CHAPTER 5: GUIDELINES AND RECOMMENDATIONS FOR USE OF KINETIC TESTS FOR COAL MINING (AMD) PREDICTION IN THE EASTERN U.S.

by

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KINETIC TESTS USED IN COAL MINING PREDICTION

Kinetic or leaching tests furnish kinetic data that static tests such as acid-base accounting (ABA) cannot. Static tests, as discussed in Chapter 4, measure and balance the intrinsic variables of the rock strata. Static tests can, for the most part, provide accurate predictions of water quality from mines operating in areas where the overburden contains high NP values, high NP-S ratios (indicating that alkaline conditions will persist) or very low NP-S ratios (indicating the potential for acidic conditions). However, post-reclamation water quality often does not correlate well with predictions based on static tests from areas where the NP is approximately equal to the MPA. Under these geochemical conditions, which are equivalent to the "gray zone" described in chapter 4, kinetic tests can provide a more accurate assessment of the strata's potential drainage quality. With many of the permits from the easier to predict areas having already been obtained, more permits are being sought from this gray zone. Kinetic tests can provide valuable information for the mining operation, so that resource management plans can be formulated, and for the regulatory agency.

Kinetic tests provide empirical data by subjecting overburden samples to simulated weathering conditions, which may be designed to either mimic or accelerate natural conditions. The rates of pyrite oxidation and the release of weathering products can then be measured quantitatively to predict drainage quality (Bradham and Caruccio, 1995). The leachates resulting from the various kinetic tests are evaluated for certain parameters such as pH, specific conductance, acidity, alkalinity, sulfate, and sometimes other constituents. These data can then be analyzed statistically and graphically to evaluate the rates of sulfide oxidation and acid production. These techniques, however, have their disadvantages. The procedures are labor intensive, typically require 12-20 weeks at a minimum to complete, and are thus relatively expensive to perform. In addition, while there is general agreement that leaching tests accelerate weathering rates over conditions encountered in an actual mine, it is not known by how much, or even how much time in the field is actually represented by laboratory tests. Also contentious is whether results gathered from a laboratory test involving as little as 100 g of finely crushed overburden in a soxhlet or weathering cell leach test can accurately be extrapolated to characterize overburden weathering at an actual mine. Comparison studies, however, indicate that kinetic tests correlate well with anticipated field conditions (Bradham and Caruccio, 1990).

A wide variety of kinetic or leaching tests have been used in research studies (Bradham and Caruccio, 1995; Hornberger and Brady, 1998; Lapakko, 1993). However, they have been used relatively rarely in mine permitting in the Appalachian Basin states (with the exception of Tennessee and in areas where the permit may be denied by the regulatory agency without additional information) (Maddox, 1988). An important obstacle to field implementation is that different kinetic tests often yield different or contradictory results. Ostensibly identical overburden samples are often observed to produce acidic results in one type of test, and alkaline results in another. One reason for this is that the conditions created to simulate

overburden weathering can be dramatically different. Another problem can result from the use of very fine-grained material, such as mine tailings, in columns, which can cause "airlocks" that can limit the transfer of oxygen and thereby inhibit acid production.

Hornberger and Brady (1998) suggested that the test methods should be as simple as possible, given the variables to be evaluated, considering that multiple arrays are frequently used concurrently to test multiple rock samples from a proposed mine site. The kinetic test apparatus, however, does require some complexity in external form or internal structure to allow fluids and gases (i.e., oxygen and carbon dioxide) to enter, circulate through, and exit the apparatus in a manner that is representative of weathering conditions of the mine environment.

As more permits are sought from the gray areas and as more regulators, consultants and industry representatives become familiar with the procedures and the tests' benefits, kinetic testing will increase. This chapter is intended to increase familiarity with the kinetic test procedures and to outline the essential elements and methodology of these tests. We will focus on: 1) the various kinetic test methods; 2) the physical, chemical, and biological considerations that should be incorporated into any kinetic test; 3) the tests' similarities rather than their differences; and 4) the factors affecting the design, performance and interpretation of the tests.

Humidity Cells

Humidity or weathering cells are usually constructed of plastic chambers that are connected by tubing to a reservoir from which humid air is pumped, thereby creating a humid environment conducive to pyrite oxidation. The sample may be purged with humid air or alternately purged with humid air and ambient humidity. Crushed rock samples (usually no greater in size than 100% passing 6.3 mm and with a weight usually between 100 and 500 g) representing various overburden units at a particular mine site are placed in separate chambers and flushed periodically by adding a leachant to the cell (Figure 5.1). The leachate is removed and analyzed.

Over the decades since the early research using weathering cells to predict water quality was published, various types, sizes and configurations have been used. The early cells (Caruccio and Parizek, 1968) were plastic chambers connected by similar length segments of tygon tubing to a large glass container of distilled water through which air was pumped. The humidified air flowed over the sample, providing an environment conducive to pyrite oxidation. An aliquot of deionized water was added to the sample, mixed and the effluent decanted. The effluent was analyzed for various chemical constituents. In Smith et al. (1974), the purging air was alternately humid and dry, but the configuration of the apparatus was similar. Rock chip samples were placed in the humidity cell type containers {10cm (4 in) x 30cm (12 in) x 15cm (6 in) plastic boxes} and "inoculated with acid mine water from a deep mine to provide the essential microorganisms for reduced sulfur and iron oxidation" (Smith et al., 1974). Moist air was passed through the plastic boxes for 3 ½ days, followed by dry air for 3 days. Then a ½ day was used to leach the samples and analyze the leachate, hence completing a 7-day cycle. Since then, a number of modifications have been applied to attempt to remove variables that were considered to be potentially problematic. Harvey and Dolhopf

Figure 5.1. Humidity cells (from Bradham and Caruccio, 1995)

(1986) developed a "computerized automated rapid weathering apparatus" (CARWA), which consists of three humidity-cell type "weathering chambers or compartments" with extensive mechanical and electrical supporting equipment. While the CARWA method allows the procedure to be computerized, one of the primary disadvantages is the leaching interval of 2.5 hours. In order for the time dependant chemical equations to approach near-equilibrium conditions, a longer time interval is required between leachings.

Recently, White and Sorini (1995) have proposed a complex apparatus for weathering cells that attempts to standardize all facets of the test procedure. While many of their concerns are valid, it has not been shown that all of the variables considered have an effect on the resultant effluent quality. It may not be necessary nor desirable to go to such elaborate lengths, given the increased cost and time required for typical mine permitting decisions.

Leaching Columns

Leaching column tests allow the leachate to flow through the rock sample rather than be added and extracted as in the humidity cells. The columns are constructed of a tube or container into which rock samples are placed. A porous barrier at the bottom retains the sample, but permits water to drain. The samples are leached by adding the leachant (usually water) to the top of the column and allowing the water to drain down through the sample. Alternately, water can be introduced from the bottom to eliminate air entrapment (Hood and Oertel, 1984) or to simulate various water table conditions (Leach, 1991). The leachate is collected at the bottom of the column. Hornberger, Parizek and Williams (1981) conducted column leaching tests on coal and overburden, which are described in Hornberger (1985). Simple leaching columns were constructed from ½ gal (1.89 l) plastic containers, which combined some features of humidity cells and leaching columns. The lower half of the leaching column was kept saturated, which provided a constant source of water and humidity within the container to facilitate the chemical reactions and promoted survival of the bacteria. Williams et al. (1982) used the same leaching columns, and essentially the same

leaching procedure as Hornberger et al. (1981) but filled the lower portion of the column with glass beads in order to place most of the rock sample in humid, but unsaturated, conditions.

Several authors, including Hornberger and Brady (1998), describe the variety of column tests available, including:

1. 15cm (6”) by 91cm (3’) plastic columns, each with a perforated plastic barrier mounted on a large diameter funnel with the water being added at the top (or modified to introduce water from the bottom) and allowed to drain (Bradham and Caruccio, 1995, 1997);
2. small (3.5cm) diameter leaching columns using glass tubes 122 cm long into which distilled water was introduced into the columns from the bottom upward (Hood, 1984; Hood and Oertel, 1984);
3. large (3.08 m) diameter columns that were actually stainless steel tanks 40 ft (12.19 m) high and 10 ft (3.08 m) in diameter (Cathles et al., 1977).

The relationship between the dimensions of the kinetic test apparatus and the dimensions of the rock samples being tested must be considered in order to prevent adverse interactions between the sample and the container. For example, in some leaching column studies, including Hood and Ortel (1984), and some studies to compare numerous overburden analysis procedures, including Bradham and Caruccio (1990, 1995), problems with airlocks within the leaching columns are discussed, especially for small grain sizes. These types of problems or artifacts of kinetic test apparatus and procedures can be prevented and hence, the interaction between the container and the sample should not be a major factor in the test results.

Figure 5.2. Leaching Columns (from Bradham and Caruccio, 1995)

Figure 5.3. Soxhlet reactor (from Bradham and Caruccio, 1995)

Potter (1981) and Cathles and Breen (1983) agree that solution flow within the column is a critical operating parameter and, to avoid undue wall effects, the column diameter (I.D) should be four times the largest particle diameter in the aggregate of particles being leached. The four times factor is a minimum ratio and should only be used when grain sizes exceed 0.5 cm (0.2 in). For smaller particles, a factor greater than four should be used. Murr et al. (1977) developed scaling factors considering the ratio of column diameter and column height and maximum rock size within the column in order to scale solution and air flow rates within the columns.

Soxhlet Reactors

Soxhlet tests employ an extraction apparatus designed to subject pulverized rock samples, screened to pass 125 μm, and contained in a cellulose thimble, to cyclic flushings with boiling water over a leaching period of several hours (Figure 5.3). This aggressive, hot water leaching is coupled with high temperature oxidation brought about by storing the overburden sample thimbles in a drying oven for two weeks at 105° C (Sobek et al., 1982; Renton et al., 1988). Usually, the acid potential is determined after five or six cycles of leaching and oxidation. Soxhlet extraction is thought to rapidly accelerate pyrite oxidation, relative to the dissolution of calcium carbonate. Although increased calcium is seen in the leachates, this is due primarily to the storage of secondary minerals or ions such as Ca^{2+} and sulfate (Bradham and Caruccio, 1995).

Shake Flasks

Another methodology, more commonly used in Canada than the United States, is the shake flask or confirmation test. It follows the B.C. Research Initial Test, which is a static test and is described in Bruynesteyn and Hackl (1984). The B.C. Research Initial Test is similar in procedure and interpretation to the ABA procedure (Smith et al., 1974; Sobek et al., 1978). If the B. C. Research Initial Test indicates the sample to be a potential acid producer, the B. C. Confirmation Test is utilized (Bruynesteyn and Hackl, 1984). The rock sample is placed in a 250-ml Erlenmeyer Flask with 70 ml of nutrient media and Thiobacillus bacteria culture. The flask is maintained in a carbon dioxide enriched atmosphere at a temperature of 35° C and placed on a gyratory shaker to monitor pH changes (see also Ferguson, 1985; Ferguson and Erickson, 1986; and Ferguson and Mehling, 1986). Additional Canadian kinetic test developments and field applications, including the use of shake flasks and lysimeters, are discussed in Davidge (1984), Duncan (1975), Ferguson and Erickson (1988), Halbert et al. (1983), Ritcey and Silver (1981), and Wilkes (1985).

Applicability of Other Kinetic Tests

A wide variety of other kinetic tests have been developed, evaluated, and employed by the metal mining industry, the waste industry, and others. Many of these test methods have been described and categorized in reports by Bucknam (in press), Environment Canada (1990), and Sorini (1997). The report by Sorini (1997) summarized 59 leaching test methods for the American Coal Ash Association, including French, German, Swiss and Dutch (Netherlands) leaching tests. According to Sorini (1997):

> "Leaching tests can be divided into two categories based on whether the leaching fluid is renewed during contact. Leaching tests involving renewal of the leaching fluid are commonly known as dynamic

tests, and those in which the leaching fluid is not renewed are commonly referred to as extraction tests. Extraction tests involve a procedure in which the material is contacted with leaching fluid for a specific amount of time. At the end of the contact time, the leaching fluid and test material are separated, and the leachate is analyzed. In dynamic tests, the leaching fluid is continuously or intermittently renewed to maintain the leaching process."

The Environment Canada (1990) report classifies the extraction tests and dynamic tests into four subcategories each. The extraction tests are agitated extraction tests, non-agitated extraction tests, sequential chemical extraction tests, and concentration build-up tests. The dynamic tests are serial batch tests, flow-around tests, flow-through tests, and soxhlet tests. According to this classification system, humidity cell and leaching column tests are included in the subcategory of flow-through tests.

Bucknam (in press) distinguishes short term leaching test methods from long-term dissolution, kinetic test methods. According to Bucknam, short-term leaching tests, such as the Nevada Meteoric Water Mobility Procedure, are fairly rapid and inexpensive survey tools. Such tests briefly contact samples with solutions that mimic water that the material may be in contact with in the mine environment in order to determine what may dissolve from these materials.

Field Tests

Field tests operate similarly to other leaching kinetic tests, but on a different scale. Occasionally, the kinetic test apparatus and type of material being tested may be large enough to use mine spoil or mine refuse samples with rock sizes (particle sizes) as large as those found in the mine environment. Examples include the studies by Renton et al. (1984, 1985) using field barrels of coal refuse samples, and the large tank studies of Cathles et al. (1977) and Murr et al. (1977), using 10 ft (3.08 m) diameter by 40 ft (12.19 m) high stainless steel tanks for copper ore tailings and leach dump samples. Caruccio and Geidel (1983) and Geidel et al. (1983) conducted field particle size studies of sandstone and shale samples in 4 ft (1.22 m) by 8 ft (2.44 m) field tubs to evaluate variations in acid production from 5 different classes of particle sizes, ranging from less than 1 in (2.54 cm) to greater than 8 in (20.32 cm) in diameter. Renton et al. (1985) conducted field tests on 10-ton piles of overburden placed on plastic liners to evaluate the effect of various reclamation amendments.

FACTORS TO CONSIDER IN KINETIC TEST DESIGN

Particle Size

The mineralogic composition and size distribution of rock materials within a backfilled surface mine are important factors to consider in conjunction with rock testing to determine whether the mine spoil produces acid or alkaline drainages. The sizes of blocks or particles of rock materials within the backfill, and the corresponding size and distribution of the voids that serve as pathways and storage spaces for the various fluids and gasses contained in and moving through the backfill are determined by several factors including:

(1) blasting practices used to fragment and cast consolidated overburden strata;

(2) effects of heavy equipment used to remove overburden and conduct backfilling and grading operations;
(3) fundamental properties of the rock units (i.e. mineralogy, grain size, hardness, degree of cementation, porosity, linear sedimentary features (e.g. bedding planes); and
(4) linear structural features (e.g. joints and fractures) within the overburden (Hornberger, 1998).

While core drilling normally provides detailed information on lithologic units and allows for rock units to be sampled and subsequently analyzed on a more discrete basis, rock samples are sometimes obtained from exploration drill holes. When exploration holes are used, the particle size distribution of the rock sample used in the kinetic test will be determined by the type and method of drilling equipment and by any subsequent crushing or other sample preparation equipment and procedures. Air-rotary drilling methods yield a maximum particle size of approximately ½ in (1.27 cm) and a nominal or mean particle size of approximately ¼ in (0.635 cm) for most overburden lithologic units, but may be finer for some lithologies (e.g. coal). The size fractions and particle size distributions produced by air-rotary drilling methods can be used for some kinetic testing, although further sample preparation may be warranted for other tests. Consideration should be given to core drilling of overburden analysis test holes in some circumstances because air rotary drilling methods may mix particles from different lithologic units encountered during drilling and cause interferences in overburden analyses such as the NP test. In addition to preventing sample mixing and resultant chemical analysis problems, core drilling provides better definition of lithologic descriptions and stratigraphic intervals, and greater control of sample preparation procedures and the resultant particle size distribution of the sample used for kinetic tests.

The particle size distribution of an overburden sample may be determined through a sieve analysis. In soil classification and analysis, a mechanical analysis is conducted using a series of sieves and other physical methods (e.g., settling, suspension) to separate soils into sand, silt, and clay-sized particles as described by Brady (1974), Terzaghi and Peck (1967), Folk (1968), and others. A number of different grain-size classification systems are used, but typically particles greater than 2.0 mm are considered to be gravel and particles less than 0.002 mm to be clay sized. The USDA system classifies particles less than 0.002 mm as clay, silt from 0.002 through 0.05 mm, sand from 0.05 through 2.0 mm, and gravel greater than 2.0 mm.

Most consolidated rock overburden strata should yield a relatively large percentage of gravel-sized particles, in samples obtained from air-rotary drilling or crushing to a nominal ¼ in (6.35 mm). Thus, it is probably not necessary to conduct a complete mechanical analysis to obtain an estimate of the particle size distribution for most kinetic test samples. However, a relatively crude mechanical analysis may be useful to determine the percentages of coarse and fine particles in a few size classes for some specific kinetic test purposes, or in general for different overburden lithologic units. For example, where samples have been crushed to a nominal ¼ in (6.35 mm) by a jaw crusher, a U.S. series #10 sieve would separate the size fraction less than 2 mm and retain the gravel-sized particles of nominal ¼ in (6.35 mm). A #200 sieve with a 74 micron (μm) opening would retain the sand-sized grains, and pass the finer silt and clay-sized grains. Alternatively, a #270 sieve equals 53 μm openings, which approximates the sand/silt size interface. Additional information on these sieve sizes and procedures is found in soils texts such as Scott and Schoustra (1968) and Bowles (1970). Sandstone overburden samples will normally possess a relatively large percentage of coarse particles and relatively few fines, especially when the sample is an indurated,

well-cemented sandstone; overburden samples from more fine-grained rocks, like shales and underclays, would possess larger percentages of silt and clay-sized particles.

The presence of a relatively large percentage of fine-grained particles in an overburden sample can definitely affect kinetic test results. According to Bradham and Caruccio (1990), the fine-grained nature of the metal mines tailings that were tested in their leaching columns caused high specific retention of fluid and created air locks within the columns, which skewed the results. In addition, the particle size at the conclusion of the kinetic test may be more fine than the original particle size distribution of the sample, due to particle decomposition during the test.

Another potential problem is that sorting by grain size can bias a sample. Several studies have shown a disproportionate percentage of total sulfur in the finer-grained portion of a sorted sample. Geidel et al. (1983) evaluated pyritic sulfur contents of 5 particle size fractions (i.e. ranging from greater than 6 in (15.2 cm) to less than 1 in (2.54 cm) of a sandstone sample and a binder sample from a West Virginia surface mine. The pyritic sulfur content of the binder increased from 0.28% to 0.74% with decreasing particle size, while the sandstone sample exhibited a general decrease in pyrite sulfur from 0.26% to 0.14% with decreasing particle size. However, in field leaching tests (i.e. using plastic lined tubs 8 ft (2.44 m) x 4 ft (1.22 m) x 2 ft (0.61 m) connected to 30 gal (113.56 l) plastic barrels) using natural precipitation, the smallest size fraction of sandstone produced the highest acid loads for the sandstone samples. In addition, the smallest size fraction of the binder produced nearly 10 times the total acid load of the larger particle sizes of binder. The cumulative acid load of the less than 1 in (2.54 cm) binder sample was approximately four times larger than the cumulative acid load of the same size fraction of sandstone sample as shown on plots of the acidity data (Geidel et al., 1983). In a study of fine-grained coal refuse from a West Virginia preparation plant, Renton et al. (1984) initially screened the refuse sample to exclude particles greater than 5/8 in (1.59 cm) diameter, and subdivided the sample into 6 size classes. The largest particle size class ranged from 0.375 in (0.953 cm) to 0.625 in (1.59 cm), while the smallest size class was less than 0.0016 in (0.004 cm). There was a general increase in total sulfur content from 2.58% to 3.90% with decreasing particle size in the coal refuse sample.

In spite of the potential operational problems with some fine-grained samples and some types of kinetic test apparatus, variations in the surface area available for reaction may have dramatic effects on the chemical reactions of acidity and alkalinity production. According to Brady (1974):

> "Surface area is the characteristic most affected by the small size and fine subdivision of silt and especially clay. A grain of fine colloidal clay has about 10,000 times as much surface area as the same weight of medium-sized sand. The specific surface (area per unit weight) of colloidal clay ranges from about 10 to 1,000 square meters per gram. The same figures for the smallest silt particles and for fine sand are 1 and 0.1 square meters per gram. Since the adsorption of water, nutrients, gas, and the attraction of particles for each other are all surface phenomena, the significance of the very high specific surface for clay is obvious."

Bradham and Caruccio (1995) studied the effects of overburden particle size on contaminant production rates and total contaminant loads. Two particle sizes were tested in soxhlets and weathering cells; the "large" size fraction of overburden particles were screened to 2.36-4mm in size and the "small" size fraction

were overburden particles that ranged from 125 to 250 µ in size. For the acid-producing overburden samples, the smaller size fraction had a higher acid production rate (APR) than the large size fraction, but a smaller total acid load (TAL), due to a higher initial acid load for the large size fraction. For the overburden samples with a high NP value, the large size fraction resulted in negative (i.e. alkaline) APR's and TAL's, while the smaller size fraction produced positive APR's and TAL's. In general, sulfate, calcium, iron, and manganese production rates and total loads were higher in the small size fraction samples than in the large size fraction.

The sensitivity of contaminant production processes in weathering cells and leaching columns to variations in size and sorting efficiency of overburden particles was also evaluated. Overburden samples were crushed and sieved into three particle size fractions: 1) a large size fraction, consisting of particles ranging in size from 12.7 mm to 50 mm; 2) a medium size fraction of particles ranging from 6.4 to 12.7 mm; and 3) a small size fraction, consisting of particles smaller than 6.4 mm. Different sorting coefficient subsplits were created by blending the three sieved size fractions into various combinations. This phase of the investigation examined: 1) 3 well sorted subsplits, created by using each size subsplit unmixed; 2) 2 medium sorted samples, created by mixing the large and the medium size fractions, and the medium and the small size fractions; and 3) 1 poorly sorted sample, created by mixing all three size fractions. Representative subsplits were packed into weathering cells and leaching columns, and leached with deionized water at 7-day intervals for a minimum of 12 weeks.

According to Bradham and Caruccio (1995), in the absence of any temperature or leaching interval effects, leachate quality variability for the second phase leaching tests was dominated by the particle size factor. Both acid and sulfate production rates were linearly correlated with the logarithm of particle size. Acid production rates for overburden samples with high NP's (>2%) exhibited a positive correlation with the logarithm of particle size, indicating that, for these samples, acidity decreased with decreasing particle size. Acid production rates for overburden samples of low NP (<1%) increased with decreasing particle size, and were thus negatively correlated with particle size. Sulfate production rates were negatively correlated with particle size for all of the overburden samples.

Particle size affected leachate quality from columns and weathering cells by controlling the size of pore spaces between overburden particles, the inter-grain surface tensional forces, and the rate of water movement through the overburden material. In overburden samples with large pore sizes, such as in the well sorted, large and medium size fraction overburden samples, surface tensional forces were small and water flowed through very quickly. Short residence times for pore water in these large grained samples limited the solubility of carbonate minerals, and resulted in little alkalinity production. By contrast, very small pore sizes in fine grained overburden rocks produced larger tensional forces, held more interstitial water, and resulted in much slower water movement. In such fine grained samples, slow water movement afforded sufficient time for carbonate minerals to dissolve and neutralize acidity. The resulting alkalinity production was much greater for the fine-grained samples than for the large-grained samples.

In overburden samples with little or no neutralization potential, however, net acid production was controlled by the rate of pyrite oxidation, rather than by carbonate dissolution. Reaction products of pyrite oxidation, such as iron sulfate minerals, are orders of magnitude more soluble than calcium carbonate. Porewater

residence time was much less critical in the dissolution and transport of these minerals. Dissolution was almost instantaneous and the rate of water movement had a smaller influence on the overall rate of acid production (Bradham and Caruccio, 1995).

They also found that although all of the factors evaluated in the leaching tests affected leachate quality to some degree, the factor of particle size was somewhat less significant than the factors of storage condition and leaching interval, and played a secondary role in influencing leachate quality. Particle size resulted in 4% to 48% of leachate quality variability for four of the overburden samples, but was responsible for 95% of the variability in APR for one overburden sample.

Antecedent Storage Conditions

The storage of samples after collection and prior to analysis can play an important role in acid production. Weathering or oxidation of the minerals within the samples begins almost immediately and care must be taken to analyze samples as quickly as possible. As an extreme example, in evaluating a site in West Virginia, Caruccio and Geidel, (1981) obtained fresh cores from the location and were also provided with cores that had been stored in a dry shed for two years. Geologically, the cores correlated well; however, the results of weathering cell testing indicated that the cores that had been stored for two years produced nearly ten times more acidity than the fresh cores. Cravotta (1994) suggests that soluble iron-sulfate hydrates form on the surface of oxidizing FeS_2 in unsaturated mine spoil and can dissolve when flushed with ground water (or in this case, with leachant during testing procedures) releasing sulfate and Fe^{3+}. Subsequent oxidation of pyritic sulfur can occur by Fe^{3+} and /or hydrolysis of Fe^{3+}, producing acidity.

One method of reducing the oxidation of pyrite during storage, if the sample must be stored prior to analysis, is to store the sample under an inert gas, such as nitrogen. This method is routinely used by the USGS for the preservation of rock samples that are collected as standards.

The temperature and humidity of the stored sample is also important. Bradham and Caruccio (1995) showed that samples stored between leaching cycles at a high temperature (105ºC) oxidized pyrite while only minor reactions occurred in the carbonate minerals. Because the storage of samples between collection and analysis is similar in many respects to interleach storage, high temperature, esp. high temperatures encountered during the summer in some coal basins, could impact the results obtained during the kinetic testing. Although these effects may be minimized after the initial or early stage leaching, depending on the extent of the oxidation, they also could significantly impact the entire analysis.

Similarly, field samples with a high moisture content tend to be reactive even in the absence of oxygen. Calcareous dissolution reactions and reactions of pyrite with Fe^{3+} will continue. Therefore, precautions should be taken when collecting samples that may be moist to minimize such reactions prior to analysis.

Interleach Storage Conditions

Bradham and Caruccio (1995) evaluated four interleach storage conditions for five mine overburden samples:

1) weathering cells: samples were placed in weathering cell chambers that were under a constant humidity and temperature (20ºC);
2) humidity: samples were stored in a humid atmosphere (approaching 100% relative humidity) and ambient temperature;
3) ambient: samples were protected from dust and disturbance, but were allowed to be exposed to the ambient temperatures (20ºC) and humidity of the laboratory; and
4) oven: samples were maintained at a constant temperature of 105° C.

Oven storage resulted in higher acid production rates (APR) and total acid loads (TAL) than the other storage conditions. For the acid-producing overburden samples, oven storage produced APRs of 0.105 mg/g sample/day, roughly a 40% increase in acid production over ambient, humid, and weathering cell storage. Oven storage also produced positive APRs and TALs in two samples, in apparent contradiction to the alkaline results produced by ambient, humid, and weathering cell storage. The largest differences in APR and TAL occurred between oven storage and the other storage conditions. In general, ambient, humid, and weathering cell storage produced roughly equivalent APRs and TALs. Similar results are reported for sulfate production rates, total sulfate loads, calcium production rates and total loads, and iron and manganese and iron production rates and total loads. These findings suggest that whether column or weathering cell samples are purged with humid or ambient air, or a combination, for various numbers of days, during interleach storage, there will be only minor, if any, effect on the resultant water/leachate quality.

Borek (1994) evaluated the effects of humidity on pyrite oxidation (without leaching the sample by flushing with water as in weathering cell, column or soxhlet reactors) and concluded that pyrites weather differently depending on the humidity. Borek suggested that high humidity conditions, in the absence of direct contact with water, can contribute the water needed for pyrite oxidation. The principal weathering products were two ferrous sulfates, melanterite and rozenite.

Degree of Saturation

The hydrogeologic setting of the mine site (i.e. groundwater recharge area, transition area, or groundwater discharge area) should be considered in determining the appropriate kinetic test procedures. Under most conditions, the overburden rock material and spoil piles will not be completely saturated, but will be affected by infiltrating rainwater and groundwater. Portions of the backfill, especially close to the pit floor, may be saturated while other areas are subject to a fluctuating water table or may remain unsaturated. Infiltrating rain and ground water will flush the accumulated weathering products that are produced during the natural weathering cycles.

Watzlaf (1992) evaluated pyrite oxidation in saturated and unsaturated coal waste samples in leaching columns using influents of distilled, deionized water and recycled AMD (i.e. previously collected leachate laden with ferric iron). The cumulative loads of sulfate, acidity, iron, manganese and aluminum produced from 189 days of leaching were much greater (i.e. 1 to 3 orders of magnitude) for unsaturated conditions, regardless of whether the influent was distilled water or recycled AMD. Watzlaf (1992) concluded that:

> "Saturation of the pyritic coal refuse significantly reduced the rate of pyrite oxidation. The sulfate load produced by the unsaturated columns after 189 days would take 118 years to be generated under

saturated conditions in the columns receiving the deionized water leachant…. Theoretical calculations, column leaching, and experience from the metal mining industry show the disposal under saturated conditions can significantly reduce contaminant concentration from pyritic material."

The effectiveness of submergence of the rock samples in kinetic tests is also discussed by Leach (1991) and Caruccio et al. (1993), who used columns that simulated vadose conditions, the zone of fluctuating water table and the zone below the water table. Their results clearly showed that submerging acid-producing material below the water table dramatically inhibits acid production. Given the effect of submergence on the leachate quality, kinetic testing should only incorporate submergence when the overburden material will be submerged continually after the backfilling is complete. Since a dramatic increase in acid production was noted to occur when materials are subjected to a fluctuating water table (Caruccio et al., 1993), kinetic testing using submergence should be limited to specific applications.

Size, Shape and Structure of Apparatus

Hornberger and Brady (1998) provided a detailed review of the wide range of kinetic test apparatus used during the past 45 years and found "relatively simple leaching columns with a wide variety of diameters and heights and some more complex leaching columns of various dimensions." For example, the leaching columns range in diameter from 1.3 in (3.30 cm) (Hood and Oertel, 1984) to 10 ft (3.08 m) (Murr et al., 1977). While humidity cells have less variation in size and shape than leaching columns, the complexity of the humidity cell apparatus and peripheral equipment has varied significantly (Hanna and Brant, 1962; Harvey and Dolhopf, 1986; White and Sorini, 1995). Other complex types of kinetic test apparatus have also been utilized, such as the Warburg respirometer (Lorenz and Tarpley, 1963) and Soxhlet reactors (Renton et al., 1973).

In general, kinetic test apparatus should be as simple as possible. However, the kinetic test apparatus may need some complexity in external form or internal structure to allow fluids and gases (i.e. oxygen, carbon dioxide, and water vapor) to enter, circulate through, and exit the apparatus, in a manner representative of the weathering conditions of the mine.

The relationship between the dimensions of the kinetic test apparatus and the dimensions of the rock samples being tested must be considered in order to prevent adverse interactions between the sample and the container. As already mentioned, fine-grained material can cause airlocks in leaching columns. Another problem that can occur is preferential flow through a segment of the sample, such as along the container wall. In the mine environment, the rock within spoil piles and surface mine backfill may or may not be placed in a manner similar to the placement of the material in the leaching columns. Spoil and backfill rarely develop a uniform wetting front (except perhaps during periods of slow snow melt), but often exhibit a pseudo-karst hydrology (Caruccio et al., 1984; Brady et al, 1996; Hawkins, 1998). These effects, however, must be minimized in laboratory studies to prevent skewing test results (as with airlocks), to provide standard testing techniques, and to minimize the interaction between the container and the sample.

Another group of studies has evaluated humidity cell performance and parameters, including Bradham and Caruccio (1995, 1997), Pool and Balderama (1994), and White and Jeffers (1994). In addition, within the last fifteen years, there have been a number of studies comparing various test methods to determine which

is the best AMD predictor, including Bradham and Caruccio (1990, 1995, 1997), Caruccio and Geidel (1986), Erickson and Hedin (1988), and Ferguson and Erickson (1986, 1987, 1988). This allows the current focus to be on similarities among the various kinetic test methods rather than the differences between them. In the remainder of this section, the physical, chemical, and biological considerations that should be incorporated in any kinetic test will be emphasized.

Volume and Placement of Overburden Samples in a Kinetic Test Apparatus

The relationship between the dimensions of the kinetic test apparatus and the dimensions of the rock samples being tested was discussed previously in the context of preventing adverse interactions between the sample and the container, particularly where the container was too small or confining. A corollary to that principle is that the amount of sample typically available for the test should be a determining factor in the dimensions of the apparatus. For example, while the 30-gal (113.56 l) field barrels used by Renton et al. (1984, 1985) were ideally suited for testing representative samples of large volumes of coal refuse, this approach would not be appropriate for testing the volume of sample available from an air-rotary drill hole. The mass of rock chips and fines from a 5 5/8 in (14.29 cm) diameter air-rotary drill hole, typically used for blast hole drilling and, in some states, for overburden analysis sampling, is approximately 12 kg of sample per foot of rock drilled. According to Sobek et al. (1978) and Noll et al. (1988), rock samples from air-rotary drilling methods should be collected at 1 ft (0.305 m) intervals, though several feet of successive samples of the same lithologic unit may be combined or composited for testing purposes. As some significant lithologic units may only be 1 ft (0.305 m) thick, and representative splits of the sample are typically needed for other overburden tests, including NP and total sulfur content, the volume of sample available for kinetic tests may be limited.

Generally, the volume of sample available for kinetic tests should be at least 100 g for each lithologic unit to be tested and could be as large as 15kg. Soxhlet reactors usually contain 100 g of fine-grained sample. This weight has been relatively uniform throughout the literature due, in part, to the size of the apparatus and the nature of the thimbles used. Weathering cells and columns tend to have a wider variation in described weights and particle sizes. Weathering cells generally contain between 100 and 1000g of sample with several authors reporting weights in the 200 and 300 g range. Leaching columns have an even greater range of sample size, from several hundred g to more than 15 kg. The important aspect of the tests is that each analysis relates weight of rock to volume of effluent to time so that results can be correlative.

Leaching Interval

A principal objective of many kinetic test procedures is to perform a weathering test that will mimic field conditions so that the samples being analyzed over a long time frame can be used to relate laboratory results to field results. However, most tests simulate accelerated weathering conditions either by decreasing the interval between leachings (leaching interval) or increasing the amount of water or leachant (i.e. simulated precipitation) used in the weathering tests. Assuming the samples being tested represent the gray zone (having both alkaline and acidic components), then the leaching interval becomes an important factor due to differences in the chemical reaction rates between the oxidation of pyrite and the dissolution rate of calcareous material.

If the leaching interval is long, the amount of pyrite which has oxidized, as reflected by the total acid load, will be increased and may overwhelm the amount of alkalinity generated from carbonate dissolution. Alternatively, for short leaching intervals, the acid production rates may be high, but the total acid load is low, thereby providing for sufficient alkalinity from the calcareous material to offset or neutralize the amount of pyrite oxidized (Geidel, 1979). This scenario is complicated by the fact that in some cases, the presence of calcareous material has been shown to actually prevent the oxidation of pyrite. Therefore, the length of time between leaching must be sufficient to allow pyrite oxidation to occur while recognizing that even with an extended time period, oxidation may be arrested. Not surprisingly then, Bradham and Caruccio (1995) found that the temperature and humidity at which overburden samples were stored between leachings and the leach interval were, by far, the most significant factors influencing leachate quality. Indeed, they found that these factors were responsible for the majority of the variability present within the total range of contaminant production. Daily leaching intervals are too short for most kinetic tests and a significant amount of data is available for leaching intervals of 7 days. Geidel (1979) evaluated 1, 7, and 14 day intervals while Bradham and Caruccio (1995) tested 2, 4, and 7 day leaching intervals and found that the leaching interval was responsible for between 14 and 100% of acid production variability.

In addition to the interval, water handling also affects the leachate quality. Frequent leaching episodes with relatively large volumes of water may not simulate the mine environment within the humid Appalachian Coal Basin or the more arid conditions of the western United States. In addition, the processes affecting the oxidation of pyrite and the dissolution of calcareous material are time dependent. Accordingly, these factors must be accounted for in the determinations by relating the chemical production rates to the volume/weight of sample per volume of leachate per time interval.

The duration of the kinetic test is also a factor to consider. Testing should be conducted until the results are definitive and consistent. Soxhlet reactor tests are the most aggressive and results can generally be completed within 10 to 12 weeks. Weathering cells and leaching columns are more difficult to predict; appropriate lengths of time range from 8 to 104 weeks. The shorter time periods are normally associated with samples that are acidic initially or that become acidic within the second or third leaching interval. Samples that become acidic during kinetic testing, do not, under normal conditions, become alkaline (Lapakko and Antonson, 1994). The acidity may decrease with time or the sample may become inert (characterized by very low specific conductance (<10 µS) and net acidity of near zero).

Influent Composition

Several studies have looked at the effect of using influent or leachant other than distilled-deionized (DI) water (Geidel, 1976; Caruccio et al., 1981, Watzlaf 1992). Geidel (1976), in weathering cell experiments, leached samples with both DI water and synthetic AMD to compare the effects of the acidity, metals and anions on sample weathering rates. Generally, samples that were acid producing with DI water, had greater total acid loads after leaching with the synthetic AMD. Caruccio et al. (1981) compared the effect of DI water, simulated acid rain and synthetic AMD on samples with varying NP-MPA ratios. The AMD had a two-prong effect; the acid and metals added to the system enhanced the oxidation of the pyrite, as well as the dissolution of the calcareous material. The simulated acid rain, however, did not produce leachates that were significantly different than the DI water leach. As expected, the samples with high sulfur and low

NP were acidic and samples with low sulfur and high NP (>40 ‰) were alkaline. For samples with critical NP-MPA ratios, within the gray zone, weathering cell leaching of the samples with synthetic AMD created conditions conducive to acid production, while depending on the NP-MPA ratio, some samples leached with the simulated acid rain or DI water were acidic and others were alkaline. Several samples initially produced alkaline leachate, but with time and as the carbonate was consumed, acid conditions prevailed. (Caruccio et al., 1981).

Rock to Water Ratio

If the ratio of the volume of influent water to volume of rock sample is much greater than will occur in the mine environment, the concentrations of contaminants in the leachate will probably be much less (i.e. more diluted) than in the actual mine drainage. For example, the fluid volume: sample volume ratio of 4:1 used in the ASTM Water-Shake Extraction Procedure (1983) floods the sample in a manner that is not representative of most surface mine backfills. For this, as well as several other reasons, this technique did not work well for AMD prediction (Hornberger, 1998). In soil testing, ratios are commonly 1:1 (weight per weight basis) and in many leaching columns and weathering cells, the ratio is less. While ratios between rock sample volume or weight and leachant volume used may be important, this factor has not been studied in detail. Under natural field conditions, the volume of influent water will vary tremendously, yet laboratory conditions should maintain certain controls. Kinetic test data is often reported as a concentration expressed in mg/weight of sample/ volume of leachate/time.

For example, Bradham and Caruccio (1995) used weathering cells containing approximately 300 or 600 gm of sample, which were leached by removing the lid of the cell and covering the sample with 100 ml of deionized water. After approximately one hour, the cells were inclined to allow leachate to drain through filter paper placed in the bottom of the cell into collection beakers. After the leachate had stopped draining, usually after three hours, the leachate was removed from the collection beakers, and the weathering cells were returned to a horizontal position. In the CARWA method, 200gm samples were leached with 200 ml over a 2.5 hours leaching cycle.

In a study evaluating the amount of alkalinity released from surface applied limestone in response to rainfall, laboratory tests were conducted in which the amount of leachant was related to a rainfall event (i.e. ¼, ½ or 1 inch of rainfall) (Geidel and Caruccio, 1982).

Similar variation in rock:water ratios exist between leaching column studies. In Bradham and Caruccio (1995), clear acrylic columns 60 cm in length by 16 cm ID and containing approximately 14kg of sample, were leached weekly with 400 ml of deionized water. In Hood and Oertel (1984) and Hood (1984), glass tubes 122 cm in length and 3.5 cm ID were flushed weekly with 250 ml of leachant. In O'Hagan (1986), columns 30 cm in length by 7.5cm ID and containing approximately 1 to 1.4 kg of sample, were leached with 250 ml leachant.

While the volume of influent water in kinetic tests is important for determining dilution of the mass of leached constituents, it must always be related to the weight or volume of the sample. Assuming a linear relationship

exists between these parameters or if ratios of water to rock volume are kept constant among the various kinetic tests, then laboratory measurements can be correlated with the field results.

Another consideration is the surface area of the rock to water volume ratio. The surface area is related to the particle size. However, Bradham and Caruccio (1995) found that particle size was not significant unless leaching interval and storage was held constant. They state:

> "Particle size affected leachate quality from columns and weathering cells by controlling the size of pore spaces between overburden particles, the inter-grain surface tensional forces, and the rate of water movement through the overburden material. In overburden samples with large pore sizes, such as in the well sorted, large and medium size fraction overburden samples, surface tensional forces were small and water flowed through very quickly. Short residence times for pore water in these large grained samples limited the solubility of carbonate minerals, and resulted in little alkalinity production. By contrast, very small pore sizes in fine grained overburden rocks produced larger tensional forces, held more interstitial water, and resulted in much slower water movement. In such fine grained samples, slow water movement afforded sufficient time for carbonate minerals to dissolve and neutralize acidity. The resulting alkalinity production was much greater for the fine grained columns than for the large."

They also found that in overburden samples with little or no NP, net acid production was controlled by the rate of pyrite oxidation, rather than by carbonate dissolution. Reaction products of pyrite oxidation, such as iron sulfate minerals, are orders of magnitude more soluble than calcium carbonate. Porewater residence time was much less critical in the dissolution and transport of these minerals. Dissolution was almost instantaneous and the rate of water movement had a smaller influence on the overall rate of acid production.

Pore Gas Composition

The pore gas composition of the sample analysis can be controlled; however, the important consideration is to determine the portion of the backfill or refuse pile that is to be mimicked by the kinetic testing. It has been suggested that a significant amount of the total weathering occurs in the upper or outermost portions of the backfill. In this instance, the pore gas composition is not significantly different from that of the atmosphere.

The effect of O_2 and CO_2 partial pressures on the production of acidity and alkalinity in the mine environment and in kinetic tests is discussed in Hornberger and Brady (1998). The composition of gases within void spaces and backfilled surface mine spoil has been studied by Cravotta et al. (1994), Jaynes et al. (1983), Lusardi and Erickson (1985), Guo et al. (1994), Guo and Parizek (1994) and others. Jaynes et al. (1983) found that decreases in oxygen concentration with depth were strongly correlated with increases in CO_2 concentrations with increasing depth, but that most of the mine site remained well oxygenated (i.e., O_2 greater than 10%) down to 12 m depth throughout the 2-year study. The highest CO_2 concentrations reported were 16.61% at 7 m depth. Cravotta et al. (1994) reported that:

> "Partial pressures of O_2 and CO_2 in spoil are expected to vary depending on the predominant reactions involving the gases, relative rates of the reactions, and rates of gas exchange with surrounding zones (Jaynes et al. 1984 a,b; Lusardi and Erickson 1985). In general, where pyrite-oxidation and carbonate-dissolution reactions are active, pO_2 will decrease and pCO_2 will increase.

> Data on pore-gas compositions at the mine indicate that pO_2 decreases from about 21 volume percent (vol %) at the land surface to less than 2 vol % at 10.7 m below the surface, with corresponding increases in pCO_2 with increasing depth in all three areas."

In determining the alkalinity generated from rocks with an alkaline potential, CO_2 variations must be considered. At pCO_2 of the atmosphere ($10^{-3.5}$ atm.), the maximum alkalinity generated from carbonate rocks is approximately 75 mg/l as $CaCO_3$. However, as the pCO_2 increases with depth, the alkalinity can increase up to about 400 mg/l as $CaCO_3$ at pCO_2 of 10^{-1} atm. Kinetic tests can be modified to incorporate various gas compositions, however, as determined from Guo et al. (1994) the pCO_2 in the backfill remains relatively low and approximates atmospheric conditions.

Modeling of pyrite oxidation in reclaimed coal strip mines by gas diffusion processes is described by Rogowski et al. (1983), Jaynes et al. (1984a, 1984b) and Jaynes (1991). According to Jaynes et al. (1984a), the air convection mechanism of oxygen movement used by Cathles and Apps (1975) represents reasonable assumptions for coarse waste dumps, but they believe that diffusion processes would dominate within backfilled coal mine spoil. However, Guo et al. (1994) concluded that the:

> "Results of both field investigation and analytical calculation suggest that the high O_2 concentration (18% or higher) observed in mine spoil cannot be the result of diffusion but, instead, is caused by advection, probably due to thermal convection."

Additional information on oxygen transport is found in Guo and Cravotta (1996). Pyrite oxidation rates were studied in laboratory kinetic tests by USBM researchers for more than 60 years, including Hammack and Watzlaf (1990), Leitch et al. (1930), Lorenz and Tarpley (1963), Watzlaf and Hammack (1989) and Watzlaf (1992). Oxidation rates of pyrite (with and without bacterial catalysis) were measured by Lorenz and Tarpley (1963) using a Warburg Respirometer, which facilitated the measurement of oxygen consumption during the kinetic test. Hanna and Brant (1962) used the Warburg Respirometer to evaluate oxygen uptake during laboratory weathering of pyrite materials in differing lithological units and particle sizes. Hammack and Watzlaf (1990) measured abiotic and biotic oxidation rates of pyrite in leaching columns, using certified gas mixtures ranging from 0.005% to 14.5% oxygen (plus 5% carbon dioxide and the remainder nitrogen gas) introduced into the leaching columns via compressed gas cylinders and a gas humidifier.

Watzlaf (1992) studied pyrite oxidation in saturated and unsaturated coal waste in leaching columns to determine the effects of dissolved oxygen in water and the presence of ferric iron upon the pyrite oxidation. Watzlaf (1992) stated:

> "To limit pyrite oxidation, oxygen levels must be reduced from an atmospheric level of 21% (0.21 atm) to extremely low levels. It has been shown that the biotic rate of pyrite oxidation is not limited unless pore gas oxygen is reduced to less than 1% (0.01 atm) (Carpenter, 1977; Hammack and Watzlaf, 1990). With current reclamation practices, limiting oxygen to less than 1% is not feasible. At the current time, the only practical method to reduce oxygen to levels low enough to limit pyrite oxidation is by saturating the pyritic material with water…. In an unsaturated system, pyrite oxidation has been found to be independent of oxygen levels down to about 1%.… Pore gas oxygen levels in surface mine spoil or in coal refuse piles are almost always above 1%…. In a saturated system, pyrite

would oxidize at a very low rate that is dependent on the amount of dissolved oxygen and ferric iron in the contacting water. Once dissolved oxygen is consumed, the rate of diffusion of pore gas oxygen through water becomes limiting."

Watzlaf (1992) also compiled data on pyrite oxidation rates from other studies (expressed in mg of sulfate per gram of pyrite per hour) ranging from 0.06 to 0.16, including data from Braley (1960), Clark (1965), Hammack and Watzlaf (1990), and Nicholson et al. (1988). Cravotta (1996) provides a more recent compilation and comparison of pyrite oxidation rates from laboratory experiments ranging from 0.02 to 0.96 (expressed in the same units as above) including data from McKibben and Barnes (1986), Moses et al. (1987), Moses and Herman (1991), Rimstidt and Newcomb (1993) and others. These studies evaluated pyrite oxidation rate differences on the basis of particle size (surface area), pH of initial solution, and availability of oxygen and ferric iron.

Bacterial Effects

The pyrite oxidation reactions are catalyzed by bacteria, primarily *Thiobaccillus ferrooxidans*, a bacterium that oxidizes Fe^{2+} to Fe^{3+} (U.S. EPA, 1971; Kleinmann and Crerar, 1979). These bacteria are indigenous to aqueous environments having pH values ranging from about 2 to 3 and defining the range and/or activity of these bacteria. This three-phase system, and the role that bacteria play in the reactions, has been described by Kleinmann et al. (1981).

In evaluating the effect of *Thiobaccillus ferroxidans* on humidity cell tests, Poissant and Caruccio (1986) found that core and highwall samples collected for the study contained viable populations of bacteria. Therefore, for samples collected from various locations in West Virginia, the samples did not require inoculation prior to testing. In fact, it was necessary that the samples be sterilized to remove the bacteria. Other researchers, however, have indicated that rock samples collected from various locations are sterile. Caruccio and Geidel (1978, 2000) suggest that the bacteria population is viable and active only when the geochemical environment model meets certain criteria, which includes pyrite content and morphology, calcareous material content, and groundwater geochemistry. Bacteria are generally active only under certain conditions. It is probable that in environments with a high calcareous and low sulfur content, and in alkaline groundwater conditions, the activity of these acid-loving bacteria will be minimized. However, in the absence of calcareous material, the rate of pyrite oxidation is enhanced even in low (1%) oxygen concentrations (Kleinmann, 1998).

Some researchers have inoculated samples during kinetic testing with bacteria and others have added mine drainage collected from field sites with AMD to the sample. Based on studies using simulated AMD, the effects of the mine drainage may out weigh the benefits of adding additional bacteria. Due to the activity of the bacteria and their generally ubiquitous nature, the activity or presence of bacteria in a sample may simply be related to the sample's geochemical properties.

Pyrite Morphology and Texture

As discussed in Chapter 2, Caruccio and Parizek (1968) found that the pyrite morphology was significantly different in samples that produced acid and those that did not, even though the total pyritic sulfur contents

were similar. In samples from the non-acid producing area, the pyrite commonly had a massive form and appeared to have been deposited after coalification. Most of the grains were >400 μm and some had a morphology that suggested that the pyrite occurred as replaced plant structures and occupied joints in the coal. The morphology of the other grains in stable pyrite categories were crystals or euhedra of pyrite that commonly had cubical or triangular shapes. These particles, although small in size (between 5-10 μm), were relatively more stable than the massive ones. In samples from the acid-producing area, however, a major portion of the pyrite occurred as clusters of spheres approximately 25 μm in diameter. Each of the spheres was an agglomeration of minute (approximately 0.25 μm) crystals of pyrite that collectively formed the globular morphology. Gray et al. (1963) called attention to this type of pyrite (often called framboidal pyrite) occurring in the Pittsburgh seam.

The framboidal pyrite was determined to be much more reactive than the massive secondary pyrite. Samples that contained only coarse-grained particles of pyrite did not show appreciable signs of weathering, and the pyrite remained shiny and brassy for indefinite periods of time. Subsequent studies by Caruccio (1973) showed that percentages of framboidal pyrite within samples of similar permeabilities multiplied by total pyrite content of that sample could be used to estimate the acid potential with the proviso that the NP was less than 20 tons/1000 tons or 2 %. Caruccio et al. (1977) confirmed that a strong correlation existed between the occurrence of AMD and pyrite morphology. The secondary massive pyrite was relatively stable, as reflected by the paucity of sulfate in mine drainage sites in non-acid areas. These relationships are valid, providing there is an absence of calcium carbonate. The results of the study established framboidal pyrite as being the most reactive of the pyrite forms and were further corroborated by Pugh et al. (1981, 1984). Caruccio (1973) and Morrison (1988) found a relationship between relative surface area and acid production, with the smaller particles being more reactive. Pyrite genesis has also been suggested as a factor influencing pyrite reactivity—sedimentary pyrite (framboidal pyrite, for example) is typically more reactive than hydrothermal pyrite (Hammack et al., 1988; Borek, 1994). Pyrite morphology can be used in conjunction with kinetic testing or the EGA techniques discussed in Chapter 4 to discern differences in acid production rates between samples with similar NP/MPA ratios.

Carbonate

While prediction of AMD rather than water quality has been the focus of many of the kinetic tests of the decades, it has been shown repeatedly that calcium or magnesium carbonates play a significant and perhaps overriding role in the process. Brady et al. (1998), Caruccio and Geidel (1978) and Caruccio and Parizek (1968) have shown that a stratum's potential to produce acidity is determined to a large extent by the amount of calcareous material ($Ca\text{-}MgCO_3$) and not the amount of pyrite. Geologic systems enriched in calcareous material produce alkalinity, and highly buffered and potentially neutralizing drainages. In these areas, the calcareous material raises the pH of the ground water regime above 7, which effectively suppresses iron bacteria microbial activity and reduces the oxidation of ferrous iron. Several studies have shown that the calcareous material also serves to inhibit the oxidation of pyrite and stabilize the sulfide (Caruccio et al., 1981; Hornberger et al., 1981; Williams et al., 1982; Perry and Brady, 1995). Bradham and Caruccio (1995) showed that when NP exceeds 38g/kg, the sample would produce alkaline leachate at the 95% confidence level. At an NP of 73 g/kg, a confidence threshold of 100% for alkaline leachates

occurred. A previous section of this handbook discussed the importance of carbonates and their measurement through static tests. For strata with high NP values, static testing provides the essential information required for determining whether the sample will produce acidic or alkaline leachate.

The acidity produced at a site that has relatively little calcareous material depends, in part, on the amount of reactive pyrite that is available for oxidation. When lack of calcareous material is coupled with a lack of pyrite, such as might occur in a sandstone or shale, the resultant leachate quality is characterized as inert (pH ~5, very low specific conductance). Given a low specific conductivity, coupled with a lack of alkalinity, this leachate or water quality is easily impacted by acidic waters.

Surface mining disturbs strata of varying chemical compositions, and the ultimate quality of the drainage is a blend of all drainage chemistries produced by each rock type. Various techniques are available to evaluate the acid and alkaline potentials of overburden material (Sobek et al., 1978; Caruccio et al. 1993; and Bradham and Caruccio, 1991). The reactive pyrite component can be related to the acid potential, whereas the calcium carbonate content in the stratigraphic section can be related to moderate amounts of alkalinity. However, the level of alkalinity that can be potentially produced by calcareous material is limited by its solubility. Unlike the acid-producing compounds (the oxidation products of the disulfide), which are extremely soluble in water, Geidel (1979) and Neuhaus (1986) have shown that dissolution of calcareous material is limited by the amount of carbon dioxide present, the time of rock-water contact, and the solubility of the specified mineral. Once equilibrium is established between the calcareous rock and water, further contact of the water with the alkaline-producing medium does not produce additional alkalinity.

At equilibrium, alkalinity levels seldom exceed 75 mg/l (as $CaCO_3$) under atmospheric partial pressure of carbon dioxide (pCO_2) ($10^{-3.5}$ atm). Increases in pCO_2 brought about by the development of a mature soil and vegetative cover could effectively increase the available alkalinity by a factor of eight. At equilibrium conditions with pCO_2 at 10^{-1} atm, the maximum amount of alkalinity that can be generated by calcareous material is about 400 mg/l (as $CaCO_3$), irrespective of the amount of calcareous material present in the section. In some cases, shales with a high ion-exchange capacity can shift the equilibrium, with an increase in alkalinity. The mechanism for this reaction is through the exchange of calcium and magnesium cations onto the clays of the shale. This shifts the carbonate equilibrium reaction leading toward greater dissolution of the carbonate mineral, with attendant increases in alkalinity (Winters et al., 1999).

Blending of acid and alkaline material initially increases the levels of alkalinity since the solubility of calcium-magnesium carbonate is greater in an acid solution. However, under aerobic conditions, ferric iron, which is soluble at low pH, will precipitate at the neutralizing sites and, if located in a fluctuating wet and dry condition, will armor the calcareous material against further reactions. In this event, the alkaline material becomes isolated from the aqueous system and most of the alkaline potential of that stratum is lost (Ziemkiewicz et al., 1995). Should anaerobic conditions be maintained, such as occurs in anoxic limestone drains, the iron remains in the ferrous state. The coating is then minimal and a portion of the calcareous material remains exposed as a viable source of alkalinity, capable of neutralizing limited amounts of acidity.

It was previously noted that the appropriate length of time for kinetic testing, especially for weathering cells and columns, ranges from 8 to 104 weeks. The shorter duration tests are normally appropriate for a sample

that becomes acid very early in the leaching process. Continued leaching of these samples may result in decreased acidity with time but will not generate net alkalinity. However, a number of samples, especially from the "gray zone," may begin leaching cycles as alkaline samples, but with time, as the alkaline components are dissolved, the sample may become acidic. One example of this is shown in Caruccio et al. (1981), in which samples with critical NP/MPA ratios were initially alkaline, but with time became acidic. When replicate samples were leached with synthetic AMD, the carbonate neutralization effect was minimized and the alkalinity was overwhelmed by the acidity in a shorter time. Certain samples, however, based on their higher carbonate content, remained alkaline throughout the study. Other researchers have evaluated samples for long periods of time and have also shown that certain alkaline samples remain alkaline.

CRITERIA FOR DETERMINING WHETHER TO CONDUCT KINETIC TESTING

The interaction between alkaline and acid-forming materials, along with the natural variability in the proportions of these two sets of variables and the differences in their reaction rates, provide a framework within which the evaluation of the potential to predict acid drainage must be evaluated. As discussed in Chapter 4, the modified NP analysis can be used to determine the amount of alkaline generating materials while the acid generating materials can be estimated using the percentage total sulfur (S). If the reaction kinetics were similar for the two processes, no further analysis would be required. However, due to fundamental differences between the two sets of reaction kinetics, the quantification of the two parameters is not always sufficient to determine the anticipated water quality from the mine site. When the NP of the rock sample exceeds a threshold value of 3.7% (Bradham and Caruccio, 1995), the alkaline system is favored, regardless of S content. Other studies have suggested that the threshold may be low as 2.1% (Chapter 4). Alternatively, when there is a paucity of alkaline material, coupled with even a low S content, the resultant leachate is usually acidic.

The NP/MPA ratio for which an accurate prediction can be made varies from one basin to another. Within one geologic basin, a ratio greater than one generates alkaline water, while a similar ratio is acid forming in another basin (Caruccio and Geidel, 1982). Graphically, the area defined by the swath created by the <1:1 ratio and the slightly >1:1 ratio, coupled with an NP threshold, is equivalent to the gray zone referred to in Chapter 4. As shown in Figure 5.4, the Neutralization Ratio (NR) =1 results only in confidence between 65 and 70%, for a 30-35% chance of an error in which an overburden sample is classified by ABA as alkaline but produces acidic leachate. However, when the NR is used with a threshold NP value, a much smaller gray zone is possible than for either the threshold NP or the neutralization ration criteria methods (Fig. 5.5). Figures 5.4 and 5.5 represent 83 coal mine overburden samples from 4 states and numerous geologic basins (Bradham and Caruccio, 1995). Within this gray zone, the likelihood of acid generation may be site specific. It is under these conditions, and especially when NP is used, that the additional information gained from kinetic testing is warranted to determine the anticipated drainage quality.

RECOMMENDATIONS/GUIDELINES FOR SELECTION OF KINETIC TEST

After it has been determined that the sample has less than the threshold NP and is within the NP/S gray zone, the kinetic test selected for laboratory analysis should approximate the anticipated field conditions of

the mine site. Therefore, field scale tests will not generally be considered as the primary laboratory test, but are more often used to validate laboratory analyses or to determine scaling factors. As noted in the prior sections, the soxhlet extraction method subjects the fine grained sample to a hot water leach and interleach storage conditions of 105°C temperature and a lack of humidity, such that pyrite oxidation is accelerated relative to carbonate dissolution. While this may be the method selected in specific instances such as mimicking surface conditions of a fine grained tailings pond in a warm climate or in a fine grained coal spoil pile, it does not reflect the conditions present in most overburden reclamation sites.

For the majority of surface mine overburden scenarios, the kinetic test selected will be either the Column or the Weathering/Humidity Cell. Due to problems associated with column tests, such as non-uniform wetting fronts due to channelized flow, and less control over the leaching time period (i.e. within course rock fractions, the leachant flows through more quickly), we recommend that laboratories making an initial selection of kinetic test apparatus choose the humidity cell. Column tests are appropriate for a number of research applications, such as evaluating the effects of differing water table conditions, pore gas compositions, etc. However, humidity cells have been demonstrated to accurately assess the post-mine drainage quality, and have been shown to be more statistically accurate (Bradham and Caruccio, 1990). Additionally, the humidity cell can accommodate a smaller sample as well as smaller size fractions and, if the rock undergoes significant physical weathering during the testing phase, the fine-grained particles are retained.

RECOMMENDATIONS/GUIDELINES FOR SAMPLE PREPARATION

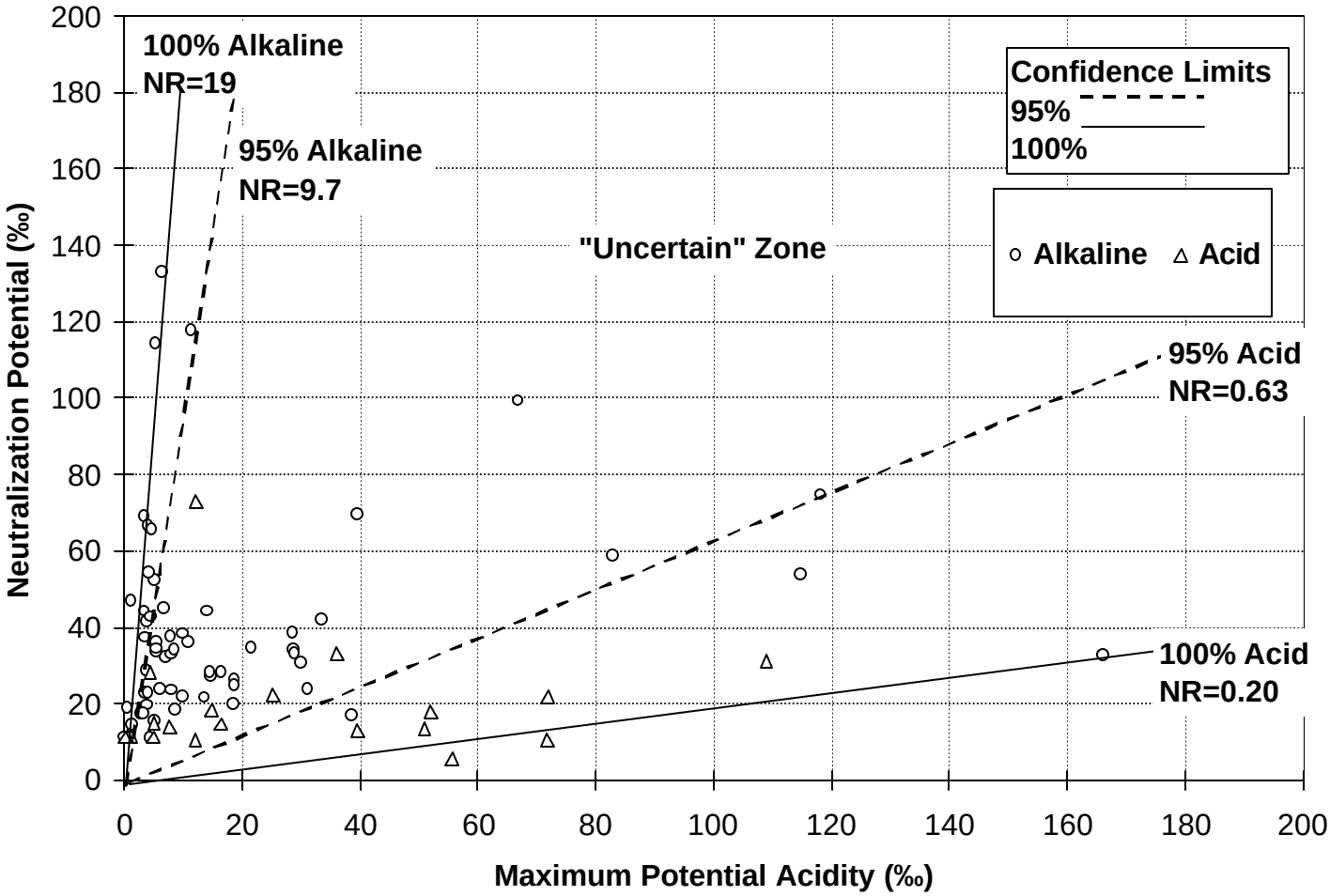
An accurate testing protocol requires both representative samples and appropriate sample preparation. Regardless of whether static and /or kinetic tests are used, the test results will be useless if the tested sample does not represent a statistically valid portion of the collected sample, which in turn is representative of the site. These issues are addressed below and in more detail in Chapters 6 and 7 of this document.

First, the sample collection and storage of samples prior to analysis should mimic conditions found in the field in order to maximize the preservation of the sample under approximate field conditions. 15°C). For samples collected from below the water table, precautions should be taken to minimize both the acid oxidation and carbonate dissolution reactions.

Equally important is that care must be taken to ensure that a statistically valid sample is apportioned from the collected sample and used in the analyses. The collected samples must be riffled to the appropriate size fractions and not merely split. This may necessitate several riffling series if the initial sample is large.

Mechanical rifflers are available and when used with the four-pan method, provide a statistically accurate sample. “Cone and quartering” manual methods may also be used. Once a representative sample of the appropriate size is prepared, the sample can be used in any of the test procedures discussed.

Figure 5.4: Neutralization Potential (NP) vs. Maximum Potential Acidity (MPA)



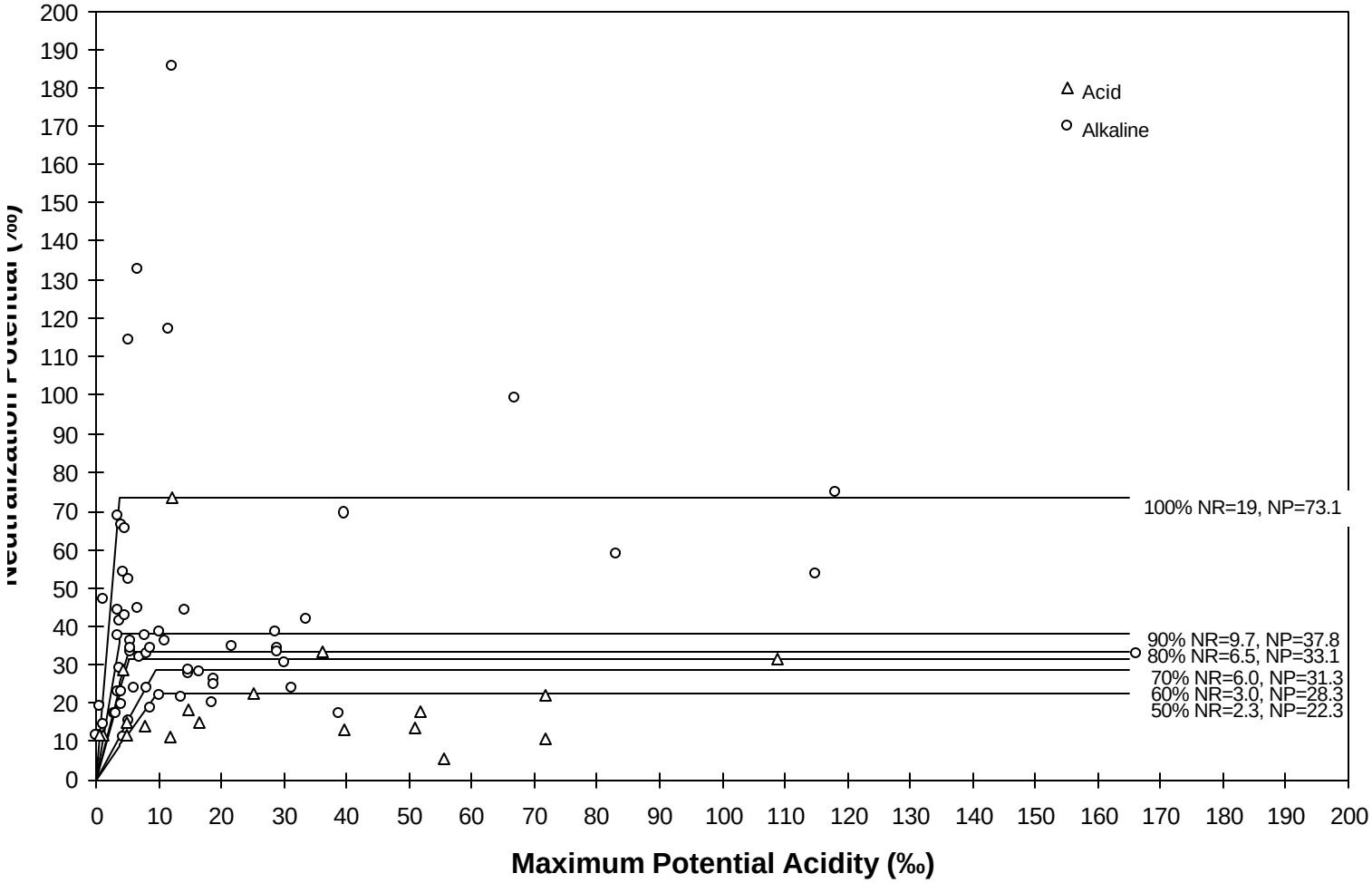
RECOMMENDATIONS FOR STANDARDIZATION OF LEACHING COLUMN TESTS

Column tests are characterized by the use of inert cylindrical columns into which rock samples are loaded and leachant is added and allowed to drain. The resultant leachate is collected and analyzed. The primary considerations and recommendations for column tests include:

Particle Size

The optimum size particle for normal or routine column tests for coal overburden samples is between 12.7 mm (1/2 inch) and 2mm (.08 in). This correlates with the lower limit of gravel (2 mm) and an upper limit for which the pore spaces are small enough to allow inter-grain surface tensional forces to be significant. In this range, the rate of water movement through the column provides for alkaline dissolution as well as the leaching of acidic reaction products. When column tests are being used to evaluate a smaller size fraction of material, such as some coal refuse, then the lower end particle size used in the column may be less than 2mm.

Figure 5.5: Combined Neutralization Ratio Criteria and Neutralization Potential Thresholds with Confidence Levels



Antecedent Storage Conditions

As noted above, samples should be stored as to mimic field conditions, usually under low oxygen conditions (airtight container should be purged with nitrogen if sample will not be immediately analyzed) and low temperatures (less than 15° C) that correlate with the average ground water temperature.

Interleach Storage Conditions

Temperature and humidity

Between the selected leaching intervals, the interleach storage conditions are important. Storing the samples at too high a temperature results in higher acid production rates and total acid loads and in some cases, results in otherwise alkaline producing samples becoming acidic. We recommend using ambient room temperature, between 20° and 25°C, for the samples between leaching intervals.

The humidity studies, while indicating that a lack of humidity (0% relative humidity and 105°C) is a major factor, also show that little difference in the resultant leachate quality occurs as long as some humidity is present. Only minor, if any, effect on the resultant water/leachate quality occurs regardless of whether the samples were stored under 100% humidity, purged intermittently with humid air or stored at normal/ambient humidity. However, given that ambient humidity levels could be very low in certain laboratories, it is recommended that the columns not be allowed to dry completely and if necessary, that the columns be purged with humidified air.

Degree of saturation

The hydrologic setting of the completed mine site should be considered in determining the appropriate column test procedure. Under most backfill conditions, the overburden and mine spoil will not be completely saturated, but will be affected by infiltrating rainwater and groundwater. Only a small fraction of the backfill will be inundated and therefore, during interleach storage, the column should be unsaturated. After the leachate is removed from the column at the end of the leaching cycle, water should not be introduced to submerge or saturate the sample until the subsequent leaching cycle begins.

Under certain conditions, such as mimicking of a submergence reclamation plan, submergence of the sample in the column may be appropriate. However, because of the significant impact on the leachate quality as a result of the submergence, this option should be limited to those occurrences when field conditions are truly reflected in the test conditions.

Size, Shape, and Structure of Apparatus

The relationship between the test apparatus and the dimensions of the rock samples being tested must be considered in order to prevent adverse interactions between the sample and the container, and therefore, is closely tied to particle size. Although it has been suggested that the column inside diameter should be at least four times the largest particle diameter to avoid undue wall effects, this represents a minimum diameter. Assuming the largest particle size is 12.7 mm (1/2 in.) then the minimum diameter column would be 51 mm (2 in). In order to avoid wall effects and to minimize channelization of the leachant in the column, it is recommended that the column diameter be between 76.2 mm (3 in) and 152.4 mm (6 in). Column height is recommended to be between 305mm (12 in) and 915 mm (36in). Larger columns could be used for special studies.

A cylindrical column is recommended to maximize the uniform distribution of particles within the column. A porous barrier incorporated at the base of the column retains the sample, but permits the leachant to drain and be collected. The top of the column should be covered to prevent extraneous particles from entering the column and to retain humidity. Although some airtight columns have been used when differing pore gas compositions have been tested, the atmospheric gas composition will simulate near surface mine conditions and conditions upon immediate closure of the backfill. Therefore, the column should not be airtight. Assuming the leachant to be added from the top, the top of the column should be fitted with a device to ensure that the leachant is uniformly distributed over the surface of the sample.

Volume of Sample and Placement within a Column

The volume of the sample used in column tests is related to the size of the column and is a function of representative sample considerations. To some extent, the amount of sample available for testing will be a determining factor in the dimensions of the column. The mass of rock chips and fines from a 5 5/8 in (14.3 cm) diameter air rotary drill hole is approximately 12 kg per foot of rock drilled and a continuous core sample would be slightly greater. However, several analyses are required from each foot (or if a uniform lithology, each 3 foot horizon) and the entire recovered volume of rock would not be available for column testing. However, the height of sample in the column should be at least twice the diameter of the column. For example, if the column is 76.2 mm (3 in), then the height of rock in the column should be contained in at least 152.4 mm (6 in) of the column or weigh roughly 1kg. The sample should be precisely weighed since an important aspect of the test is that each analysis relates weight of rock to volume of effluent to time. Also, the rock sample should be placed in the column, but not packed under pressure.

Leaching Interval

As noted above, the factors of interleach storage and leaching interval were the most significant factors influencing leachate quality and were responsible for the majority of variability present in the total range of contaminant production. Therefore, it is important to maintain a leaching interval that allows sufficient time for the time dependent chemical reactions to occur. Based on a number of studies, a leaching interval of 7 days is recommended.

The duration of the column test is also important. Testing should be conducted until the results are definitive and consistent. The time of testing can vary from 8 to 104 weeks. The shorter time periods represent samples which become acidic within the early leaching cycles. Samples that become acidic do not, under normal conditions, become alkaline with time. In many cases, a 12 week test will provide definitive and consistent results.

Influent Composition and Addition

Although a number of leachant compositions have been used, including simulated AMD, simulated acid rain and distilled or deionized water, the leachate characteristics of the water leached samples and simulated acid rain leached samples were not significantly different. Therefore, the recommended leachant is distilled/deionized water for normal conditions.

Studies have reported water being added from both the bottom of the column as well as the top. The primary difference between the two methods is the degree of flushing of the sample. Water introduced from the bottom and then allowed to drain represents a fluctuating water table condition, which has been shown to generate a slightly higher acid production potential than samples subjected to top additions or infiltrating rainwater/surface water simulations. Since most backfill configurations are dominated by surface wetting, the authors prefer the surface/top introduction of leachant. Care should be taken when using this approach to ensure that the distribution of leachant is uniform over the surface of the column.

Rock to Water Ratio

In addition to the leaching interval, the water volume also effects the resultant leachate quality. Since the chemical production rates are related to the weight of the sample per volume of leachate per time interval, it is important to hold these factors constant. Although in weathering/humidity cell tests the weight of sample to weight/volume of leachate varies, from 1:1 to about 3:1, column samples have been noted to have a greater ratio range from about 4:1 (wt of rock to wt of leachant) to 35:1. If a linear relationship is assumed to exist between these parameters, then laboratory results can be correlated with field results. Therefore, it is recommended that for sample sizes between 0.5 kg and 2.5 kg, that 250 ml of leachant be used, and that for samples sizes greater that 2.5 kg and up to 10kg, that 500 ml of leachant be used as influent in each leaching cycle.

Pore Gas Composition

The pore gas composition of the column test can be controlled to mimic placement in a portion of the backfill or refuse pile. However, a number of researchers have evaluated the pore gas composition within backfills. Although CO_2 levels may be elevated and O_2 levels may be somewhat depressed (at depth, variations from >18% to 2% O_2 have been observed), none of the O_2 levels observed would have a significant inhibitory effect on pyrite oxidation. In addition, since it has also been suggested that a significant portion of the total weathering takes place in the upper and most outward portions of the backfill, the ambient atmospheric gas composition is the preferred pore gas composition for column tests.

Bacterial Effects

The bacteria that are active in the pyrite oxidation reactions are indigenous to aqueous environments having pH values ranging from around pH 2 to 5, and *Thiobaccillus ferrooxidans* appears to be ubiquitous. However, due to the important role that these bacteria play in estimating the acid production potential, it is recommended that column samples tested for the presence of bacteria prior to leaching or be inoculated at the initiation of the testing to ensure a healthy population. While leaching samples with synthetic or simulated AMD has shown that the acid production rates are increased, the inoculation of the sample with 1 ml of either cultured bacteria or fresh AMD should provide a viable bacteria population while having little impact on the leachant quality.

Pyrite Morphology and Texture

While pyrite morphology has a significant impact on the acid production potential of a sample, this variable cannot be controlled within the column test. Discerning the pyrite morphology of a particular sample by reflected light microscopy or other technique will, however, provide a tool to explain variations in sample response and characterization.

Carbonate

Similarly, the carbonate content of a rock unit plays a significant role in determining not only the acid production potential, but also whether column or other kinetic tests are necessary to adequately evaluate

the sample's anticipated leachate quality. The carbonate content of the individual sample is fixed, however, with the acceptance of alkaline additions into the mine reclamation plan, it has been suggested that the effect of alkaline additions on mine drainage quality can be evaluated through kinetic testing. The primary difficulty with this approach is the scaling factor. The addition of 100 tons per acre of limestone or even 1000 tons/acre is significant on a mine scale, but when extrapolating to a column, it presents numerous difficulties. Therefore, it is suggested that the limestone to be used on the site be subjected to individual kinetic testing to determine the rate of alkaline production. The rate of alkalinity production will also be effected by the pCO_2 of the backfill. Alkaline additions applied near the surface of the backfill will produce alkalinity levels on the order of up to 75 mg/l while alkaline additions within portions of the backfill exhibiting higher pCO_2 will provide greater alkalinity. The rate of alkalinity production can be translated to field applications.

Data Presentation

Data are entered on spreadsheets and typically include the following: sample weight, date, number of days, leachate volume, pH, specific conductance (or normalized specific conductance (uS/g)), alkalinity (including sample volume, titrant normality, titrant volume, alkalinity in mg as $CaCO_3$), acidity, and any other cation or anion analyses. Data are then presented graphically as either cumulative ion versus time (if acidity and alkalinity are presented, the net value is graphed as mg of acidity as $CaCO_3$/g of sample/time) (Figure 5.6) or as the net daily value versus time. In Figure 5.6, 2 of the samples are net alkaline and one sample is a low acid producer.

RECOMMENDATIONS FOR STANDARDIZATION OF HUMIDITY OR WEATHERING CELL TESTS

Generally, humidity or weathering cells are constructed of inert chambers which are connected by tubing to a reservoir from which air is pumped into the cell. The sample may be purged with humid air or alternately purged with humid and ambient air. By these leaching tests, kinetic data are derived from empirical results by subjecting the overburden samples to simulated weathering conditions that, in theory, mimic natural conditions. The rates of pyrite oxidation and the release of weathering products can then be measured quantitatively to determine whether a sample will produce acidity, and then predict acid loads.

Particle Size

The recommended particle size for normal or routine humidity cell tests for coal overburden is between 6.3 mm (1/4 in) and 1 mm (0.04 in). This size fraction includes the particles that can be readily oxidized, yet the effect and concerns associated with the fine fraction are minimized.

Antecedent Storage Conditions

Samples should be stored in such as manner as to duplicate field geochemical conditions. Care should be taken to minimize oxidation of the sample. This would include storage under low oxygen conditions in an airtight container and, if the sample is to be stored for an extended period of time, the sample should be purged with nitrogen. Samples should also be stored at a low temperature.

Interleach Storage Condition

After the sample has been leached and before it is leached again (the interleach period), storage conditions are important. The recommended temperature for the samples between leaching intervals is ambient room temperature (20°-25°C). However, the temperature should be held constant.

Humidity studies indicate that there is little difference in the resultant leachate quality regardless of whether the samples are stored under 100% humidity, purged with humid air or stored at normal/ambient humidity. However, given that ambient humidity levels could be very low in certain laboratories, it is recommended that the humidity cells be purged with humidified air to prevent the samples from complete drying. Under humid conditions, pyrite oxidation reactions will continue and alkaline dissolution in the water entrained in the pore spaces will attain equilibrium.

Size, Shape and Structure of Apparatus

A number of sizes and configurations of humidity cells have been used. In most cases, the cells are used as part of the procedure to hold the sample under constant environmental conditions (i.e. temperature, humidity, and gas composition), while the sample is being analyzed. Humidity cells in many ways are similar to leaching columns; however, due to their construction, the humidity rates can be better controlled. The primary differences are: the humidity cell usually contains a smaller sample size, water usually drains through the column while it may be extracted, decanted or drained from a humidity cell, and the length of time that the water is in contact with the sample is usually more defined in a weathering cell.

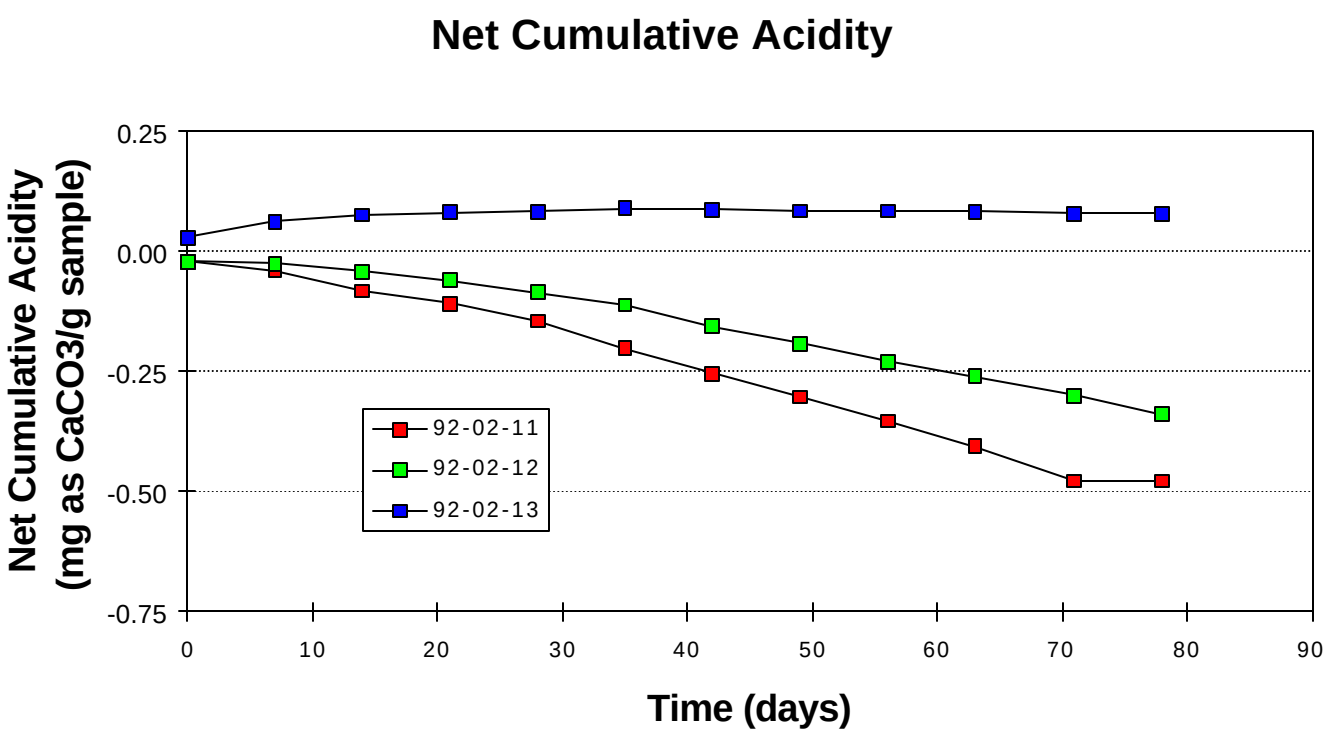


Figure 5.6. Net cumulative acidity data from leaching tests for three overburden samples.

In constructing a humidity cell, the shape of the container generally makes little difference. The cell may be rectangular (as large as 10 cm (4") by 15cm (6") by 20cm (8"), or as small as 8cm (3") by 10cm (4") by 15cm (6")) or cylindrical (approximately 20 cm (8") in diameter by 8 to 10 cm (3-4")). These ranges in container sizes have been used by a variety of labs, all giving good results. The diameter of the container, however, should exceed the height.

To maintain humid conditions, the container should be connected by tubing to a reservoir in which air is bubbled through water. The resulting humid air is pumped into the cell and creates an environment conducive to pyrite oxidation. When a series of cells are connected to a common reservoir, tubing length should be similar to hold the airflow to each cell constant. The samples are leached periodically (typically weekly) by adding the leachant (usually distilled/deionized water) to the cell. The leachate can be drained, decanted or extracted. It is recommended that the cell have a discharge tube near the bottom, which is fitted with a filter, through which the water is drained.

Volume or Weight of Rock

Based on the literature, the weight of the rock sample place in the chamber should be between 100 and 500g, precisely weighed. A maximum sample weight of 300 g is recommended, however, to ensure that the sample is thoroughly wetted and inundated during the leaching process, and that the weathering products are entrained in the leachate.

Leaching Interval, Influent Composition and Rock to Water Ratio

A leaching interval (the length of time overburden samples were stored between leachings) of seven days is recommended. Bradham and Caruccio (1995) found that the leaching interval was responsible for between 14 and 100% of acid production variability, so it is important to hold this factor constant.

A related factor is the length of time the test should be continued. The leaching cycles should be continued until the samples exhibit stable results, which may occur as quickly as 8 weeks or be as prolonged as 104 weeks. However, most samples become stable between 12 and 20 weeks and therefore, a minimum of 12 weeks is recommended, with the understanding that tests must go longer if the sample analyses have not attained a consistent weekly composition.

In addition to the leaching interval, the volume of leachant also affects the resultant leachate quality. In as much as the chemical production rates are normally related to the weight of the sample per volume of leachate per time interval, it is important to hold these factors constant. Reported variations in the weight of sample to weight/volume of leachate varies for weathering/humidity cell tests from 1:1 to about 3:1. If a linear relationship in the chemical character of the leachate is assumed to exist between sample weight and leachant volume, then laboratory results can be correlated with field results. Therefore, it is recommended that a uniform leachant volume be added to each cell; we have found that a leachant volume of 100 ml works well. Also, while several influent compositions have been researched, for standard humidity cell tests, it is recommended that distilled-deionized water be used as the leachant.

Pore Gas Composition

For standard humidity cell analyses, the pore gas composition should be atmospheric. Even though gas levels may vary in the completed backfill, atmospheric conditions will prevail at the surface where a significant amount of the weathering occurs.

Other Effects

Due to the important role that iron-oxidizing bacteria play in estimating the acid production potential, it is recommended that humidity cell samples be tested prior to testing to determine whether a viable bacteria population exists. If not, then the sample should be inoculated at the initiation of the testing to ensure a healthy population. To avoid increasing acid production rates, as was shown to occur with some samples using simulated AMD, it is suggested that only 1 ml of either cultured *Thiobacillus ferrooxidans* bacteria or fresh AMD be used to provide a viable bacteria population without having a significant impact on the leachant. Pyrite morphology and carbonate content of the sample similarly play an important role in weathering cells, as discussed in the leaching column section.

Data Presentation

The data are presented in a manner similar to the column leaching tests shown in Fig. 5.6. Figure 5.7 presents data on a daily, rather than a cumulative basis. While Net Acidity is presented in both 5.6 and 5.7, other parameters, such as sulfate and metals, can also be presented in a similar manner. Note the variations in the kinetic behavior of the samples. Three increase in acidity during the first three leaching cycles and then show decreasing acid loads while the other two simply decrease over time.

Data Interpretation

Few field calibration studies and screening criteria for kinetic tests are published. This stems from the application of kinetic tests on a case by case basis, rather than on a broad scale. Figure 5.6 shows an example of a plot of net cumulative acidity (as mg of acidity/gm of sample) in which two of the samples were alkaline and one exhibited low acidity. Either daily or cumulative data can be plotted and the interpretation is related to the differing slopes of the lines. With cumulative data, the chemical weathering attributes are usually defined by one of three trends. Figure 5.6 is an example of relatively straight slopes indicating that the acid and alkaline production potentials vary little with time and that few weathering products had accumulated in the sample prior to leaching. This is common for all alkaline samples.

A second common trend is a steep acid slope for 3 to 6 weeks and then a gently increasing slope for the remainder of the test. This suggests that acidic weathering products had accumulated during the sample collection and processing stage and that the second slope is more indicative of the expected field conditions. In some cases, depending on the nature of the rock, the decreasing slope could indicate a decline in the rate of acid production. However, a very steep slope also indicates that this particular sample will weather quickly when exposed during the mining operation. This may be related to the physical attributes of the sample and suggests that reclamation efforts must deal quickly with this rock type.

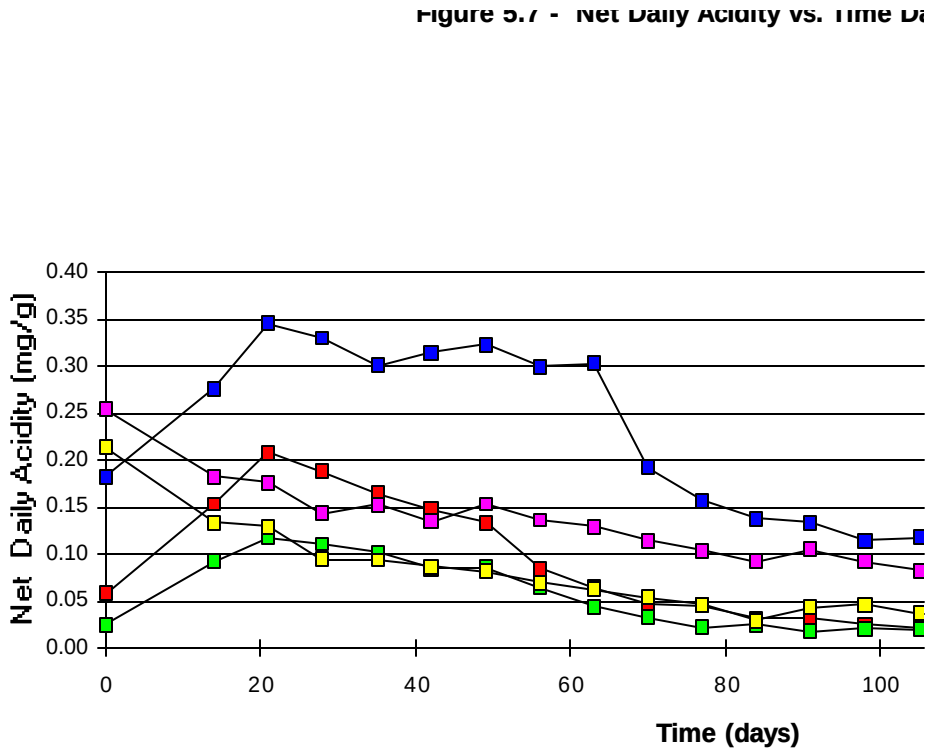


Figure 5.7. Net daily acidity vs. time for five samples, plotted on a daily basis.

The third major trend, which is seen in acid samples, is the inverse of the second trend. The sample may exhibit low acidity or sulfate values initially and after several weeks, begin to produce significant acidity. These samples are normally high acid producers. The slow initiation of acid formation could be due to a number of factors, such as carbonate suppression or carbonate neutralization. These include rock types that initially exhibit no problem, but if reclamation is delayed for any reason, the rocks begin to produce acidity.

Because the data are calculated on a weight per weight per time basis, samples can be compared and evaluated. Furthermore, the slopes of the lines can be statistically evaluated to compare multiple samples and rock types.

RECOMMENDATIONS FOR STANDARDIZATION OF FIELD SCALE TESTS

Field tests can be divided into three basic types, all of which mimic column tests: 1) small tubs or barrels, 2) constructed tubs, tanks or cribs, and 3) piles. In small tub or barrel studies, the rock samples are weighed and placed in small tubs on the order of 1m (3') by 0.7m (2') by 0.5m (1.5') or in barrels. The units are then allowed to weather under natural rainfall conditions, and the effluent or leachate is collected after each rainfall event. Alternatively, these tests have been subjected to simulated rainfall conditions in which deionized-distilled water was showered over the sample on a weekly interval to augment natural rainfall. Rainfall is an important element of any field test; in areas where rainfall is minimal or when drought conditions occur, the interval between leachings may be significant.

In constructed tubs, tanks or piles, usually large, weighed sample volumes are used and the weathering cycle is dependent on natural rainfall events. Often these tests have been used to evaluate specific field or reclamation techniques that could not be represented adequately in laboratory sized experiments.

Constructed tubs vary in size, but generally have been on the order of 1.3m (4') x 2.6m (8') x 1.3m (4') to 1.3m (4') x 2.6m (8') x 4m (12'). The wooden tubs are lined with plastic and an outflow/discharge pipe is incorporated into the base. The leachate is diverted to a collection device. Large tanks have also been used. Rainfall must be monitored as well as volume of leachate collected.

For even larger field scale tests, rocks can be piled on top of contoured plastic liners into which a network of collection pipes is incorporated. The piles can be constructed in several configurations, although the most common one is a relatively shallow pile (1-1.5m (3-5') thick) and approximately 6m (20') square. Similarly, the leachate is collected following each rainfall event and analyzed. Depending on the rainfall frequency and intensity, the length of time that field scale tests must be run is difficult to determine in advance; however, a minimum of one year, to evaluate the seasonal variations, is warranted in most situations.

As noted above, laboratory kinetic tests, including columns, humidity cells or soxhlets, derive empirical results by subjecting the overburden samples to simulated weathering conditions which, in theory, mimic natural conditions. In essence, due to the smaller grain sizes and the periodicity of the leaching events, they represent accelerated weathering conditions. The results of laboratory tests have been extrapolated to field scale tests; however, the length of time necessary for field scale tests (unless artificial rainfall rates are used) is usually much longer than in the laboratory and environmental conditions cannot be held constant. Therefore, for standard practices, field scale tests are generally not recommended, however, they can be useful when used in comparison with lab tests.

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