Chapter 10. Summary, Conclusions and Applications

Roger J. Hornberger, Eric F Perry, Keith B. C. Brady, Joan E. Cuddeback

The original objectives of this project were: (1) standardizing humidity cell and leaching column procedures, (2) improving the test methods by (a) maintaining a carbon dioxide-enriched environment to optimize carbonate mineral dissolution, and (b) quantifying particle size variables to evaluate reaction kinetics, and (3) providing flexibility in test method implementation consistent with EPA guidelines for Performance-Based Measurement Systems (PBMS). These objectives have all been met as described in this report and in the test method document for EPA Method 1627: Kinetic Test Procedure for the Prediction of Mine Drainage Quality.

As these kinetic test methods were developed under the auspices of the Acid Drainage Technology Initiative (ADTI), the humidity cell procedure was named ADTI-WP1 (for weathering procedure 1) and the leaching column procedure was named ADTI-WP2. Consistent with EPA guidelines for PBMS, flexibility was provided in the construction of the weathering apparatus to allow the use of readily available low-cost materials. The leaching columns were constructed from clear plastic pipe and the humidity cells were constructed from rectangular plastic freezer containers.

Method 1627 was developed and validated in two multiple laboratory studies (2002 and 2003) and one interlaboratory study (2006) involving laboratories from the Federal, commercial, mining industry and academic sectors. In the 2002 weathering study, the performance of the leaching columns was found to be superior to the humidity cells, and the humidity cells were constructed from the rectangular plastic containers. In the 2003 weathering study, the humidity cells were constructed from the same diameter plastic pipe as the leaching columns, but the saturation and humidified-air drying cycles were different for the humidity cells and leaching columns. In the full interlaboratory weathering study involving eight laboratories in 2006, only the ADTI-WP2 Leaching Column Method was employed. Therefore, standard procedures have been developed for the humidity cell and leaching column test methods, but only the ADTI-WP2 leaching column method has undergone the rigors of the interlaboratory study and posting on the EPA website as a final draft standard test method.

The objective of maintaining a carbon dioxide-enriched environment was met, but achieving a relatively constant 10 percent CO_2 gas mixture was found to be the most difficult procedure to control. Flexibility in method implementation was allowed by specifying three different methods of achieving the 10 percent target mixture: a single tank of an industrial grade gas mixture of 10% CO_2, 10% oxygen and 80% nitrogen; a tank of CO_2 and a tank of compressed air with regulators to control the mixture; and a tank of CO_2 mixed with “house air” used in the laboratory. In the 2006 interlaboratory study, the use of rotometers to control gas flow and a portable CO_2 meter to monitor consistency improved the control of the 10% CO_2 target mixture.

The objective of quantifying particle size variables was achieved by performing a particle size distribution of the rock sample using six sieves and standardizing the percent of total weights of the various particle size classes (see Table 3.3) through a reconstructed particle size distribution, prior to the start of the weathering test. This procedure was performed for a geochemical reason

and an operational reason. The initial particle size distribution is an artifact of the rock crushing process; it is not a natural particle size distribution. Two laboratories crushing the rock sample with two different pieces of crushing equipment would produce two different particle size distributions, as would two different rock types (e.g. sandstone, shale, limestone). By reconstructing to the standard particle size distribution, all rock samples have the same starting point, regardless of rock type or crushing equipment. This procedure is important for evaluating weathering rates of the various rock samples. The operational reason for using the standard reconstructed particle size distribution is that if there are too many fines (i.e. -60 mesh) in the leaching column, it causes clogging which impedes water flow and air flow through the leaching column. The standard particle size distribution was readjusted in the 2006 weathering study, by reducing the -60 mesh fraction from 10% to 5% of the total sample weight in order to prevent clogging.

Key Findings and Principles from Previous Chapters

The major difference between static and kinetic tests is that static tests provide measurements of the amount of selected chemical constituents in the rock sample (e.g. total sulfur, neutralization potential), while kinetic tests provide measurements of the amount of selected chemical constituents that come out of the rock samples in leachate (e.g. acidity and iron concentrations) under specified conditions. If the physical, chemical and biological conditions of the kinetic tests are representative of those found in the mine environment, the concentrations of the water quality parameters in the leachate may be used to predict or estimate the concentrations of these parameters that would be produced by the proposed mining operation.

The pore gas composition within the kinetic test apparatus should be similar to that within reclaimed surface mine spoil, particularly to have a partial pressure of carbon dioxide sufficient to facilitate the dissolution of carbonate minerals. The results of these preliminary tests in 2002 indicated that the introduction of 10% CO_2 does significantly increase alkalinity production. For the shale leaching columns described in Chapter 2, the alkalinity concentrations were approximately three times greater in the columns with the additional CO_2 than the air-only columns (Figure 2.2a). In the sandstone leaching column results the alkalinities are approximately three times greater with CO_2 addition, similar to that found with the shale columns. The humidity cells produced consistently lower conductivity values than the leaching columns, indicating lower total dissolved ionic species (i.e. total dissolved solids) and less aggressive weathering on these shale samples.

The bacteria *Thiobacillus ferroxidans* catalyzes the formation of acid mine drainage (AMD) (Singer and Stumm, 1970 and Kleinmann et al., 1981). The most probable number (MPN) for iron-oxidizing bacterial (including *Thiobacillus*) was determined by the methods of Alexander (1982) and Greenberg et al., (1992). These results demonstrate that these iron-oxidizing bacteria populations are suppressed under alkaline conditions, but can be superabundant under acidic conditions. The results also show that the humidity cells and leaching columns do not have to be inoculated with the bacteria to catalyze acid producing reactions, particularly in high sulfur samples.

The results of the 2003 phase of weathering tests in Chapter 3 indicate that the leaching columns are superior to the humidity cells in rock weathering performance, and the 2 inch diameter

columns used in this second phase performed as well as the 6 inch diameter columns used in the first phase (2002) of weathering tests. The results also show that the continuous flow of CO_2-enhanced air was a superior gas handling method in comparison to the exposure of influent water saturated with CO_2-enhanced air. The standardized particle size distribution appears to be an improvement in the performance and the data interpretation of the method. The removal of fine (<35 mesh) particle components affected sulfate concentrations, but had essentially no effect upon alkalinity concentrations. The coal refuse sample exhibited the greatest change in effective surface area.

Chapter 4 presents the results of an interlaboratory study designed to further evaluate the draft leaching column method across multiple laboratories, each evaluating the method procedures in replicate samples. To evaluate method performance in multiple laboratories, and to ensure the generation of at least six useable datasets, the 2006 study involved eight participating laboratories implementing method procedures in 9 columns over a 15-week period and analyzing weekly column leachate samples for conductivity, pH, alkalinity, and net acidity. Each of seven laboratories also shipped a filtered sample aliquot from each of its 9 weekly leachate samples (one from each column) to a metals laboratory for measurement of dissolved metals and sulfate.

Results of this interlaboratory study are consistent with both ASTM and U.S. EPA guidelines, using at least six datasets generated by laboratories representing the community of potential users of the method. Results of the study represent the variability and accuracy that would be expected across laboratories and support the method's use as a standard method for predicting mine drainage, particularly in samples representing gray zone areas that would be expected to need additional evaluation by the method.

Chapter 5 includes bulk rock chemical data and detailed mineralogical and textural data for unweathered starting materials used in the interlaboratory validation study, and for two samples used in the early phases of leaching column tests (Wadesville Sandstone, Leechburg Coal Refuse). Leach test starting materials were characterized by a number of methods, including whole-rock chemistry, optical microscopy, powder x-ray diffraction (XRD), scanning electron microscopy (SEM), and electron probe microanalysis (EPMA). Microscopy and XRD were used to identify the types of minerals present in each lithology and to estimate their relative abundances. Microbeam techniques (SEM and EPMA) were used to identify fine-grained minerals and determine mineral composition.

The rock characterization study demonstrates the chemical variability of the starting materials and the mineralogical source of leaching analytes. Differences in mineralogy among the five lithologies tested are reflected in leach column effluents. Some target analytes are present in several minerals that have different weathering characteristics; others are largely confined to a few mineral groups. Based on the data presented in this chapter, the main sources for the target analytes are as follows:

- Aluminum: Micas (muscovite, biotite, phengite), clay (illite, kaolin), chlorite, feldspar
- Calcium: Calcite, ankerite, apatite
- Iron: Pyrite, ankerite, siderite, micas, chlorite
- Manganese: Ankerite, calcite, siderite, pyrite, chlorite, biotite

- Potassium: Micas, feldspar
- Magnesium: Ankerite, chlorite, micas
- Selenium: Pyrite, organic material (?)
- Zinc: Sphalerite
- Sulfur (sulfate): Pyrite, gypsum, barite

Surface areas were measured on the starting material sieve fractions and at the completion of the testing; the resultant rock was again sieved and remeasured. The bulk surface areas for each column could be determined for the post-leaching rock by taking the individual masses of the sieve fractions specified in the protocol, multiplying each mass by the surface area (SA), and combining their fractional percent of the total as a weighted linear average as shown in Chapter 6.

Shales are mixtures of quartz, feldspars, clays and chlorite plus or minus calcite or dolomite and minor amounts of accessory minerals. They are fine grained with a large, but variable, volume fraction of its constituents made up of phyllosilicates, all of which contribute to a measured BET surface area that is about a factor of 3 to 10 times larger than limestone or sandstone.

Underlying the practical leach test is the basic physical chemistry of the dissolution process. The dissolution of mineral matter involves the transfer of chemical elements from the solid surface to the surrounding fluid. The rate at which the transfer process occurs depends on the surface area exposed to the solution, on the rates of chemical reactions on the mineral surface, on transfer rates across the static boundary layer of fluid on the mineral surface, and on any diffusion barriers that build up on the surface during the course of reaction. Reaction rates are usually sensitive to the effects of other ions in solution which can act as either catalysts or inhibitors. All of these are potentially important when measuring reaction kinetics in such heterogeneous materials as crushed rock or coal waste samples.

The first step in evaluating the leaching column data, especially for rock samples in the ‘gray zone”, should be to examine the acidity and alkalinity data, and related mine drainage indicator parameters of pH, conductivity and sulfates. These data should be compared to the acid-base accounting data for these rock samples. The primary goal of the leaching test is to determine or predict whether the mine drainage is likely to be acidic or alkaline, and to what degree. The secondary goal is to determine whether the metals concentration data are indicative of the weathering of these rock samples in the mine environment and the resultant metals concentrations in mine drainage discharges. The plots of accumulated release give the best indication of the overall kinetics of the column leaching experiments.

Sulfur is the primary element responsible for the generation of acidity so accordingly, sulfur extraction in the leaching columns was examined in somewhat more detail in Chapter 7, as was carbonate mineral dissolution. By far the most common and most soluble minerals containing calcium and magnesium on mine sites are calcite, dolomite and ankerite. Calcium is almost exclusively present in carbonate minerals. Although there are other sources of magnesium, the carbonates are by far the most soluble sources of magnesium found in overburden rocks.

Whether a sample through time will produce acidic or alkaline water is a function of the relative weathering rates of the carbonates and pyrite. If the carbonates exhaust first, the sample will

probably become acidic. If the pyrite is exhausted first, the sample will remain alkaline. In order to determine which will win the race (remain the longest) the pyrite oxidation rate will also need to be determined. The same approach that was used for determining carbonate dissolution rates in Chapter 7 is used to determine pyrite oxidation rates and the amount of sulfur weathered each week. This is then compared to the mass of sulfur in the rock.

The data for the major cations, calcium, magnesium and potassium plot on very smooth curves that give excellent power function fits with values of the statistical goodness of fit parameter, R^2, in the range of 0.94 to 0.99. If the leaching process were purely diffusion controlled, the exponent, n, should be 0.500. The fitted values scatter around the ideal value with the rather wide range of 0.3 to 0.7. It is probably reasonable to conclude that the release of these elements from the columns is a diffusion-controlled process. Because of dissolution kinetics of calcite, dolomite, and gypsum – the main calcium and magnesium-bearing minerals, are not diffusion controlled when measured on single phases, it can be further concluded that the movement of these ions through the mass of generally inert material in the columns is the source of the diffusion barrier.

Concerning the leaching behavior of elements, the test successfully distinguished weathering characteristics of the five rocks on concentration, flux and leachate composition bases as described in Chapter 8. Solid rock chemistry and mineralogy, mineral solubility, gas pressure, pyrite and carbonate content all combined to influence the rate and intensity of chemical weathering and leachate chemistry. Calcium, magnesium, sodium, potassium, sulfate and alkalinity were typically present as macro constituents (mg/L range) in all samples. Selenium and zinc are present in trace amounts in the rocks, and were usually as micro constituents (ug/L to a few mg/L) in leachates.

Elemental concentrations declined substantially from week 1 to week 14. Calcium and magnesium concentrations at week 14 were 22 to 71% lower than initial values for 4 samples and sulfate values were 60 to 88% lower. Alkalinity data (in Figure 8-1) reflect both carbonate content and mineralogy, and the high partial pressure of CO_2 used in the columns. Each rock produced significant alkalinity, and two rocks generated water with more than 400 mg/L. These data show that the test produced a weathering environment similar to that found in a spoil pile or underground mine.

The lack of significant concentrations of iron and aluminum in most leachates should not be interpreted as lack of weathering of iron and aluminum bearing minerals. Significant weathering did take place within the columns, as described in the Chapter 5 comparisons of pre- and post-leaching mineralogical observations. Iron and aluminum were largely removed from solution by the formation of new secondary minerals in four samples, rather than being leached from the columns.

Chemical flux or load varied among the rocks, both on an absolute basis, and as relative fraction of the total elemental content. HCS-IN leached chemicals most aggressively, while the blank MKSS-PA and KBF-WV were the least reactive rocks. HCS-IN leached the most element fractions overall, while KBF-WV and MKSS-PA leached the least. As described in Chapter 5,

these rocks both contain more quartz and other less reactive minerals than the other three samples.

Several conclusions on leaching behavior of the rock samples were expressed in Chapter 8. Calcium and magnesium were the dominant cations, while sulfate and bicarbonate were the principal anions. Weathering intensity paralleled sulfur content. High sulfur rocks weathered most aggressively, while low sulfur rocks leached the least.

Time dependent concentration trends were approximated by a natural log decay function for most elements. Alkalinity decay was slower than sulfate for most rocks, suggesting it will persist over acid generation in those samples. Time dependent fluxes were well described by power function or natural log regression models.

The strengths and weaknesses of Acid-Base Accounting (ABA) data for the rock samples used in the interlaboratory validation study were evaluated in Chapter 9. The two biggest problems found in the use of the original ABA test methods specified in Sobek et al., (1978) and other publications are with the NP test, including: a potential siderite interference problem and, accuracy and precision problems in NP test results related to the subjectivity of the fizz rating step in the NP test procedure. Both of these problems were addressed and essentially resolved in a revised NP test method published by Skousen et al., (1997).

The fizz rating problems described in Skousen et al., (1997, 2000) above are very relevant to the NP data from the rock sample splits used by the eight participating labs in the present ADTI-WP2 interlaboratory study. The difficulties noted with obtaining reproducible NP analysis are serious enough to affect the reliability of mine drainage quality prediction.

Methods of Interpreting the Leaching Column Data

There are three general approaches or methods of interpretation of the leaching column results. These data analysis procedures are not entirely separate and distinct; rather they are on a continuum of increasing complexity.

The most basic method of data evaluation is to look at the concentration data from the weekly leaching episodes (e.g. acidity, alkalinity, iron, sulfate, etc.) and construct simple plots of the data variations through time. Masters of statistical analyses such as Dr. John C. Griffiths and Dr. John Tukey state that the first steps in data analysis should be to get a feel for the data or to conduct exploratory data analysis before proceeding to more sophisticated methods of data analyses (see Griffiths, 1967, 2000 and Tukey, 1977). Griffiths, in particular, suggests the simple time plots as a first step in the data analysis algorithm described in Griffiths et al., (2000).

At numerous places throughout this report statements were made of how concentrations in the leachate data are similar to concentrations of specific water quality parameters in the mine environment. These observations are simple, yet valuable uses of the leaching column data. These observations are also testimonials to the validity of the ADTI-WP2 method, if the range in leachate data concentrations are directly comparable to the range of concentrations of water quality parameters in ground water or mine water (i.e. they are realistic comparisons without transforming the leachate data).

In addition to the simple time plots, there are other univariate data analysis procedures that may be used, such as the histograms shown in Chapters 2, 3 and 4. In essence, these simple methods of evaluating the leaching column data are meaningful and realistic.

The second approach or level of leachate data analysis involves the evaluation of loads or fluxes and the use of graphical methods of classifying the data. Caruccio and associates typically plot cumulative acidity or alkalinity expressed in milligrams per gram or kilogram of sample (e.g. Caruccio and Geidel, 1983; Caruccio and Bradham, 1995 and Geidel et al., 2000). In Chapter 8 of this report fluxes were discussed extensively and numerous cumulative leaching plots are included. Chapter 8 also included a Durov plot based on dominant cations and anions expressed in percentage milliequivalents. Other types of plots of leachate composition include Stiff or Pieper diagrams. This second level of data evaluation involves a deeper understanding of weathering characteristics or leaching behavior of the rock samples, without the use of sophisticated geochemical models. However, bivariate statistical and graphical analyses may be employed.

The third approach or level of leachate data analysis involves the evaluation of weathering rates, saturation indices, the use of geochemical equilibrium computer models such as PHREEQCI (Parkhurst and Appelo, 1999) and the fitting of power functions to the data. Examples of this approach with the ADTI-WP2 data are included in Chapters 7 and 8 of this report, and in Brady et al., (2004) and Perry et al., (2008). The use of surface area data and surface area to volume ratios (SA/V) is also included in this domain of evaluating weathering rates as shown with ADTI-WP2 leaching column data, in Brady et al., (2004), Hornberger et al., (2005) and Chapters 6 and 7 of this report. There is almost no limit to the level of detail that may be pursued under the auspices of this third level of leachate data analysis. For example, multivariate statistical analyses of mine drainage data are contained in Cravotta (2008 a) and Hornberger (1985). This third level of data evaluation is typically used for research purposes, rather than regulatory agency functions such as permit reviews.

Applications of the ADTI-WP2 Leaching Column Method

There are primary and secondary applications or uses of the ADTI-WP2 Leaching Column Method. The method can be used as a stand alone mine drainage prediction tool; it typically will be used in concert with other prediction tests, such as Acid Base Accounting.

The primary use of the method is in the preparation and review of new surface mine permit applications, particularly where specific rock samples or the overburden analysis of an entire mine site falls into the “gray area” or “uncertain zone” described in previous chapters of this report. The Federal regulations of the Office of Surface Mining Reclamation and Enforcement found at 30 CFR Part 7--- require that a determination be made of the Probable Hydrologic Consequences (PHC) of a proposed surface mine, as well as the development of a Cumulative Hydrologic Impact Assessment (CHIA). The overburden analysis data is a major component of the PHC and CHIA. The Federal regulations of the Environmental Protection Agency found at 40 CFR Part 434 pertain to the effluent limitations for point-source discharges from a new surface mine or a remining operation. Again the overburden analysis data is a key component in predicting whether there is the potential for pollution in a post-mining discharge at a new mine

site, or determining which overburden strata are causing the acid mine drainage at remining sites. Many state regulatory agencies, such as the Pennsylvania Department of Environmental Protection, are delegated the authority to review and write surface mining permits under the Surface Mining Conservation and Reclamation Act (SMCRA), and to review and write NPDES permits under the Federal Clean Water Act (CWA). The state and federal permit reviewers will be primary users of the ADTI-WP2 Leaching Column Method, as will the geologists and engineers who prepare the permit applications for the coal mining industry. Most importantly, the laboratories that implement the detailed steps of the method will be primary users of EPA Method 1627.

The secondary users or applications of the standardized leaching column method (i.e. ADTI-WP2 or EPA Method 1627) are researchers in the field of geochemistry, hydrogeology and mine drainage chemistry. Researchers in this field in the United States and internationally have used leaching columns for many years (e.g. Braley, 1949), but is has been difficult to compare the results of these studies to each other due to the lack of a standard method that incorporates provisions for the partial pressure of CO_2 within the column, and the particle size distribution of the material being subjected to weathering. It is the hope of the Principal Investigators of this method development project that other researchers will find the method to be useful and practical.

In most applications of the ADTI-WP2 Leaching Column Method, it will be used on selected rock samples, after Acid-Base Accounting has been performed on all of the rock samples from a drill hole. In fact, Section 8.1.2 of EPA Method 1627 concerning sample characterization states "Prior to method implementation, samples should be analyzed for neutralization potential (NP) and percent total sulfur... If the overall change in particle size, NP, percent sulfur, or other parameters will be determined, these analyses also may be performed on the sample after the last leachate sample has been collected and the sample is removed from the column."

Acid-Base Accounting is much less expensive than the ADTI-WP2 Leaching Column Method, and ABA is the most common overburden analysis tool. The most economical use of EPA Method 1627 would be to review all of the ABA data from a series of overburden analysis drill holes and determine which stratigraphic intervals are uncertain and in need of further analysis. These selected samples should then be subjected to weathering with the ADTI-WP2 Leaching Column Method.

There are numerous tools in the mine drainage prediction tool box as described by Kania (1998) and Perry (2002). No one tool will answer all the questions or solve all of the problems of the prediction of mine drainage quality or the remediation of acid mine drainage. Static tests such as ABA are useful prediction tools as described in Skousen et al., (2000), but they have limitations. For example, the NP test is a surrogate measure of potential alkalinity of a rock, not a true measure of the alkalinity concentration that will be produced in the mine environment. If there is a need to determine whether the carbonate minerals will outlast the acid-producing sulfide minerals, or whether iron, manganese and aluminum concentrations in mine drainage are likely to be relatively high, a kinetic test is needed and numerous kinetic test methods have been used in the past 5 or 6 decades. However, there has been a lack of standardization and continuity, regardless of how complicated the kinetic test methods have been.

The objectives of this ADTI-WP2 Leaching Column Method, (also known as EPA Method 1627) development project are stated in the first paragraph of this chapter and in Chapter 1. By developing standard leaching column procedures that meet EPA guidelines for Performance-based Measurement Systems (PBMS) and ASTM Standards specified in ASTM Method D2777, we have met the objective of standardization. By maintaining a carbon-dioxide enriched pore gas (i.e. 10% CO_2) and quantifying particle size variables, we have made improvements over some previous leaching column methods. By describing three approaches to the interpretation of the leachate data, we have expressed the latitude of applications of the method. Hopefully, this standardized leaching column method will be found to be useful to mining permit preparers and reviewers, commercial and governmental laboratories, and a variety of researchers.