Effects of Dissolution Time and Particle Size on Kinetic Test Results

Kim Lapakko
Jennifer Haub
David Antonson

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

This paper was presented at The 1998 SME Annual Meeting & Exhibit in Orlando Florida, March 9-11, 1998. Several typographical errors have been corrected in this version.

ABSTRACT

Kinetic tests results are influenced by methodological variables, including test duration and mine waste particle size. Some samples tested produced neutral drainage in kinetic tests for more than two years prior to drainage acidification. The potential for long "lag times" can be assessed based on the mine waste mineralogy. The lag time duration can be estimated using this mineralogy in conjunction with dissolution rates observed in the kinetic tests. The influence of particle size on the drainage quality is dependent on the variation of the availability of acid-producing and acid-neutralizing minerals with particle size.

INTRODUCTION

Kinetic tests are commonly used as tools to predict whether or not abandoned hard rock mine wastes will generate acidic drainage. This information is then used to design appropriate mine waste management methods and provide for their financing. Several tests have been used for this purpose (Bradham and Caruccio 199 1, Brodie et al. 199 1, Lapakko 1993, Lapakko et al. 1995). The concept on which such tests were developed was to provide an accelerated simulation of the dissolution of mine wastes in the field. Thus, if a sample generated non-acidic (acidic) drainage in the laboratory, it was concluded it would generate non-acidic (acidic) drainage in the field. This approach is becoming more sophisticated, with test results being used as input to models for more refined predictions.

There are, of course, significant differences between the laboratory tests and actual dissolution of abandoned mine wastes, and these discrepancies introduce uncertainty to prediction. Two key differences are the time frame used for dissolution tests and, with waste rock, particle size subjected to testing. First, the duration of laboratory testing must be short relative to the field situation, in which mine waste drainage quality over a period of decades and centuries is the concern. This is an obvious necessity and must be considered in dissolution test design and data interpretation. Second, there are potential compositional differences between samples tested in the laboratory and those which will be generated in the operation. To some extent, the compositional variation in the field can be accounted for. Dissolution tests can be conducted on tailings generated in bench tests and on drill core samples which represent the chemical and mineralogic compositional ranges of wastes to be generated (Lapakko 1990). The particle size distribution of tailings generated in thew tests will likely provide a reasonable approximation of that in the operation phase. For waste rock, however, it is unlikely that simulation of particle size will be possible for pre-operational testing.

The objectives of this paper are to 1) provide examples which demonstrate uncertainty introduced by kinetic test duration and the influence of waste rock particle size on drainage quality and 2) provide methods for designing test and interpreting their results to provide more accurate empirical predictions. The cases presented provide examples of drainage quality prediction uncertainty introduced kinetic tests are viewed in isolation from other data, and are not intended to imply that use of kinetic test data in drainage quality prediction is of no benefit. To the contrary, such testing provides valuable information in the drainage quality prediction process.

BACKGROUND

Acid Production

The potential for generation of acidic mine waste drainage is the primary water quality concern, and this potential is largely determined by mine waste composition. Iron sulfide minerals such as pyrite, marcasite, and pyrrhotite are often present in mine wastes, and their oxidation leads to the production of acid (reactions 1, 2). The rate of iron sulfide oxidation by oxygen is proportional to the available sulfide surface area (Nelson 1978) and dissolved oxygen concentration (McKay and Halpern 1958, Nelson 1978) with only a slight dependence on pH (Nelson 1978). However, Nordstrom (1982) indicates that "as pH decreases to 4.5, ferric iron becomes more soluble and begins to act as an oxidizing agent." As pH decreases further, bacterial oxidation of ferrous iron becomes the rate limiting step in the oxidation of pyrite by ferric iron (Singer and Stumm 1970), which is the only significant oxidizing agent in this pH range (Nordstrom 1982, Singer and Stumm 1970, Kleinmann et al. 1981). It should be noted that with this mechanism, the rate of pyrite oxidation is independent of the pyrite surface morphology and available surface area (Stumm and Morgan 1981).

Acid Neutralization

Calcium carbonate or magnesium carbonate minerals such as calcite, dolomite, ankerite, or magnesite ($CaCO_3$, $CaMg(CO_3)_2$, $CaFe(CO_3)_2$, $MgCO_3$ respectively) present in sulfidic mine wastes will dissolve neutralize some or all of the acid produced (reactions 3-6). For systems open to the atmosphere, reactions 3 and 5 are dominant above pH 6.4, while reactions 4 and 6 are dominant below pH 6.4 (Drever, 1988). Calcium and magnesium carbonate mineral dissolution rates are relatively rapid and, therefore, these are the most effective minerals for neutralizing acid. However, dissolution rates do vary among these carbonates. Rauch and White (1977) and Busenberg and Plummer (1986) reported that the rates of magnesium carbonate and calcium-magnesium carbonate dissolution are substantially slower than that of calcium carbonate.

$$\begin{aligned}&FeS_2(s) + (5/2)H_2O + (15/4)O_2(g) = \\ &FeOOH(s) + 4H^+(aq) + 2SO_4^{2-}(aq)\end{aligned} \tag{1}$$

$$\begin{aligned}&FeS(s) + (3/2)H_2O + (9/4)O_2(g) = \\ &FeOOH(s) + 2H^+(aq) + SO_4^{2-}(aq)\end{aligned} \tag{2}$$

$$CaCO_3(s) + H^+(aq) = HCO_3^-(aq) + Ca^{2+}(aq) \tag{3}$$

$$CaCO_3(s) + 2H^+(aq) = H_2CO_3(aq) + Ca^{2+}(aq) \tag{4}$$

$$\begin{aligned}&CaMg(CO_3)_2(s) + 2H^+(aq) = \\ &2HCO_3^-(aq) + Ca^{2+}(aq) + Mg^{2+}(aq)\end{aligned} \tag{5}$$

$$\begin{aligned}&CaMg(CO_3)_2(s) + 4H^+(aq) = \\ &2H_2CO_3(aq) + Ca^{2+}(aq) + Mg^{2+}(aq)\end{aligned} \tag{6}$$

$$\begin{aligned}&FeS_2(s) + (5/2)H_2O + (15/4)O_2(g) + 4CaCO_3(s) = \\ &FeOOH(s) + 2SO_4^{2-}(aq) + 4Ca^{2+}(aq) + 4HCO_3^-(aq)\end{aligned} \tag{7}$$

Acid can also be neutralized by dissolution of silicate minerals such as anorthite and forsterite, but their dissolution rate and associated rate of acid neutralization is very slow relative to that of carbonate minerals. These minerals dissolve more rapidly as pH decreases, however, the rate of acid production must be relatively slow for this dissolution to maintain drainage pH in the neutral range (Lapakko 1988).

Lag Time to Drainage Acidification

Concurrent pyrite oxidation (reaction 1) and calcite dissolution (reaction 3) is presented in reaction 7. Mine waste drainage will not acidify as long as the rate of acid neutralization equals or exceeds the rate of acid production. This is to a large degree dependent upon the relative surface areas of iron sulfide and calcium/magnesium carbonate minerals available for reaction.

To simplify discussion, three types of iron sulfide bearing mine waste are qualitatively defined based on their relative neutralizing mineral contents and the consequent temporal variation of drainage pH in predictive dissolution tests. A Type I mine waste contains virtually no neutralizing minerals. The acid-producing nature of these mine wastes can be readily identified in dissolution tests since their drainage will become acidic almost immediately. A Type 2 mine waste contains a small amount of neutralizing minerals, the dissolution of which will initially neutralize the acid produced as a result of iron sulfide oxidation. If the neutralizing minerals are depleted while iron sulfides remain and are oxidizing, the drainage will acidify. The period during which neutralizing minerals are being depleted prior to drainage acidification has been called the lag time. Lag times of 20 weeks (Lapakko 1988) to as long as 1.5 to 2 years of dissolution (Lapakko 1990b) have been reported, and longer periods are possible.

A Type 3 mine waste contains a substantial amount of neutralizing minerals. The acid produced as a result of iron sulfide oxidation will be neutralized for an extended period. If the neutralizing minerals are depleted while iron sulfides remain and are oxidizing, the drainage will acidify. If the iron sulfide minerals are depleted while reactive neutralizing minerals are yet present, the drainage will remain neutral. In addition, precipitates may gradually accumulate over time on the surfaces of both iron sulfide minerals and acid neutralizing minerals. Such coatings will inhibit the reactivity of the minerals on which they form. If coatings form on the acid-neutralizing minerals and iron sulfide oxidation continues, drainage from the waste will become acidic. If coatings form on the iron sulfide minerals and the rate of iron sulfide oxidation is adequately inhibited, the drainage will not acidify. At present it is not possible to quantitatively model the formation of coatings with the accuracy required to predict the effects on drainage quality.

As is clear from the previously cited Type 2 examples, a very long dissolution test would be required to identify the acid producing character of mine wastes with a substantial calcium/magnesium carbonate mineral content. Such a test would be conducted until the drainage acidified or until the iron sulfide minerals present became unreactive. The decrease in this reactivity would be indicated by a decrease in sulfate release.

In summary, laboratory dissolution tests can readily simulate the acidic nature of drainage from tailings which contain an abundance of acid-producing minerals and a scarcity of acid-neutralizing minerals (Type 1 mine wastes). However for tailings (or other mine wastes) in general, there is considerable uncertainty in using solid-phase composition or short-term laboratory dissolution tests to predict the quality of drainage from tailings after a mine has been abandoned. In order to simulate the long-term quality of drainage from some wastes, dissolution tests would have to be continued for years. Such durations would introduce more than minor inconvenience into the time table for mine permitting.

Effects of Particle Size

Particle size reduction is often a necessity for predictive dissolution testing of waste rock. Unfortunately the quality of drainage, in particular drainage pH, from small waste rock particles may not accurately simulate the quality of drainage from operational scale waste rock. Iron sulfide oxidation and calcium/magnesium carbonate mineral dissolution are responsible, respectively, for the generation and neutralization of acid. The rates of these reactions are generally proportional to the surface area of the respective mineral available for reaction. This surface area is a function of the amount of mineral present, its grain size, extent of liberation (extent to which it is liberated from the rock matrix), and surface morphology (e.g. surface "roughness").

As rock particle size is reduced, the balance of available iron sulfide and calcium/magnesium carbonate mineral surface areas may change due to changes in the relative amounts of these minerals present or in their specific surface areas. The relative amounts of the minerals present may change due to the preferential breakage of certain rock components. Changes in the relative amounts of surface areas may occur due to preferential reduction in grain size (i.e. one grain breaks down more readily than another) or in preferential liberation of one mineral from the rock matrix. As a result, particle size reduction may result in preferential enhancement of acid-producing or acid-neutralizing mineral surface areas. This in turn will affect the relative rates of acid generation and acid neutralization and, consequently, drainage pH. Thus, it is possible that acid would be produced by one particle size fraction of a given rock, and not by another, due to variations in relative contents and availabilities of iron sulfide and calcium/magnesium carbonate minerals.

METHODS

One tailings sample and one waste rock sample were subjected to dissolution testing. Both tailings and waste rock samples were subjected to weekly rinses with distilled-deionized water, and stored in a controlled temperature and humidity room between rinses. Additional information on the solid-phase characteristics of the tailings, as well as analytical methods is presented in Lapakko (1992). Additional information on waste rock sample RK4 is presented in Lapakko (1994) and Lapakko et al. (1995).

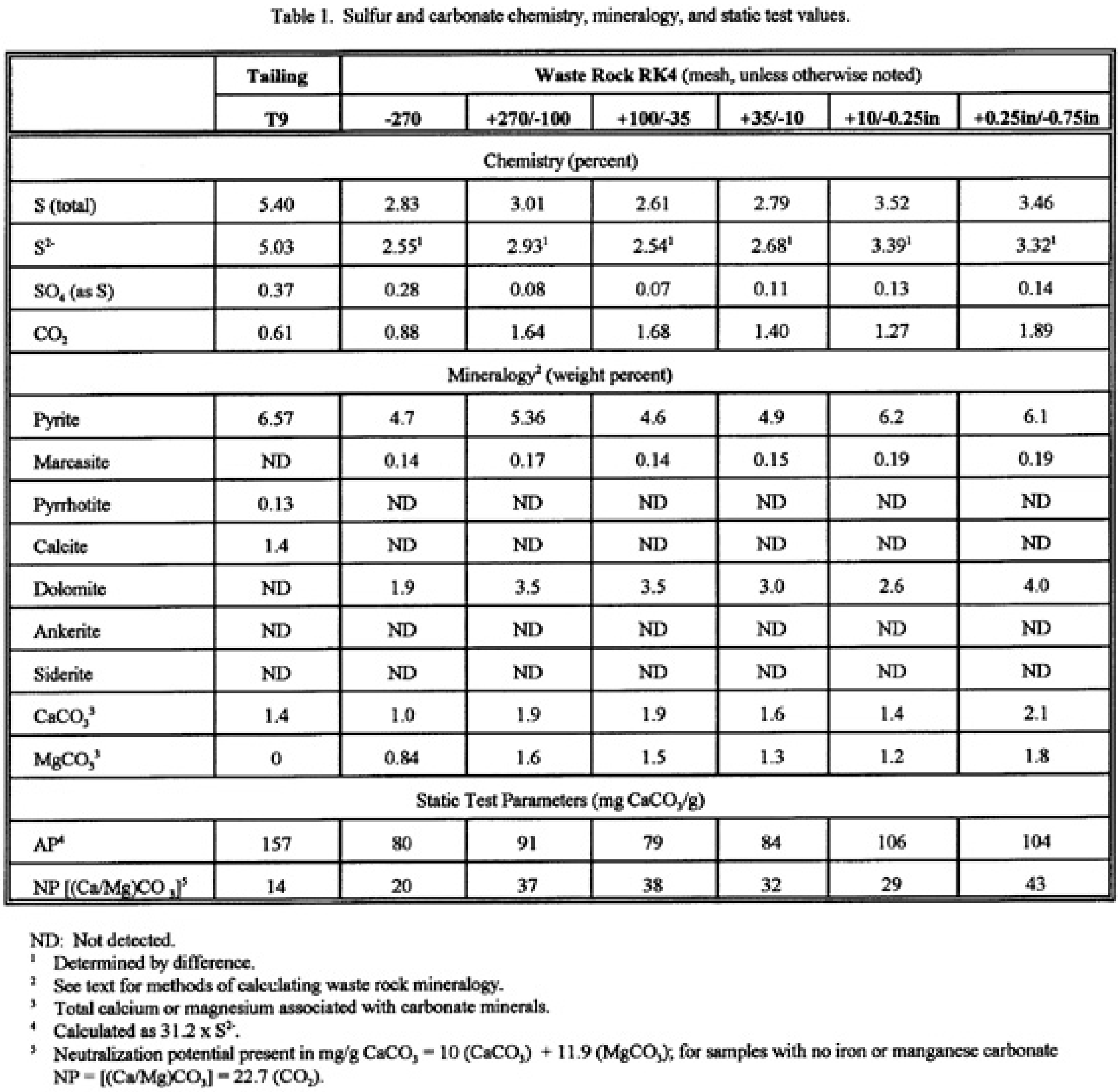

Table 1. Sulfur and carbonate chemistry, mineralogy, and static test values.

	Tailing	Waste Rock RK4 (mesh, unless otherwise noted)					
	T9	-270	+270/-100	+100/-35	+35/-10	+10/-0.25in	+0.25in/-0.75in
Chemistry (percent)							
S (total)	5.40	2.83	3.01	2.61	2.79	3.52	3.46
S^{2-}	5.03	2.55[1]	2.93[1]	2.54[1]	2.68[1]	3.39[1]	3.32[1]
SO_4 (as S)	0.37	0.28	0.08	0.07	0.11	0.13	0.14
CO_2	0.61	0.88	1.64	1.68	1.40	1.27	1.89
Mineralogy[2] (weight percent)							
Pyrite	6.57	4.7	5.36	4.6	4.9	6.2	6.1
Marcasite	ND	0.14	0.17	0.14	0.15	0.19	0.19
Pyrrhotite	0.13	ND	ND	ND	ND	ND	ND
Calcite	1.4	ND	ND	ND	ND	ND	ND
Dolomite	ND	1.9	3.5	3.5	3.0	2.6	4.0
Ankerite	ND	ND	ND	ND	ND	ND	ND
Siderite	ND	ND	ND	ND	ND	ND	ND
$CaCO_3$[3]	1.4	1.0	1.9	1.9	1.6	1.4	2.1
$MgCO_3$[3]	0	0.84	1.6	1.5	1.3	1.2	1.8
Static Test Parameters (mg $CaCO_3$/g)							
AP[4]	157	80	91	79	84	106	104
NP [(Ca/Mg)CO_3][5]	14	20	37	38	32	29	43

ND: Not detected.
[1] Determined by difference.
[2] See text for methods of calculating waste rock mineralogy.
[3] Total calcium or magnesium associated with carbonate minerals.
[4] Calculated as 31.2 x S^{2-}.
[5] Neutralization potential present in mg/g $CaCO_3$ = 10 ($CaCO_3$) + 11.9 ($MgCO_3$); for samples with no iron or manganese carbonate NP = [(Ca/Mg)CO_3] = 22.7 (CO_2).

ND: Not detected.

1. Determined by difference.
2. See text for methods of calculating waste rock mineralogy.
3. Total calcium or magnesium associated with carbonate minerals.
4. Calculated as 31.2 X S^{2-}
5. Neutralization potential present in mg/g $CaCO_3$ = 10 ($CaCO_3$) + 11.9 ($MgCO_3$); for samples with no iron or manganese carbonate NP = [(Ca/Mg)CO_3] = 22.7 (CO_2).

Lag Time Example: Tailings Sample T9

Materials: The tailings sample, identified as T9, was from a hydrothermal quartz-carbonate gold deposit and was tested as received. The tailing particles were quite fine, with over 98 percent finer than 0. 149 mm and about 70 percent finer than 0.053 mm. T9 contained 5.03 percent sulfide, which was present largely as pyrite (table 1). The acid production potential inferred by the sulfide content was 157 mg/g $CaCO_3$ (5.03 x 31.2 = 157). The only carbonate mineral present was calcite, and its content (1.4%) implied a neutralization potential of 14 mg/g $CaCO_3$.

Dissolution Test Procedure: A 75-g sample of tailings (as received) was placed into the upper segment, or reactor, of a two-stage filter unit. The unit was similar to that depicted in Lapakko (1994b), except the standpipe and 0.45-micron filter were removed. Samples were rinsed weekly with 200 mL distilled-deionized water, to remove mineral dissolution products. The water was added slowly with a burette, to minimize solids disturbance, and allowed to drain overnight through the mine waste sample into the receiving flask of the two-stage unit.

Between rinses the solids were retained in the reactors and stored for further oxidation within individual compartments in a box. A thermostatically controlled heating pad was placed beneath the box to control temperature. The box was stored in a small room equipped with an automatic humidifier and dehumidifier, to maintain a stable range of humidity. During the 15 1 -week experiment temperature and relative humidity were monitored a total of 538 times, typically three to four times a week, using a Taylor wet-bulb/dry-bulb hygrometer. The average weekly temperatures ranged from 21.7 to 29.0^0C, with an average of 25.8^0C and a standard deviation of 1.5^0C (n=148). The average weekly relative humidities ranged from 42 to 80%, with an average of 54% and a standard deviation of 6.7% (n=148).

The volume of rinse water, or drainage, was determined by weighing the lower stage (receiving flask) of the reactor. pH and specific conductance were determined directly in the lower stage of the reactor, after which a 20 mL sample was taken for analysis of alkalinity (if pH exceeded 6.30) or acidity. The remaining sample was then filtered for subsequent analysis for metals and sulfate. Samples taken for metal analyses were acidified with 0.2 mL AR Select nitric acid (Mallinckrodt) per 50 mL sample.

Drainage Analysis: An Orion SA 720 pH meter equipped with a Ross combination pH electrode (8165) was used for pH analysis, and a Myron L EP conductivity meter was used to determine specific conductance. Alkalinity and acidity were analyzed using standard titration techniques (American Public Health Association et al. 1992). Sulfate was analyzed using an HF Scientific DRT-100 nephelometer for the barium sulfate turbidimetric method (American Public Health Association et al. 1992). Metals samples collected through week 51 were analyzed using ICP. Subsequent metal samples were analyzed for calcium and magnesium only using a Perkin Elmer 603 atomic absorption spectrophotometer in the flame mode.

Influence of Waste Rock Particle Size

Materials: The waste rock, identified as RK4, was an adularized-pyritized mudstone and was separated into six separate size fractions for testing (-270 mesh ($d \leq 0.053$ mm), +270/400 mesh ($0.053 < d \leq 0.149$ mm), +100/-35 mesh ($0.149 < d \leq 0.500$ mm), +35/4 0 mesh ($0.500 < d \leq 2.000$ mm), +10 mesh/-0.25 in ($2.000 < d \leq 6.35$ mm), +0.25/-0.75 in ($6.35 < d \leq 19.05$ mm)). Size fractions were separated by subjecting rock samples (150 - 200 g) to 15 minutes on a ro-tap apparatus loaded with U.S. standard mesh sieves. (Due to a missing 10 mesh sieve of compatible size, the - 10/+ 12 mesh was separated from the -1/4-inch/+12 mesh fraction by hand sieving.) After the separation, the various size fractions were wet sieved by placing approximately 150 g of solid on the plus size sieve and rinsing it repeatedly with tap water, agitating the rock while rinsing. When the water ran clear, the rock was rinsed with distilled water and then oven dried at about 38^{0}C. The drying times for the various fractions ranged from one to three days. Portions of each size fraction were retained for dissolution testing to assess the effect of particle size on waste rock dissolution.

A -100 mesh sample of the rock was analyzed for both chemistry and mineralogy. The sulfide content of this sample was 2.82 percent, most of which was present as pyrite (5.16%) and marcasite (0. 16%). The only carbonate mineral present was dolomite, at a concentration of three percent. The individual size fractions were analyzed for sulfide and sulfate content and evolved carbon dioxide. It was assumed that the ratios of sulfide content (calculated as the difference between total sulfur and sulfur present as sulfate) to the content of pyrite and marcasite did not vary as a function of particle size. Similarly it was assumed that the ratio of carbon dioxide evolved to dolomite was constant among particle sizes. These ratios were then used to calculate the pyrite, marcasite, and dolomite contents of the individual size fractions.

The individual size fractions of RK4 were also subjected to microscopic analysis, in an attempt to describe the relative surface areas of acid-producing and acid-neutralizing minerals. These analyses revealed that both the sulfide and carbonate minerals occurred with quartz in veinlets. However, the sulfide veinlets were "relatively open and porous" as opposed to the "tight" veinlets containing carbonate minerals. This suggests that in larger rock particles, the sulfide minerals would be accessible to air and water and, therefore, be available for oxidation and acid production. In contrast, the tight structure of the carbonate veinlets would limit the reactivity of the carbonate minerals present in larger rock particles.

Dissolution Test Procedure: The -270,+270/-100, and +100/-35 mesh fractions were leached with the apparatus and methods used for the T9 tailings sample. For larger size fractions (+35/-10 mesh, +10 mesh/-0.25 inch, and +0.25/-0.75 inch) a 1-kg mass was placed into a clear cylindrical acrylic reactor. The reactor measured 4.0 inches in diameter, 7.5 inches in height, and was equipped with a 1/8-inch outlet port and a cover with a 1/8-inch vent hole. The solids rested on a glass fiber filter placed on the bottom of the reactor.

At the start of the experiment (week 0) the solids were rinsed between four and seven times to remove reaction products which had accumulated since the samples were rinsed during sieving. The rinse water was analyzed for specific conductance to provide an indicator of the decreasing masses of oxidation products removed from the solids. Prior to each of the subsequent weekly rinses, which extended over 134 weeks, the reactors were weighed to determine the moisture retained. A 400-mL volume of distilled-deionized water was used to rinse the three larger size fractions. The drainage was analyzed on site to determine pH, alkalinity (if pH ≥ 6.3) or acidity, and specific conductance. Samples taken for sulfate and metals analyses were filtered through a 0.45-micron filter. Metals were acidified with 0.2 mL

AR Select nitric acid (Mallinckrodt) per 50 mL sample.

Between rinses the solids were stored in the reactors in a room in which temperature and humidity were controlled. The smaller reactors were stored in the same box used to store the tailings reactors. For the larger reactors, a thermostatically controlled heating mat was placed onto each of two shelves and covered with a piece of perforated tag board. Each of the larger reactors was supported 3.8 cm (1.5 inches) above the tag board by a pair of wooden spacers. The humidity was maintained within a stable range with an automatic humidifier/dehumidifier. Temperature and relative humidity were monitored three to four times weekly. The mean weekly temperatures for the three smaller particle sizes and three larger particle sizes were 24.2^0C and 24.4^0C, respectively. The corresponding relative humidity values were 57% and 54%. The corresponding n values were 131 and 127. It should be noted that, based on the weekly weights and the presence of moisture on the inside walls of the covered reactors, it was assumed that the relative humidity was near 100%.

Between week 0 and week 1 the reactors were left uncovered and weighed on a daily basis to determine the variation in water retained over time. Due to the wide discrepancy of drying among reactors, it was determined that the covers be left on the reactors between rinses, except for reactors containing the -270 fractions, which would not drain under wet conditions. The water remaining on top of these solids was pipetted from the reactor and added to the drainage before analysis. The percentage of the total volume decanted from the -270 mesh fraction was approximately 39%.

<u>Drainage Analysis:</u> Drainage analyses for pH, alkalinity, acidity, and specific conductance were conducted in the same manner as for the T9 tailings samples. Prior to week 16, sulfate was determined at the MN DNR laboratory using an BF Scientific DRT-100 nephelometer for the barium sulfate turbidimetric method (APHA et al. 1992). For week 16 through 33, determinations were made using ICP at Midland Research Center. Subsequently, sulfate concentrations were determined at the Minnesota Department of Agriculture using a Technicon AA2 automated colorimeter. Calcium and magnesium were determined with a Perkin Elmer 603 atomic absorption spectrophotometer in flame mode through week 33. Subsequent determinations were made at the Minnesota Department of Agriculture using a Varian 400 SPECTRAA.

RESULTS

The results presented demonstrate certain features of kinetic test design and interpretation which can introduce error into the conclusions reached regarding whether or not mine wastes will produce acidic drainage. The examples are presented from the viewpoint that kinetic test results are evaluated in absence of other relevant data. This, of course, should never be done. Indeed, static test data on the solids used in the examples strongly suggests they are acid producing. Although that may be true for these solids, it is conceivable that the same kinetic test problems could arise with solids that static tests do not identify as acid producers. This could result due to errors introduced by assumptions inherent in static testing or in the measurement made in static tests (Lapakko 1994a).

<u>Lag Time</u>

Sample T9, with an NP[(Ca/Mg)CO_3] of 14 kg $CaCO_3$/t and an AP of 156 kg $CaCO_3$/t, is consistent with the Type 2 profile described in the introductory section. The pH of drainage from the T9 tailings was in the approximate range of 7.7 to 8.1 during the initial 100 weeks of the experiment. At this time drainage pH began to decline, dropping below pH 6.0 after 122 weeks and ultimately reaching pH 3.45 after 151 weeks (figure 1). Alkalinity concentrations followed a similar trend.

Sulfate concentrations generally increased throughout the experiment, indicating an increasing rate of iron sulfide oxidation and consequent acid production (figure 1).

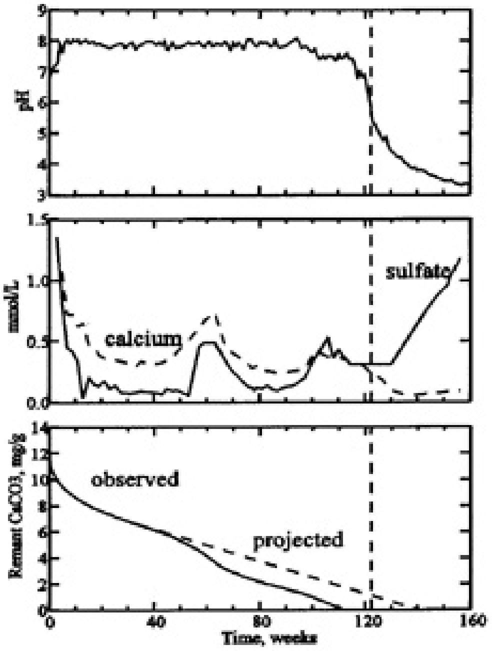

Figure 1. At week 122, pH decreased below 6.0. At approximately this time calcium concentrations decreased below those of sulfate indicating that the rate of acid neutralization was lower than that of acid production. Cumulative calcium release indicated the calcite originally presented was depleted at week 112.

Anomalously high sulfate concentrations were observed between weeks 50 and 65. The relative humidity was also high during this period and apparently accelerated the rate of sulfide oxidation (Morth and Smith 1966, Hammack 1987, Borek 1994). The elevated sulfate concentrations after week 130, when drainage pH was in the range of 3.4 to 4.4, were roughly eight times those typical of the earlier phase of the experiment, when drainage pH was near neutral. The elevated sulfate concentrations near the end of the experiment were probably due to increased biologically mediated ferric iron oxidation of the sulfide minerals as pH decreased below 4.0 (Nordstrom 1982, Singer and Stumm 1970, Kleinmann et a]. 1981). The rate of chemical oxidation may have increased also, although the extent of this increase was most likely slight relative to that of biological oxidation (Nordstrom 1982).

In contrast, calcium concentrations in the drainage generally decreased throughout the experiment. This decrease was particularly pronounced as the drainage pH declined (figure 1), suggesting that the calcium carbonate initially present had been depleted or rendered unreactive at week 122. The calcium release at this time was calculated as 11 millimoles, which is consistent with the depletion of the 10.5 millimoles of calcite initially present. At this time, less than eight percent of the total sulfur initially present in the sample had been depleted. The remaining iron sulfides (mostly pyrite) continued to produce acid, of which only a small fraction was neutralized, and the drainage pH decreased. The calcium and magnesium present in the drainage indicate the relatively small fraction of acid neutralized during this phase was apparently due to dissolution of feldspar and mica, which comprised about 40% of the sample.

Lapakko (1990a) presented a method of using short term kinetic test data to project if and when kinetic test drainage would acidify. Such estimation, if accurate, would allow extrapolating short term data over a longer time frame and, thus, shorten the test duration required to determine long-term drainage quality. The accuracy of this method was tested using rates of sulfate and calcium release observed over the first 30 weeks (the short term) in conjunction with the initial solid-phase sulfide and carbonate content. It was assumed that the rates would remain constant over time and that all pyrite and calcite present was available for reaction. This approach indicated that the NP[(Ca/Mg)CO_3] would be depleted in 146 weeks, and that substantial pyrite would remain at this time. This prediction agreed reasonably well with the drainage acidification observed after 122 weeks (figure 1). The actual time to depletion was shorter than that projected due to two periods during which calcium release was faster than the assumed constant rate. These periods occurred around week 60 and 110 (figure 1).

The good agreement between the estimated time to drainage acidification and that observed suggests that this method can be applied to address the question of lag time duration. Despite the accuracy of the method in this case, a sound understanding of the assumptions involved is necessary to apply it to mine wastes in general. The estimation assumes all calcium and magnesium carbonate minerals, and only these minerals, will dissolve to neutralize acid. This implies all of these carbonate minerals will be available for reaction. Since this is unlikely to be true for waste rock (in which carbonate minerals may occur interstitially or as inclusions, and therefore be unavailable for reaction), the method is most applicable to tailings, in which the carbonate minerals present are likely to be liberated. It further assumes that the dissolution rates of these minerals will be constant. This assumption ignores the formation of precipitate coating on carbonate mineral surfaces. Although these coatings are known to form, and inhibit mineral dissolution, knowledge of their formation in mine wastes is inadequate to quantify their influence on drainage quality. Such coatings are less likely to inhibit dissolution of small carbonate grains as opposed to large mineral grains. Thus, this method is appropriate for extrapolating short-term kinetic data on tailings to longer time frames.

Long term dissolution tests can reduce the uncertainty associated with predicting precipitate coating formation on sulfide and carbonate mineral surfaces and the influence of these coatings on mine waste drainage quality. Testing operational size waste under field conditions provides the best simulation of the environmental behavior of the mine waste. Long term laboratory testing provides the next best approximation.

Particle Size

Rock sample RK4 provides an excellent example of the influence of particle size on waste rock drainage quality, and the resulting uncertainty which must be addressed in waste rock drainage quality prediction. The drainages from the two largest size fractions of RK4 were acidic, while the pH of drainage from the smaller size fractions typically ranged from 7 to 8 (figure 2). The release rates of sulfate from the larger particles exceeded that of calcium plus magnesium (figure 3). This indicates that, for the larger particles, the rate of sulfide oxidation exceeded the rate of dolomite (the only calcium/magnesium carbonate mineral present) dissolution and, consequently, the drainages acidified. In contrast, the rate of sulfide mineral oxidation for the smaller particles was less than the rate of carbonate mineral dissolution, therefore these drainages remained in the slightly basic range. (It should be noted that the method presented in the "Lag Time" results predicts that these solids will eventually produce acidic drainage.)

Sulfate release rates further indicate that rates of sulfide oxidation for the larger particles were faster than those for the smaller particles. It should be noted that release from the -270 mesh fraction may have been limited by the fact that all of the rinse water was not transmitted through the solids. This may have resulted in incomplete removal of reaction products. Secondly, the fine nature of these solids, in combination with the moisture retained, may have limited the transport of oxygen through the solids. This would, in turn, limit the rate of sulfide oxidation.

Although the larger particles contained more pyrite and calcium/magnesium carbonates that the fine fraction, there was no consistent variation in these mineral contents as a function of particle size (table 1). More specifically, the ratio of acid-producing minerals to acid-consuming minerals in the large fractions was not larger than that in the fine fractions. This indicates that the lower drainage pH in the large particles was not due to an abundance of pyrite relative to dolomite.

This suggests the differences in drainage pH were the result of sulfide and carbonate mineral availability. Both the sulfide and carbonate minerals in RK4 occurred in veinlets, very possibly along fracture planes. However, the sulfide veinlets were "relatively open and porous" and, therefore, were accessible to air and water even in the larger particles. That is, the available sulfide surface area was relatively constant among the size fractions examined. In contrast, the carbonates were present in "tight" veinlets. The available carbonate mineral surface area in the larger particles was apparently limited by this mode of occurrence. As a result, the dissolution of carbonates in the larger particles was inhibited to the extent that they could not dissolve fast enough to neutralize the acid produced by the oxidation of iron sulfides. The acidic conditions apparently gave rise to bacterial mediation of the sulfide mineral oxidation, thereby accelerating the oxidation rate. In the smaller particle size fractions, a greater extent of the carbonate mineral surface area was available for reaction. Consequently, the carbonate mineral dissolution was adequately rapid to neutralize the acid produced by the iron sulfide mineral oxidation.

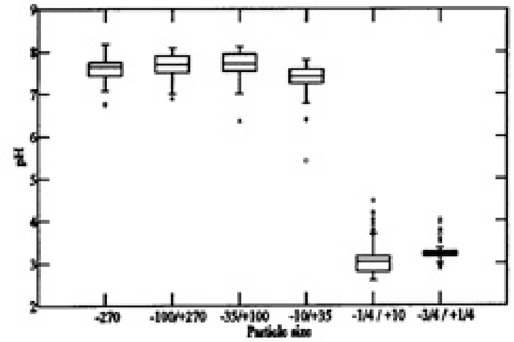

Figure 2. The drainage pH from the two largest size fractions was acidic, while that from the four smaller size fractions was slightly basic.

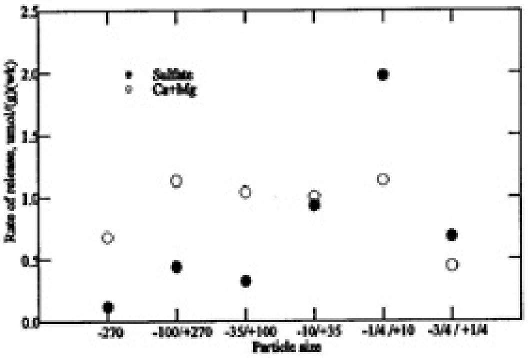

Figure 3. For the two largest solids, the release rate for sulfate exceeded that for the sum of calcium and magnesium. This indicates the rate of acid production (by iron sulfide oxidation) exceeded the rate of acid neutralization (dolomite dissolution). This is consistent with the observed acidic pH values. Sulfate release from the larger particles exceeded that from smaller particles.

Physical factors associated with the finer size fractions may have enhanced the interaction of acid generated and alkaline components present. Reduction of particle size decreases the distance between sulfide and carbonate mineral grains. Consequently, there is more intimate contact between carbonates and sulfides, and carbonate mineral surfaces are more likely to contact and neutralize acid. The increased moisture retention by finer particles may have further enhanced the interaction of acidic and alkaline components by providing a transport medium. For example, acid generated at sulfide mineral surfaces can diffuse through the water to reach calcium carbonate surfaces and be neutralized. These factors allow neutralization reactions to occur more or less continuously.

In contrast, with larger particles neutralization reactions would occur only if sulfide grains and calcium/magnesium carbonate grains were adjacent or when rinse water was added. For example, the +35/40 fraction produced neutral drainage from week I to week 30, when the moisture content in the cell was 12.9 percent. However, at week 0 when the solids were essentially dry, a drainage pH of 3.92 was produced. During the 30-week experiment, the moisture content of the +35/40 fraction was roughly 2.5 times values observed for the larger particle size fractions which produced acidic drainage.

Furthermore, with the more intimate contact of sulfide and carbonate mineral contact and elevated moisture content, acid is more likely to be neutralized before acidic microenvironments develop to a great extent. This in turn would inhibit bacterial acceleration of oxidation rates. Elevating the pH near sulfide minerals also enhances the precipitation of iron oxyhydroxides on the sulfide mineral surfaces, thereby inhibiting the rate of oxidation.

Clearly, waste rock particle size can have a profound influence on drainage quality. At present it is difficult, if not impossible, to quantitatively determine the influence of particle size on drainage quality. However, detailed description of sulfide and calcium/magnesium carbonate abundances and modes of occurrence will provide a sound qualitative indicator of this influence. It is important to note that while, with this sample, drainage pH decreased with increasing particle size, the opposite trend might occur with another rock type.

SUMMARY

Tailings sample T9 produced circumneutral drainage for 120 weeks and at week 121 the drainage pH dropped below 6.0, eventually reaching pH 3.45 at week 151. The decline in drainage pH coincided with die depletion of calcite from the sample, as calculated from the initial calcite content and the measured calcium release in the drainage. Thus, the quality of drainage generated in short term dissolution experiments may not accurately simulate drainage quality generated by mine wastes over a longer time.

The rates of sulfate, calcium, and magnesium release over the first 30 weeks of the experiment, in conjunction with the AP and NP[$(Ca/Mg)CO_3$] of the tailing were used to reasonably predict that, and when, the drainage would acidify. The approach used provides a first-cut estimate of whether drainage will become acidic (NP depleted before AP) or remain basic (AP depleted before NP).

Drainage pH for large particles was lower than that from fine particles. The pyrite grains in the large particles were fine and available for oxidation and the consequent acid production. The carbonate mineral occurred in "fight" veins and their reactive availability was limited. Consequently, their rate of dissolution was too slow to neutralize the acid produced. As particle size was reduced, the carbonate mineral veins were broken up and the reactive surface area increased. As a result, the carbonate minerals in the finer particle size fractions neutralized the acid produced, and the resultant drainage was mildly basic. It must be noted that this dependence of drainage quality on particle size will not hold for all types of waste rock. In general, drainage pH mill be determined by the variation of the relative abundance of iron sulfide and carbonate mineral surface areas with particle size. This variation can be qualitatively assessed by detailed mineralogic analysis of the iron sulfide and calcium/magnesium carbonate surface areas in various particle size fractions of the rock.

In summary, kinetic tests provide valuable data for predicting the acidic nature of mine waste drainage. With any tests, deviations from the conditions simulated are inevitable and introduce uncertainty. To reduce this uncertainty, the factors controlling acid production and acid neutralization must be understood. This understanding is essential to the design of kinetic tests and meaningful interpretation of their results. Included in a kinetic testing program must be rigorous analysis of the mine waste, with a focus on the abundance and availability of iron sulfide and calcium/magnesium carbonate minerals. Testing must account for the variation of these parameters with particle size. The data generated must allow for determination of the reaction rates of these minerals. Both solid-phase characteristics and drainage quality must be considered in the analysis of test result, which may require extrapolation of short-term results to a longer time frame.

ACKNOWLEDGEMENTS

Dissolution of the T9 tailings was part of a larger study funded by the Minnesota Minerals Coordinating Committee and the MN DNR Division of Minerals. The particle size experiment was part of a study funded by the US Environmental Protection Agency.

REFERENCES

American Public Health Association, American Water Works Association, Water Environment Federation. 1992. Standard Methods for the Examination of Water and Wastewater. 18th edition. American Public Health Association, Washington, DC.

Borek, S.L. 1994. Effect of humidity of pyrite oxidation. In Environmental Geochemistry of Sulfide Oxidation, ACS Symposium Series No. 550. C.N. Alpers and D.W. Blowes (eds.). American Chemical Society, Washington, DC. p. 3144.

Brodie, M.J., Broughton, L.M., Robertson, A.M. 1991. A conceptual rock classification system for waste management and a laboratory method for ARK prediction from rock piles. In Proceedings Second Annual Conference on the Abatement of Acidic Drainage. Montreal, Quebec, Canada, September 16-18, 1991. p. 119-135.

Bradham, W. S., Caruccio, F. T. 199 1. A comparative study of tailings analysis using acid/base accounting, cells, columns, and soxhlets. In Proc. of the Second International Conference on the Abatement of Acidic Drainage, V. 1, CANMET, Montreal, Quebec, Canada. p. 157-173.

Busenberg, E., Plummer, L.N. 1986. A comparative study of the dissolution and crystal growth kinetics of calcite and aragonite. U.S. Geol. Surv. Bull. 1578. p. 139-168.

Drever, J.I. 1988. The geochemistry of natural waters: Prentice Hall, Englewood Cliffs, New Jersey, 437 p.

Hammack, R.W. 1987. Pyrite oxidation under unsaturated conditions part 1: Abiotic oxidation. In Proceeding: Billings Symposium on Surface Mining and Reclamation in the Great Plains and American Society for Surface Mining and Reclamation. Billings, MT. Montana State University Reclamation Research Unit Report No. 8704. p. 289-295.

Kleinmann, R. L. P., Crerar, D. A., Pacelli, R. R. 1981. Biogeochemistry of acid mine drainage and a method to control acid formation. Mining Eng. March 198 1.

Lapakko, KA. 1988. Prediction of acid mine drainage from Duluth Complex mining wastes in northeastern Minnesota. In Mine Drainage and Surface Mine Reclamation. v. 1. Mine Water and Mine Waste. Proceeding 1988 Mine Drainage and Surface Mine Reclamation Conference. BuMines IC 9183. p. 180-190.

Lapakko, KA. 1990a. Regulatory mine waste characterization: A parallel to economic resource evaluation. In Proceedings Western Regional Symposium on Mining and Mineral Processing Wastes, F. Doyle (ed.), Society for Mining, Metallurgy, and Exploration, Inc., Littleton, CO. p. 31-39.

Lapakko, KA. 1990b. Solid phase characterization in conjunction with dissolution experiments for prediction of drainage quality. IQ Proceedings Western Regional Symposium on Mining and Mineral Processing Wastes, F. Doyle (ed.), Society for Mining, Metallurgy, and Exploration, Inc., Littleton, CO. p. 81-86.

Lapakko, KA. 1992. Characterization and static testing of ten gold mine tailings. In Proceeding 1992 American Society for Surface Mining and Reclamation Meeting. Duluth, MN, June 14-18,1992. p. 109-119.

Lapakko, KA. 1993. Evaluation of tests for predicting mine waste drainage pH: Report to the Western Governors' Association. Minnesota Department of Natural Resources, Division of Minerals, St. Paul, MN. 76. p. plus appendices.

Lapakko, KA. 1994a. Evaluation of neutralization potential determinations for metal mine waste and a proposed alternative. In Proc. International Land Reclamation and Mine Drainage Conference and Third International Conference on the Abatement of Acidic Drainage, v. 1. United States Department of the Interior, Bureau of Mines Special Publication SP 06A-94. p. 129-137.

Lapakko, KA. 1994b. Subaqueous disposal of mine waste: Laboratory investigation. in Proc. International Land Reclamation and Mine Drainage Conference and Third International Conference on the Abatement of Acidic Drainage, v. 1. United States Department of the Interior, Bureau of Mines Special Publication SP 06A-94. p. 270-278.

Lapakko, KA., Wessels, J.N. 1995. Release of acid from hydrothermal quartz-carbonate hosted gold-mine tailings. In Proceedings of Sudbury '95, Conference on Mining and the Environment, Sudbury, Ontario, May 28th - June 1 st, 1995. p. 139-148.

Lapakko, K.A., Wessels, J.N., Antonson, DA. 1995. Long term dissolution testing of mine wastes. Report to the United States Environmental Protection Agency, Minnesota Department of Natural Resources, Division of Minerals. 85 p. plus appendices.

McKay, DR., Halpern, J. 1958. A kinetic study of the oxidation of pyrite in aqueous suspension. Trans. Of Metall. Soc. Of A.I.M.E., June.

Morth, A.H., Smith, E.E. 1966. Kinetics of the sulfide-to-sulfate reaction. In Symposium on Fossil Fuels and Environmental Pollution, ACS Division, Fuel Chemistry Preprints, v. 10. p. 83-92.

Nelson, M. 1978. Kinetics and mechanisms of the oxidation of ferrous sulfide. Ph.D. Thesis, Stanford University, Palo Alto, CA.

Nordstrom, D. K. 1982. Aqueous pyrite oxidation and the consequent formation of secondary iron minerals. In Acid Sulfate Weathering. J.A. Kittrick, D.S. Fanning, and L.R. Hossner (eds.), Soil Sci. Soc. Am. Spec. Pub. 10. p. 37-56.

Rauch, H.W., White, W.B. 1977. Dissolution kinetics of carbonate rocks 1. Effects of lithology on dissolution rate. Wat. Resour. Res., v. 13, no. 2. p. 381-394.

Singer, P. C., Stumm, W. 1970. Acid mine drainage: The rate determining step. Science, 167. p. 1121-1123.

Stumm, W., Morgan, J.J. 1981. Aquatic chemistry - An introduction emphasizing chemical equilibria in natural waters. John Wiley & Sons, Inc. p. 470.