

## RELIABILITY OF ACID ROCK DRAINAGE TESTING

Dr. A. MacG. Robertson, P. Eng. and Linda M. Broughton, P.Eng.  
Steffen, Robertson and Kirsten, Vancouver, B.C. (604) 681-4196

### ABSTRACT

*It is the quality of drainage water from sulphitic rocks in the field that determines the actual or potential environmental impact of acid rock drainage (ARD). It determines the need for, and success of, alternative control measures. Accurate estimation and prediction of ARD is therefore a critical pre-requisite to successful ARD control.*

*The development of acid generation from sulphide bearing rocks is a time dependant process. Acid generation varies with time, as does the quantity of acidic products stored on, or about, the source. The mobility of these (stored) oxidation products will determine the quality of the drainage as infiltration flushes the oxidation sites. Seasonal and climatic controls on infiltration rates result in large variations in drainage water quality, both in the short term on a daily or weekly basis (for some rock piles) and in the long term. Static tests measure the theoretical potential for acid generation. A soluble product extraction test provides a measure of the accumulated soluble products of acid generation at any instant in time, reflecting the sample history to that date. Kinetic tests determine the evolution of the acid generation process and yield drainage water quality which is dependant on both the test configuration and method and on the mineralogy of the sample. Results can vary widely depending on sample collection, storage, preparation and resting methods.*

*Appropriate methods of sampling and testing are necessary if even moderately reliable estimates or predictions of field drainage water quality are to be made from laboratory tests. It is the intention of this paper to describe the factors which control the reliability and model similitude of prediction testing for ARD. This paper examines some of the conditions controlling ARD quality in prediction testing, variability of results obtained from various sampling and test methods, and makes recommendations as to appropriate procedures to improve reliability. The techniques described herein refer to prediction for all mine site components, however much of the discussion relates to mine rock piles, for which sampling and testing is the most complex*

### OBJECTIVES OF ACID ROCK DRAINAGE TESTING

ARD testing is usually performed for one of two purposes:

- i) To determine the maximum concentrations of contaminants which will be released to the environment from deposits of sulphide bearing rock (mine walls, mine rock piles or tailings). The objective is to determine if ARD control measures will be required, or if proposed measures are adequate. Such testing must enable water quality estimates to be made which are sufficiently accurate to safely proceed with project development or remediation measure implementation. To be useful, the testing and water quality prediction methods must have a reasonably high reliability.
- ii) To obtain estimates of average contaminant contents and loadings, and the probable range of variation, for the purpose of designing con-

taminated drainage collection and water treatment systems. For such estimates the accuracy is often acceptable at an 'order of magnitude' level, as there is flexibility and additional control inherent in the water management and treatment system. Reliability of the ARD water quality prediction testing is considerably less critical than for the first purpose.

### EVOLUTION OF ACID ROCK DRAINAGE QUALITY

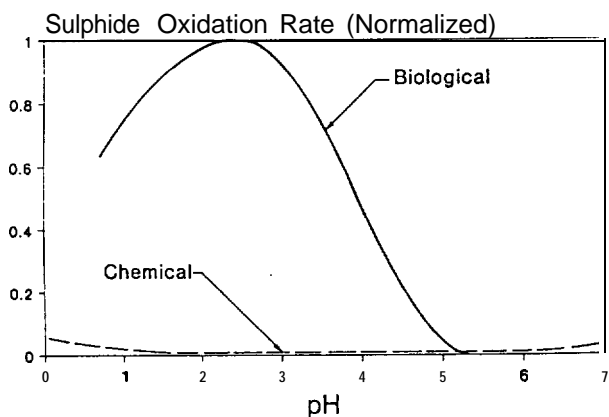
The development of acidic drainage, its characteristic water quality, and the rate controls at each stage of the acid generation process, must be recognized before reliable interpretation of prediction tests is possible.

ARD does not occur instantaneously but develops over a period of time as conditions favouring acid generation evolve. Conditions controlling the rate of acid generation are:

- presence of the reactive sulphides, water and oxygen (the **necessary** ingredients)
- presence and activity of *Thiobacillus ferrooxidans* and other oxidation catalyzing bacteria
- **pH**
- temperature

The acid generation process is started when a particle of rock containing reactive sulphides is exposed to air and water. The evolution of the acid generation processes is then dependent on the ‘environmental’ conditions influencing the rock particle. The rate of acid generation varies with time and from location to location, depending on the specific site conditions.

For a sulphide sample, the typical **normalized** rate of acid generation as a function of **pH** is shown in Figure 1.

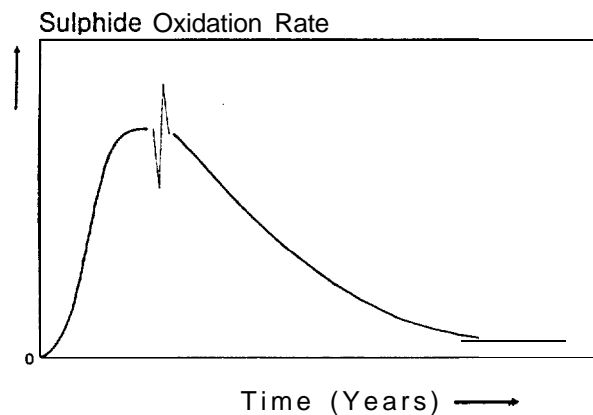


**Figure 1** Sulphide Oxidation Rate as a Function of pH

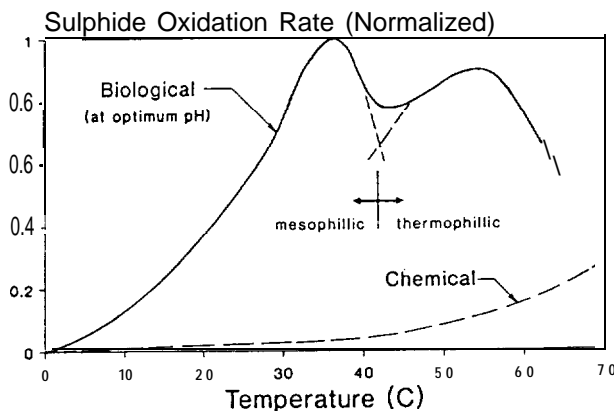
Of particular interest is the acid generation rate at near neutral **pH**, as this is the most difficult range to interpret in kinetic testing (Ferguson and Morin, 1991). In this range, acid generation is primarily due to chemical oxidation. The rate is relatively low and acidity is immediately neutralized by available alkalinity in the sample to maintain near neutral **pH**. The solubility of most metals are low at neutral **pH** and consequently **leachate** contaminant concentrations are usually low in most metals. Once the basic minerals are consumed the **pH** begins to drop and below a **pH**

of about 4.5 biological oxidation rapidly accelerates the acid generation process. **Thus** there may be a long period of slow acid generation required to achieve the initial **pH** drop followed by comparatively rapid increases in acid generation and a large decline in the **leachate** quality as the metals are more soluble at lower **pH**. Acid generation may proceed at a rapid rate until the sulphides are depleted and the oxidation rates decline.

This lag time can extend for weeks, months or years in the field and in lab testing, as illustrated in Figure 2. The effect of temperature on acid generation is illustrated in Figure 3.



**Figure 2** Sulphide Oxidation Rate as a Function of Time



**Figure 3** Sulphide Oxidation Rate as a Function of Temperature

As the exothermic reactions of acid generation increases temperatures in the field, the rate of acid generation **also** increases **to a limiting value at about 60°C.**

The quality of the drainage water emanating from an acid generating rock pile also varies, depending not only on the presence or absence of acid generation, but on the:

- rate of acid generation, hence amount (load) of acidity produced;
- rate of leaching, hence concentration of acidity in leachate;
- history of acid product accumulation and hence load available for leaching during flushing events;
- metals (and other leachable contaminants) present; and
- the acidity buffering and contaminant attenuation that occurs along the flow path before the **leachate** is collected.

If a sample of reactive sulphitic rock has **been** exposed to oxygen and water for some time, without complete flushing to remove the acid products, it will contain a finite load of readily leachable acid generation products in either or both the liquid and solid phase. When such a sample is tested in a leaching test, it may yield the **leachate** quality curve illustrated in Figure 4. Initially high concentrations of contaminants are leached as the load of acidic products in storage in the flow pathways are released. After declining to some minimum **value** the contaminant concentrations may again begin to increase as conditions evolve which are favourable to higher rates of acid generation and associated contaminant leaching. All alkalinity, originally available in the sample, may have been consumed prior to testing or rendered unavailable by coating, resulting in a much more rapid development of the maximum acid generation rate than **may** apply to a fresh sample.

For the above reasons, old and fresh samples may yield very different **leachate** qualities on **first** flushing and very different acid generation evolution and **leachate** quality characteristics. Sample selection, aging, storage, preparation and testing methods all have large effects on the quality of **leachate** generated from different ARD tests. These differences, as well

as recommendations for appropriate methodology, are reviewed below.

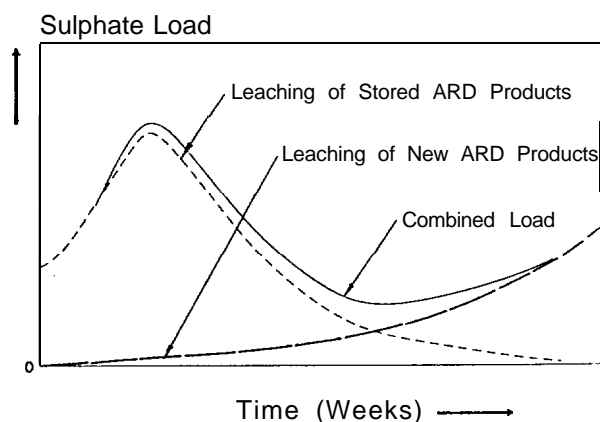


Figure 4 *Sulphate Leaching as a Function of Time*

#### OLD MINES VS NEW MINES

Sampling and testing for new mines (mines yet to be developed) usually have different concerns and requirements compared with old mines. A comparison of ARD conditions and information available from new and old mines is provided on Table 1. At new mines the primary concern is the potential for acid generating conditions which may develop, and, if ARD can **occur**, the effectiveness of alternative control measures. Prediction is based on fresh samples, often representative of an uncertain geology and mineralogical distribution, **with** a requirement for accurate prediction of drainage water qualities (and contaminant loads) a long time into the future.

For old mines the ARD is often well established providing a clear demonstration of material behaviour and contaminant loads and concentrations to the environment **Questions** that **need to** be answered relate to the quantity of acid products stored in the waste (which are available for leaching regardless of additional acid generation), the evolutionary stage of acid generation in the various waste piles, and how future waste production will compare with the waste produced in the past. The geology and sulphide distribution in the mine and remaining ore body is often well

TABLE 1  
COMPARISON OF INFORMATION ON ARD AVAILABLE FROM NEW AND OLD MINES

Information Type	New Mines	Old Mines
Geology and sulphide mineralization distribution	<ul style="list-style-type: none"> <li>- Limited by size of exposures and volume of rock investigated</li> <li>- Continuity, distribution and relative quantities of rock classes more difficult to define</li> </ul>	<ul style="list-style-type: none"> <li>- often extensive exposures allowing sound understanding of geology and in-situ <b>sul-</b>phide mineralization distribution</li> <li>- distribution in piles may be unknown</li> </ul>
Acid generation behaviour	<ul style="list-style-type: none"> <li>- Lack of field data: potential must be determined from small samples, often of 'fresh' rock</li> </ul>	<ul style="list-style-type: none"> <li>- Long term exposure of various rock types permits field observation of acid generation evolution</li> </ul>
Acid product storage	<ul style="list-style-type: none"> <li>- No acid products stored in rock mass - must be assessed from kinetic test on 'fresh' samples</li> </ul>	<ul style="list-style-type: none"> <li>- Various stages of acid product storage</li> <li>- Storage nature and load can be determined <b>from</b> representative field samples</li> </ul>
Drainage Water Quality	<ul style="list-style-type: none"> <li>- No field seeps representative of acid generation conditions. No data available for ARD <b>leachate</b> quality model calibration</li> </ul>	<ul style="list-style-type: none"> <li>- Field seeps in various stages of acid generation evolution. May be used for ARD water quality model calibration</li> </ul>

understood (or determinable) but the distribution, as placed on the rock piles (waste dumps), may not have been recorded. The detailed composition of the rock piles may therefore be uncertain. For old and new mines the establishment of an inventory of mine rock and tailings piles, existing and to be produced, is essential. For new mines this **will** be based on mine planning and scheduling but for old mines it requires site reconnaissance and investigation of the form described in Broughton et al 1992. This must be followed by ARD characterization of the materials that are in, or will be, in the various piles. Finally the long term acid generation and drainage water quality must be predicted with and without ARD control or remediation measures, in order to establish control potential and costs. The control potential and costs are essential information for decisions relating to permits, for on-going mine operation, and for the selection and financing of appropriate control options.

The environmental liability associated with inappropriate decisions based on inaccurate prediction methodology is huge.

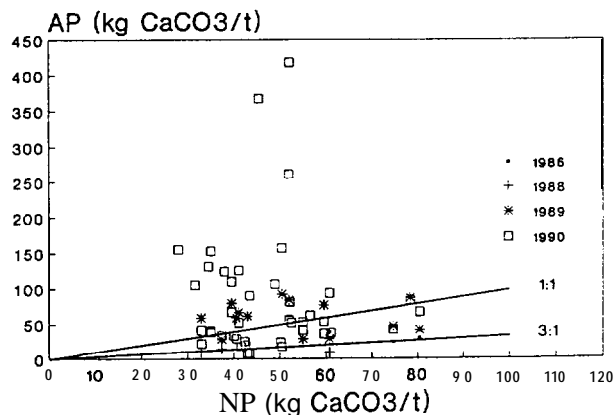
#### INFLUENCES OF SAMPLING

##### Representativeness of Sampling

Sulphide distribution, as for all mineral distribution, is variable through and about an ore deposit. Just as it is necessary to take a large number of assay samples to define an ore body, so it is necessary to take a sufficient number of acid/base accounting (ABA) samples to define the acid generating potential of the “waste” rock about an ore body. Similar sampling and **geostatistical** evaluation techniques are applicable. The Draft ARD Technical Guide prepared by the BC Task Force on ARD, SRK (1989), provides guidelines as to minimum sample numbers.

Most recently, additional complementary guidelines have been issued by the province of Saskatchewan as the “Mine Rock Guidelines for the Design and Control of Drainage Water Quality”, SRK (1992), which describes a geological evaluation and sample selection process. Samples should be taken with a geographical spread throughout the zone of interest for each ARD rock class as defined by the ARD rock classification process described by Brodie et al, 1991.

Representative sampling is the most critical, and perhaps most difficult, part of a testing program. An example of inappropriate sampling is illustrated for an un-named mine, for which the ABA results are illustrated in Figure 5.



**Figure 5** Results of Annual ABA Tests for an Unnamed Mine

The results of ABA tests on “representative” mine rock samples for each year 1986 to 1990 are shown in the figure. Based on the **first** series of samples taken it was concluded that the mine rock was not acid generating and no ARD control measures were implemented. Sampling from successive years clearly indicates a “shift” in the ARD potential. The mine is now faced with an acid generating problem. Had the original sampling program recognized the rock variability, changes in sulphide content approaching the ore zone, and been designed to be more representative of the entire mining zone, then appropriate control technology could have been implemented and current problems avoided or reduced.

##### Composites

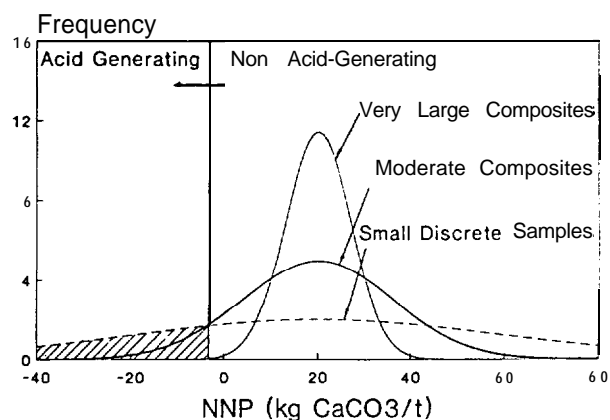
All samples represent a composite of rock minerals over some extent; often mixing rock materials which have a large variation in sulphide and alkali content. The larger the dimensions over which the composite is taken, the greater the extent of mixing and the more likely the sample will be representative of some mean value.

Indiscriminate mixing of rock material from different localities results in a composite with properties which are not necessarily representative of any of the material types included in the composite. A number of sampling strategies result in composites:

- i) sampling over an interval of core length
- ii) combination of different rock types to produce a sample representative of some larger deposit (such as a rock pile)
- iii) sampling of the same rock type (from ARD considerations) from different locations.

Compositing may be required to provide sufficient sample for a kinetic test, in which case it is essentially bulk sampling, or when small-scale heterogeneities would effect an individual sample. The greatest concern is with the **first** two strategies.

Figure 6 illustrates the effect on the distribution of net neutralization potential (NNP) values that would be obtained for random sampling with different composite sizes from a rock mass with a highly variable sulphide content.



**Figure 6** Frequency Distribution of NNP Values

For the example chosen, acid generation would occur (as demonstrated by kinetic testing) in samples with a NNP of less than -4. From the figure it is apparent that the percentage of “potentially acid generating”

samples increases as the composite size (or length) decreases. In the extremes, a single composite of the entire sample population would be “not acid generating” while the distribution for a large number of small samples (each representing about 1 kg of rock taken over a lateral dimension of 10 cm) may indicate 30% of the samples to be potentially acid generating. The potential for acid generation within the resulting mine rock pile depends on the degree of mixing of rock types. If the various samples were intimately mixed, as would occur for a tailings deposit, then large composites may be representative of the final deposit. However, if the various samples are not intimately mixed, as occurs in a mine rock pile, then some layers and portions of the rock pile may be acid generating while other layers or portions are acid consuming. Contaminated drainage from the portions of the rock pile which are acid generating will result in contaminated ARD.

It is essential that compositing lengths be restricted to enable the micro and macro behaviour of a rock pile to be evaluated. Our current practice for drill core is generally to restrict **compositing** to 0.5 m lengths, depending on the occurrence of mineralization and heterogeneity of the sample. If appropriate to the evaluation, the ABA results of adjacent samples can be numerically summed to derive the ABA values for larger composites.

## STATIC & KINETIC TESTING

### Static Tests

Static tests are designed to determine if the “ingredients” necessary for acid generation are available in sufficient quantities and appropriate proportions so that acid generation could occur if all the other conditions necessary for acid generation were present. They are intended as **YES/NO** index tests of the theoretical potential for acid generation, and are cheap and quick to allow rapid initial assessment of large numbers of samples.

Since the static test determines only the balance between the “basic ingredients” in a sample and, as the name implies, does not address a number of critical kinetic parameters which contribute to the potential for acid generation, these tests are only reliable (definitive) when:

- values are clearly acid generating or consuming; or
- values are “calibrated” by other testing.

There is a low reliability in the near marginal “potentially acid generating” conditions.

Based on earlier eastern US coal mine experience and comparative testing (Ferguson, 1991; personal communication), this “grey” area in interpretation is found between plus and minus 20 kg/tonne  $\text{CaCO}_3$  equivalent as illustrated in Figure 7. More recently experience in the evaluation of mine rock piles at Canadian metal mines has shown that in addition to the NNP value, the ratio between neutralization potential (NP) and acid potential (AP) should also be considered. Based on NP:AP ratios a zone of uncertainty may exist between a ratio of 1:1 and 3:1 as illustrated in Figure 8.

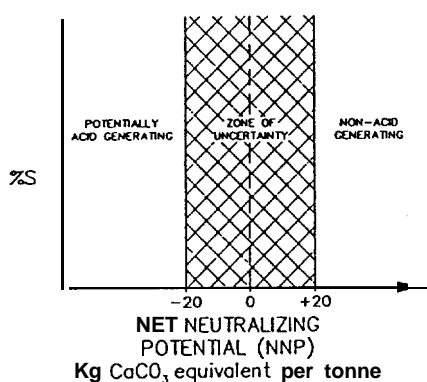


Figure 7 Interpretation of ABA Results by NNP

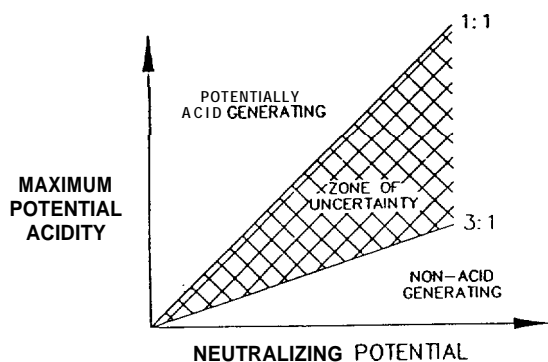


Figure 8 Interpretation of ABA Results by NP:AP

To reduce this wide range in which static testing alone is not definitive of ARD potential, it is necessary to use kinetic testing to satisfy the YES/NO question.

Static tests cannot determine the rate of acid generation nor provide an estimate of the drainage water quality.

Short Term Leach Extraction Tests (static tests)

Short term leach extraction tests are used to determine the readily soluble constituents in a sample. Many rock types have readily soluble constituents, available for immediate leaching, quite independent of any acid generation that may occur.

On exposure to air, oxidation will commence for any exposed oxidizable products contained in drill core, bulk samples or mined rock. The rate of oxidation, and the accumulation of oxidation products will depend on the conditions of air and water availability and leaching conditions to which the samples or rock are subjected.

The accumulation (load) of soluble oxidation products can be determined by an appropriate leach extraction test. If the leachate is selected to represent field leachate quality (simulated rain water or groundwater), then the total load available for release in the field can be determined.

The rate of leaching in the field is dependent on the flow paths, and flow rates that will occur in the field. Simulation of the seasonal variation of flow is essentially a kinetic test and is considered in the next section.

Kinetic Testing

Kinetic tests are intended to subject the sample in a controlled environment to conditions under which the kinetic processes of acid generation and contaminant leaching can proceed. The evolution of the process is monitored and the results used for the purposes of acid generation prediction, drainage water quality estimation and alternative control technology evaluation.

The reaction kinetics which develop are dependant on a large number of conditions in the test sample, thus

the accuracy with which the test duplicates the conditions that will exist in the field, and the field results, depends on the accuracy **with** which appropriate field conditions can be duplicated. Alternatively the differences between laboratory and field kinetic behaviour must be understood and appropriate corrections applied when extrapolating laboratory results to **field** estimates.

In the following sections some of the factors affecting the kinetic test results, and therefore the reliability of field water quality prediction from kinetic laboratory testing, are reviewed, based on the current understanding. It is recognized that there is not yet a definitive answer on the “best” method to predict field drainage water quality, particularly for mine rock.

#### Field Tests

Field tests have the very substantial advantage that they:

- can be conducted using sample gradings representative of field gradings;
- are subject to weather conditions typical of the site; and,
- can be conducted at a scale representative of the waste piles that would be developed in the field.

They represent the most reliable method for the determination of ARD quality. Unfortunately they suffer from the following disadvantages:

- expensive to construct and maintain, particularly at remote sites, therefore only a few, representing a limited **range** of sample variability, can be performed;
- often the **field** kinetic rates are very slow requiring long testing periods (years);
- test results must be interpreted in light of the actual climatic conditions during the testing period, i.e. particularly dry, cold, etc.; and
- test conditions are site specific and results to be applied to other sites must be “calibrated” for site conditions and rock geochemistry.

For existing mines where tailings or mine rock piles exist, these represent large field tests and much insight into future behaviour with respect to ARD can be obtained from a site ARD reconnaissance in

accordance with the procedures proposed in the Saskatchewan Mine Rock Guidelines (**SRK**, 1992).

A combination of field tests, laboratory kinetic tests and static tests may provide the optimum for any investigation program.

#### SIMILITUDE OF TEST AND FIELD CONDITIONS

##### Particle Size Distribution

The rate of sulphide oxidation is directly proportional to the surface area of sulphides exposed to oxidation. In a graded material the surface area per unit weight of material is inversely proportional to the particle diameter. Thus the greatest part of the total surface area is associated with the **finer** fraction of the material. For this reason there is usually justification for testing only the finer fraction of the material to determine the reaction kinetics, and then correlating the reaction rates and results between samples and/or field conditions by correcting for the total surface area of particles in the various samples and deposits. With such corrections, good correlations have been obtained between tests at different scales and with particle size distributions as illustrated by Norecol 1988 and Figure 9. where the results of long term conventional humidity cell tests and large scale field pad tests show similar sulphate production rates once the test data is corrected to reflect production per unit area.

Particle size is also important in that it affects the chemical and physical conditions in the sample in the following ways:

- in fine materials the acid generating and alkali materials are in close proximity, thus the alkali source can effectively control the **pH** conditions and hence the acid generation **rate**;
- the convective and **advective** transport of air and oxygen occurs more freely through coarse materials than fine materials; and
- the moisture holding capacity, hence chemical storage capacity and leaching characteristics differ between fine and coarse materials.

The effect of the proximity of sulphidic and alkaline materials can be large. Conventional humidity cell

testing illustrated in Figure 10 requires sample crushing to minus 2 mm. Thus test similitude is appropriate for **ARD** conditions in tailings deposits as illustrated in Figure 11, but not for mine rock piles. To adequately represent the conditions in mine rock piles, Figure 12, requires the testing of samples with a size and grading representative of a larger range of the particle size fraction of the field grading. In order to appropriately test coarser materials, the authors have proposed the **SRK** cell test (Brodie et al, 1991), as illustrated in Figure 13.

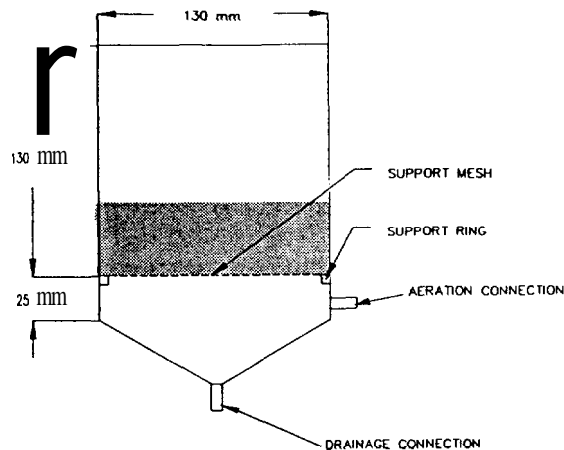


Figure 10 Conventional Humidity Cell

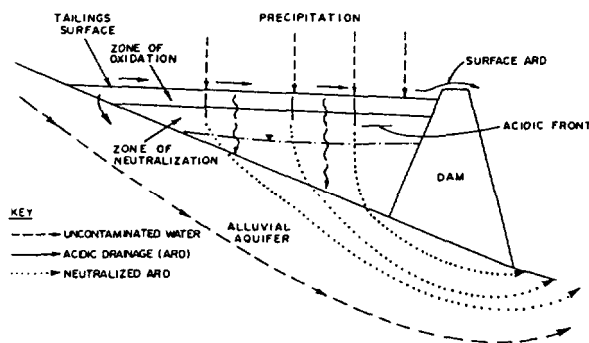
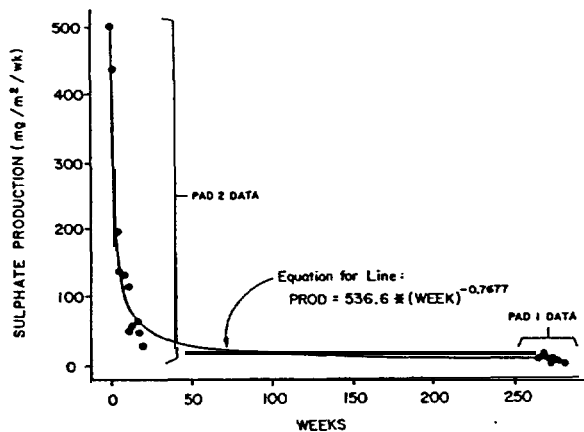


Figure II ARD and Contaminant Front Development in a Tailings Impoundment

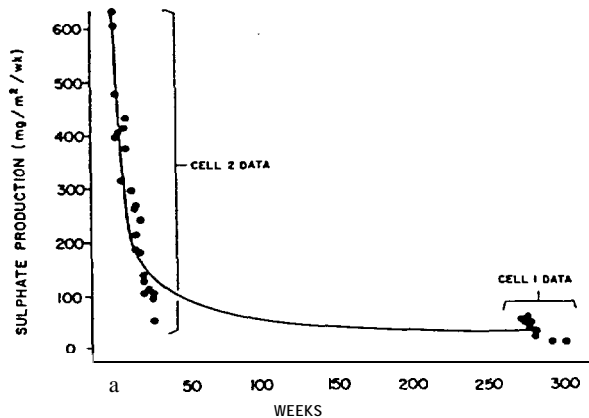


Figure 9 Comparison of Sulphate Production Rates per Unit Area for Equivalent Samples Tested in Small Scale Lab and Large Scale Field Pad Tests

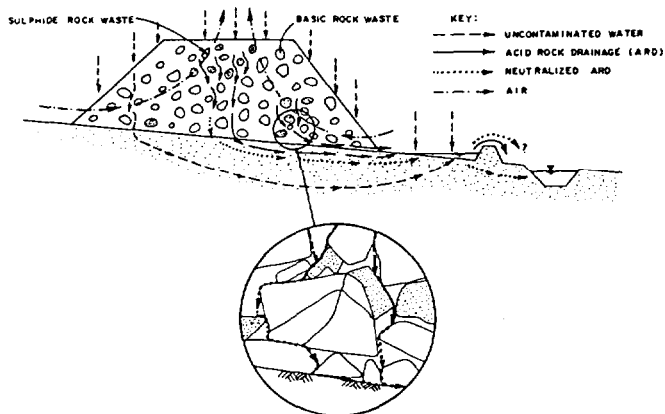
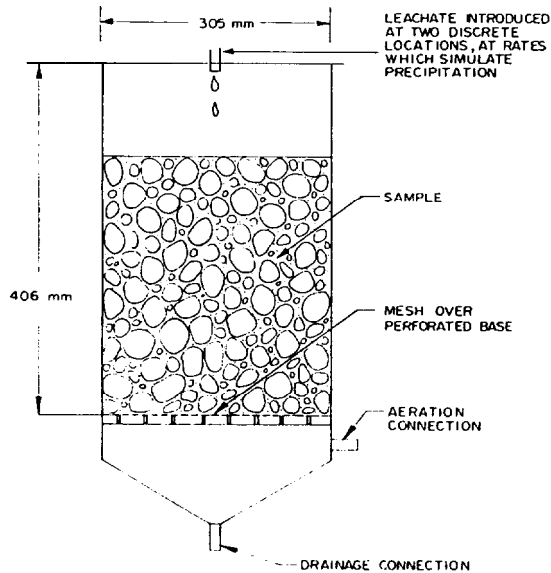


Figure 12 ARD and Contaminant Front Development in a Mine Rock Pile



**Figure 13** SRK Cell Test

#### Configuration

The configuration of the test should reasonably duplicate, within the test sample, the field conditions of:

- oxygen availability;
- water availability;
- acid generation (chemical) product storage;
- flushing (leaching) rates and patterns; and,
- drainage path length.

If field conditions are not duplicated, there is uncertainty in how the field conditions can be estimated from laboratory results. Because of limitations to the conventional humidity cell test the SRK cell test was developed to provide greater similitude. The influence of flowpath length on acid generation and water quality prediction, and how this influence can be tested and/or modelled, has not been resolved, particularly for mine rock piles.

#### Samples

Samples selected for laboratory testing should be representative of the materials that they are selected

to represent in the field. This includes representative mineralogy, AP and NP and equivalent ARD classification, as described by Brodie et al (1991). which accounts for sulphide type and distribution, alkali type and distribution, grain size and slaking characteristics. Fresh or aged samples with representative acid product storage must be selected to represent the appropriate conditions in the field.

## Weather

These are a number of weather determined conditions which affect reaction kinetics. These are:

- temperature, as illustrated in Figure 2. A field test plot at the Faro mine, Yukon, **Canada**, has demonstrated the effect of low temperatures and freezing in controlling acid generation;
- precipitation and infiltration patterns and rates determine the moisture conditions and flushing patterns; and
- barometric “pumping”, convective (temperature) and **advective** (wind pressure) induced transport of air into air filled void spaces.

Corrections can be applied for temperature conditions mathematically, but the effects of moisture conditions and flushing patterns must be provided for in the test configuration and procedure. **Modelling** of both flushing patterns and oxygen transport (other **than** diffusive transport) by mathematical means is still in the early stages of development (Broughton and Robertson, 1991).

## Time

Kinetic tests are time dependant Usually the time period required for the evolution of the full history of kinetic behaviour (Figure 2) is too long for the full kinetic cycle to be determined and tests are terminated when **the** maximum rate of acid generation is achieved.

The laboratory conditions (temperature, moisture addition, etc.) applicable to kinetic testing are usually very favourable to acid generation. Despite this, it is the author’s experience **that** more **than** 70% of kinetic tests are usually required to be continued for longer than 10 weeks, and a substantial percentage require testing for more than 20 weeks. This is in large part a function of the initial alkali content (neutralization potential) of **the** material (**Ferguson and Morin**, 1991).

Acceleration of Kinetic Tests by ‘Spiking’ and ‘Inoculating’

Acid generation conditions can be accelerated by spiking the sample **with** acid and/or inoculating the sample with *Thiobacillus ferrooxidans*. However such

activities modify the sample and there is a question as to how reliable (and overly pessimistic) the resulting drainage water quality is of the field conditions. When such accelerated testing is necessary then the authors **favour** the simultaneous testing of two identical samples, (one with and one without acceleration) and to consider **the** results as “bracketing” the probable terminal value. As the two test methods provide results which trend to a common value, an estimate can be made of the common value at an earlier stage than if only one test type is used. **The** proportion of **the** sample which is ‘spiked’ should not exceed 5% of **the** sample. Such ‘spiking’ is analogous to **the** effect of high sulphide ‘trigger\*’ spots in a rock pile

## SAMPLE PREPARATION

### Grading

As the rule of thumb, the grading in **the** test sample should simulate the grading of the minus 10 cm grading anticipated for the mine rock in the field. For existing mines such samples are usually best obtained from the rock piles in the field. For proposed new mines it may have to be generated from core. Since breaking up or crushing of the core to minus **10** cm does not generate the percentage of **finer** that would occur from blasting and handling in the field, it may be necessary to **fine** crush and grind part of the sample to achieve the desired sample grading.

### Size

The sample (and test) size should be as large as can be economically achieved, with the test cell size preferably being at least 8 times the size of the largest particle. Relatively small samples, approximately 0.2 kg, can be used for conventional humidity cell tests. Sample sizes between 25 and 50 kg are required for **the SRK** cell test.

The drainage **path** length through the sample for waste rock testing should allow for the development of discrete flow paths along which acid product storage, contaminant migration and flushing kinetics can fully develop. The authors recommend a sample height of at least **40** cm for the SRK cell.

A comparison between drainage water quality obtained from a sample tested by four different methods: conventional humidity cell, SRK cell,

unsaturated column (unflooded) leach and saturated column (flooded) leach is illustrated in Figures 14a and 14b. While **pH** and molar ratio of sulphate to calcium plus magnesium values are similar for the three unflooded tests, significant differences in the sulphate concentration in the **leachates** are indicative of differences in water quality. The decline in **the** flooded column concentrations after 17 weeks results from **the first** complete replacement of (flushing) of pore water in the flooded column.

### Aging

The significance of the age and past oxidation history on **the** acid product storage and ARD evolution of a sample has been mentioned. Sample storage and aging conditions must be taken into account when initiating the test and designing the test method. The effect of stored acid products is apparent from **the** initial **pH** rise for the unflooded column test and the initial sulphate yield from the flooded column in Figure 14. Preferably samples should be collected and stored in such a manner that acid generation conditions are prevented by the sampling and storage conditions. Typically, samples should be aluminum foil and plastic film wrapped and/or sealed in heavy plastic bags stored in buckets **with** air tight lids to prevent additional oxidation. If the sample tends to oxidize rapidly, it may be necessary to fill the container **with** nitrogen gas to displace air (O<sub>2</sub>).

### Crushing

Crushing of a sample increases the total surface area of exposed **sulphides** and exposes new minerals for leaching. It has been the authors' experience that the crushing of coarse mine rock, which is already exhibiting a reduced **pH** as a result of acid generation, will release alkali and result in an increase in the paste **pH** and a consequential short-term reduction in the acid generation rate and reduction in contaminant concentrations in short term leach extraction tests. The effect of small additions of basic minerals (limestone) on acid generation kinetics and ARD quality is illustrated by the test results in Figure 15.

Crushing to a **finer** material also changes **the** average **spacial** distance between the alkali and the acid generating sulphide minerals as previously discussed. These differences **are** responsible for significant differences in the kinetics of acid generation and

ARD quality as illustrated by the comparison of ARD evolution in a finely crushed sample tested in a conventional humidity cell and a coarse sample in a **SRK** cell as shown on Figure 16.

### TEST PROCEDURES

Having set up (configured) a test, **the** quality of the seepage water from **the** test will still be dependant on the test procedures. Some of **the** variations are reviewed below.

#### Initial Flushing

The initial flush may be:

- extensive, designed to remove all soluble products. Such a flush, involving large quantities of water will allow the determination of the total soluble product load, in the same manner as a short term leach extraction. The water quality of **the leachate will**, however, not be representative of a trickle leach. By flushing out all the acid products in storage, changing the sample **pH** and the kinetics of acid generation in **the** test specimen, as well as **the** pattern of contaminant migration into future flush paths, subsequent seepage quality is severely altered.
- a trickle, to flow along a discrete flow path, with the minimum quantity of water being introduced intermittently in a slow trickle to provide a discharge from the base of the sample. The resulting discharge contains only a portion of the acid products in storage in the sample, the balance being available for migration into the future flush paths, as well as maintain the acid generating environment in the sample. Since only portion of the acid products are flushed out it is not possible to determine the total quantity of acid products in storage. **The** seepage from the base of **the** test specimen may be indicative of the quality of water to expect from field seepage, from a layer with a thickness equivalent to that of **the** test specimen.

Figure 17 illustrates the difference in acid generation and flushing rate, when columns of identical material are subjected to a trickle leach, repeated flushing to remove soluble products, or kept under water all **the** time.

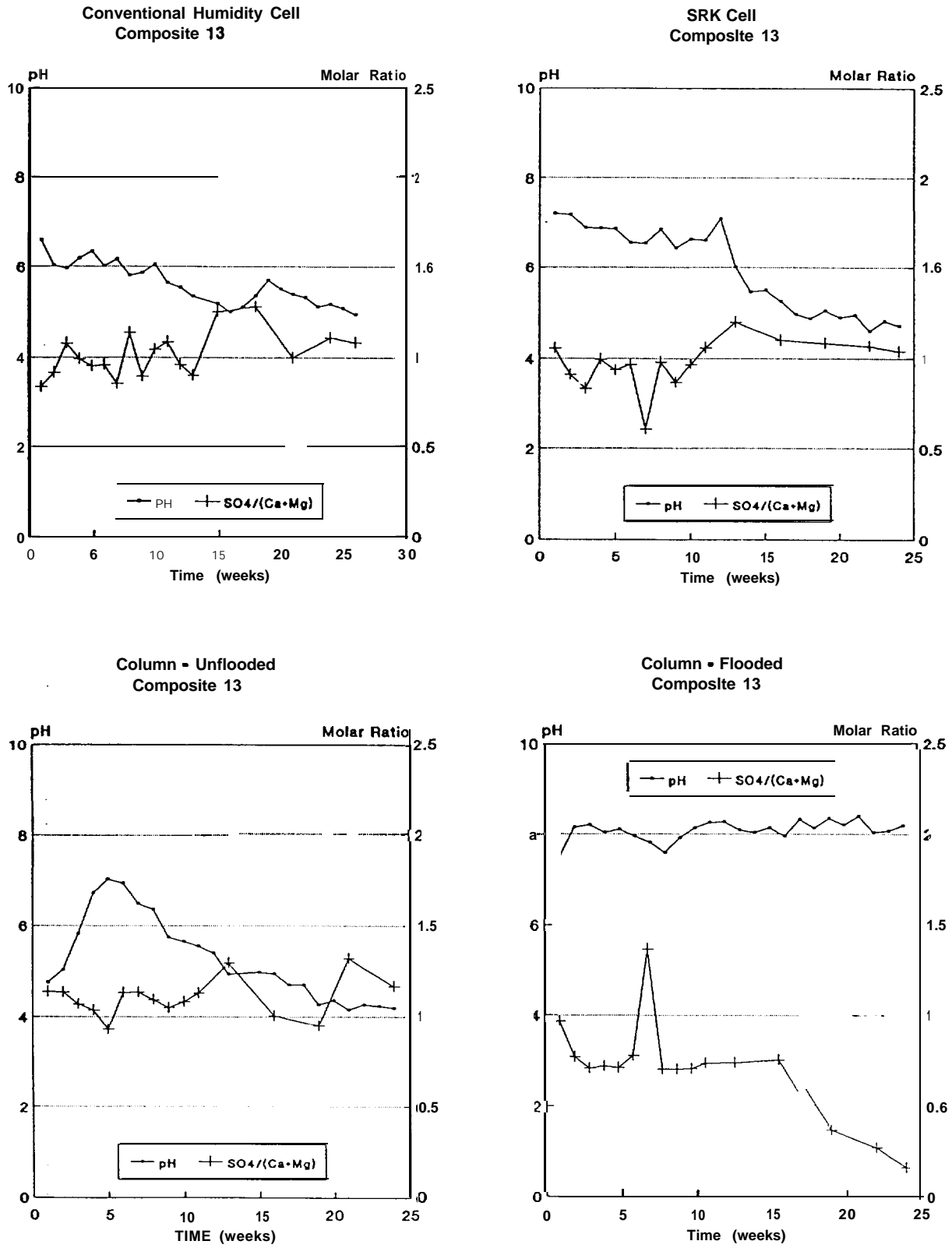


Figure 14a Comparison of Results from Four Different Kinetic Test Methods

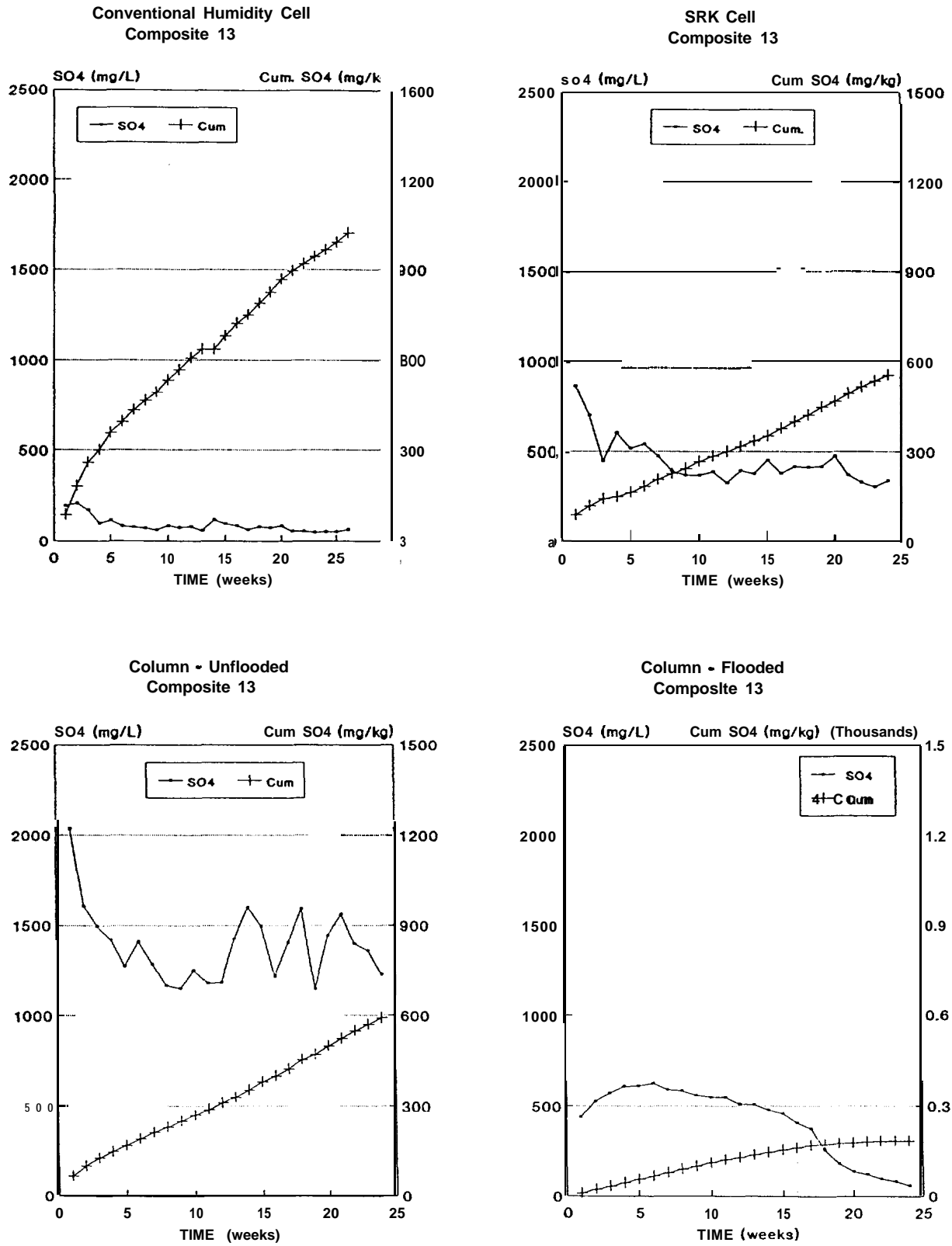


Figure 146 Comparison of Results from Four Different Kinetic Test Methods

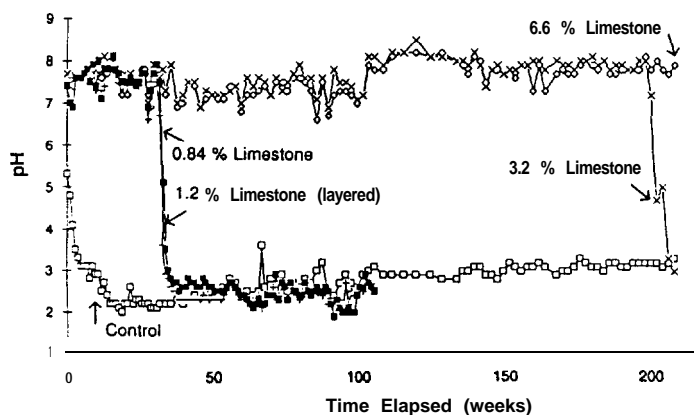


Figure 15 Effect of Small Additions of Finely Crushed Limestone on ARD Kinetics (Unsaturated Column Leach Tests) Norecol. 1992.

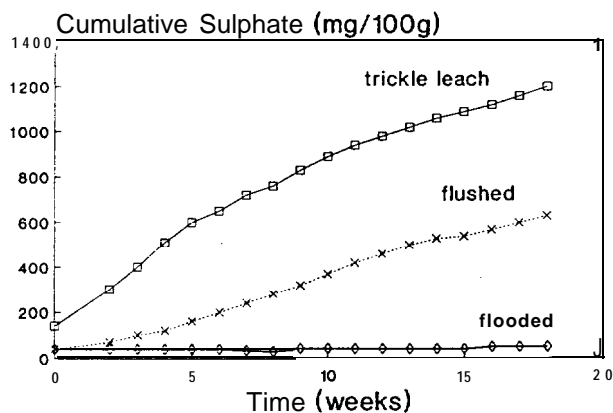


Figure 17 Variation of Acid Generation With L-each Method (Norecol, 1988).

The conventional humidity cell with its weekly complete flush does not represent field conditions and is therefore considered to be a poor test for water quality prediction purposes.

#### Flushing Rate

For a given rate of acid product production the seepage quality will be inversely proportional to the rate of flow introduced for flushing. This assumes the flush rate and path for each test remains uniform and the load generated or migrating into the flush path in each flushing period is constant.

Mathematical adjustment for flushing rate dilution effects should provide adequate correction for this effect.

#### Flushing Pattern

If the flushing pattern is varied, that is, there are periods with higher and lower flushing rates, then the concentration profile over time will be more complex. After a period of low or no flushing, an increase in the flushing rate will result in a disproportionate increase in the contaminant concentration as acid

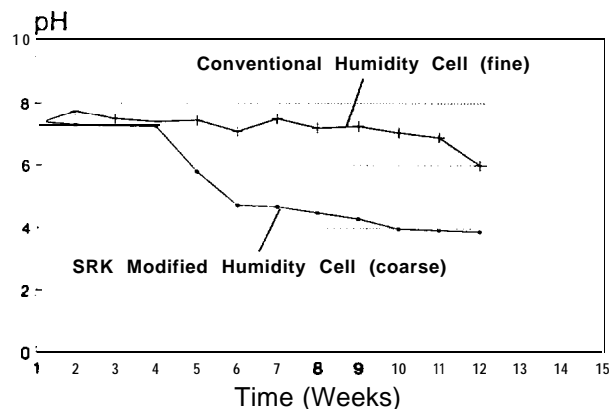


Figure 16 Effect of Crushing and Test Type on ARD Quality

products which have migrated into, or been generated in, **the** flow channels occupied by **the** increased flush flow are leached. If **the** increased flush rate is maintained then the concentration will again reduce to a typical value. Should the flow be further **decreased** the flush flow channels retreat into well flushed, narrower channels, and there is a decrease in the concentrations. Thus during, or immediately following an increase in the flush rate **there** is an increase in the contaminant concentration, contrary to the expectations of the second point above. **This** is the same mechanism as is observed in **the** field where early spring freshet flows show increased concentrations of contaminants even as the flow rate is increasing.

The *spatial* flushing pattern through a test sample must reflect the tendency towards **channelling** (discrete flow paths) evident in mine rock piles if representative water qualities are to be obtained. Further, the *temporal* flushing pattern should also reasonably represent the flushing pattern and rate per unit area that will occur in the field. The configuration and **the** flushing rates and pattern of **the** SRK cell test attempts to simulate these.

### Leachant Quality

The acid generation conditions in the flow paths are determined partly by **the** *influent* quality of the leachate. Thus if a strongly alkaline **leachate** is used for flushing, simulated groundwater for example, then the high **pH** control of acid generation (Figure 1) may be sufficient to prevent the initiation of biological oxidation. Under these circumstances, the **Ph** of the test sample may remain high, resulting in “good” drainage water quality with low dissolved **metals**. The same sample when subjected to leaching from a lower **pH** leachate, simulated acid rain for example at **pH** 4.5, may develop biological oxidation conditions rapidly **with** a resulting decreases in **pH** and increased contaminant concentrations.

The **influent** water qualities that will be applicable in the field should be used for test purposes.

The change in quality of a **leachate** as it passes through successive layers of acid generating rock can be determined by passing the effluent from one SRK cell on to become the **influent** for the next This also permits **the** effects of layering and blending in a rock pile to be evaluated.

### Flooded vs Unflooded

Acid generation under flooded conditions has two main controls:

- limitation of oxidation by oxygen exclusion, The rate of oxidation will depend on the rate of oxygen transfer which depends both on the flush rate and the oxygen concentration in the water.
- **pH** control throughout the sample as a **consequence** of the water bath providing **the** transfer medium for any available alkalinity to neutralize acid products throughout **the** sample.

Flooded or unflooded testing should be conducted to represent the field conditions that **will** occur. It is unrealistic to perform flooded (but oxygen rich) kinetic tests and expect **these** to provide useful data regarding water quality for unflooded mine rock in the field.

On initial flooding, the stored oxidation products will dissolve as is clearly illustrated by the relatively high sulphate concentrations initially measured for the flooded column test in Figure 14.

### Spiking and Inoculation

The practice of initiating acid generation by performing an initial acid flush of the entire sample to remove surface alkalinity is considered too radical an alteration of the sample to yield representative results, **although** not in all cases (**Ferguson**, 1985). As an alternative **the** authors prefer to “spike” a small portion of **the** sample (less than 5% of the sample by weight) with such an initial acid or peroxide flush and with inoculation of bacteria. Also to perform an unspiked test in parallel, in the anticipation that **the** long term field conditions are bracketed by the two sets of results. Figure 18 provides an example of spiked and unspiked conventional humidity cell tests of the same sample. **The** idealized ‘stepped’ **pH** curve in Figure 18 **(b)** indicates **pH** is buffered at about **pH** 5.4 and 4.5 before dropping to **pH** 3.4 in a series of additional steps. After 220 days of testing **the** un-inoculated cell is still on the **pH** 4.5 step. The cumulative sulphate production for (a) is 400 **mg/100** g at 220 days for **(b)** this value is reached in 45 days at which time the sample is at **the** same **pH** of 4.5.

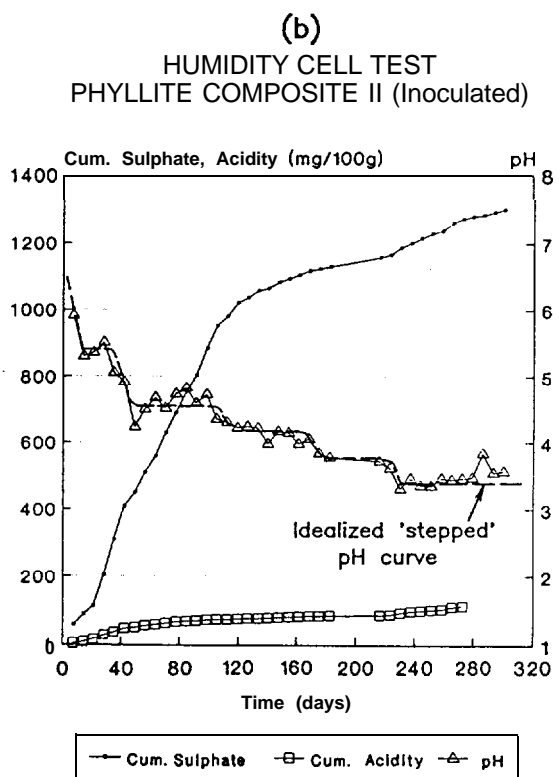
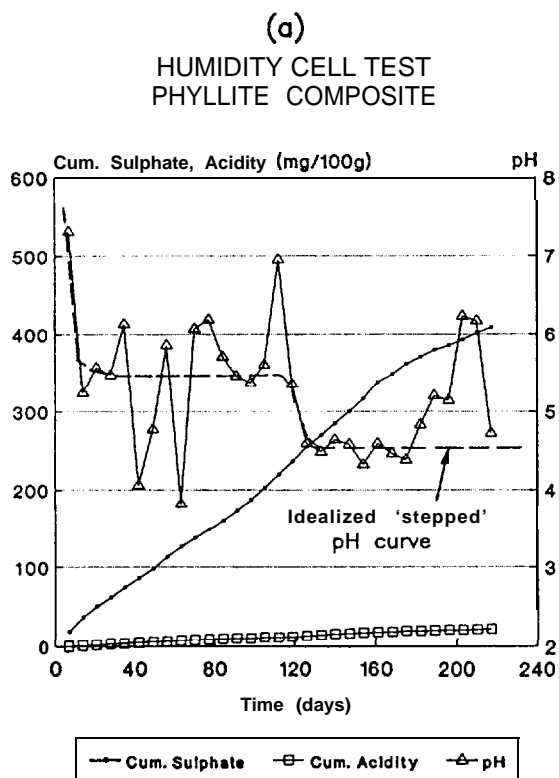


Figure 18 Comparison of Spiked, Inoculated and Similar Unspiked, Uninoculated Samples Tested in Conventional Humidity Cell Tests.

## Period of Testing

The length of time for which a test must be continued will depend on the results of the weekly flushing, and the objectives of the test: ten weeks is considered the minimum test duration, but 70% of fresh sample tests are required to run for periods of 20 weeks or longer to achieve maximum rates of acid generation. The lag time, until acid production is evident, will depend on the neutralization potential of the sample, as indicated by the **acid/base** accounting, and **the** availability of the carbonate and sulphide minerals. Initially the rate of release of sulphate (from the oxidation of **sulphides**), and **the** release of alkalinity and changes in acidity provide an indication of the reaction process and hence the lag time until the onset of rapid, biological oxidation and acid generation. As **pH** decreases below 5.5, changes in other parameters will become more rapid; conductivity and **redox** potential increase, and elevated acidity and dissolved metal levels become more apparent.

## SUMMARY OF TEST METHODS AND THEIR APPLICABILITY

Table 2 provides a summary of most of the common parameters that are measured for **ABA**, humidity cell and column tests. A comparison of some of these test procedures, advantages and disadvantages, was presented by Ferguson (1985). Standard analyses and measurements that should be conducted for all samples, for each test, are listed. Additional procedures have been recommended that may not be required on all samples, or **all** test programs, but should be considered.

## INTERPRETATION OF RESULTS

There are two aspects to **the** interpretation of the results of a kinetic test program:

- what do the results mean in terms of the sample geochemistry and -acid generation potential; and
- how do the lab results relate to field conditions and prediction of field drainage water quality.

TABLE 2  
Prediction Test Methods for Mine Evaluation

TEST PROCEDURE	ACID-BASE ACCOUNT	LEACH EXTRACTION	CONVENTIONAL HUMIDITY CELL	SRK CELL	COLUMN LEACH
Typical Analyses	<ul style="list-style-type: none"> <li>Total Sulphur - Leco</li> <li>Titration for NP</li> <li>Paste pH</li> </ul>	<b>Solids</b> <ul style="list-style-type: none"> <li>ICP before/after test Solution</li> <li>Dissolved metals</li> </ul>	<b>Solids</b> <ul style="list-style-type: none"> <li>ICP before/after test Solution</li> <li>Acidity, alkalinity</li> <li>Sulphate</li> <li>Conductivity</li> <li>Dissolved metals,</li> <li>Radionuclides</li> </ul>	<b>Solids</b> <ul style="list-style-type: none"> <li>ICP before/after test Solution</li> <li>Acidity, alkalinity</li> <li>Sulphate</li> <li><b>Conductivity</b></li> <li>Dissolved metals,</li> <li>Radionuclides</li> </ul>	<b>Solids</b> <ul style="list-style-type: none"> <li>ICP before/after test Solution</li> <li>Acidity, alkalinity</li> <li>Sulphate</li> <li>Conductivity</li> <li>Dissolved metals,</li> <li>Radionuclides</li> </ul>
Optional Analyses	<ul style="list-style-type: none"> <li>Sulphur Species</li> </ul>	<ul style="list-style-type: none"> <li>Organics</li> </ul>	<ul style="list-style-type: none"> <li>Mineralogy of solids</li> <li>before/after test</li> </ul>	<ul style="list-style-type: none"> <li>Mineralogy of solids</li> <li>ABA before/after test</li> </ul>	<ul style="list-style-type: none"> <li>Mineralogy of solids</li> <li>ABA before/after test</li> </ul>
Variations to Test Procedure	<ul style="list-style-type: none"> <li>Hydrogen peroxide oxidizable sulphur</li> </ul>	<ul style="list-style-type: none"> <li>ASTM 03987</li> <li>B.C. SWEP</li> <li>US EPA 1312</li> <li>US EPATCLP</li> <li>Conduct test on uncrushed (as-received) sample</li> </ul>	<ul style="list-style-type: none"> <li>Inoculation with bacteria</li> </ul>	<ul style="list-style-type: none"> <li>Wet/dry cycles</li> <li>Flushing rate</li> <li>Single pass or recirculation of water through the sample</li> <li>Inoculation with bacteria</li> <li>Cells in series</li> </ul>	<ul style="list-style-type: none"> <li>Wet/dry cycles</li> <li>Flushing rate</li> <li>Single pass or recirculation of water through the sample</li> <li>Inoculation with bacteria</li> <li>Columns in series</li> </ul>
Particle Size	-3 mm	Depends on test typically -0.6	-0.6 cm	10 cm	2 to 20 cm
Amount of Sample required (kg)	0.002 to 0.500	0.1 to 2.0	1 to 5	25 to 40	30 to 500
Cost per Test	\$75 to \$150	\$175	\$3000	\$4000	\$5000
Time to Complete Test	2 days	2 days	3-6 months	3-6 months	6-36 months
Certainty in Results	<ul style="list-style-type: none"> <li>Very good</li> <li>Static test only</li> </ul>	<ul style="list-style-type: none"> <li>Indicative of leachable contaminants but not of field behaviour</li> </ul>	<ul style="list-style-type: none"> <li>Indicative of ARD potential but not of field behaviour for mine rock</li> </ul>	<ul style="list-style-type: none"> <li>Good</li> </ul>	<ul style="list-style-type: none"> <li>Good</li> </ul>

Notes: 1) Laboratory Costs only - Canadian \$  
2) Depends on number of samples submitted  
3) 10-week testing period (\$90/each additional week) of the dissolved metals.  
4) 26 week testing period (\$105/each additional week)  
5) ICP, or selected metals by AA and less frequent ICP analysis

The focus of this discussion is the interpretation of the sample geochemistry, and prediction of “whether it will go acid” in the field. Extrapolation of kinetic data to predict long term drainage water is much more difficult, particularly for mine rock (Broughton et al, 1991).

The results of the weekly analysis of the **leachate** will indicate changes in solution and solid chemistry over time. The information that should be tabulated for each cycle includes:

- sample description, cycle number, duration, **leachate** volume;
- readings or concentrations of all measured parameters;
- calculated acidity and alkalinity (**mg/L CaCO<sub>3</sub>** equiv.), sulphate (**mg/L SO<sub>4</sub><sup>2-</sup>**) production;
- cumulative production of acidity, alkalinity, and metals (**mg/kg** or **mg/kg/m<sup>2</sup>**); and,
- cumulative sulphate production (**mg SO<sub>4</sub><sup>2-</sup>/kg** or **mg SO<sub>4</sub><sup>2-</sup>/kg/%S/m<sup>2</sup>**).

The relative rate and sequence of oxidation will be indicated by changes in **pH** and conductivity, and the results of calculations of production rates of sulphate, acidity, alkalinity and dissolved metals in terms of sample weight and/or surface area.

The evaluation of data should include the following steps:

- check for inconsistencies or errors; however, unusual values should be reviewed to determine if they are **analytical** errors or actual indications of change in the water quality;
- plotting of changes in key indicator parameters over time, cycle, or pore volume; **pH**, sulphate, alkalinity, acidity. Changes in sulphate and alkalinity can indicate the onset of oxidation before changes in **pH** are apparent
- plotting of cumulative sulphate and acidity production and alkalinity consumption with time;
- plotting of metals **as** a function of time and of **pH**;
- plotting of contaminant production per unit time, pore volume, or unit surface area;
- plotting of **geochemical** ratios of parameters such as sulphate, alkalinity-, calcium, magnesium with time, particularly for samples with near neutral **pH**;
- review of mine rock classification and AI3 A results;
- comparison with other data from the site, and from other sites.

Care must be taken in evaluating the initial flushing cycles when the sample contains stored oxidation products or a readily soluble load, as shown in Figure 4, where there has been sample pre-treatment, or if control measures are being evaluated (eg. water cover, alkali addition), as these early cycles may reflect the flushing out of stored products and not long term trends in acid generation and contaminant leaching.

As previously discussed, the peaks of these curves may reflect one or both of the two sources of contaminants;

- stored oxidation products or readily soluble constituents;
- on-going oxidation, acid generation and metal leaching.

Typically, for flushing of stored products or leaching of readily soluble constituents there would be:

- a high initial flush of contaminants within the **first** 1 to 2 pore volume replacements;
- a decreasing load with time, the period of which varies with the rate of flushing, available load, and solubility;

For on-going ARD there would be:

- gradually increasing sulphate and acidity values with associated decreasing alkalinity;
- gradually increasing iron levels and decreasing **pH** lagging somewhat behind the sulphate peaks; and then,
- increasing dissolved **metals** in the drainage.

It is expected for most sites that the drainage water quality will be controlled by both mechanisms. The extent to which one or the other dominates will depend on the nature of the rock and the time period for which it has been exposed.

Prediction of the long-term acid generating potential of a sample, and potential water quality issues, from interpretation of the results of the humidity cell testing can be complicated, and requires some experience in ARD testing. A discussion of the interpretation of results of kinetic testing is provided in the Draft ARD Technical Guide, and forms the basis for the following general guidelines in interpreting test data.

**pH** > 5.0 sample is not strongly acid generating and/or the chemistry is dominated by release of alkalinity from **calcareous** material, during the testing period.

**pH** 3.0 to 5.0 sample is generating acid although some **pH** neutralization is occurring. Biological oxidation becomes more significant (iron oxidizing bacteria).

**pH** < 3.0 sample is strongly acid generating and the role of *Thiobacillus ferrooxidans* can be significant

**Sulphate** Sulphate is a direct by-product of complete sulphide oxidation, and can be indicative of the rate of sulphide oxidation and acid generation. Depending on the test procedure, there are a number of factors that must be checked in the interpretations: whether all of the oxidized sulphur is flushed from the sample, and whether **solubility constraints result** in precipitation of gypsum or other sulphate salts. Elevated sulphate analyses may indicate the presence of strong acid generation although the **pH** is neutral due to release of alkalinity from carbonate minerals. An increase in sulphate concentrations and the rate of sulphate **production** over the test period would indicate that the rate of acid generation was increasing. Release of sulphate in the initial weeks of testing may indicate only the dissolution of sulphate salts or release of stored oxidation products.

**Acidity** Acidity is a cumulative measure of several aqueous species such as  $Fe^{2+}$ ,  $Fe(OH)^{2+}$ ,  $Al^{3+}$ , and  $HSO_4^-$ . Thus, acidity can be used as a rough approximation of acid generation. The change in acidity/alkalinity and release of elements such as calcium and magnesium associated with alkali minerals is indicative of the rate and extent of acid generation and neutralization reactions. A correlation between sulphate and acidity frequently exists unless there is significant neutralization of the drainage.

**Metals** Analyses of dissolved metals will indicate the rate of metal depletion from the sample, by comparison with the original metal content of the sample. An increase in dissolved metals does indicate that either flushing of readily soluble products or acid generation and metal mobilization is occurring in the cell; however, it is not a good indicator of the rate of acid generation due to secondary effects such as hydrolysis and precipitation of secondary minerals.

One of the most difficult aspects of prediction is evaluation of near neutral drainage. Ferguson and Morin (1991) describe techniques for, and examples of interpretation of acid generation potential in drainage that remains in the near neutral range throughout the testing period. Indications of acid generation and neutralization are

- increasing or constant sulphate production;

- decreasing alkalinity release;
- rate of sulphate production exceeding availability of alkalinity (as indicated by Ca and Mg in solution; or
- release of “indicator” metals such as **Zn**, **Al**, or **Fe**.

Evaluation of data should be done throughout testing, to determine if the results are useful and if changes should be made to the schedule of sample analysis, or if the tests can be concluded. As soon as the tests indicate that the material does generate unacceptable drainage water, the focus of the prediction program should change to the evaluation of control measures. Typically, kinetic tests are required to run for twenty weeks or more before analyses indicate final steady state conditions. Testing is often terminated **if**:

- **pH** becomes acidic (< 5) indicating acid generation is occurring (**but final water** quality is not of interest); or
- after 20 weeks, if **pH** is neutral or alkaline and **NP/AP** > 1.0 and there are no indications of increased sulphate production.

Tests should be continued as long as the data indicates that there are changes in water quality that indicate that the leaching or oxidation processes are developing or neutralizing minerals are **being** depleted. Testing should continue:

- if **pH** is decreasing;
- if sulphate production is constant or increasing;
- if metal concentrations are elevated or increasing in the leachate; or
- if test is critical to assessment of the control plan or environmental impact or can be modified to **evaluate ARD controls**.

## REFERENCES

- Brodie**, M.J., Broughton, L.M., and Robertson A.MacG., 1991, A Conceptual Rock Classification System for Waste Management and a **Laboratory** Method for ARD Prediction from Rock Piles. Proceedings of the Second International Conference on Abatement of Acidic Drainage. Montreal, Quebec, September 1991. Volume 3 pp (119-136)
- Broughton, L.M. and Robertson **A.MacG.**, 1991 'Modelling of **Leachate** Quality from Acid Generating Waste Dumps' Proceedings of the Second International Conference on the Abatement of Acid Drainage, Montreal, Quebec, September 1991. Volume 3.
- Broughton, L.M., Robertson, A.MacG., 1992. Acid Rock Drainage from Mines - Where We are Now. In publication.
- Ferguson, **K.D.**, and **Morin**, 1991. The Prediction of Acid Rock Drainage - Lessons from the Database. Proceedings of the Second International Conference on the Abatement of Acid Drainage - Montreal, Quebec, September 1991. Volume 3.
- Ferguson, K.D., 1985. Static and Kinetic Methods to Predict Acid Mine Drainage. Presented at the **International** Symposium on Biohydrometallurgy. Vancouver, B.C., August 22-24.
- Norecol Environmental Consultants Ltd., 1988. Cinola Gold Project, Stage II Report, Volume V, Environment Research and Special Studies. Report for City Resources (Canada) Ltd.
- Norecol Environmental Consultants Ltd., 1992. MEND Cinola Project - Year 2 Progress Report - Draft.
- Steffen, Robertson and Kirsten (Canada) Inc., Norecol Consultants and Gormely Process Engineering, 1989. Draft Acid Rock Drainage Technical Guide - Volume I. British Columbia Acid Mine Drainage Task Force.
- Steffen, Robertson and Kirsten (Canada) Inc, 1992. 'Mine Rock Guidelines - Design and Control of Drainage Water Quality' prepared for Saskatchewan Environment and Public Safety - Mine Pollution Control Branch.