COMPARISON OF DULUTH COMPLEX ROCK DISSOLUTION IN THE LABORATORY AND FIELD[1]

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Abstract: The quality of drainage and the release of sulfate, calcium, and magnesium from five field test piles of Duluth Complex rock with sulfur contents of 0.63% (three piles), 0.79%, and 1.41% were determined for periods of 12 to 14 yr. The pH of drainage from the piles decreased over time and with increasing solid-phase sulfur content. The ultimate drainage pH values for the 0.63% S piles ranged from 4.8 to 5, similar to values observed in the laboratory. Ultimate drainage pH values for sulfur contents of 0.79% (pH 4) and 1.41% (pH 3.5) were about one unit lower than the corresponding laboratory values for these sulfur contents. Over the entire period of record, average rates of sulfate release (2.1 to 10.5 mmol/mt/d) and magnesium release (0.55 to 3.7 mmol/mt/d) increased as the solid-phase sulfur content of the pile increased, while those of calcium release (1.2 to 2.4 mmol/mt/d) were relatively constant with respect to solid-phase sulfur content. Annual release rates for sulfate and calcium were relatively constant over time, while those for magnesium tended to increase over time. Annual release rates for all three parameters increased with increased annual drainage volume, a variable not examined in the laboratory. Release rates in the field were typically 10% to 30% (and in one case, nearly 40%) of those observed in the laboratory. Empirical neutralization potentials in the field decreased as solid-phase sulfur content decreased and were typically 10% to 50% of the corresponding average laboratory values. The empirical neutralization potentials to maintain drainage pH above 6.0 were approximately 0.5% to 8% of ABA NP values for Duluth Complex rock.

Additional key words: acid mine drainage, sulfide mineral oxidation, pyrrhotite, field test, rates.

Introduction

In the mid-1970's AMAX Exploration Inc. was evaluating the potential for developing copper-nickel resources of the Duluth Complex in northeastern Minnesota. At this time little information existed on the potential drainage problems associated with copper-nickel development in Minnesota. The State and AMAX agreed to commence field leaching tests on Duluth Complex rock. AMAX began excavation of a shaft in 1975 and in 1977 constructed six test stockpiles containing lean ore material. Water quality samples were collected periodically from each pile in 1977, and the data were compiled by AMAX Environmental Services Inc. (1978). The test pile studies were conducted from 1978 through the present by the Minnesota Department of Natural Resources (MNDNR), Division of Minerals (Eger and Lapakko 1981, 1985). As part of a cooperative research project with the U. S. Bureau of Mines, the compilation and analysis of data from the test piles were updated through 1991 to aid in development of a dissolution model by the Salt Lake City Research Center. This paper presents data on the quality and quantity of drainage from five of the test piles and the rates of mineral dissolution observed from 1978 through 1991. The period of record for pile 4 was only 5 yr, and these data are not presented. The data are compared with those previously presented on laboratory studies on the dissolution of Duluth Complex rock.

Objectives

The objectives of this paper on the quality of drainage from Duluth Complex rock field test piles are to

1. Describe the variation of drainage quality with respect to solid-phase sulfur content, time, and flow.
2. Determine the rates of sulfate, calcium, and magnesium release.
3. Describe the variation of drainage quality and mass release with respect to sulfur content, time, and flow.

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4. Determine the empirical acid neutralization potentials of the Duluth Complex rock samples examined.
5. Compare field results with those generated in the laboratory.

Methods

Climate

Annual precipitation in the study area averages 72.1 cm (Hickok and Associates 1977), and the average watershed runoff is 26.2 cm/yr (Siegel and Ericson 1980). Temperatures are extreme, averaging -14° C in January and 19.1° C in July, with an annual mean of 3.6° C; the ground is covered with snow for an average of 140 days per year (Hickok and Associates 1977).

Test Pile Construction

Materials. Six test stockpiles containing 820 to 1300 metric tons (mt) of low-grade copper-nickel material were constructed in 1977. The piles were approximately 4 m high and 15 m by 25 m at the base. Stockpiles 1 to 4 were constructed of rock mined during the shaft-sinking operation, while piles 5 and 6 contain material from underground drifts. The chemical compositional ranges for the piles are 0.63% to 1.41% S, 0.30% to 0.35% Cu, and 0.083% to 0.085% Ni (table 1). A grab sample was taken from test pile 1 for more extensive chemical and mineralogical analyses (Eger and Lapakko 1981). The major sulfide minerals identified and their volume percentages were pyrrhotite (0.844%), chalcopyrite-cubanite (0.769%), and pentlandite (0.037%). The major silicate minerals and their approximate volume percentages were plagioclase (59%), clinopyroxene (11%), olivine (11%), orthopyroxene (3.7%), and monocrystalline amphibole (3.6%).

Approximately 40% of test pile 4 was removed in 1982 for use in another study of stockpile reclamation techniques (Eger et al. 1984, Lapakko et al. 1986). At this time a representative sample weighing over 3 mt was collected for analysis of particle size distribution, specific surface area, chemistry, and mineralogy. The methods and detailed results of this characterization are presented in Lapakko et al. (1986). The particle size analysis revealed that 11% of the grains were larger than boulder/cobble size classification (d > 305mm), 6.8% were boulder/cobble (76.2 < d ≤ 305 mm), 63% were gravel (2 < d ≤ 76.2 mm), 15.8% were sand (0.074 < d ≤ 2 mm), and 4.7% were silt/clay (0.053 < d ≤ 0.105 mm). The sand, silt, and clay fractions were analyzed for specific surface area, chemistry, and mineralogy. The specific surface area of the fine fractions was roughly inversely proportional to the particle size diameter (table 2). The pH decreased and the sulfide and trace metal content increased with decreasing particle size of the rock. The finer sand, silt, and clay fractions had S, Cu, and Ni contents above the 0.634% S, 0.348% Cu, and 0.083% Ni levels estimated for pile 4 as a whole.

Table 1. Summary of chemical and physical characteristics of test piles.

	Pile 1	Pile 2	Pile 3	Pile 6	Pile 5
Date completed	4/20/77	4/20/77	4/20/77	9/30/77	9/10/77
S . . . . %	0.63	0.63	0.63	0.79	1.41
Cu . . . . %	.35	.35	.35	.34	.30
Ni . . . . %	.083	.083	.083	.084	.085
Mass . . . . mt	1,100	1,100	830	1,300	815
Volume . . . . m³	540	530	400	630	400
Collecting area . . . . m²	290	340	300	320	340
Surface area . . . . . m²	330	450	430	390	370
Cover material	None	Topsoil	Glacial till (coarse sand)	None	Sandy till over coarse sand
Ave. cover depth . . cm	0	23	34	0	54
Vegetated	No	Yes	Yes	No	Yes

Table 2. Characterization of fine fractions from test pile 4.

Size fraction, mm	pH	Total sulfur, %	Sulfide, %	Cu, %	Ni, %	Co, %	Zn, %	Specific surface area, m²/g
Sand								
0.50 -2.00	6.56	0.67	0.65	0.337	0.062	0.012	0.015	0.60
.177- .50	6.37	.80	.75	.381	.078	.013	.015	.78
.149- .177	6.18	.88	.80	.391	.103	.015	.015	1.1
.105- .149	NA	1.12	1.05	.495	.147	.019	.017	1.6
.075- .105	5.95	1.37	1.30	.585	.221	.022	.019	1.7
Silt and clay								
.053- .075	5.78	1.65	1.57	.647	.253	.024	.019	2.6
< .053	5.77	1.94	1.86	.814	.295	.027	.023	4.7

NA Not available.

X-ray diffraction (XRD) analyses were conducted on the 0.053- to 0.075-mm, the 0.075- to 0.105-mm, and the 0.105- to 0.149-mm size fractions of the rock. Approximately half of this material was plagioclase (with a Na:Ca ratio of about 2:3), and half was a mixture of olivine (with a Fe:Mg ratio of 1:4 to 1:9), pyroxene, and biotite. Lesser amounts of magnetite, amphibole, chlorite, and possibly smectite and/or vermiculite were also identified. The phyllosilicate minerals (biotite, chlorite, smectite, vermiculite) were more common in the finer size fractions.

Piles 1, 3, and 6 were partly covered by plastic at the end of the 1989 field season, for the practical purpose of reducing the volume of drainage the MNDNR is required to treat. The plastic covers were shredded during 1990 by exposure to the elements. A more robust Hypalon cover was placed onto pile 3, thereby terminating flow from this pile at the end of the 1989 field season.

Reclamation Treatments. Three of the piles were left uncovered, as controls, and the remaining three piles were covered (May 1978) with 18 to 29 cm of soil obtained from a nearby borrow pit. Pile 2 was covered with fertile topsoil obtained from the top 30 cm of the borrow pit, while piles 3 and 5 were covered by infertile coarse sand. In 1980 an additional 30 cm of sandy till was added to pile 5. Additional details on vegetation, fertilization, and the application of lime-stabilized sludge to pile 3 (1980, 1982) and a sodium-lauryl-based bactericide to pile 5 (1982) are available in Eger and Lapakko (1981, 1985).

Water Sampling and Analysis. For drainage collection, each pile is underlain by an impervious Hypalon liner (30 mil) which is sloped toward a 15.2-cm perforated plastic pipe. The drainage collected from the piles flows to a common sump. A limited number of water quality samples were collected in 1977, but no flow measurements were made. Since methods in this year deviated from those over the remainder of the study and the data were sparse, the results are not addressed in the text. During 1978, each pile was fitted with a cumulative flow meter and a flow-weighted composite sampler (Eger and Lapakko 1981). For each pump discharge, a fixed volume of sample was placed into the compositing container.

The composite samples were analyzed weekly through 1990 and biweekly subsequently. Samples were filtered through 0.45-μm filters to remove suspended materials prior to analysis. Routine analyses included pH, alkalinity, specific conductance, sulfate, copper, nickel, cobalt, zinc, calcium, and magnesium, although calcium and magnesium were not analyzed in 1983. (Some samples were also analyzed for sodium, potassium, chloride, and dissolved organic carbon.) Specific conductance was analyzed using a Myron L conductivity meter. pH was determined using a Radiometer 29 pH meter from 1978 to 1988, and subsequently using an Orion SA 720 with a

Ross combination electrode (8165). Sulfate was analyzed using the barium sulfate turbidimetric technique (APHA et al. 1992). Metals were analyzed with a Perkin Elmer 603 atomic absorption spectrophotometer.

Calculations

For each period over which composite samples were collected, the mass release was calculated as the product of the concentration in the composite sample and the volume of flow during the period over which the composite was collected. Annual mass release was calculated as the sum of the mass release values for the individual periods for each year. Annual flow-weighted mean concentrations were calculated by dividing the annual mass release by the annual flow. The annual rates of release were calculated as the annual mass release divided by the product of the number of days of flow and the mass of the pile (mt). Average rates of release for the entire period of record were calculated by dividing the total mass release by the number of days of flow.

Empirical neutralization potentials (ENP) were calculated to determine the amount of acid neutralized by the solids prior to the drainage pH decreasing and, for the duration of the period of record, remaining below pH values of 7, 6, 5, 4.5, and 4. The acid neutralized was calculated as the cumulative calcium and magnesium release (expressed as kilograms of $CaCO_3$ per metric ton of rock, or kg/mt $CaCO_3$) prior to the drainage pH decreasing and remaining below the specified pH value. If the drainage pH from a given solid never decreased permanently below a specified value, the ENP was reported as "greater than" the total calcium plus magnesium release for the period of record. Sulfate release was not used for the ENP calculation since some of the sulfate was the product of trace metal sulfide oxidation. The sulfate released from oxidation of copper and nickel sulfides, which comprised 15% to 35% of the sulfide mineral content of the test piles, does not necessarily result in acid production.

Results

Drainage Quality

The test piles typically produced drainage between the middle of March and the middle of November, with an average flow season of 245 days. The pH of drainage from the test piles generally decreased over time, and decreased as the solid-phase sulfur content increased (fig. 1). At the beginning of 1978, the pH of drainage from all piles was between 7 and 8. For the three piles containing 0.63% sulfur, drainage pH decreased gradually from circumneutral to the range of 4.8 to 5.3. The pH of drainage from the piles containing 0.79% and 1.4% sulfur decreased and plateaued within a range of about 0.2 to 0.3 pH unit. The pH of drainage from the 0.79%-sulfur pile decreased until 1982 and subsequently oscillated in the typical range of 4.0 to 4.3. The pH of drainage from the 1.41%-sulfur pile decreased to a lower level, from a median value of 5.5 in 1978 to a typical range of 3.4 to 3.6 from 1979 to 1991. The annual median values actually increased from 1982 (3.40) to 1991 (3.60).

Annual flow-weighted mean sulfate concentrations for the individual piles tended to increase during the first 3 to 4 yr and then oscillated within a fairly constant range, increased as the solid-phase sulfur content increased, and were independent of the annual flow volume. Some deviations from the general trends were observed. Most notably, sulfate concentrations in drainage from the 1.41%-sulfur pile increased to peak levels between 1981 and 1985 and then decreased. From 1987 to 1991 the flow-weighted mean sulfate concentrations from this pile were comparable to, or lower than, those from the 0.79%-sulfur pile. Sulfate concentrations from the 0.79%-sulfur pile increased over time. However, these temporal variations from 1981 through 1991 were relatively small. In general the maximum annual flow-weighted mean sulfate concentrations were typically within a factor of 2 of the minimum value observed during this period.

Annual flow-weighted mean magnesium concentration variations over time were generally parallel to those observed for sulfate and were independent of annual flow volume. Magnesium concentrations were lowest in drainage from the 0.63%-sulfur piles, typically ranging from 2 to 6 mmol/L. The corresponding range for the two piles of higher sulfur content was 7 to 15 mmol/L. For the individual piles, annual flow-weighted mean magnesium

concentrations tended to increase as the annual median pH decreased.

Annual flow-weighted mean calcium concentrations were typically fairly constant, ranging from about 4 to 7 mmol/L. As implied by the constant range, there was little dependence of annual flow-weighted mean calcium concentrations on time of dissolution, sulfur content, or annual flow. The values for the 1.41%-sulfur pile appeared to parallel the decreasing trend observed for sulfate concentrations from 1985 to 1991.

Annual Rates of Release

The annual rate of sulfate release from each pile oscillated within a fairly constant range (fig. 2). In general, annual sulfate release increased with the solid-phase sulfur content of the pile, although the rates for the 0.79%-sulfur pile were comparable to or exceeded those for the 1.41%-sulfur pile from 1984 to 1991. Sulfate release also increased with annual flow, and temporal variations in the annual rate were largely due to variations in annual flow volume. A graphic example of the flow dependence is the low sulfate-release rate from the 0.79%-sulfur pile in 1990, while the pile was partly covered with plastic. The drainage volume and sulfate mass release were consequently low.

Variations in magnesium release followed similar trends. Similar to the sulfate-release rates from 1984 through 1991, magnesium release from the 0.79%-sulfur pile was usually higher than that from the 1.41%-sulfur pile. In contrast, the annual rates of calcium release typically fell into the range of 1 to 3 mol/mt/d. They did not vary with time or solid-phase sulfur content, but did increase linearly with annual flow.

Figure 1. Annual median pH from 1978 to 1991. Drainage pH decreased over time and as solid-phase sulfur content increased.

Empirical Neutralization Potential (ENP)

The pH of drainages from the 0.63%-sulfur rock did not decrease permanently below 5.0. The approximate ranges of ENP values determined for endpoint pH values of 7.0 and 6.0 (ENP_{pH7} and ENP_{pH6}, respectively) were 0.2 to 0.4 and 0.4 to 1.3 kg/mt $CaCO_3$, respectively. The pH of drainage from pile 3 approached 5 at the end of 1989. The 1.3 kg/mt $CaCO_3$ ENP value determined for this pile is assumed to be near the ENP_{pH5} for this pile. The lowest ENP endpoint pH values for the piles with sulfur contents of 0.79% and 1.41% were pH 4.5 and pH 4.0, respectively. The ENP values for any pH value tended to decrease as sulfur content increased.

Comparison of Field and Laboratory Data

Certain qualitative similarities were apparent between the field data and laboratory data (Lapakko 1988, Lapakko and Antonson 1993).
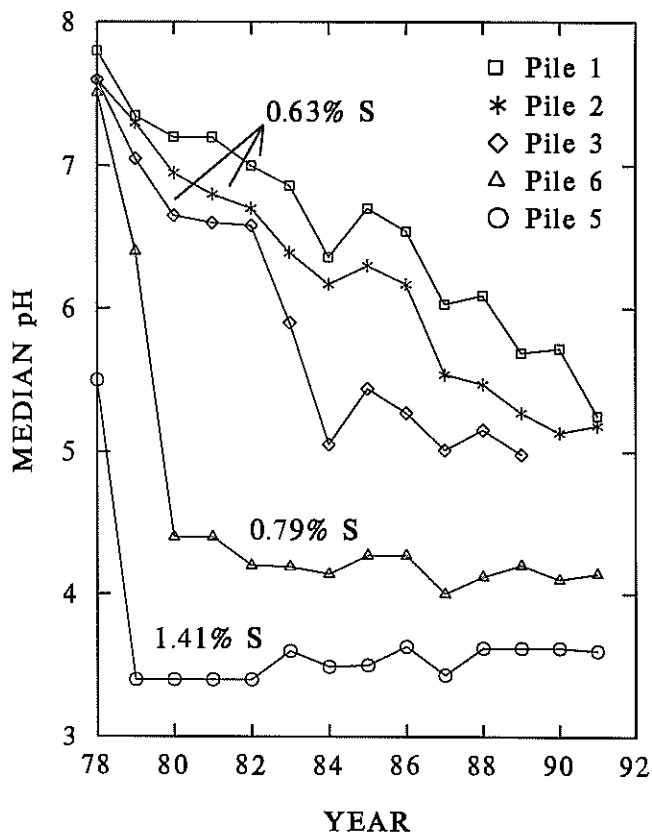
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1. Drainage pH generally decreased, or decreased and plateaued, as the time of dissolution increased. A subtle variation on this trend was a possible slight increase in the pH of drainage from the 1.41%-sulfur pile from 1982 to 1991 (median annual pH values of 3.40 and 3.60, respectively).

2. In both laboratory and field, drainage pH values decreased as solid-phase sulfur content increased.

3. The rates of sulfate release were fairly constant over time. The ratio of maximum-sulfate-release rate to minimum-sulfate-release rate for a laboratory sample was typically less than 3:1. This ratio was observed to increase if drainage pH decreased below about 4. The corresponding ratios for the test piles ranged from 2.7:1 to 3.9:1.

4. In both laboratory and field tests the rate of sulfate release increased with solid-phase sulfur content. Sulfate release rates from the test piles also increased with drainage volume, a variable not examined in laboratory tests.

5. Rates of calcium release were relatively constant over time, although it must be noted that laboratory data on calcium release are limited.

6. Rates of calcium release were relatively constant with respect to sulfur content. The rates of calcium release from the test piles also increased with drainage volume, a variable not examined in laboratory tests.

7. Rates of magnesium release increased as time increased, although it must be noted that laboratory data on magnesium release are limited.

8. Rates of magnesium release increased as solid-phase sulfur content increased. The rates of magnesium release from the test piles also increased with drainage volume, a variable not examined in laboratory tests.

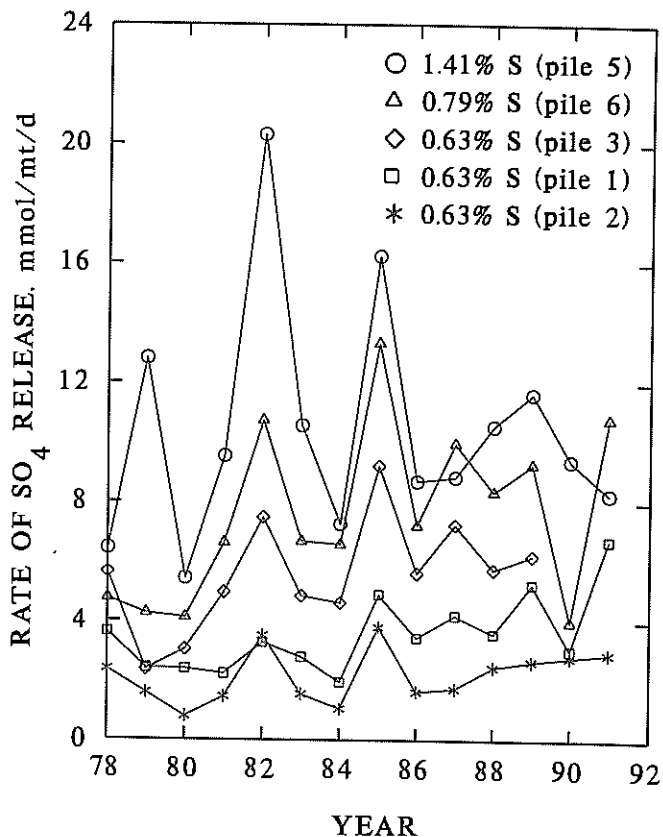9. Neutralization potential values were low and decreased with increasing sulfur content.

Figure 2. Annual sulfate release rate from 1978 to 1991. Sulfate concentrations generally increased with solid-phase sulfur content and were within a constant range over time.

Field and laboratory data were also quantitatively compared based on drainage pH, neutralization potentials, and rates of release. The minimum drainage pH values observed for the 0.63%-sulfur rock in the field ranged from 4.71 to 4.96 and were reasonably consistent with the laboratory relationship between drainage pH and solid-phase sulfur content. However, the minimum pH values for drainages from the test piles with sulfur contents of 0.79% and 1.41% were about one unit lower than expected based on laboratory data (fig. 3). The minimum pH values observed were typically occasional excursions, and recurrent low pH values were typically 0.1 to 0.2 unit higher.

For the entire period of record, average rates of sulfate release ranged from 2.0 to 10 mmol/mt/d, and increased as sulfur content and drainage volume increased. The average rates of calcium release ranged from 2.1 to 2.4 mmol/mt/d and were fairly constant with respect to sulfur content. Average rates of magnesium release ranged from 0.55 to 3.7 mmol/mt/d and were lowest for the low-sulfur solids and highest for the solids containing 0.79% sulfur.

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The rates of sulfate, calcium, and magnesium release observed for the test piles were compared to laboratory rates for the Duluth Complex samples of similar sulfur content (Lapakko and Antonson 1993). The laboratory rates were from the last 15 to 36 weeks of the period of record. The ratios of field rates to laboratory rates, or retardation factors, ranged from 0.053 to 0.46, with most values in the range of about 0.1 to 0.36 (table 3). This indicates that the laboratory rates were roughly 3 to 10 times those in the field.

The neutralization potentials of the test piles were lower than those for laboratory samples, which is consistent with the lower drainage pH levels observed in the field. The ENP values for the 0.63%-sulfur rock were roughly 25% to 50% of those observed for laboratory samples of similar sulfur content (table 4). Although the ENP_{pH6} and ENP_{pH7} values from pile 3 were higher than this range, the ENP_{pH5} value was 46% of the corresponding value for laboratory samples.

The field ENP values for the 0.79%-sulfur rock were 13% to 54% of the corresponding values for laboratory samples of similar sulfur content. The ratios of field to laboratory ENP were lowest for the 1.41%-sulfur rock, typically 5% or less than those determined in the laboratory.

Discussion

There were several differences between the conditions in the laboratory dissolution experiment and those in the field study. Laboratory particles were smaller than the average particle in the field, ranging from 0.053 mm to 0.149 mm in diameter, and therefore had a higher specific surface area. Due to the relatively uniform particle size, the available mineral surface area was roughly proportional to the amount of the mineral present. In contrast, the fraction of the rock surface area comprised of iron sulfide minerals in the field was most likely higher than that indicated by the sulfur content of 0.63%. Sulfide minerals comprised a disproportionately large fraction of the fine material the field, as indicated by the elevated sulfur content of this fraction (table 2). This material also had the highest specific surface area of the field rock. Therefore, iron sulfide minerals comprised a larger fraction of the field rock surface area than indicated by the sulfur content alone.

Hydrologic differences also existed. The volume of rinse water per unit mass rock yielded approximately 300 L per ton of rock per day of drainage in the laboratory, roughly three orders of magnitude greater than the yields of 0.27 to 0.38 L per ton of rock per day in the field. Furthermore, the flow of the laboratory rinse water through the solids was fairly uniform, whereas preferential flow was probable in the field setting.

Despite these differences there were numerous similarities between the field and laboratory results. As cited earlier, the variations of drainage pH and chemical mass release were qualitatively comparable in the two settings.
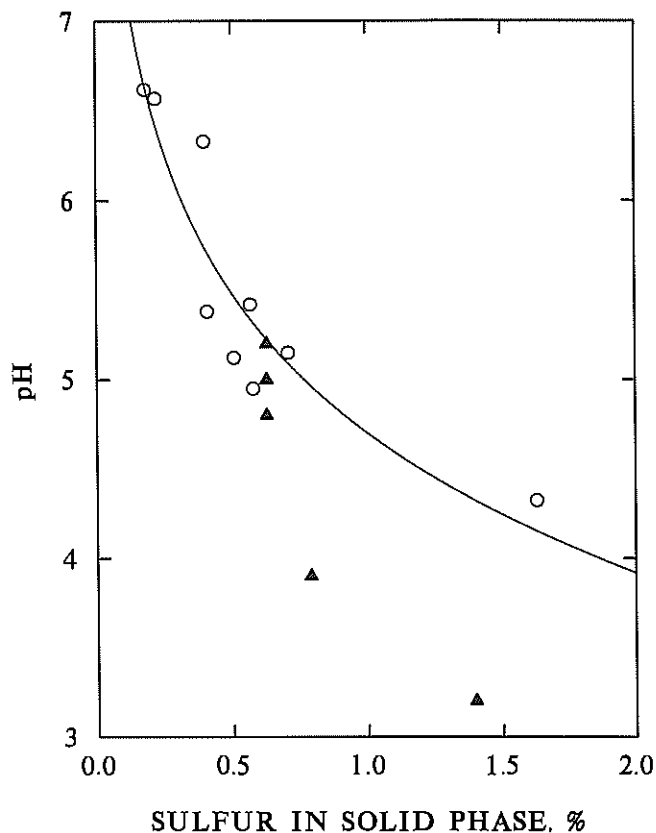

Figure 3. Comparison of recurrent minimum drainage pH in field (▲) and laboratory (○). Laboratory data represents drainage pH after 150 weeks of dissolution of Duluth Complex samples (Lapakko and Antonson 1993).

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Table 3. Comparison of field and laboratory release rates. Rates in moles per gram rock per second x 10^{-14}.

Sulfur, %	Field rate			Lab rates			Retardation factor			
	SO_4	Ca	Mg	SO_4	Ca	Mg	SO_4	Ca	Mg	Ave.
0.63[1] (pile 1)	3.9	2.5	0.86	[1]25	[1]6.7	[1]12	0.16	0.37	0.072	0.20
.63[1] (pile 2)	2.4	1.4	0.64	25	6.7	12	0.096	0.21	0.053	0.12
.63[1] (pile 3)	6.4	2.8	2.4	25	6.7	12	0.26	0.42	0.20	0.29
.79[2] (pile 6)	8.5	2.8	4.3	[2]26	[2]6.1	[2]12	0.33	0.46	0.36	0.38
1.41[3] (pile 5)	12	2.7	3.7	[3]66	[3]19	[3]21	0.18	0.14	0.18	0.17

[1] The arithmetic mean of average rates from samples with sulfur contents of 0.57%, 0.58%, and 0.71% (150 week period of record) was used for comparison with 0.63%-sulfur rock. Minimum pH values for these samples ranged from 4.82 to 5.38, as compared with 4.7 to 5.0 in the field.

[2] Rates were linearly extrapolated based on sulfur content using average rates from samples with sulfur contents of 0.71% and 1.16% (150- and 69-week periods of record, respectively). Minimum pH values for these samples ranged from 4.6 to 5.0, about 1 unit higher than the pH 3.7 minimum value for the field pile.

[3] The arithmetic mean of average rates from samples with sulfur contents of 1.40% and 1.44% was used (69-week period of record) for comparison with the 1.41%-sulfur pile. Minimum drainage pH for these samples ranged from 4.4 to 4.9, about 1.5 units higher than the minimum drainage pH for the field pile and and 1 unit higher than its recurrent minimum pH.

Table 4. Comparison of field and laboratory neutralization potentials.

S, %	pH 7	pH 6	pH 5	pH 4.5	pH 4	pH 3.5
FIELD NEUTRALIZATION POTENTIAL[1]						
0.63 (pile 1)	0.346	0.781	>1.059	>1.059	>1.059	>1.059
.63 (pile 2)	.179	.393	>.642	>.642	>.642	>.642
.63 (pile 3)	.442	1.254	>1.340	>1.340	>1.340	>1.340
.79 (pile 6)	.157	.172	.226	1.702	>2.074	>2.074
1.41 (pile 5)	.044	.044	.096	.130	.136	>1.889
RATIO OF FIELD ENP TO LABORATORY ENP						
0.63 (pile 1)	0.52	0.52	NAp	NAp	NAp	NAp
.63 (pile 2)	.27	.26	NAp	NAp	NAp	NAp
.63 (pile 3)	.66	.84	NAp	NAp	NAp	NAp
.79 (pile 6)	.54	.23	0.13	NAp	NAp	NAp
1.41 (pile 5)	.17	.056	<.056	<0.045	<0.044	NAp

[1] kg/mt $CaCO_3$
NAp Not applicable.

Quantitatively, the drainage from 0.63-percent sulfur rock in the laboratory approximated that in the field. However, pH of field drainages from the 0.79%- and 1.4%-sulfur rock were about 1 and 1.5 units, respectively, lower than the corresponding laboratory values. These field drainage pH values may have been lower due to a higher iron sulfide surface area than indicated by the sulfur content alone. The low rinse water to rock ratio in the field would also lend to increased H^+ concentrations.

Both the rates of mineral dissolution and subsequent reaction product transport probably contributed to the lower sulfate, calcium, and magnesium release rates (per unit mass) observed in the field. First, the larger field particles have a lower specific surface area (surface area per unit mass) than the smaller particles used in the laboratory. The lower surface area in the field would retard the sulfate, calcium, and magnesium release per unit mass rock, since both sulfide mineral oxidation and silicate mineral dissolution are surface reactions. The reaction environment in the field, where temperatures are colder, may also retard reaction rates. Limitation of sulfide oxidation by oxygen transport seems unlikely due to the small test pile size.

Limited transport of reaction products in the field also may have reduced rates of release. Hydrologic variables, which were not influential in the laboratory, could have contributed to this transport limitation. The relatively low flow in the field may have limited transport. This is supported by the observation that release rates in the field increased with flow. Preferential flow would limit the transport of reaction products from some rock surfaces. This would essentially reduce the amount of rock in the test piles that was actually contributing to the observed chemical release. The degree of transport in the field may also be limited by chemical precipitation of dissolution reaction products. In particular, the formation of gypsum might limit the rates of sulfate and calcium release. Gypsum formation was not a problem in the laboratory since the high rinse-water-to-solid ratio produced relatively low concentrations of sulfate and calcium in the drainages.

In addition to the larger particle size in the field, the low field ENP values may have been influenced by factors similar to those discussed regarding drainage pH. First, preferential flow in the field piles would reduce the amount of silicate minerals, which could contribute to acid neutralization. For example, if flow through the pile contacted only half the silicate minerals, the observed neutralization potential of the rock would be half the actual value for the entire pile. Second, if the fraction of rock surface area comprised of silicate minerals in the laboratory samples exceeded that in the test piles, the laboratory solids would be expected to neutralize acid more efficiently. Third, the ratio of available reactive surface area of sulfide minerals to that of silicate minerals present in the test pile rock may have been greater than that in the laboratory. This would be equivalent to increasing the sulfur content of rock in the laboratory. As was observed in the laboratory, neutralization potential tended to decrease as sulfur content increased.

More rigorous analysis of the recently compiled laboratory and field data is presently in progress at the Minnesota Department of Natural Resources. The data are also being used to aid development of a geochemical predictive model for acid mine drainage at the US Bureau of Mines Salt Lake City Research Center.

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