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MEASURED RATES OF COPPER AND ZINC LEACHING IN THE INTERNATIONAL KINETIC DATABASE

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ABSTRACT

The objective of the International Kinetic Database (IKD) is to characterize bulk reaction rates in alkaline, neutral, and acidic minesite drainage. The IKD currently contains 307 kinetic tests from around the world, and is growing. Of the 307 tests, 185 provided leaching rates for copper and zinc. Scatterplots of these rates against pre-test parameters such as solid-phase copper and acid-base accounting failed to reveal any clear relationships. Consequently, leaching rates cannot be predicted accurately from pre-test characterization of a sample. Some correlation was noted among leaching rates, sulfate (acid) production, neutralization rate, and aqueous pH. However, the strength of these correlations was too weak to allow the accurate estimation of one parameter from another. All these observations point to the importance of kinetic testing in the assessment and prediction of mine drainage, and the inability to estimate rates prior to testing.

INTRODUCTION

A standard procedure for the prediction of minesite-drainage chemistry is known as "kinetic testing", involving periodic rinsing of a sample to remove all reaction products. The rinse water is then analyzed to obtain unit-weight reaction rates. Air is typically pumped over or through the sample to promote the oxidation of sulfide minerals for acidic drainage or in ingassing of atmospheric CO_2 to regulate alkaline drainage.

In all cases, the objective of the testwork should be to obtain bulk reaction rates, not to obtain a direct estimate of on-site drainage chemistry. The bulk reaction rates can then be combined with other physical and geochemical aspects to explain current chemistry or to predict future chemistry (e.g., Morin and Hutt, 1994a). From a large-scale perspective, these rates define $RATE_1$ from Geochemical Reservoir #1 of sulfide and oxide minerals (Figure 1).

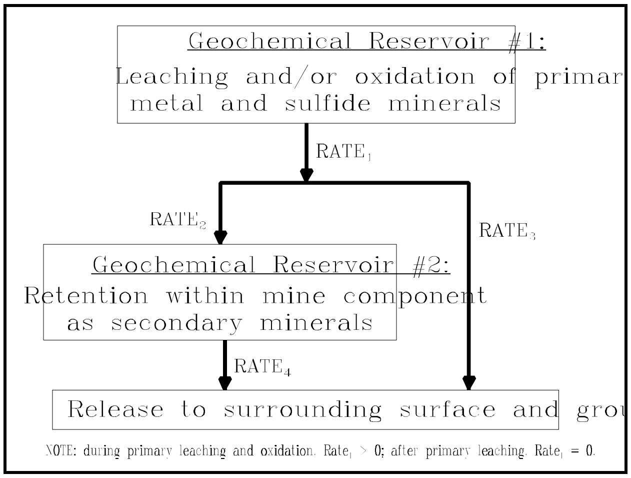

FIGURE 1. Geochemical Reservoirs and Rates Affecting Drainage Chemistry (from Morin et al., 1995a).

The most popular type of laboratory-based kinetic test is a "humidity cell" (Figure 2). The sample within a cell is typically rinsed once a week. A second, less popular type of kinetic test involves a column of rock with water periodically or continuously poured onto the top of the sample. Columns can suffer from more complexities than humidity cells, but apparently provide information that is consistent with data from cells (discussed in Morin et al., 1995b). As a result, there seems to be no major advantage to either approach, except that cells are often easier and less expensive to prepare and operate.

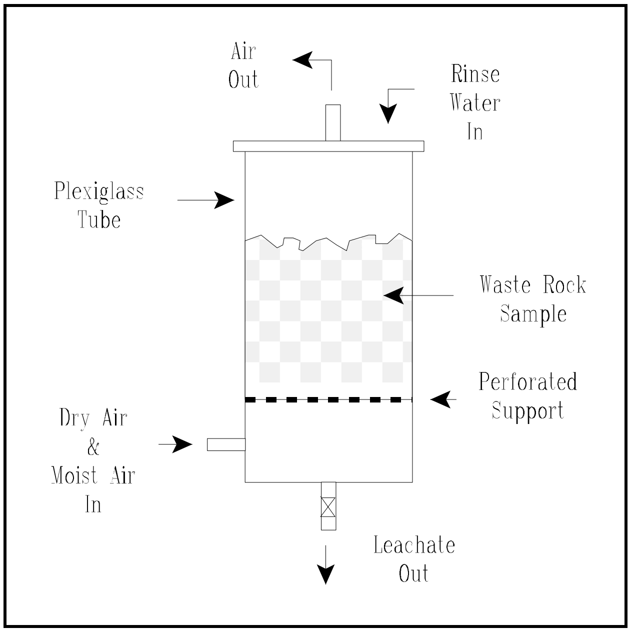

FIGURE 2. Example of a Humidity Cell.

Based on the weight of a kinetic-test sample (e.g., 1 kg), the volume of rinse water (e.g., 0.5 L), and the concentration (e.g., 400 mg/L), a reaction rate can then be calculated (200 mg/kg of sample/week). If particle-surface area is known (e.g., 5 m^2/kg), a unit-area rate can also be calculated (40 mg/m^2/week).

There is some disagreement on value of kinetic tests due to (1) the scaling of kinetic-test results to full-scale mine components and (2) the biased enhancement or acceleration of oxidation in kinetic tests for acidic drainage. However, these complications do not necessarily invalidate kinetic testing, but require such testing for proper characterization. First, scaling is not necessary in some cases since fine-silt-to-sand material similar to a cell sample (less than 0.25 inches) often dominates bulk reaction rates in coarser rock dumps (Morin and Hutt, 1994b). These authors reported similar bulk rates (per kg) for five scales of kinetic tests ranging from 1 kg to 30,000 kg. Second, active movement of moist, or alternating dry and moist, air as well as periodic rinsing by water are not unusual in some rock dumps and mine walls (e.g., Morin et al., 1991; Morin and Hutt, 1995). As a result, kinetic tests should not often enhance the rate of oxidation over that expected in the field.

In fine-grained materials such as tailings, humidity cells can provide a reasonable oxidation rate representative of full exposure to the atmosphere and moisture. In cases where oxygen is expected to be limited by diffusion (Jambor and Blowes, 1994) or submergence (Morin, 1993), lower rates can be calculated from the maximum rate. Consequently, scaling of reaction rates and enhancement of oxidation rates are not considered problems with properly operated and interpreted kinetic tests.

INTERNATIONAL KINETIC DATABASE

Rates of sulfide oxidation, acid neutralization, alkaline neutralization, and metal leaching have long been recognized as factors determining the chemistry of minesite drainage. However, there have apparently been little systematic compilation and evaluation of these rates for mine rock and tailings (Ferguson and Morin, 1991). In response, Morin et al. (1995b) compiled data from 281 kinetic tests from around the world. The database is called the "International Kinetic Database" (IKD) and the number of tests is now 307.

The rates of sulfide oxidation and neutralization, and the relationships of these rates to other rates and pre-test measurements such as acid-base accounting (ABA), are discussed in Morin et al. (1995b). For this paper, the focus is on the leaching rates of copper and zinc in the IKD. Scatterplots are used here to find if a relationship exists between leaching rate and another rate or pre-test parameter. The implications of the relationships are discussed at the end of this paper.

The minimum, average, and maximum number of weeks that kinetic tests in the IKD operated were 5, 27, and 159, respectively. Of the 307 tests in the database, 185 provided data on the leaching of copper and zinc (reported as averaged rates, see next paragraph). The minimum, arithmetic average, and maximum leaching rates for copper were 0.0003, 0.387, and 9.354 mg Cu/kg sample/week, respectively. Corresponding values for zinc were 0.0007, 3.06, and 109 mg Zn/kg of sample/week, respectively. Because the minimum and maximum values span more than four orders of magnitude, arithmetic averages are biased towards the highest values. As a result, clearer representations of the rates are made on logarithmic scales so that the variability is more obvious and correlations are more obvious.

Where all weekly metal analyses were available for a kinetic test, two leaching rates were calculated for each metal. An "overall" rate was based on the average value over the entire length of the test. A "stable" rate was based on the last few weeks, typically five weeks, which represented stabilized long-term values. A comparison of the overall and stable rates for copper (Figure 3) and zinc (Figure 4) show that the two rates were similar, often within a factor of three (0.5 log cycles). Because of this similarity, the overall rates will be used through the remainder of this paper for simplicity. Additionally, the overall rates for copper and zinc (Figure 5) correlate well, so only copper will be examined further in this paper. Nevertheless, all following observations for copper leaching have also been confirmed as valid for zinc.

One common assumption is that the rate of metal leaching is proportional to the amount of solid-phase metal in the sample. This is not true for copper and zinc in the International Kinetic Database (Figure 6). This is similar to

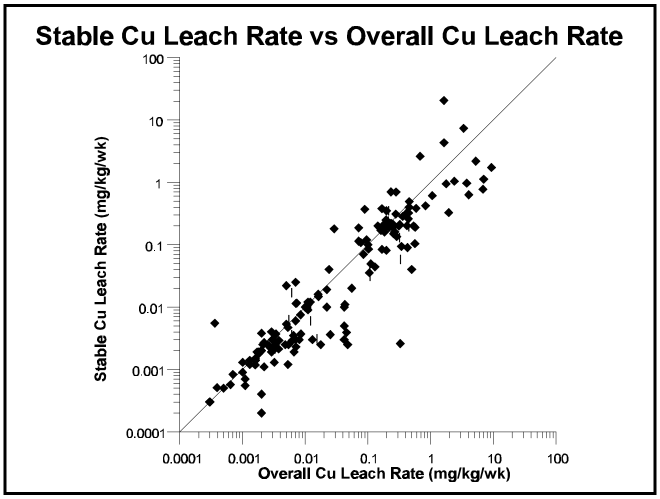

FIGURE 3. Stable Cu Rate vs. Overall Cu Rate.

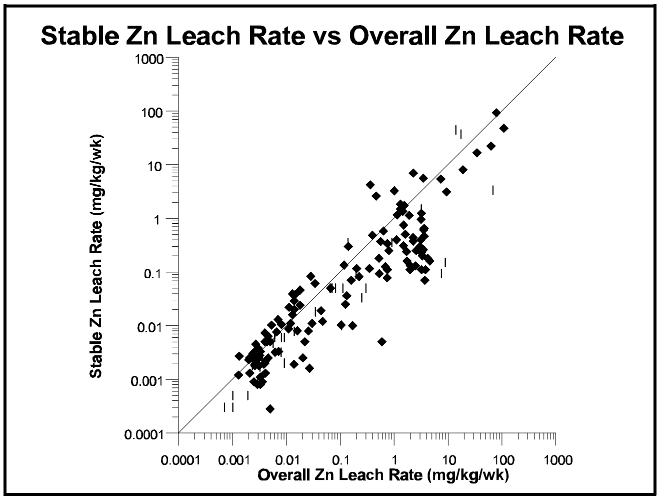

FIGURE 4. Stable Zn Rate vs. Overall Zn Rate.

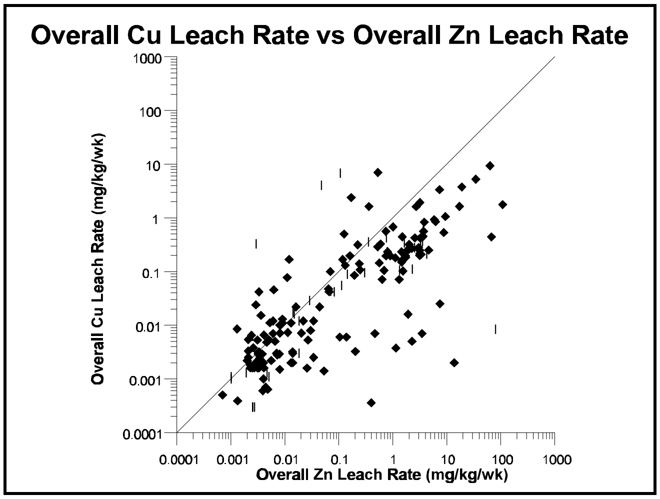

FIGURE 5.Overall Cu Rate vs. Overall Zn Rate.

the observation that the rate of sulfide oxidation and acid generation is not dependent on the amount of solid-phase sulfide (Morin et al., 1995b).

Since copper and zinc often occur as sulfide minerals in sulfide-bearing samples, it is possible that the leaching rates could be dependent on the amount of solid-phase sulfide. This dependency does not exist in the Database (Figure 7).

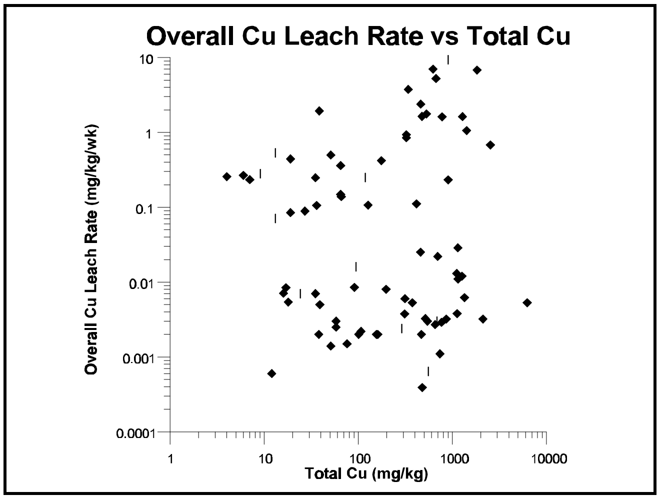

FIGURE 6. Total Solid-Phase Copper vs. Cu Rate.

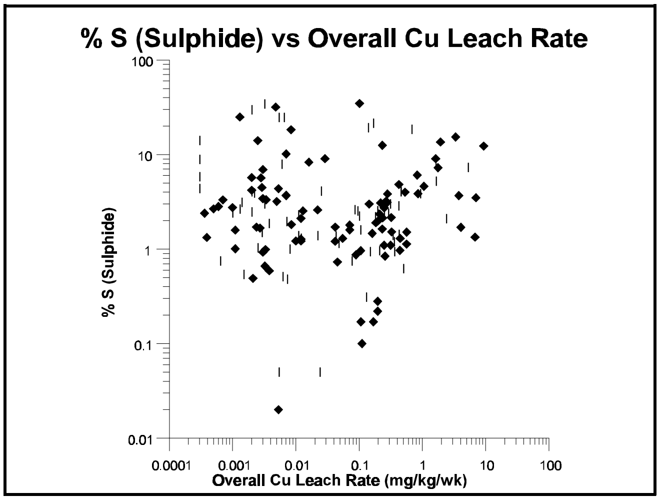

FIGURE 7. Solid-Phase Sulfide vs. Cu Rate.

Because reaction rates are typically dependent on the exposed surface area of grain particles, a relationship can be expected between leaching rates and surface area. The Database does not show this relationship (Figure 8), where surface areas were calculated from the size distribution and shape of grains (geometrical surface area). If any trend can be discerned in Figure 8, the leaching rate increases as surface area decreases. However, measurements of any type of surface area are fraught with difficulties and with inaccuracies of up to three orders of magnitude (Anbeek, 1993; White and Peterson, 1990). As a result, any real correlation between surface area and leaching rate may not be readily apparent or incorrectly portrayed.

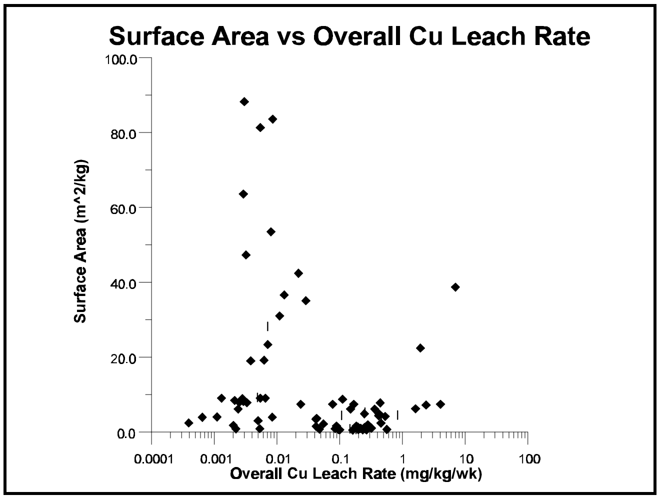

FIGURE 8. Geometric Surface Area vs. Cu Rate.

With acid-base accounting, the Acid Potential (AP) based on sulfide content and the Neutralization Potential (NP) can be compared mathematically through subtraction (Net Neutralization Potential: NNP = NP - AP) or through division (Net Potential Ratio: NPR = NP/AP). No clear relationship exists between NNP and the leaching rate of copper (Figure 9). In fact, the highest rates were measured at relatively minor negative values, which was also noted for the rate of sulfide oxidation.

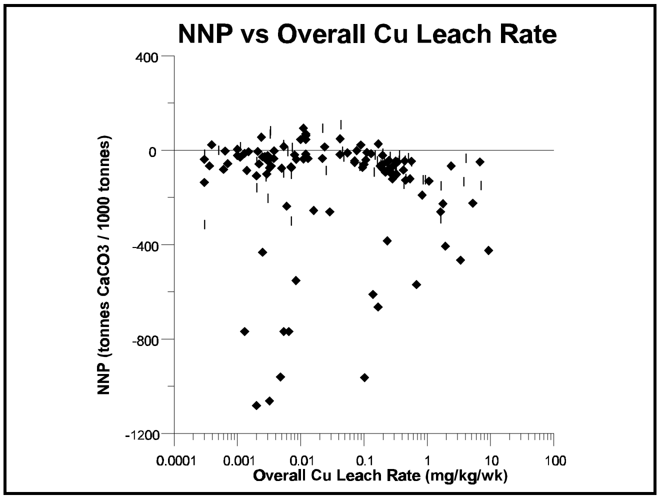

FIGURE 9.Net Neutralization Potential vs. Cu Rate.

For NPR (Figure 10), all leaching rates above roughly 0.1 mg/kg/wk were correlated with NPR < 0.5. However, rates as low as 0.0003 mg/kg/wk were also measured in this range of NPR. Thus, NPR provides only a minor advantage over NNP by showing that no samples in the IKD with NPR above 0.5 produced copper at a rate above 0.1 mg/kg/wk.

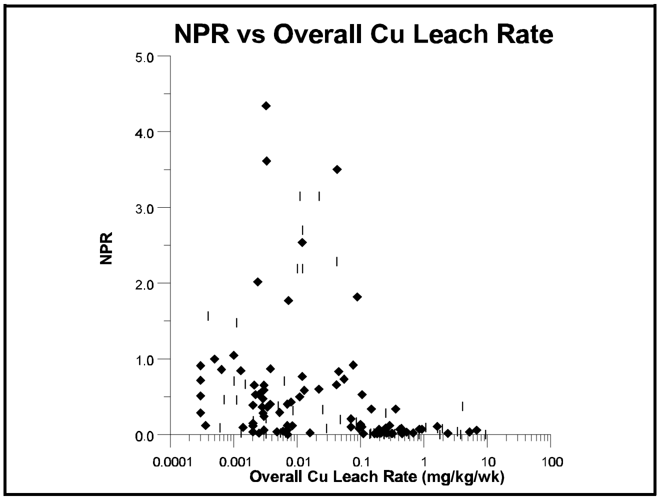

FIGURE 10. Net Potential Ratio vs. Cu Rate.

Now that the general lack of relationships with many parameters has been documented, the parameters that correlate with leaching rates can be discussed. It is important to note here that a correlation between two parameters does not imply a cause-and-effect relationship. For example, both parameters could be simply responding to a third parameter. This is discussed further at the end of this paper.

As mentioned above, the rate of sulfate production, which is an indicator of the rate of sulfide oxidation and acid generation, is not dependent on the amount of solid-phase sulfide. Also, the leaching rates of copper and zinc are not dependent on their solid-phase concentrations. However, the leaching rate does roughly correlate with the rate of sulfate production (Figure 11). Some of the lower rates of metal leaching were below detection limits, which were thus divided by two for use in the figures. This partly explains the vertical line on the left side of Figure 11.

Some kinetic tests in the Database became acidic during the test period, which often caused overall rates to increase. For this reason, Morin et al. (1995) compared the lowest pH recorded in each test to other parameters, and found that the rate of sulfate production correlated well with lowest pH. The rate of copper leaching also correlates well with lowest pH (Figure 12), which is not surprising since the leaching rate also correlated with sulfate production (Figure 11). This mesh of related parameters will be discussed in more detail below.

Figure 12 also shows that pH tends to cluster around near-neutral values and moderately acidic values. This clustering of pH is typical of minesites, which have a favored, typical value for pH-neutral waters and acidic waters reflecting mineralogy, climate, etc. For example, Morin et al. (1995c, these proceedings) show that near-neutral pH and acidic pH at Island Copper Mine is typically 7.0 and 4.0, respectively. At Bell Mine, the values are 7.0 and 3.0 (Morin and Hutt, 1993).

A relationship has also been noted between leaching rate and the aqueous molar ratio (Figure 13) representing carbonate dissolution (Ferguson and Morin, 1991; Morin and Hutt, 1994b). This ratio generally represents the rate of acid neutralization in the samples relative to the rate of acid generation.

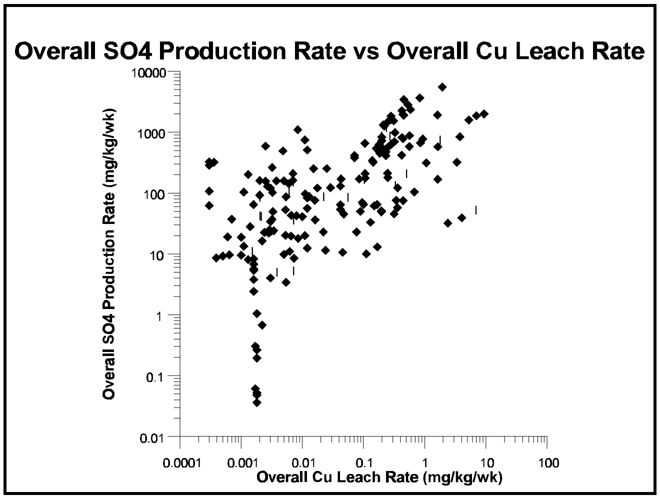

FIGURE 11. Sulfate Production Rate vs. Cu Rate.

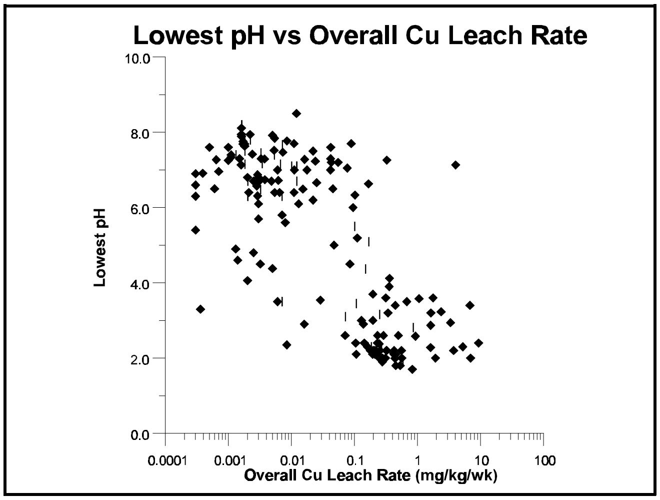

FIGURE 12. Lowest pH in a Test vs. Cu Rate.

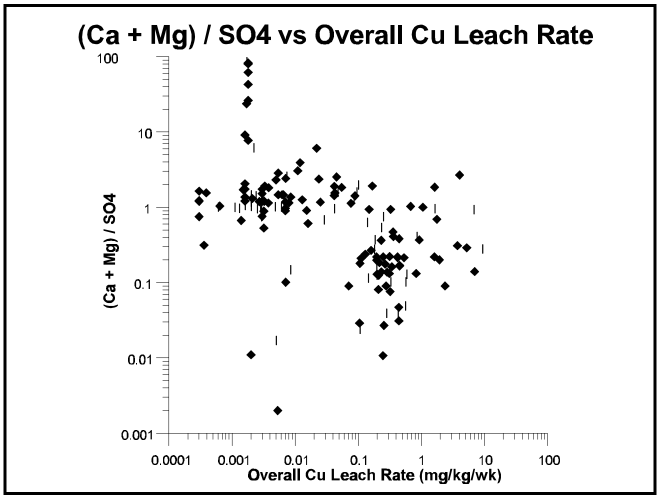

FIGURE 13. Carbonate Molar Ratio vs. Cu Rate.

Lower values of the ratio correlated with lowest pH (Morin et al., 1995b), and thus the ratio also generally correlates with leaching rate.

CONCLUSION

Based on the diagrams presented above and in Morin et al. (1995b) for the International Kinetic Database, there are four related parameters in kinetic tests: aqueous pH, sulfate (acid) production rate, neutralization rate, and copper/zinc leaching rate. However, the correlations are not sufficiently strong to predict one from another. Additionally, these parameters do not correlate well with other parameters such as solid-phase sulfide or copper. As a result, reaction rates cannot be estimated prior to kinetic testing, which in turn demonstrates the importance of such testing for drainage-chemistry assessments or predictions (e.g., Morin and Hutt, 1994a).

It is interesting to ponder which of the four related parameters is the true independent variable that determines in part the other three. In reality, none of the four are probably independent. For example, the rate of sulfate (acid) production affects pH, and pH in turn affects the rate of sulfate production. Additionally, there may be other parameters not monitored, not well understood, or not yet identified that are truly independent variables in determining these reaction rates and pH. Whatever the case, the ability at this time to estimate or predict reaction rates without kinetic testing is poor.

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