MIXING OF ALKALINE SOLIDS WITH FINELY-CRUSHED ACID-PRODUCING ROCK

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April 1998

Minnesota Department of Natural Resources Division of Minerals 500 Lafayette Road St. Paul, MN 55155-4045

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10.

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0. EXECUTIVE SUMMARY

Rotary kiln fines (RK fines; a waste product generated by the conversion of limestone to lime), -10 mesh limestone, and +10 mesh/-0.25 inch 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. With regard to operational application, the focus was to determine the ability of the additions to 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. 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 calcium content of the RK fines indicated a combined calcium carbonate/oxide content of 63 percent, while the combined calcium and magnesium carbonate (96.7% and 2.1%, respectively) content of the limestone was 99.1 percent as CaCO₃.

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) of each solid were mixed with 75 g Duluth Complex rock. (Duplicate reactors were also used for the 1.0 and 3.0 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 for 397 weeks. Over a 117-week period **the rock alone** produced drainage pH as low as 3.3 and maximum copper and nickel concentrations in the range of 1 to 2 ppm. The sulfate release did not decrease over time. In contrast, the alkaline mixtures (except the large limestone) maintained drainage pH above 6.0, a common minimum water quality standard, for 75 to 397 (still in progress) weeks. While pH was maintained 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 which 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. 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 3.5 after 397 weeks. The cumulative calcium release to the drainages which acidified 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. 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 3:1 loadings began to oscillate occasionally into the sevens. Such oscillations preceded acidification of drainages from the 1:1 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) with time (weeks) over the period during which pH remained above 6. The values of b for the 6 cases ranged from -0.016 to -0.0031.

The -10 mesh limestone additions elevated drainage pH and net alkalinity and inhibited 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 5.5 to 6.3 through week 397. The lack of more extreme acidification was due to an 84 percent decrease in the rate of sulfide oxidation, possibly due to coating of iron sulfide grains by products of precipitation reactions enhanced by the presence of the limestone. Dissolution of silicate minerals such as plagioclase and olivine was adequately rapid to neutralize most of the acid produced at the resultant low rate of iron sulfide oxidation. 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 for the fine limestone were considerably higher than those for the RK fines. Earlier work on **larger limestone** (-1/4-inch/+10 mesh) indicated that it was only minimally effective in neutralizing acid and reducing trace metal concentrations.

Keywords: acid rock drainage, mine waste, tailings, Duluth Complex, sulfide minerals, pyrrhotite, oxidation, dissolution, drainage chemistry, mitigation, limestone, calcium carbonate

1. INTRODUCTION

The major water quality concern for mining operations is the generation of acidic drainage from mine wastes such as tailings, waste rock, and the mine itself. In order to meet water quality standards, mitigation measures for acid-producing mine wastes may be required during operation, after the cessation of operation and before closure measures are applied, and/or during the long-term post-closure period. The present study describes laboratory experiments on finely-crushed sulfidic rock, simulating tailings or a fine waste rock fraction.

With waste rock, the blending and layering of acid-neutralizing solids are reported to be of minimal mitigative success, due to problems such as inadequate homogeneity of mixtures and preferential flow through acid-generating layers (Mehling et al. 1997). The large particle sizes of waste rock (the dimensions of which can reach several feet) and the acid-neutralizing solids most likely contribute to these problems. With finer mine wastes and alkaline solids a homogeneous mixture can be more readily attained, and, due to more uniform particle sizing, flow tends to be more uniform. Blending of alkaline solids with tailings is further attractive due to 1) the fine and relatively homogeneous composition of tailings and 2) the potential to achieve more intimate blends by moderate modification of standard tailings handling procedures. Furthermore, it may be necessary to treat only those tailings above the water table, since the rate of sulfide mineral oxidation below this level will be limited by oxygen diffusion through water.

For tailings, the operational phase is least problematic since drainage acidification tends to be limited by 1) the subaqueous environment in which the majority of tailings are disposed and 2) the typical addition of alkaline processing reagents to tailings impoundments. Furthermore, any problematic drainage that is generated can be collected and returned to the impoundment. However, after operations cease and before final closure measures are implemented, mitigation measures may be required, particularly in areas in which sulfidic tailings are not submerged. The addition of limestone to tailings as the tailings are generated may be an effective, low-cost method of neutralizing acid produced during this period. It is also possible that such addition would accelerate the formation of precipitate coatings on the iron sulfide minerals responsible for acid production and, thereby, render these minerals much less reactive.

1.1 Mine Waste Dissolution Chemistry

Acid is produced as the result of the oxidation of iron sulfide minerals (reactions 1, 2) and can be neutralized by the dissolution of calcium and magnesium carbonate minerals (reactions 3, 4). Trace metal sulfide oxidation will produce acid if and only if the trace metal released precipitates as an oxide, hydroxide, or carbonate. Drainage from a mine waste will become acidic if the rate of acid production exceeds the rate of acid neutralization.

$$FeS_{2}(s) + (5/2)H_{2}O + (15/4)O_{2}(g) = FeOOH(s) + 4H^{+}(aq) + 2SO_{4}^{2-}(aq)$$
[1]

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

$$CaCO_3(s) + 2H^+(aq) = H_2CO_3(aq) + Ca^{2+}(aq)$$
 [3]

$$CaCO_{3}(s) + H^{+}(aq) = HCO_{3}(aq) + Ca^{2+}(aq)$$
 [4]

The oxidation of iron sulfides by oxygen is only slightly dependent on pH. For the mixture of sulfides present in Duluth Complex rock the sulfide-oxidation rate was reported as proportional to $[H^+]^{0.2}$ over the pH range of 5 to 8 (Lapakko 1980). Nicholson and Scharer (1994) observed little variation in the abiotic pyrrhotite oxidation rate over the pH range of 2 to 6, reporting "maximum differences in oxidation rates were about a factor of 2 or within 50% of the mean rate at a specified temperature." Nelson (1978) reported that the rate for mackinwite by oxygen at pH 6.5 was five times that at pH 9.0.

Under low pH conditions, bacteria can accelerate the ferric iron oxidation of iron sulfide minerals, yielding a reaction rate considerably higher than that for the oxidation by oxygen alone (McKibben and Barnes 1986, Moses et al. 1987, Nicholson et al. 1988). Research on pyrite oxidation indicates that as "pH decreases to 4.5, ferric iron becomes more soluble and begins to act as an oxidizing agent" (Nordstrom 1982). As pH decreases further, bacterial oxidation of ferrous iron becomes the rate limiting step in the oxidation of pyrite by ferric iron (Singer and Stumm 1970), which is the only significant oxidant in this pH range (Nordstrom 1982, Singer and Stumm 1970, Kleinmann et al. 1981). Arkesteyn (1980) reported that bacterial acceleration was initiated as pH decreased below 4.0. Under these low-pH conditions the reaction is independent of sulfide-mineral surface area (Stumm and Morgan 1981).

The rate of iron sulfide oxidation may decrease over time due to formation of either a leached layer or a precipitate coating. Pratt et al. (1994) reported three compositional zones at the surface of pyrrhotite which had been air-oxidized for 50 hours. The outer zone, less than 10 Ångstroms thick, was enriched in oxygen and deficient in sulfur. Beneath this layer was a compositional continuum from FeO_{1.5} (surface), to FeS₂, Fe₂S₃, and Fe₇S₈ (unaltered pyrrhotite). The formation of zones was attributed to the migration of electrons and iron from the interior to the surface, where adsorbed molecular oxygen was reduced to O²⁻. The reduction was hypothesized to be the result of electron transfer from the interior, and iron diffusion from the the interior was conjectured to be enhanced by "vacancies" in the nonstoichiometric pyrrhotite.

Nicholson et al. (1990) reported a layer of ferric oxide, on the order of 0.6 microns thick, on the surface of pyrite which had been air-oxidized for about 10,000 hours (60 weeks) in a carbonatebuffered system. The rates observed were fit to a shrinking core model. The surface layer was postulated to form as lepidocrocite, which dehydrated to maghemitite during preparation for SEM analysis. Molar volume decreases during these transformations from pyrite were reported as 12% and 26%, respectively. The authors conjectured that, based on the observed reaction rates, the surface layer did not crack during sulfide oxidation. Results were compared to previous reports on pyrite coatings by Burkin (1969) and Goldhaber (1983). Additional information on oxidation and surface coatings has also been presented for pyrrhotite (Janzen 1996; Buckley and Woods 1984; Ingraham et al. 1972) and pyrite (Yanful et al. 1997; Borek 1994; Batarseh 1989; Frost et al. 1977).

1.2 Alkaline Solids Addition

The elevated pH associated with calcium or magnesium carbonate mineral dissolution has three notable secondary environmentally relevant effects. First, the elevated pH yields an environment unfavorable for *Thiobacillus ferrooxidans*, a strain of bacteria which accelerates sulfide mineral oxidation. The inhibition of these bacteria limits the rate of sulfide oxidation and, therefore, the rate of acid production. Second, the elevated pH enhances the oxidation of ferrous iron and the subsequent precipitation of ferric oxyhydroxides. If the pH is elevated in the immediate neighborhood of iron sulfide mineral surfaces, precipitates will form on the mineral surface. This would impede chemical transport to and from the iron sulfide mineral surface and, consequently, inhibit iron sulfide oxidation and the attendant acid production. Third, as pH increases, aqueous trace metal concentrations decrease due to increased trace metal precipitation (as oxides, hydroxides, and/or carbonates) and adsorption.

An important factor in the balance between acid production and acid neutralization is the relative masses of the iron sulfide and carbonate minerals. This balance may be particularly important since an increase in the rate of pyrite oxidation has been reported at low applications of alkaline solids (Burt and Caruccio, 1986). The limestone requirement can be estimated based on theory or on empirical evidence. The theoretical alkalinity requirement can be calculated by assuming each mole of sulfur produces two moles of acid (reactions 1, 2) and each mole of calcium carbonate neutralizes two moles of acid (reactions 3). If no other solids neutralize acid, the limestone mass required would be 3.12 times that of sulfur (one mole of CaCO₃/mole of S = [40.1 + 12.0 + (3x16)]g/32.1g = 3.12). The limestone requirement would be doubled to 6.24 times the sulfur content if each mole of calcium carbonate neutralized only one mole of acid (reaction 4).

The theoretical estimate of the limestone requirement can be refined by accounting for the acid neutralizing capacity of the host rock and the fact that some sulfur is bound in minerals which do not produce acid. For example, a laboratory experiment (MNDNR unpublished data for the Duluth Complex Blast Hole Experiment) has demonstrated that dissolution of silicate minerals present in Duluth Complex rock, and the resultant acid neutralization, can maintain drainage pH above 6.0 providing sulfur content does not exceed 0.4 percent (Lapakko and Antonson 1994). (It should be noted, however, that one of the reactors in this experiment contained 0.41% S yet produced drainage with pH values as low as 4.1.)

Calculation of the acid-producing sulfur content should be based on sulfur associated with iron sulfide minerals. This concept can be applied by assuming that:

- 1. the silicate minerals present in Duluth Complex rock can neutralize the acid produced by a sulfur content of 0.4 percent,
- 2. 93 percent of the sulfur is associated with acid producing minerals (assuming all trace metals in this sample are present as sulfides; see Section 3.1 for trace metal contents),
- 3. each mole of iron sulfide present produces two moles of acid,
- 4. each mole of calcium carbonate neutralizes two moles of acid, and
- 5. drainage pH must be maintained above 6.0.

Using this approach, the estimate of the theoretical limestone required can be refined as follows:

$$L = 3.12[0.93(P - 0.4)] = 2.9P - 1.16$$
[5]

where: L = limestone requirement (percent of rock mass) and P = the sulfur content of the Duluth Complex rock (percent of rock mass).

For a sulfur content of 2.1 percent the limestone requirement would be:

$$L = 3.12[0.93(2.1 - 0.4)] = 6.1 - 2.61 = 4.93\%.$$
 [6]

This limestone addition represents a limestone to sulfur ratio of 2.3, roughly 25 percent lower than the minimum value obtained by the first theoretical estimation of 3.12.

Laboratory data have been generated on drainage quality from sulfidic mine wastes in the presence of naturally-occurring calcite and calcite added in the form of limestone. Such experiments have been conducted on fine materials, including tailings, and larger materials simulating waste rock. Earlier experiments on the dissolution of finely-crushed Duluth Complex solids indicated that a calcium carbonate/sulfur ratio of 2.6 produced neutral drainage over a period of 33 weeks of wet/dry cycle leaching (Lapakko 1988).

However, over a longer period the calcium carbonate (which was naturally present, a rare occurrence for Duluth Complex rock) may have been depleted or rendered ineffective by precipitate coating. If this occurred, and iron sulfide minerals remained and oxidized, the drainage would have become acidic. Such depletion and acidification was reported after a period of 122 weeks for pyritic tailings (5 percent sulfide) containing 1.4 percent calcite (Lapakko and Wessels 1995). Day (1994) concluded that limestone (d < 0.6 mm) mixed with acid producing rock (2.1% sulfur) should provide neutralization potential (NP) at least twice the acid-producing potential (AP) of the rock in order to ensure neutral drainage. (It should be noted that MEND (1994) indicates that 60 percent of the limestone was finer than 0.6 mm, and that 81.9 percent of the rock was finer than 3.35 mm.) Day (1994) further noted that iron precipitate coatings did not reduce the availability of the limestone during the 5-year column study.

In column experiments lasting a total of 24 weeks, O'Hagan (1986) found that a 5 percent CaCO₃ addition was required to neutralize drainage from shale with 1 percent sulfur and 0.7 percent pyritic sulfur. The 2.0 to 5.6 mm limestone and shale particles were well blended. Rose and Daub (1994) conducted a 15-week column experiment, and concluded that the 2 to 5 mm limestone particles mixed with 7.0%-sulfur pyritic shale (d < 1 cm; NP/AP = 1) were ineffective because they did not impart adequate alkalinity to the pore water. This ineffectiveness was hypothesized as being due to their large size and observed coating by iron precipitates.

Analysis of field data from coal mining areas, in conjunction with consideration of aqueous carbonate equilibria, suggests that one mole of calcium or magnesium carbonate will neutralize one mole of acid (reaction 4; diPretorio and Rauch 1988; Cravotta III et al. 1990; Brady et al. 1990). diPretorio and Rauch (1988) found that neutral drainage was consistently produced by coal seams containing "greater

than 40 tons $CaCO_3$ equivalent of total NP per thousand tons of overburden." This value was subsequently modified to 30 tons/1000 tons "with fizz" by Brady and Hornberger (1990). The "with fizz" provision was added to ensure than the NP was present as calcium and magnesium carbonates as opposed to iron carbonates.

Donovan and Ziemkiewicz (1994) added limestone layers to 400-ton piles of sandstone and shale coal overburden roughly one to eight inches in diameter, to produce limestone contents of 0.46, 1.07, and 1.26% (0.56 < NP/AP < 2.38). The authors concluded that these and other layered alkaline additions did not consistently affect drainage quality during the year after construction "due to their inhomogeneous distribution, to heterogeneity in NP or MPA [Maximum Potential Acidity] within the piles, to hydroxide armoring of the amendment layers, or to time lag in reaching the outflow." The site was resampled 11 years later and drainage from the two higher limestone additions was "circumneutral" (Ziemkiewicz and Meek 1994).

Evans and Rose (1995) added lime kiln flue dust (an alkaline waste product) to 360 tons pyritic shale (1.9% S) in amounts providing neutralization potential 0 to 1.71 times the acid production potential. All conditions produced acidic drainage throughout the 10-month field test, although drainage pH increased from 1.9 to 2.6 as the flue dust loading increased. Incomplete mixing of the flue dust and shale, as well as preferential flow were cited as limitations to the effectiveness of the treatment.

Stewart et al. (1994) reported on column studies on mixtures of fly ash, limestone, or rock phosphate with acid-producing coal refuse. The loadings of mitigative solid were varied and the tests were conducted for periods of two to three years. Coal refuse (2.3% S) was mixed with Westvaco ash mix (20% ash with an NP of 5 kg/t CaCO₃) in ratios of 4:1 and 2:1. Both ratios produced neutral drainage (pH 8) for three years, as compared to a control pH of 1.9. In a second phase, column experiments were conducted on various mixtures of coal refuse (4% S) with the Westvaco ash (5, 10, 20, and 33% loadings) and Clinch River fly ash (20 and 33% loadings). With the Westvaco ash, only the highest loading remained neutral after two years. The Clinch River ash (which was more alkaline than the Westvaco ash) maintained neutral drainage for two years, as did a 13% limestone mixture.

2. OBJECTIVES

This experiment examined the influence of five different loadings of RK fines, -10 mesh limestone, and -1/4-inch/+10-mesh limestone on the quality of drainage from finely-crushed Duluth Complex rock containing 2.1 percent sulfur in a wet-dry cycling environment. More specifically, the objectives were to determine the loadings required to 1) neutralize acid produced by the oxidation of iron sulfide minerals present in Duluth Complex rock and 2) reduce the rate of iron sulfide oxidation to a level at which host rock minerals can neutralize the acid produced. These two objectives represent 1) interim mitigation between operation cessation and implementation of final closure measures and 2) a final closure measure. This paper presents the results from 17 May 1988 through 26 December 1995, the first 397 weeks of the experiment. The initial findings on the effects of blending and limestone particle size on acid and trace metal release were reported by Lapakko and Antonson (1990, 1991).

3. METHODS

3.1 Materials

Sulfidic Duluth Complex rock from northeastern Minnesota (drill core sample 355-1338) was blended with rotary kiln fines (RK fines), minus 10 mesh (d < 2 mm) high-calcium limestone, and +10 mesh/-0.25-inch high calcium limestone. The Duluth Complex rock was crushed and dry-sieved to obtain particles in the -100/+270 mesh fraction (0.053 < d \le 0.149 mm), simulating tailings or relatively fine waste rock. The dominant host rock minerals in the Duluth Complex are plagioclase, olivine, and pyroxenes; the major sulfide mineral is pyrrhotite; chalcopyrite, cubanite, and pentlandite are also present; and carbonate minerals are rare (Stevenson et al. 1979). The sulfur, copper, nickel, cobalt, and zinc contents were 2.1, 0.17, 0.053, 0.007, and 0.069 percent, respectively. The 2.1 percent sulfur content yielded an acid production potential (AP) of 65.5 kg/t CaCO₃. The neutralization potential (NP; Sobek et al. 1978) was 11.3 kg/t CaCO₃.

The RK fines, a waste product generated when limestone is converted to lime (CaO), were obtained from the Cutler-Magner Company in Duluth, Minnesota. Particle size analysis indicated that 96.7% of the particles were finer than 200 mesh (74 microns, table 1). The calcium and magnesium contents, as oxides, were 36% and 1.1%, respectively (table 2). Assuming the calcium and magnesium were present solely as carbonates, oxides, or hydroxides yields neutralization potentials of 640 and 27 kg/t CaCO₃, respectively. A subsequent analysis yielded slightly higher calcium and magnesium values, with a total NP of 726 kg/t CaCO₃ (table 2). This analysis was conducted several years after the beginning of the experiment, and the initial analysis will be used for all NP calculations. The second analysis provides compositional information on a wider range of trace parameters. Samples were also collected from five of the reactors at week 91 and analyzed for sulfur content, NP, and CO₂ (table 3).

The limestone was obtained from the Presque Isle Company (Alpena, MI). The limestone percentages finer than 35, 80 and 270 mesh were 52.9, 31.1 and 19.8, respectively (table 1). The particle size analysis was repeated with similar results (appendix 11). The calcium and magnesium oxide contents indicated calcium carbonate and magnesium carbonate contents of 96.68 and 2.07 percent, respectively. This is equivalent to a neutralization potential of 99.1% CaCO₃ (991 mg CaCO₃/g limestone).

In addition to the fresh samples of Duluth Complex rock and alkaline solids, samples were also removed from five reactors after 91 weeks of dissolution. A 12-g mass was removed from reactor 1 (0.11 NP/AP quotient loading [hereafter referred to as "quotient"] of RK fines), 13 g from reactor 2 (0.22 quotient of RK fines), 14 g from reactor 5 (0.65 quotient of RK fines), 14 g from reactor 10 (0.32 quotient of -10-mesh limestone), and 14 g from reactor 12 (0.96 quotient of -10-mesh limestone). These samples were analyzed for total sulfur content, NP, and carbon dioxide (appendix 11). In addition, samples of the unleached Duluth Complex rock, the 0.65 quotient RK fines leached for 460 weeks, and the 0.96 quotient limestone leached for 458 weeks were subjected to visual examination, light microscopy, and SEM (appendix 11).

Table 1. Particle size analyses.

Limestone:

Screen analysis of RK fines:

	% (of total		
Sieve#	· 1990	1991	Size	% passing by weight
10		0.2	3/4 inch	100
35	48.6	47.0	5/8 inch	100
80	20.4	21.6	1/2 inch	100
100	4.4	3.2	3/8 inch	100
200	5.9	6.6	4 mesh	100
270	2.3	1.6	20 mesh	99.97
-270	18.4	19.5	200 mesh	96.74

 Table 2.
 Chemical composition of RK fines and Presque Isle limestone. (Values are percents unless noted otherwise.)

Chemex	LTV/DNR	Limestone
< 0.2		
2.55		
170		
3.0		
12		
>25.0	30.8	
< 0.5		
11	40	
57		
66	20	
1.12	0.48	
1.50	1.16	
0.59	0.6	
145		
. 23		
0.33	0.6	
305	310	
290		
	Chemex < 0.2 2.55 170 3.0 12 > 25.0 < 0.5 11 57 66 1.12 1.50 0.59 145 23 0.33 305 290	$\begin{array}{c ccccc} < 0.2 & \\ 2.55 & \\ 170 & \\ 3.0 & \\ 12 & \\ > 25.0 & 30.8 \\ < 0.5 & \\ 11 & 40 \\ 57 & \\ 66 & 20 \\ 1.12 & 0.48 \\ 1.50 & 1.16 \\ 0.59 & 0.6 \\ 145 & \\ 23 & \\ 0.33 & 0.6 \\ 305 & 310 \\ 290 & \\ \end{array}$

RK Fines

	RK F	ines		
-	Chemex	LTV/DNR	Limestone	
Pb (ppm)	624			-
Sr (ppm)	298			
Ti	0.15	5		
V (ppm)	785			
W (ppm)	< 10			
Zn (ppm)	64	160		
S _T			0.085	
S ²⁻				
SO ₄ (as S)				
CO ₂	15.8			
Al_2O_3	4.53	3 3.71	0.27	
CaO	39.38	35.9	54.14	
Cr ₂ O ₃	<0.	01		
Fe ₂ O ₃	1.63	3 2.63 ^A	0.23	
K ₂ O	1.61			
MgO	0.98	8 1.10	0.99	
MnO	0.0	l 0.03		
Na ₂ O	0.40	5		
P_2O_5	0.07			
R_2O_3			0.49	
SiO ₂	9.03		0.75	
TiO ₂	0.24			
LOI	32.47	26.33	43.63	
H ₂ O		0.17		
Equiv. CaC	O ₃		96.68	
Equiv. MgC	CO ₃		2.08	

 Table 2.
 Chemical composition of RK fines and Presque Isle limestone; continued. (Values are percents unless noted otherwise.)

A: reported as 1.84% Fe --: not analyzed

Table 3.	Chemical	analyses	of	samples	removed	at week 91	•
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Reactor #	Alkaline Solid	NP/AP	Amount removed (g)	S	NP	CO ₂
1 2 5	RK fines RK fines RK fines	0.11 0.22 0.65	12 13 14	1.81 1.69 1.85	6.31 7.79 26.2	0.02 0.02 0.91
10 12	-10 mesh limestone -10 mesh limestone	0.32 0.96	14 14	1.61 1.47	16.3 39.4	0.70 1.86
Control Limestone				1.82	11.3 880	0.04 11.7
RK fines				0.03	755	

3.2 Leaching Procedure

Varying masses of RK fines or limestone were blended thoroughly with 75 g rock by passing them through a sample splitter 10 times. The NP/AP quotients resulting from these mixtures were 0.11 to 1.1 for the RK fines and 0.16 to 1.6 for the limestone (table 4). The mixtures were placed onto a 1.6 micron Whatman GF/A glass fiber filter (5.5 cm diameter) resting on a perforated plastic plate (into which a standpipe was fitted) in the upper section of a two-stage filter unit or reactor (figure 1; modification of Lapakko 1994a).

The alkaline solids/rock mixtures were subjected to oxidation in the presence of atmospheric oxygen and water throughout the course of the experiment. The solids were rinsed weekly with 200-mL volumes of distilled deionized water that was added to the upper section. After the water rose into the standpipe, it was drawn through the solids, glass fiber filter, plastic plate, a 0.45 micron Millipore filter resting on another perforated plastic plate, and into a receiving flask under a vacuum of 4 inches (10.2 cm) mercury.

Between rinses the reactors and solids were stored in a compartmentalized wooden housing to dry and oxidize. A cover was initially placed about 5 cm above the upper edge of the housing to allow drying of the solids while minimizing the input of airborne debris, but the cover was removed on 16 July 1990 to allow better drying of the solids between rinses. A thermostatically controlled heating pad was placed beneath the box to maintain a fairly constant temperature. A humidifier and dehumidifier controlled by humidistats were placed in the room to control humidity. Over the 397-week period of record, temperature and relative humidity in the box were monitored two to three times per week. The temperature ranged from 19.4 to 32.0° C, with a mean of 25.4° C and a standard deviation of 1.7° C (n=1299). The relative humidity ranged from 18 to 92 percent, with a mean of 55.8 and a standard deviation of 7.4 (n=1287).

Alkaline material	Reactor #	Alk. mass added (g)	Alk. mass/sulfur (NP added/AP)	NP/AP
RK Fines	1 2 3 4 5 6 7	0.788 1.575 1.575 3.150 4.725 4.725 7.875	$ \begin{array}{c} 0.5\\ 1.0\\ 2.0\\ 3.0\\ 3.0\\ 5.0\\ \end{array} $	$\begin{array}{c} 0.11 \\ 0.22 \\ 0.22 \\ 0.43 \\ 0.65 \\ 0.65 \\ 1.08 \end{array}$
-10 mesh limestone	8 9 10 11 12 13 14	0.788 1.575 1.575 3.150 4.725 4.725 7.875	$\begin{array}{c} 0.5 \\ 1.0 \\ 1.0 \\ 2.0 \\ 3.0 \\ 3.0 \\ 5.0 \end{array}$	0.16 0.32 0.32 0.64 0.96 0.96 1.60
Controls	22 23	0 0	0 0	0 0

Table 4. NP/AP quotients in the RK fines and -10 mesh limestone reactors.

Notes: Reactor 4 inadvertently fell on the floor and was thus terminated early in the experiment. The (largely ineffective) larger limestone (-0.25 inch/+10 mesh) was added to reactors 15-21 in the same ratios as the -10 mesh limestone.

3.3 Analyses

The rinse water, or drainage, was analyzed for specific conductance, pH, alkalinity, acidity, calcium, magnesium, and sulfate. Trace metal concentrations were also determined but are not discussed in this publication. The volume of rinse water, specific conductance, pH, alkalinity, and/or acidity were determined weekly. Sulfate was analyzed every two weeks (biweekly) for the first 38 weeks and monthly thereafter. Calcium and magnesium concentrations were determined biweekly for the first 20 weeks and monthly thereafter.

Water samples were analyzed for specific conductance, pH, alkalinity, and acidity at the Minnesota Department of Natural Resources laboratory (MN DNR) in Hibbing. Specific conductance was analyzed using a Myron L conductivity meter, while either a Radiometer 29 or an Orion SA720 meter



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was used for pH analyses. Alkalinity (for pH \ge 6.3) and acidity were determined using standard techniques for endpoints of 4.5 and 8.3, respectively (APHA et al. 1992). For the first 303 weeks, metals and sulfate concentrations were determined at the MN DNR. Samples were analyzed for calcium and magnesium using a Perkin Elmer 603 atomic absorption spectrophotometer, and sulfate concentrations were determined using an HF Scientific DRT-100 nephelometer for the barium sulfate technique (APHA et al., 1992). Subsequent metal and sulfate determinations were conducted at the Minnesota Department of Agriculture (MN DA). Metal concentrations were determined with a Varian 400 SPECTRAA. Sulfate concentrations were determined using a Technicon AA2 automated colorimeter or, for concentrations less than 5 mg/L, a Dionex ion chromatograph.

The calcium and magnesium values from weeks 16 through 139 were discovered to be somewhat in error. This error was introduced when the Ca and Mg values from the blanks were inadvertantly not subtracted from the sample values, which resulted in values that were somewhat elevated. The values of the blanks were obviously low, but they were high enough to cause significant error in this experiment, where the sample values themselves are also quite low. Details of how these calcium and magnesium values were revised is presented in Appendix 1.

4. RESULTS AND DISCUSSION

4.1 Controls

During the first five to seven weeks of the experiment, the two controls generated circumneutral drainage, with pH in the range of 6.2 to 6.8. Drainage pH then decreased steadily, dropping below pH 6 by week 8 and to pH 4 by about week 20. Subsequent values decreased very gradually, ultimately reaching the range of 3.3 to 3.4 by week 114 (figure 2). The pH and net alkalinity (net alkalinity = alkalinity - acidity) reflect the balance between the acid production resulting from iron sulfide oxidation and acid neutralization by host rock silicate mineral dissolution. In addition to acid production, iron sulfide mineral oxidation also leads to sulfate release. Over the first six weeks the sulfate concentrations decreased from about 50 to 15 mg/L, reflecting release of oxidation products accumulated between sample crushing and experiment initiation. Subsequently sulfate concentrations increased through about week 24 and then oscillated in the typical range of 35 to 70 mg/L, with the exception of elevated concentrations between approximately weeks 50 and 70. The temporal variation was similar to that for pH and net alkalinity but was in the opposite direction (figure 2). (Calcium data from weeks 0 and 2 were 20 mg/l, and data from weeks 0-5 were omitted for all figures in order to retain a legible calcium scale.)

It should be noted that there was no trend of decreasing sulfate concentration, which would have been the case had precipitate layers formed on the sulfide mineral surfaces. Unfortunately, the controls were terminated after 117 weeks to conserve funds and personnel time. At that time it was clear that the solids produced acidic drainage, but the longer term variations in mineral dissolution were not addressed. Fortunately, other experimental data were available which indicated no decreasing trend in sulfate release from unmitigated Duluth Complex rock (1.63% S) over a 395-week period (figure 3; Lapakko and Antonson 1994, Lapakko 1993, MNDNR unpublished data).

Figure 2. SO₄, Ca, Mg, net alkalinity and pH vs. time for weeks 3-114 for the control reactors. Note: data from weeks 0-5 were omitted in order to retain a legible scale for Ca.







With Duluth Complex rocks, in which carbonate minerals are rare, the calcium and magnesium in the drainage reflect the dissolution of acid-neutralizing minerals such as anorthite and olivine (reactions 7, 8 from Busenberg (1976) and Hem (1970), respectively).

$$CaAl_2Si_2O_8(s) + 2H^+ + H_2O = Ca^{2+} + Al_2Si_2O_5(OH)_4(s)$$
 [7]

$$Mg_2SiO_4(s) + 4H^+(aq) = 2Mg^{2+}(aq) + 2H_4SiO_4(aq)$$
 [8]

As was the case with sulfate, the release of calcium and magnesium decreased during the first six weeks, and reflected the removal of cations solubilized from the time samples were crushed to the beginning of the experiment. For the two controls, the average calcium and magnesium released during this period were 0.34 and 0.074 millimoles, respectively. Subsequently the temporal variation of calcium and magnesium concentrations roughly paralleled that for sulfate concentrations. However, the sum of the molar concentrations of calcium and magnesium was only about 35 percent of the sulfate concentration, indicating that silicate mineral dissolution neutralized only about a third of the acid produced. Thus, despite the acid neutralization by silicate mineral dissolution, the drainage pH did not meet water quality standards.

The capacity of host rock mineral dissolution to neutralize acid while maintaining pH above 6.0, or Empirical Neutralization Potential (ENP), was determined to be 0.52 to 0.56 kg CaCO₃ per metric ton rock. This calculation was based on the mass of sulfate released prior to pH decreasing below 6.0 (Lapakko and Antonson 1991). The ENP is considerably lower than the 11.3 kg/t value determined by the method of Sobek et al. (1978). This underestimation of effective NP has been reported previously (Lapakko 1990, 1994b, 1994c) and could lead to erroneously predicting neutral drainage from acid-producing rock. Apparently the dissolution of plagioclase, olivine, and/or pyroxenes present in the rock at low pH contributed to the neutralization potential determined by the method of Sobek et al. (1978). However, the dissolution of these minerals was too slow to neutralize the acid produced by pyrrhotite oxidation and maintain a drainage pH above 6.0 in the laboratory test.

Trace metal concentrations peaked at week 8 or 10, immediately after the drainage pH decreased below 6.0. Concentrations then decreased to a constant range until week 75, and subsequently increased steadily as pH decreased into the mid-threes. Maximum copper and nickel concentrations were on the order of 1 to 2 mg/L.

4.2 -0.25 inch/+10 mesh limestone

The -0.25 inch/+10 mesh limestone was only minimally effective at acid neutralization and reduction of trace metal release. The drainage pH decreased over time, reaching values from 3.75 to 4.05 at week 40. In comparison, the pH values for drainage from the controls were 3.9 and 4.0. Net alkalinities at week 40 ranged from about -20 to -60 mg/L, as compared to about -35 mg/L for the controls. These comparisons indicate the ineffectiveness of the larger limestone particles in buffering the acid produced by iron sulfide oxidation. Due to the ineffectiveness of this treatment the reactors were terminated after week 40. Upon termination iron staining was clearly visible on virtually all of the limestone surface.

For weeks 16 to 40 the average sulfate concentrations typically ranged from 27 to 47 mg/L, roughly 50 to 90 percent of the 52 mg/L average for the controls. However, the 2:1 ratio reactor drainage averaged 67 mg/L sulfate.

Nonetheless, there was some inhibition of iron sulfide oxidation in most of the reactors. Average calcium concentrations for this period typically ranged from 5 to 7 mg/L, as compared with 4.6 mg/L for the controls. This indicates that the larger limestone was neutralizing some of the acid produced. Magnesium concentrations were slightly greater than or equal to those observed for the controls.

With the exception of cobalt, average trace metal concentrations occasionally exceeded the values observed for the controls. Copper concentrations were particularly high, with five of the seven averages exceeding the copper averages for the controls. Although the periods over which the control averages were calculated were different, it is clear that the larger limestone particles were of little benefit in reducing trace metal concentrations. The average iron concentrations ranged from 1 to 20 mg/L, indicating that treatment for iron release was also marginal at best.

4.3 **RK** fines

4.3.1 Introduction

The RK fines elevated pH and inhibited sulfate release for time periods which increased with the mass of RK fines present. The drainage from the 0.11 and the duplicate 0.22 quotients decreased below 6.0 after 75 to 172 weeks. The higher RK quotients produced drainage pH values above 7 for the entire 397-week period of record.

4.3.2 0.11 and 0.22 NP/AP quotients (quotients of RK fines that produced acidic drainage)

The pH of drainage from the **0.11 quotient** decreased below 6.0 after 75 weeks of dissolution, indicating that the RK fines added were no longer effective in neutralizing acid and maintaining an acceptable pH. Drainage pH reached a minimum of 3.6 after 117 weeks (figure 4), at which time the reactor was terminated. Temporal variation of net alkalinity was consistent with that of pH.

Sulfate concentrations were typically near 20 mg/L during the period of neutral drainage and increased to almost 100 mg/L prior to termination (figure 4). This increase was likely due to biological acceleration of iron sulfide mineral oxidation as pH decreased below 4.0, the point at which bacterial acceleration becomes active (Arkesteyn 1980). The bacteria accelerate the rate of oxidation over that which occurs by oxygen alone (McKibben and Barnes 1986; Moses et al. 1987; Nicholson et al. 1988).

Calcium concentrations were typically in the range of 10 to 20 mg/L for the first 70 weeks, at which time they declined and ultimately leveled at about 3 mg/L (figure 4). The concurrent decline in pH and calcium concentrations suggests that the calcic neutralization components present in the RK fines were depleted. The mass of calcium released after 75 weeks was 256 mg, which represents 127% of the calcium added with the RK fines (table 5). Further examination of the calcium concentrations indicated an anomalously high value at week 47. When this value was replaced by the average of previous and subsequent values, the resultant mass calcium release was 103% of that added with the RK fines. It is therefore concluded that the RK fines provided the vast majority of the acid neutralization observed, and the decrease in pH (and calcium concentration) occurred upon their depletion.

The duplicate RK fines reactors with an NP/AP quotient of 0.22 acidified after 98 and 172 weeks. The general temporal trend of pH was similar to that observed for the 0.11 NP/AP sample; pH remained near 9 then declined (figures 5 and 6). The pH decline for the reactor which acidified first (reactor 2) was more rapid, and may have been influenced by the removal of 13 grams of solids from the reactor at week 91. This reactor was terminated after 117 weeks, and the drainage quality discussion will focus on the reactor with the 397-week period of record (reactor 3). After falling below 6 at week 172, the drainage pH from this reactor continued to decline steadily, reaching 3.5 after 397 weeks. (Drainage quality data for the terminated reactor are presented in figure 5 and appendix 1. The temporal variations in drainage quality for the two reactors were similar (i.e. the "shapes" of concentration vs time profiles), although the timing varied.)



Figure 4. SO₄, Ca, Mg, net alkalinity and pH vs. time for the 0.11 NP/AP quotient of RK fines (reactor 1). Note: data from weeks 0-5 were excluded to retain legible scale for Ca.

Reactor	Ratio	Period	Percent limestone dissolved								
		of record	Mass of alk. material added (g)	Mass of CaCO ₃ added (g)	Mass of Ca added** (g)	Cum. Ca mass released at end of period of record (g)	Cum. Ca mass released when pH dropped below 6.0 (g)	Percent of Ca released at end of record	Percent of Ca released when pH dropped below 6.0	Mass of CaCO ₃ remaining (g)	Percent of CaCO ₃ remaining
RK Fines											
1 2 3 5 6 7	0.5:1 1:1 1:1 3:1 3:1 5:1	117 117 397 397 397 397 397	0.788 1.575 1.575 4.725 7.725 7.875	0.504 1.008 1.008 3.024 4.944 5.040	0.202 0.403 0.403 1.210 1.210 2.016	0.269 0.371 0.442 0.929 1.050 1.307	0.256 (week 75) 0.364 (week 95) 0.404 (week 170) 	133* 92 110 78 87 65	127* 90 100 	0 0.080 0 0.281 0.160 1.769	0 8 0 22 13 35
-10 mesh limestone											
8 9 10 (a) 11 12 (a) 13 14	0.5:1 1:1 2:1 3:1 3:1 5:1	397 397 397 397 397 397 397 397	0.788 1.575 1.575 3.150 4.725 4.725 7.875	0.762 1.523 3.046 4.569 4.569 7.615	0.305 0.610 0.610 1.218 1.828 1.828 3.046	0.333 0.344 0.380 0.480 0.517 0.491 0.525	0.301 (week 270) 	109 56 63 39 28 27 17	99 	0 0.664 0.574 1.849 3.278 3.343 6.305	0 44 37 61 72 73 83
Controls											
22 23	0 0	117 117	0 0	0 0	0 0	0.077 0.075	0.016 (week 6) 0.018 (week 8)	na na	na na	na na	na na

Table 5. Calcium mass release.

* These (anomalously high) values appear to be the result of a single data point at week 47. When the data set is modified to limit the effect of this data point, the percent calcium released when pH dropped below 6.0 is 103% instead of 127%. See Appendix 4 for more detail.

** The mass of alkaline material added (g) was first converted to the mass of CaCO₃ added (g); for RK fines this was done by multiplying by 64%, and for the -10 mesh limestone this was done by multiplying by 96.7%. These values were then multiplied by 0.4 to convert into the mass of calcium added (g). (a): 20 g of material was removed from reactors 10 and 12 for NP testing on 2/13/90 (after 90 weeks). na: Not applicable

Figure 5. SO_4 , Ca, Mg, net alkalinity and pH vs. time for the 0.22 NP/AP quotient of RK fines (reactor 2). Note: data from weeks 0-5 were excluded to retain legible scale for Ca.



Figure 6. SO₄, Ca, Mg, net alkalinity and pH vs. time for the 0.22 NP/AP quotient of RK fines (reactor 3). Note: data from weeks 0-5 were excluded to retain legible scale for Ca.



Sulfate concentrations in drainage from the reactor with the 397-week period of record were initially about 40 mg/L, decreased below 10 mg/L after 150 weeks, and dropped below 3 mg/L at week 200. Concentrations began to increase at about week 320, as pH decreased into the middle fours, and continued to increase with decreasing pH, reaching 100 mg/L as pH fell to 3.5 (figure 6). Calcium concentrations decreased throughout most of the experiment, with the most pronounced decrease occurring as pH dropped below 6. At this time, concentrations fell below 1 mg/L and remained in this range until pH dropped to the upper threes, after which concentrations typically ranged from 1 to 2 mg/L. This increase was apparently due to dissolution of host rock minerals, such as plagioclase, under the low pH conditions.

At the time of acidification the calcium release from the duplicate reactors represented dissolution of 90 and 100 percent of the calcium present in the RK fines added. Thus, the behavior was parallel to that at the lower loading (NP/AP = 0.11). The acid produced by iron sulfide oxidation was initially neutralized by the RK fines. When the alkaline fraction of these solids was depleted, pH dropped below 6 and calcium concentrations in the drainage decreased sharply.

4.3.3 0.66 and 1.1 NP/AP quotients (quotients of RK fines that produced alkaline drainage)

The 0.66 and 1.1 quotients produced alkaline drainage over the 397-week period of record, with drainage pH values typically ranging from 8.5 to 9 (figures 7, 8 and 9). It should be noted however that pH of drainage from the 0.66:1 loadings began to oscillate at roughly week 340. This behavior was observed prior to acidification of drainages from the 0.22:1 loadings.

Concentrations of both sulfate and calcium decreased over the first 200 weeks and subsequently leveled within a fairly constant range (figures 7, 8 and 9). Sulfate concentrations in the later stages were on the order of two percent of those during the first 10 weeks. The calcium release ranged from 65 to 87 percent of that added with the RK fines (table 5), indicating the majority of the neutralization potential has been depleted. In contrast, only 44 to 62 percent of the sulfur has been depleted, with remnant concentrations of 38 to 56 percent.

4.3.4 Decrease in sulfate release from RK fines reactors

The decrease in sulfate release was described using the equation

$$[SO_4^{2-}] = ae^{bt}$$
 [9]

or equivalently, $\ln[SO_4^{2}] = \ln a + bt$ [10]

with sulfate concentration in mg/L and time t in weeks. The variable "a" represents the initial sulfate concentration. The ranges of values for a and b, determined by linear regression analysis, were 13.00 to 38.02 and -0.0031 to -0.016, respectively. It should be noted that the correlations were not strong, as indicated by the r² values determined (table 6).

μd Net Alkalinity. mg/L -10 -20 1/gm .[80 40 20 [Ca], [Mg], mg/L Ca 阳 Time (weeks)

Figure 7. SO₄, Ca, Mg, net alkalinity and pH vs. time for the 0.44 NP/AP quotient of RK fines (reactor 5). Note: data from weeks 0-5 were excluded to retain legible scale for Ca.

Figure 8. SO₄, Ca, Mg, net alkalinity and pH vs. time for the 0.66 NP/AP quotient of RK fines (reactor 6). Note: data from weeks 0-5 were excluded to retain legible scale for Ca.



ЪН Net Alkalinity. mg/L $[SO_4]$, mg/L |Cal. |Mgl. mg/L Ja Ì311 and the second second

Figure 9. SO₄, Ca, Mg, net alkalinity and pH vs. time for the 1.1 NP/AP quotient of RK fines (reactor 7). Note: data from weeks 0-5 were excluded to retain legivle scale for Ca.



Table 6. Decrease in sulfate release vs. time.

The data used to calculate these statistics omitted data from the first four weeks (i.e. the rinseoff period). For the RK Fines reactors, the data after the time when pH values were consistently below 6.0 was also omitted. (None of the -10 mesh limestone reactors were consistently below pH 6.0 as of week 397.)

Reactor	NP/AP quotient	Time period (weeks)	b	e ^b	Y- int.	a, mg/L ([SO ₄] ₀)	r ²	n
1	0.11	5 - 75	-0.00306	0.997	3.231	25.305	0.037	26
2	0.22	5 - 96	-0.01633	0.983	3.638	38.017	0.552	[.] 33
3	0.22	5 - 172	-0.00606	0.994	3.005	20.187	0.255	59
5	0.44	5 - 397	-0.00572	0.994	2.565	13.001	0.428	113
6	0.66	5 - 397	-0.00435	0.996	2.594	13.383	0.178	115
7	1.1	5 - 397	-0.00582	0.994	2.872	17.673	0.445	112

RK Fines

-10 mesh limestone

Reactor	NP/AP quotient	b	e ^b	Y-int.	a, mg/L ([SO ₄] ₀)	r ²	n
8	0.16	-0.00658	0.993	3.156	23.477	0.686	113
9	0.32	-0.00750	0.993	2.468	11.799	0.601	113
10	0.32	-0.00893	0.991	2.848	17.253	0.671	111
11	0.64	-0.00801	0.992	2.692	14.761	0.723	110
12	0.96	-0.01121	0.989	3.043	20.968	0.832	112
13	0.96	-0.00891	0.991	3.009	20.267	0.768	112
14	1.6	-0.01028	0.990	2.844	17.184	0.804	111

Leached solid analysis was conducted in hopes of identifying potential mechanisms for the inhibition of sulfate release. After 460 weeks of reaction, one of the 0.65 quotient reactors (reactor 5) was terminated and the solids were subjected to examination by light microscopy. Copper sulfide coloration on the surface of sulfide minerals was reported, as were "local clumps of iron oxide cemented grains" and "hematitic cemented grains associated with pyrrhotite." Additional work is in progress to further describe the surface alteration of pyrrhotite and particle cementation.

4.4 -10 mesh limestone

4.4.1 Introduction

The lowest quotient of -10 mesh limestone produced some mildly acidic drainage. Drainage remained continuously in the circumneutral range for all of the higher quotients. Sulfate concentrations decreased with time with all quotients.

4.4.2 0.16 NP/AP quotient of -10 mesh limestone (the quotient that produced acidic drainage)

The lowest limestone loading was produced by adding 0.788 g of limestone (comprised of 0.761 g calcium carbonate and 0.016 g magnesium carbonate) to 75 g of Duluth Complex rock. Assuming neutralization by reaction 3, this addition represents about 16 percent of the stoichiometric 3.12 g of CaCO₃ required to neutralize the acid produced by oxidation of iron sulfide minerals containing 1 g of sulfur (i.e. NP/AP = 0.16). This loading produced neutral drainage for 109 weeks. At that time the drainage pH dropped below 6.0, decreased to the minimum observed pH of 5.0 at week 116, and subsequently increased to a typical range of 5.5 to 6.3. Drainage pH slowly decreased between about week 200 and 350, with only five values above 6.0 reported after week 327 (figure 10).

In the limestone-amended reactors, calcium and magnesium could be released from silicate minerals present in Duluth Complex rock or from the limestone added. It is assumed that calcium and magnesium solubilized between the time of sample crushing and the start of the experiment as it had with the controls, yielding an estimated release of 0.34 and 0.074 millimoles, respectively. Most of the subsequent release, however, was probably the result of carbonate mineral dissolution, which is far more rapid than silicate mineral dissolution. Adding the calcium and magnesium release estimated from silicate minerals during the initial six weeks to that present in the limestone (7.61 and 0.19 millimoles respectively) yields totals of 7.94 and 0.26 millimoles, respectively. Calcium release reached 7.94 millimoles at approximately week 327, suggesting that the calcium carbonate was near depletion. As discussed above, drainage pH was decreasing as the carbonates were apparently being depleted. Furthermore, and generally consistent with carbonate mineral depletion, only five pH values after week 327 exceeded 6.0 (figure 10).

Despite the estimated depletion of carbonate minerals and a remnant sulfur content of approximately 1.8 percent, drainage pH did not decrease below 5.38. This moderate pH may indicate that acid was being neutralized by small amounts of remaining carbonates. For certain, the lack of more extreme acidification was influenced by a decrease in iron sulfide oxidation, as indicated by the decrease in sulfate concentrations over time (figure 10). Indeed, the sulfate release from the 0.16 quotient loading

Figure 10. SO₄, Ca, Mg, Net alkalinity and pH vs. time for the 0.16 NP/AP quotient of -10 mesh limestone (reactor 8). Note: data from weeks 0-5 were excluded to retain legible scale for Ca.



over 397 weeks was about half that from the controls over 117 weeks (table 6). At this low rate, dissolution of silicate minerals in the host rock may have neutralized the acid generated. This possibility is addressed in section 4.5.

4.4.3 0.32 to 1.6 NP/AP quotients of -10 mesh limestone (which all produced alkaline drainage)

At quotients of 0.32 to 1.6, drainage pH was in the alkaline range and continuously met the common minimum pH standard of 6.0 (figures 11-16). Drainage pH generally increased with the limestone loading, as did the release of alkalinity, calcium and, to a lesser extent, magnesium (table 7). These observations clearly demonstrate that dissolution of limestone at loadings greater than NP/AP = 0.16 readily neutralized the acid produced by iron sulfide oxidation and produced an environmentally acceptable pH over the experimental duration.

The elevated pH, net alkalinity, and calcium concentrations in drainages from these samples indicate that the carbonate minerals have not been depleted. Estimations based on the limestone addition, initial calcium and magnesium release from the controls, and total calcium and magnesium release from the limestone-amended solids indicate that 5 to 62 millimoles of calcium/magnesium carbonate remain in the 0.32 to 1.6 quotients. It is of interest to note that the sum of calcium and magnesium released exceeded sulfate release, often substantially (table 7), indicating that some of the carbonate mineral dissolution occurred in the absence of acid attack, that is by reaction 11. As the mass of blended mine waste increases, the fraction of carbonate minerals dissolving by this reaction is expected to decrease (Lapakko and Antonson, 1991).

$$CaCO_3 = Ca^{2+} + CO_3^{2-}$$
 [11]

Sulfate concentrations and the sulfate mass release were lower than those observed for the 0.16 quotient, but did not strictly decrease as the quotient increased (table 7). The concentrations decreased over time, as was the case for the 0.16 quotient (see section 4.5).

4.4.4 Decrease in sulfate release vs. time for the -10 mesh limestone reactors

For the lowest loading of -10 mesh limestone (0.16 NP/AP quotient), the decrease in sulfate concentrations over time, excluding removal of sulfate generated before the experiment began, was quantified using linear regression to obtain the equation:

$$[SO_4^{2-}] = 23.5e^{-0.00658t}$$
[12]

where $[SO_4^{2}] = \text{concentration of sulfate in mg/L and t} = \text{time in weeks (figure 17)}$. This decrease represented a decrease in the sulfide oxidation rate from 44 to 6.9 micromoles/week over the course of the experiment (table 7). The ultimate rate was about seven percent of that observed for the

Figure 11. SO₄, Ca, Mg, Net alkalinity and pH vs. time for the 0.32 NP/AP quotient of -10 mesh limestone (reactor 9). Note: data from weeks 0-5 were excluded to retain legible scale for Ca.



Figure 12. SO₄, Ca, Mg, Net alkalinity and pH vs. time for the 0.32 NP/AP quotient of -10 mesh limestone (reactor 10). Note: data from weeks 0-5 were excluded to retain legible scale for Ca.



Figure 13. SO₄, Ca, Mg, Net alkalinity and pH vs. time for the 0.64 NP/AP quotient of -10 mesh limestone (reactor 11). Note: data from weeks 0-5 were excluded to retain legible scale for Ca.



Figure 14. SO₄, Ca, Mg, Net alkalinity and pH vs. time for the 0.96 NP/AP quotient of -10 mesh limestone (reactor 12). Note: data from weeks 0-5 were excluded to retain legible scale for Ca.



Figure 15. SO₄, Ca, Mg, Net alkalinity and pH vs. time for the 0.96 NP/AP quotient of -10 mesh limestone (reactor 13). Note: data from weeks 0-5 were excluded to retain legible scale for Ca.



Figure 16. SO₄, Ca, Mg, Net alkalinity and pH vs. time for the 1.6 NP/AP quotient of -10 mesh limestone (reactor 14). Note: data from weeks 0-5 were excluded to retain legible scale for Ca.



Reactor	NP/AP	Weeks	Cumulative mass release (mmol)					
	quotient		Ca	Mg	Ca+Mg	Net alkalinit y	SO4	
RK Fines								
1 2 3 5 6 7	$\begin{array}{c} 0.11 \\ 0.22 \\ 0.22 \\ 0.44 \\ 0.66 \\ 1.1 \end{array}$	117 117 397 397 397 397 397	6.71 9.25 11.03 23.17 26.18 32.60	$\begin{array}{c} 0.75 \\ 0.72 \\ 1.30 \\ 1.53 \\ 1.53 \\ 1.46 \end{array}$	7.46 9.97 12.33 24.70 27.71 34.06	0.03 4.70 0.80 17.5 17.9 24.4	6.87 4.66 9.27 7.23 9.01 10.2	
-10 mesh limestone								
8 9 10 11 12 13 14	$\begin{array}{c} 0.16 \\ 0.32 \\ 0.32 \\ 0.64 \\ 0.96 \\ 0.96 \\ 1.6 \end{array}$	397 397 397 397 397 397 397 397	8.30 8.58 9.49 11.97 12.91 12.24 13.10	1.16 1.12 1.11 1.12 1.16 1.10 1.22	9.47 9.70 10.59 13.09 14.06 13.37 14.32	0.68 5.38 5.41 7.44 8.04 7.99 9.98	6.97 3.70 4.76 4.55 4.72 5.23 3.83	
-¼"/+10 mesh limestone								
15 16 17 18 19 20 21	0.16 0.32 0.32 0.64 0.96 0.96 1.6	40 40 40 40 40 40 40	1.29 1.06 1.13 1.66 1.70 1.33 1.73	$\begin{array}{c} 0.54 \\ 0.50 \\ 0.51 \\ 0.52 \\ 0.50 \\ 0.41 \\ 0.40 \end{array}$	1.83 1.56 1.64 2.18 2.20 1.74 2.13	-3.34 -1.95 -2.95 -3.32 -2.45 -1.26 -0.80	3.48 2.66 3.08 4.19 3.40 2.10 2.23	
Controls 22 23	0 0	117 117	1.93 1.86	1.14 1.14	3.07 3.00	-14.58 -14.13	13.5 13.2	

Table 7. Cumulative mass release (Ca, Mg, Ca+Mg, SO_4 and alkalinity).

Note: Net alkalinity mass was calculated to be:

((alkalinity-acidity)*volume)/100

Figure 17. For the 0.5:1 loading of -10 mesh limestone (Reactor 8) sulfate concentrations decreased according to the equation: $[SO_4] = 23.477 * e^{-0.00658*week}$, $r^2=0.686$, n=113. The pH of this reactor never fell below 6.0.



controls. The sulfate concentrations from the higher quotients were also fit to exponential curves (figure 18; $14.8 \le a \le 21$, $-0.0112 \le b \le -0.00658$, $0.601 \le r^2 \le 0.832$). The rates in the latest phase of the experiment ranged from 2 to 4 micromoles/week (table 8). Although limestone was still present in these mixtures, previous data indicate that dissolution of host rock silicate minerals present in the Duluth Complex rock are capable of neutralizing acid at this rate (Lapakko and Antonson 1994; see section 4.5).

The decrease in the sulfide oxidation rate may have been due to 1) precipitate formation on the sulfide mineral surfaces, 2) formation of a leached layer at the surface of pyrrhotite, 3) depletion of a more reactive sulfide mineral phase, with a subsequent slow oxidation of less reactive phases, and/or 4) concretion of the solids bed with a subsequent limitation of sulfate release due to a consequent limitation of oxygen or water transport to the mineral surface.

After 458 weeks of dissolution, the 0.96 quotient mixture was subjected to visual examination and light microscopy (appendix 11). This analysis indicated that the sulfides present had coloration of "bornite" and/or "covellite". This suggests a thin layer of copper sulfides formed on the surface of the pyrrhotite. Furthermore, it was reported that "less common sulfide grains appear to be nuclei with surrounding iron oxide cementation of grains (a radius of 2-4 grains)" and "only where iron oxide patches occur (around oxidizing sulfide grains") is there any coherent cementing [of grains]." Additional work is presently in progress to further examine both surface characteristics of the sulfide minerals and the role of cementation.

4.5 Acid neutralization by Duluth Complex at low rates of sulfate release

Thorough mixing of alkaline solids with acid-producing rock elevated drainage pH and decreased the rate of sulfate oxidation. The decrease in the sulfide oxidation rate may have implications beyond the point at which the alkaline solids have been depleted. In particular, if the rate of pyrrhotite oxidation is reduced to a low level, the dissolution of silicate minerals in the Duluth Complex may be adequately rapid to neutralize the acid produced.

During the first 70 weeks of reaction, the **controls** (to which no carbonates were added) produced drainage pH as low as 3.6. The low pH was the result of iron sulfide oxidation rates as high as 0.125 mmoles/week and the consequent acid production. In contrast, the rate of sulfate release from the **0.16 limestone quotient** was only 0.007 mmoles/week after week 327. Mass release calculations for the 0.16 limestone quotient indicated the calcium and magnesium carbonates were depleted by week 327 (section 4.4.2). Despite this depletion, drainage pH typically remained above 5 during the entire 397-week period of record. Silicate mineral dissolution apparently neutralized most of the acid produced at this low rate. Since the sulfate release rates were lower yet for the higher limestone quotients, silicate dissolution could also neutralize the acid produced at these loadings if the sulfide oxidation rates remained low.

Previous work on 75-gram samples of Duluth Complex rock $(0.053 < d \le 0.149 \text{ mm})$ indicated that drainage pH exceeded 6.0 whenever the rate of sulfate release was less than 0.005 mmoles/week, although it should be noted that neutral drainage was also often produced at higher rates of sulfate release (Lapakko and Antonson, 1994). Furthermore, drainage pH values were almost always above 5.0 when sulfate release rates were less than 0.020 mmoles/week. These values suggest that, for the 0.16 quotient,

Figure 18. Sulfate release from all of the -10 mesh limestone reactors decreased according to the equation $[SO_4] = ae^{bt} (0.601 < r^2 < 0.832)$, with $[SO_4]$ in mg/L and t in weeks. (For clarity only three lines are depicted.)



Time, weeks

Table 8.Linear regression statistics for sulfate release vs. week.for the alkaline addition
reactors (1988-1995 data).

Reactor	Time period (weeks)	Alkaline solid	NP/AP quotient	Sulfate release rate (mmol/week)	Y- intercept	R	R ²
1	0-2 3-38 39-110 111-117	RK Fines	0.11	0.217 0.040 0.036 0.165	0.306 0.769 1.659 -12.427	1.000 0.995 0.998 0.998	1.000 0.991 0.996 0.997
	0-117			0.049	0.637	0.993	0.987
2	0-12 13-38 39-62 63-117	RK Fines	0.22	0.080 0.044 0.053 0.013	0.540 0.883 0.555 3.192	0.977 0.996 0.999 0.999	0.955 0.993 0.997 0.992
	0-117			0.035	1.119	0.973	0.947
3	0-12 13-38 39-92 93-144 145-320 321-368 369-397	RK Fines	0.22	0.078 0.036 0.015 0.025 0.006 0.018 0.105	0.494 0.968 1.804 0.837 3.755 -0.161 -32.715	0.988 0.999 0.997 0.998 0.989 0.989 0.996 0.980	0.976 0.998 0.994 0.996 0.979 0.993 0.961
	0-397			0.014	1.779	0.959	0.920
5	0-6 7-28 29-38 39-58 59-108 109-118 119-256 257-397	RK Fines	0.66	0.272 0.029 0.006 0.039 0.018 0.029 0.005 0.007	1.310 2.853 3.483 2.112 3.400 2.260 5.279 4.651	0.966 0.986 0.994 0.997 0.997 0.996 0.937 0.994	0.933 0.973 0.988 0.994 0.995 0.995 0.992 0.878 0.987
	0-397			0.010	3.781	0.910	0.829
6	0-14 15-36 37-63 64-110 111-118 119-264 265-340 341-397	RK Fines	0.66	0.156 0.026 0.053 0.017 0.037 0.005 0.014 0.005	1.617 3.205 2.124 4.316 2.275 6.203 3.928 6.923	0.916 0.995 0.989 0.990 0.989 0.960 0.996 0.997	0.839 0.989 0.977 0.981 0.979 0.921 0.991 0.994
	0-397	ļ		0.014	4.104	0.934	0.872
7	0-4 5-38 39-63 64-116 117-397 0-397	RK Fines	1.1	0.546 0.029 0.050 0.026 0.007 0.015	1.875 4.010 3.547 4.772 7.499 5.283	0.987 0.989 0.991 0.957 0.989 0.912	0.975 0.979 0.982 0.916 0.978 0.832

Reactors with RK Fines

Note: Reactor 4 (the 0.44 NP/AP reactor) was accidentally knocked over early in the experiment.

Table 8.Linear regression statistics for sulfate release vs. week for the alkaline addition reactors
(1988-1995 data); continued.

Reactor	Time period (weeks)	Alkaline solid	NP/AP quotient	Release rate (mmol/week)	Y- intercept	R	R ²
8	0-63 64-92 93-140 141-397 0-397	-10 mesh limestone	0.16	0.044 0.019 0.035 0.007 0.015	0.399 1.964 0.399 4.319 1.962	0.990 0.995 0.988 0.997 0.932	0.980 0.990 0.975 0.994 0.868
9	0-38 39-140 141-397	-10 mesh limestone	0.32	0.041 0.011 0.002	4.496 1.381 2.682	0.972 0.991 0.990	0.946 0.982 0.979
10	0-62 63-120 121-397	-10 mesh limestone	0.32	0.040 0.013 0.003	0.473 2.124 3.417	0.984 0.978 0.990	0.967 0.956 0.980
11	0-397 0-45 46-120 121-397	-10 mesh limestone	0.64	0.009 0.037 0.015 0.004	1.972 0.390 1.654 3.190	0.873 0.953 0.976 0.990	0.762 0.908 0.952 0.980
	0-397			0.009	1.775	0.884	0.782
12	0-62 63-120 121-397	-10 mesh limestone	0.96	0.043 0.012 0.002	0.418 2.453 3.891	0.986 0.991 0.953	0.973 0.982 0.908
	0- 397			0.009	2.143	0.831	0.690
13	0-58 59-120 121-397	-10 mesh limestone	0.96	0.039 0.018 0.004	0.413 1.838 3.843	0.980 0.992 0.985	0.960 0.984 0.970
	0-397			0.010	2.005	0.878	0.771
14	0-62 63-132 133-397	-10 mesh limestone	1.6	0.031 0.012 0.002	0.563 1.619 3.065	0.968 0.997 0.971	0.937 0.995 0.942
	0-397			0.007	1.728	0.868	0.753

Reactors with -10 Mesh Limestone

Table 8.Linear regression statistics for sulfate release vs. week for the alkaline addition reactors
(1988-1995 data); continued.

Reactor	Time period (weeks)	Alkaline solid	NP/AP quotient	Release rate (mmol/week)	Y-intercept	R	R ²
15	0-10 11-28 29-40	-0.25"/ +10 mesh limestone	0.16	0.064 0.118 0.049	0.094 -0.311 1.542	0.999 0.997 0.999	0.999 0.995 0.998
	0-40			0.096	0.014	0.990	0.980
16	0-4 5-30 31-40	-0.25"/ +10 mesh limestone	0.32	0.081 0.051 0.097	0.114 0.217 -1.206	0.999 0.999 1.000	0.999 0.998 1.000
	0-40			0.057	0.130	0.993	0.987
17	0-12 13-28 29-40	-0.25"/ +10 mesh limestone	0.32	0.057 0.121 0.044	0.124 -0.814 1.340	0.993 0.997 0.999	0.986 0.994 0.997
	0-40			0.084	-0.036	0.989	0.978
18	0-10 11-24 25-40	-0.25"/ +10 mesh limestone	0.64	0.065 0.166 0.074	0.142 -1.106 1.257	0.990 0.999 0.999	0.980 0.998 0.998
	0-40			0.115	-0.125	0.990	0.979
19	0-6 7-28 29-40	-0.25"/ +10 mesh limestone	0.96	0.054 0.099 0.065	0.121 -0.315 0.816	0.992 0.994 0.995	0.983 0.987 0.990
	0-40			0.090	-0.094	0.994	0.988
20	0-40	-0.25"/ +10 mesh limestone	0.96	0.048	0.103	0.999	0.997
21	0-40	-0.25"/ +10 mesh limestone	1.6	0.050	0.181	0.999	0.998

Reactors with larger limestone (-0.25"/+10 mesh)

Controls

Reactor	Time period (weeks)	Alkaline solid	NP/AP quotient	Release rate (mmol/week)	Y- intercept	R	R ²
22	0-16 17-117	na	0	0.060 0.125	0.072 -1.258	0.993 0.998	0.986 0.995
	0-117			0.120	-0.767	0.997	0.993
23	0-18 19-46 47-62 63-117	na	0	0.056 0.095 0.276 0.088	0.032 -0.497 -9.241 2.697	0.989 0.994 0.999 0.999	0.978 0.988 0.999 0.988
	0-117			0.986	-0.758	0.993	0.986

dissolution of host rock silicate minerals such as plagioclase, clinopyroxene, and olivine was adequately rapid to neutralize almost all of the acid produced at the low rate of iron sulfide oxidation (6.9 micromoles/week). Thus, it appears that this limestone loading is slightly less than that which would be required to maintain, at least temporarily, drainage pH above the common water quality standard of 6.0. It must, however, be noted that an acceleration of iron sulfide mineral oxidation, such as that observed after week 100, could drive pH further into the acidic range (figure 10). Such acceleration was apparently due to elevated humidity and has been reported previously (Lapakko and Wessels 1995; Lapakko and Antonson 1994).

Ignoring dissolution rates, the mass of silicate minerals present in the rock is sufficient to neutralize the maximum acid generation possible from oxidation of iron sulfides present. The Duluth Complex is a long arcuate mafic intrusion of Keweenawan age. Based on mineralogy and texture, the Duluth Complex can be considered to consist of three gross units. The following is summarized from Stevenson et. al 1970.

1. Anorthositic series

This series consists of rocks that are generally >80% plagioclase, with olivine, augite, and oxide minerals occurring interstitially to the tabular plagioclase crystals.

2. Troctolitic series

This series is made up of plagioclase, olivine, pyroxenes and oxides. Plagioclase is the predominant mineral, comprising 50 to 80% of the rocks, with olivine the second-most abundant mineral, at 10 to 40% of the rock.

3. Felsic series

These rocks have gradational to sharp contacts with rocks of the anorthositic and troctolitic series. They vary from being clearly intrustive into the older rocks to having an ambiguous relationship to the other units of the Duluth Complex.

The Duluth Complex rock used in this experiment came from a drill core (sample #355-1338) collected from the Minnamax site located near Babbitt, MN, which is part of the troctolitic series. Plagioclase is the predominant mineral in this series, and typically accounts for approximately 60 to 80% of the rock, while olivine typically accounts for about 20 to 30%. Other minerals such as pyroxenes and oxides may also be present (and may account for anywhere between 0 and 15% of the entire volume); if this is the case, there is proportionately less plagioclase and olivine (Miller 1998). In any case, the ratio between plagioclase and olivine stays close to 2:1. Approximately 50 to 65% of the plagioclase is anorthitic (i.e. the ratio of Ca/(Ca+Na) is about 0.5 to 0.65), and approximately 45-60% of the olivine is forsteritic (Mg/(Mg+Na) = 0.45 to 0.6); Miller 1998, Severson and Barnes 1991).

While recognizing that any particular rock from this series may differ significantly from these values, for the sake of these calculations we will assume that 60% of the rock is plagioclase (the low end of the reported typical range) and that 50% of this plagioclase is anorthitic; this yields a value of 30% for the percentage of the Duluth Complex that is anorthite. Assuming that 20% of the rock is olivine (again, the low end of the reported average range) and that half of this olvine is forsterite yields a value of 10%

for the percentage of Duluth Complex that is forsterite. The acid-neutralizing potential of these two silicate minerals is equivalent to 11 and 14 percent calcium carbonate, respectively, yielding a total acid-neutralizing potential of 25 percent calcium carbonate, or 250 kg/t CaCO₃. In comparison, the acid producing potential of about 66 kg/t CaCO₃ would exist for rock containing 2.1 percent sulfur present as iron sulfides. Thus, dissolution of these silicate minerals would be more than adequate to neutralize the acid produced by oxidation of all iron sulfides present, providing the sulfide oxidation rate remained low.

Whereas acid production rates have been low for a period of years, it must be noted that it is not known how long they will remain low. For example, if rates are controlled by precipitate coatings on sulfide minerals, they will remain low only as long as these coatings remain intact on the iron sulfide mineral surfaces. Precipitate coatings on pyrite have been reported to be "poorly adhered" and "susceptible to desiccation" (Yanful et al. 1997). If coatings on the pyrrhotite in the Duluth Complex rock were similar, the reduced rate of acid production may be of limited duration. If so, this technique will be limited to application as a relatively short-term interim mitigation measure rather than as a "stand alone" mine waste abandonment method. Pratt et. Al (1994) has reported the formation of a leached layer during air oxidation of pyrrhotite. The competence of such a leached layer may differ from the "poorly adhered" precipitate coating on pyrite discussed above. Additional work is presently in progress to determine the mechanism by which sulfide mineral oxidation is inhibited.

5. CONCLUSIONS

Rotary kiln fines (RK fines), -10 mesh limestone, and +10 mesh limestone were each mixed with finely crushed 2.1-percent-sulfur Duluth Complex rock to determine their effectiveness in reducing the release of acid and trace metals with drainage from the rock. 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) of each solid were mixed with 75 g rock. 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 for 397 weeks. Over a 117-week period the rock alone produced drainage pH as low as 3.3 and maximum copper and nickel concentrations in the range of 1 to 2 ppm. The sulfate release did not decrease over time. In contrast, the alkaline mixtures maintained drainage pH above 6.0, a common minimum water quality standard, for 75 to 397 weeks (still in progress). While pH was maintained in this range, sulfate concentrations decreased and trace metal concentrations were typically three to ten percent of those observed in drainage from the controls.

Drainage from the lowest two loadings of RK fines (the reactor with an NP/AP quotient of 0.11, and the duplicate reactors that have NP/AP quotients of 0.22) neutralized drainage for 75 to 192 weeks. Drainage quality and mass release calculations, in conjunction with solid-phase analyses, indicated that essentially 100% of the neutralization potential of the RK fines was depleted when drainage pH decreased below 6.0. Thus, the drainage remained in acceptable range only while RK fines were available to neutralize acid.

A 0.16 quotient of -10 mesh limestone produced drainage pH above 6.0 for 109 weeks and above 5.0 for 397 weeks. Limestone loadings of 1:1 to 5:1 produced drainage pH above 6.0 for 397 weeks. 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 would be 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. Thus, 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.

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 formation, may be specific to this rock formation. In addition, the dissolution of host rock minerals of other rock types are 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. 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. Cooperators are presently being sought to conduct small-scale field tests to better assess the influence of these variables.

The -0.25 inch/+10 mesh limestone was only minimally effective in neutralizing acid and trace metal release.

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