August 1990.) The following discussion pertains to only the initial 15 Duluth Complex samples. Data from the early stage of the experiment were presented by Lapakko and Antonson (1993) and Lapakko (1993a).

Presently in progress is a report that analyzes as much as 866 weeks of drainage quality data. These data are used to update classifications of rock reactivity based on sulfur content. The drainage quality data are also used, in conjunction with solid-phase characterization (particle

size, bulk chemistry, mineral content, mineral chemistry, surficial features of leached solids) to estimate mineral dissolution rates.

The particle size of the rock samples tested in the small MN DNR reactors was in the range of 0.053 to 0.149 mm and the sulfur contents ranged from 0.18 to 3.12 percent. Detailed analyses were conducted on these samples to determine chemistry, mineral content, and mineral chemistry. 75-g samples were rinsed weekly with 200 mL of deionized water, and the drainage was regularly analyzed for pH, specific conductance, sulfate, calcium and magnesium. Concentrations of other solutes were determined on a less frequent basis. Between rinses the samples were stored in a room in which temperature and humidity were controlled. Analyses were also conducted on rock samples for which dissolution testing was terminated.

Rates of sulfate release tended to increase and drainage pH tended to decrease as solid-phase sulfur content increased. Two drainage pH values are of particular interest with regard to managing the associated mine wastes in an environmentally sound manner. The first is pH 6.0, a common regulatory requirement for drainages. The second critical pH value is that below which microbial catalysis of sulfide mineral oxidation accelerates the rate of sulfide mineral oxidation and, consequently, acid production and trace metal release. Provisionally a pH value of 4.0 will be used for this threshold. Drainage with pH values in the range of 4.0 to 6.0 will have trace metal concentrations exceeding regulatory standards. Since this type of drainage is not highly acidic, it may be possible to mitigate the acid release by passive treatment (e.g. limestone beds, sulfate reduction). Rock that generates, drainage pH values below 4.0 will also require mitigation of both acid and trace metal release. In contrast to the previous case, the levels of acidity and metals in this low-pH drainage may be excessively high for practical application of passive treatment. Thus, rock that generates drainage of this nature would require the most rigorous management.

Samples with sulfur contents of 0.18 and 0.22 percent consistently generated drainage pH values above 6 and, therefore met standards for pH. Trace metal concentrations in drainage from this rock might still exceed regulatory standards. Thus, mine waste management plans for this rock might require mitigation of trace metal release but not acid neutralization.

The remaining samples produced drainage pH values below 6.0. Drainage pH from samples of higher sulfur (S ≥ 0.40%) contents generally decreased for five to seven years, plateaued for one to two years, and then increased. Samples with sulfur contents of 0.40 to 0.58 percent produced minimum drainage pH values near 4.0. Samples with sulfur contents of 0.71 to 1.64 percent generated minimum pH values in the approximate range of 3.0 to 3.5. Dissolution testing of samples with sulfur contents of 2.06 and 3.12 percent was terminated after 78 weeks, and it is likely that these samples would have generated minimum drainage pH values of 3.0 or lower had testing continued. Mine waste management plans for waste rock generating drainage pH values below 6.0 must mitigate release of both acid and trace metals. The mitigation of the highest sulfur group would be most rigorous.

3.3.2.2. Partridge River Intrusion (PRI)

3.3.2.2.1. Babbitt Prospect

Several laboratory testing studies were conducted on Babbitt prospect rock from AMAX drill core, AMAX test piles, and a 1996 bulk sample. **AMAX drill core and a test pile** sample were subjected to dissolution experiments using the small MN DNR reactors described above. The experiment was the first laboratory dissolution testing of Duluth Complex rock at the MN DNR and was initiated in March 1985. The intent was to investigate the effect of solid phase sulfur content on the quality of drainage from 14 rock samples ($0.47 \leq \%S \leq 2.57$) from the Babbitt prospect of the PRI. Thirteen of the samples were from AMAX drill core and one sample was collected from AMAX test pile FL4. The samples were subjected to dissolution testing for periods of 30 to 49 weeks, and rinse intervals varied from one to five weeks (Lapakko 1993e, 1988a). It should be noted that the experiment was somewhat exploratory in nature, given the short duration and changing rinse intervals.

The use of sulfur content alone as the controlling variable for drainage pH assumes that acid neutralization by host rock mineral dissolution is relatively constant in Duluth Complex rocks of similar particle size. The solids examined were divided into three groups based on sulfur content, maximum rate of sulfate release, and minimum pH of the drainages (Lapakko 1993e). Group 1 samples contained 0.47 to 0.80 percent sulfur and produced maximum sulfate release rates of 5.8×10^{-6} to 16×10^{-6} mol week^{-1}. The sum of calcium and magnesium release rates exceeded the sulfate release rates (that is, the rates of acid neutralization exceeded the rates of acid production) and, consequently, the drainage pH of Group 1 solids remained higher than 6.0.

Group 2 (0.92 - 1.26% S) and Group 3 (1.35 - 2.57% S) solids had higher sulfur contents, exhibited higher sulfate release rates (20×10^{-6} to 190×10^{-6} mol week^{-1}), and produced minimum drainage pH values in the range of 3.77 to 4.50. For all solids examined, less than nine percent of the sulfur in the samples was oxidized (Lapakko 1993e), suggesting that extrapolating the data for long-term predictions was tenuous. The drainage pH values were higher than those generated by the SKI samples from the Dunka Mine (section 3.3.2.1). The higher pH values were partly the result of the short duration of these tests.

The composition of the Duluth Complex rock examined in the aforementioned experiment was subsequently characterized using more sophisticated methods (Pignolet-Brandom and Lapakko 1990). The QEM*SEM automated scanning electron microscope image analysis system was used to quantify the volumetric abundances of iron sulfides, copper-iron sulfides, nickel-iron sulfides, and calcite, as well as the general categories of silicate, oxide and phosphate minerals. The sulfur, nickel, and copper contents based on volumetric abundances were typically within 20 percent of the values determined by standard chemical analyses. QEM*SEM can quantify other parameters affecting mine waste dissolution, including mineral grain and rock particle size, particle surface mineralogy, extent of sulfide liberation, as well as total and liberated mineral surface area per unit volume.

Four PRI Babbitt prospect samples were subjected to dissolution testing along with SKI samples in the small MN DNR reactors beginning in August 1997 (see also section 3.3.2.1). One sample

was from a **bulk sample** collected in 1996 and three samples were from **AMAX exploration drill cuttings** generated in the mid-1970s. Respective sulfur contents of these samples were 0.67, 0.72, 0.92, and 1.71 percent. The 1.71% S drill core sample was terminated after 143 weeks, and testing of the remaining samples continues. The drill cutting tests resulted in markedly lower sulfate release and higher pH than samples of similar sulfur content from the SKI samples with which they were tested (see section 3.3.2.1) or subsequently tested PRI samples (see section 3.3.2.2.1.).

The **United States Bureau of Mines** Salt Lake City Research Center (USBM) initiated dissolution tests on larger Duluth Complex particles (d < 6.25 cm) using a different method (ASTM 5744-96 method) in July 1992. Tests were conducted on eight Duluth Complex samples that were collected randomly in 1992 from the surface of AMAX test piles FL1 and FL6 (Babbitt prospect of the Partridge River intrusion). Samples with sulfur contents ranging from 0.56 to 1.39 percent (White 1998), virtually all of which was present as sulfide, were run in duplicate and the duplicates were terminated after 60 weeks. The remaining eight samples were continued for 168 weeks. Drainage pH and rates of sulfate, calcium, and magnesium release from the eight pairs of samples during the initial 59 weeks replicated well (White and Lapakko 2000). Data from the first 125 weeks were used for comparison with those from two other laboratories (Lapakko and Antonson 2000a; Lapakko and White 2000; White and Lapakko 2000; Lapakko et al. 2002a), but data from week 125 through 168 have not been reported.

Minimum pH values ranged from approximately 4 to 5, and were in general agreement with values observed at MN DNR for Dunka blast hole samples of similar sulfur content. However, the USBM drainage pH values did not decrease strictly (nor did sulfate release rates increase strictly) with increasing sulfide content, and the lowest pH values were produced by a sample containing 0.97 percent sulfide. The rates of sulfate, calcium, and magnesium release from the USBM samples were typically 25 to 75 percent of those observed in MN DNR experiments on Dunka blast hole samples of similar sulfur contents. The difference in rates was most likely due to the particle size in the USBM experiments, which was large relative to the 0.053-0.149 mm diameter particles used in the MN DNR experiments. A similar effect of particle size on release rates was observed in an experiment conducted as part of an EPA project (see section 3.3.2.3). However, testing of particle size fractions of Duluth Complex rock indicated drainage pH decreased with decreasing particle size. In contrast, the drainage pH values from the USBM study were roughly equal to or, in the case of the 0.97 percent sulfide sample, lower than the associated MN DNR samples.

Beginning in 1996 the **MN DNR conducted additional testing on the 1.39% S** sample tested by the USBM using method ASTM 5744-96 and three modifications of this method (Lapakko 1998b, 1999a; Lapakko and White 2000; White and Lapakko 2000; Lapakko and Antonson 2000a; Lapakko et al. 2002a). (As discussed in section 3.3.1.2, the results were compared to those from the USBM and a commercial laboratory.)

After 265 weeks of testing using the MN DNR drip and flood alternatives to the ASTM method (Lapakko et al. 2002a), the minimum drainage pH values observed were in the range of 4.4 to 4.6. These values were considerably higher than the minimum annual median pH values observed for the 0.8 and 1.4 percent sulfur test piles (see section 3.2.3), which were 4.0 and 3.4,

respectively. That is, the drainage pH values from these laboratory tests did not reach the minimums observed in the field for rock of similar or lower sulfur content. The copper and nickel contents of the laboratory sample were 0.35 and 0.06 percent, respectively, and these values were similar to those for the field test piles. This suggests that the sulfur speciation for the laboratory and field samples was similar. Therefore, the differences in drainage pH values do not appear to be the result of differences in sulfide mineral contents.

The reason for the differences cannot be conclusively identified at present. Possible contributing factors are 1) differences in particle size distribution of laboratory and field rock (for example, a more influential fine size fraction in the field), 2) reduced sulfide mineral reactivity of the laboratory rock because it had been weathered in the field for 15 years, 3) influence of a wider range of sulfur contents for the rock in the field piles, 4) excessive neutralization in laboratory tests resulting from excessive water retention (see Lapakko and White 2000), or 5) development of microbial communities in the field that accelerated sulfide mineral oxidation. It should be noted that drainage pH values reported for another laboratory conducting testing on this sample were as low as 3.7. The low pH was attributed to higher temperatures in this laboratory during the summer months and, therefore, the closer agreement with field conditions might be somewhat fortuitous.

3.3.2.2.2. Babbitt and Dunka Road Prospects

In August 2003 tests were initiated on the dissolution of Duluth Complex rock samples from the **Babbitt and Dunka Road prospects** of the **Partridge River intrusion (PRI)**. Tests were conducted on 75-g samples of −100/+270 mesh (0.053 <d < 0.149 mm) rock and on 1000-g samples of rock finer than 0.25 inches (6.35 mm) in diameter. Seven fine samples were tested, consisting of six samples from the Babbitt prospect and one from the Dunka Road prospect. Sulfur and carbon dioxide content ranges were 0.07 to 0.94 percent and 0.07 to 0.21 percent, respectively. Ten larger samples were tested, seven from the Babbitt prospect and three from the Dunka Road prospect. Sulfur and carbon dioxide content ranges were 0.13 to 1.36 percent and 0.05 to 0.21 percent, respectively. These experiments remain in progress and the following comments assess data generated through week 126 (Lapakko and Antonson 2006).

For both experimental methods drainage pH tended to decrease and SO_4, Ni, Cu, Co, Zn, Ca, Mg, Na, K release rates tended to increase with increasing sulfur content. The -100/+270 mesh rock produced lower drainage pH and higher rates of sulfate and metal release per unit mass than the −0.25-inch rock.

Comparison of the Babbitt prospect and Dunka Road prospect rocks is tenuous because of the limited number of Dunka Road samples, thus the following comments must be viewed as tentative. The variations of drainage pH with solid-phase sulfur content for Babbitt prospect and Dunka Road samples were not substantially different, although sulfate release from the Babbitt prospect samples was greater than or equal to that from the Dunka Road samples. Babbitt prospect samples tended to have a lower ratio of calcium to magnesium release than the Dunka Road samples. Trace metal release from the Babbitt prospect rock tended to be higher than that from the Dunka Road rock. Additional solid-phase analyses will provide insight on the behavior of these samples.

The dissolution behavior of PRI rock (both Babbitt and Dunka Road prospects) was compared to that of the South Kawishiwi rock (samples from the Dunka Mine) using data from laboratory experiments on -100/+270 mesh samples. Data from seven PRI samples ($0.07 \leq$ percent sulfur $\leq$ 0.94) and nine South Kawishiwi intrusion samples ($0.18 \leq$ percent sulfur $\leq$ 1.16) were used. The PRI samples tended to generate slightly lower pH and higher sulfate release rates than the SKI samples. For a specified sulfur content, drainage pH from the PRI samples was generally 0.1-0.2 units lower than that from the SKI samples. Sulfate release from the PRI samples tended to be about 50 percent higher than that for the SKI samples of the same sulfur content.

Comparison of trace metal release from the Partridge River and South Kawishiwi intrusions is limited to data prior to week 72. Trace metal concentrations from the SKI samples were determined only sporadically after this time. Prior to week 72, nickel release from the PRI samples was roughly 70% higher than that from the Dunka Mine samples. Copper and cobalt release from the PRI samples was not obviously different from that from the Dunka mine samples. Zinc release from the PRI samples was roughly 70% of that from the Dunka Mine samples.

The detailed chemistry, mineral content, and mineral chemistry of the PRI samples have not been determined. These analyses may shed light on the reasons for the observed drainage quality differences relative to the Dunka Mine samples.

3.3.2.3. Effects of Rock Particle Size

To determine the effects of particle size on drainage quality, Duluth Complex rock was separated into six different size fractions and subjected to dissolution testing in December 1993 (Lapakko et al. 1995, 1998, 2004a, 2006). The sample was from AMAX test pile FL6 (0.8% S, Babbitt prospect of the Partridge River intrusion), and its mineral content indicated it was a norite (Lapakko et al. 2006). The particle size diameter ranges for the six size fractions were <0.053, 0.053-0.149, 0.149-0.5, 0.5-2.0, 2.0-6.35, and 6.35-19 mm. The drainage quality results through week 465, reported by Lapakko et al. (2004a, 2006), indicated that as particle size decreased, lag times to pH decreasing below 6.0, minimum drainage pH values, and the ratio of neutralizing mineral dissolution rates to acid producing mineral oxidation rates tended to decrease. These three drainage quality descriptors correlated well with the degree of sulfide mineral exposure. This indicates that particle size reduction increased the acid-producing mineral surface area to a greater extent than the acid-neutralizing mineral surface area.

All size fractions produced drainage pH values below 6.0, and the dissolution time prior to pH decreasing below 6.0 varied from 16 weeks for finer size fractions to 403 weeks for the largest size fraction. The three finest fractions produced minimum pH values ranging from 4.0 to 4.2 after roughly 200 weeks of dissolution, and pH followed a generally increasing trend after 200 to 400 weeks of dissolution. Examination of unpublished data through week 652 revealed ultimate drainage pH values of approximately 6, 6.3, and 5.2 for the <0.053, 0.053-0.149, 0.149-0.5 mm fractions, respectively. Drainage pH values from the three larger fractions tended to decrease slowly and then plateau after 300 to 600 weeks. The minimum values for the 0.5-2.0 mm and 2.0-6.35 mm fractions ranged from 4.8 to 4.9, and the largest fraction produced a minimum value

of 5.8. After 652 weeks the drainage pH values were approximately 4.8, 5.0, and 5.8 for the 0.5-2.0, 2.0-6.35, and 6.35-19 mm fractions, respectively. Average sulfate release rates ranged from 0.014 to 0.80 mmol $(kg \bullet wk)^{-1}$ for the first 465 weeks and increased as particle size decreased.

3.3.2.4. Comparison of Field and Laboratory Data

A similar trend in drainage pH with respect to time and sulfur content was observed in both the laboratory after 78 and 150 weeks, and field test piles experiments over 17 years (Lapakko 1994a). The ultimate drainage pH values for the 0.63% sulfur test piles were similar to values observed in the laboratory. However, minimum pH values for higher sulfur content test piles were about one unit lower than the corresponding laboratory values for these sulfur contents. The rates of sulfate, calcium, and magnesium release in the laboratory were 3 to 10 times higher than those for the test piles.

The lower field rates may be due to several factors. First, field rates of sulfide mineral oxidation may be slower due to differences in the sulfide mineral surface area available for reaction. Since the iron sulfide mineral oxidation produces the acid that drives silicate mineral dissolution, lower release of calcium and magnesium in the field would be expected due to the lower sulfate release. Second, cooler temperatures in the field, and possibly lower oxygen concentrations (although oxygen transport is not likely limiting in the small piles), would retard oxidation. Third, lower field release may be due to limited transport of reaction products resulting from factors related to the magnitude of water addition in the laboratory rinse phase. The amount of water added in laboratory tests is designed to enhance reaction product transport. In comparison, reaction product transport in the field might be limited owing to 1) limited water available to transport reaction products from the piles or 2) increased chemical precipitation in the field due to higher solute concentrations. (That is, solute concentrations in the laboratory tend to be lower due to the relatively large amount of water added during the rinse.)

The observation of field pH values lower than laboratory values at the higher sulfur contents was puzzling.   Considering the decrease of pH with decreasing particle size observed in the laboratory (Lapakko et al. 1995, 1998, 2006), drainage pH from the larger field particles would be expected to exceed that from the small laboratory particles. Continued laboratory testing shed light on this apparent contradiction, revealing that the pH of drainage from samples with sulfur contents exceeding 0.40 percent continued to decrease (see also the laboratory section on blast holes at the Dunka site). After 404 weeks of dissolution in the laboratory, the higher sulfur content samples generally approximated field pH values (MN DNR 1997, unpublished data). In contrast, the pH values for the lower sulfur content samples in the laboratory were typically a unit lower than those in the field. This is consistent with the particle size dependence of drainage pH observed in laboratory experiments.

However, given the laboratory-field agreement for drainage pH from the higher sulfur solids, it may also suggest that pH of drainage from the 0.63 percent sulfur field piles would have continued to decrease had the piles not been dismantled. A visually estimated relationship between pH and time was graphed for the low sulfur field piles, which suggested that drainage pH values asymptotically approach a minimum value in the range of 4.6 to 4.8. The 404-week

dissolution pH values observed in the laboratory are in better agreement with the estimated minimum drainage pH values for the low sulfur field piles.

Drainage pH values in the circumneutral range associated with the low-sulfur gabbro at dimension stone quarries (pH 6.5 to 6.8 for sulfur contents less than 0.05%; Lapakko and Oberhelman 1993) are also semiquantitatively consistent with the observed dependence of laboratory drainage pH on sulfur content. Correlation of field data from the Dunka site to laboratory data was tenuous due to uncertainties in field pile composition. The lowest pH at the site, 4.2, was associated with a stockpile reported to contain only 0.24 percent sulfur. Higher sulfur content rock at the site produced higher drainage pH values. It is assumed that the lack of correlation between sulfur content and drainage pH at the site is the result of inadequate data on stockpile composition and/or the presence of relatively small amounts of highly reactive mineralized Virginia formation hornfels in some piles. The presence of this rock could depress drainage pH even when present in small amounts.

3.3.3. Tailings

3.3.3.1. Field Tests

In November 1978, a tailings plot approximately 20 ft x 30 ft x 2 ft deep, denoted FL7, was constructed (Borovsky et al. 1983). A 30-mil Hypalon synthetic liner was placed at the base of the plot to provide an impermeable base for a drainage collection system. The tailings used in the plot were generated from Duluth Complex ore from the Minnamax site, which was processed by the Twin Cities Research Center of the U.S. Bureau of Mines. The tailings were placed on top of the liner, which was sloped to a six-inch PVC perforated pipe that collected leachate. The MN DNR monitored water quality from the plot from 1979 to 1981 (MN DNR 2004).

Based on analyses for a subsequent study, the total sulfur concentration in the tailings was 0.38%, and the copper, nickel, cobalt and zinc contents were 420, 350, 110, 180 parts per million. The pH of drainage from the tailings remained above 7 for the course of the study. Based on laboratory testing with Duluth Complex waste rock, acid drainage could occur at total sulfur contents of 0.2 to 0.4%. Some of these waste rock samples produced circumneutral drainage for 14 years then acidified. Consequently, the comparatively short three-year field study is inadequate to determine if the tailings would generate acidic drainage. Even though the tailings did not produce acid, low levels of trace metals, particularly nickel were released to solution. The maximum concentrations observed for copper, nickel, cobalt, and zinc in the drainage were 0.2, 0.4, 0.09, and 0.03 mg L^{-1}.

Drainage from this plot also contained elevated chloride and sulfate concentrations. Sulfate is generally produced from the oxidation of sulfide minerals present in the tailings, but the source of chloride is not known. Chloride concentrations in the Duluth complex are very low, and the chloride may have been added during the processing or there may have been some contamination of the tailings during the storage at the U S Bureau of Mines.

3.3.3.2. Laboratory Tests

A bulk sample of Duluth Complex rock was collected from the Babbitt prospect of the Partridge River intrusion in April 2001. The sulfide flotation used produced tailings with a 0.2% sulfur content. In February 2002, dissolution tests were begun on 75-g samples in uncovered and covered reactors (both in triplicate) and in duplicate 1000-g humidity cells (Lapakko et al. 2003, Lapakko and Berndt 2009).

Drainage pH from the small, uncovered reactors decreased from near 8 at week 0 to approximately 7 at week 100, and oscillated in the typical range of 6.8 to 7.1 to week 220. Sulfate concentrations decreased from a typical range of 10-20 mg L^{-1} during the first 20 weeks, to about 2 mg L^{-1} at week 100, and subsequently oscillated in the approximate range of 1 - 2 mg L^{-1}. Drainage pH from the small, covered reactors was slightly lower, decreasing from near 8 at week 0 to 6.5 at week 70, with subsequent values in the typical range of 6.5-6.8. Concentrations remained above 10 mg L^{-1} for roughly 60 weeks, and declined to a typical range of 2-4 mg L^{-1} after week 100. For cell 5, a subtle peak in sulfate concentrations occurred between weeks 40 and 66, concurrent with the decline in pH. Drainage pH values from the 1000-g humidity cells decreased slowly and steadily from near 8 initially to 7 at week 220. Sulfate concentrations decreased from 20-30 mg L^{-1} initially to 10 mg L^{-1} at week 100, and subsequently typically ranged from 8-10 mg L^{-1}. These results suggest that the potential for acid production in the first four years of dissolution is low.

If the tailings do not generate acid, trace metal release would potentially be the major environmental concern. For the small, uncovered reactors, nickel and zinc concentrations during the first three weeks typically ranged from 0.004 to 0.008 mg L^{-1} and decreased to a typical range of <0.002 (detection limit) to 0.004 mg L^{-1} subsequently. Copper and cobalt were at or near this same detection limit throughout the period of record. Trace metal concentrations in drainage from the covered reactors were considerably higher. Nickel concentrations were generally near the detection limit during the first 40 weeks and peaked roughly 50 to 80 weeks into the experiment, reaching values near 0.1 mg L^{-1}. The elevated nickel concentrations were concurrent with the decline of drainage pH below about 6.8. Concentrations subsequently decreased and generally ranged from 0.002-0.005 mg L^{-1} after week 150. During the period of maximum nickel concentrations, zinc concentrations peaked near 0.01 mg L^{-1} and cobalt concentrations reached 0.005-0.008 mg L^{-1}. Copper concentrations remained below or near the detection limit.

For the 1000-g humidity cells, nickel concentrations in the first rinse were near 0.05 mg L^{-1}, decreased immediately to near 0.01 mg L^{-1}, and were typically below or near the detection limit of 0.002 mg L^{-1} after week 50. However, concentrations from one of the duplicate cells (cell 7) were consistently reported as 0.03 mg L^{-1} after week 170. Copper concentrations in the intial two rinses were near 0.006 mg L^{-1} and decreased to values typically below detection (0.002 mg L^{-1}) within the first 10 weeks. Cobalt and zinc concentrations were almost always reported as less than detection (0.002 mg L^{-1}). The dependence of heavy metal release on test design, drainage pH, and water retention is discussed in more detail based on a roughly 200-week period of record by Lapakko and Berndt (2009).

Two tailings samples generated from bench scale tests on titanium ore from the Duluth Complex were also subjected to solid phase characterization and dissolution testing described above (Lapakko 1991a, 1993c). The test was very preliminary, and since the two tailings were generated from the same ore, the results do not represent the potential range of ore and tailings composition. The tailings were relatively coarse and contained very few sulfide or carbonate minerals. However, they did contain elevated concentrations of chromium, copper, and nickel. The neutralization potentials determined by static tests greatly overestimated the total calcium carbonate and magnesium carbonate content of these two samples.

These tailings generated drainage of neutral pH during the 52-week dissolution test, and presented virtually no potential for acid production since the sulfide content of both samples was reported as less than 0.01 percent. Copper, nickel, and zinc concentrations (to a lesser extent) were elevated in these tailings and in the initial drainage. Concentrations subsequently decreased, suggesting that only a small fraction of the metals present in the solid phase were readily leachable under the conditions of this experiment (Lapakko 1991a, 1993c).

3.4. Mineral Dissolution Literature Summaries

Extensive research has been conducted elsewhere that benefit interpretation of laboratory and field data on the dissolution of Duluth Complex rock. Thus, a series of annotated bibliographies focusing on rates of mineral dissolution was generated to identify and help summarize those studies most relevant to reactions taking place or expected to be taking place in Minnesota mine wastes. These include acid-producing reactions involving oxidative dissolution of pyrite (Leopold and Lapakko 2001a) and pyrrhotite (Leopold and Lapakko 2001b) and acid-neutralizing reactions involving carbonates (Doctor et al. 2001) and silicates (Phillips et al. 2001).

4. MITIGATION TECHNIQUES

4.1. Introduction

The degree of mitigation required for mining wastes depends directly upon the potential for problematic mine waste drainage quality at a site. Appropriate methods of mitigation can be designed and optimized based, in part, upon the predicted drainage quality. The MN DNR Division of Lands and Minerals has studied both passive and active mitigation techniques in the laboratory and on an operational scale. Results from these studies are presented below.

4.2. Literature Reviews.

Extensive literature exists on the subject of mitigation techniques. The MN DNR has compiled and summarized the current state of environmental mine waste technology, specifically as it relates to present and possible future ore deposits located in Minnesota. Fifteen environmental mine waste strategies were identified, which could be subdivided into three separate categories: those focused on prevention, control and treatment of problematic mine waste drainages (Jakel and Lapakko 1999; Leopold and Lapakko 2000, 2001c).

4.3. Operational Scale Mitigation

In the early 1980s, the U.S. Bureau of Mines funded a two-phase program examining the feasibility of removing trace metals (Cu, Ni, Co, Zn) from stockpile drainage using readily available materials (peat, till, wood chips, Cu-Ni tailings, zeolite) in low-cost, low maintenance systems. Following the initial literature review and laboratory experimental phase that used batch and column tests to evaluate metal sequestration by the materials, a field study phase was conducted at the AMAX/Kennecott site. The results of the entire program are presented in two reports (Lapakko et al. 1986a, 1986b), and synopses of various research segments are presented in several symposium proceedings (Eger et al. 1984; Lapakko and Eger 1988, 1983, 1981a; Lapakko et al. 1983).

Passive and active mitigation techniques have been applied to stockpiles and stockpile seepages at the Dunka Mine to prevent, control, and treat known and potential water quality problems (LTV Steel Mining Company 1996). Prevention methods include stockpile capping, diversion ditches, and moving rock off site (STS Consultants Ltd. 1993, 1994a, 1994b). Stockpile capping techniques were selected based on the stockpile drainage quality and chemical composition. Stockpiles with no known water quality problems and relatively low sulfur contents were capped using standard mineland reclamation (two feet of overburden). Stockpiles with known water quality problems or elevated sulfur contents were capped with either enhanced mineland reclamation (two feet of minus 6-inch uncompacted material with at least 10% in the -200-mesh fraction: stockpiles 8011, 8031, and 8012); enhanced mineland reclamation with linear low density polyethylene (LLDPE) membrane lined ditches (stockpiles 8013 and 8014); or covered with a LLDPE membrane liner (8018 and the hornfels pile on the 8014) (STS Consultants Ltd. 1994a).

Limestone was also added to the hornfels pile on the 8014 stockpile (LTV Steel Mining Company 1996). This pile was constructed of random hornfels rock identified on top of the 8014 and 8031 stockpiles (LTV Steel Mining Company 1996). The hornfels presence was the result of blast contamination "at the interface between the gabbro and/or waste rock" (LTV Steel Mining Company 1996). LTVSMC estimated that such contamination was on the order of "a few thousand tons on a 5 to 10 million ton stockpile."

Diversion ditches to reduce surface and ground water input to stockpiles were constructed on the west side of the 8014 draining to the pit; the west side of the 8013 draining to the pit; a bedrock cut in Unnamed Creek east of Seep 1 to lower the water table at the toe of the 8013 stockpile; from the Environmental Sump to the pit; on the south side to the 8011 draining into the Environmental Sump and subsequently into the pit; and to redefine the east 8011 drainage ditch.

A mass of 262,652 long tons of mineralized Virginia Formation hornfels rock was moved off site to LTV's tailings basin. The rock, which had a sulfur content of 3.2 percent, was mixed with 31,468 tons of dolomitic limestone (to neutralize acid) and buried in the tailings to inhibit oxygen transport to the rock and consequent oxidation of the sulfide minerals present. The limestone addition yielded a value of 1.2:1 for the ratio of NP added to acid production potential

present as sulfur. The tailings also contained ankerite for additional neutralization potential and iron oxyhydroxide minerals as potential trace metal adsorbing surfaces.

Treatment methods at Dunka include passive wetland treatment systems (Eger 1992; Eger et al. 1996, 1997, 1998) and an active treatment plant (STS Consultants Ltd. 1994b). Constructed wetland treatment systems include limestone/peat systems at seeps W2D/W3D (061) and Seep X (044), a limestone pretreatment followed by a limestone/peat system at W1D (051), and a limestone pretreatment followed by a peat system at Seep 1 (043). A limestone/peat system was constructed in 1998 for EM8 (041). The active treatment plant is a lime precipitation system designed to treat flow from EM8, Seep1, Seep X, and W1D treatment systems.

4.4. Blending Alkaline Solids with Mine Waste

4.4.1. Introduction

The addition of alkaline solids to acid-producing mine waste may provide 1) short-term mitigation by neutralizing acid produced by iron sulfide oxidation and 2) long-term mitigation by facilitating the passivation of iron sulfide mineral surfaces. Laboratory experiments blending Duluth Complex with rotary kiln fines and with limestone have been in progress since 1988. Field tests blending Archean greenstone with limestone were initiated on 24 October 2000.

4.4.2. Laboratory experiment with Duluth Complex rock

In a laboratory experiment which began in May 1988, rotary kiln fines (RK fines; a waste product generated by the conversion of limestone to lime), 10 mesh (d < 2 mm) limestone, and +10 mesh/ 0.25 inch (0.2 mm ≤ d < 6.35 mm) limestone were each mixed with finely-crushed Duluth Complex rock (0.053 < d 0.149 mm) to examine their effectiveness in reducing the release of acid and trace metals in drainage from the rock. The finely crushed Duluth Complex rock, simulating tailings or fine waste rock, contained 2.1 percent sulfur and the predominant iron sulfide mineral was pyrrhotite. The combined calcium and magnesium carbonate (96.7% and 2.1%, respectively) content of the limestone was 99.1 percent as $CaCO_3$. The calcium content of the RK fines indicated a combined calcium carbonate/oxide content of 63 percent and 96.7 percent of the mass was finer than 0.075 mm.

In addition to duplicate control reactors, five loadings (0.5, 1.0, 2.0, 3.0, and 5.0 g alkaline solid (g sulfur in rock)$^{-1}$) of each solid were mixed with 75 g Duluth Complex rock. Duplicate reactors were used for the 1.0 and 3.0 g loadings. This produced neutralization potential to acid production potential quotients (NP/AP) of 0.11 to 1.1 for the RK fines and 0.16 to 1.6 for the limestone. The mixtures were subjected to a "wet-dry cycle" laboratory test, which is yet in progress. The following section summarizes the results of the experiment for the first 585 weeks. Additional detail on this study is available in three status reports (Lapakko and Antonson 1989a, 1990a; Lapakko et al. 1998a) and three papers (Lapakko and Antonson 1991; Lapakko et al. 1997, 2000).

The pH of drainage from the rock alone decreased below 6.0, a common minimum water quality standard, after 8 weeks and reached a minimum of 3.3 in 117 weeks, at which time the controls

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were terminated. Maximum copper and nickel concentrations ranged from 1 to 2 ppm. The sulfate release did not decrease over time. The minus 0.25-inch/+10 mesh limestone treatment produced drainage similar to that of the controls and was discontinued after 40 weeks. In contrast, the RK fines and -10 mesh limestone maintained drainage pH above 6.0 for 75 to 585 (still in progress) weeks. While pH was in this range, sulfate concentrations decreased and trace metal concentrations were typically three to ten percent of those observed in drainage from the controls.

The RK fines elevated pH and inhibited sulfate release for time periods that increased with the mass of RK fines present. The pH of drainage from the 0.11 quotient (NP/AP) loading decreased below pH 6.0 after 75 weeks of dissolution and reached a minimum of 3.6 after 117 weeks, at which time the reactor was terminated. Drainage from the duplicate 0.22 quotient loadings of RK fines decreased below 6.0 after 95 and 170 weeks. The former was terminated after 117 weeks, and the latter (still in progress) reached a minimum pH of 2.8 after 512 weeks. Drainage pH from the 0.66 quotient decreased below 6.0 after 581 weeks. For the drainages that acidified, the cumulative calcium release indicated that 92 to 103 percent of the calcium carbonate/oxide initially present in the RK fines was dissolved at the time pH decreased below 6.0. Concentrations of nickel, cobalt, and zinc reached maximums after pH declined below 6.0, and copper concentrations tended to increase steadily as pH decreased. The pH of drainage from the 1.1 quotient, which remains operative, typically remained above 8.0 throughout the 585 week period of record.

Sulfate concentrations in the drainage generally declined until pH decreased below 6, and the highest values were observed after drainage acidification. With the 0.65 and 1.1 quotient loadings, drainage pH values were typically near 9.0, although after week 340 the pH of drainage from the 0.65 loadings began to oscillate occasionally into the sevens. Such oscillations preceded acidification of drainages from the 0.22 quotient loadings. Sulfate concentrations in the drainage from the 0.65 quotient loadings have decreased throughout the period of record. For each mixture, regression analysis for the equation $[SO_4] = ae^{bt}$ was used to describe the decrease of sulfate concentrations (mg L^{-1}) with time (t, weeks) over the period during which pH remained above 6. The variables "a" and "b" are constants, and the values of b for the six cases ranged from -0.016 to -0.0031 (Lapakko et al. 1998a).

The - 10 mesh limestone additions elevated drainage pH and net alkalinity while inhibiting sulfate release. The pH of drainage from the 0.16 quotient (NP/AP) loading was initially neutral, decreased below 6.0 after 109 weeks, reached a minimum of 5.0 at week 116, and subsequently increased to a typical range of 5.3 to 6.3 through week 709. This is in contrast to the pH from the lower loadings of RK fines, for which pH continued to decline after falling below 6.0. The lack of more extreme acidification was due to a decrease in the rate of sulfide oxidation by more than 80 percent. It is of interest to note that the sulfide oxidation rate did not increase after pH decreased below 6.0. Drainage pH from the higher limestone loadings remained above 6.0 and sulfate concentrations decreased with time.

As with the RK fines, regression analysis was used to describe the decrease of sulfate concentrations with time (see above), and the constant "b" for the seven cases ranged from - 0.011 to -0.0066. The correlations for the fine limestone were considerably higher than those

for the RK fines. All loadings reduced the sulfide mineral oxidation rates, and the loadings of 1:1 and greater reduced them to levels at which host rock silicate mineral dissolution was adequate to neutralize the resultant acid production. Furthermore, the amount of silicate minerals present was large enough that their dissolution would neutralize the acid produced if the pyrrhotite present continued to oxidize slowly. The decline in sulfide oxidation may have been due to creation of a leached layer at the pyrrhotite surface, pyrrhotite coating by products of precipitation reactions enhanced by the presence of the limestone, or cementation of pyrrhotite grains due to reactions within the bed. Fresh and leached solids were examined using scanning electron microscopy (SEM). These examinations identified varying degrees of oxidation features on leached sulfide mineral grains but did not provide a clear indication of the mechanism producing the superior mitigation by the limestone (Nicholas et al. 2006, 2007).

This mitigative technique has excellent potential for neutralizing acid produced over a period of several years as an interim measure and promising potential for long term mitigation. However, certain precautions must be taken with the conclusions. First, the results are specific to the Duluth Complex mineralogy. For example, if sulfide minerals were coated by precipitates the coating composition, as well as mechanisms and rates of coating, may be specific to this rock formation. In addition, the dissolution of host rock minerals of other rock types is likely to provide different rates and capacities of acid neutralization than those of the Duluth Complex.

Second, these results were determined under laboratory conditions. The extent of limestone/mine waste mixing in the field is likely to be less complete than in the laboratory, and this extent is likely to influence the effectiveness of acid neutralization and sulfide mineral coating. In particular, it is difficult to obtain intimate contact when mixing relatively fine limestone with large waste rock particles. Environmental variables such as large fluctuations in temperature may also produce results deviant from those observed in the closely controlled laboratory environment. Of particular importance is determination of the longevity of the acid production inhibition.

4.4.3. Field Experiment with Archean Greenstone Rock

In October 2000 a field experiment was initiated to examine the effect of mixing limestone with Archean greenstone rock that was expected to produce acidic drainage (Lapakko et al. 2001, 2003). The tests are being conducted in six polyethylene plastic tanks (d = 48 in., h = 42 in.), consisting of two control tanks (tanks 1 and 6), two tanks with limestone mixed at a 1:1 ratio (tanks 2 and 5), and two tanks with limestone mixed at a 3:1 ratio (tanks 3 and 4). The 1:1 ratio represented a limestone loading that would neutralize all acid produced by oxidation of the iron sulfides present in the rock, assuming complete reaction of both limestone and iron sulfides. The 3:1 ratio represented a safety factor of three for the limestone addition. The tanks were fitted with 2-inch slotted PVC outlet pipe on the bottom, which drains into a 22-gallon polyethylene plastic sample collection sump. The tanks were filled on 24 October 2000 and input to the tanks is limited to precipitation. The tanks are housed in a 20' x 20' lined bin that serves as a double containment.

The 0.67% sulfur rock used in test pile 4 of the Archean greenstone prediction study was selected for use in the alkaline mixing experiment. The rock was screened to pass a 1.5-inch

screen at Casper Construction Inc. in Grand Rapids, MN. A bobcat loader was used to fill the tanks with the exception of tank 5 which could not be reached with the loader and was filled using five gallon buckets.

For the tanks that had the rock mixed with limestone, the loader scooped a bucket of rock and then the limestone (1/3 of the total addition), which had been weighed, was added to the bucket. A sample of rock was taken from each loader bucket, prior to adding the limestone for the alkaline mixing tanks, for a total of three samples per tank. A total of 55 pounds of limestone was added to the 1:1 ratio tanks and 165 pounds to the 3:1 ratio tanks.

The drainage pH from all tanks was initially slightly alkaline, ranging from the upper sevens to middle eights. Drainage pH from the controls decreased below 6.0 in September 2004. As of September 2011 pH values are in the low fours and acidity is in the range of 40 to 50 mg L^{-1}. Drainage pH values from the tanks with limestone added have been consistently above 7.3. The 1:1 limestone addition tanks presently have pH values in the middle to upper sevens and alkalinity ranging from 35 to 50 mg L^{-1} as $CaCO_3$. The 3:1 limestone addition tanks presently have pH values near eight and alkalinities in the range of 40 to 70 mg L^{-1} as $CaCO_3$. These tests remain in progress with the objective of determining the effectiveness of the limestone addition over time.

4.5. Drainage Treatment with Limestone Beds

4.5.1. Laboratory tests

Column laboratory experiments to examine the ability of limestone beds to neutralize acidic stockpile drainage began in April 1988. Triplicate columns containing 780 grams of minus 0.25-inch/+10-mesh high calcium limestone were used to treat each of three different drainages. Flow rates were adjusted to maintain an effluent in which the alkalinity exceeded the acidity. Although the columns were successful in treating all three drainages, problems with plugging typically led to termination of columns. These problems occurred at different times and, consequently, periods of record for the columns varied. The termination dates for individual columns ranged from September 1990 to December 1998. Excluding periods when columns were nonfunctional, the periods of operation ranged from 856 to 3682 days.

For Seep 1, input flow was maintained at an average of 4.9 bv d^{-1} (bed volumes per day) for most of the experiment, with total flow volumes ranging from 4200 to 5700 bed volumes. The mean input values for pH and net alkalinity were 5.6 and -22 mg L^{-1} as $CaCO_3$. Limestone dissolution elevated these values to 7.5 and 20 mg L^{-1} as $CaCO_3$ in the column effluent.

For FL3, input flows averaged 0.15 bv d^{-1}, with total flow volumes ranging from 160 to 610 bv. The mean pH and net alkalinity were 4.9 and -210 mg L^{-1} as $CaCO_3$. Dissolution of limestone elevated drainage pH and net alkalinity to approximate respective values of 7.9 and 75 mg L^{-1} as $CaCO_3$ in the column effluent.

For FL6, input flows averaged 0.51 bv d^{-1}, with total flow volumes of 550 to 990 bv. The mean input pH and net alkalinity were 4.1 and 580 mg L^{-1} as $CaCO_3$. Dissolution of limestone

elevated these values to respective means of 7.6 and 120 mg L^{-1} as $CaCO_3$ in the column effluent.

Copper concentrations were reduced by 85 to 98%. Nickel, cobalt and zinc concentrations were reduced to a lesser extent (Ni: 11-24%, Co: 7-22%, Zn: 35-65%). These results indicate that limestone beds are capable of neutralizing these stockpile drainages and substantially reducing copper concentrations if adequate detention time is allowed. Problems with maintaining flow, due to cementation of the bed, were encountered. Use of larger particles would reduce potential for such problems in the field but decrease the reactivity per mass limestone. Additional detail is available in the final report (Lapakko et al. 2002b), status reports (Lapakko and Antonson 1989b, 1990b), and a shorter technical publication (Lapakko and Antonson 1990d).

4.5.2. Field test

A field scale limestone treatment bed (1.4 m^3 bed volume) began treating the Seep 1 drainage at the Dunka site on 26 September 1988 (Lapakko and Antonson 1989c, 1990c; Lapakko et al. 1998). The objectives of this project were to:

1) elevate the pH and alkalinity while reducing the acidity and trace metal concentrations in the Seep 1 drainage;

2) describe the variation of treatment efficiency in terms of pH elevation and trace metal removal with the volume of drainage treated; and,

3) describe the variation of treatment efficiency as a function of detention time, or equivalently, flow rate.

The bed contained 2020 kg of high-calcium limestone (minus 6.4 mm), and was 1.3 m in diameter and 1 m deep. It received Seep 1 flow from 26 September to 28 October 1988, from 26 April until 31 October 1989, and from May 5 to July 3. Operation was terminated in 1988 and 1989 when freezing conditions were impending. The bed clogged persistently throughout the study and, consequently, the limestone was replaced with a coarser-sized limestone (6.4 to 38.1 mm) July 12, 1990 (Lapakko et al. 1998).

The total flow volumes through the fine particle-size limestone bed during 1988, 1989, and 1990 were 580, 6600, and 3600 m^3, respectively, yielding an average flow of 13, 25, and 45 bed volumes per day, respectively. The bed was 100% efficient in neutralizing acid in the seepage, raising the pH from approximately 5.1 to 7.0, and the net alkalinity from approximately -46 mg $CaCO_3$ L^{-1} to 28 mg $CaCO_3$ L^{-1}. Copper removal by the bed increased each year, reaching 68% in 1990. Zinc removal also increased from about 12% in 1988 and 1989 to 42% in 1990. Nickel and cobalt concentrations were reduced by approximately 10% throughout the study. The flow volume treated or the range of detention times observed in this study did not influence treatment efficiencies for acid neutralization and trace metal removal.

The average rates of acid neutralization by the fine particle-size limestone bed were 14, 32, and 72 mg $CaCO_3$ s^{-1} in 1988, 1989, and 1990 respectively, implying that 0.84 T of limestone was dissolved during the operation of this bed. The release rate was independent of the volume of

treatment, indicating that the treatment capacity of the bed was not taxed. The release rate did increase with flow, indicating that for the range of flows observed, the initial reaction of the Seep 1 drainage with the limestone was relatively rapid. Although the bed provided acceptable elevation of pH and net alkalinity, as well as some reduction in trace metal concentrations, the observed flow impedance was a problem that had to be addressed.

Larger-sized limestone particles were tested from July 12 to August 6, 1990, and although no overflow occurred, treatment efficiency decreased below acceptable levels. Total flow through this bed during the 24-day period of operation was 790 m^3, or 23 bv day^{-1}. However, the bed was only 25% efficient in neutralizing acidity in the seepage. The mean effluent pH only reached 4.9, and the effluent net alkalinity averaged -64 mg $CaCO_3$ L^{-1}. Furthermore, no more than 10% of copper, zinc, nickel, or cobalt was removed from the drainage. The mean rate of acid neutralization was a nominal 10 mg s^{-1}, indicating that only 0.02 T of limestone was dissolved.

The flow rates were too high to allow an adequate detention time for the larger limestone particles to effectively treat Seep 1 drainage quality. The rate of calcite dissolution is proportional to surface area. Since the surface area of the fine particles was approximately seven times that of the coarse particles, their dissolution rate would be approximately seven times faster than those of the coarse particles. It would therefore be expected that a limestone bed using the larger particles would require a detention time seven times that of the fine particles for adequate acid neutralization to occur. To achieve this detention time, a minimum bed volume of 3024 L would be required. However, only 25% of the Seep 1 drainage acidity was neutralized by the large particles in the limestone bed. This indicates that the bed volume should be increased by at least a factor of four to achieve adequate neutralization for the flow rates encountered.. Additional investigation will be necessary to determine the actual bed volume required to neutralize Seep 1 drainage.

4.6. Subaqueous Disposal

4.6.1. Introduction

Five laboratory experiments and one field experiment were conducted to examine the effectiveness of subaqueous disposal and subaqueous disposal with various barrier layers for controlling the oxidation of sulfide minerals present in mine wastes. 1) Unmodified subaqueous disposal tests were initially conducted in 2-liter Erlenmeyer flasks. 2) Subsequent tests were conducted in 2-inch-diameter columns to describe the release of sulfate as a function of sulfidic mine waste depth for two different mine waste particle sizes. 3) In a second phase of the Erlenmeyer flask experiment, composted yard waste was added to some of these flasks to determine if organic amendments would further inhibit sulfide oxidation. 4) Composted yard waste and fresh rock, as well as controls for compost and rock, were subjected to subaqueous dissolution in the laboratory. 5) A column experiment was conducted to determine the effectiveness of taconite tailings, yard waste compost/tailings mixtures, and limestone layers above tailings as potential oxygen diffusion barriers above sulfidic mine waste. 6) Barriers of tailings, a yard waste compost/tailings mixture, and limestone are presently under examination in small-scale field tests.

4.6.2. Unmodified subaqueous disposal

4.6.2.1. Laboratory flask experiments

The first 120 weeks of the flask experiment begun in September 1990 were summarized by Lapakko (1994c). The experimental objective was to determine the effect of three different subaqueous disposal techniques on the oxidation of sulfide minerals present in Virginia Formation hornfels rock containing about 5.5 percent sulfur and about 14 wt% pyrrhotite ($Fe_{0.9}S$). The subaqueous techniques were unmodified subaqueous disposal, subaqueous disposal with alkaline addition, and pretreatment (rinsing and neutralization) of rock prior to subaqueous disposal and subsequent alkaline addition. The pH of drainage from the two unsaturated controls, representing on-land disposal, ranged from 3.7 to 4.2 during the initial 100 weeks, then decreased rapidly to 3.2 at 120 weeks. During the first 100 weeks the sulfate release rates averaged roughly 2.0×10^{-12} mol (g rock)$^{-1}$ s^{-1}; concurrent with the pH decrease, rates for controls increased to 5.6×10^{-12} and 13×10^{-12} mol (g rock)$^{-1}$ s^{-1}. For unmodified subaqueous disposal, pH declined steadily from 4.5 initially to 3.5 after 120 weeks. Pyrrhotite oxidation rates for the three subaqueous disposal techniques were 1.5×10^{-12}, 1.7×10^{-12}, and 2.2×10^{-12} mol (g rock)$^{-1}$ s^{-1}, respectively. With the exception of some initial rapid sulfate release from rock that was not pretreated, these rates were relatively constant over the course of the experiment. The rates observed in the laboratory were used, along with oxygen transport theory, to determine acid production rates for disposal of similar mine waste in a flooded open pit.

4.6.2.2. Laboratory column experiments

Assuming oxygen transport was limited by diffusion through a quiescent layer of water, it was estimated that the depth of solids in the flasks (see previous section) was near that at which oxygen transport became limiting. Due to the uncertainty of values for variables necessary for this calculation, an experiment was initiated in March 1997 to 1) determine the depths of fine (0.053 < d   0.149 mm, 1.22 percent S) and coarse (0.635 < d   1.905 mm, 0.6 to 1.0 percent S) sulfidic Duluth Complex rock at which oxygen transport limited the rate of sulfide mineral oxidation and 2) better estimate values for oxygen transport variables for the materials used. Bed depths of 1 to 20 cm were used for the fine particles, and two standard Wet-Dry Cycle reactors were added after the columns were underway. Coarse particle bed depths of 5 to 150 cm were used. A 25-cm depth of water was maintained above the submerged beds, and unsaturated columns were run at three depths of fine and coarse particles for comparison with oxidation rates under saturated conditions.

The depth of solids at which oxygen transport limited the rate of sulfide mineral oxidation in the fine and coarse tailings was on the order of 20 and 100 cm, respectively. The respective maximum sulfate release rates observed were 2.5×10^{-8} and 1.5×10^{-8} mole m^{-2}s (m^2 represents the horizontal cross sectional area of the bed). These values are about an order of magnitude higher than those preliminarily predicted based on oxygen diffusion alone, perhaps due to advective oxygen transport due to thermal currents.

Although higher than indicated by preliminary theoretical calculations, sulfate release from the subaqueous bed was lower than that from the unsaturated beds. Sulfate release from the deeper fine unsaturated columns was apparently limited by formation of a saturated layer at the top of the bed and, consequently, duplicate 75-g masses were subjected to unsaturated oxidation in standard MN DNR wet-dry cycle reactors to obtain data for an unsaturated condition. Weekly sulfate release from these reactors (3.0×10^{-8} mole $m^{-2}s^{-1}$ = 0.50×10^{-6} mole (g rock•wk)$^{-1}$) exceeded the observed range of 1.2×10^{-8} to 2.5×10^{-8} mole $m^{-2}s^{-1}$ from all masses of saturated tailings (38 to 555 g). The sulfate release rates (per unit cross-sectional area) for the unsaturated coarse particle bed depths of 5, 50, and 150 cm were 1.5 to 3 times those for the corresponding saturated beds.

The sulfate release from the unsaturated fine and coarse rock was in good agreement with rates previously reported for unsaturated Duluth Complex rock. Release per unit mass unsaturated fine rock (0.50×10^{-6} mol (g rock•wk)$^{-1}$) was in good agreement with average values previously reported by Lapakko (1993a) for similarly sized samples with sulfur contents of 1.12 and 1.16 percent (0.59×10^{-6} and 0.31×10^{-6} mol (g rock•wk)$^{-1}$, respectively). Sulfate release from the unsaturated beds averaged 0.017×10^{-6} mole (g rock•wk)$^{-1}$, which agreed well with the 0.02×10^{-6} mole (g rock•wk)$^{-1}$ rate observed for the 0.25-0.75 inch fraction of 0.9-percent-sulfur gabbro (Lapakko et al. 1995).

The two experiments discussed above revealed that separating sulfidic mine waste from the atmosphere with a layer of water would reduce the rate of oxidation of sulfide minerals present. However, oxidation would continue and possibly produce acidic waters. Consequently, various modifications to subaqueous disposal are presently being examined.

4.6.3. Subaqueous Disposal with Modifications

4.6.3.1. Organic Amendment Flask and Beaker Experiments

The potential benefit of adding an oxygen consuming layer between sulfidic rock and the overlying water in the flasks experiment is under examination (MN DNR Hibbing laboratory, unpublished data). After 238 weeks the addition of alkalinity to the flasks was terminated (see above), and 75 grams of yard waste compost was added to one of each pair of duplicate reactors. The quality of water was monitored for an additional year, at which time the pH of water in the three reactors receiving no compost was in the range of 3.4 to 4.3. For reactors receiving compost, the pH remained near seven or, in the case of the initial unmodified subaqueous treatment, increased to this level shortly after the addition. After 26 weeks of reaction, the pH in one of the compost amendment reactors (initial treatment 3) decreased below pH 6.0. At the end of the period of record, the pH in the two remaining organic amendment reactors was in the upper sixes to the lower sevens. Rates of sulfide oxidation were calculated for the different disposal techniques based on the rate of sulfate appearance in solution. The aqueous concentrations of phosphorous, ammonia-ammonium nitrogen, total Kjeldahl nitrogen, nitrate, and nitrite from the organic substrate were also determined. These results have not been formally analyzed and compiled.

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The solids in the previous experiments had been weathering in a subaqueous environment for roughly 4.5 years prior to the addition of compost. A second experiment was begun using six 4-liter beakers: two composted yard waste controls (75 g/3.6 L), two unleached mineralized Virginia Formation hornfels controls (4.47% S, 200 g/3.6 L), and two with the compost (75 g/3.6 L) and hornfels rock (200 g/3.6 L). The composted yard waste controls were run for 20 weeks and pH was in the typical range of 7.5 to 7.8. The rock controls initially had pH values in the upper fours, and then gradually decreased to near 3 at week 91. The pH for the combined rock and compost was initially in the mid-sevens, dropped below 6.0 at week 113, and decreased to the mid-fives at week 125. In contrast, the solids subjected to the initial subaqueous oxidation (in the aforementioned flask tests) maintained pH above 6 for 179 weeks. It is possible that during the 224-238 weeks of subaqueous oxidation in the previous test, a) some of the more reactive sulfides were removed or b) the sulfide mineral surface had become less reactive. Such a reduction in reactivity could be the result of formation of a leached layer on the pyrrhotite. The difference in effectiveness may also have been due to differences in the initial compositions of the rock and/or compost in the two experiments. Additional analysis and formal reporting of these results is in progress.

4.6.3.2. Subaqueous Disposal plus Barrier Layers Column Experiment

A second laboratory experiment, conducted in columns, was initiated in March 1997 to examine the effect of placing various barriers above sulfidic wastes (-4/+14 mesh rock) disposed in a subaqueous setting. The intent of these barriers is to further inhibit oxygen transport to the mine waste and, therefore, decrease the rate of sulfide mineral oxidation. The barriers under examination are tailings (1, 2, 3, 5, 10 cm depths), tailings/yard waste compost mixtures (0.1 percent compost with tailings at depths of 1, 3, 10 cm; 0.5 and 1.0 percent compost with tailings at 3 cm depth), and a layer of limestone above tailings (1 cm limestone over tailings depths of 0, 1, 3, 10 cm). Controls were included for unamended -4/+14 mesh rock and unscreened -3/4-inch rock in a subaqueous setting, and -4/+14 mesh rock in an unsaturated condition. Initial calculations indicated that sulfate release rates from the thicker covers were 15 to 50 percent of those from the subaqueous controls. Rates also tended to decrease as the amount of compost added increased. Rates from some of the thinner covers were similar to those for the subaqueous control, likely due to visible physical flaws in these covers. The initial results suggest that these modifications warrant additional examination. Additional analysis and formal reporting of these results is in progress.

4.6.3.3. Field Tests on Subaqueous Disposal plus Barrier Layers

A field test examining the effectiveness of limestone, tailings, and a tailings compost mixture above sulfidic rock in a subaqueous environment began in December 1997 at the MN DNR Research Site in Hibbing. The subaqueous tests are being conducted in large cylindrical tanks (d = 46 in., h = 120 in.), fitted with a 30 mil PVC liner. Inside the PVC liner was a filter fabric liner that extended to a height of 48 inches. Wells (i.d. = 1 in.) were installed to sample at distances of 3 and 39 inches from the bottom of the tanks.

The tanks were filled to a depth of 48 inches with -3/4-inch Duluth Complex rock, originally collected from a 1996 bulk sample and subsequently crushed at the NRRI Coleraine Research

Center. The sulfur contents of composites from each of the four tanks averaged 0.66% (0.63 to 0.69%). These values compare favorably with values determined for the same rock in the column experiments (0.63%), a composite sample taken from the barrels in which the samples were shipped (0.71%), and two grab samples taken by the NRRI from a larger pile of this material at Coleraine (0.76%).

The rock was placed into the tanks 5 November 1996, and water from the Hibbing Taconite Scranton Mine pit was added to the tanks from above (to a level one foot from the top of the tank) on 10 December 1996. The bottom port and surface water were sampled eight times and the middle port six times prior to the addition of barrier layer amendments. In August 1997, water was drained from the tanks and well water was added from below to the surface of the rock. Water addition to the control tank was continued to a level one foot from the top of the tank.

To the remaining three tanks, the amendments were added prior to filling the tanks to this level. 53 liters (14 gallons) of each amendment were added, representing an amendment depth of approximately 4.4 cm (1.75 inches). The mass additions of limestone, tailings, and tailings plus compost were 87 kg, 81 kg, and 81 kg, respectively (191, 179, 179 lbs). The limestone and tailings were added on 26 August and the tailings/compost mixture on 27 August. The tailings/compost mixture contained 0.406 kg dry compost, or five percent of the mixture. Over time, water quality samples will be collected from the two well depths and the surface water to determine the rate of sulfate release and, by implication, the rate of sulfide mineral oxidation in the various settings. The first samples were collected on 28 August 1997 (week 0).

Two unsaturated tanks (d = 48 in., h = 42 in.) were also established to generate comparative water quality data for an on-land disposal scenario. These tanks were fitted with 1-inch slotted PVC outlet pipe on the bottom and were filled to a height of 38 inches with the same Duluth Complex rock. Subsequently a bulk density of 106.5 lb ft^{-3} (also 37% porosity, 2.7 specific gravity) was determined, indicating the rock mass was approximately 1930 kg. On 28 August 1997, 65 gallons of tap water was added to each tank to check for plumbing leaks and to attain field capacity. A grab sample (week 0) was collected on the same day from the initial drainage. Subsequent input to the tank will be limited to precipitation.

Through week 222, pH of water in the four subaqueous treatments ranged from 7.0 to 8.9, and values did not vary markedly among the four tanks. Values for all subaqueous tanks tended to be higher in the surface water. In contrast, pH values for the unsaturated controls at week 222 ranged from 4.2 to 4.5. Additional analysis and formal reporting of these results is in progress.

5.   Acknowledgements

6. References

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APPENDIX 1

MINE WASTE DISSOLUTION CHEMISTRY

1.   Acid Production

1.1.   Iron Sulfide Mineral Oxidation.

When metal sulfide minerals are exposed to the oxidizing conditions present in waste rock stockpiles, mine walls, and tailings basins, sulfide is oxidized and the associated metals (Fe, Cu, Ni, Co, Zn) are released (Nelson 1978; Garrels and Christ 1965; Sato 1960a, 1960b). Acid is produced as a result of the oxidation of iron sulfide minerals present in mine waste, as indicated by reaction 1 (Nelson 1978) and reaction 2 (Stumm and Morgan 1981). Two moles of acid are produced for each mole of sulfur oxidized.

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

$$FeS_2(s) + (5/2)H_2O + (15/4)O_2(g) = FeOOH(s) + 4H^+(aq) + 2SO_4^{2-}(aq) \qquad (2)$$
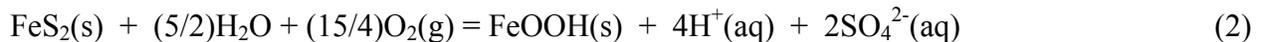
The rate of iron sulfide oxidation by oxygen is proportional to the available sulfide surface area (Nelson 1978; Sato and Mooney 1960; Sato 1960a, 1960b), and dissolved oxygen concentration (Nelson 1978; Dobrokhotov and Maiorova 1962; McKay and Halpern 1958), with only a slight dependence on pH (Nelson 1978; Majima and Peters 1966). These oxidation reactions can elevate aqueous concentrations of iron, sulfate, and acid. These components can 1) accelerate the oxidation of other sulfide minerals, 2) precipitate hydrated iron-sulfates or other minerals, 3) contact host rock minerals which react to neutralize some or all of the acid, and/or 4) exit the mine waste as acidic flow, referred to as acid mine drainage (AMD) or acid rock drainage (ARD).

Ferric iron oxidizes iron sulfides more rapidly than oxygen (Singer and Stumm 1970). Research on pyrite oxidation indicates that as "pH decreases to 4.5, ferric iron becomes more soluble and begins to act as an oxidizing agent" (Nordstrom 1982). As pH further decreases, bacterial oxidation of ferrous iron becomes the rate-limiting step in the oxidation of pyrite by ferric iron (Singer and Stumm 1970), which is the only significant oxidizing agent in this pH range (Nordstrom 1982; Singer and Stumm 1970; Kleinmann et al. 1981). Under these conditions the reaction is independent of sulfide-mineral surface area (Singer and Stumm 1970).

1.2.   Sulfate Mineral Dissolution.

Hydrated iron sulfate minerals may precipitate due to evaporation of acidic, iron- and sulfate-rich water within mine wastes. This essentially stores acid generated by iron sulfide mineral oxidation for potential subsequent release. The more common of these minerals that occur as efflorescent salts on the surfaces of weathering pyrite include melanterite, rozenite, szomolnokite, romerite, and copiapite ($FeSO_4 \cdot 7H_2O$, $FeSO_4 \cdot 4H_2O$, $FeSO_4 \cdot H_2O$, $Fe^{2+}Fe^{3+}_2(SO_4)_4 \cdot 14H_2O$, and $Fe^{2+}Fe^{3+}_4(SO_4)_6(OH)_2 \cdot 20H_2O$ respectively; Alpers et al. 1994). These salts are highly soluble and provide an instantaneous source of acidity upon dissolution

(Nordstrom 1982, Cravotta 1994).   For example, dissolution of one mole of melanterite contributes two moles of acid (reaction 3). Similarly, Cravotta (1994) reported that dissolution of one mole of romerite produces six moles of acid. Reactions such as this may be largely responsible for increased acidity loadings during rainstorm events.

The formation of hydrated iron sulfates is an important intermediate step that precedes the precipitation of slightly soluble iron minerals such as jarosite (Nordstrom 1982). Jarosite is slightly soluble (Alpers et al. 1994) and yields 1.5 moles of H^+ per mole dissolved (reaction 4). In studies conducted at the U.S. Bureau of Mines, Salt Lake City Research Center (USBM SLRC), the pH of deionized water dropped from 6 to 3 or 4 after contact with synthetic and natural jarosites (White et al. 1997a). Because of jarosite's relatively low solubility, the acid contributed by its dissolution is small relative to that by dissolution of more soluble hydrated iron sulfates, although hydronium jarosite can contribute acid at a more rapid rate (Lapakko and Berndt 2003). It should be noted that sulfate minerals such as anhydrite ($CaSO_4$, reaction 5) or barite ($BaSO_4$) will not produce acid.

$$FeSO_4 \cdot 7H_2O + (1/4)O_2(g) = FeOOH(s) + 2H^+(aq) + SO_4^{2-}(aq) + (11/2)H_2O \qquad (3)$$

$$KFe_3(SO_4)_2(OH)_6(s) = 3FeOOH(s) + 3H^+(aq) + 2SO_4^{2-}(aq) + K^+(aq) \qquad (4)$$

$$CaSO_4(s) = Ca^{2+}(aq) + SO_4^{2-}(aq) \qquad (5)$$
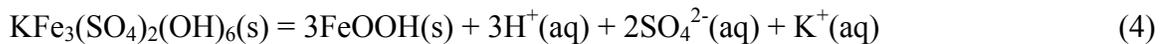
2.   Acid Neutralization

2.1.   Calcium and Magnesium Carbonate Mineral Dissolution

The most effective minerals for neutralizing acid are calcium carbonate and magnesium carbonate (reactions 6-9). Reactions 6 and 8 are dominant above approximately pH 6.3, while reactions 7 and 9 are dominant below this pH.

$$CaCO_3(s) + H^+(aq) = Ca^{2+}(aq) + HCO_3^-(aq) \qquad (6)$$

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

$$MgCO_3(s) + H^+(aq) = Mg^{2+}(aq) + HCO_3^-(aq) \qquad (8)$$

$$MgCO_3(s) + 2H^+(aq) = Mg^{2+}(aq) + H_2CO_3(aq) \qquad (9)$$
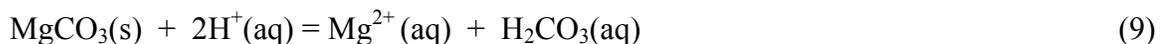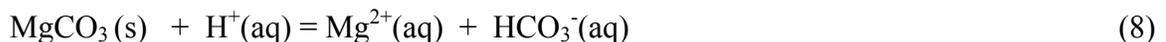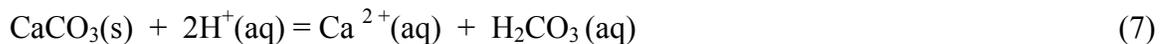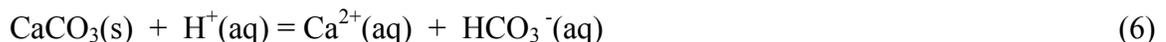
Iron carbonates will provide no net neutralization of acid. The initial dissolution of one mole of iron carbonate will consume one or two moles of acid (reactions 10, 11). However, under environmental conditions the one mole of ferrous iron released will oxidize to ferric iron (reaction 12), which will precipitate as ferric oxyhydroxide (reaction 13). The oxidation of ferrous iron is slower than the subsequent ferric oxyhydroxide precipitation, and is reported to be second-order with respect to hydroxide ion concentration (Sung and Morgan 1980; Eary and

Schramke 1990). The oxidation and precipitation reactions will yield two moles of acid (reaction 14). Thus, iron carbonate will not contribute to acid neutralization.

$$FeCO_3(s) + H^+(aq) = Fe^{2+}(aq) + HCO_3^-(aq) \qquad (10)$$

$$FeCO_3(s) + 2H^+(aq) = Fe^{2+}(aq) + H_2CO_3(aq) \qquad (11)$$

$$Fe^{2+}(aq) + (1/4)O_2(g) + H^+(aq) = Fe^{3+}(aq) + (1/2)H_2O \qquad (12)$$

$$Fe^{3+}(aq) + 2H_2O = FeOOH(s) + 3H^+(aq) \qquad (13)$$

$$Fe^{2+}(aq) + (1/4)O_2(g) + (3/2)H_2O = FeOOH(s) + 2H^+(aq) \qquad (14)$$
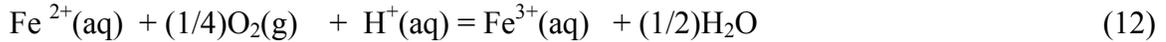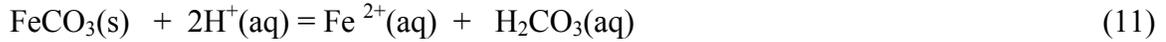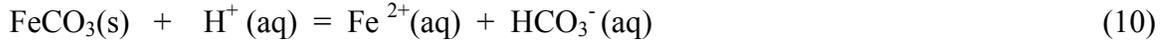
2.2.   Silicate Mineral Dissolution

Other minerals, such as anorthite and forsterite, can also consume acid but their dissolution rate (and associated rate of acid neutralization) is typically slow in the neutral pH range (reactions 15, Holdren and Berner 1979; and reaction 16, Hem 1970). These minerals dissolve more rapidly as pH decreases, and therefore, provide more buffering under acidic conditions.

$$CaAl_2Si_2O_8(s) + 2H^+(aq) + H_2O = Ca^{2+}(aq) + Al_2Si_2O_5(OH)_4(s) \qquad (15)$$

$$Mg_2SiO_4(s) + 4H^+(aq) = 2Mg^{2+}(aq) + H_4SiO_4(aq) \qquad (16)$$
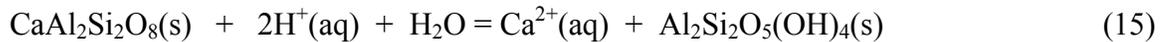
3.   Trace Metal Sulfide Oxidation

The oxidation of trace metal sulfide minerals releases trace metals and sulfate but does not necessarily contribute acid (reaction 17). Reactions subsequent to sulfide mineral oxidation affect

$$CuS(s) + 2O_2(g) = Cu^{2+}(aq) + SO_4^{2-}(aq) \qquad (17)$$
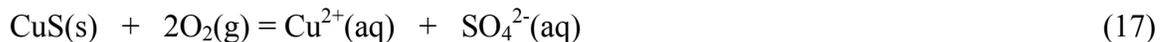
the net trace metal release to the environment. The transport of a given component in the environment is the net result of release to solution by dissolution and removal from solution by precipitation, coprecipitation, exchange reactions, and adsorption. The degree of trace metal transport is dependent upon drainage composition (particularly pH), the chemistry of the released component, and the chemical character and surface area of solid surfaces present. Concentrations of trace metals tend to increase exponentially as solution pH decreases, therefore acidic drainages often contain elevated trace metal concentrations. However, circumneutral drainages can contain elevated concentrations of trace metals such as nickel (Eger and Lapakko 1985) and molybdenum (Brown 1989) that, compared to other trace metals, are relatively soluble in this pH range.

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Attachment 1. Dunka NPDES permit monitoring requirements.

Seeps WS001, WS003, WS004, WS005 monitored twice monthly, prior to treatment, for:

       Total Co
       Total Cu
       Total Ni
       Total Zn
       pH
       Total Hg (twice annually and at WS001 only)
       Flow

Discharges SD005, SD006, SD007, SD008, SD009 monitored twice monthly (or monthly as noted), <u>after</u> treatment, for:

       Total Cu
       Total Ni
       Total Zn
       Hardness
       pH
       Toxicity (Additive Acute Toxicity for Cu, Ni and Zn)
       Total Hg (twice annually and at SD005, SD007, SD009 only)
       Sulfate (monthly)
       TSS (monthly)
       Dissolved Fe (monthly)
       Flow

Key to Outfalls/Seeps

       WS001, SD007 = Seep EM-8
       WS003, SD008 = Seep 1
       WS004, SD009 = Seep X
       WS005, SD005 = Seep W-1d
       SD006 = Seep W-2/3d