

IN: Proceedings of the Second International Conference on the Abatement of Acidic Drainage, Montreal, Quebec, September 16-18, 1991, Volume 3, p. 85-106.

**The Prediction of Acid Rock Drainage
- Lessons from the Database**

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The Prediction of Acid Rock Drainage - Lessons from the Database

ABSTRACT

For over 15 years, attempts have been made to predict the formation of Acid Rock Drainage (ARD) for many metal and coal mines in Canada using laboratory geochemical tests. Both static and kinetic tests have been conducted on many samples of waste rock and tailings. A portion of the ARD database, primarily for metal mines in British Columbia, is examined to summarize the approaches used to date for prediction and to identify common trends and important differences in the results. The results of laboratory studies are compared to field observations where possible and the kinetic database is assessed to determine differences in sulphide reactivity, carbonate dissolution, and long term trends. Recommendations are made for interpreting laboratory geochemical test results, and for future research into their use for the prediction of ARD.

KEYWORDS: Acid drainage, acid-base accounting, static tests, kinetic tests, acid generation, acid neutralization, water-quality predictions

1. INTRODUCTION

There are two objectives in the prediction of acid rock drainage: to predict qualitatively prior to mining whether ARD is likely to be formed, and to predict quantitatively after mining has been initiated the contaminant levels in the mine drainage. This paper examines some of the pre-mine qualitative prediction tools - static and kinetic geochemical tests as described by Ferguson and Erickson (1988).

The static tests were developed in both Appalachia and British Columbia (B.C.) in the early 1970's. Variations in test procedures have arisen but they have the same basis; the maximum potential for acid generation (determined by sulphur assay) is compared to the maximum potential for acid neutralization (determined by acid digestion and titration):

$$\text{NNP} = \text{NP} - \text{AP} \quad (\text{Eq. 1})$$
$$\text{and AP} = 31.25 * \%S \quad (\text{Eq. 2})$$

where: NNP = Net neutralization potential as tonnes CaCO₃ equivalent/1000 tonnes
(parts of CaCO₃ per thousand)

NP = Neutralization potential as tonnes CaCO₃ eq/1000 tonnes

AP = Acid potential as tonnes CaCO₃ eq/1000 tonnes

%S = Sulphur as percent

Equation 1 and the NNP are often called the "acid/base account" or ABA of the sample. The NP/AP ratio is also sometimes used in ARD prediction (NNP = 0 is equivalent to NP/AP = 1).

ratio of the tailings at depth. We recalculated the Swedish values as NP/AP ratios assuming that calcite was the only neutralizing mineral present, and plotted them versus surface pH (Figure 1) including B.C. data for comparison. Some of the B.C. sites were operating mines whereas the Swedish sites were all abandoned. The results of the two studies are in general agreement. Lindahl concluded that the sulphur/calcite ratio could be used to predict whether a tailings pond would generate ARD in the future. Our data combined with the Swedish information support the use of the NP/AP ratio for the prediction of ARD for tailings.

2.2 Waste Rock

The prediction of acid generation in waste rock is usually more difficult than tailings because of extreme heterogeneity in mineralogy, stacking sequence, and particle size in waste rock dumps. Surprisingly, there are very little static testing data available for existing waste rock dumps, especially for samples obtained by drilling which are the most representative. ABA data have been obtained by drilling waste rock dumps at only three minesites in B.C.: Island Copper, Mt. Washington, and Westmin.

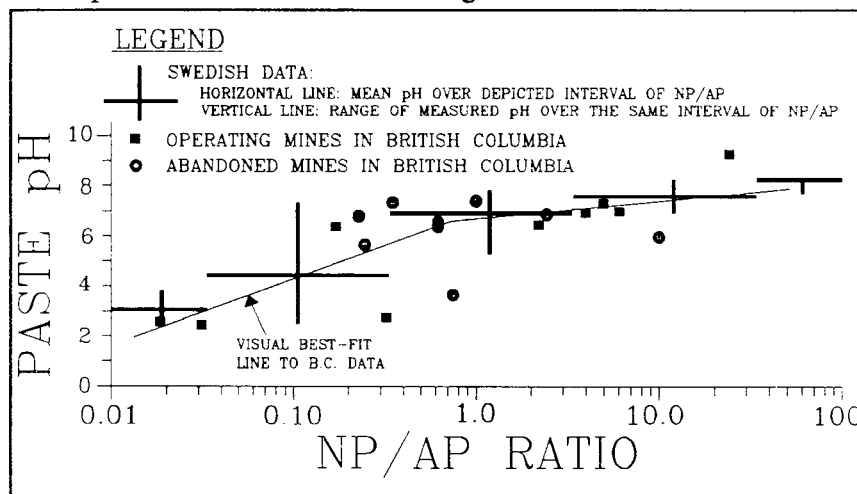


FIGURE 1. Paste pH vs. NP/AP Ratio for Mines in British Columbia and Sweden.

The sulphur content and neutralization potential in individual waste dump holes varied so that the NNP ranged from positive to negative through depth and the sulphur contents were relatively low compared to several of the tailings sites (Table 1). The mean NNP values were

TABLE 1
Summary of Static Test Results for Waste Rock Dumps

Mine	Dump	Size ¹	Holes (tests)	Mean ²			
				%S	NP	NP/AP	NNP
Island Copper	NW	954000	5 (45)	1.8	51	2	-5
	North	84000000	7 (64)	1.1	30	1.4	-4
Mt. Washington	N/east	150000	3 (21)	0.94	10	0.46	-19
	N/west	100000	2 (7)	0.62	13	0.7	-6
	South	200000	1 (6)	0.48	17	3.4	+2
	N/pit	500000	11 (46)	1.64	14	0.54	-37
Westmin	No. 1	1000000	56 (168)	3.57	24	0.81	-88

¹ units are tonnes

² units are tonnes CaCO₃/1000 tonnes, except %S - percent

becoming more common in B.C. Most tests were on weekly cycles including equal durations of wet and dry air. The sample volume varied significantly with the least sample used in standard humidity cells and relatively large amounts in some column experiments. Particle size of the sample also varied, but, was generally less than 6 mm. Different water volumes have been used and flushing rates ranged from 0.5 to 1.75 L/kg/wk. The tests were conducted from 10 to 100 weeks, but in general the duration has been increasing and 20 week tests are now common in B.C. Although not shown in Table 2, the majority of the samples (74%) had a negative NNP.

3.2 General Results

The results of the kinetic leaching tests can be categorized as (Figure 2):

Type I - Alkaline - alkaline throughout test

Type II - Acid - acidic throughout test (pH <4.5)

Type III - Alkaline to acid - initially alkaline but became acidic

Type I results are the most common representing 63% of the database. Type II represent 29% of the database and were found at only a few minesites representing a large number of tests. Therefore, Type II rocks may not be that common in the overall population of minesites. Type III are rare being only 8% of the database. Since the development of acidic conditions in a kinetic test is often used in the prediction of ARD, it is of concern that so few samples have produced an acid leachate in the laboratory despite the vast majority of these samples indicating a potential to generate ARD according to ABA (NNP=0 criterion).

The Type I results can be further divided into three subgroups (Figure 3):

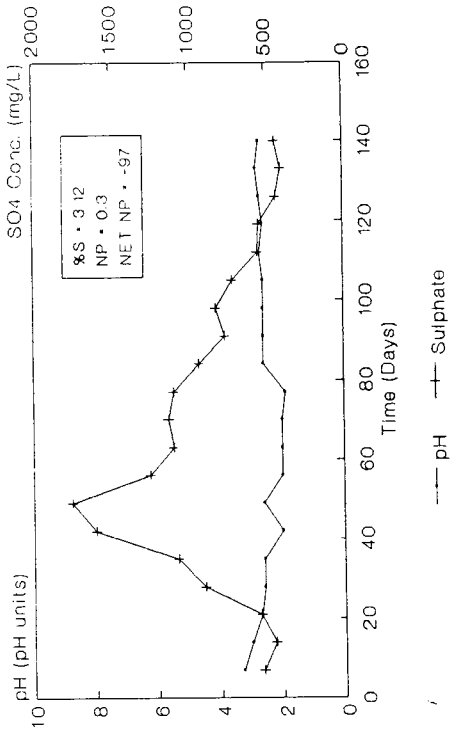
Type Ia - linear cumulative sulphate production

Type Ib - convex cumulative sulphate production

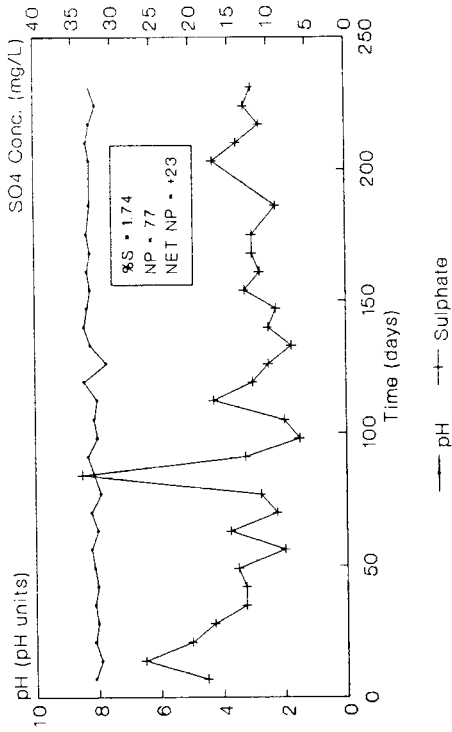
Type Ic - concave cumulative sulphate production

Type Ib are by far the most common. The convex shape of the cumulative sulphate production curve can be explained in four ways. First, for many tests, significant quantities of oxidation products (eg. gypsum) are formed and stored prior to testing. These are dissolved during the early leaching cycles causing elevated sulphate concentrations. This would explain the initial convex shape but would not apply in later leaching cycles. Second, as oxidation proceeds, a weathered rind develops and, therefore, the rate of reactant transport (such as oxygen) from the outer rind to the internal reactive surfaces decreases. The rate of transport may be related to the intergrain porosity, water content, and degree of fracturing resulting in different shapes to the convex cumulative sulphate production curve. Third, coatings of secondary minerals may form on the sulphide surfaces, especially if significant concentrations of contaminants are present in the water film around particles. These coatings could be expected to form during the dry period of the leaching cycle. In field studies, thin coatings on pyrite surfaces were noted by Kwong and Ferguson (1990) for waste rock at the abandoned Mt. Washington site. The coating was believed to be amorphous hydrated iron oxides (eg. ferric hydroxide and limonite) and appeared to retard the extent of oxidation of the pyrite. The fourth explanation for the convex production curve involves the variation of reactions rates with

TYPE II - Acid



TYPE 1 - Alkaline



TYPE III - Alkaline to Acid

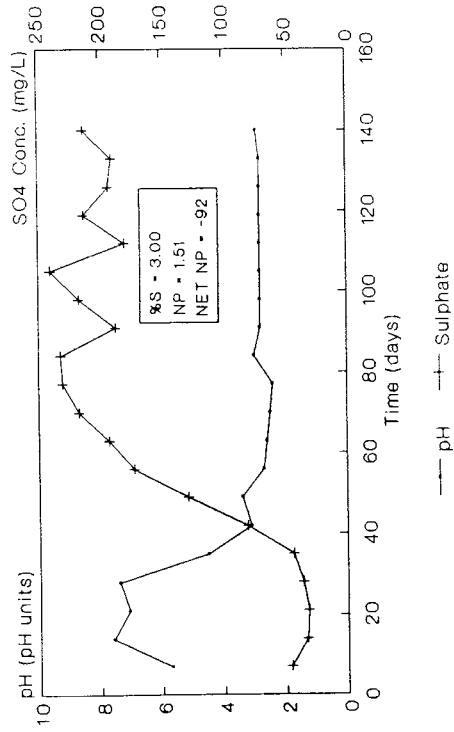


FIGURE 2
TYPES OF KINETIC CELL RESULTS

negative, except in the Mt. Washington South dump which is the only dump not generating ARD. However, several dumps with a mean NP/AP > 1 are apparently generating ARD.

The above analysis indicates the mean NNP (but not the mean NP/AP ratio depending upon the cutoff criterion) determined by static tests would have been accurate in predicting ARD, although caution is warranted since the database is small. Data were found for only one waste rock dump with a positive mean NNP.

3. KINETIC TESTS

3.1 The Database

Kinetic tests are conducted for two purposes: (1) to examine reactivities of individual rock samples and (2) to investigate the effectiveness of ARD prevention techniques. The results from the latter tests are not summarized here, but a few examples are cited in Section 4.

The details of 166 kinetic tests conducted on single rock types from 27 minesites in Canada (20 sites), the western United States (6 sites), and a New Zealand mine are summarized in Table 2. Standard humidity cells were conducted for the majority of tests, but modified cells are

TABLE 2
Summary of Kinetic Tests

Mine/study	Year	No. of Tests	Type ¹	Leaching Cycle ²	Mass of Sample (g)	Particle Size (passing, mm)	Duration	
							Leachate Add (L)	Test (wk)
Waihi	1986	2	C	continuous	1500-3000	4	1-3.9	100
Kutcho-I	1985	2	C	6d rest/26hr leach	3600	6.35	4.8	15
EP	1984	7	H	3d dry/3d wet	200	2.38	0.2	10
Quinsam	1984	2	C	7d rest/2.75 leach	27000	6.35	12.3	25
Cinola	1988	41	H	6d wet	200	4	0.25	20-28
Silbak	1989	3	H	3d dry/3d wet	200	5	0.2	10
Curragh	1989	2	MH	3d dry/3d wet	1000	6	0.5	30
Snip	1989	5	H	6d wet	200	0.3	0.5	39
Sulphurets	1988	6	MH	3d dry/3d wet	1000	6	0.5	10
Energex	1987	5	H	3d dry/3d wet	200	4	0.5	31
Coastech	1988	4	H	3d dry/3d wet	200	6	0.25	20
Minnova	1990	2	C	1d rest/6d leach	11400-30500	19	20	58+
Kutcho-II	1989	20	MH	3d dry/3d wet	1000	6.35	0.5	20
Mt. Milligan	1990	7	C	3d dry/3d wet	40000	19	20	33
Mt. Hundere	1990	5	MH	3d dry/3d wet	1000	6	0.5	20+
Mt. Poiley	1990	3	MH	3d dry/3d wet	1000	6	0.5	10-13
US-A	1990	12	H	3d dry/3d wet	200	4	0.15	10
US-B	1989	12	H	3d dry/3d wet	200	4	0.15	10
US-C	1989	8	H	3d dry/3d wet	200	4	0.15	10
US-D	1989	1	H	3d dry/3d wet	200	4	0.15	10
US-E	1989	6	H	3d dry/3d wet	200	4	0.15	10
US-F	1989	10	H	3d dry/3d wet	200	4	0.15	10
Ketza	1990	1	MH	3d dry/3d wet	1000	6	0.5	35+

¹ C=column; H=humidity cell; MH=modified humidity cell

² Short-term leach occurred on 7th day unless otherwise noted

Several criteria have been used to interpret static test results. Originally in the coal mining region of Appalachia, only samples with a NNP less than $-5 \text{ t CaCO}_3/1000 \text{ t}$ were considered to be potentially acid producing because many soils in the region exhibited a NNP of this value. In B.C., an NNP equal to zero has been used as a criterion for metal mines. More recently, predictions for samples with an NNP between -20 and $+20$ were considered uncertain because of potential errors in the test and differences in kinetics of the acid consumption and production reactions (Steffen Robertson and Kirsten, 1989). Smith and Barton-Bridges (1991) proposed a 3:1 (NP/AP) ratio so that samples below this value should be subjected to kinetic testing. Cravotta et al (1990) recommended the acid potential value be multiplied by 62.5 rather than 31.25 because the neutralization reaction to neutral pH will not exsolve all the CO_2 (Section 4).

Kinetic tests were developed because the static tests did not address differences in the rates of acid production and consumption. Historically, a simple criterion was used to interpret kinetic test results: "Did the sample generate an acidic leachate (often a pH less than 4.5)?" If yes, the sample was classified as an acid producer. If no, the sample was classified as a non-acid producer.

The underlying assumption in both static and kinetic tests is that the basic factors controlling acid production can be reduced to the relative quantities of the major acid generating and consuming minerals (static tests) or the relative rates of reaction in the laboratory (kinetic tests).

In this paper, the available static and kinetic database is examined, primarily from British Columbia, to examine the accuracy and value of the tests, the differences in test methods, and possible improvements. The next two sections address the acid production process with static test results for tailings and waste rock discussed in Section 2 and kinetic tests for waste rock discussed in Section 3. The acid consuming reactions are examined in more detail in Section 4. Where possible in Sections 2 and 3, laboratory predictions are related to field behaviour, whereas Section 4 refers only to the interpretation of laboratory results.

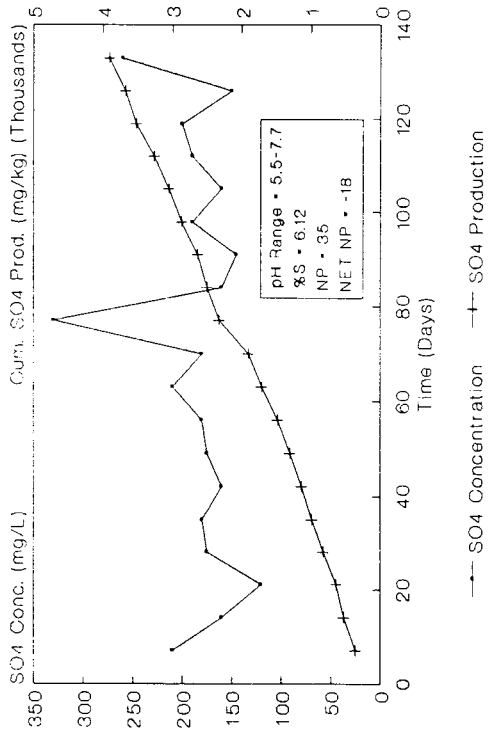
2. STATIC TESTS

2.1 Tailings

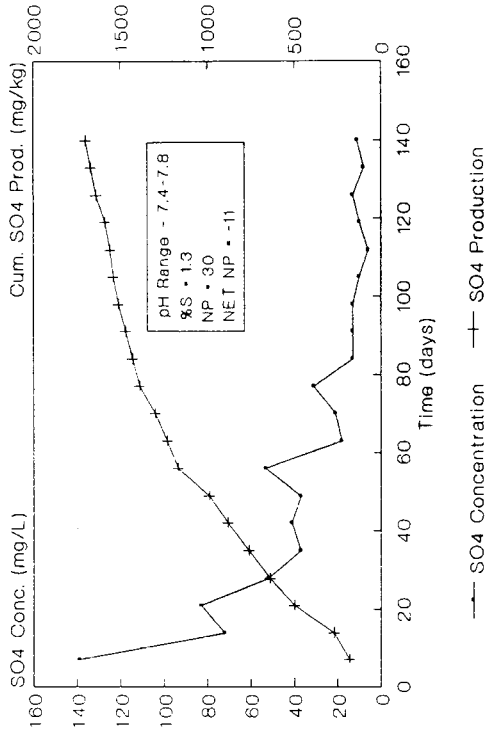
Between 1987 and 1990 Environment Canada collected samples from 20 active or abandoned tailings ponds in B.C.. Samples were obtained from the surface and, in some cases, at depth. For abandoned sites, the depth samples were assumed to represent the acid production potential as originally deposited and the paste pH of the surface sample was used to determine if ARD was present. With only one exception, only abandoned sites exhibited an acidic paste pH. The dry surfaces of the operating tailings ponds almost always exhibited alkaline conditions on surface because of lime addition during milling. Overall, only tailings with a negative NNP produced ARD.

A similar study was conducted in Sweden of 15 tailings ponds as reported by Lindahl (1990). Results were presented as a mean and range of surface layer pH versus sulphur/calcite

TYPE Ia - Linear



TYPE Ib - Convex



TYPE Ic - Concave

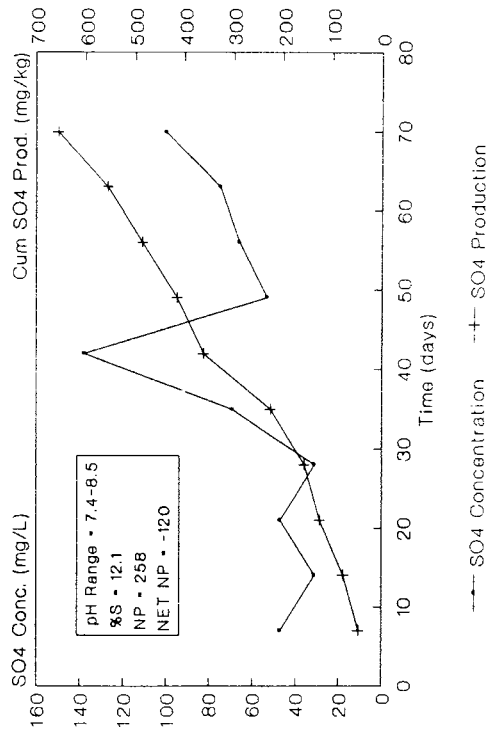


FIGURE 3
 VARIATIONS OF TYPE I RESULTS

sulphide morphologies and crystal sizes. The oxidation rate would decrease as progressively less reactive sulphide mineral surfaces become dominant in controlling the rate of reaction. Detailed mineralogical analysis are required to determine which of these mechanisms are dominant in a particular test.

A linear sulphate production rate (Type Ia) would be observed if the reaction was strictly kinetically controlled, (ie. controlled by the rate of mineral oxidation not by the flux of reactants). This might reflect the presence of small, relatively pure sulphide minerals liberated during crushing of the sample which would control the initial oxidation rate. As sulphur content increases more fine sulphide particles would be liberated and the Type Ia behaviour may be observed longer (note high percent sulphur for Type Ia and Ic examples in Figure 3). Type Ic behaviour would be observed if sulphide particles broke down, resulting in higher surface area, or if low-pH microenvironments developed, increasing the oxidation rate (Section 5). Although the Types Ia and Ic kinetic cell results can be explained by this model, with sufficient time, most of the results would ultimately resemble Type Ib.

3.3 Controls of Acid Production

The results of kinetic tests may afford a better understanding of the factors that control acid production in a particular sample (Figure 4). No sample with a NP/AP greater than one (NNP > 0) has produced an acid leachate (pH < 6) in the laboratory. However, several samples with a NP/AP ratio less than one have produced alkaline leachates because the NP content buffered the system preventing acid production in the short term lab tests (Figure 4b). Generally a NP/AP of approximately less than 0.1 seems necessary to produce an acid leachate in the timeframe of most laboratory tests. If tests were conducted for a very long time, the boundary between acid and alkaline leachates would be expected to shift to the right towards the NP/AP=1 line. But, would it shift beyond? That is, do samples with a positive NNP produce

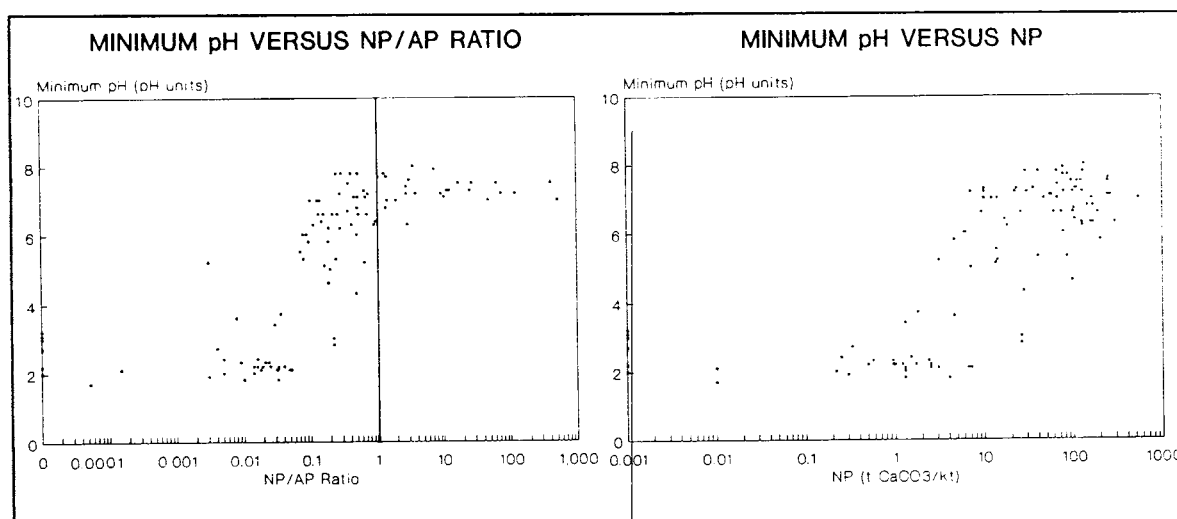


FIGURE 4. Minimum pH vs. (a) NP/AP Ratio and (b) NP.

ARD in the long term? These questions cannot be answered from this analysis, but are examined in Section 4.

The relative reactivities of sulphide minerals can be examined in a cursory way by comparing sulphate production rates and by accounting for differences in particle size. The initial sulphate production rates were ignored because dissolution of sulphate salts produced prior to testing affected some of the results. For cells exhibiting Type Ib behaviour, only the longer term sulphate production rates at near neutral pH were used. To account for differences in particle size the average sulphate production rate (SO_4 Prod in mg/week) was adjusted according to half the maximum particle diameter (D in mm) in the cell. From data obtained by Ferguson (1985) for four particle sizes of a waste rock tested in humidity cells, the following relationship ($r^2 = 0.93$) was determined:

$$\text{SO}_4 \text{ Prod} = 73D^{-0.10} \text{ (Eq. 3)}$$

This equation was used to scale the results from the humidity cells (standardized to maximum 6mm diameter) to account for differences in particle size. This is only an approximate adjustment since it is unlikely that all of the test samples had the same particle size gradation and Equation 3 may only apply to the sample tested. A comparison of the sulphate production rate per kilogram of sample per week is shown in Figure 5.

Three fields of low, medium, and high reactivity were arbitrarily drawn. Some samples do correlate with field behaviour. The "high" reactive sample "A" was the only coal sample included in the database and is known to be a significant acid producer in the field. On the other hand, some of the "low" reactivity samples are not producing ARD in the field. Samples with very high percent sulphur generally exhibited low reactivities, possibly because as sulphur content increases a larger amount is within the interior of the particle

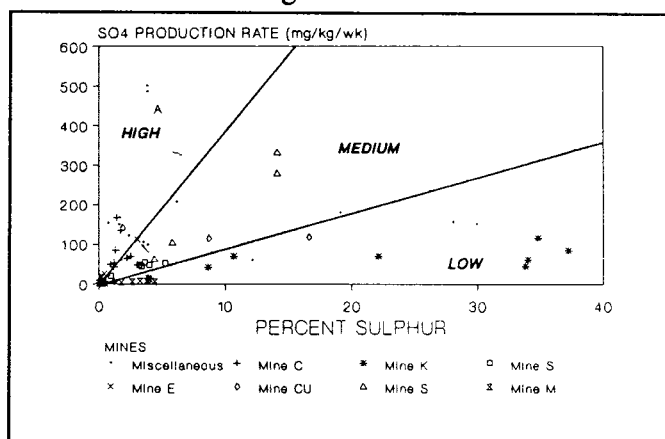


FIGURE 5. Sulphate Production Rate vs. %Sulphur at Near-Neutral pH.

unavailable for reaction and, also, more large coarse grained sulphide minerals, less amenable to oxidation, may be present. Data suggest some difference in reactivity of sulphides at neutral pH, but Figure 5 should be used with caution since the test methods varied and oxygen content and humidity may have limited oxidation rates in some cells. Moreover, while only cells at near neutral pH were considered, there was some variation in the pH and this affected the results. Mineralogical identification are needed to compare better sulphide reactivities.

3.4 Lag to Acid Production

Only 14 tests generated acid from an initial alkaline condition (Type III behaviour). With one exception, all of these samples contained relatively low neutralization potential. Assuming that all of the NNP was present as calcium carbonate and that one mole of carbonate mineral (NP) was depleted for each mole of sulphate produced to reach pH 4.5, then the quantity of NP consumed can be calculated for each sample. This calculation gave a mean of 27% of the initial NP depleted. However, there was a fairly high standard deviation (26%) and coefficient of variation (97%).

Figure 6 presents the data as the NP/AP ratio. As this ratio increases, the time (DURATION in weeks) for the leachate pH to fall from near-neutral to pH 4.5 also increases. The formulae for the best fit curve ($r^2 = 0.52$) is:

$$\text{NP/AP} = 0.00033 \text{ DURATION}^{2.0} \text{ (Eq. 4)}$$

There is a rather poor correlation which may be due to differences in reactivities. However, this curve and formula may serve as a rough guide to decide prior to testing if a sample is likely to generate ARD in the laboratory. Results from two field test plots are also included in Figure 6, and they agree with the laboratory results.

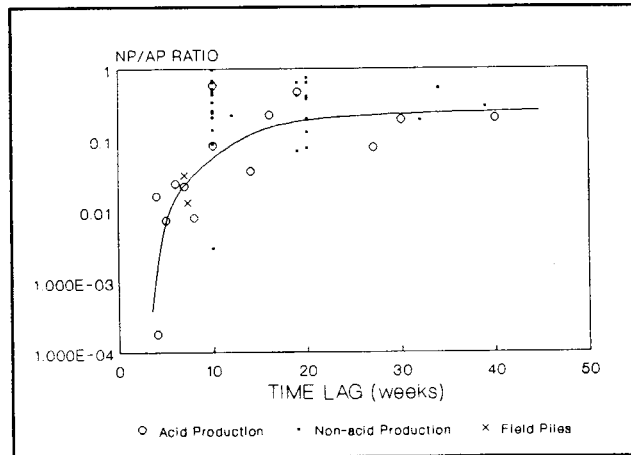


FIGURE 6. NP/AP vs. Time Lag to pH 4.5.

Little long term data for samples with a NP/AP ratio close to unity could be located for Figure 6 and more experiments are needed. Samples with a $\text{NP/AP} < 1$ that did not generate ARD in the lab are also plotted in the figure.

As expected, most of these results plotted above the line of acid production, but there were a few exceptions. Differences in reactivities of acid producing and consuming minerals may explain why some of those samples did not generate ARD in the laboratory test although they would be predicted to do so by Equation 4.

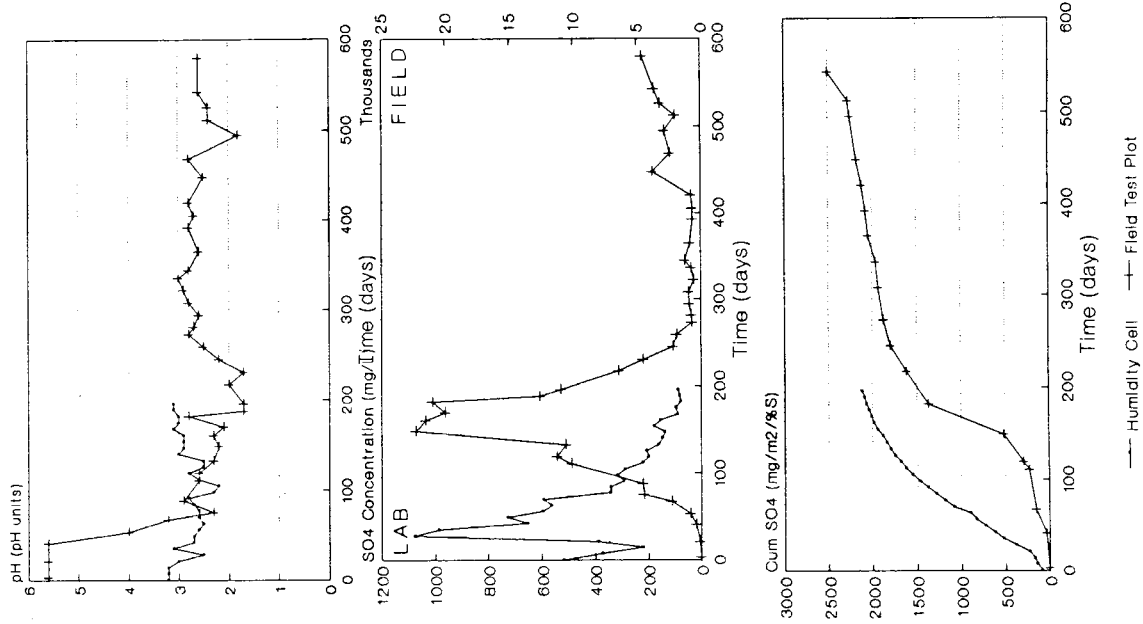
3.5 Comparison of Laboratory Results to Field Data

Because of the heterogeneity of waste rock dumps there are very few single laboratory humidity cells that are thought to quantify field conditions. However, comparisons between laboratory and field behaviour are critical if laboratory results are to be used with confidence in predictions. Humidity cell tests were conducted on samples collected from 30 tonne field test piles at one minesite in B.C. and one pair of data are examined here.

The humidity cells exhibited Type II behaviour while the pile was Type III (Figure 7). The

FIGURE 7
COMPARISON OF LAB TO FIELD

ABA CHARACTERISTICS				
	pH	%S	NP	NNP
CELL	3.7	1.45	-4	-49
FIELD PAD	7.2	2.96	3	-90



humidity cell initially generated acid leachate because the rock was exposed in the field for one month prior to collection and start of the laboratory test. The field pile achieved a lower pH and much higher sulphate concentrations. Therefore, the concentrations of contaminants obtained from laboratory tests cannot be used directly for estimates of field concentrations.

The time to peak sulphate concentration was much shorter in the humidity cell, even correcting for the one month weathering of the sample in the field prior to starting the laboratory test. This is shown in the lower graph in Figure 7 with the cumulative sulphate production rate normalized to surface area and percent sulphur. Overall, the humidity cell released sulphate at a higher rate. The final cumulative sulphate production of 2115 mg/m²/ %S achieved in the humidity cell by 196 days was not achieved by the field test plot until 420 days.

If the one month preweathering of the humidity cell sample is deducted, the field test plot took 2.3 times as long to reach the same cumulative rate. However, extrapolating the humidity cell line suggests that the pad may ultimately produce more sulphate. This may be due to particle breakdown under field conditions and the resulting exposure of fresh sulphide mineral surfaces for reaction.

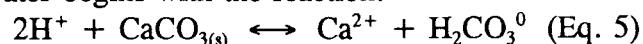
4. NEUTRALIZATION IN pH-NEUTRAL LABORATORY EXPERIMENTS

In the previous section, aspects of sulphide oxidation and acid generation were discussed. In this section, neutralization reactions and accompanying secondary mineral precipitation will be addressed. Specifically, theoretical issues will be reviewed to illustrate the complexities in interpretation of pH-neutral laboratory tests, and then examples from the database will illustrate the approach to interpretation and the manner in which consumption of neutralization potential might occur in the future. This information is critical for calculating the potential lag to net acid production (Section 3.4) and the long-term differentiation between Type I and Type III conditions (Section 3.2).

4.1 Theoretical Considerations

The neutralization of acidic solutions to near-neutral pH in natural systems virtually depends on the carbonate system because (1) aqueous alkalinity is often comprised predominately of some form of aqueous carbonate and (2) carbonate minerals are often responsible for neutralizing acidic water to near-neutral pH. Aqueous carbonate takes the basic forms of H₂CO₃⁰ which is dominant below pH 6, HCO₃⁻ (bicarbonate) which is dominant between pH 6 and 10, and CO₃²⁻ (carbonate) which is dominant above pH 10. Although each basic form is dominant within a specific range of pH, the other forms are still present and, furthermore, bicarbonate and carbonate ions form numerous ion pair and complexes with cations such as Ca²⁺ and Mg²⁺. For the purposes of this paper, only the simplistic scenario of the three basic forms will be considered.

When an acidic water encounters a carbonate mineral such as calcite (CaCO_{3(s)}), neutralization of the water begins with the reaction:

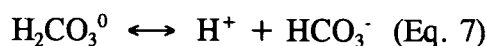


Depending on the amount of H_2CO_3^0 generated by the neutralization, some portion will be lost from the water by exsolution of CO_2 gas which in laboratory experiment is removed by the air flow over the sample:

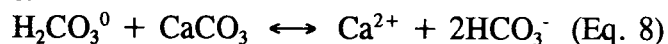


At least several minutes are required for most of the excess H_2CO_3^0 to be exsolved from the water.

If sufficient carbonate is present and neutralization continues, pH will increase towards 6 and, just above pH 6, H_2CO_3^0 begins to release acidity through dissociation, temporarily slowing the neutralization of pH:

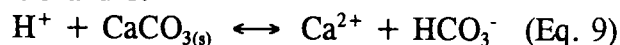


In this example, calcite is providing the continuing neutralization so that the net reaction involving Equation 7 is:



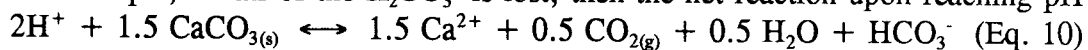
After most of the H_2CO_3^0 is converted to bicarbonate, then pH is free to rise above 6 with further calcite dissolution.

Although the previous equations have expressed neutralization in discrete steps, the full neutralization of acidic water to pH 7 without loss of CO_2 would be equivalent to the combination of Equations 5 and 8:



As a result, neutralization above pH 6 uses carbonate less effectively than neutralization below pH 6 because only one mole of H^+ , rather than 2 (Equation 5), is neutralized by one mole of CaCO_3 .

A key point in our interpretation of pH-neutral experiments in the database is the distinction between gradual, stepwise neutralization to $\text{pH} > 6$ (Equations 5 through 8) during which CO_2 is lost and nearly instantaneous or closed-system neutralization to $\text{pH} > 6$ (Equation 9). Acid-base accounting (Section 1) implicitly assumes the former scenario applies (Morin, 1990). These two scenarios can be differentiated under laboratory and field conditions by the resulting ratio of alkalinity (as bicarbonate) to calcium (plus magnesium because magnesium-bearing carbonate minerals are common). According to Equation 9, the ratio should be 1.0. On the other hand, if significant amounts of H_2CO_3^0 are lost as carbon dioxide, then the ratio would be less than 1.0. For example, if half of the H_2CO_3^0 is lost, then the net reaction upon reaching pH 7 is:



and the ratio of alkalinity as bicarbonate to (calcium+magnesium) would be 0.67.

An important complexity at this point lies in the definition of alkalinity between laboratory analysts and geochemists. Throughout this paper, alkalinity is quantitatively defined as the aqueous concentration of bicarbonate (HCO_3^-). In fact, there are various types of alkalinity such as carbonate and total alkalinity, but we must assume due to lack of additional data that bicarbonate alkalinity represents the major portion of the reported total alkalinity in each experiment. The alkalinity measured in laboratory analyses expressed as CaCO_3 must then be

mathematically converted to the alkalinity used in this paper. Alkalinity as CaCO_3 is typically measured by titration with a diprotic acid such as H_2SO_4 , and one mole of the acid (2 moles of H^+) is assumed to be neutralized by one mole of CaCO_3 (Equation 5). As discussed above, the neutralization to pH 7 actually requires 2 moles of CaCO_3 for each 2 moles of H^+ (combination of Equations 5 and 8). To adjust standard carbonate alkalinity, we used:

$$\text{Molar concentrations: Alk as HCO}_3^- = 2 \times \text{Alk as CaCO}_3 \text{ (Eq. 11)}$$

In addition to the alkalinity/calcium+magnesium ratio, the ratio of sulphate to alkalinity as bicarbonate is useful for interpretations of the database. The "standard equation" for pyrite oxidation dictates that 1 mole of sulphate is generated for each 2 moles of H^+ (Morin, 1990). Consequently, nearly instantaneous or closed-system neutralization (Equation 9) will yield a value of 0.5 for sulphate/alkalinity whereas neutralization with attendant loss of carbon dioxide would provide a higher value such as 1.0.

The preceding discussion has assumed that all aqueous ions originate with the aforementioned minerals, remain in solution, and are eventually removed from an experimental chamber as effluent. However, secondary mineral precipitation-dissolution can cause some ions to precipitate from solution or can represent a secondary source of ions upon dissolution, leading to anomalous geochemical ratios of sulphate/alkalinity and alkalinity/calcium+magnesium. One relevant secondary mineral is gypsum (hydrated calcium sulphate). Because of the common presence of gypsum where sulphide oxidation is occurring, this mineral can greatly complicate interpretations. For interpretation of the database, the potential interference of gypsum was determined by calculating an approximate solubility coefficient from concentrations of calcium and sulphate and, if the coefficient was close to gypsum solubility, precipitation-dissolution was assumed to be occurring and distorting the geochemical ratios. The gypsum coefficient was calculated by assuming that all complexation of calcium and sulphate was minimal, ionic strength was negligible, and pH was essentially neutral. Based on concentrations of sulphate, the value of the sulphate/calcium ratio below which gypsum was likely present in the sample was determined (Figure 8).

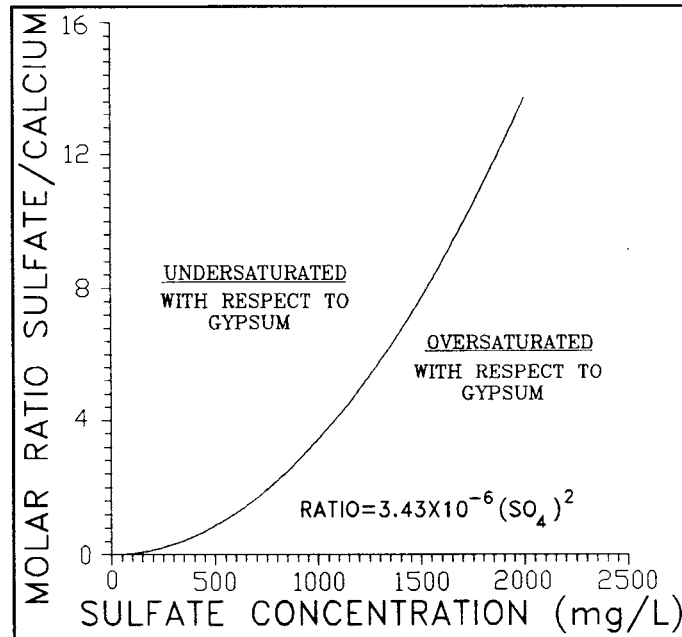


FIGURE 8. Ratio of sulfate/calcium vs. sulfate concentration as an approximate indicator of gypsum presence at neutral pH.

In light of the limiting assumptions of no complexation and minimal ionic strength, some error (at least a factor of 2) must be included in these sulphate/ calcium ratios. In fact, the error reaches a factor of orders-of-magnitude around pH 2 because of the formation of the bisulphate complex (HSO_4^-), but this is not relevant here because only neutral-pH conditions are examined.

In summary, there are definable geochemical ratios that can reflect differences in rates of neutralization and carbonate consumption under several limiting assumptions (Table 3). The violation of the limiting assumptions, such as caused by secondary precipitation-dissolution, can have significant effects on the ratios.

TABLE 3
Geochemical Molar Ratios Reflecting Rates of Neutralization and Carbonate Consumption Under Several Limiting Assumptions

	<u>Alk/Ca+Mg</u>	<u>SO₄/Alk</u>	<u>SO₄/Ca</u>
Rapid or Closed-System Neutralization:			
no loss of CO ₂	1.0	0.5	0.5
Stepwise Neutralization			
loss of 1/2 of CO ₂ , Eq.10	0.67	1.0	0.67
loss of 3/4 of CO ₂	0.40	2.0	0.80

4.2 Examples from the Database of pH-Neutral Experiments

With the theoretical aspects of neutralization and limitations of geochemical ratios established (Section 4.1), the database of pH-neutral experiments can be examined for information on the nature of neutralization and for predictions of carbonate consumption.

In one experiment, the ratios for SO₄/Ca indicated gypsum was likely not at saturation in the experimental chamber (Figure 9) so that the geochemical ratios should be providing valid information at least in later weeks on the nature of neutralization. In the initial weeks, the values for SO₄/Alk were relatively high, the values for Alk/Ca+Mg were relatively low, and the values for SO₄/Ca were relatively constant around 1.0. This behaviour is consistent with the gradual dissolution of some gypsum from the sample which was not associated with a release of acidity and the accompanying release of alkalinity. As mentioned above, concentrations of calcium and sulphate did not reach gypsum-solubility levels.

Following the initial peak, the values of Alk/Ca+Mg were less than 1.0 (Figure 9), often around 0.5-0.7, reflecting significant loss of carbon dioxide according to Table 3. In agreement, values for SO₄/Alk and SO₄/Ca were greater than 0.5, also indicating loss of carbon dioxide during neutralization. As a result, neutralization resulted in a relatively smaller rate of carbonate-mineral consumption, prolonging the ability of the sample to neutralize acidity.

In a leach column containing acid-generating rock mixed with crushed limestone (Figure 10), the initial sulphate concentration of 667 mg/L in Week 1 exceeded gypsum solubility based on the SO_4/Ca ratio of 0.89 (Figure 8) which accounts for the anomalous values of $\text{Alk}/\text{Ca}+\text{Mg}$ and SO_4/Alk and the value close to 1.0 of SO_4/Ca in Week 1. By Week 2, the effluent was undersaturated with respect to gypsum, although trace amounts probably continued to dissolve for some time. Some loss of carbon dioxide likely occurred based on values of SO_4/Alk greater than 0.5, SO_4/Ca of approximately 0.6, and $\text{Alk}/\text{Ca}+\text{Mg}$ of approximately 0.5.

A leach column identical to that from Figure 10 was assembled with significantly less crushed limestone. Values of the ratios (Figure 11) were similar to those of Figure 10 in early weeks, but, after Week 5, the values of $\text{Alk}/\text{Ca}+\text{Mg}$ were less than Figure 10 and the values of SO_4/Alk and SO_4/Ca were greater than Figure 10, indicating stepwise neutralization with loss of CO_2 . The ratio of SO_4/Alk

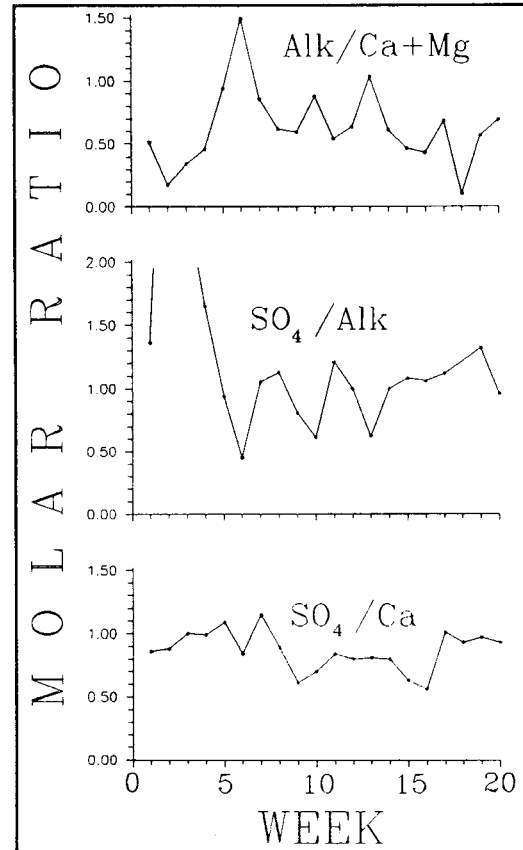


FIGURE 9. Geochemical Ratios from a Humidity-Cell Test.

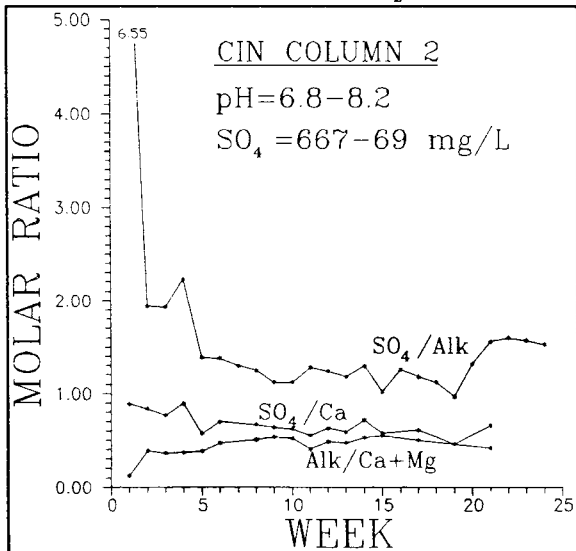


FIGURE 10. Geochemical Ratios from a Leach Column with Crushed Limestone.

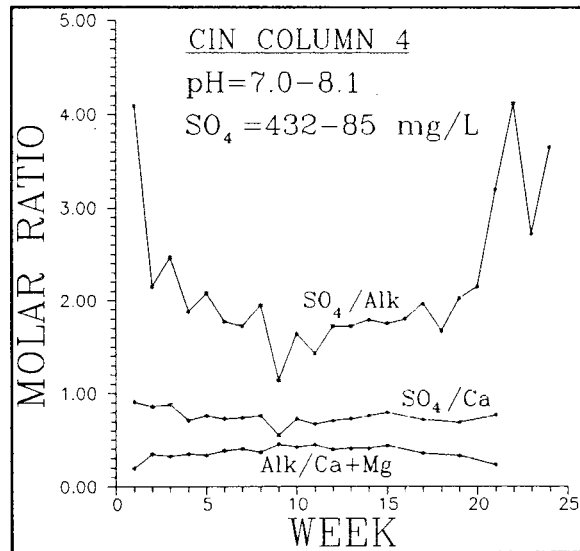


FIGURE 11. Geochemical Ratios from a Leach Column with Less Crushed Limestone Than Fig 10.

was particularly anomalous, especially after Week 21 when the value rose to about 4 and sulphate concentrations doubled to approximately 200 mg/L. A few weeks after Week 25, sulphate concentrations reached a few thousands of mg/L, similar to the control column at pH 2.0-3.5, and an additional few weeks later, pH dropped sharply to control values. As a result, the ratio of SO_4/Alk apparently provided an early warning by several weeks that NP was nearly consumed and that acid drainage would soon appear.

In another example (Figure 12), the ratios of SO_4/Alk and SO_4/Ca do show a sharp decrease to stabilize by Week 3 suggesting that gypsum dissolution was relatively rapid. After Week 3, the values of SO_4/Ca and SO_4/Alk around 0.5 and of $\text{Alk}/\text{Ca}+\text{Mg}$ around 1.0 suggest little loss of carbon dioxide and thus rapid neutralization (closed-system neutralization is ruled out because this was a humidity-cell test). However, values of SO_4/Alk below 0.5 indicate an enhanced leaching of alkalinity over that required by sulphide oxidation based on sulphate concentrations. Furthermore, values of $\text{Alk}/\text{Ca}+\text{Mg}$ greater than 1 indicate the excess alkalinity is apparently not derived from Ca-Mg-based carbonates, but apparently from other carbonates such as siderite (iron-bearing carbonate) or heavy-metal oxide-hydroxide-based minerals. The concept of excess leaching of alkalinity will be further addressed in the following example.

As a final example, there were a series of leach experiments conducted over 70 weeks on layered blends of two rock types. The first type was acid-generating rock with carbonate minerals and the second was non-acid-generating with carbonate minerals. For these experiments, calcium and magnesium concentrations were not measured so that the only available ratio is SO_4/Alk (Figure 13) and the complexity of gypsum precipitation-dissolution cannot be addressed.

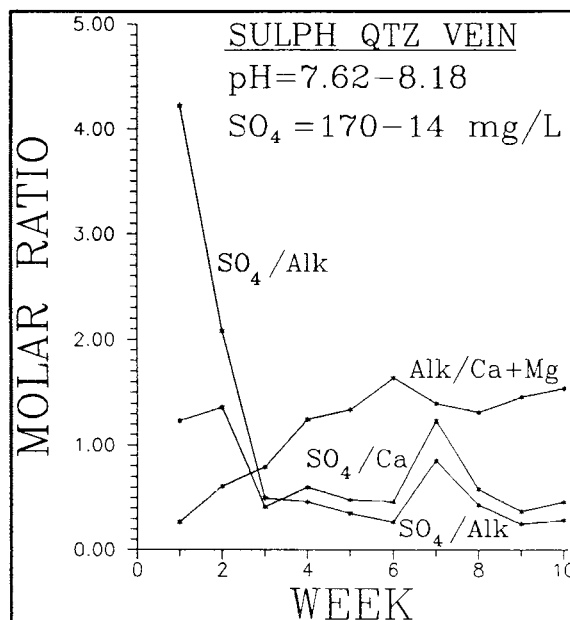


FIGURE 12. Geochemical Ratios from a Humidity Cell.

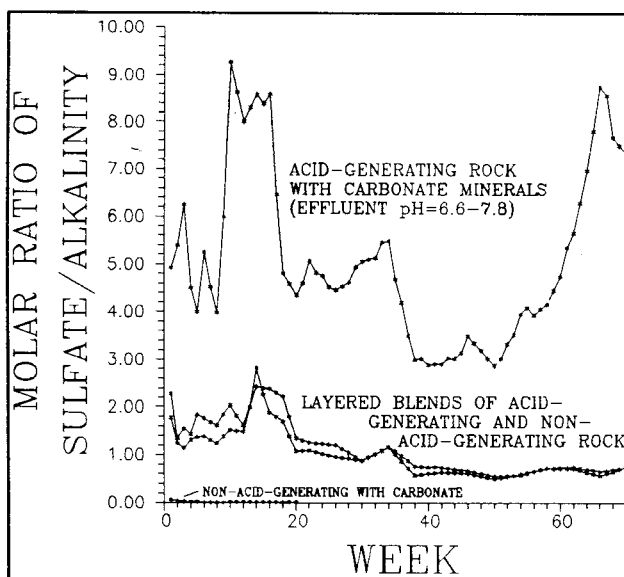


FIGURE 13. Series of Control and Blended Tests on Two Rock Types: Acid-Generating and Non-Acid-Generating Rock, Both with Carbonate.

In this series of tests, the non-acid-generating rock produced low sulphate concentrations on the order of 1-2 mg/L and, because carbonate solubility exceeds this concentration, the values of SO_4/Alk are on the order of 0.02. This value is significantly less than the value of 0.5 which indicates no loss of carbon dioxide during neutralization, and thus obviously reflects a process other than neutralization of acidic water (i.e., there was no significant acid generation). On the other hand, the acid-generating rock produces initial ratio values around 4-5, indicating significant loss of carbon dioxide. Between Week 10-20, there was a significant increase in the rate of acid and sulphate generation; however, the carbonate was able to maintain neutral pH and the SO_4/Alk ratio suggests that significant loss of CO_2 occurred, perhaps reflecting a longer period of time to neutralize more acidic water. Although the ratio decreased to around 3 by Week 40, the rapid increase after Week 60, corresponding to an increase in sulphate concentration, suggest that the neutralizing capacity might soon be exhausted and that acidic water may soon appear in the effluent. This is similar to the trend in Figure 11.

The layered blends of the two rocks types had significantly less loss of carbon dioxide than the acid-generating rock alone. As flowpaths and additional neutralizing reactions by the non-acid-generating layers presumably became established, the ratio dropped towards 0.5 (no loss of CO_2), but remained elevated around 0.6-0.7. This may indicate that closed-system conditions developed in the carbonate-rich layers, leading to a relatively higher rate of carbonate consumption.

In summary, the examples from the database have shown the manner in which the geochemical ratios can be informative, misleading, and ambiguous. In experiments where the ratios are valid, information can be obtained on the rate of carbonate consumption relative to acid production.

4.3 Conceptual Models of Neutralization and Carbonate Consumption

The preceding analysis indicates a wide range in geochemical ratios can arise during laboratory testwork and conceptual physical models are valuable in visualizing the conditions under which a particular ratio might be expected. The following discussion outlines one model that fits the data, but others are possible. This model is based on mineralogical microenvironments and water films surrounding the microenvironments. Neutralization of acid solutions occurs in two separate periods of the kinetic leaching test. During the first, at relatively dry periods between leaching, acid and sulphate are produced by oxidation of the sulphide minerals and released to the water film surrounding the particles in which they are imbedded. If carbonate minerals, either on the same particle or on adjacent particles, are also surrounded by the same water film, the overall bulk pH of the film could be neutral but there could also be differences within the film. For example, adjacent to the sulphide minerals, the pH would be more acid and more alkaline next to the carbonate minerals. During these dry periods, the acidity may be neutralized by relatively slow diffusion and there may be zones of various pH within the water film between the minerals. This could lead to relatively slow stepwise neutralization and loss of CO_2 . Some water films may be entirely acid or alkaline if

only acid producing or acid consuming minerals are present. In the second neutralization period, water is added to the kinetic cell to leach the oxidation and neutralization products. The water films are displaced and mixed. If minor in extent, acid water films would be quickly neutralized when contacting carbonate minerals and alkaline films and, as such, there may be little loss of CO₂. As a result, the procedure of the test has critical impacts on the outcome and the associated predictions.

Three scenarios are observed in the data and can be explained by the preceding models. The low sulphate to alkalinity ratio found in the layered experiments in Figure 13 may occur because of separate acid water films and fast neutralization during flushing rather than closed-system neutralization in the calcite-bearing layers. The high ratio in the blended experiments in Figure 10 and 11 may occur because of more neutral water films and slow neutralization. In the third case with poor blends or samples with insufficient carbonate minerals, a water film may still connect sulphide and carbonate minerals. As oxidation proceeds the microenvironments adjacent to the sulphide minerals may become quite acid because carbonate minerals close to these sites have been consumed. As long as the overall pH remains neutral, then the water films must be extensive to contact sufficient carbonate minerals and the rate of acid and alkaline ion transport might be slow, resulting in progressively more CO₂ release, relatively less NP consumption, and an increase in the sulphate/alkalinity ratio in the leachate until the NP is fully consumed. This is equivalent to the "spreading acid microenvironment" concept discussed in some references. Also, if the microenvironments become more acid, the concentration of contaminants, especially gypsum, in the water film may exceed saturation. Coatings would form, especially on carbonate minerals because it is adjacent to these minerals that high concentrations of both sulphate and calcium would be present. As coatings began to slow the rate of carbonate dissolution and neutralization there could be more CO₂ loss (higher sulphate/alkalinity ratio) as observed in some kinetic tests. This conceptual model is consistent with the results of kinetic tests discussed in this paper but requires further confirmation.

5. PREDICTION OF ACID GENERATION AND NEUTRALIZATION

A critical objective of the experiments in the database is to determine if acid drainage can arise at the minesites. For the experiments that generate acid drainage during the tests, the prediction is straightforward. However, if net acidity is not generated during the tests, then the data must be extrapolated into the future. The validity of these extrapolations and predictions depends on the proper interpretation of the experimental data.

For future predictions, the extrapolation of experimental data can be divided into short-term (a few months), medium term (a few years) and long-term (many years). Short-term predictions can be based on the trends of the geochemical ratios towards the end of the tests. This short-term extrapolation can be seen in Figures 11 and 13 where significant increases in values of SO₄/Alk suggested imminent breakthrough of acid drainage in the effluent, although such a breakthrough was later confirmed by analytical data for Figure 11 only.

Medium-term predictions require an assessment of the consumption rate of carbonate through time. As the examples have shown, alkalinity can be preferentially leached with respect to sulphide from a sample when there is little acid generation. As a result, there is a minimal leaching rate which is applicable to each sample whether any acid is being actively generated. The delineation of this minimal rate can be based on solubility constraints of carbonate minerals (not discussed in this paper) or on experimentally determined alkalinity data where the values of SO_4/Alk are significantly less than 0.5 (e.g., bottom of Figure 13). After this minimal leaching value is obtained, the potentially higher rates from sulphide oxidation are determined by the procedures discussed in Sections 4.1 and 4.2. Specifically, if neutralization is relatively rapid or occurs in a closed system, no CO_2 is lost, and the final pH is above 6.5, then each mole of sulphate in the effluent will represent a leaching of 2 moles of alkalinity as HCO_3^- . Because one mole of bicarbonate is derived from one mole of CaCO_3 , then one mole of sulphate will also represent a removal of two moles of CaCO_3 from the sample. On the other hand, if nearly all carbon dioxide is lost from solution, the ratio of SO_4/Alk will be significantly greater than 1, but this ratio should not be used in the calculations because at least minimal neutralization according to Equation 5 (which does not contribute significantly to alkalinity) has occurred. Equation 5 indicates that one mole of sulphate (2 moles of H^+ from acid generation) in the effluent will represent a leaching of one mole of CaCO_3 from the sample. Consequently, calculations and extrapolations of carbonate consumption should use ratios of SO_4/Alk between 0.5 and 1.0 based on the limiting assumptions in this paper and experiments providing ratios of SO_4/Alk between 0.5 and 1.0 can be extrapolated using the exact value of the ratio. Although a maximum variation of a factor of 2 (from 0.5 to 1.0) can seem negligible and may not affect predictions in the medium term, significant differences could arise in long-term predictions.

This analysis assumes that the rates obtained from a short term leaching test can be extrapolated into the medium term, that all the sulphide and carbonate minerals are available for reaction, and that the geochemical ratios will remain constant. The most important assumption is probably that all the sulphide and carbonate minerals are available for reaction. The reactivity of the sulphide and carbonate minerals will vary with crystal size, composition, and morphology. Euhedral, coarse grained sulphide minerals may be less reactive. Tests are needed to determine the actual minerals available for reaction and this information, combined with the geochemical ratios determined by leaching tests, may provide the best means to predict whether ARD will be formed in the medium term.

Because all the sulphide minerals are assumed to be reactive in acid-base accounting (Section 1), this incorporates in a "safety factor" that may explain the success at least for tailings for this prediction method (Section 2), despite a poor theoretical basis. Nevertheless, long term projections of whether a rock is likely to generate ARD are extremely difficult. It is expected that the development of a weathered rind and the rate of diffusion of reactants and products through that rind may determine the long-term rates of acid production and consumption. Therefore, a more mechanistic approach will be needed to make long-term predictions. Finally, this analysis has arrived at approaches that may be useful in predicting whether a sample will generate ARD in the laboratory. Further work is needed to test and develop approaches for the

field.

6. CONCLUSIONS AND RECOMMENDATIONS

- 1) Based solely on the field data, the static tests (NP/AP ratio) appear to predict qualitatively whether ARD is likely to be formed in tailings deposits. The mean NNP might be useful for waste rock prediction, but the database is very small. Further field tests of tailings, with various ages and NP/AP ratios, and of all types of waste rock are required to validate this conclusion.
- 2) Only 37% of the samples in the database generated acid leachates in the laboratory (Type II and III) despite the vast majority of samples exhibiting an acid generation potential by static tests (NNP=0 criterion). Relatively high neutralization potential in many samples buffered the system in the short term, preventing acid leachates within the short duration laboratory tests (Type I). Conclusions on longer-term net acid or non-acid production based solely on whether acid leachates are found in the laboratory are uncertain.
- 3) Figures were developed which may aid in comparing reactivities of sulphide minerals and determining the time to acid production for laboratory experiments. More data are needed relating reactivity to exposed surface area, and determining the time to acid production for samples with a NP/AP between 0.1 and 1.
- 4) Concentration data obtained from laboratory kinetic tests cannot be extrapolated directly to field conditions. Normalized sulphate production rates per unit surface area and percent sulphur can be related but the laboratory rates should apparently be reduced. Studies comparing laboratory and field rates are needed, particularly for the initial stages of the ARD process, to determine how laboratory rates should be modified.
- 5) The leachate geochemical ratios reveal the acid production and consumption conditions that could be important in ARD prediction. These ratios can indicate the rate of carbonate consumption relative to the rate of acid production as well as the imminent release of net acidity in kinetic tests. However, dissolution of secondary minerals such as gypsum can greatly complicate interpretation particularly during the initial leaching cycles. Therefore, testing must be sufficiently long to ensure these minerals are not affecting leachate chemistry. Leachates from kinetic tests should be tested for sulphate, alkalinity, calcium, and magnesium to allow calculation of these ratios.
- 6) Both static and kinetic tests suffer from limitations in ARD prediction. In static tests, the existing criterion (NNP=0 criterion) may not be theoretically supported and actual available acid producing and consuming minerals are not determined. In kinetic tests, short duration laboratory tests may not resemble the field conditions in the medium and long term. Development of static methods to determine reactive sulphide and carbonate minerals is recommended to redefine the ABA based on the available mass of reactive minerals, rather than the total mass used in conventional ABA.

7) The approaches discussed in this paper should be useful in assessing the factors that control ARD production, in the short and medium term in the laboratory and for characterizing or classifying kinetic leach test results. These approaches, however, will not be ready for full qualitative predictions until further cases are tested. Little is known about the factors that control ARD production in the long term, especially for waste rock. Long term experiments and studies of old wastes, not yet generating ARD, are clearly needed.

BIBLIOGRAPHY

Cravotta III, C.A., Brady, K.B.C., Smith, M.W., and R.L. Beam, 1990. "Effectiveness of the Addition of Alkaline Materials at Surface Coal Mines in Preventing or Abating Acid Mine Drainage: Part I. Geochemical Considerations". In: 1990 Mining and Reclamation Conference and Exhibition, April 23-26, Charleston, West Virginia.

Ferguson, K.D., 1985. "Static and Kinetic Methods to Predict Acid Mine Drainage". Environmental Protection Manuscript Report, Conservation & Protection, Environment Canada, Pacific and Yukon Region.

Ferguson, K.D. and P.M. Erickson, 1988. "Approaching the AMD Problem - from Prediction and Early Detection." In: Proceedings, International Conference on Control of Environmental Problems from Metal Mines, June 20-24, Roros, Norway.

Kwong, Y.T.J. and K.D. Ferguson, 1990. "Water Chemistry and Oxidation Mineralogy at Mount Washington - Implications to Acid Generation and Metal Leaching". In: Acid Mine Drainage Designing for Closure - GAC/MAC Joint Annual Meeting, May 16-18, 1990, Vancouver, British Columbia.

Lindahl, L-A, 1990. "Acid Mine Drainage - Research and Remedial Actions in Sweden". In: Acid Mine Drainage Designing for Closure - GAC/MAC Joint Annual Meeting, May 16-18, 1990, Vancouver, British Columbia.

Morin, K.A., 1990. Problems and proposed solutions in predicting acid drainage with acid-base accounting. Proceedings of Acid Mine Drainage - Designing for Closure, GAC/MAC Conference, Vancouver, B.C., May 16-18.

Smith, A. and J.B. Barton-Bridges, 1991. "Some Considerations in the Prediction and Control of Acid Mine Drainage Impact on Groundwater from Mining in North America". In: Proceedings of the EPPIC Water Symposium, Johannesburg, May 16-17.

Steffen Robertson and Kirsten, 1989. Draft Acid Rock Drainage Technical Guide - Volume 1. Prepared for B.C. AMD Task Force.