# PREDICTION OF ACID MINE DRAINAGE FROM DULUTH COMPLEX MINING WASTES IN NORTHEASTERN MINNESOTA[1]

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Abstract.  Ten Duluth Complex drill core samples, with sulfur contents ranging from 0.47 to 2.17 percent, were leached in a laboratory experiment.  The variation in sulfur content was due largely to fluctuations in iron sulfide content. Solids containing 0.8 percent sulfur or less produced neutral drainage while, with one exception, solids with sulfur contents of 0.92 percent or more produced acidic drainage.  The results indicated that acid production due to oxidation of sulfide minerals containing iron, such as pyrrhotite, increased linearly as the sulfur content increased. The acid consumption due to silicate mineral dissolution was relatively constant despite minor variations in the silicate mineralogy.  A sample containing 1.17 percent sulfur produced neutral drainage due to the buffering provided by a calcium carbonate content of three percent.  Leaching of a sample from a test stockpile indicated that the fine fraction of stockpile solids exerted a major influence on the drainage chemistry.  The pH range and temporal variation of drainage from solids containing 0.92 percent sulfur was similar to that from a test stockpile with a bulk sulfur content of 0.6 percent.  Analysis of the test stockpile solids indicated that particles smaller than 2.0 mm in diameter comprised about 12 percent of the stockpile mass and had a sulfur content of 1 percent.  The laboratory results suggest these small particles exert a major influence on stockpile drainage quality, most likely due to their elevated sulfur content and specific surface area.

## INTRODUCTION

The Duluth Complex, located in northeastern Minnesota, is an intrusive formation containing low-grade copper and nickel sulfides (Listerud and Meineke 1977).  These deposits comprise 25 percent of the United States' copper resource and the nation's largest nickel sulfide resource (Minnesota Environmental Quality Board 1980, Kingston et al. 1970).

Development of these resources would require open pits which will eventually fill and discharge water, possibly containing elevated concentrations of trace metals, to the environment (Thingvold et al. 1979).

Based on conceptual models, the open pits could produce an estimated 4 to 10 $km^2$ of waste rock stockpiles (Sturgess 1981; Veith 1978), which would generate an estimated runoff of 1.5 to 3.8 billion liters in a year of average precipitation (Hewett 1980).  Trace metal concentrations in runoff from waste rock stockpiles at the Erie Mining Company Dunka Mine were 10 to 10,000 times natural background levels of streams in the area (Eger et al. 1981). Since these metals have been shown to be toxic at low aqueous concentrations (United States Environmental Protection Agency 1976), means of mitigating the impacts of mining drainage will be required for these resources to be developed.

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The degree of mitigation required may be a function of the potential for trace metal and acid release from a given stockpile. This potential is dependent upon, among other factors, the composition of the stockpiled rock. Examining dissolution with respect to all chemical and mineralogical variables would, at best, be extremely complicated. Characterizing mine wastes with respect to these variables in the course of operations is also impractical. Consequently, a more simplistic course of experimentation, using sulfur content as the independent variable, was adopted.

The effect of sulfur content on the leaching of Duluth Complex mining wastes has been examined for a limited number of samples. Field tests were conducted on test stockpiles constructed of rock removed from a test shaft. Over a 6-year period, test stockpiles containing 0.8 and 1.4 percent sulfur produced acid leachate while piles containing 0.6 percent sulfur did not (Eger and Lapakko 1985). Subsequent data indicate the drainage pH has at times decreased below pH 5 at one of the four piles containing 0.6 percent sulfur. In shake flask tests, neutral leachate was generated by tailings containing 0.92 percent sulfur or less, while acidic leachate was generated by tailings with sulfur contents equaling or exceeding 2.65 percent (Natarajan and Iwasaki 1983).

The rate of metal sulfide oxidation has been reported to be directly proportional to the reactive sulfide mineral surface area available (Lapakko 1980; Nelson 1978; Sato 1960a, 1960b; Sato and Mooney 1960). In turn, the available surface area of nonporous solids is a function of the sulfide content of the rock, particle size, and the roughness of the surface. Since the copper and nickel content of mine wastes is small, the sulfur content is an indicator of iron sulfide minerals, which are of major importance due to their role in acid production.

Since other sulfides are present in limited quantities, their influence is diminished and to some extent uniform. By using uniformly small solids, the influence of particle size and host rock association of the iron sulfides is normalized. If the sulfides are liberated in small size fractions, the sulfur content will represent the available sulfide surface area, assuming specific surface area does not vary greatly among sulfide minerals of the same particle size. Since all the sulfide surface area is known to be available, acid production rates per unit sulfide surface area can be determined. Using this normalized value, the acid production rate can be extrapolated to mining wastes based on their available sulfide surface area. This extrapolation will allow appropriate mitigation based on the rock composition.

The use of sulfur content as the independent variable neglects the effects of many other variables, environmental as well as compositional, on the leaching of mine wastes. Although there is a given degree of compositional uniformity within an ore body, there are deviations from the norm. To accurately assess the leaching potential of mining wastes from a given body, a large number of samples must be analyzed. This implies the use of efficient and accurate laboratory techniques from which results can be extrapolated to operational conditions. This study involved examination of the leaching behavior of a small number of Duluth Complex samples with variable sulfur contents, and determination of the feasibility of extrapolating laboratory results to operational conditions.

## METHODS

### Materials

An experiment was conducted to examine the effect of solid phase sulfur content on the quality of drainage from Duluth Complex mining wastes. The sulfur content of the 11 samples examined ranged from 0.47 to 2.17 percent. Acid digestion (U.S. Bureau of Mines 1980) and subsequent analysis revealed typical solid phase copper and nickel contents of 0.13 to 0.23 and 0.05 to 0.09 percent, respectively (table 1). The samples were selected to approximate mining wastes, based on a 0.2 percent copper cutoff. Mine waste would, of course, be larger with a maximum diameter of approximately 45 cm for under-ground mines and 120 cm for open pits. Plagioclase, olivine, pyroxenes, and biotite were the predominant minerals, as determined by examination of polished thin sections with an optical microscope (table 2). Specific surface area was determined by single point BET nitrogen adsorption by A. U. Baes of the Soil Science Department at the University of Minnesota, St. Paul.

With one exception, the solids were MINNAMAX core samples which had been drilled from 1974 to 1977. The core samples had been crushed to minus 1/4 inch, placed into plastic bags, and stored inside 55-gal barrels at the MINNAMAX site near Babbitt, MN. Under the direction of Karl Smith, the samples were processed for experimental use at the Mineral Resource Research Center at the University of Minnesota. The plus 10-mesh fraction was selected for experimentation in order to minimize the amount of surface area exposed to oxidation while the samples had been stored after drilling. This fraction was stage crushed using a pulverizer and wet-screened to segregate the -100/+270 mesh fraction for use in laboratory tests.

The remaining sample (1.26 pct S) was collected from a test stockpile which was constructed in April 1977 at the MINNAMAX

Table 1.--Elemental composition of 11 Duluth Complex samples, values in weight percent.

| S | Cu | Ni | Co | Zn | S with FeS[1] | Fe | Ca | Mg | Na | K | Pct of total S bound by Fe |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 0.47 | 0.23 | 0.060 | 0.011 | 0.017 | 0.31 | 15.2 | 7.8 | 7.9 | 2.6 | 0.37 | 65 |
| .59 | .13 | .072 | .013 | .0070 | .44 | 11.5 | 11 | 7.1 | 3.1 | .27 | 75 |
| .80 | .19 | .067 | .011 | .010 | .66 | 13.7 | 9.8 | 6.6 | 3.0 | .42 | 82 |
| .92 | .091 | .049 | .014 | .016 | .83 | 24.6 | 8.0 | 11.8 | 2.2 | .42 | 90 |
| 1.17 | .23 | .082 | .011 | .015 | 1.0 | 16.3 | 14.6 | 10.5 | 1.4 | .42 | 85 |
| 1.24 | .19 | .066 | .012 | .013 | 1.1 | 15.4 | 6.8 | 10.1 | 2.3 | .42 | 91 |
| 1.35 | .23 | .086 | .018 | .011 | 1.2 | 18.4 | 9.4 | 7.3 | 2.4 | .30 | 87 |
| 1.87 | .17 | .088 | .021 | .011 | 1.7 | 19 | 9.6 | 8.7 | 7.5 | .86 | 92 |
| 2.01 | .20 | .055 | .012 | .020 | 1.9 | 19.6 | 5.3 | 5.1 | 2.2 | 1.10 | 93 |
| 2.17 | .20 | .078 | .010 | .027 | 2.0 | 8.5 | 1.7 | 2.9 | 2.6 | 1.83 | 93 |
| 1.26[2] | .55 | .20 | .018 | .014 | .97 | 18 | 8.0 | 8.0 | 2.7 | .44 | 77 |

[1]Calculated as the sulfur not bound by Cu, Ni, Co, or Zn assuming all trace metals were bound by sulfur in a 1:1 mole ratio of sulfur to metal.
[2]Sample from test pile.


Table 2.--Approximate modal compositions of Duluth Complex Samples.
    (By Tatiana Sabelin, Mineral Resources Research Center, University of Minnesota).

Mineralogy (%)

| PCT S | Olivine | Pyroxene | Plagioclase | Biotite | Opaque | Amphibole | Other | Calcite |
|---|---|---|---|---|---|---|---|---|
| 0.47 | 30 | 10 | 45 | 5 | 8 | -- | 2 | -- |
| .59 | 17 | 4 | 68 | 2 | 5 | -- | 4 | -- |
| .80 | 20 | 8 | 59 | 4 | 7 | -- | 2 | -- |
| .92 | 31 | 27 | 24 | 2 | 16 | -- | -- | -- |
| 1.17 | 19 | 15 | 28 | 2 | 8 | -- | 25 | 3 |
| 1.24 | 17 | 27 | 47 | 1 | 5 | -- | 3 | -- |
| 1.35 | 10 | 14 | 57 | -- | 9 | -- | 10 | -- |
| 1.87 | 18 | 4 | 57 | 2 | 10 | -- | 9 | -- |
| 2.01 | 7 | 15 | 59 | 6 | 13 | -- | -- | -- |
| 2.17 | 15 | 8 | 51[1] | 6 | 17 | -- | 3 | -- |
| 1.26[2] | 15 | 11 | 49 | 3 | 16 | 2 | 4 | -- |

[1]Includes plagioclase and quartz; of this total maybe as much as 1/3 to 1/2 is quartz.
[2]Sample from test pile.


site. The pile was constructed of rock mined during the development of a test shaft. When part of the test pile was removed in September 1982 a representative sample, weighing over 3 tons, was collected for analysis of particle size distribution, specific surface area, chemistry, and mineralogy (Lapakko et al. 1986). A subsample of stockpile material in the -100/+270 mesh fraction was collected for use in the experiments.

Leaching Procedure

Several techniques have been used in laboratory leaching of mining wastes (Caruccio 1986; Ferguson and Mehling 1986). The method used was based on the principle that sulfide minerals oxidize in the presence of atmospheric oxygen and water (Gottschalk and Buehler 1912; Caruccio et al. 1980). Samples (75 g) of -100/+270 mesh rock were placed into the upper segment, or reactor, of a two-stage filter unit and rinsed with 200-mL volumes of distilled deionized water. Seven of the solids were run in duplicate while single reactors were used for the remaining four solids (0.47, 0.59, 1.35, and 2.01 pct S). The rinse water was allowed to remain in contact with the solids for five minutes and filtered through a 0.45 micrometer filter. Between rinses the solids were kept in the upper segment and stored in a box to dry. A cover was placed about 3 cm above the upper edge of the box to allow drying of the solids and prohibit the input of airborn debris. A thermostatically

controlled heating pad was placed beneath the box to maintain a constant temperature. Water containers were placed in the box in an attempt to maintain a fairly constant humidity. Temperature and relative humidity in the box were monitored four to five times per week. The average temperature was $25^{\circ}$C with a standard deviation of $1.0^{\circ}$C, while the corresponding values for relative humidity were 56 and 9.1 percent.

At the beginning of the experiment, the solids were rinsed five times to remove oxidation products generated after crushing and wet sieving. After this initial washing the solids were rinsed weekly. Four rinses were used after one week and three rinses after two weeks. Two rinses were found to remove the majority of sulfate from the solids and were used in subsequent weeks.

The rinse water, or drainage, was analyzed for specific conductance, pH, sulfate, copper, nickel, cobalt, zinc, calcium, magnesium, sodium, and potassium. Specific conductance was analyzed using a Myron L conductivity meter, while a Radiometer 29 pH meter was used for pH analyses. Sulfate was analyzed using either the barium sulfate turbidimetric technique (APHA et al. 1975) or a Technicon autoanalyzer. Metals were analyzed with a Perkin Elmer 603 atomic absorption spectrophotometer. The experiments were conducted at the site previously leased by MINNAMAX, which is presently leased by Kennecott Minerals (fig. 1).

## RESULTS AND DISCUSSION

### Laboratory Data

Drainage pH generally decreased as the solid phase sulfur content increased and as the duration of leaching increased. The pH of drainage from solids containing less than 0.9 percent S was consistently above 6, while drainage from solids containing more than 1.3 percent S was typically below pH 6. Between 0.9 and 1.3 percent S was a transition zone. Drainage pH from one of the three transitional solids continuously remained above 7.5 (fig. 2). The drainage pH from the other two transitional solids was initially in the neutral range, but steadily decreased to about 4.2 where it plateaued. The tendency for drainage pH to decrease and level over time was observed with most solids, but the decrease was most pronounced with these transitional solids. These pH trends were the net result of acid production by the oxidation of iron sulfide minerals and acid consumption by the dissolution of silicate minerals.

The dissolution of iron sulfide minerals leads to the production of acid, as indicated by reaction 1 (Nelson 1978).
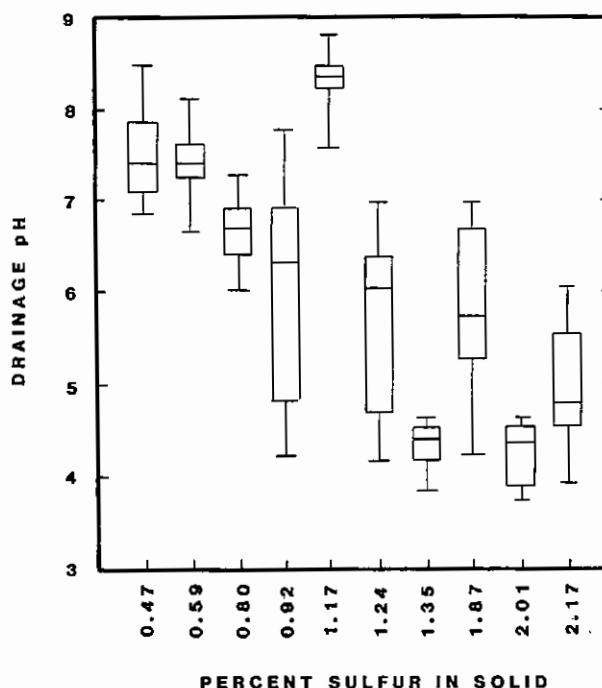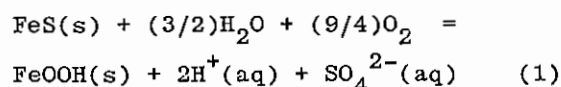


Figure 1.--Project site in northeastern Minnesota.



PERCENT SULFUR IN SOLID

Figure 2.--Drainage pH versus sulfur content of the solid phase. Horizonal lines represent 25, 50 and 75 per percentiles, as well as the minimum and maximum values during the entire experiment.

The iron sulfide oxidation may be

$$FeS(s) + (3/2)H_2O + (9/4)O_2 =$$

$$FeOOH(s) + 2H^+(aq) + SO_4^{2-}(aq) \qquad (1)$$

influenced by microbial activity (Natarajan et al. 1982) and galvanic interactions with other sulfide minerals (Natarajan and Iwasaki 1983), as well as other factors. The oxidation of sulfide to the hexavalent sulfur in sulfate does not contribute acid. The two moles of acid produced are the net result of the oxidation of ferrous iron

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and the subsequent precipitation of ferric iron, as lepidocrocite for example (Nelson 1978; Sung and Morgan 1980).

The rate of iron sulfide oxidation was reflected by the appearance of sulfate in solution. In an oxidizing environment, sulfate is the ultimate reaction product of sulfide oxidation. Over the aqueous concentration range observed in the laboratory samples, sulfate will remain in solution as opposed to precipitating.

The hypotheses that sulfate was the dominant oxidation product and was stable in solution were supported by the fact that sulfate concentrations in stored samples were constant over several months. If reduced sulfur species were present they would have oxidized over this period and increased the sulfate concentration. Similarly there was no decrease in sulfate concentration which would result if sulfate precipitated from solution. The fact that more than 90 percent of sulfate concentrations were less than 50 mg/L, with none exceeding 130 mg/L, further indicates that sulfate precipitation or adsorption was unlikely. Some sulfate, or other sulfide oxidation products, may have been adsorbed onto the solids in the reactor. However, the multiple rinses indicated that little sulfate was removed from the solids by distilled water after the two rinses.

Since sulfide was oxidized to sulfate and aqueous sulfate was stable, the rate of sulfide oxidation equals the rate of appearance of sulfate in solution at steady state. Since 82 to 93 percent of the sulfide present in these samples was bound by iron (table 1), oxidation of these iron sulfides was most likely the major sulfate source. Pyrrhotite is the predominant iron sulfide in the Duluth Complex (Bonnichsen 1972), and in these samples.

The rate of sulfate appearance was proportional to the mean sulfate concentration, since the rinse volumes were essentially equal, the mass of solids leached was constant at 75 g, and the rinse interval was constant. Mean concentrations from weeks 6 through 17 were used since a) sulfate concentrations during the initial 5 weeks were typically low and not representative of the sulfate release in general, and b) after the initial 17 weeks, the rinsing interval for some of the solids was extended beyond the standard duration of 1 week, which affected the rate of sulfate release. The weekly sulfate concentrations were fairly constant over this period, suggesting the oxidation of sulfide to sulfate had approached steady state. However, some of the solids subsequently generated sulfate concentrations which fluctuated from this narrow range. Although a steady-state condition may not have been reached for all solids, the sulfate data provide the best approximation of the sulfide

oxidation rate during the initial stage of experimentation. The phrase "initial apparent steady-state period" best describes this phase.

The rate of sulfide oxidation, as reflected by mean sulfate concentrations, correlated highly with the solid phase sulfur content. The percent sulfur in the solid phase accounted for 77.6 percent of the variation in the sulfide oxidation rate ($r = 0.776$). The r value increased to 0.963 when two outlying data points at 1.35 and 1.87 percent S were ignored.

The degree of correlation for the entire data set increased when variations in specific surface area among the solids were taken into account. The anomalous sulfate concentrations, from the solids containing 1.35 and 1.87 percent S, were higher than predicted by the linear model describing the eight remaining points (fig. 3). Although all solids were in the −100/+270 mesh size fraction, limiting particle diameter to the range of 0.053 to 0.149 mm, there were minor variations in specific surface area. The specific surface areas, as determined by BET nitrogen adsorption, of the two anomalous solids were 65 to 80 percent higher than the average of the remaining solids. To account for this variation, the available sulfide surface area per gram solid was estimated as the product of the sulfur content and the specific surface area. The correlation coefficient was 0.846 for the linear variation of sulfate release rate with respect to this available sulfide surface area. This dependence is consistent with a surface reaction dominating the sulfide oxidation.

The r value increased to 0.962 when the data for the solid containing 1.17 percent sulfur was omitted. Sulfate release from this solid was lower than predicted by the linear model describing the remaining nine data points. This was the only sample containing calcium carbonate, which may have been responsible for the elevated surface area of this sample. The elevated pH of the drainage from this sample may also have inhibited the rate of sulfide oxidation (Nelson 1978).

Some of the acid generated was consumed, or neutralized, by the dissolution of silicate minerals. Plagioclase, olivine, and pyroxenes are the silicate minerals which comprise the majority of the host rock. The dissolution of anorthite, which is a member of the plagioclase solution series, is represented by the following reaction (Stumm and Morgan 1981).

$$CaAl_2Si_2O_8(s) + 2H^+(aq) + H_2O =$$
$$Ca^{2+}(aq) + Al_2Si_2O_5(OH)_4(s) \qquad (2)$$
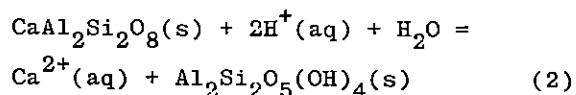
The dissolution of these minerals in laboratory experiments has often been reported as parabolic with respect to time. Initially the hydrogen ions in solution are
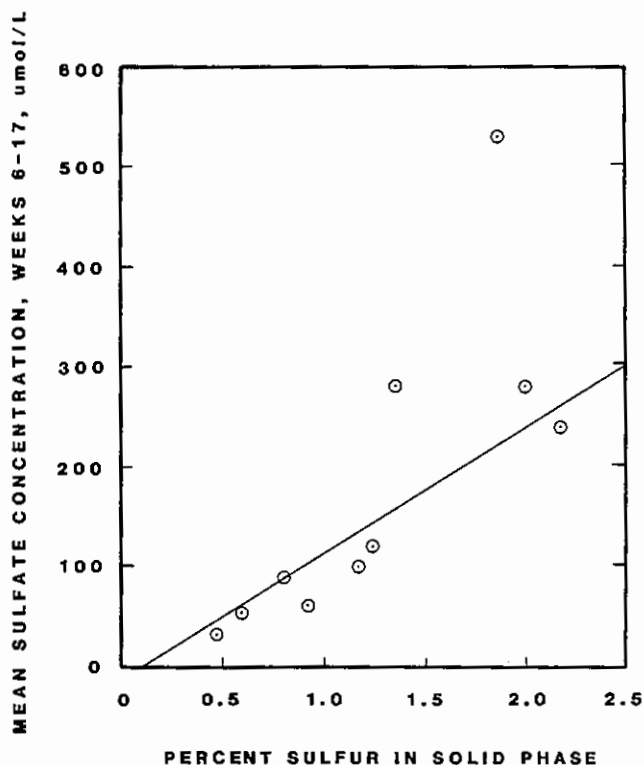
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Figure 3.--Sulfide oxidation rate, as represented by mean sulfate concentration, versus percent sulfur. Points at 1.35 and 1.87 percent S were excluded from the regression analysis which determined line shown.

rapidly and reversibly exchanged with alkalai ions on the mineral surface (Holdren and Berner 1979, Busenberg and Clemency 1976). The rate of release subsequently decreases, eventually becoming linear with respect to time (White and Classen 1979, Busenberg and Clemency 1976). The rate of dissolution during this phase is relatively slow (Siegel 1981, White and Classen 1979, Busenberg and Clemency 1976).

Dissolution of the silicate minerals was rapid enough to neutralize the acid generated by iron sulfide oxidation in the solids containing 0.8 percent S or less. The pH of drainage from these solids remained above 6. For the solids containing at least 1.35 percent S, reflecting the higher content of iron sulfides, the acid production rapidly overwhelmed the buffering capacity. The drainage from the solids containing 0.92 and 1.24 percent S was initially neutral but gradually decreased, indicating that the rate of iron sulfide oxidation ultimately exceeded the dissolution rate of the silicate minerals present.

The balance of acid production by iron sulfide oxidation and acid consumption by silicate mineral dissolution is illustrated semiquantitatively by comparing sulfate concentrations with the sum of calcium and magnesium values. The release of one mole of sulfate represents the production of two moles of acid, while the release of one mole of calcium or magnesium represents the consumption of two moles of acid (reactions 1 and 2, respectively). Initially the sum of calcium and magnesium concentrations exceeded the sulfate concentration, thus the ratio of the sum to sulfate was greater than one. This indicates that the rate of acid consumption by silicate mineral dissolution initially exceeded the rate of acid production by iron sulfide oxidation. This is borne out by the fact that the drainage pH was initially in the neutral range (fig. 4).

The rate of acid production gradually increased over the first 18 weeks, but the rate of acid consumption increased concomitantly and neutralized the acid produced. After 20 weeks the acid production increased dramatically and the silicate mineral buffering was overcome. At this time, the ratio of the sum of calcium and magnesium concentrations to sulfate concentration dropped below a value of one and pH decreased, ultimately reaching 4.5.
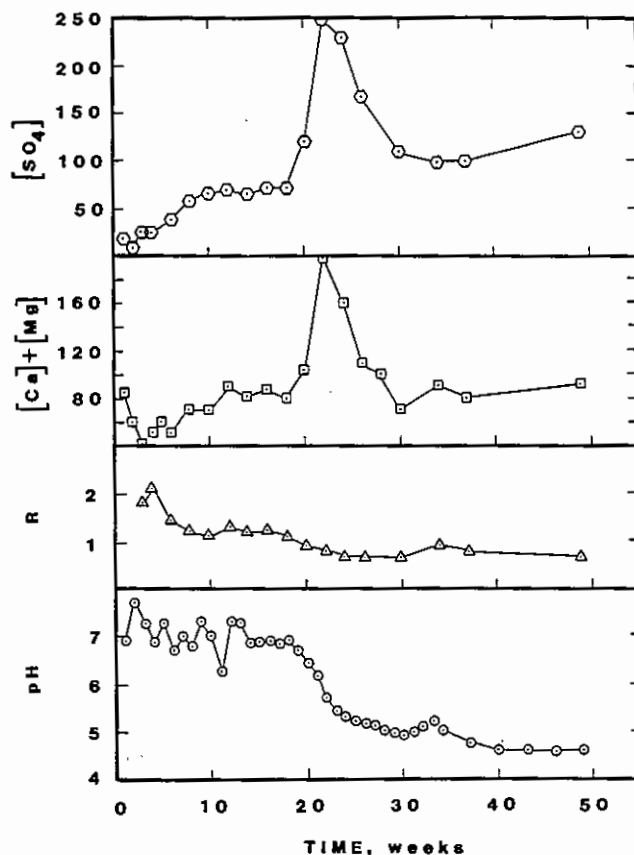


Figure 4.--Drainage from 0.92 percent S solids versus time. Concentrations are in micromoles per liter, and R is the ratio of the sum of Ca and Mg concentrations to the sulfate concentration.

The buffering supplied by the silicate minerals was fairly uniform among the solids, despite differences in silicate mineralogy (table 2). Apparently these differences had little effect on the overall rate of silicate mineral dissolution. The sample containing 1.87 percent S did exhibit slightly greater buffering and calcium release, and its composition is being examined in greater detail.

The uniformity in buffering among the silicate minerals is particularly important in predicting drainage pH. The primary copper-nickel mineralization of the Duluth Complex occurs as disseminated sulfides in a troctolitic-gabbroic series of rocks which intrudes an anorthositic and felsic series of older rocks (Weiblen and Morey 1975). About 90 percent of the host rock is composed of silicate minerals, predominantly plagioclase, olivine, and pyroxenes (Stevenson et al. 1979). If the buffering supplied by these minerals is somewhat uniform, the drainage pH will be controlled by the rate of acid generation due to oxidation of iron sulfides. Pyrrhotite is the predominant form of these iron sulfides (Bonnichsen 1972). Determination of the oxidation rate based on sulfur content will allow prediction of the acid-producing potential of mining wastes based on their sulfur content. Investigation of a wider variety of rocks will lend further insight into the influence of the various silicate minerals on buffering, as well as other factors.

In contrast to the general uniformity in buffering, the solid containing 1.17 percent S, despite exceeding the sulfur content of one of the acid solids, produced drainage pH values which were typically above pH 8. Mineralogical analysis of this solid indicated a calcium carbonate content of about 3 percent. Dissolution of this calcium carbonate was reflected by calcium concentrations in drainage from this solid which were three to five times those in drainage from all but one other solid. Due to its rapid dissolution, the small amount of calcium carbonate was able to provide more buffering than the silicate minerals, which typically comprised more than 80 percent of the solids. This further emphasizes the slow kinetics of, and limited buffering by, dissolution of the silicate minerals.

The effectiveness of the silicate mineral buffering may have been further limited by the physical factors in the reaction environment. Iron sulfides can be oxidized by the oxygen and water vapor present in the air, while silicate dissolution due to the presence of oxygen and water vapor is negligible. The acid resulting from iron sulfide oxidation may contact only the silicate minerals in the immediate vicinity of the iron sulfides. Dissolution of these silicates can leave a less reactive solid phase such as kaolinite (reaction 2; Busenberg 1978),

which may further inhibit the transport of acid to other mineral surfaces and further limit buffering. This inhibition of buffering reactions may contribute to the increased metal recovery associated with the "resting" of leach columns and dumps in metallurgical work.

In a submerged reaction environment, such as that in batch reactors, the acid generated could be readily transported to silicate mineral surfaces via the aqueous medium. As a result, batch reactor data may overestimate the buffering available in an environment subject to wet-dry cycling, such as stockpiles and unsubmerged mine walls.

As drainage pH decreased, trace metal release increased, and this increase was quantified by linear regression analysis of the base 10 logarithm of metal concentration versus pH. For the log copper concentration versus pH plot, the slope was -1.11 (r=-0.944, n=38); and the corresponding slope for nickel was -0.99 (r=-0.902, n=40). Similar trends were observed for cobalt and zinc. This increase in trace metal concentrations further magnifies the problems of acid drainage. The slopes indicate that as pH decreases one unit, copper and nickel concentrations will increase by about an order of magnitude.

Comparison of Laboratory and Field Data

Laboratory data on the test stockpile solids suggested that the smaller particles had a marked influence on the stockpile drainage quality. Particles smaller than 2.0 mm in diameter comprised about 12 percent of the total stockpile mass. The weighted average sulfur content of these particles was 1.0 percent as compared with 0.6 percent S for the bulk rock. The sulfur content of these particles tended to increase as particle size decreased, with particles of diameter less than 0.053 mm having a sulfur content of 1.86 percent (Lapakko et al. 1986).

The pH range generated in the laboratory was quite close to that observed for the test stockpile drainage in 1982, when the solids were collected (fig. 5). Comparison with field data from subsequent years is somewhat tenuous since the stockpile was dismantled, and the rock was divided among six different test plots. The diameter of the particles used in the laboratory tests was in the range of 0.053 to 0.147 mm, and particles in this size range comprised only about 3 percent of the stockpile mass. The sulfur content of the particles was 1.26 percent, as compared with 0.6 percent for the bulk rock. The laboratory pH was slightly lower than that observed in the field. This suggests that the particle size range dominating the stockpile drainage chemistry may be slightly larger than that used in
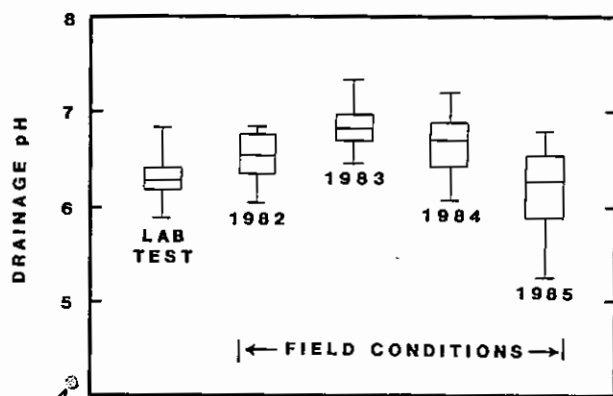
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Figure 5.--Drainage pH in laboratory
  compared to field values.  Note:
  In September 1982 the test pile from
  which these laboratory solids were
  taken was dismantled and placed into
  test plots.  Field data subsequent to
  1982 are from these plots.

the laboratory, assuming similar sulfide
oxidation rates in the two settings.  The
field rates may have differed from labora-
tory rates due to fluctuations in ambient
temperature and humidity, or inhibited by
restricted oxygen transport.  If so,
another size range may have been the
dominant influence on the stockpile
drainage chemistry.  Nonetheless, drainage
pH from the 0.053 to 0.147 mm particles in
the laboratory was quite close to that
from the test stockpile in the field.

Particle size is important for
several reasons.  As previously mentioned,
sulfur content increased as particle size
decreased.  Sulfide minerals are softer
than the silicate minerals and, therefore,
are more prone to breakdown.  Consequent-
ly, they tend to concentrate in the
smaller size fractions.  Secondly, the
surface area of the fines is relatively
high since specific surface area increases
as particle size decreases.  Since the
rate of iron sulfide oxidation was propor-
tional to the available surface area, the
rate of sulfide oxidation per unit mass of
these particles is magnified.

Thirdly, sulfide minerals in the
small size fractions are most likely to be
free rather than occurring as interstitial
or included minerals. For Duluth Complex
samples, the diameter at which sulfides
are liberated from the host rock has been
estimated as 0.074 mm (Weiblen and Morey
1976); mineral beneficiation studies
suggest a value of about 0.2 mm (Vifian
and Iwasaki 1968). In particles larger
than this critical size, a large fraction
of the total sulfide surface area would be
protected by the host rock, and therefore
unavailable for reaction. Leaching tests
run with larger particles tended to yield
lower rates of sulfide oxidation and acid
production.  For example, the leaching of

minus 10 mesh (diameter less than 2 mm)
tailings containing 0.92 percent S produced
neutral leachate (Natarajan and Iwasaki
1983), while 0.053-mm to 0.147-mm solids of
the same sulfur content produced acidic
drainage in the present study.  As dis-
cussed earlier, the submerged reaction
environment in the shake flask leaching of
tailings may also have increased buffering
efficiency by permitting acid contact with
a larger silicate surface area.

The pH of drainage from test stock-
piles also decreased as the sulfur content
increased. The most recent annual median pH
values from piles containing 0.6 percent S
were in the range of 5.25 to 6.5. The
corresponding pH values for stockpiles with
sulfur contents of 0.8 and 1.4 percent were
about 4.25 and 3.6, respectively. These
values suggest that stockpiles containing
0.6 percent S are near the boundary of acid
production. In the laboratory this boundary
occurred between 0.80 and 0.92 percent S.
This indicates that the laboratory tests
simulate the leaching behavior of stock-
piled solids having a bulk sulfur content
roughly 68 to 79 percent of the laboratory
solids. This "effective sulfur content" of
stockpiled rock will, however, vary depend-
ing on the particle size distribution of
the stockpiled solids.  Additional study on
the effects of both composition and
particle size on drainage quality are
required in order to more accurately
extrapolate laboratory results to stock-
piles in the field.

The laboratory data also closely
simulated other aspects of stockpile
drainage chemistry, indicating that the two
reaction regimes were similar. The varia-
tion of pH over time was similar in both
cases. The drainage pH in the field tended
to decrease over time, reflecting the
decrease in buffering by silicate mineral
dissolution.  For the stockpiles containing
0.6 percent S the pH decrease over time was
gradual, but for the higher sulfur piles
the decrease was relatively rapid (fig. 6).
After the initial pH decrease, the drainage
pH from the high sulfur piles was fairly
stable.  In the laboratory tests, a rapid
pH decrease and subsequent period of
relatively stable pH was also observed for
samples with relatively high sulfur con-
tents.  The ratio of the sum of calcium and
magnesium release to sulfate release traced
pH fluctuations in the field as in the
laboratory.

Metals concentrations increased as pH
decreased in both laboratory and field
settings. The slopes for the log metal
versus pH relationships, however, were
steeper in the laboratory than in the
field. As previously mentioned, the labora-
tory data for the 0.92 percent solids
indicated slopes of -1.11 for copper and
-0.99 for nickel. Using the annual median
values for metal concentration and pH for
all stockpile drainages, the slopes for
copper and nickel were -0.76 and -0.66,
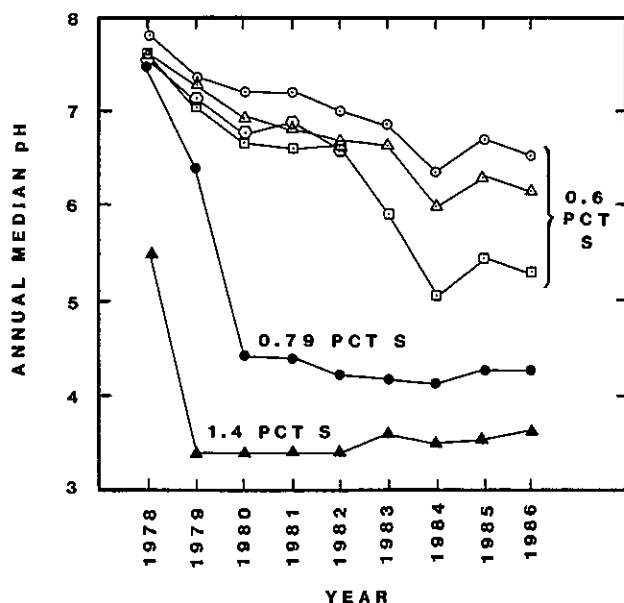respectively (Eger and Lapakko 1985).

Figure 6.--Annual median pH values of test
   stockpile drainage from 1978 to 1986
   (modified from Eger and Lapakko 1985).

The pH decrease and concomitant trace
metal concentration over time were ob-
served in drainage from an operational
scale stockpile at the LTV Dunka site near
Babbitt, MN. A drainage denoted as Seep 1
flows from 1.5 million tons of stockpiled
Duluth Complex rock removed from an open
pit taconite mine. The stockpile was
constructed in 1976 and drainage has been
monitored since this time. From 1976 to
1986 the annual median pH decreased from
7.3 to 5.4 and annual median trace metal
concentrations increased by factors of
roughly 5 to 20 (Minnesota Department of
Natural Resources 1988).

CONCLUSIONS

Ten Duluth Complex samples, obtained
from core drilled by MINNAMAX exploration,
were leached in a laboratory experiment.
The number of samples was extremely small
relative to the vast extent of the Duluth
Complex. This experiment represents the
starting point for examination of a wider
compositional range, as well as the
influence of other variables on the
dissolution reactions.

The sulfur content of the samples
examined ranged from 0.47 to 2.17 percent,
the variation due largely to variable
content of iron sulfides, in the form of
pyrrhotite. Solids with sulfur contents
of 0.8 percent or less produced neutral
drainage while, with one exception, solids
containing at least 0.92 percent S pro-
duced acidic drainage. The rate of iron
sulfide oxidation, and the attendant acid
production, increased linearly with sulfur

content, consistent with first order depen-
dence on available sulfide surface area.
The rate of acid neutralization, which was
controlled by silicate mineral dissolution,
was relatively constant among the samples
despite variations in the relative amounts
of plagioclase, olivine, and pyroxenes
present. This uniformity in neutralization
rates adds credence to the possibility of
predicting acid producing potential based
on the sulfur content of Duluth Complex
mining wastes, since they will be comprised
primarily of these silicate minerals. At
the 0.92 percent sulfur content, the rate
of acid production due to iron sulfide
oxidation exceeded the dissolution rate of
silicate minerals which comprised 80 to 92
percent of the solid phase.

A solid containing 1.17 percent S did
not produce acidic drainage since it
contained about 3 percent calcium carbon-
ate, or calcite, which is rare in the
Duluth Complex (Stevenson et al. 1979).
Unlike the silicate minerals, the calcite
was able to neutralize the acid produced by
the iron sulfide oxidation. The influence
of this small mineralogical anomaly on
drainage quality emphasizes the importance
of examining the leaching behavior of
numerous samples. Only then can leaching be
described in terms of more general char-
acteristics, such as sulfur content.

The laboratory leaching results were
consistent with field observations on the
variation of pH with respect to percent
sulfur and time. The range of 0.8 to 0.92
percent sulfur in the laboratory appeared
to be similar to a bulk sulfur content of
approximately 0.6 percent for stockpiled
rock. The drainage chemistry of stockpiles
appears to be strongly influenced by the
small particle size fraction, in which the
softer sulfide minerals are concentrated.
In conjunction with an elevated specific
surface area, this produces a high sulfide
surface area available for chemical
reaction.

The equilibration period for the
drainage pH is variable, and the experi-
mental time frame must allow for steady
state to be reached. Under field condi-
tions, the drainage pH from three gabbro
stockpiles containing 0.6 percent S has
decreased for nine years, indicating that
equilibrium has not yet been reached.
Drainage pH from a stockpile containing 0.8
percent S approached apparent equilibrium
after two years, while about one year was
required for 1.4 percent S rock.

Although the pH dependence for test
stockpiles was not as strong as that
observed in the laboratory, trace metal
concentrations increased as pH decreased.
Projections based on the first year of
drainage from these stockpiles would have
underestimated subsequent release of acid
and trace metals by at least two orders of
magnitude (Eger and Lapakko 1985). The
decrease in pH and attendant increase in
trace metal concentrations was also

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observed in drainage from operational scale stockpiles. This temporal pH decline and trace metal concentration increase underlines the importance of allowing adequate reaction time for steady state to be approached.

## Acknowledgements

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