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KINETIC TESTS AND RISK ASSESSMENT FOR ARD

by
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ABSTRACT

This paper examines the relationship between geochemical kinetic tests and the assessment of risk for ARD. A classic definition of risk depends on the likelihood that ARD will appear and the consequence if it does. The consequence of ARD is generally independent of kinetic tests, so the focus in this paper is placed on the relationship between kinetic tests and the prediction of ARD likelihood.

Standard international practice involves the "Wheel" approach, in which several types of static and kinetic tests are conducted and compared. Therefore, kinetic tests alone should never be used for ARD predictions. This minimizes errors in ARD likelihood.

The most common kinetic tests are laboratory-based columns and humidity cells and field-based test pads. Unlike columns and pads which often do not often provide any unique information under the Wheel, humidity cells typically provide primary-mineral rates without the complication of secondary-mineral precipitation. For ARD likelihood, they provide the relative rates of NP consumption and acid generation, which are critical for (1) estimating the duration of these reactions and (2) separating net-acid-generating from net-acid-neutralizing rock with a site-specific NPR (=NP/AP) value under acid-base accounting.

Calculations show that gypsum precipitation can lead to significant errors in the aqueous rate ratio of NP consumption to acid generation after only 15-30% of the initial aqueous calcium precipitates. For example, an actual rate ratio of 1.5, which means that NP consumption is 1.5 times faster than acid generation, will be measured as 6.0 after roughly 60% of the calcium is precipitated in a magnesium-free kinetic test. This falsely indicates that all samples with NPR values less than 6.0 will generate net acidity at some point, which is an incorrect prediction of high ARD likelihood. Data from the International Kinetic Database suggest this error is rare in kinetic tests, but appropriate kinetic-test closedown procedures should always be conducted for confirmation.

On the other hand, human misinterpretations of kinetic tests are apparently more common. They tend towards the opposite error of gypsum precipitation, that is, incorrect predictions of low ARD likelihoods.

1. INTRODUCTION

A classical definition of risk is based on two basic factors, likelihood and consequence. Therefore, a basic risk assessment for ARD addresses both the likelihood that ARD will appear and the consequence if it does.

Geochemical kinetic tests, like columns and humidity cells, provide estimates of concentrations or reaction rates. These estimates indicate the severity and duration of ARD and metal leaching, and thus are related to consequence. However, in many environmental settings, the consequence of ARD is often considered moderate to severe, mostly independent of pH and acidity. In other words, the environmental consequence is often considered at least moderate whether pH is 2 or 4 and whether acidity is 100,000 or 1,000 mg/L.

Because the consequence of ARD is mostly independent of kinetic-test results, this paper instead focusses on the relationship of kinetic tests to the likelihood of ARD. Specifically, we address the question of, "How do kinetic tests contribute to the accurate prediction of the likelihood of ARD?".

2. IMPORTANT INFORMATION PROVIDED BY KINETIC TESTS

International standard practice has evolved into the "Wheel" approach (Figure 1). This requires that all the tests be conducted and compared, because the redundancies and cross-checks in the Wheel are critical for accurate predictions of ARD and metal leaching. If there is a discrepancy between one or more tests, then additional work must be done to explain and resolve it. For this reason, kinetic tests should never be used alone for predictions of ARD. In turn, the potential for predictive error on the likelihood of ARD is minimal, except for the parameters that are provided solely by one test like kinetic tests.

The main kinetic tests are laboratory-based columns and humidity cells and field-based test pads. Column tests and pads have not been widely standardized and thus they come in all shapes, sizes, and water-rinse rates. Rinse rates are typically low, such as through trickle leaching or rainfall simulation. As a result, not all reaction products are removed from many columns and pads, and secondary

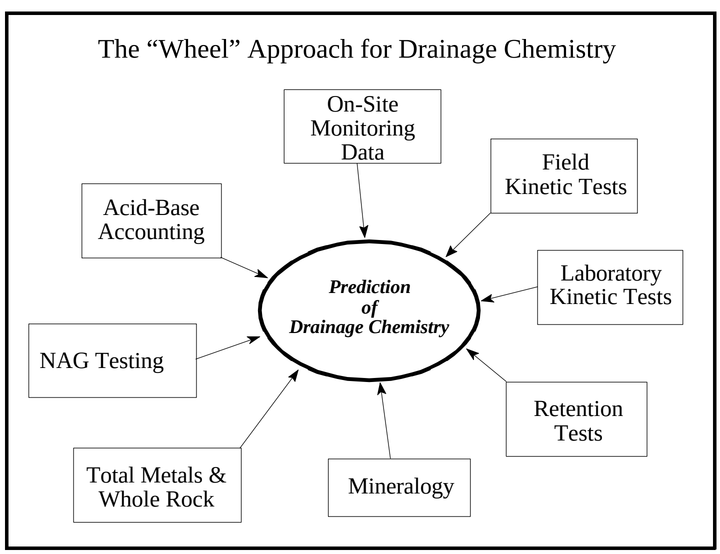

FIGURE 1. The "Wheel" Approach for Predicting Drainage Chemistry and the Likelihood of ARD.

minerals accumulate in them. In terms of overall drainage-chemistry predictions (Figure 2), columns often provided estimates of "Rate2", which is the actual concentration as mg/L expected in the drainage. In the Wheel (Figure 1), on-site kinetic tests and on-site monitoring actually provide better estimates of Rate2 than laboratory columns, but columns are useful when the others are not yet available.

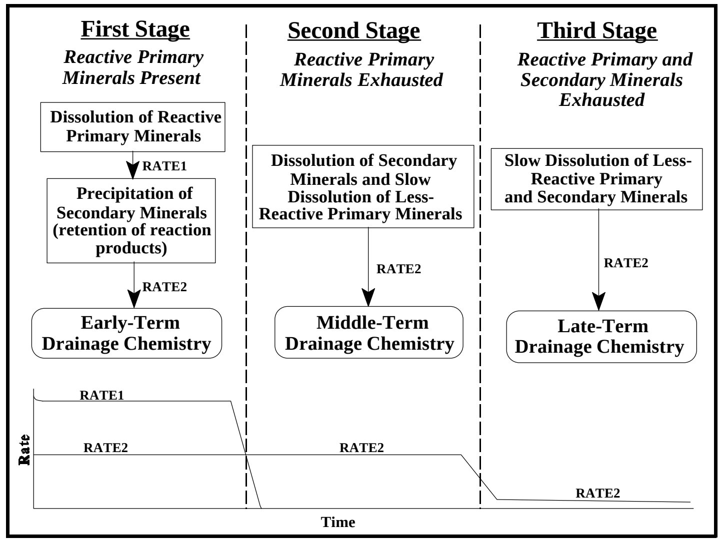

FIGURE 2. Three Stages of Minesite-Drainage Chemistry (from Morin and Hutt, 1997a).

Since columns and field pads often do not provide anything unique under the Wheel, the redundancies from the other tests minimize the error on ARD likelihood from columns. Nevertheless, if a column or pad alone yields pH 4.0 instead of 2.0, the likelihood of ARD is still properly predicted. However, it is important to note that information from a pH-neutral column or pad cannot necessarily be used to predict whether the column will be acidic later, as explained below in Section 3.

Unlike columns and field pads, humidity cells have been standardized with minor modifications for the last 30 years. More importantly, they have a different objective than columns, that is, to provide primary-mineral reaction rates without the interference of secondary-mineral accumulation (Rate1, Figure 2). To accomplish this, excess water must be added and, in some cases, the water and sample must be stirred. Interestingly, because secondary-mineral precipitation is minimized, some inexperienced people mistakenly consider cells as "accelerated" compared to columns and field data, when in fact they are simply providing different information.

As with columns, a pH of 2.0 or 4.0 from a cell does not affect the prediction of ARD likelihood. However, unlike columns at neutral pH, pH-neutral cells do provide something unique: primary-mineral rates of acid generation (based on sulphate production) and acid neutralization (as NP consumption). These rates from cells are critical to the accurate prediction of ARD likelihood. For example, if NP is consumed twice as fast as sulphide, then any related sample with an NPR value (= NP/AP from acid-base accounting) less than 2.0 should be given a high likelihood of ARD. Similarly, if NP is consumed 1.5 times as fast as sulphide, then any related sample with an NPR less than 1.5 is assigned a high likelihood of ARD.

Thus this ratio of rates represents a site-specific or unit-specific criterion for NPR, and eliminates the "uncertain" range given to ABA results in preliminary stages. The following section discusses how errors can arise in the aqueous rate ratio from columns tests, field pads, and improperly operated cells.

3. POTENTIAL ERRORS IN THE SITE-SPECIFIC NPR CRITERION DUE TO KINETIC TESTS

As explained in Section 2, humidity cells uniquely provide primary-mineral reaction rates and the ratio of rates of acid generation and NP consumption, whereas columns and field pads often include secondary-mineral precipitation. This section illustrates the resulting error in ARD likelihood when a secondary mineral, gypsum in this case, is allowed to accumulate in a column, pad, or in an improperly operated humidity cell.

If gypsum ($CaSO_4 \bullet 2H_2O$) precipitates from water within a kinetic test, it removes calcium and sulphate from the water. Since calcium reflects the rate of NP dissolution, at least in part and depending on mineralogy, the loss of aqueous calcium to gypsum means that the rate of NP consumption is underestimated and that the duration of neutralization is overestimated. The rate of carbonate-based NP consumption is actually represented by calcium plus magnesium, to include magnesium-bearing carbonates like dolomite. Similarly, the loss of aqueous sulphate to gypsum means that the rate of acid generation is underestimated and that the duration of sulphide oxidation is overestimated. These errors can lead to predictive errors on the likelihood and extent of ARD.

In carbonate and some aluminosilicate systems, the rate of NP consumption is represented by aqueous concentrations of calcium plus magnesium, and the rate of acid generation and sulphide oxidation are represented by aqueous concentrations of sulphate. For carbonate systems, the rate ratio of NP consumption to acid generation should usually be greater than 1.0 and less than 2.0 (Morin and Hutt, 1997a). For any “initial” ratio (before gypsum precipitation) greater than 1.0, the measured “apparent” ratio (after gypsum precipitation) from a kinetic test will be affected by (1) the degree of gypsum precipitation and (2) the aqueous Ca:Mg value, as explained below.

For example, if the initial ratio is 1.5 (Figure 3a), then the apparent ratio begins to differ significantly after roughly 30% of the initial calcium is precipitated as gypsum. If nearly 60% of the calcium is precipitated in a magnesium-free kinetic test, the test will erroneously indicate the NP is being consumed six times faster than acid is being generated, that is, the rate ratio is 6.0. This could lead to a prediction of high likelihood of ARD if the initial ABA analysis indicated the sample had an NPR of less than 6.0. In reality, the likelihood would be very low for NPRs above 1.5 because the real rate ratio is 1.5. In other words, gypsum precipitation can overestimate the likelihood of ARD.

Numerically, this can be seen by starting with kinetic-test water containing 1.000 moles of calcium, no magnesium, and 0.667 moles of sulphate, yielding an initial rate ratio of 1.5 (1.000/0.667). If 60% of the calcium (0.600 moles) precipitates as gypsum, then 0.600 moles of sulphate is also precipitated, leaving 0.400 moles of calcium and 0.067 moles of sulphate in the water. Thus, the apparent rate ratio is 6.0 (0.400/0.067).

This effect is even stronger at a higher initial rate ratio of 2.0 (Figure 3b). The apparent ratio begins to differ significantly from the initial ratio after roughly 15% of initial calcium is precipitated. In a magnesium-free cell, the apparent rate ratio reaches 6.0 after only roughly 25% of the calcium is precipitated.

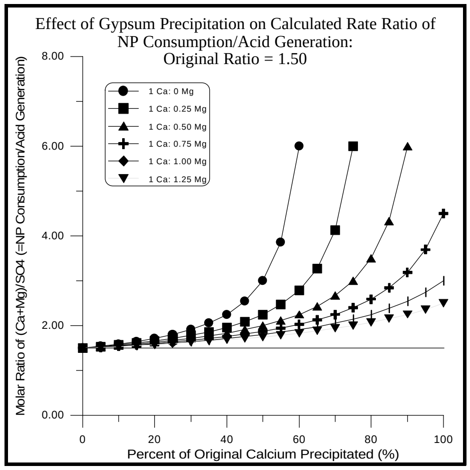

FIGURE 3a.

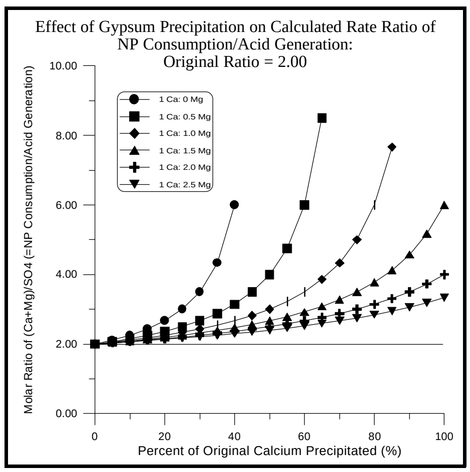

FIGURE 3b.

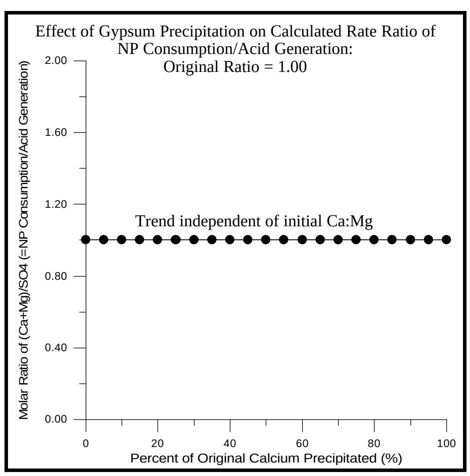

FIGURE 3c.

FIGURE 3. Effect of Gypsum Precipitation on the Calculated Ratio of NP Consumption to Acid Generation Based on Initial Ratios of (a) 1.50, (b) 2.00, and (c) 1.00.

This effect of gypsum precipitation for rate ratios greater than 1.0 is lessened as the relative proportion of aqueous magnesium increases (Figures 3a and 3b). Calcium becomes a relatively minor species and the precipitation of gypsum removes relatively little sulphate and no magnesium. As a result, the apparent rate ratio is not affected as strongly.

The effect of gypsum precipitation is different if the initial rate ratio is exactly 1:1 in the absence of gypsum precipitation. In this case, the rate ratio will not change as any gypsum is precipitated and it is also independent of the value of Ca:Mg in the water (Figure 3c).

Based on this theory, it is interesting to question whether significant gypsum precipitation typically occurs in kinetic tests and if this has resulted in errors of ARD likelihood. As a general empirical assessment of this, the International Kinetic Database (IKD), Version 98.3 (MDAG Publishing, 1998) was checked for anomalies. This was done by plotting aqueous pH against the rate ratio from 448 humidity cells from 61 minesites (Figure 4a). The objective was to search for rate ratios around near-neutral pH that might be anomalous, that is, above 2.0, although these ratios can be normal for certain mineralogies and conditions.

Some near-neutral cells did have elevated rate ratios (Figure 4a), which might imply significant gypsum precipitation. However, it is well known that cells with low acid-generation rates produce high rate ratios simply through the weekly addition of rinse water (Morin and Hutt, 1997a). In other words, the addition of water causes much more NP consumption than that caused by the acid generation. This can be seen in the IKD cells (Figure 4b) below an acid-generation rate of approximately 30 mg SO_4/kg/wk. Therefore, many of the elevated rate ratios from the cells are due to the rinsing effect, rather than gypsum precipitation. In fact, to initiate gypsum precipitation, concentrations of sulphate have to be relatively high, so gypsum effects should appear primarily at high sulphate-production rates. However, they are not seen (Figure 4b).

As explained in Sections 1 and 2, columns often have slower rates of rinsing and may thus promote gypsum precipitation. Although the IKD contains fewer columns than cells (Figures 5a and 5b), the same trends noted for cells are visible: elevated rate ratios appear below approximately 20 mg SO_4/kg/wk and are thus apparently not attributable to gypsum precipitation.

One might think that gypsum saturation within a kinetic test would be apparent from the elevated concentrations of calcium and sulphate, around 600 and 1200 mg/L, respectively, in the rinse waters. However, if only the water layers around some mineral grains have reached gypsum saturation and have precipitated gypsum, then the bulk rinse water may instead contain only tens of mg/L of calcium and sulphate. Similarly, if all mineral grains are not rinsed regularly and well, the bulk rinse water may contain relatively low concentrations of calcium and sulphate. Therefore, aqueous concentrations from kinetic tests are not appropriate for determining gypsum saturation within kinetic tests. This is why the kinetic-test Closedown Procedure (e.g., Appendix C in Morin and Hutt, 1997a) is important. The 24-hour 3-L agitation of the entire sample will reveal whether gypsum has accumulated in a cell through elevated concentrations despite the larger water volume. This Closedown Procedure provides a valuable check on the precipitation of gypsum and other secondary minerals during a kinetic test.

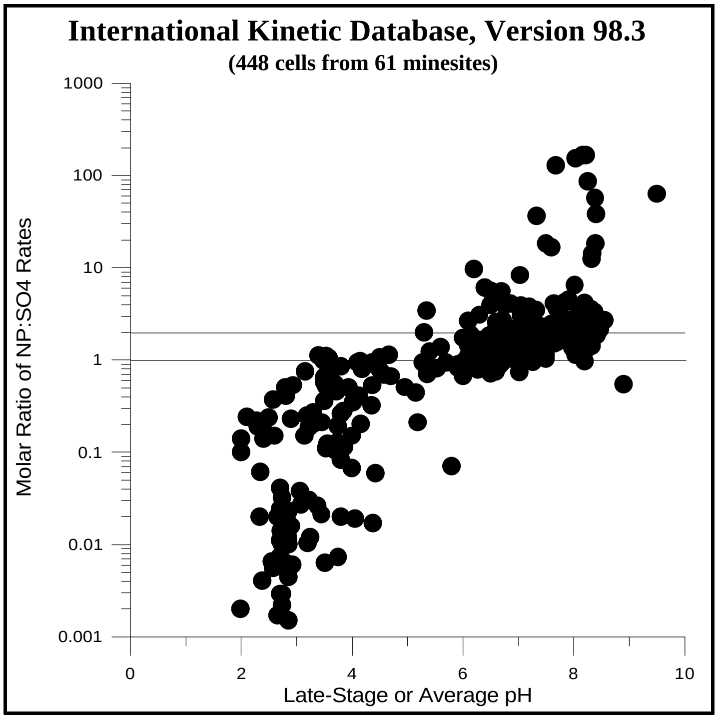

FIGURE 4a.

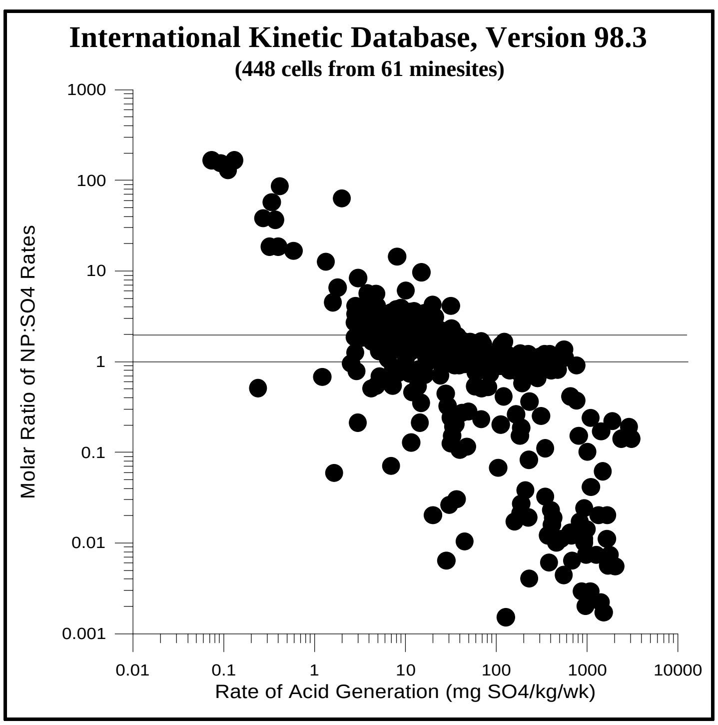

FIGURE 4b.

FIGURE 4. Molar Ratio of NP-Consumption to Sulphate-Production Rates vs (a) Aqueous pH and (b) Rate of Acid Generation (Sulphate Production) from Humidity Cells in the International Kinetic Database, Version 98.3 (MDAG Publishing, 1998).

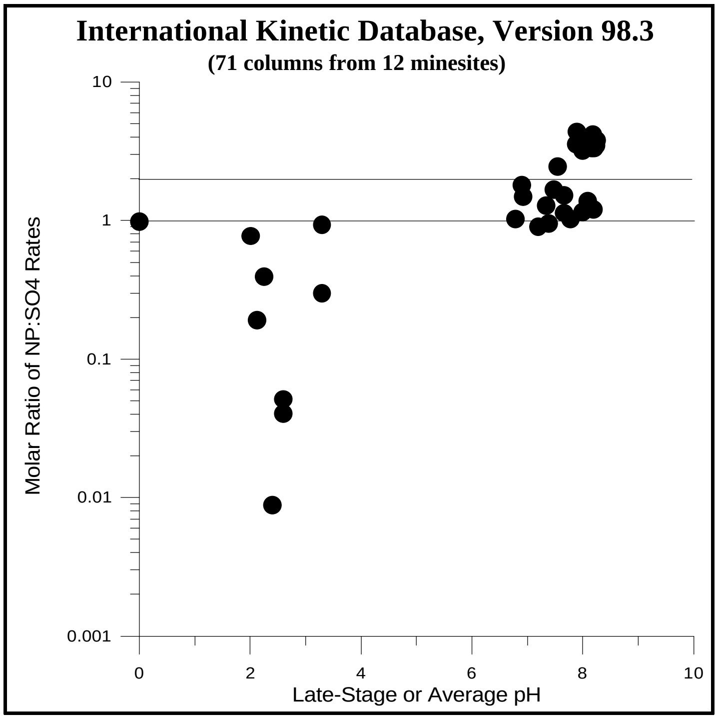

FIGURE 5a.

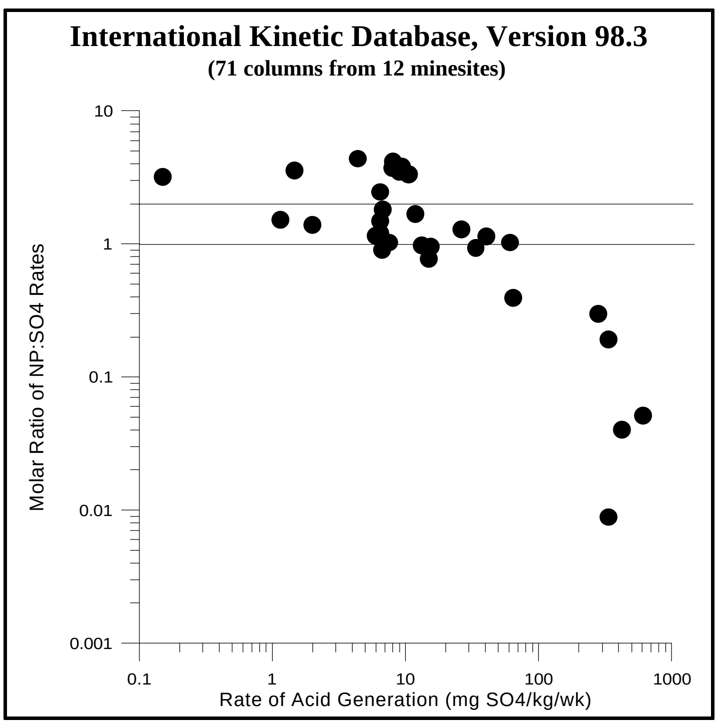

FIGURE 5b.

FIGURE 5. Molar Ratio of NP-Consumption to Sulphate-Production Rates vs (a) Aqueous pH and (b) Rate of Acid Generation (Sulphate Production) from Columns in the International Kinetic Database, Version 98.3 (MDAG Publishing, 1998).

In summary, the ratio of NP consumption to acid generation can be affected by gypsum precipitation with kinetic tests. This can lead to significant overestimation of the likelihood of ARD. However, the International Kinetic Database suggests that this error is rare. Nevertheless, to be more certain, the accumulation of secondary minerals within kinetic tests can be checked with appropriate kinetic-test closedown procedures.

4. OTHER ERRORS IN ARD LIKELIHOOD RELATED TO KINETIC TESTS

The primary, known error in ARD likelihood related to kinetic tests is actually human error in interpretations. For example, an international conference once received a draft paper indicating ABA criteria, like net acid generating rock at NPR<1.0, were wrong based on kinetic tests. Cells containing selected samples, with NPs up to approximately 100 t/1000 t and NPRs less than 1.0, were operated for 20 weeks. When these high-NP samples did not become acidic after 20 weeks, the NPR criterion was declared erroneous. The authors were apparently not familiar with lag times to net acidity in high NP samples. The paper was rejected, but the point remains that there are still serious misinterpretations of kinetic tests occurring.

Another, detailed example involves the Samatosum minesite (Morin and Hutt, 1997a and b). This minesite implemented an expensive and thorough waste-management plan, involving double handling of rock with layering and final covering of net-acid-generating and net-acid-neutralizing rock in the on-site waste-rock dump. This plan was partly based on laboratory columns containing similar layers of rock. The effluents from these columns were not analyzed for calcium and magnesium, and NP consumption was calculated solely from alkalinity. Based on this, the columns were predicted to remain near neutral pH indefinitely. However, alkalinity typically underestimates NP consumption (Figure 6) according to the International Kinetic Database (MDAG Publishing, 1998), so some of the Samatosum columns may actually have become acidic at some point. However, it made little difference for the Samatosum waste-rock dump, because physical factors caused ARD to appear despite the excess NP.

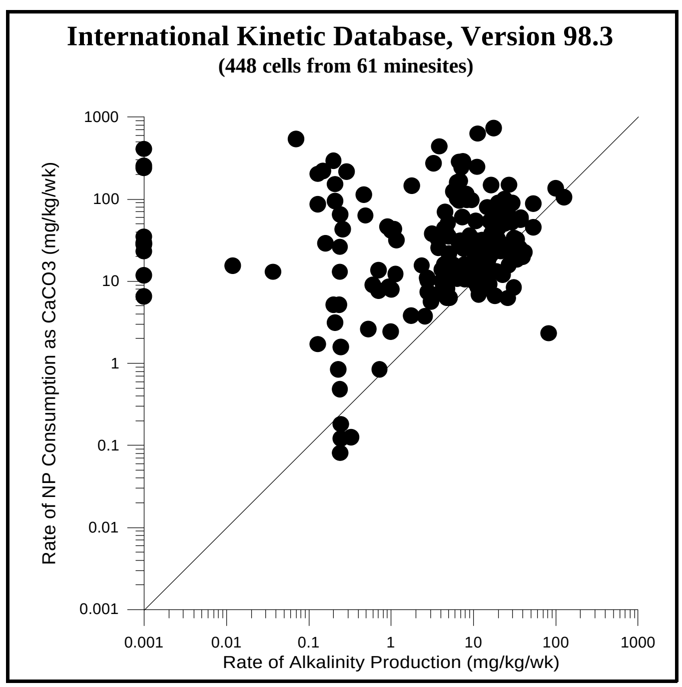

FIGURE 6. NP Consumption vs Alkalinity Production in the International Kinetic Database, Version 98.3 (MDAG Publishing, 1998).

Interestingly, these human errors in ARD likelihood tends toward the negative, that is, to underestimate the likelihood of ARD. This is in contrast to gypsum precipitation (Section 3) which overestimates the likelihood.

5. CONCLUSION

A significant potential error in predicting ARD likelihood and risk from kinetic tests can be traced to the precipitation of minerals like gypsum during kinetic testing. Calculations indicate that the precipitation of as little as 15-30% of the original calcium as gypsum can lead to incorrect predictions of high ARD likelihoods. However, data from the International Kinetic Database suggest this error is rare. Nevertheless, appropriate kinetic-test closedown procedures will reveal whether secondary-mineral have accumulated.

On the other hand, human misinterpretations of kinetic tests are apparently more common. They tend towards the opposite error than gypsum precipitation, that is, incorrect predictions for low ARD likelihoods.

6. REFERENCES

Morin, K.A., and N.M. Hutt. 1997a. Environmental Geochemistry of Minesite Drainage: Practical Theory and Case Studies. MDAG Publishing, Vancouver, British Columbia. ISBN 0-9682039-0-6.

Morin, K.A., and N.M. Hutt. 1997b. Control of Acidic Drainage in Layered Waste Rock at the Samatosum Minesite: Laboratory Studies and Field Monitoring. MEND Report 2.37.3.

MDAG Publishing. 1998. The International Kinetic Database (IKD), Version 98.3. MDAG Publishing, Vancouver, British Columbia.