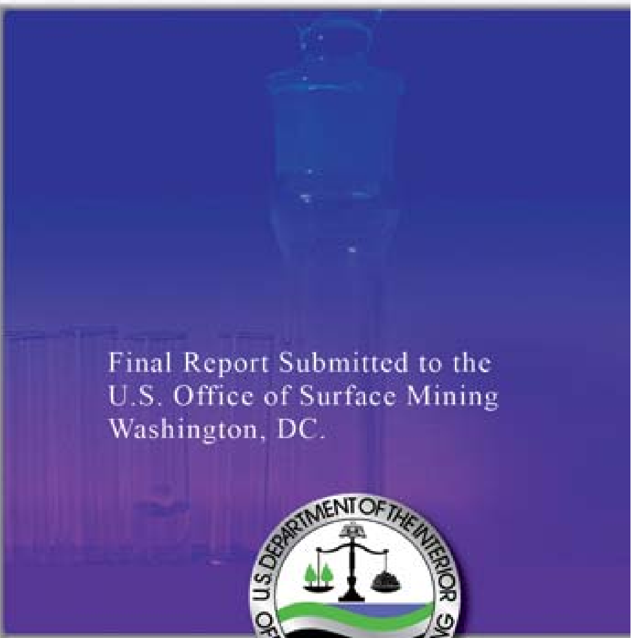
DEVELOPMENT AND INTERPRETATION OF THE ADTI-WP2 LEACHING COLUMN METHOD

(Kinetic Test Procedure for the Prediction of Coal Mine Drainage Quality)

EPA Method 1627



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Roger J. Hornberger and Keith B.C. Brady, Editors

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(Kinetic Test Procedure for the Prediction of Coal Mine Drainage Quality)
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Pennsylvania Department of Environmental Protection in cooperation with
the Pennsylvania State University
CSC Dyncorp
US Office of Surface Mining Reclamation and Enforcement
The US Environmental Protection Agency
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This report represents more than 7 years of work by a team of scientists from various locations to develop and validate this kinetic test method. The project is a cooperative effort between the U.S. Office of Surface Mining Reclamation and Enforcement (OSM), the U.S. Environmental Protection Agency (EPA), the Acid Drainage Technology Initiative (ADTI), the Pennsylvania Department of Environmental Protection (DEP), Pennsylvania State University and CSC Dyncorp. The OSM project coordinator is Eric F. Perry. The EPA project coordinator is Joan E. Cuddeback with CSC Dyncorp. The DEP Principal Investigators for this project are Keith B.C. Brady and Roger J. Hornberger. Dr. Barry E. Scheetz and Dr. William B. White of the Materials Research Institute of the Pennsylvania State University played a key role in the test method development. Jane Hammarstrom and her associates of U.S. Geological Survey (USGS) provided a great amount of detailed information on rock characterization.

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The numerous authors of the chapters of this report are given credit at the front of each chapter. These chapters and the appendices of this report document essentially all of the information compiled in this project.

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Chapter 1: Background Information on Kinetic Tests

Roger J. Hornberger and Keith B.C. Brady

Introduction

The ADTI-WP2 Leaching Column Method development project described in this report is intended to provide a standardized kinetic test method for coal mine drainage prediction, which essentially fulfills a technological need that has existed for many years, and was developed under the auspices of the Acid Drainage Technology Initiative (ADTI). The project was jointly funded by the Office of Surface Mining Reclamation and Enforcement (OSM) of the U.S. Department of the Interior and the U.S. Environmental Protection Agency (EPA); with significant technical input, cooperation and guidance provided by scientists from both of these federal agencies. Additional financial and/or technical assistance was provided by numerous other project cooperators including the Pennsylvania Department of Environmental Protection, the U.S. Geological Survey, the Materials Research Institute of the Pennsylvania State University, the National Mine Land Reclamation Center at the West Virginia University and the Interstate Mining Compact Commission (IMCC). Also, eight laboratories participated in the various phases of weathering tests conducted during the method development process and assisted in the operational refinements of the test method. They will be acknowledged individually in a later section of this report, but they collectively possess a great diversity of experience and interests including four commercial labs, two university research labs, a mining industry research lab, and a Federal government agency research lab.

This introductory chapter provides some background information on kinetic tests and their relationship to static tests for mine drainage prediction; briefly describes the goals and milestones of this ADTI-WP2 Leaching Column Method development process (and the related ADTI-WP1 Humidity Cell Method); briefly outlines the contents of the other chapters of this final report; and provides some information on the applications of this standardized kinetic test method for the various members of the user community.

This report describes results of the 2006 interlaboratory study for validation of the ADTI-WP2 Leaching Column Method, involving eight participating laboratories simultaneously conducting weathering tests on five different lithologic units using an array of nine leaching columns. The report also describes results of weathering studies conducted in 2002 and 2003 as part of the method development. This interlaboratory study satisfies key requirements in the EPA method development process, however, there is a dual purpose to the report as reflected in the structure and contents of the following chapters. OSM is not in the business of developing standard test methods; they rely upon EPA to perform this essential function. However, OSM is closely involved with state and federal mining regulatory personnel and other users of mine drainage prediction and monitoring test methods, and OSM has a very active technology transfer program to disseminate information on new technological developments including geochemical interpretive information on mine drainage prediction tools. Hence, this report is designed to: (1) document the EPA method development process, including the analytical data from the participating laboratories, and (2) present geochemical interpretations of the practical and theoretical aspects of the leaching behavior of the various overburden rock types evaluated during the weathering studies.

The long-term technological need referred to above arose from some inherent limitations of static tests, and two major problems encountered in the use of kinetic tests for mine drainage quality prediction. Both static and kinetic tests produce site-specific geochemical evaluations of potential acidity or alkalinity, and other parameters of predicted water quality. 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. Static tests for coal mine drainage prediction have been in use for about 30 years (e.g. Smith et al., 1974 and Sobek et al., 1978), and kinetic tests have been used in coal mine drainage research for more than 50 years (e.g. Braley, 1949).

The static test most commonly used to predict mine drainage quality in the eastern United States is acid-base accounting (ABA). This method involves a comparison of the maximum potential acidity (MPA), typically calculated from the total sulfur in the sample, to the neutralization potential (NP). Although other static tests have been developed and used in coal mine drainage prediction, ABA is the most routinely used method for coal mine drainage prediction. The three main limitations of static tests, such as acid-base accounting are: (1) the total sulfur content and neutralization potential (NP) are surrogate measurements of the potential acidity and alkalinity of a rock sample, respectively, and they may not be accurate indicators of the actual concentrations of acidity or alkalinity that can be produced, (2) there is an area of uncertainty, often referred to as the “gray zone” (see Geidel, et al., 2000) where the magnitude of the sulfur and NP values make it very difficult, if not impossible, to accurately predict whether a rock sample will produce substantial acidity or alkalinity, and (3) it is generally not possible to predict metals concentrations from static tests. Despite these limitations, static tests including acid-base accounting have been very useful in many evaluations of mine drainage permit applications.

The most commonly used kinetic tests for mine drainage prediction are leaching columns and humidity cells. While these kinetic test methods and others have been used in hundreds of mine drainage studies as shown in the chronology contained in Hornberger and Brady (1998) and other references (e.g. Sorini, 1997), they have rarely been used in coal mine permitting by either regulatory agencies or the mining industry. The two major related problems impeding the routine use of these kinetic test methods are : (1) there are a considerable number of variables in the design and operation of these kinetic tests and the variety of test apparatus and procedures in use is so great that it is very difficult to interpret the results and make meaningful comparisons of data from different studies in similar or different lithologic settings, and (2) in the absence of standardized, accepted (e.g. by EPA or ASTM) test methods, mine operators and consultants shy away from kinetic tests because they do not know which apparatus or procedure to use, nor how to interpret the results.

While the ADTI-WP2 Leaching Column method discussed in this report does not preclude the use of other kinetic test methods or solve all of the problems associated with kinetic prediction tests, it does fulfill a technological need by providing a standardized method, and by providing a tool to reduce the effects of the three limitations of static tests.

The role of the ADTI

The Acid Drainage Technology Initiative (ADTI) was initiated in 1995 by federal agencies, the National Mining Association and the Interstate Mining Compact Commission to identify, evaluate, and develop cost-effective and practical acid drainage technologies. In 1999, ADTI was expanded through the addition of the Metal Mining Sector (MMS). ADTI addresses drainage quality issues involving metal mining and related metallurgical operations and acid drainage from coal mines, for abandoned, active and future mines. The guiding principle of ADTI is to build a consensus among industry, federal and state regulatory agencies and academia. With this array of varying interests and expertise in acid mine drainage problems, it was envisioned that a consensus could be developed on reliable, standard static and kinetic test methods and other aspects of mine drainage prediction in the Appalachian Coal Basin.

ADTI includes the Coal Mining Sector (CMS) and the Metal Mining Sector (MMS) under the overall guidance of the ADTI Operations Committee. The Coal Mining Sector has produced two publications on the prediction and prevention of acid drainage (Skousen et al., 1998 and Kleinmann et al., 2000). Three ICARD (International Conference on Acid Rock Drainage) papers presented background information and details of the ADTI (Hornberger, et al., 2000; Williams, 2003 and vanZyl, et al., 2006).

The project to develop standard kinetic test procedures (i.e. ADTI-WP1 Humidity Cell Method and ADTI-WP2 Leaching Column Method) is a good example of cooperation, technology development and consensus building among various ADTI stakeholders. The need for these standardized procedures has been recognized since the inception of ADTI in 1995 as described in Hornberger and Brady (1998) and Geidel, et al., (2000). ADTI members in the MMS and the CMS have extensive experience in kinetic tests and the methods development process, and they provided comments and suggestions in the peer review phase of the project. Kinetic tests have historically been used more by industry and regulatory agencies in metal mining in the western U.S. and Canada (e.g. Lapakko, 1988; Lapakko et al., 1995; White et al., 1994; and Sorini, 1997). This project has been a high priority for the ADTI-CMS.

Background Information on Kinetic Test Methods

A major advantage of kinetic tests for the prediction of mine drainage quality is that, since these types of tests produce an effluent of simulated mine drainage quality, the effluent may be tested for the same water quality parameters as the actual mine drainage that would be monitored during the proposed mining operation. The water quality parameters typically included in the leachate analyses are pH, acidity, alkalinity, sulfates, iron, manganese and aluminum. These are the same water quality parameters typically monitored under the National Pollutant Discharge Elimination System (NPDES) permit requirements for an active mining operation. 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.

Hornberger and Brady (1998) compiled a comprehensive chapter on kinetic tests for mine drainage prediction that included: (1) a chronology and synopsis of scientific literature on these kinetic tests as they have developed over approximately 50 years, (2) an evaluation of the factors to be considered involving physical, chemical, and biological processes, and (3) general guidelines for test procedures, data interpretations, and recommendations for further research to develop standard methods. That chapter and a related chapter by Geidel, et al., (2000) in the ADTI prediction book formed much of the basis for members of the ADTI prediction working group to commence development of the ADTI-WP1 Humidity Cell and ADTI-WP2 Leaching Column standard test methods described in this report.

The chronology in Hornberger and Brady (1998) documents the historical development of kinetic tests for mine drainage prediction and practical applications of the test results on mine sites in the Appalachian coal fields and elsewhere. In citing more than 275 scientific references it demonstrates that most of the kinetic test methods in use today were substantially developed and applied more than 40 or 50 years ago, including leaching columns (Braley, 1949), humidity cells (Hanna and Brant, 1962) Soxhlet reactors (Pedro, 1961) and field scale tests with actual precipitation (Glover and Kenyon, 1962).

physical, chemical and biological factors: The kinetic tests described in the chronology referred to above, incorporate physical, chemical and biological processes and constraints. Physical factors include: the size, shape and structure of the apparatus used to conduct the tests; the volume, texture and particle size distribution of the sample to be tested; and the volume, pathway and resultant saturation conditions (e.g. saturated zone, capillary fringe or relative humidity of pore spaces) of the fluids introduced into or removed from the apparatus for analysis.

Chemical factors include: the mineralogical composition of the rock sample, the composition (i.e. concentration of cations and anions) of the influent and effluent fluids; the solubility controls on the acidity and alkalinity generating processes, the interrelationships between these processes and other constraints affecting the reaction kinetics, and the composition of gaseous phases (e.g. partial pressures of oxygen and carbon dioxide) in the fluids and void spaces within the kinetic test apparatus.

Biological factors include: the presence and relative abundance of bacteria (e.g. *Thiobacillus*), that catalyze the AMD producing reactions; the availability of nutrients and other life-supporting ingredients; and the interrelationships among controls on the biological system, such as temperature and pH, which determine whether various organisms flourish, barely survive, or die.

It is useful to briefly review the controls and range of acidity, alkalinity, sulfate, and metals concentrations which may be found in nature, particularly mine environments, in order to demonstrate the variations in mine drainage composition associated with the range of geologic settings in Pennsylvania and elsewhere, and to place some expectations on the variations in leachate composition from kinetic tests. Lovell (1983), and Hornberger and Brady, (1998), list ranges of component concentrations in Appalachian acid mine drainage where pH may be as low as 1.4, and maximum concentrations for the following parameters are : acidity of 45,000 mg/L, total iron or ferrous iron of 10,000 mg/L, aluminum of 2,000 mg/L, and sulfate of 25,000 mg/L.

The alkalinity production process has a dramatically different set of controls, and the resultant maximum alkalinity concentrations are typically one or two orders of magnitude less than the maximum acidity concentrations found in mine environments. The carbonate rocks which produce significant alkalinity or bicarbonate concentrations in groundwater, surface-water, and mine drainage samples (i.e. coal surface mines, stone quarries, and coal and noncoal underground mines) are limestones and dolomites and the principal carbonate minerals are typically calcite (calcium carbonate) and dolomite (calcium-magnesium carbonate).

Very thorough discussions of the chemical reactions of carbonate mineral dissolution and precipitation and associated solubility and chemical equilibria controls are found in Stumm and Morgan (1970), Krauskopf (1967), Garrels and Christ (1965), Freeze and Cherry (1979), Plummer et al. (1978), White (1988), and Langmuir (1997). Rose (1997) calculated the range of bicarbonate concentrations for calcite dissolution in pure water from 83 mg/L at PCO_2 of 10^{-3} to 370 mg/L at PCO_2 of 10^{-1} using the methods (i.e. Case 4) described in Garrels and Christ (1965). Figure 1.1 from White (1988) shows solubility curves for calcite as a function of carbon dioxide partial pressure, and Rose and Cravotta (1998) depict bicarbonate and alkalinity concentration for a similar range of PCO_2, based upon Case 2 of Garrels and Christ (1965, p. 81).

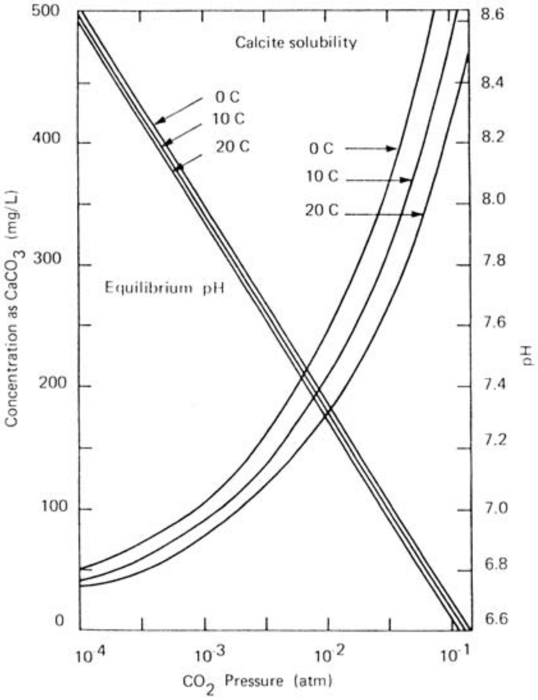


Figure 1.1 Solubility curves for calcite as a function of carbon dioxide partial pressure (from GEOMORPHOLOGY AND HYDROLOGY OF KARST TERRAINS by William B. White. Copyright © 1988 by Oxford Univ. Press, Inc.).

Typical bicarbonate and alkalinity concentrations associated with limestone and dolomites in Pennsylvania are found in Langmuir (1971), Shuster (1970) and Shuster and White (1971). Langmuir (1971) reported bicarbonate concentrations ranging from 81 to 438 mg/L for wells and springs in limestone of central Pennsylvania. Given the ranges and extreme values of pH, acidity, alkalinity, iron, aluminum, and sulfate reported above, it is reasonable to expect that kinetic tests for AMD prediction should be capable of producing leachate with acidity and sulfate concentrations of several thousand to tens of thousands mg/L, and metals concentrations of several hundred mg/L from worst-case AMD producing rock samples, and leachate with alkalinity concentration of several hundred mg/L from best-case carbonate rock samples.

Of all of the physical, chemical and biological factors to be considered in kinetic tests, two of them warrant special attention in the development of the ADTI-WP2 Leaching Column Method, and in kinetic tests in general: (1) the partial pressure of carbon dioxide (PCO_2) used in the gas handling provisions of the test, and (2) the effects of the particle size distribution, and the related surface area to volume ratio of the water handling provisions of the test.

partial pressure of carbon dioxide (PCO_2): The significance of oxygen and carbon dioxide in acidity and alkalinity production in the mine environment and in kinetic tests to predict mine drainage quality has been noted throughout this chapter and elsewhere. Without sufficient oxygen and aeration of the rock samples, pyrite oxidation and weathering will be impeded and AMD production will not reach its full potential. Without sufficient carbon dioxide, the dissolution and maximum solubility concentration of carbonate rocks will be reduced dramatically, and alkalinity production will not reach the full potential of the carbonate rocks.

Concerning the role of gases in laboratory kinetic tests, Hyman et al. (1995, p. 11) state, "Gas phases, such as oxygen and carbon dioxide, that occur in field conditions may not be represented appropriately in the laboratory test conditions." Gas handling provisions in kinetic test design and operation should: (1) account for percentages of oxygen and carbon dioxide within the test apparatus that are representative of field conditions of the mine environment (e.g. pore gas composition of a backfilled surface mine) and (2) include mechanisms to circulate the gas mixture through the apparatus to ensure that chemical reactions (oxidation and dissolution) may take place and promote weathering of the rock samples. From the discussion on pyrite oxidation above, it is presumed that there should be more than enough oxygen available for pyrite oxidation in the normal laboratory setting if the kinetic test apparatus is open to the air and the rock samples are not entirely saturated within the apparatus. However, the amount of carbon dioxide needed to facilitate significant dissolution of carbonate minerals is more than can be achieved under normal atmospheric conditions as described above. Therefore, carbon dioxide generally needs to be added to or concentrated within the kinetic test apparatus to enrich the carbon dioxide concentration within the gas mixture unless interactions of minerals (e.g. pyrite) and fluids will increase the PCO_2. If the partial pressure of carbon dioxide in the gas mixture is $10^{-3.5}$ bars (i.e. atmospheric conditions) within the kinetic test apparatus, the maximum alkalinity/bicarbonate concentrations in the leachate will be less than 100 mg/L, even with pure limestones and dolomites. If there is too much carbon dioxide in the gas mixture (e.g. greater than 10^{-1} bars, PCO_2 typically found in groundwater systems and pore gas of surface mine backfills) the bicarbonate and alkalinity concentrations may be greater than 500 mg/L, for example, as shown on Figure 1.1.

In summary, 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. To ensure a representative and realistic gas mixture in kinetic tests for mine drainage prediction, it may be necessary to have the kinetic test apparatus fitted with gas ports to enable the constant or intermittent introduction of a controlled gas mixture into the apparatus (i.e. for carbon dioxide enrichment). For example, a mixture of 10% oxygen, 10% carbon dioxide and 80% nitrogen in a compressed gas cylinder would supply adequate and representative amounts of oxygen for pyrite oxidation and carbon dioxide for carbonate mineral dissolution.

particle size distribution and surface area of rock samples: Concerning particle size and surface area effects, the goals of sampling for kinetic testing should be to obtain rock samples that are representative of the physical (i.e. particle size distribution) and chemical (i.e. mineralogic composition) characteristics of the consolidated overburden strata, or backfilled mine spoil, or waste dump to be simulated in the test. Consideration should be given to the percentage of relatively coarse (i.e. gravel sized) particles and relatively fine grained particles in the sample. A greater percentage of fine particles increases the surface area available for reaction, which is a critical parameter in the production of acidity or alkalinity.

Usually, for the purposes of pre-mine prediction of AMD potential, the rock samples will be obtained from exploration drill holes, and 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.

Most consolidated rock overburden strata should yield a relatively large percentage of gravel-sized particles in samples obtained from air-rotary drilling. It could be expected that sandstone overburden samples would possess a relatively large percentage of coarse particles and relatively few fines, especially where the sample is indurated, well-cemented sandstone; and that 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 may have positive and negative effects upon the kinetic test results. According to Bradham and Caruccio (1990), the fine-grained nature of the Canadian metal mines tailings that they tested in leaching columns, caused high specific retention of fluid and created air locks within the columns which skewed the results. In addition, the particle size distribution at the conclusion of the kinetic test may be different (i.e. more fine) than the original particle size distribution of the sample, due to particle decomposition during the test.

Notwithstanding 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 upon the chemical reactions of acidity and alkalinity production. According to Brady (1974, p. 43) concerning silt and clay-sized particles in soil: “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.”

According to Rose and Cravotta (1998): "Kinetic studies indicate that the rate of acid generation depends on the surface area of pyrite exposed to solution, and on the crystallinity and chemical properties of the pyrite surface" (e.g. McKibben and Barnes, 1986). The consideration of surface area available for reaction in kinetic tests leads to the evaluation of the ratio of the surface area to the volume of leachate, which may be the most important factor in kinetic test design, performance, and data interpretation.

One of the shortcomings of previous leaching studies has been not considering the effects of surface area and particle size. This factor was extensively studied in the decade from the mid-1970's through the mid-1980's by scientists who were investigating the stability of materials used for the sequestration of nuclear waste (e.g. Ethridge et al., 1979; Hench et al., 1980; Buckwalter et al., 1982; Oversby, 1982; Pederson et al., 1982). The work of John K. Bates and associates at Argonne National Laboratory on nuclear waste glass also provides relevant information on surface area/leachate volume ratios (Aines et al., 1986; Ebert and Bates, 1992; Feng and Bates, 1993; and Feng et al., 1994).

It was recognized by this group of researchers that the particle size of the leached materials and the volume of fluid that was available for the leaching process had a significant impact on the experimental results. Figure 6.3 in Chapter 6 of this document demonstrates this dependence. Shown is the release of silica from a nuclear waste form as a function of time with specific control of the surface area to volume ratio. What is important in Figure 6.3 is that by specifically including the surface area/volume parameter, leaching rates varying over 3 orders of magnitude can be scaled onto the same plot. Surface area must also be taken into account in coal overburden leaching experiments. Otherwise the cross-laboratory experiments, although individually correct, cannot be compared, and the results cannot be compared with other results in the literature, and cannot be used to extract quantitative rate constants. The observed leach rates would be an accurate result of the individual experiment, but meaningless as a fundamental property of the material itself.

For this study, the surface area of each fraction of sieved starting material was determined by BET (Brunauer et al., 1938; and Yates, 1992) instrumentation using N_2 gas bulk adsorption. This method is a routine analytical approach to measure the accessible surface of the rock to gas molecules. Additional discussion of surface area measurements and their relationships to porosity and reaction kinetics are given by Brantley and Mellott (2002) and Brady et al., (2004).

Goals and Milestones of the ADTI-WP2 Method Development Process

The three major goals of the project are: (1) standardizing kinetic test procedures; (2) improving 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). The importance of the carbon dioxide enriched leaching environment and the particle size and surface area factors was explained in the preceding section on background information. The EPA guidelines for PBMS will be explained in Chapter 2.

There have been three phases or episodes of weathering tests in this standard method development process. The original concept was to develop two standard kinetic test methods under the auspices of ADTI: the Weathering Procedure 1: Humidity Cell Method and the Weathering Procedure 2: Leaching Column Method. The first phase of weathering tests occurred in 2002 and is described in greater detail in Chapter 2 and Hornberger, et al., (2003). This initial phase involved the weathering of three lithologic units (Brush Creek Shale, Wadesville Sandstone and Valentine Limestone) by 2 laboratories. A commercial laboratory (Geochemical Testing) constructed 8 humidity cells and 8 leaching columns and tested 4 shale and 4 sandstone splits of the rock samples, using duplicate apparatus set-ups on two different gas handling procedures. A university laboratory (Materials Research Institute of the Pennsylvania State University) (MRI) evaluated different gas handling options and particle size factors on 3 single leaching columns of shale, sandstone and limestone.

The second phase of weathering tests occurred in 2003 and is described in greater detail in Chapter 3 of this report and in Hornberger, et al., (2004) and Brady, et al., (2004). This second phase of kinetic test development involved the weathering of three rock samples (Brush Creek Shale, Vanport Limestone and Lower Kittanning Coal refuse) by 2 commercial laboratories (Geochemical Testing and Mahaffey Laboratories) and a university laboratory (MRI). The 2 commercial laboratories each constructed 12 leaching columns and 12 humidity cells in order to test 4 shale, 4 limestone and 4 refuse representative splits of the rock samples, using duplicate apparatus set-ups on two different revised gas handling procedures. The MRI laboratory evaluated the weathering behavior of shale samples in leaching columns of three different diameters, and performed detailed surface area measurements on all particle size classes, pre- and post-weathering.

The third phase of weathering tests, which is the major component of this report, occurred in 2006, and is the full inter-laboratory study for validation of the ADTI-WP2 Leaching Column Method. This final phase of weathering studies in the method development process is described in greater detail in Chapter 4 (the data report and statistical evaluation of inter-laboratory method performance criteria), and related chapters (5 through 10). Chapter 5 provides a detailed mineralogical characterization of the unweathered rock samples, plus characterization of some of the post-weathering rock samples and trace element content in leachate from the leaching columns, conducted by USGS researchers. Chapter 6 is an evaluation of particle size and surface area effects from BET measurements of effective surface areas pre- and post-weathering, conducted by Penn State researchers from the Materials Research Institute, while Chapter 7 is a related evaluation of weathering rates, surface area to volume (SAV) ratios and kinetic data. Chapter 8 is principally an interpretation of the metals data and related water quality parameters from the large database of metals data compiled from the 9 leaching columns at each of the 8 participating laboratories; this chapter is also closely related to the interpretive content of Chapter 7. The strengths and weaknesses of the acid-base accounting data conducted for this project are described in Chapter 9, because these static test data are typically a companion or precursor to the kinetic test data. Finally, Chapter 10 is a guide to the overall interpretation and conclusions of the ADTI-WP2 leaching column results in several levels of sophistication and detail. The revised final draft of the ADTI-WP2 Leaching Column Method is contained in Appendix A of this report.

This third phase of kinetic test development involved the weathering of four shale samples (Brush Creek Shale and Lower Kittanning Shale from PA, Kanawha Black Flint Shale from WV, and Houchin Creek Shale from IN), and a sandstone sample (Middle Kittanning Sandstone from PA) by eight participating laboratories, using an array of nine identical leaching columns (i.e. duplicate columns for each of the four shale samples and a single relatively inert sandstone column to represent a "blank" sample). The eight participating labs comprise a diverse cross-section of four commercial labs from two states, two university labs, a coal industry research lab and a federal agency research lab. This is a sufficient number of laboratories to satisfy conformance with the protocol in ASTM Standard D-2777 on Standard Practice for Determination of Precision and Bias of Applicable Test Methods of Committee D-19 on Water.

In addition to these three phases of weathering tests, a peer review study on the draft ADTI-WP2 Leaching Column Method was conducted in 2004. Results of the peer review are included in Appendix B.

Applications and Users of The ADTI-WP2 Leaching Column Method

The need for standardized kinetic test methods is recognized by OSM and EPA to provide improved predictions of coal mine drainage quality and overburden strata characterizations for use by state and federal regulatory agencies and the mining industry. Such predictions can be used in addressing the Probable Hydrologic Consequences (PHC) and Cumulative Hydrologic Impact Assessment (CHIA) requirements of the SMCRA, associated federal and state regulations, and surface mining permit applications and NPDES permits. OSM is administering this project and EPA is ensuring that the method development process meets their rigorous requirements to become an approved EPA method.

Following the completion and distribution of this final report, the final draft of the ADTI-WP2 Leaching Column Method, (contained in Appendix A of this report) will have to be published in the Federal Register in accordance with 40 CFR Part 136 in order to become an approved EPA method. That publication of the draft method would be in the format of a proposed EPA method, followed by a public comment period, and ultimately publication as a final approved EPA method.

It is anticipated that the user community for the standard ADTI-WP2 Leaching Column Method will consist of three main groups: (1) state and federal agency permit reviewers who evaluate and write SMCRA permits and NPDES permits for mine drainage discharges, (2) mining industry geologists, engineers and chemists who prepare mining permit applications, and who evaluate mine drainage problems during active mining operations and the abatement of any unanticipated post-mining discharges, and (3) laboratory personnel who conduct the weathering tests in their laboratories to produce the leaching data for use in the permit applications or other purposes.

Two major advantages of developing standard kinetic procedures are that almost everyone, especially for mine permitting purposes, would be using the same test procedures (which facilitates data comparison and data base building) and that scientific and legal controversies between government and industry users of prediction techniques over interpretations of the test results and accuracy of the predictions would be substantially reduced.

It is recognized, however, that kinetic tests alone are not the answer to the prediction of mine drainage quality. These tests should be used in combination with static tests and other predictive techniques including evaluation of background water quality, mine drainage quality produced at nearby mine sites or mines in similar lithologic settings, and detailed stratigraphic analyses. Kinetic tests will usually be more expensive and more time consuming than static tests; therefore the kinetic tests should be used selectively, in cases when the static tests are inconclusive or require augmentation.

Chapter 2: First Phase of Weathering Tests (2002)

Joan E. Cuddeback, Roger J. Hornberger, Keith B.C. Brady and William A. Telliard

Standard Method Development Process of EPA

EPA's cradle-to-grave analytical methods development process typically involves evaluation of existing documented techniques and development of procedures for an intended EPA application in a single laboratory. Single laboratory results and observations are used to prepare a draft method that is tested further in one or several multiple laboratory studies, including an interlaboratory study in which each laboratory evaluates identical unknown samples. Results of each study are used to revise the method, as appropriate, towards the goal of providing a method that can be sued for an intended purpose by a variety of laboratories. EPA methods that are intended to be required by EPA for use by industries monitoring compliance with regulations, are subjected to a federal rulemaking proposal process, and may be further revised prior to promulgation. In the case of the ADTI-WP2 Leaching Column Method, the method procedures were drafted based on published results of similar existing procedures, and the draft procedures were evaluated and further developed first in a single laboratory, followed by a multiple laboratory study, peer review, and finally, an interlaboratory study. Following each stage of method development, the draft method was revised as needed to address study results or reviewer comments.

Many EPA method development efforts include a built-in approach for providing performance-based criteria that can be used to (1) evaluate the validity of analytical results, and (2) allow the use of alternative equivalent procedures or equipment. This is consistent with the flexibility provided by EPA's Performance Based Measurement Systems (PBMS) approach to method development. Examples include study requirements for laboratories to analyze quality control samples to determine analytical precision and bias, such as statistical differences between results of replicate samples and recoveries of known spiked analyte concentrations. Statistical assessments of the results of these quality control samples are used to establish method performance criteria based on application of the procedures in multiple laboratories. Because of the complex nature of the samples and analytical components involved in the ADTI-WP2 method, it was not feasible to include an evaluation of bias in the method validation studies (i.e. the method is designed to evaluate the long-term effects of weathering, rather than the total amount of a contaminant that can be recovered in a singe analysis). The studies described in this report, for validation of the draft ADTI-WP2 method, included requirements for laboratories to evaluate duplicate samples throughout the weathering process. Results of these analyses were used to determine the precision that should be expected from laboratories analyzing replicate samples, and a requirement for analysis of replicate samples is built into the method as a means of evaluating data validity. Specifically, results of replicate samples were used to determine and establish the relative percent difference (RPD) in analytical results that can be expected between duplicate samples evaluated in a single laboratory and the relative standard deviation (RSD) that can be expected between more than two samples evaluated in a single laboratory. These criteria are based on the following equations:

Relative Percent Difference (RPD):

$$RPD = \frac{|C1 - C2|}{(C1 + C2)/2} * 100\%$$

Where: C1 and C2 are the concentrations of the original and duplicate results.

Relative Standard Deviation (RSD):

RSD = (Standard deviation / mean) x 100%

Rock Samples Tested during Method Development

Several rock samples were used during the initial development and testing of the humidity cell and leaching column kinetic test methods to determine how the procedures would perform using a variety of sample types that could be expected to encounter in overburden analysis. Neutralization Potential (NP) and total sulfur contents of these samples are provided in Table 2.1. The Brush Creek shale outcrop near Greensburg PA was selected as the primary rock sample for use in this project for several reasons: it has moderately high total sulfur and NP values classifying it as a “gray zone” type of sample; the sample site was selected in 1999 to be the first ADTI Coal Mining Sector standard reference material (thus, there is extensive geochemical characterization data available); the site stratigraphy has been confirmed and described by Skema (1995) in a published field guidebook; the sample site (Route 66 road cut) has long term accessibility for future sampling needs; and finally, the lithologic unit is known throughout Pennsylvania’s Bituminous Coal Region to have sufficient NP to produce significant alkalinity in mine drainage discharges and pit waters (described in Brady et al., 1998). The range in total sulfur content of four splits of the Brush Creek shale is 0.90 to 0.93 % (see Table 2.1). The range of NP values is 133.39 to 138.28 parts per thousand (ppt), thus documenting the moderately high sulfur and NP characteristics of the sample (i.e. a gray zone sample) and the homogeneity of the sample splits.

The Wadesville sandstone was selected as the secondary rock sample for this project because it represents a hard lithologic unit, in distinct contrast to the more friable Brush Creek shale. For this reason, it was expected to allow evaluation of much different physical weathering characteristics. Wadesville sandstone samples were collected within the pit of a large anthracite open-pit surface mine in Schuylkill County, PA that has been operated by Reading Anthracite Co. since before 1950. This sandstone represents the only lithologic unit at the site containing appreciable carbonate minerals; yet the mine pool discharge is one of the most naturally high alkaline discharges in the state (i.e., alkalinity greater than 400 mg/L) as documented in Hornberger and Brady (1998) and Brady et al. (1998). X-ray diffraction on this sample determined the carbonate mineral to be ferrodolomite; with 2 or more percent additional iron content, this mineral could be properly classified as ankerite. The range of NP values for this sample is 255.84 to 281.96 ppt (see Table 2.1), and the total sulfur contents are negligible.

Table 2.1 Total Sulfur and Neutralization Potential Values of Rock Samples

Split Sample ID	Total% Sulfur	*Fizz	Neutralization Potential (ppt)
Brush Creek Shale			
#8	0.90	2	138.28
#16	0.92	2	135.58
#24	0.91	2	133.39
#32	0.93	2	135.83
Wadesville Sandstone			
#4	0.00	2	255.84
#8	0.00	2	274.24
#16	0.01	2	261.50
#24	0.00	2	281.96
Highwall "A"	0.01	2	225.62
Valentine Limestone			
"A"	0.00	3	928.99
"I"	0.00	3	926.68
"K"	0.00	3	931.82
"P"	0.02	3	928.35
Leechburg Coal Refuse			
S-1	1.68	0	0.91
S-2	3.03	0	-1.32
S-3	1.58	0	3.29
S-4	2.01	0	5.27
S-5	2.42	0	1.29
Ernest Coal Refuse			
1A	4.38	0	1.16
1B	4.03	0	1.65
2A	3.75	0	2.29
2B	4.19	0	1.36
3A	3.91	0	1.09
3B	3.45	0	1.02
4A	1.23	0	-0.37
4B	0.99	0	-0.21
5A	1.28	0	1.38
5B	1.39	0	1.13

The Valentine limestone and the Ernest and Leechburg coal refuse samples were not as rigorously tested as the primary and secondary samples described above (i.e., no duplicate samples were analyzed during kinetic test evaluation). However, results from these samples provide some useful additional information on the performance of the draft weathering methods as described in Hornberger, et al., (2003). The Valentine limestone is described in a PA Geologic Survey publication (O'Neill, 1964) and Brady et al., (1998, p. 8-46) as the purest limestone in Pennsylvania, typically having calcium carbonate content greater than 97%. The specific Valentine limestone sample used in this project was collected from a quarry and underground mine operated by Graymont (PA), Inc. in Centre County, PA. That Valentine Limestone sample was collected from a stock pile located at the mine site near the town of Pleasant Gap. The stock pile consists of high-calcite bench material known to have 98.5% $CaCO_3$ and essentially zero sulfur.

The Ernest coal refuse sample was collected from a large coal refuse pile associated with the abandoned underground coal mine at the town of Ernest in Indiana County, PA. The Leechburg coal refuse sample was collected from the large refuse deposit associated with the abandoned underground Leechburg coal mine near the town of Apollo in Armstrong County, PA. The Leechburg site produces some of the most acidic mine drainage in PA as described in Hornberger and Brady (1998, p. 7-7), wherein acidity concentrations greater than 16,000 mg/L are reported.

sample collection and preparation: Prediction of the effects of weathering is limited by the extent to which samples are representative of the overburden being evaluated. Samples were collected using standard procedures described in Sobek et al., 1978; Block et al., 2000; Griffiths, 1967; and Tarantino and Shaffer, 1998. Samples were collected by the Pennsylvania Department of Environmental Protection and were homogenized and split into sample aliquots by Geochemical Testing. The sampling team collected approximately 800 pounds each of Brush Creek Shale, Wadesville Sandstone, Valentine Limestone and the two coal refuse piles. Bulk sample volumes were crushed to approximately ½" maximum diameter, mixed, and homogenized using procedures described in ASTM C-702-98 and Noll, et al., 1988.

Samples were air dried overnight and crushed through a Marcy jaw crusher, with the opening set for approximately ½" top size. Once an entire sample was passed through the jaw crusher, the sample was spread evenly, mixed, and long piled. Finally, the sample was riffled through a bulk splitter with openings set at 1.5". The bulk sample was used to prepare a total of 32 sample aliquots weighting approximately 25 pounds each. Prior to exposure to the weathering conditions described in the draft methods, the sample aliquots were stored in clean 5-gallon opaque buckets. Sample aliquots were selected randomly for analysis of total sulfur, neutralization potential, maximum potential acidity, and fizz rating. Results of these analyses are presented in Table 2.1.

The particle size distribution of the crushed sample was determined using a series of sieves (#4 (4.76 mm), #10 (2.00 mm), #20 (0.84 mm), #40 (0.42 mm), #100 (0.149 mm) and #200 (0.74 mm) sieve sizes) to yield 8 particle size classes (i.e. including >3/8" (9.52 mm) and <200 (0.074 mm) fines). The homogenized samples were then chemically analyzed for percent total sulfur and neutralization potential as shown in Table 2.1.

Study Design and Laboratory Tasks

Toward the goal of developing standardized and effective test procedures, draft humidity cell (ADTI-WP1) and leaching column (ADTI-WP2) methods were developed for test application in two laboratories. The draft methods were designed to require low cost materials and minimal apparatus construction, maximize weathering efficiency, and produce reliable and verifiable data. The leaching columns were constructed from 6-inch diameter clear polycarbonate plastic tubing. The humidity cells were constructed from rectangular plastic food storage containers with airtight lids. Schematic diagrams describing the construction of the humidity cells, leaching columns, and humidified gas reservoir are presented in Figures 2.1a through 2.1c.

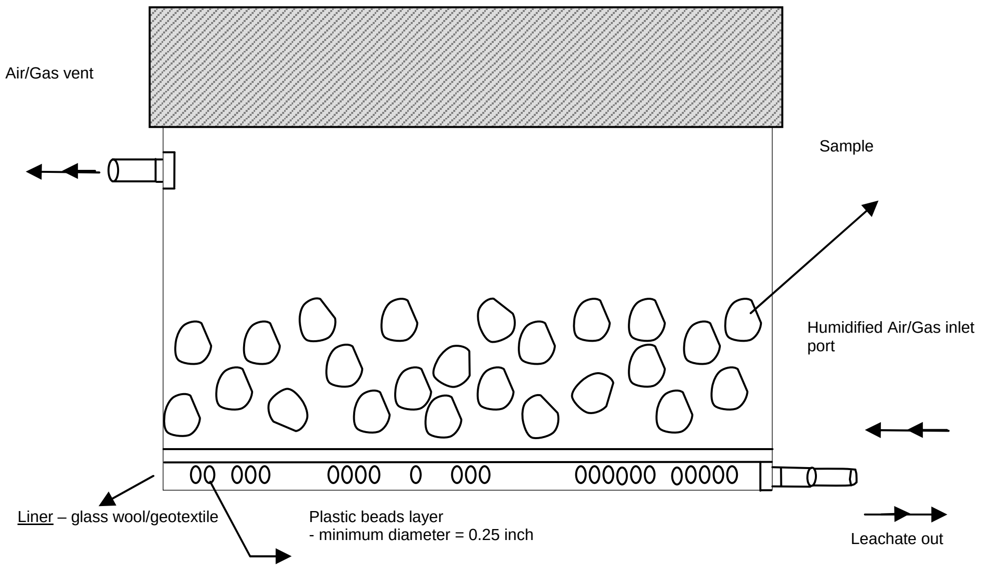


Figure 2.1a. Humidity Cell

To evaluate the performance of draft test methods and evaluate the effects of CO_2-enhanced air, the study involved two laboratories and the three sample types described above (shale, sandstone, and limestone). Laboratory 1 (Geochemcial Testing) was tasked with implementing both draft leaching column and humidity cell methods using duplicate samples exposed to two

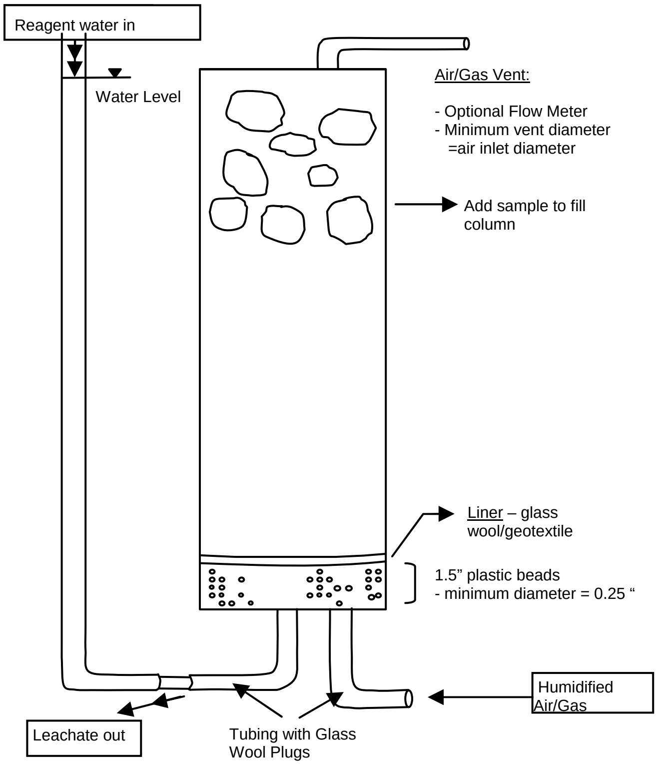


Figure 2.1b. Leaching Column

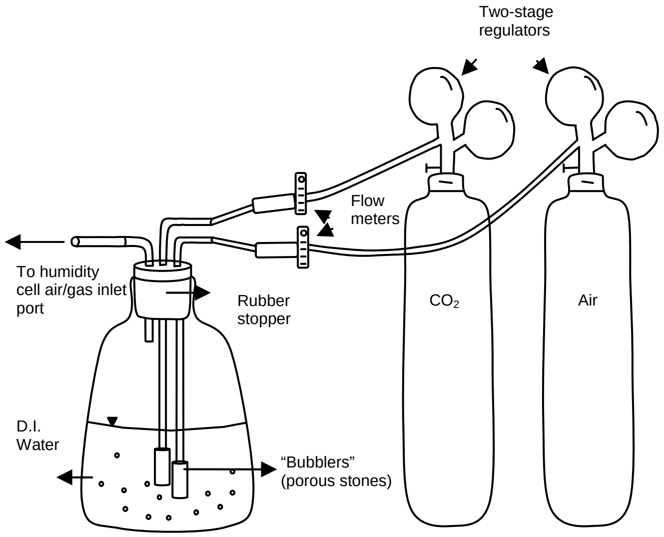


Figure 2.1c. Humidified Gas Mixture Schematic.

gas-mixture scenarios (i.e., air-only, and CO_2-enhanced air). Laboratory 2 (Materials Research Institute at Penn State University) was tasked with implementing the draft leaching column method using single samples exposed to CO_2-enhanced air. For a period of 15 weeks, each laboratory collected weekly samples from all columns and cells, and analyzed the samples for specific conductance and pH. Biweekly samples were filtered and analyzed for dissolved calcium, sulfate, acidity, alkalinity, iron, and manganese using EPA-approved methods. Data results of the analyses are included in Appendix C of this report.

Humidity cells were filled to 2/3 cell height; columns were filled to column height. Approximate weights of each sample added to the humidity cells were 1 kg and approximate weights added to the leaching columns was 13 kg. To provide an assessment of method precision, Laboratory 1 prepared duplicate samples for exposure to identical weathering conditions. Table 2.2 presents the weight of each sample added to each leaching column/humidity cell and exposed to either air only or CO_2-enhanced air.

Table 2.2.Sample Weights

		Column		**Cell**		
Lab	**Sample**	**Air**	**CO_2-Air**	**Air**	**CO_2-Air**	**Total # Samples**
1	Shale	12,722.6 g	12,825.8 g	1003.6 g	1006.5 g	8
		12,749.7 g	12,650.1 g	1003.2 g	1001.3 g	(4 duplicate pairs)
	Sandstone	12,476.5 g	12,612.6 g	1002.1 g	1005.9 g	8
		12,491.1 g	12,769.9 g	1004.9 g	1007.0 g	(4 duplicate pairs)
2	Shale	NA	13,284.0 g	NA	NA	1
	Sandstone	NA	13,227.5 g	NA	NA	1
	Limestone	NA	14,350.0 g	NA	NA	1

gas-mixing and handling procedures: Two alternative gas-mixing procedures were evaluated to attempt to achieve the target 10% CO_2 atmosphere in the weathering apparatus in a practical, cost-efficient manner. In the interest of economy, Laboratory 1 used one tank of CO_2 with a regulator, and mixed it with filtered house air (i.e. the compressed air piped throughout the lab) in the reagent water reservoir, prior to entry in the leaching columns and humidity cells. Precautions were taken to trap any drops of oil from the air compressor in the air lines prior to gas mixing, because any oil residue coating the rock samples would cause serious interferences in the weathering test. Laboratory 2 pursued a more rigorous mixing procedure, using separate tanks of CO_2 and compressed air, each equipped with regulators and mixing valves. A third alternative that was not evaluated would be to obtain an industrial grade gas mixture of 10% CO_2, 10% oxygen and 80% nitrogen in one tank, but it was determined that the cost of that prepared gas mixture was significantly higher than the other two alternatives.

water handling procedures/leaching cycles: The ADTI-WP1 & 2 simulated weathering procedures consist of alternating cycles of saturation and humidified air. A humidified gas mixture is introduced continuously through the gas inlet port of each leaching column and humidity cell during the periods of time between leaching episodes. These interleach periods of time are called “humidified air cycles” or “drying cycles”. The leaching episodes are called “wetting cycles” or “saturation cycles”. The gas mixture was also introduced into the leaching columns and humidity cells during periods of saturation (i.e. when the apparatus is filled with water).

In the ADTI-WP2 leaching column method once the leaching column has been filled with the rock sample and sealed, reagent water is introduced through the water inlet port at the bottom of the column (shown on Fig. 2.1a) until the column is full and all visible pore spaces are saturated. The first leaching episode is called the “initial flush”, in which the reagent water was drained from the column after a 1-hour contact time. During this initial flush the column is filled and drained again until the conductivity of the flush water (leachate) stabilizes. This initial flush is intended to wash the rock samples of any oxidized materials that have accumulated during handling and storage.

The initial flush is followed by a one-week humidified air cycle. Following this first and each successive humidified air cycle, reagent water (distilled, deionized) was introduced through the water inlet port to just above the rock sample surface, and the saturation cycle begins. During this saturation cycle, the rock sample is in contact with the reagent water in the column for a 24-hour period. Following this 24-hour saturated condition, the column is drained and the leachate is tested for analytes of concern (e.g. acidity, alkalinity, Fe, Mn, Al, sulfate). Then the next one-week humidified air cycle commences, followed by the next 24-hour saturation cycle. This weekly pattern of alternating humidified air cycles and saturation cycles continues until method implementation is complete (e.g. 15 weeks).

The ADTI-WP1 humidity cell method includes alternating weekly wetting and drying cycles similar to the procedures described above for the leaching columns. The main difference between these two weathering procedures is that the humidity cells have a one-hour saturation period on the 7th, 14th, 21st day, etc. until method implementation is complete. The comparison of the effects of this one-hour contact time to the 24-hour contact time of the leaching columns is discussed below.

Results of Weathering Tests

The leaching column and humidity cell weathering procedures were conducted in 2002 for a period of 16 weeks in the two laboratories. Evaluations were made of: (a) the effect of the CO_2-enhanced gas mixture (i.e. 10% CO_2) as compared to normal atmospheric air conditions (i.e. 0.035% CO_2), (b) comparison of the leaching efficiency of the columns and cells, (c) comparison of calcite saturation indices and partial pressures of carbon dioxide within the columns and cells, (d) preliminary determination of the effects of the weathering procedure on particle size and surface area, (e) the abundance of iron-oxidizing bacteria related to rock type, and (f) the relative percent difference (RPD) of analyte concentrations produced between duplicate columns and cells, plus statistical comparison of gas mixtures.

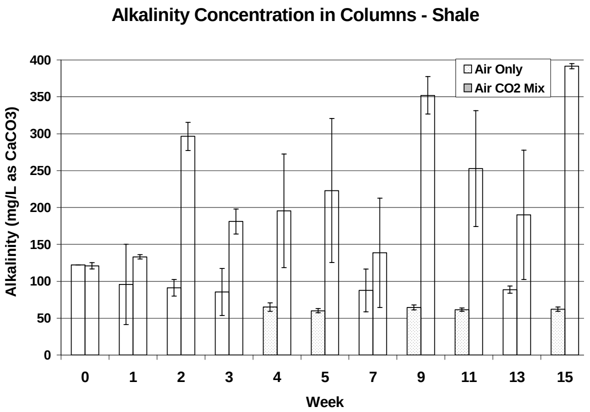


Figure 2.2a. Alkalinity concentrations from shale sample in leaching columns.

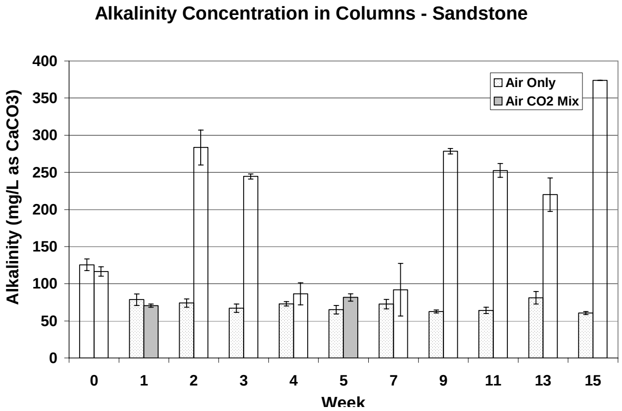


Figure 2.2b. Alkalinity concentrations from sandstone sample in leaching columns.

comparison of gas mixtures: Figures 2.2a and 2.2b were drawn from the alkalinity data set produced by Laboratory 1, but were developed specifically to facilitate the comparison of the air-only and CO_2-enhanced gas mixtures for the shale and sandstone samples using each of the draft methods (humidity cell and leaching column). In Figure 2.2a for the shale leaching columns, the highest alkalinity concentration for the air-only columns is 122 mg/L, while the highest alkalinity for the CO_2-enhanced columns is 394 mg/L; hence, the alkalinities were approximately three times greater in the columns with the additional CO_2 (in weeks 9 and 15 the alkalinities were 6 or 7 times greater). In the sandstone leaching column results shown in Figure 2.2b, the highest alkalinity concentration for the CO_2-enhanced gas mixture is 374 mg/L, while the highest alkalinity for the air-only columns is 120 mg/L; therefore the alkalinities are approximately three times greater with CO_2 addition, similar to that found with the shale columns. The histograms in Figures 2.2a and 2.2b depict the average or median values of alkalinity, and the bar diagrams in the top center of each histogram show the range in alkalinity concentrations of the duplicate samples.

Figures 2.2a and 2.2b show a lack of consistency in alkalinity concentrations with the CO_2-enhanced gas mixture from week to week, especially comparing the high values in weeks 2, 3 and 15 of the shale and sandstone humidity cells to the other weeks. That observation prompts further study of whether it is due to inconsistencies in the control of carbon dioxide partial pressures in the apparatus through time, or due to some geochemical factors in the weathering process.

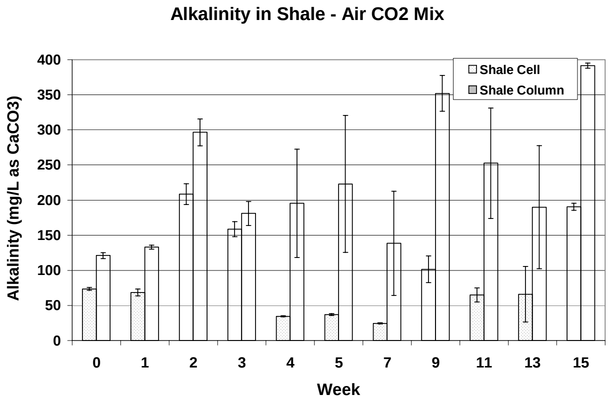


Figure 2.3a. Comparison of Humidity Cell and Leaching Column Performance on Alkalinity Production in Shale Sample Using CO_2 Enhanced Mixture

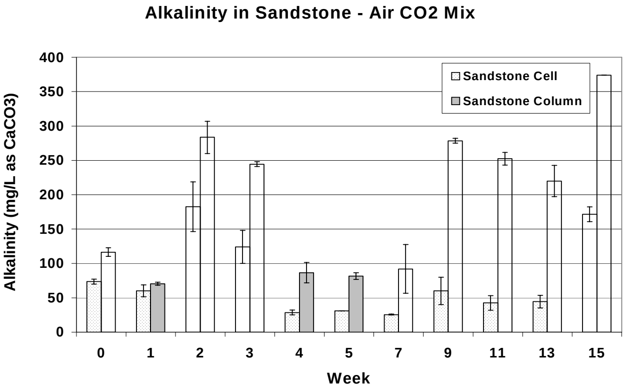


Figure 2.3b Comparison of Humidity Cell and Leaching Column Performance and Alkalinity Production in Sandstone Samples Using CO_2 Enhanced Gas.

<u>comparison of leaching efficiency of columns and humidity cells:</u> Figure 2.3 shows the comparison of humidity cell and leaching column performance on duplicate samples of shale and sandstone with air only and CO_2-enhanced gas mixtures. In comparing the performance of the humidity cells and leaching columns with the CO_2-enhanced gas mixture on the same shale sample, it is obvious that the alkalinities are much greater (i.e. often 2 to 6 times greater) in Figure 2.3a for the columns. The humidity cells in Figure 2.3a generally have alkalinities that are much lower than the leaching columns, and there is usually less variability between the duplicates and through time.

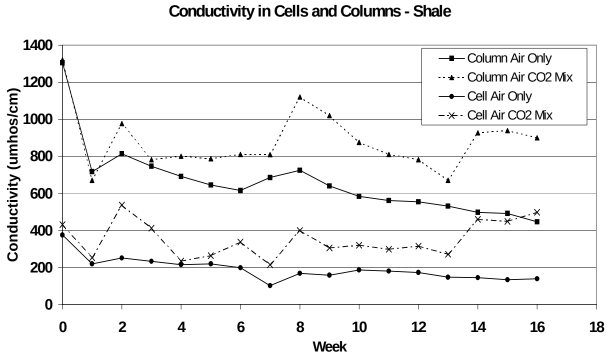


Figure 2.4a. Conductivity in Leachate from Shale in Humidity Cells and Leaching Columns

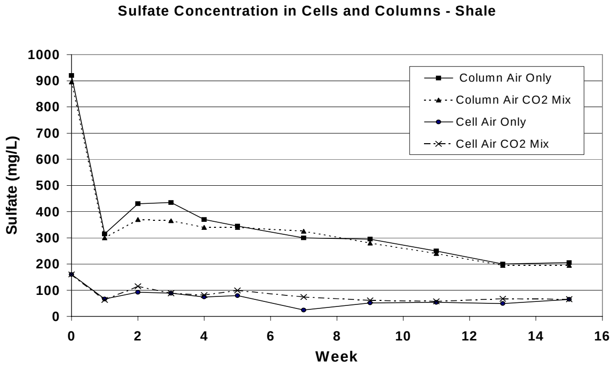


Figure 2.4b. Sulfate in Leachate from Shale in Humidity Cells and Leaching Columns

The leaching columns in Figure 2.3a exhibit alkalinity concentrations similar to alkaline mine drainage discharges from the Brush Creek shale interval in weeks 2, 9 and 15 (i.e. 300 to 400 mg/L), with relatively little difference between duplicates; but the variability from week to week and between duplicates is large in some of the 15 weeks shown. Figure 2.3b shows performance patterns for humidity cells and leaching columns on the Wadesville sandstone sample using the CO_2-enhanced gas mixture that are very similar to those described above for the shale in Figure 2.3a, except the variation in duplicate samples for the sandstone leaching columns is less than those for the shale.

Figures 2.4a and 2.4b depict variations in conductivity and sulfate concentrations throughout the 15-week weathering tests of the shale sample, using both draft test methods and both gas mixtures. These figures confirm that the humidity cells produce 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. Figure 2.4a shows the CO_2-enhanced gas mixture cells and columns have somewhat higher conductivity than their air-only companions, indicating that the influence of the additional CO_2 increases the dissolution of the carbonate minerals and adds calcium and magnesium cations and bicarbonate anions to the leachate.

Figure 2.4b shows that the CO_2-enhanced gas mixture has a negligible effect upon the sulfate concentrations, which follow a gradually declining trend after the initial flush. The leaching column sulfates are consistently higher than the humidity cell sulfates, and the response to the initial flush is much more dramatic in the columns; both observations being indications of more aggressive weathering conditions in the leaching columns. Finally, the apparently curious increase in conductivity in the last 3 weeks of the tests in both the columns and cells having the CO_2-enhanced gas mixtures has a rational explanation, because the authors decided to change the gas and water handling procedures at Laboratory 1 to determine the effect of using CO_2 saturated influent water rather than DI water (i.e. distilled, deionized) at that point, for possible future modifications in the draft procedures.

partial pressures of carbon dioxide (PCO_2) and calcite saturation indices: A goal of this project was to leach calcareous rock samples under conditions that are likely to be encountered in mine spoil, where O_2 concentrations tend to be diminished and CO_2 concentrations tend to be elevated relative to those in the ambient atmosphere. The concentration of CO_2 in the atmosphere is 0.03%, whereas in mine spoil it can exceed 10% (Cravotta et al., 1994; Lusardi and Erickson, 1985). Under subsurface conditions, where CO_2 is elevated, the weathering rate of calcareous materials can be accelerated and high concentrations of alkalinity can result (e.g. Cravotta et al., 1994). The target for CO_2-enriched leaching was equilibration with CO_2-enriched air containing 10% CO_2 (and 19% O_2 and 71% N_2).

A comparison of the water chemistry between the two laboratories showed significant differences in the leachate pH, alkalinity and corresponding computed values for PCO_2 and calcite saturation index. High pH and low PCO_2 values for many samples leached under high PCO_2 conditions indicated that leachate samples had evolved upon exposure to air outside the columns: CO_2 was degassed and, consequently, pH increased and calcite supersaturation was indicated. However, inside the columns, one would expect that calcite would have been saturated or undersaturated in association with higher PCO_2 and lower pH. Therefore, we recalculated the pH for equilibrium with calcite and the corresponding PCO_2 assuming that Ca and alkalinity were conservative.

The partial pressure of carbon dioxide in the leaching columns and humidity cells was calculated through geochemical modeling using a spreadsheet developed by Dr. Charles A. Cravotta of USGS. The equilibrium computations were performed utilizing thermodynamic data from Ball and Nordstrom (1991) to estimate the PCO_2 and pH of solutions within the columns and cells, prior to equilibration with the atmosphere. The following chemical parameters were determined every other week: pH, alkalinity, acidity, iron, manganese, calcium, magnesium, and specific conductance. Additionally temperature was known. The spreadsheet estimates ionic strength from conductance using relationships explained in Hem (1985) and Langmuir (1997) and was well suited for limited chemical analyses resulting from the study. The activity coefficients were determined using the Debye-Huckel equation (see Hem, 1985). Temperature correction was by the van't Hoff equation (Hem, 1985) and the equilibrium pH was computed simply by subtracting the calcite saturation index from the reported pH of the leachate. Then, the PCO_2 at equilibrium with calcite was recalculated considering this equilibrium pH and the reported alkalinity.

Table 2.3. Partial pressure CO_2 as determined from geochemical modeling. "Calculated" values were determined for water that was saturated or oversaturated by assuming the saturation index for calcite was 0.0 (i.e., at saturation). Q1 and Q3 are the 25th and 75th percentiles respectively.

Description	N	Median $\%PCO_2$ Unadjusted	Q1 $\%PCO_2$ Unadjusted	Q3 $\%PCO_2$ Unadjusted	Median $\%PCO_2$ Calculated	Q1 $\%PCO_2$ Calculated	Q3 $\%PCO_2$ Calculated	Median Saturation Index Calcite
Shale Air Column Lab 1	22	0.12	0.10	0.21	0.25	0.18	0.55	+0.290
Sandstone Air Column Lab 1	22	0.08	0.05	0.11				-0.236
Shale 10% CO_2 Column Lab 1	22	0.28	0.17	0.41	2.50	1.08	6.54	+0.963
Sandstone 10% CO_2 Column Lab 1	22	0.19	0.07	0.40	1.48	0.07	0.24	+0.494
Shale Air Humidity Cell Lab 1	22	1.48	0.07	0.12				-0.972
Sandstone Air Humidity Cell Lab 1	22	0.12	0.03	0.08				-1.044
Shale 10% CO_2 Humidity Cell Lab 1	22	0.90	0.10	1.06				-0.431
Sandstone 10% CO_2 Hum. Cell Lab 1	22	0.75	0.06	0.82				-0.822
Limestone 10% CO_2 Lab 2	12	10.45	9.09	11.36	14.97	12.25	16.79	+0.147
Sandstone 10% CO_2 Lab 2	13	10.05	9.07	11.31	9.71	6.61	13.18	-0.030
Shale 10% CO_2 Lab 2	14	12.55	9.27	16.19	30.19	21.27	32.79	+0.383

Table 2.3 shows the median and quartiles of PCO_2values for the columns and humidity cells, and recalculated PCO_2 assuming equilibrium with respect to calcite. The calculated PCO_2 values in Table 2.3 showed that the PCO_2 in humidity cells with and without the enhanced CO_2 gas mixture were nowhere near the 10% target CO_2 value; also leaching columns with carefully controlled CO_2 introduction usually met the target 10% value, while columns with less rigorous CO_2 introduction fell short of the target value.

The distribution of calculated saturation indices for leachate from the leaching columns and humidity cells is shown in a series of boxplots in Figure 2.5. Boxplots 5 through 8 are humidity cells, all others are columns. Stippled boxplots represent columns and cells that had air enriched with 10% CO_2 circulated through them. The boxplots that are not stippled represent apparatuses with atmospheric air only. Where duplicate columns were run, the data were combined (items 1 through 8 in Fig. 2.5). In general, the columns were supersaturated, or nearly saturated with respect to calcite. The humidity cells were almost always undersaturated with respect to calcite.

The gas handling procedures at Laboratory 2 differed from those of Laboratory 1, in that each of the three leaching columns had separate flow meter controls connected to the regulators of the tanks of compressed gas. Further evaluations of the kinetic test procedures demonstrated the importance of incorporating most of these Laboratory 2 gas handling procedures into the draft method, in order to maintain the target mixture within the leaching column (or humidity cell) apparatus throughout the weathering test. Laboratory 2 conducted leaching column tests on shale, sandstone and limestone samples for 16 weeks, using the ADTI-WP2 draft method. The rock samples were representative splits of the same Brush Creek shale and Wadesville sandstone samples used by Laboratory 1, plus a Valentine limestone sample. Figure 2.6 shows the alkalinity concentrations for the sandstone, shale and limestone samples for the 16 week weathering period.

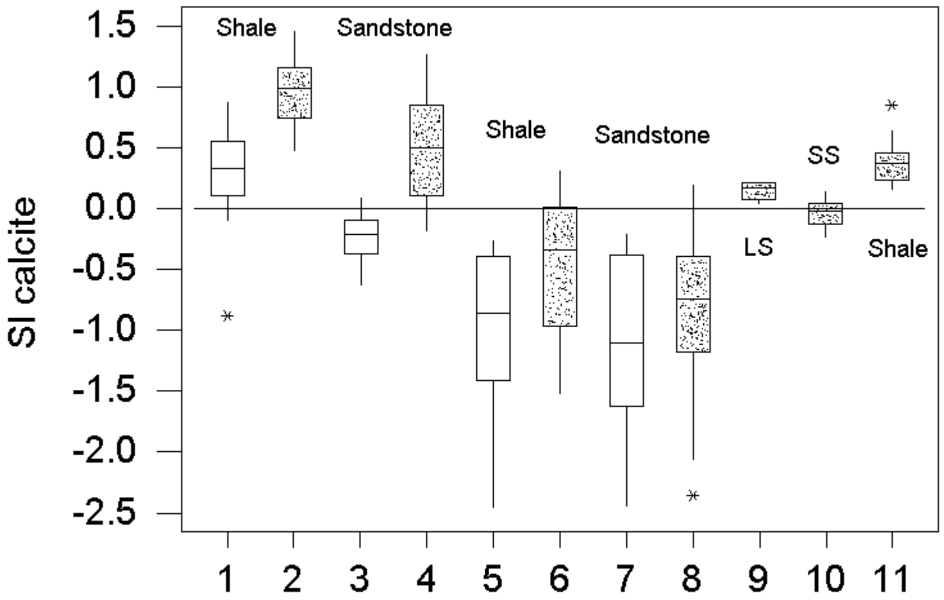


Figure 2.5. Boxplots showing the distribution of saturation indices for calcite for leaching apparatuses.

Three main observations are made from examining Figure 2.6 and comparing it to Figures 2.2a and 2.2b for the same shale and sandstone samples: (1) the alkalinity concentrations for the shale and sandstone samples are more consistent (i.e. exhibit less week to week variability) throughout the weathering test period than the weekly variations shown in Figures 2.2a and 2.2b, (2) the shale sample produced more alkalinity than the sandstone for each week of the test (and more than the limestone for each week except week 4), and (3) the alkalinity concentrations for the shale and sandstone samples in Figure 2.6 are significantly higher than shown for the same lithologic units in Figures 2.2a and 2.2b. The range of alkalinity concentrations for the sandstone sample in Figure 2.6 are 386 to 535 mg/L with a median alkalinity of 435.5 mg/L. The highest alkalinity concentration for the same sandstone sample in Figure 2.2b is 374 mg/L, which is much less than the median in Figure 2.6 and slightly less than the lowest alkalinity in Figure 2.6. The corresponding range of alkalinity concentrations for the shale sample in Figure 2.6 are 458 to 770 mg/L, with a median of 551.5 mg/L. The highest alkalinity concentration for the same shale sample in Figure 2.2a is 397 mg/L, which is considerably less than the median and the lowest alkalinity in Figure 2.6.

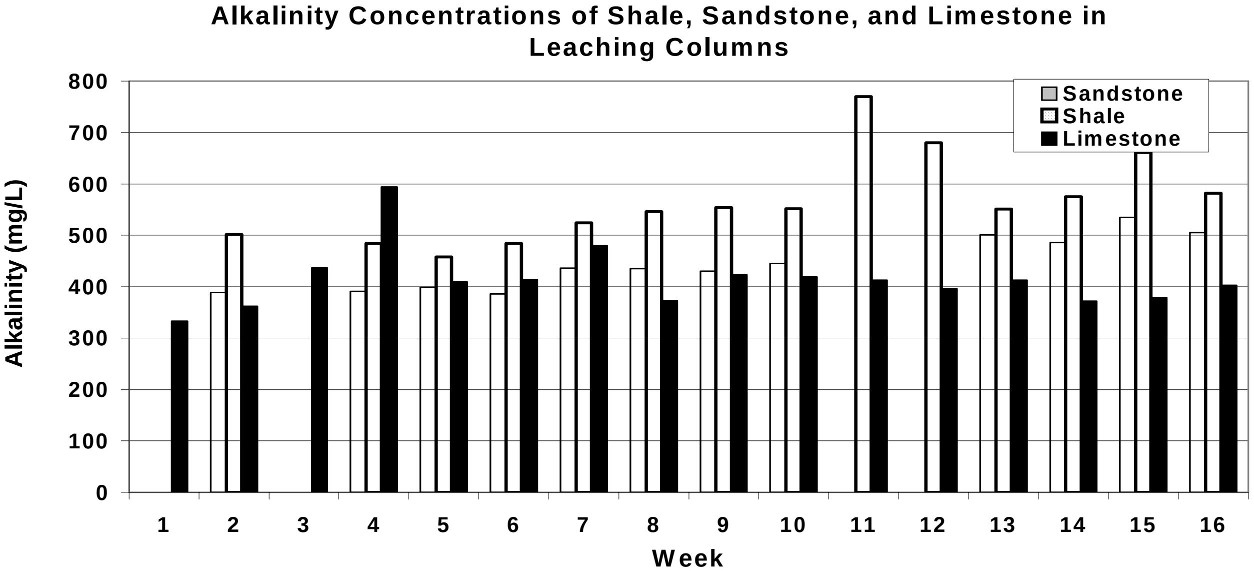


Figure 2.6. Alkalinity Concentrations of Shale, Sandstone, and Limestone Samples in Leaching Columns

<u>preliminary study of particle size and surface area effects:</u> The MRI researchers at Penn State University evaluated the differences in the sieve analyses of the shale and sandstone samples performed prior to the start of the weathering test and after the completion of the 16 week test in the leaching columns. The differences in the post-leaching particle size distributions were not as great as expected, but the shale sample did have a greater amount of fines in the 100 and 200 mesh size classes prior to weathering and had a greater percentage of loss in these size classes post-leaching, than the sandstone, as was expected.

The researchers at MRI also conducted some preliminary surface area measurements on the sandstone sample using BET equipment. The measurement of surface areas by the Brunauer, Emmett and Teller (BET) Method was originally described in Brunauer et al. (1938) and more recently in Yates (1992). The MRI researchers found that sandstone sample from the #8 sieve had a surface area of 0.76 square meters per gram, while sandstone sample from the #20 sieve had a surface area of 1.33 square meters per gram. Additional work on surface area measurements was needed in order to obtain measurements on a greater range of particle sizes and different lithologic units. These measurements would lead to further work on surface area to volume ratios as discussed in Hornberger and Brady (1998, p. 7-15).

bacteria populations: 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 bacteria (including *Thiobacillus*) was determined by the methods of Alexander (1982) and Greenberg et al., (1992). The abundance of iron-oxidizing bacteria in leachate drawn from humidity cells and leaching columns was determined in the fourth week and the last week of the 15 week weathering tests performed in Laboratory 1. The most probable number counts per 100 mL of sample ranged from <30 to 11,000 for shale and sandstone leaching columns and humidity cells. Both of these rock types produced alkaline leachate. The MPN values for the highly acidic coal refuse humidity cells ranged from 4.6 billion to >24 billion. 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.

Method Performance Data

statistical comparison of duplicate samples in Laboratory 1: Results from Laboratory 1 were used to evaluate method implementation, assess method precision (through comparison of duplicate results), and evaluate the effects of air vs. CO_2-enhanced air weathering conditions. Because the study was designed to assess the effect of CO_2-enhanced conditions on alkalinity production, this section presents an evaluation of the effects of the test methods on production of alkalinity, sulfate, calcium, and specific conductance. The precision of the draft leaching column and humidity cell test procedures was assessed using results of duplicate samples exposed to identical weathering procedures. Relative percent differences (RPD) were calculated for duplicate samples prior to implementation of method procedures (initial flush at week 0) and as pooled RPDs for all sample weeks beginning with week 1 (15-week RPD). Resulting RPDs are presented in Table 2.4. RPDs between duplicate samples were determined as RPD = [(2A - B2)/(A + B)] x 200. Fifteen week Pooled RPDs were determined as the square root of the average squared weekly (Weeks 1 - 15) RPDs for each parameter.

Pooled RPDs ranged between 0 and 58%. RPD results could be largely due to precision inherent to the analytical methods used to measure the parameters of interest. However, pooled RPDs were greater than the initial flush RPDs, indicating that the implementation of weathering procedures increased variability between duplicate samples. EPA methods often include RPD performance criteria of up to 30% for duplicate analyses. (e.g. EPA draft Method 200.7, May 2001, includes RPD criteria ranging from 0.5 to 20%. EPA draft Method 1630 includes an RPD criterion of 35%).

Table 2.4: Relative Percent Differences (RPD) of Duplicate Samples

Sample Type	Method	Gas Mix	Conductivity (RPD) umhos/cm	Calcium (RPD) mg/L	SO_4 (RPD) mg/L	Alkalinity (RPD) mg/L $CaCO_3$
Shale (Initial Flush)[1]	Column	Air	5.36	2.96	4.35	0
		Air-CO_2	6.06	6.83	10.06	4.96
	Cell	Air	1.60	1.94	0	4.44
		Air-CO_2	0.70	3.39	0	4.08
Shale (15-week pooled) [2]	Column	Air	7.77	10.77	17.47	33.25
		Air-CO_2	13.85	21.73	18.09	41.86
	Cell	Air	12.19	8.52	21.21	36.47
		Air-CO_2	17.62	17.36	16.45	28.20
Sandstone (Initial Flush)[1]	Column	Air	5.36	2.96	4.35	0
		Air-CO_2	6.06	6.83	10.06	4.96
	Cell	Air	1.60	1.94	0	4.44
		Air-CO_2	0.70	3.39	0	4.08
Sandstone (15-week pooled) [2]	Column	Air	12.55	10.66	13.78	10.54
		Air-CO_2	18.53	21.35	28.08	19.25
	Cell	Air	28.34	26.04	58.43	5.61
		Air-CO_2	21.11	25.08	25.93	24.60

[1] RPD between duplicate samples is determined as RPD = [(2A - B2)/(A + B)] x 200.

[2] 15-week Pooled RPDs are determined as the square root of the average squared weekly (Weeks 1 - 15) RPDs for each parameter

Out of thirty-two pooled RPD results, only four were above 28% (see shaded cells in Table 2.4). Pooled RPDs for alkalinity in duplicate shale samples ranged from 28.2 to 41.9%. Because alkalinity production is directly related to the presence of O_2 and CO_2, it is possible that the gas flows through the systems containing these duplicate shale samples were not identical.

statistical comparison of gas mixtures: Statistical comparisons between samples exposed to air-only and CO_2-enhanced gas mixtures were determined using paired t-tests. For each parameter, sample type, method type, and week, the difference was calculated between the mean of the two log transformed results for samples exposed to CO_2-enhanced air and the mean of the two log transformed results for samples exposed to air-only conditions. The mean of the weekly differences was then calculated for each parameter, sample and method type, and the paired t-tests were run to determine whether the mean of the differences was significantly greater or less than 0. A mean significantly greater than 0 suggests that the CO_2-enhanced gas type yields higher results than the air only gas type, while a mean significantly less than 0 suggests that the CO_2-enhanced gas type yielded significantly lower results than the air-only gas type.

With the exception of sulfate, the resulting mass and concentrations of all parameters were significantly greater in the samples exposed to CO_2-enhanced air during drying cycles. Because sulfate is the result of pyrite oxidation and is therefore influenced by the concentration of oxygen, it is not likely to be influenced by the addition of CO_2.

The results of these preliminary tests indicate that the introduction of 10% CO_2 does significantly increase alkalinity production. Most importantly, the alkalinity concentrations, particularly in samples taken from the leaching columns, are similar to the alkalinity concentrations found in mine drainage samples taken from these particular rock units in the natural environment.

Chapter 3: Second Phase of Weathering Tests (2003)

Roger J. Hornberger, Joan E. Cuddeback and Keith B.C. Brady

Following evaluation of the 2002 weathering test results described in Chapter 2, the draft methods were revised for use in the 2003 weathering tests as follows: (a) the humidity cell apparatus was constructed identical to the cylindrical leaching column apparatus, (b) the diameter of most of the leaching columns and humidity cells was reduced to 2 inches (from 6 inches in 2002), (c) the rock samples were crushed to a nominal 3/8" diameter, and procedures for reconstructing rock samples according to specified particle size partitioning were included in each method, and (d) two options were provided for exposing rock samples to the CO_2-enhanced gas mixture during saturation periods. Those two options were the introduction of a continuous flow of CO_2-enhanced air into the columns during periods of saturation as well as drying periods, and exposure to influent water saturated with CO_2-enhanced air during periods of saturation.

Rock Samples Tested

The three rock samples used in the 2003 weathering tests were: (1) the Brush Creek shale sample used in the 2002 weathering tests (and described in more detail in Chapter 2), (2) the Vanport Limestone, and (3) a Lower Kittanning coal refuse sample.

Two limestone samples were selected to serve as high-alkalinity producing end members in the 2202 and 2003 weathering tests. The Valentine limestone is the purest limestone in Pennsylvania (O'Neill, 1964) and Brady et al. (1998, p. 8-46), typically having calcium carbonate content greater than 97%. The Valentine limestone sample used in the first phase of this project during 2002 was collected from a quarry and underground mine operated in Centre County, PA. The Valentine is a marine limestone of Ordovician Age. For the 2003 weathering tests, the Vanport limestone was selected because it is a Pennsylvanian Age limestone, stratigraphically positioned between the Clarion and Lower Kittanning coals. The Vanport limestone samples were collected in a quarry and coal mining operation in Butler County, PA. The range of NP values of this sample is 900 to 916 ppt as shown in Table 3.1, while the total sulfur content is negligible.

Two coal refuse samples were selected to serve as high-acidity producing end members in the weathering tests (i.e. Ernest and Leechburg abandoned coal refuse piles). The Leechburg coal refuse samples used in 2002 were collected from the large refuse deposit associated with the abandoned underground Leechburg coal mine, and the samples used in 2003 were from an active adjacent underground mine on the Lower Kittanning coal located near the town of Apollo in Armstrong County, PA. The abandoned mine refuse site at Leechburg produces some of the most acidic mine drainage in PA as described in Hornberger and Brady (1998, p. 7-7), wherein acidity concentrations greater than 16,000 mg/L are reported. The 2002 weathering tests were conducted on samples collected from the abandoned coal refuse piles having sulfur contents between 2.42 and 4.38%. The 2003 weathering tests were conducted on samples of a fresh refuse pile at the end of a conveyor belt from the active underground mine, which have total sulfur contents greater than 6.5% as shown in Table 3.1.

Samples of a relatively inert sandstone, stratigraphically positioned between the Middle Kittanning and Upper Kittanning Coals, were collected from a quarry in Clearfield County, PA.

This lithologic unit was selected to serve as a "blank" in these weathering tests, but was not included in the 2003 weathering experiments due to financial constraints on the number of different rock types to be tested. The range in total sulfur contents of this sample is 0.03% to 0.08% as shown in Table 3.1, while the range of NP values is 14.3 to 20.9 ppt. This Middle Kittanning sandstone sample was stored in sealed containers and was used as the "blank" sample in the 2006 interlaboratory weathering tests described in Chapter 4.

Table 3.1: Sample Characterization

Description	Total Sulfur %	Fizz Rating	Neutralization Potential
SH Bucket #26 Shale PSU Brush Creek [1]	0.90	3	112.05
SH Bucket #28 Shale PSU Brush Creek [1]	0.90	3	121.42
SH Bucket #32 Shale PSU Brush Creek [1]	0.91	3	120.78
LRBT Bucket #4 Coal Refuse [2]	6.64	0	2.64
LRBT Bucket #9 Coal Refuse [2]	6.94	0	-0.39
LRBT Bucket #14 Coal Refuse [2]	7.67	0	-1.71
VLS Bucket #1 Limestone [3]	0.00	3	902.94
VLS Bucket #9 Limestone [3]	0.01	3	915.77
VLS Bucket #11 Limestone [3]	0.00	3	899.73
HSS Bucket #2 Sandstone [4]	0.08	0	20.87
HSS Bucket #8 Sandstone [4]	0.04	1	17.70
HSS Bucket #12 Sandstone [4]	0.03	1	14.29

[1] Brush Creek Shale from Route 66 road cut near Greensburg, PA

[2] Lower Kittanning Coal Refuse from Rosebud deep mine near Leechburg, PA

[3] Vanport Limestone from Allegheny Minerals mine in Butler County, PA

[4] (Not used in method evaluation) Middle Kittanning Sandstone - Hawbaker quarry in Clearfield County, PA

Study Design and Laboratory Tasks

To further evaluate performance of the draft methods, the 2003 study involved three laboratories and the three sample types described above (shale, limestone, and coal refuse). Laboratories 1 and 2 (Geochemical Testing and Mahaffey Laboratories) were tasked with evaluating (1) the two exposure scenarios (constant exposure to CO_2-enhanced air vs. exposure to water saturated with CO_2-enhanced air) and (2) the leaching column (24-hour saturation periods) vs. humidity cell (1-hour saturation periods) methods. Laboratory 3 (Materials Research Institute at Penn State University) was tasked with implementing the leaching column method using three sizes of cylindrical testing structures (i.e., 2-inch, 4-inch, and 6-inch diameter). Laboratory 3 (MRI) also performed surface area measurements, using BET methods, on each of 8 particle size classes, before and after the weathering tests, on selected lithologic units.

For a period of 15 weeks (12 weeks for Laboratory 3), each laboratory collected weekly water samples from all columns and cells, and analyzed the samples for pH, specific conductance, alkalinity, acidity, and sulfate. Samples also were filtered and analyzed for dissolved calcium, sulfate, acidity, alkalinity, iron, and manganese using EPA-approved methods. Data results of the analyses are included in Appendix D of this report.

The original type of humidity cell apparatus, used in the 2002 weathering tests, was constructed from rectangular plastic food storage containers with airtight lids. This approach was consistent with the project goals of requiring low cost materials and minimal apparatus construction. However, the humidity cells yielded consistently lower concentrations of key analytes reflecting less aggressive weathering than the leaching columns. A reason for this difference between humidity cells and leaching columns, particularly for carbonate minerals, may be the large amount of air space above the rock sample in the rectangular cells. As some humidity cell tests reported in the literature use a cylindrical apparatus resembling a short leaching column (e.g. White et al., 1994), the shape and dimensions of the humidity cells used in the 2003 weathering tests were made equivalent to the leaching columns.

Standardized Particle Size Distribution and Surface Area Measurements

The reconstruction of the particle size distribution following the crushing of each rock sample was included in the methods because variations in particle size distribution of the same lithologic unit can occur due to differences in crushing equipment, and the particle size distribution may vary significantly by rock type as shown in Table 3.2.

Table 3.2. Particle size distribution (by percent total weight) of as prepared rock samples.

	Limestone				Shale					Coal Refuse				
Lab	**1**	**2**	Mean	SD	**1**	**2**	**3**	Mean	SD	**1**	**2**	**3**	Mean	SD
***Sieve Size**														
+3/8	0.1	0.0	0	0.1	0.0	0.0	0.0	0	0.0	0.0	0.0	0.0	0	0.0
3/8-#4	40.2	41.9	41	1.2	22.5	23.7	28.8	25	3.4	46.1	49.3	54.0	50	4.0
#4-#10	25.3	26.5	26	0.8	32.6	32.1	33.4	33	0.6	27.8	23.1	23.5	25	2.6
#10-#16	12.1	9.7	11	1.7	16.4	12.8	8.1	12	4.2	10.6	9.5	7.1	9	1.8
#16-#35	8.2	10.2	9	1.4	10.8	15.7	12.2	13	2.5	6.4	9.3	8.0	8	1.4
-30+#60							10.5					5.3		
#35-#60	5.1	3.8	5	0.9	6.8	4.9			1.3	3.7	3.2			0.3
-#60	9.1	8.0	8	0.8	10.8	10.9	7		2.2	5.3	5.7	2.2		1.9

*US sieve # or equivalent mesh size; SD represents standard deviation

Since the particle size distribution of the crushed rock sample is largely an artifact of the crushing process, rather than a natural systems process (like the particle size distribution of a soil or an unconsolidated sedimentary deposit), it was determined that the standardized particle size distribution, shown in Table 3.3 would promote operational consistency of the weathering test procedures and facilitate better control in determining reaction kinetics. Regarding operational consistency of the method, large amounts of fine particles within specific zones of the leaching columns were found to impede uniform fluid flow and/or gas flow in this study, and similar problems with fines are described in Bradham and Caruccio (1990, 1995) and Hornberger and

Brady (1998). Regarding the determination of reaction kinetics, the importance of surface area to volume ratios is described in Brady et al., 2004, and other references discussed in Chapter 1 and Chapter 6, and significant differences in crushed particle size distributions and effective surface areas were found among the lithologic units tested in this study. Standardizing the particle size distribution in each leaching column and humidity cell promotes control of that variable at the start of the weathering test, and facilitates the evaluation of surface area and related kinetic variables after weathering.

Table 3.3. Particle size distribution of reconstructed samples.

Sieve Size	Percent of Total Weight
+3/8 (9.52 mm)	-
3/8 - #4 (4.76 mm)	40
#4M - #10 (2.00 mm)	25
#10 - #16 (1.19 mm)	10
#16 - #35 (0.50 mm)	10
#35 - #60 (0.250 mm)	5
-#60 (0.250 mm)	10

surface area effects on selected rock samples from 2002 and 2003 weathering tests:
Laboratory 3 performed BET surface area measurements on three distinctly different lithologic units to evaluate the effects of weathering by particle size classes and by rock type characteristics. Table 3.4 shows the particle size distributions for the Brush Creek shale and Wadesville sandstone samples used in the 2002 weathering tests and the LRBT coal refuse sample used in the 2003 weathering tests at Laboratory 3.

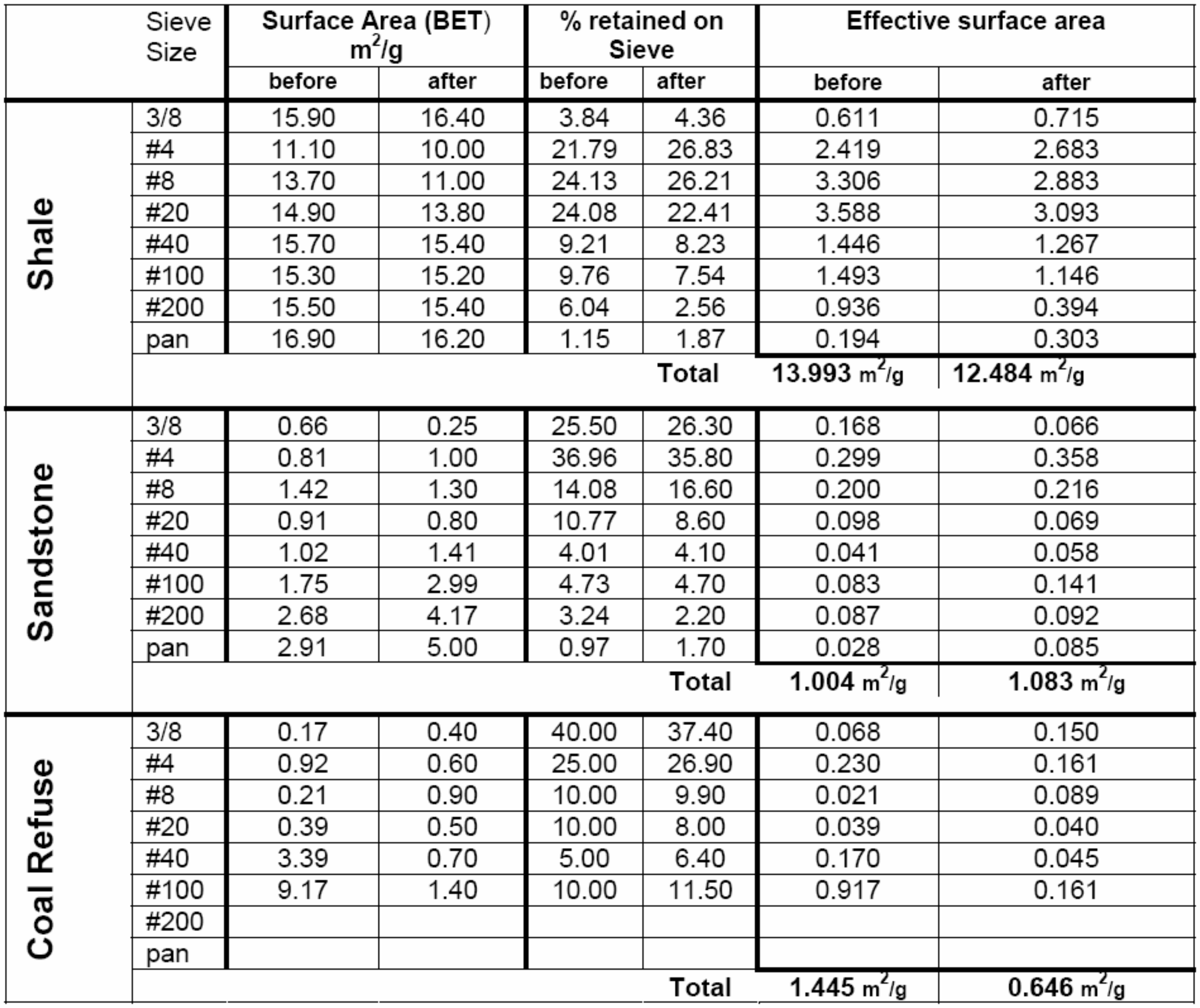
For this study, the surface area of each fraction of sieved starting material was determined by BET (Brunauer et al., 1938; Yates, 1992) instrumentation using N_2 gas bulk adsorption. This method is a routine analytical approach to measure the accessible surface of the rock to gas molecules. Additional discussion of surface area measurements and their relationships to porosity and reaction kinetics are given by Brantley and Mellott (2002), Lasaga (1984, 1998) and Brady et al., (2004).

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 were determined for the post-leaching rock by taking the individual masses of the sieve fractions specified in the protocol above, multiplying each mass by the surface area (SA), and combining their fractional percent of the total as a weighted linear average.

$$A \times SA_{\text{sieve1}} + B \times SA_{\text{sieve2}} + C \times SA_{\text{sieve3}} = SA_{\text{bulk}}$$

Where: $A + B + C = 1$
A = fraction of total sieve 1 size
B = fraction of total sieve 2 size
C = fraction of total sieve 3 size

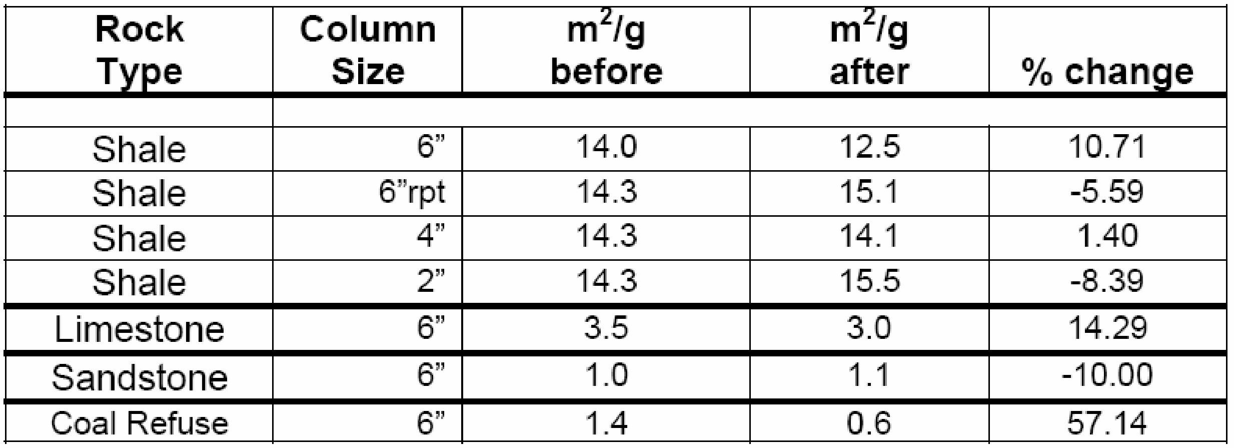
Table 3.4. Surface area measurements, sieve analysis, and calculations of effective surface areas before and after weathering tests.



	Sieve Size	Surface Area (BET) m^2/g		% retained on Sieve		Effective surface area	
		before	after	before	after	before	after
Shale	3/8	15.90	16.40	3.84	4.36	0.611	0.715
	#4	11.10	10.00	21.79	26.83	2.419	2.683
	#8	13.70	11.00	24.13	26.21	3.306	2.883
	#20	14.90	13.80	24.08	22.41	3.588	3.093
	#40	15.70	15.40	9.21	8.23	1.446	1.267
	#100	15.30	15.20	9.76	7.54	1.493	1.146
	#200	15.50	15.40	6.04	2.56	0.936	0.394
	pan	16.90	16.20	1.15	1.87	0.194	0.303
					Total	**13.993 m^2/g**	**12.484 m^2/g**
Sandstone	3/8	0.66	0.25	25.50	26.30	0.168	0.066
	#4	0.81	1.00	36.96	35.80	0.299	0.358
	#8	1.42	1.30	14.08	16.60	0.200	0.216
	#20	0.91	0.80	10.77	8.60	0.098	0.069
	#40	1.02	1.41	4.01	4.10	0.041	0.058
	#100	1.75	2.99	4.73	4.70	0.083	0.141
	#200	2.68	4.17	3.24	2.20	0.087	0.092
	pan	2.91	5.00	0.97	1.70	0.028	0.085
					Total	**1.004 m^2/g**	**1.083 m^2/g**
Coal Refuse	3/8	0.17	0.40	40.00	37.40	0.068	0.150
	#4	0.92	0.60	25.00	26.90	0.230	0.161
	#8	0.21	0.90	10.00	9.90	0.021	0.089
	#20	0.39	0.50	10.00	8.00	0.039	0.040
	#40	3.39	0.70	5.00	6.40	0.170	0.045
	#100	9.17	1.40	10.00	11.50	0.917	0.161
	#200						
	pan						
					Total	**1.445 m^2/g**	**0.646 m^2/g**

The before-weathering distributions for the shale and sandstone samples are exactly what resulted from crushing the samples; the particle size distribution for the coal refuse sample was reconstructed/adjusted to meet the specification of the revised method as shown in Table 3.3. The BET measurements of surface area for the shale are an order of magnitude greater than the sandstone and coal refuse surface areas for most size classes (except the 0.149 mm coal refuse pre-weathering). This is probably due to much greater intrinsic porosity in the shale laminae. The sandstone sample was from a very hard and well-cemented lithologic unit, thus there was little difference in the particle size distributions or surface area measurements after weathering. The coal refuse sample showed the greatest change in effective surface area of all samples tested at Laboratory 3 in the 2002 and 2003 weathering tests (Table 3.5). This change is largely due to the reduction in surface area of the two finest size classes (Table 3.4). Two factors that probably contributed to this reduction are (a) loss of fines during weekly sample collection and (b) weathering of fine-grained pyrite in these size classes.

Table 3.5. Summary of changes in surface areas after weathering.



Rock Type	Column Size	m^2/g before	m^2/g after	% change
Shale	6”	14.0	12.5	10.71
Shale	6”rpt	14.3	15.1	-5.59
Shale	4”	14.3	14.1	1.40
Shale	2”	14.3	15.5	-8.39
Limestone	6”	3.5	3.0	14.29
Sandstone	6”	1.0	1.1	-10.00
Coal Refuse	6”	1.4	0.6	57.14

calculation of SA/V ratio: The design of the column experiments allows a direct calculation of the surface area to volume ratio. The surface area for the reconstituted rock mass in the column is calculated as shown above. This quantity is then scaled to the total rock mass in the column. The volume is simply the volume of water drained from the column after each weekly 24-hour fill-and-drain cycle.

$$\frac{SA}{V} = \frac{1000\, m\, SA_{Bulk}}{V}$$

Where:

SA/V = surface area to volume ratio (meters $^{-1}$)
m = mass of solids in column (grams)
SA $_{Bulk}$ = BET surface area of solids (meter-squared/gram)
V = volume of leachate from each drain cycle (liters)

The significance of the surface area to volume ratio in leaching processes is described in Machiels and Pescatore (1983), Pederson et al., (1983), White (1986) and Scheetz et al., (1981).

Method Preparation, Implementation and Results

The laboratories assembled leaching columns and humidity cells as described in Figure 3.1 from the draft leaching column method (see Appendix A of this report). Samples were reconstructed after sieving according to the particle size distributions presented in Table 3.3 above. To provide an assessment of method precision, Laboratories 1 and 2 prepared duplicate Shale and Coal Refuse samples for exposure to identical weathering conditions. Table 3.6 presents the weight of each sample added to each leaching column/humidity cell exposed to either constant flow of CO_2-enhanced air or CO_2-Air saturated water during wet weathering conditions.

The leaching column and humidity cell weathering procedures were conducted for a period of 15 weeks in the three laboratories. Evaluations were made of: (a) the two options for introducing the CO_2-enhanced gas mixture into the leaching columns, (b) laboratory performance on duplicate samples by calculation of relative percent differences (RPD’s) and relative standard

deviations (RSD's), (c) the leaching effectiveness of the column and humidity cell methods
(d) the effect of removing the fines (i.e. 2 smallest particle size classes < #35 mesh), and
(e) influence of different leaching column diameters (i.e. 2", 4" and 6"). The concentration data for leaching column and humidity cell effluent for the 3 rock types are presented in Appendix D.

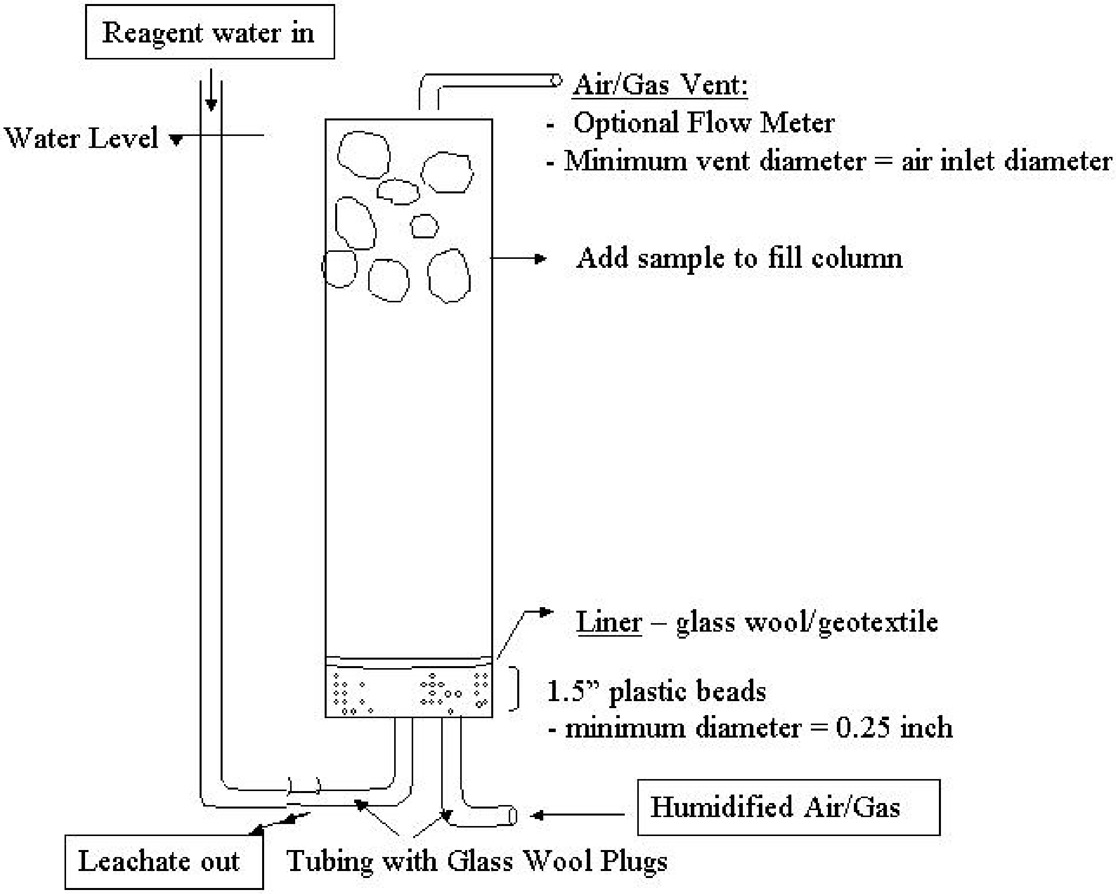


Figure 3.1. Revised Leaching Column Design.

comparison of the two gas mixture options: Statistical comparisons between samples exposed to a constant flow of CO_2-enhanced air and those exposed to reagent water saturated with Co_2-enhanced gas mixture during wet weathering were determined using paired t-tests. For each parameter, sample type, method type, and week, the difference was calculated between the mean of the results for duplicate samples exposed to constant CO_2-enhanced air and the mean of the results for duplicate samples exposed to saturated reagent water. The mean of the weekly differences was then calculated for each parameter, sample and method type, and paired t-tests were run to determine whether the mean of the differences was significantly greater or less than 0. Sample results were evaluated as (1) straight concentrations, and (2) "normalized" to account for the volume of sample collected and the weight of sample exposed to weathering. Sample results were normalized by multiplying concentration by the volume of sample collected, then dividing by the total weight of the sample to obtain mg/kg.

Table 3.6: Sample Weights (in grams)

		Column		Cell		
Lab	**Sample**	**CO_2-Air Constant Flow**	**CO_2-Air - Saturated H_2O**	**CO_2-Air Constant Flow**	**CO_2-Air - Saturated H_2O**	**Total # Samples**
1	Shale	1770.45 1765.24 1583.11 [1]	1764.77 1764.84	-	1764.97 1764.93	7 (3 duplicate pairs, one extra)
	Coal Refuse	-	1129.52 1129.48	-	1130.42 1129.51	4 (2 duplicate pairs)
	Limestone	1771.11	1765.52	-		2
2	Shale	2025.3 2025.4	1873.8 2025.5	-	2054.4 2054.1	6 (3 duplicate pairs)
	Coal Refuse	-	1278.1 1278.4	-	1278.4 1278.1	4 (2 duplicate pairs)
	Limestone	2008.6	2008.1	-	-	2
3	Shale [2]	1198 (2” column) 5430 (4” column) 12,608 (6” column)	-	-	-	1

[1] Lab 1 prepared an extra Shale sample small particle fractions removed (<35M sieve).

[2] Lab 3 evaluated Shale in three leaching columns of varying diameters (2-inch, 4-inch, and 6-inch)

Comparisons were made on alkalinity, sulfate, calcium and conductivity. Results of the paired t-tests indicate that for all four parameters, mean concentrations were significantly greater for samples exposed to a constant flow compared to those exposed to the saturated water (i.e. significant at the 99% confidence interval). A graph depicting the comparisons run on alkalinity results for the two gas mixture scenarios is shown in Figure 3.2.

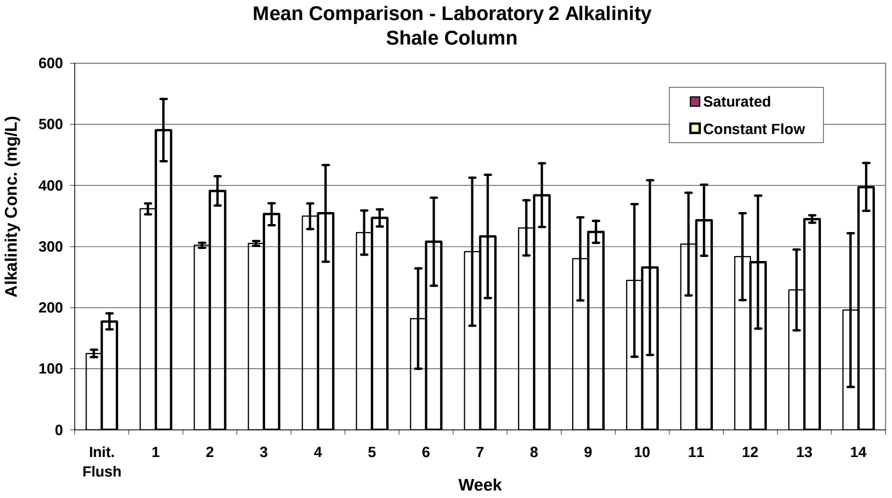


Figure 3.2. Alkalinity concentrations of two gas mixture scenarios.

In this Figure, the vertical lines extending symmetrically in each direction from the average concentration result (top of each column) represent the range of results from the duplicate samples. In Figure 3.2, the alkalinity concentrations produced by the constant-flow scenario generally appear to be 50 to 100 mg/L higher than those produced by the CO_2-saturated water scenario. Paired t-tests also were performed on normalized results, but there were no significant differences between samples exposed to constant flow and samples exposed to the saturated gas mixture for any of the four parameters in Laboratory 1. For Laboratory 2, however, normalized results were significantly higher for samples exposed to the CO_2-saturated water compared to those exposed to constant gas flow.

Figure 3.3 is a comparison of calculated PCO_2 among the three labs for the columns with continuous air flow. Horizontal lines within the "boxes" are medians and the values are plotted next to the box. The "boxes" extend from the 25th to 75 percentile of data and thus encompass the middle 50% of the data. "Whiskers" (the vertical lines) show the range of the data to 1.5 times the interquartile range. Asterisks indicated statistical outliers.

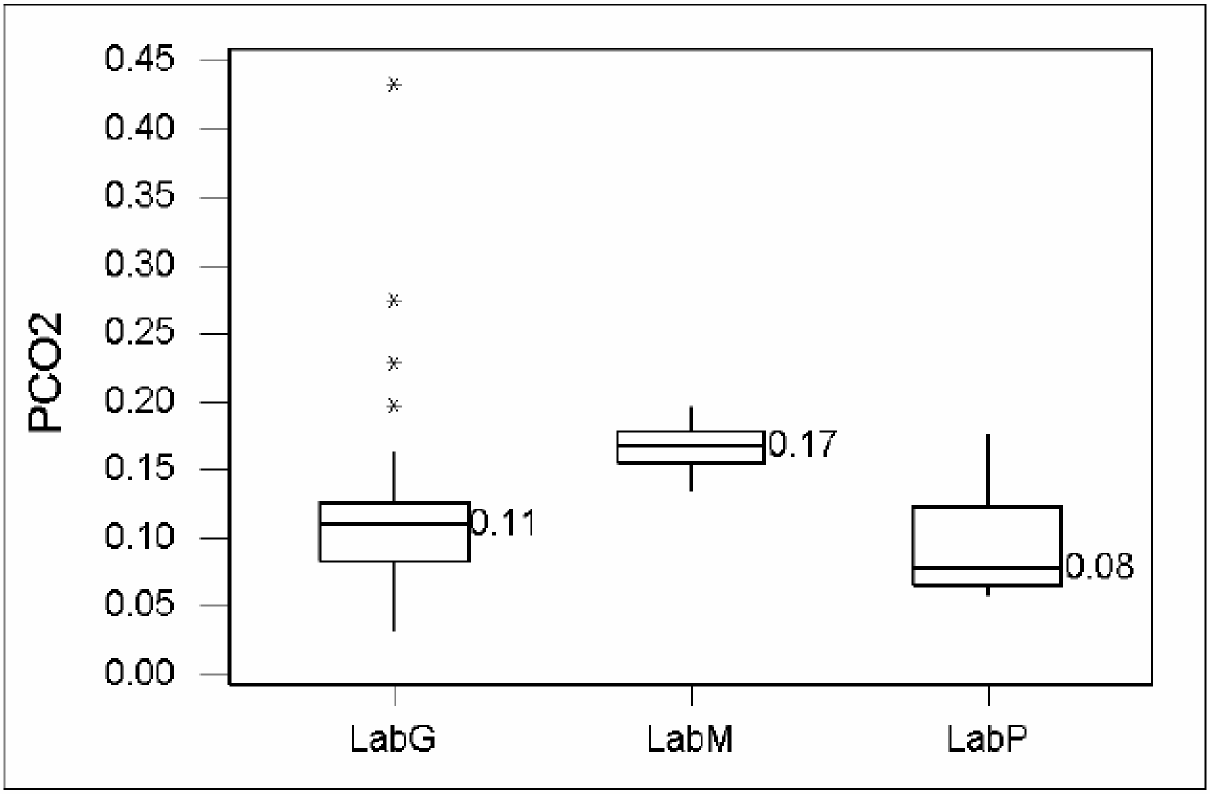


Figure 3.3. Comparison of PCO_2 among laboratories for the leaching columns that had continuous flows of 10% air.

comparison of duplicate samples: The precision of the methods was assessed using concentration results of duplicate samples exposed to identical weathering procedures. Relative percent differences (RPD) were calculated for results of duplicate samples prior to implementation of method procedures (initial flush at week 0) and as pooled RPDs for all sample weeks beginning with week 1 through week 14. Pooled RPDs were determined as the square root of the average squared weekly (weeks 1 to 14) RPDs for each parameter. For Laboratory 1, pooled RPDs ranged between 3.3 and 41.5%. For Laboratory 2, pooled RPDs ranged between 6.5 and 50%. These ranges were based on concentrations of alkalinity, sulfate, calcium and conductivity measured in shale samples, and on concentrations of acidity, sulfate, conductivity, calcium, manganese and iron measured in coal refuse.

In addition to calculating RPDs between the measured concentrations of the duplicate samples, RPDs were also calculated using normalized results. Pooled RPDs based on normalized results ranged from 7.5 to 47% for Laboratory 1, and from 8.5 to 50.2% for Laboratory 2. Out of 96 pooled-RPD results from the two laboratories, 26 were above 30%. It is important to note that EPA methods often include RPD performance criteria of up to 30% for duplicate analyses.

comparison of leaching column and humidity cell methods: Results of samples exposed to humidity cell weathering procedures (exposure to 1-hour wet weathering) were compared to the results of samples exposed to leaching column weathering procedures (24-hour wet weathering) to determine if increased sample immersion in water produces significantly more of the target parameters. Based on results of this analysis, shale samples were affected by method type most significantly in terms of alkalinity and conductivity. Conductivity and alkalinity concentrations were significantly greater in leaching columns than humidity cells for both laboratories. Calcium concentrations from shale samples also were significantly greater in leaching columns evaluated in Laboratory 1 but not in Laboratory 2. The method type did not have a significant effect on sulfate for either laboratory. Normalization had little effect on the results of this analysis.

The type of weathering method had a lesser effect on coal refuse samples than on shale samples. In general, these results show that the leaching column weathering procedures are more aggressive than the humidity cell procedures.

effects of removal of small particle size fraction: In addition to the duplicate shale samples evaluated using leaching columns by Laboratory 1, a third sample was also analyzed. Unlike the duplicate pair, this third column did not include particles less than 35 mesh. Based on the results of the paired t-tests, removal of fine particles decreased the concentration of sulfate, calcium and conductivity significantly, but did not have a significant effect on alkalinity. These results did not change after data normalization.

Figure 3.4a displays the effect of fine particle removal on sulfate concentration. The difference in sulfate concentrations between the column without the fines and the columns with fines at week 1 (approximately 275 mg/L) showed that the concentration of sulfates in the column without fines decreases steadily until week 9, and in weeks 13 and 14 the difference is less than 50 mg/L. This may be due to a depletion of the fines in the other columns as a result of the weathering process. However, it is uncertain whether this convergence of sulfate plots in the last 5 weeks in Figure 3.4a is due to: (a) a reduction or consumption of fine particles by dissolution (e.g. carbonate minerals) or some other weathering process, (b) a reduction in the reactivity of remaining fine particles (e.g. sulfur/sulfate depletion) or (c) the loss of fine particles during weekly leachate collection procedures (leaving the columns as suspended solids in the leachate).

Figure 3.4b shows that the removal of fine particles from the third constant-flow leaching column had essentially no effect upon alkalinity concentrations produced by the Brush Creek shale samples. The time plots of the three constant-flow columns in Figure 3.4b are nearly identical, and represent consistently higher alkalinity concentrations than the pairs of columns and humidity cells with CO_2-saturared influent water. These findings support the principle that the major factors controlling alkalinity production from a rock sample with a high neutralization potential are the solubility of the carbonate minerals and the partial pressure of carbon dioxide in the system (i.e. in the pore spaces in the leaching column or in the spoil gas mixture in a mine environment). The concentration of alkalinity produced tends to be independent of particle size and surface area, if sufficient time is available to reach saturation. Saturation with respect to $CaCO_3$ was reached in all instances within the 24-hours that the sample was inundated with water. The ultimate alkalinity that can be produced under inundated conditions is a function of the PCO_2, whereas, the major factors controlling sulfate (and acidity) production from a rock sample with appreciable total sulfur content include particle size and surface area.

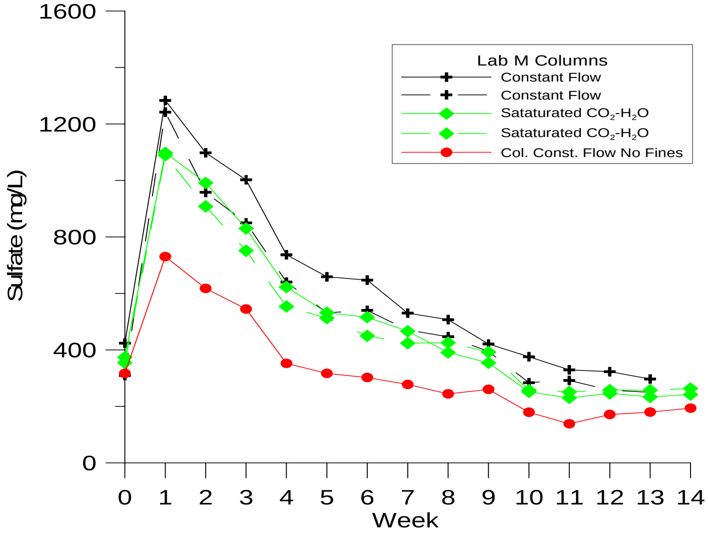


Figure 3.4a. Effects of fine particle fractions on sulfate production in shale.

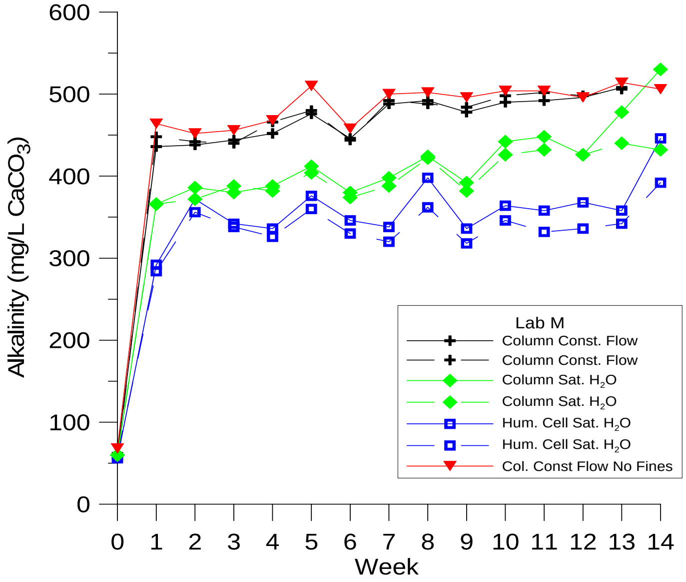


Figure 3.4b. Effects of fine particle fractions on alkalinity in shale.

effect of varying leaching column diameter: Comparison of Column Sizes (2-inch, 4-inch, and 6-inch diameters). Laboratory 3 evaluated the effects of the leaching column weathering procedures on samples of shale in three cylindrical column structures of identical height (24-inches) and different diameters (2-inch, 4-inch, and 6-inch). Results of this comparison are presented in Figures 3.5a and 3.5b. A comparison of the effect of leaching column sizes upon analyte concentrations showed that mean and maximum alkalinity concentrations produced from the shale sample in the 6 inch column were not greater than those corresponding to the smaller column diameters. Curiously, the calcium concentrations produced in the leachate from the 2 inch and 4 inch columns declined significantly through time, while that from the 6 inch column did not decline – resulting in a much higher median calcium concentration from the 6 inch column.

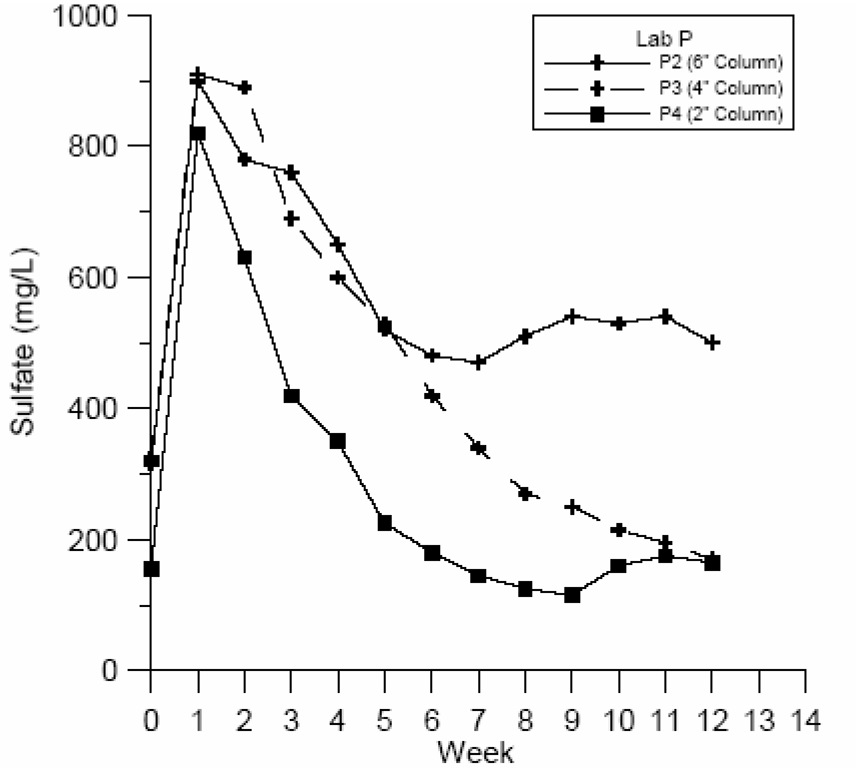


Figure 3.5a. Sulfate concentrations of Brush Creek shale using two inch, four inch, and six inch column diameter.

Figures 3.4 and 3.5 show concentrations of sulfate and alkalinity through time for the Brush Creek shale from various leaching columns. Sulfate concentrations from the three diameters of leaching columns at Lab 3 are plotted in Figure 3.5a. These plots resemble the classic leaching behavior shown in White (1986), with the steep initial slope, followed by supersaturation, and then a flattening (6-inch column) or decline (2-inch and 4-inch columns) in concentration through time for the remainder of the weathering test. Notice that these plots do not originate at zero, they extend to negative weeks time, indicating that weathering of the shale samples commenced prior to the start of the leaching column tests (i.e. prior to the initial flush).

Figure 3.5b is the time plot of alkalinity concentrations of the Brush Creek shale from leaching columns. The plots resemble the leaching behavior of a combination of the initial linear and latter diffusion-controlled mechanisms, shown in White (1986). Laboratory 3, which evaluated different diameter columns, had similar alkalinities in the three columns.

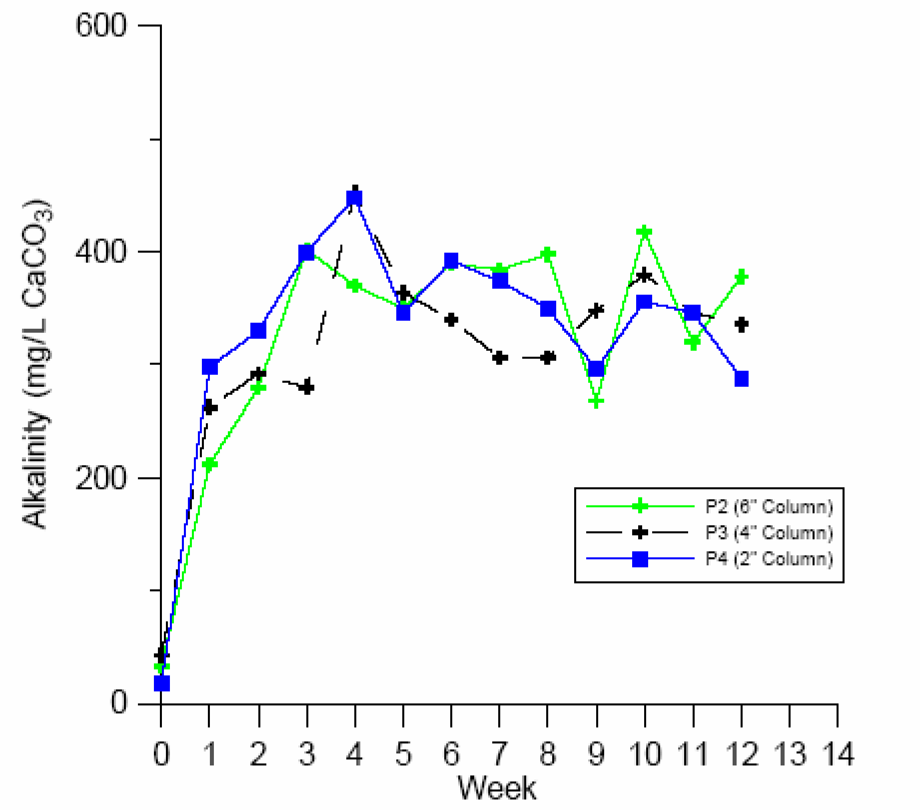


Figure 3.5b. Alkalinity concentrations of Brush Creek shale using two inch, four inch, and six inch column diameter.

Conclusions:

The results of this second phase of weathering tests 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: Results of Interlaboratory Study

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Background

In November 2001, a project team consisting of the U.S. Department of Interior's Office of Surface Mining (OSM), U.S. Environmental Protection Agency (EPA), Pennsylvania's Department of Environmental Protection (PADEP), and Computer Sciences Corporation (CSC, formerly DynCorp Systems and Solutions) drafted ADTI-WP1 (Humidity Cell) and ADTI-WP2 (Leaching Column) test methods for predicting the quality of mine drainage. The methods were based on weathering procedures already used by the mining industry and mine drainage researchers, and were designed to be cost efficient and practical.

During 2001 - 2003, the methods were tested in two studies, involving three laboratories, to evaluate the effects of weathering conditions on samples of shale, limestone, sandstone, and coal refuse. These studies and the resulting data are described in *Development of Test Methods for Prediction of Coal Mine Drainage Water Quality*, August 2002 and *Development of Test Methods for Prediction of Coal Mine Drainage Water Quality*, September 2003. Results of this testing demonstrated cylindrical (column) test structures (as opposed to rectangular humidity cells) and continuous exposure to humidified mixed gas facilitated uniform sample exposure to weathering conditions. The draft ADTI-WP2 Column Test Method was revised to reflect the results of these studies, and the revised method was distributed for expert review by representatives of the U.S. Bureau of Land Management, U.S. Department of Energy, Minnesota Department of Natural Resources, University of South Carolina, Pennsylvania State University, and the Western Research Institute.

Following test method review and evaluation of the 2001 - 2003 study results, the draft method was revised as follows:

- Relative percent differences (RPDs) between results of duplicate samples exposed to identical weathering conditions were included based on results of duplicate samples run in each of two laboratories that can be expected when implementing method procedures.
- Procedures for reconstructing samples according to particle size partitioning were included.
- Previous draft included two options for exposing samples to CO_2-enhanced air during saturation periods: (1) continuous flow of CO_2-enhanced air, and (2) exposure to water saturated with CO_2-enhanced air. The method was revised to specify use of Option 1 only.
- The diameter of the leaching columns was revised to 2 inches (from six inches).

- In order to assess the effects of the weathering conditions on overburden samples, it is important to remove residual target analytes from the samples prior to method implementation. Once samples were added to the leaching columns, the systems were flushed with reagent water until the reagent water demonstrated stable conductivity results (i.e., changes in conductivity ≤10%).

This report 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. Study results will be used to revise the draft method to include improved procedures and criteria for evaluating method performance in a single laboratory.

Study Description

Sample Collection and Characterization

The draft test method is intended for use in evaluating the effects of weathering on consolidated rock or mining overburden samples with geochemical characteristics that fall into a gray zone (e.g., containing moderate amounts of neutralization potential and sulfur) in cases where more information is needed than can be provided by acid/base accounting. For these sample types, acidity or alkalinity production is difficult to predict, and more information is needed than can be provided by typical leachate or acid base accounting tests. To represent this gray zone and at the same time include some geological diversity across study samples, aliquots of the following samples were provided to each of eight laboratories participating in the method validation study:

- **Brush Creek Shale (BCS3-PA):** Brush Creek Shale from Route 66 road cut near Greensburg, PA. Selected because it is well known and because of its high alkalinity and total sulfur content.
- **Kanawha Black Flint Shale (KBF-WV):** Kanawha Black Flint Shale. Selected with the assistance of West Virginia (WV) University National Research Center for Coal and Energy and the WV Department of Environmental Protection as a gray-zone shale sample from a terrain where selenium problems are believed to occur. [Note: Results of rock characterization performed concurrent with this interlaboratory study demonstrated that this sample contained low NP and sulfur.]
- **Lower Kittanning Shale (LKFC-PA):** Lower Kittanning Shale from the Redbank Creek watershed in Pennsylvania. Selected because coal and overburden in this watershed are known to produce alkaline drainage even though the neutralization potential (NP) is not high.
- **Houchin Creek Shale (HCS-IN):** Houchin Creek Shale from the Eastern Interior Coal Basin. Selected with input from OSM, as a gray zone sample containing high sulfur and low NP, but producing alkalinity.
- **Middle Kittanning Sandstone (MKSS-PA):** Middle Kittanning Sandstone from Hawbaker quarry in Clearfield County, PA. Selected for use as a blank study sample, because of its expected low production of target analytes (i.e., low sulfur and relatively low NP).

Laboratories evaluated duplicate columns of each of the four shale samples and a single column containing Middle Kittanning Sandstone.

Prior to exposure to the weathering conditions in the draft method, sample aliquots were selected randomly for analysis of neutralization potential. Results of these analyses are presented in Table 4.1.

Table 4.1: Sample Characterization

Sample	**Neutralization Potential**		
	Total Sulfur (%)	1978 (1) (ppt)	1997 (2) (ppt)
Brush Creek Shale (BCS3-PA) - 1	0.59	96.97	49.68
Brush Creek Shale (BCS3-PA) - 2	0.59	96.96	49.31
Brush Creek Shale (BCS3-PA) - 3	0.56	96.98	47.61
Brush Creek Shale (BCS3-PA) - 4	0.59	96.97	47.07
Kanawha Black Flint Shale (KBF-WV) - 1	0.35	15.17	13.17
Kanawha Black Flint Shale (KBF-WV) - 2	0.30	16.76	13.34
Kanawha Black Flint Shale (KBF-WV) - 3	0.21	17.17	13.65
Kanawha Black Flint Shale (KBF-WV) - 4	0.32	18.69	14.26
Lower Kittanning Shale (LKFC-PA) - 1	0.93	12.71	15.63
Lower Kittanning Shale (LKFC-PA) - 2	0.90	16.47	16.36
Lower Kittanning Shale (LKFC-PA) - 3	0.89	12.57	15.65
Lower Kittanning Shale (LKFC-PA) - 4	0.92	12.41	16.06
Houchin Creek Shale (HCS-IN) - 1	5.27	41.85	41.05
Houchin Creek Shale (HCS-IN) - 1	5.21	41.29	45.27
Houchin Creek Shale (HCS-IN) - 1	4.73	45.87	47.55
Houchin Creek Shale (HCS-IN) - 1	5.10	47.53	48.27
Middle Kittanning Sandstone (MKSS) - 1	0.08	20.9	-
Middle Kittanning Sandstone (MKSS) - 2	0.04	17.7	-
Middle Kittanning Sandstone (MKSS) - 3	0.03	14.3	-

(1) Results obtained using 1978 NP method (Sobek, et al., 1978).
(2) Modified neutralization potential method (Skousen, et al., 1997).

Laboratory Tasks

To evaluate method performance in multiple laboratories, and to ensure the generation of at least six useable datasets [1] the 2006 study involved seven 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 laboratory 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. An eighth participating laboratory joined the study during the third week of the 15-week study period.

This laboratory was responsible for measuring conductivity, pH, alkalinity, net acidity, metals, and sulfate in all weekly leachate samples generated in that laboratory. All eight participating laboratories also recorded daily measurements of room temperature, gas flow into each column, and %CO_2 discharge from each column.

The analytes to be measured by laboratories and the analytical methods used are listed in Table 4.2. Data results of the analyses are included in Appendix E.

Table 4.2: Analytes Measured and Analytical Methods Used

Frequency	Analyte	Analytical Method
Daily	Room temperature	EPA Method 150.1; Standard Methods 4500-H; ASTM D1293; USGS I-1586
	Gas inlet flow rate	Rotameter attached between humidified gas source and column
	%Carbon dioxide (CO_2) discharge	Portable meter capable of measuring 10% CO2 with a tolerance of +/- 2%
Weekly	pH	EPA 150.1; Standard Methods 4500-H; ASTM D1293; USGS I-1586
	Conductivity	EPA 120.1; Standard Methods 2510B; ASTM D1125; USGS I-1780
	Net acidity	EPA 305.1; Standard Methods 2310; ASTM D1067
	Alkalinity	EPA 310.1, 310.2; Standard Methods 2320B; ASTM D1067; USGS I-1030, I-2030
	Dissolved metals (Al, Ca, Fe, K, Mg, Mn, Se, Zn)	EPA Method 200.7
	Dissolved sulfate (SO_4)	EPA Method 300.0

Method Preparation

column construction: Column assemblies for all but two of the participating laboratories were constructed in a single laboratory familiar with implementation of method procedures from participation in the 2003 evaluation study. This laboratory constructed setups for Laboratories 2, 3, 4, 5, 6, 7 and 8, each setup consisting of nine columns, nine flow meters (one flow meter attached to each of nine columns) a carboy (for introduction of the humidified gas mixture), and all necessary tubing, clamps, and seals. An example of these assemblies is provided in Figure 4.1. Because Laboratory 1 initiated weathering procedures approximately 3 months prior to Laboratories 2 through 8, this laboratory was responsible for construction of their column assemblies.

column preparation: The size of the particles within each sample being evaluated is a contributing factor to the effects of exposure to weathering (i.e., the smaller the particle size, the greater the surface area exposed). For this reason, and because particle size distributions within the samples that will be evaluated using this method are largely the result of mechanical sample crushing, the method developers have determined that the method should include a procedure for reconstructing samples according to a standardized particle-size distribution. This standardized distribution can facilitate comparison of the effects of weathering on various sample types. Laboratories participating in this study were tasked with preparing samples for each column according to the particle-size distributions listed in Table 2 of the draft method and in Table 4.3 below.

Table 4.3: Particle Size Distribution of Reconstructed Samples

U.S. Sieve # (or equivalent mesh size)	Percent of Sample (by weight)
3/8" to 4	40
4 - 10	25
10 - 16	15
16 - 35	10
35 - 60	5
Less than 60	5
Total	**100**

To provide an assessment of method precision, laboratories were tasked with preparing aliquots of each shale samples for exposure to identical weathering conditions in separate duplicate columns. Laboratories were also tasked with preparing a sandstone sample to evaluate weathering effects in a sample known to produce only small amounts of target analytes (i.e., contain low sulfur and relatively low NP).

Method Evaluation

Laboratories evaluated column test procedures as written and according to study requirements, with the following exceptions:

- **sample duplicates:** Laboratories were instructed to evaluate weathering procedures in duplicates of all four shale samples and in a single sandstone sample. Laboratory 8 evaluated procedures in duplicates of three of the four shale samples, in duplicates of the sandstone sample, and a single Kanawha Black Flint Shale sample.

- **study schedule:** Due to laboratory contracting schedules, not all laboratories were available to initiate study activities concurrently. Six of the eight participating laboratories initiated the test procedure on January 9, 2006. Laboratory 1 began the study approximately 12 weeks before these laboratories, using a slightly different column construction. Laboratory 8 began method activities approximately 4 weeks following study initiation, performing metals analysis in the laboratory rather than sending samples to the metals laboratory.

- **net acidity and alkalinity measurements:** Laboratories were instructed to measure net acidity and alkalinity in weekly leachate samples using methods listed in Table 4.2. Laboratory 6 did not measure net acidity and measured alkalinity in samples using indicator paper. For this reason, alkalinity and acidity results from this laboratory were not comparable to results generated in the other participating laboratories and were not used in determining method performance.
- **initial flush of samples:** Section 7.4.1 of the method describes procedures for performing an initial flush of the samples prior to exposing the samples to weathering procedures. This initial flush is intended to remove precipitates and salts that may have accumulated during sample storage. Laboratories flushed each column with reagent water, from three to four times during this initial flush period. With the exception of Laboratory 8, laboratories reported the volume of water added and removed from each column during the initial flush.
- **weekly saturation:** Columns in Laboratory 1 were exposed to a two-week period of saturation during Weeks 13 and 14. Laboratory 1 results submitted during these weeks are not comparable to results submitted by other laboratories, and were therefore eliminated from method performance evaluations.
- **metals measurements:** Analytical results for measurement of metals in samples from Laboratories 1 through 7 were reported in µg/L by the metals laboratory. Laboratory 8 reported analytical results for measurement of metals in mg/L. These results were not comparable to the results reported µg/L and therefore, were not included in determinations of interlaboratory RPD or relative standard deviation (RSD).

Figure 4.1 Leaching Column Assembly.

Data Results and Evaluation

The precision of this test method is dependent on numerous factors, including but not limited to:

- sample reconstruction and compaction,
- water volumes added and collected,
- total sample weight,
- column preparation,
- exposed surface areas,
- particle surface area to volume ratio,
- partial pressure of CO_2,
- mixed gas introduction, and
- results of water analyses (e.g., analytical precision for metals, acidity, alkalinity, sulfate, conductivity, pH).

Results of the interlaboratory study were used to evaluate and improve the test method, and to determine the precision that can be expected in a single laboratory implementing method procedures using duplicate samples. Single laboratory precision is determined as:

$$RPD = \frac{|C1 - C2|}{(C1 + C2)/2} * 100\%$$

Where:
C1 = result in original sample
C2 = result in duplicate sample

Single laboratory RPDs, representing the community of laboratories that are expected to use this method, were determined by pooling the RPDs resulting from duplicate columns across all the interlaboratory results according to the following equation:

$$RPD_{pool} = \sqrt{\frac{1}{m}\sum_{i=1}^{m} RPD_i^2}$$

Where:
RPD_i = the RPD for laboratory *i*
m = the number of laboratories

To compensate for the effects of sample size and of the volume of water collected from each column, RPDs were determined in terms of both analyte concentration (weight of analyte per volume of water analyzed) and weighted results (analyte concentration multiplied by the volume of water collected and divided by total sample weight). RPD results are presented in a later section of this chapter.

Precision that can be expected in multiple laboratories testing replicate (more than two duplicate) samples also was evaluated in terms of RSD in both concentration and weighted results in replicate samples across laboratories. RSDs and pooled RSDs were determined using the following equations:

$$RSD = \frac{StDev(C_1,...,C_n)}{Mean(C_1,...,C_n)} * 100\%$$

<u>Where</u>:
C_1 = The original sample result from Laboratory 1
C_2 = The duplicate sample result from Laboratory 1 (or the original sample result from Laboratory 2 if no duplication)
C_n = The duplicate sample result from Laboratory 7 (or the original sample result from Laboratory 7 if no duplication)

$$RSD_{pool} = \sqrt{\frac{1}{n_t - m}\sum_{i=1}^{m}(n_i - 1) * RSD_i^2}$$

<u>Where</u>:
RSD_i = the RSD for laboratory *i*
m = the number of laboratories
n_i = the number of measurements for laboratory i
n_T = the total number of measurements over all laboratories

The effect of the test method on the production of the analytes discussed in this report also was evaluated, but that evaluation is not the subject of this report. Detailed results of this study are presented in Appendix E.

Water Volumes

Laboratories reported the volume of water that was added to and collected from each column throughout the study, including during the initial flush. Volumes were used to evaluate data in terms of weighted results and to provide information regarding the amount of water remaining in the columns. Volumes also were used to assess the amount of water absorbed by samples during the initial flush, prior to sample weathering. Tables 4.4a through 4.4e present the volume (mL) of water remaining in each column throughout the study (determined by subtracting the volume collected from the volume added). Detailed Volume In / Volume Out measurements are provided in Appendix E. Volumes added to columns in Laboratory 8 were not reported, and therefore, are not included in this evaluation.

Fifty three of the fifty five columns run in Laboratories 1 through 7 retained significantly more water during the initial flush period than during any of the subsequent testing weeks. The exceptions were one HCS-IN column run in Laboratory 6 and one KBF-WV shale column run in Laboratory 3. Excluding these two columns, volumes of water added by laboratories during the initial flush ranged from 940 to 2406 mL; volumes collected ranged from 197 to 2177 mL. Volume differences indicate that columns retained from 85 to 1098 mL of water during the initial flush period, and that water volumes overall were retained in all columns. Columns in Laboratory 1 retained the most water (500 – 1098 mL) out of all other columns during the initial flush and retained much of that water throughout the 15 weeks; with only one HCS-IN sample from Laboratory 3 coming close at 566 mL initially. The different column packing technique of Laboratory 1 could account for this water retention. Differences also indicate that collection of retained water volumes during a subsequent collection period (indicated by negative Volume Added – Volume Collected results) occurred across several laboratories through approximately Week 6, but most often through Week 3.

In evaluating the analytical results submitted during this study, it is assumed that the concentration of analytes measured is consistent throughout the aqueous phase within each column (i.e., the concentration of each analyte measured in the sample volume collected is representative of the concentration of the analyte in the water throughout the column). It is also assumed that analytes will continue to partition or dissolve into any water that is retained in the column. With these assumptions in mind, it is important to note that the amount of water that is added, collected, and retained in each column must be considered as a variable affecting sample discharges. This is true irrespective of the sample being evaluated. It is also important to note that evaluation of data in terms of weighted results (analyte concentration, multiplied by the volume of water collected and divided by total sample weight) will compensate for the volume of water collected and the sample weight, but will not compensate for the impact of water retained from a previous week or weeks.

Table 4.4a: Houchin Creek Shale Volume Differences

Sample ID: HCS-IN														
	Lab 1		Lab 2		Lab 3		Lab 4		Lab 5		Lab 6		Lab 7	
	Sample Weight (grams)													
	2000	*2000*	*1298*	*1589*	*1521*	*1489*	*1487*	*1515*	*1482*	*1521*	*1361*	*1410*	*1412*	*1487*
Week	**Volume (mL) Remaining In Column (Volume of Water Added - Volume of Water Collected)**													
Initial	1098	1024	230	390	475	566	220	300	267	252	85	245	310	315
1	25	-41	-15	-45	54	-55	25	20	125	75	90	115	90	180
2	35	16	25	-55	81	93	30	20	56	95	-65	-40	140	10
3	17	31	-10	5	17	-115	25	50	54	123	35	65	284	160
4	28	20	25	20	52	107	70	55	76	50	45	50	120	190
5	71	52	5	0	102	26	35	35	58	49	-10	15	182	120
6	40	38	-5	5	58	75	40	25	69	82	65	80	240	172
7	28	33	10	50	125	194	50	40	57	78	10	5	246	240
8	25	46	15	10	131	27	55	60	84	100	20	10	210	210
9	60	64	15	5	28	10	65	60	90	73	10	80	85	100
10	82	14	10	5	73	42	60	40	80	84	40	65	85	120
11	35	40	10	20	34	37	45	55	60	55	25	55	70	110
12	84	62	5	15	28	24	55	60	75	88	35	20	125	75
13	-	-	5	10	14	-8	80	55	103	115	40	75	130	80
14	56	7	0	5	19	10	60	50	59	43	5	0	200	200
Net	**1684**	**1406**	**325**	**440**	**1291**	**1033**	**915**	**925**	**1313**	**1362**	**430**	**840**	**2517**	**2282**

Table 4.4b: Kanawha Black Flint Shale Volume Differences

Sample ID: KBF-WV														
	Lab 1		Lab 2		Lab 3		Lab 4		Lab 5		Lab 6		Lab 7	
	Sample Weight (g)													
	2000	*2000*	*1653*	*1883*	*1819*	*1849*	*2055*	*2039*	*2079*	*2056*	*1999*	*2002*	*1862*	*1912*
Week	**Volume (mL) Remaining In Column (Volume of Water Added - Volume of Water Collected)**													
Initial	824	848	270	235	305	12	260	155	322	235	345	300	345	315
1	-87	-55	-35	-20	51	52	25	30	66	50	35	35	155	245
2	34	23	0	20	125	69	15	20	35	35	15	15	240	90
3	45	30	5	0	22	11	40	35	28	39	45	45	209	215
4	22	23	25	25	23	34	30	45	37	17	60	55	245	175
5	25	31	-5	0	79	58	50	35	81	65	25	35	200	170
6	36	60	0	0	38	46	40	30	63	71	55	65	190	170
7	29	46	0	25	49	38	40	30	74	68	35	-5	140	160
8	36	35	10	30	39	45	50	50	64	61	45	60	77	255
9	28	38	5	5	27	25	50	50	100	82	60	40	60	4
10	23	60	10	10	44	30	30	15	78	73	30	55	50	20
11	29	28	10	5	42	32	70	30	66	50	20	70	30	50
12	22	44	5	5	51	76	50	50	54	61	160	55	20	15
13	-	-	5	5	22	10	60	70	65	55	5	25	20	80
14	29	50	5	5	28	44	55	50	67	50	100	65	60	100
Net	**1095**	**1261**	**310**	**350**	**945**	**582**	**865**	**695**	**1200**	**1012**	**1035**	**915**	**2041**	**2064**

Table 4.4c: Brush Creek Shale Volume Differences

Sample ID: BCS3-PA														
	Lab 1		Lab 2		Lab 3		Lab 4		Lab 5		Lab 6		Lab 7	
	Sample Weight (grams)													
	2000	*2000*	*1802*	*1807*	*1691*	*1828*	*1850*	*1922*	*1879*	*1904*	*1833*	*1859*	*1900*	*1836*
Week	**Volume (mL) Remaining In Column (Volume of Water Added - Volume of Water Collected)**													
Initial	918	1061	217	215	229	415	195	260	206	228	295	300	225	350
1	105	96	-40	-10	70	82	3	30	86	79	70	75	70	175
2	0	27	10	10	95	51	20	25	-10	15	5	-5	100	100
3	72	68	10	10	18	34	25	15	49	70	35	35	55	45
4	34	16	35	20	66	69	35	30	25	31	80	65	160	50
5	31	88	10	5	81	61	40	45	100	66	5	15	175	50
6	67	36	5	15	91	86	40	40	56	72	65	95	180	180
7	64	55	20	10	95	69	35	35	70	66	50	0	40	110
8	65	29	10	0	17	30	55	45	86	85	35	55	125	170
9	62	30	5	15	10	16	60	60	63	81	50	65	65	75
10	67	19	20	15	61	51	25	40	80	81	35	25	85	95
11	57	33	10	15	60	57	65	60	64	63	15	20	80	80
12	54	44	5	5	53	25	75	60	60	57	35	45	50	70
13	-	-	5	5	1	53	80	90	81	63	20	30	50	60
14	78	37	0	5	3	40	50	55	80	78	15	0	140	120
Net	**1674**	**1639**	**322**	**335**	**950**	**1139**	**803**	**890**	**1096**	**1135**	**810**	**820**	**1600**	**1730**

Table 4.4d: Lower Kittanning Shale Volume Differences

Sample ID: LKFC-PA														
	Lab 1		Lab 2		Lab 3		Lab 4		Lab 5		Lab 6		Lab 7	
	Sample Weight (grams)													
	2000	*2000*	*1896*	*1842*	*2011*	*1884*	*2078*	*2038*	*2014*	*2002*	*1971*	*1934*	*1970*	*2010*
Week	**Volume (mL) Remaining In Column (Volume of Water Added - Volume of Water Collected)**													
Initial	755	500	335	215	319	284	225	305	212	240	285	270	445	360
1	0	28	-5	-10	42	111	25	30	45	60	85	75	125	135
2	21	13	0	20	67	68	30	30	57	80	-55	20	220	100
3	28	26	-5	5	19	24	30	35	68	51	30	20	194	146
4	24	29	20	15	45	42	65	50	76	70	65	55	135	110
5	27	35	0	0	102	68	30	40	63	70	15	5	130	120
6	33	27	0	5	39	19	25	40	61	66	60	40	210	174
7	40	19	30	10	64	62	40	40	71	52	30	55	180	230
8	15	21	5	10	60	48	55	60	61	66	60	25	190	210
9	27	38	15	10	28	15	65	60	99	80	50	35	135	80
10	24	24	15	5	39	23	35	40	74	78	35	30	95	180
11	27	35	10	30	46	60	40	65	55	60	35	20	80	190
12	26	39	0	5	20	14	60	65	90	60	20	35	90	120
13	-	-	10	0	37	19	60	60	88	74	35	25	140	180
14	22	32	0	0	16	21	45	60	53	78	5	-10	110	200
Net	**1069**	**866**	**430**	**320**	**943**	**878**	**830**	**980**	**1173**	**1185**	**755**	**700**	**2479**	**2535**

Table 4.4e: Middle Kittanning Sandstone Volume Differences

Sample ID: MKSS - PA							
	Lab 1	Lab 2	Lab 3	Lab 4	Lab 5	Lab 6	Lab 7
	Sample Weight (g)						
Week	*2000*	*1684*	*1751*	*1964*	*1896*	*1905*	*1790*
Volume (mL) Remaining In Column (Volume of Water Added - Volume of Water Collected)							
Initial Flush	883	440	233	285	200	485	245
Week 1	41	45	83	30	73	-15	95
Week 2	57	35	74	15	67	-35	70
Week 3	15	55	13	35	45	35	160
Week 4	49	55	52	45	86	95	95
Week 5	60	30	56	5	60	15	115
Week 6	52	30	42	35	69	90	145
Week 7	53	35	62	50	59	-35	150
Week 8	49	5	49	65	95	80	155
Week 9	42	5	11	50	111	40	85
Week 10	60	5	52	40	93	40	110
Week 11	46	10	30	50	40	40	90
Week 12	43	5	40	55	78	90	70
Week 13	-	15	25	75	65	15	130
Week 14	54	15	44	45	105	10	140
Net	**1504**	**1325**	**866**	**880**	**1246**	**950**	**1855**

Sample Weights

As described previously, laboratories reconstructed samples according to the particle size distribution in Table 4.2. All laboratories, with the exception of Laboratory 8, prepared duplicates of four shale samples and a single sandstone sample. Laboratory 8 prepared a single Kanawha Black Flint Shale sample and duplicates of all other samples, including sandstone. Weights of reconstructed samples added to columns in each laboratory are presented in Table 4.5.

Table 4.5: Sample Types and Weights (in grams)

Lab	Brush Creek Shale (BCS3-PA)	Kanawha Black Flint Shale (KBF-WV)	Lower Kittanning Shale (LKFC-PA)	Houchin Creek Shale (HCS-IN)	Middle Kittanning Sandstone (MKSS)
1	2000	2000	2000	2000	2000
	2000	2000	2000	2000	-
2	1801	1653	1895	1298	1684
	1807	1883	1841	1589	-
3	1691	1819	2011	1521	1751
	1828	1849	1884	1489	-
4	1850	2055	2078	1487	1964
	1922	2039	2038	1515	-
5	1880	2079	2014	1482	1896
	1904	2056	2001	1521	-
6	1833	1999	1971	1361	1905
	1859	2002	1933	1410	-
7	1900	1862	1970	1412	1790
	1836	1912	2010	1487	-
8	1900	1800	2000	1800	2000
	1900	-	2000	1800	2000

Columns in Laboratory 1 were prepared in accordance with initial method instructions to add approximately 2 kg sample to each column. The remaining laboratories initiated study activities approximately three months later, following revised instructions to fill columns to approximately 4 inches below the top of the column, using little to no packing. Discussions with Laboratory 1 indicated that sample compaction was needed to add 2000g to each HCS-IN column. All other laboratories added from 1361 to a maximum of 1800g to HCS-IN columns. Recorded water volumes indicate that sample compaction could have affected the amount of water added to and collected from samples, particularly the HCS-IN samples.

Method Performance

Method performance, in terms of the precision that can be expected to be achieved in a single laboratory, was evaluated in terms of the RPD in unweighted (concentration) results and weighted (concentration multiplied by water volume collected over the total weight of the sample) results between duplicate samples. Precision that can be expected in multiple laboratories testing replicate (more than two) samples was evaluated in terms of the RSD in concentration and weighted results in replicate samples across laboratories.

<u>analytical precision and recovery:</u> In addition to the effects of water volumes and total sample weight, the RPDs between duplicate samples are due in part to the variability and accuracy that is inherent to the analytical methods that were used to measure the analytes of interest.[1] For example, EPA methods often include RPD performance criteria of up to 35% for duplicate analyses. EPA draft Method 200.7 (which was used to measure the concentration of metals during this study) includes RPD criteria ranging from 0.5 to 20%. In this study, analytical RPDs between duplicate analytical QC samples for dissolved metals and sulfate measurements that were above the laboratory's minimum detection limit (MDL) ranged from 0 to 109%, with 4.5 percent falling outside method prescribed analytical RPD of 20%. The highest RPDs were observed for datasets that included a majority of results that were below or near laboratory detection level, as indicated by the percentage of sample pairs with results falling below the laboratory MDL (see Table 4.6). Analytical recoveries in spiked samples run by the metals laboratory, ranged from 62 to 134%.

For each analyte measured by the metals laboratory, Table 4.6 lists (1) the percent of total sample pairs with results below the laboratory MDL, (2) the range of RPDs across analytical duplicate QC samples, (3) the pooled RPD across all analytical QC duplicates, and (4) the range of percent recovery in analytical spikes. To isolate the results of weathering as much as possible from the variability introduced by sample analysis, data results for the analytes listed in Table 6 and associated with quality control samples (i.e., analytical duplicates or analytical spikes) that fall above an RPD of 20 or outside a % recovery range of 75 to 125, were eliminated from the assessment presented in this report. The percentage of results eliminated based on analytical quality control also are included in Table 4.6.

Table 4.6: Relative Percent Differences (RPD) Between Analytical QC Duplicates

Analyte	%Total Pairs with results <MDL	Analytical RPDs (excluding results < MDL)	Pooled Analytical RPD	% Recovery Range	% of Column Results Eliminated based on analytical QC Failures
Fe	41	0 – 109	29	78 – 122	1.7
Mn	0	0 – 30.1	5.4	80 – 130	0.2
Al	80	0 – 30.3	10.3	81 – 112	0.2
Ca	0	0 – 7.5	2.2	65 – 128	0.4
Mg	0	0 – 7.9	2.3	80 – 133	0.2
Se	16	0 – 75.7	24.6	62 – 134	2.2
Zn	8	0 – 20.1	4.6	78 – 112	0.1
Na	0	0 – 37.8	7.8	75 – 115	0.4
K	0	0 – 15.4	4.8	80 – 110	0
SO_4	0	0 – 4.8	1.2	90 – 125	0

Only a subset of the laboratories measuring acidity, alkalinity, pH and conductivity reported laboratory detection limits and/or results of analytical quality control (QC) samples. All QC results reported for these analytes passed method-specified criteria; therefore, none of these data were eliminated based on association with failed QC results.

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[1] EPA methods often include RPD performance criteria of up to 30% for duplicate analyses. EPA draft Method 200.7 (May 2001) includes RPD criteria ranging from 0.5 to 20%. EPA draft Method 1630 for measurement of methylmercury includes an RPD criterion of 35%.

comparison of duplicate weathering samples: Method precision was assessed using unweighted and weighted results from duplicate samples exposed to identical weathering procedures. Relative percent differences (RPD) were calculated for analytical results prior to weathering (initial flush at Week 0) and as pooled RPDs for all sample weeks beginning with Week 1 and continuing through Week 14 (14-week RPD). The following results were eliminated from RPD calculations:

- Results associated with analytical QC failures
- Results reported at less than the laboratory MDL
- Results identified as outliers using Grubbs Test for outlying results (Grubbs, 1972)
- Laboratory 6 did not submit acidity results. This laboratory also submitted alkalinity results obtained using indicator paper; these results were not comparable to results submitted by other laboratories.
- Laboratory 1 did not include a saturation period during Week 13. Results submitted by this laboratory during Weeks 13 and 14 were not comparable to results submitted by other laboratories
- Analytical results for measurement of metals in samples from Laboratories 1 through 7 were reported in µg/L by the metals laboratory. Because Laboratory 8 joined the study several weeks following the study's initiation, it was responsible for measurement of all study analytes, including metals, in samples collected. Laboratory 8 reported analytical results for measurement of metals in mg/L. These results were not comparable to the results of the metals laboratory (reported as µg/L) and therefore, were not included in interlaboratory RPD or RSD determinations.

Pooled RPDs calculated based on unweighted and weighted results for each sample type are presented in Tables 4.7a and 4.7b. Pooled RPDs calculated using unweighted and weighted results for all samples are presented in Table 4.7c. Because pH measurements are not reported in units of concentration, comparative pH results are presented as the mean absolute difference.

Table 4.7a: Pooled RPDs based on analyte concentrations in duplicate sample pairs

(Note: Highlighted cells contain RPDs >50.)

	BCS3-PA				LKFC-PA			
	Unweighted		Weighted		Unweighted		Weighted	
Analyte	Initial Flush	14-week	Initial Flush	14-week	Initial Flush	14-week	Initial Flush	14-week
Fe	19.1	85.5	17.0	86.6	13.2	79.7	24.5	75.9
Mn	10.6	53.5	24.0	53.7	18.4	18.5	11.3	22.7
Al	–	9.6	–	13.2	50.8	79.8	50.4	54.5
Ca	17.7	16.6	29.5	16.3	18.7	20.2	11.5	22.2
Mg	14.0	18.1	14.2	16.3	12.4	18.0	12.8	22.1
Se	17.2	38.5	28.6	38.2	13.7	24.8	10.0	19.8
Zn	66.4	74.7	54.6	73.1	14.2	33.0	8.7	32.8
Na	13.2	23.3	28.0	19.2	18.6	18.2	14.9	24.5
K	8.5	11.9	28.8	17.9	13.7	14.6	12.7	21.4
SO_4	18.6	34.6	28.9	26.0	17.6	20.0	13.1	22.9
Alkalinity	17.5	20.9	28.4	30.3	12.5	24.3	37.8	29.8
Acidity	18.9	40.9	36.8	43.5	40.6	176	20.5	158
Conductivity	14.4	15.4		■	9.36	9.21		■
	Mean absolute difference				**Mean absolute difference**			
pH	0.15	0.18		■	0.18	0.22		■

Table 4.7b: Pooled RPDs based on analyte concentrations in duplicate sample pairs

(Note: Highlighted cells contain RPDs >50.)

	HCS-IN				KBF-WV			
	Unweighted		Weighted		Unweighted		Weighted	
Analyte	Initial Flush	14-week	Initial Flush	14-week	Initial Flush	14-week	Initial Flush	14-week
Fe	65.7	104.7	74.3	103.6	36.7	77.1	36.1	79.7
Mn	18.8	34.0	20.7	36.3	86.2	82.9	86.2	82.2
Al	20.1	76.6	25.6	74.1	–	–	–	–
Ca	19.4	7.7	72.4	25.1	4.1	17.5	11.0	23.2
Mg	20.4	21.9	25.0	24.4	4.8	17.1	10.6	21.8
Se	20.8	61.1	21.7	59.3	33.3	38.8	36.9	45.0
Zn	15.2	46.8	22.5	49.7	102.3	83.6	104.6	80.3
Na	14.5	34.2	24.6	29.9	6.9	23.5	13.1	25.5
K	18.0	23.2	27.9	32.9	3.5	13.5	9.2	20.5
SO_4	15.2	28.2	23.4	34.2	7.3	21.2	10.9	25.5
Alkalinity	53.1	28.7	53.4	34.4	7.9	15.4	19.6	20.9
Acidity	23.8	65.7	28.2	78.5	17.8	35.6	28.0	36.4
Cond.	13.0	12.7		■	5.6	14.6		■
	Mean absolute difference				**Mean absolute difference**			
pH	0.3	0.4		■	0.1	0.1		■

Table 4.7c: Overall RPDs based on analyte

(Note: Highlighted cells contain RPDs >50.)

	Initial Flush		14-week period		
Analyte	Unweighted	Weighted	Unweighted	Weighted	Analytical (from Table 6)
Fe	44.8	50.9	91.5	90.4	29.0
Mn	43.1	44.1	52.1	52.5	5.4
Al	37.0	38.6	76.9	72.5	10.3
Ca	36.0	38.8	16.1	21.9	2.2
Mg	15.6	16.4	18.9	21.4	2.3
Se	23.5	26.2	44.2	42.9	24.6
Zn	54.5	52.0	61.4	60.2	4.6
Na	14.5	21.1	25.6	25.1	7.8
K	12.2	21.5	16.3	23.7	4.8
SO_4	15.3	20.4	26.8	27.5	1.2
Alkalinity	32.2	35.2	22.1	28.7	[redacted]
Acidity	20.0	27.0	106	99.9	[redacted]
Conductivity	11.1	[redacted]	13.2		[redacted]
	Mean absolute difference				[redacted]
pH	0.2	[redacted]	0.2		[redacted]

The largest pooled RPD in all weathered samples resulted between measurements of iron, aluminum, manganese, and acidity; for the metals, this corresponds to the analytes with the greatest number of results falling below the laboratory MDL (see Table 4.6). The lowest variability between duplicates occurred with magnesium, sodium, potassium, and sulfate. With the exception of sulfate, these analytes were measured in mg/L or g/L ranges in water samples collected from the test columns (compared with µg/L levels for iron, aluminum, and manganese).

For most analytes, the RPDs between duplicate samples during the 14-week weathering period were similar to or decreased from the RPDs between duplicate samples during the initial flush, indicating that the method weathering procedures do not impose a notable increase in variability between duplicate samples. RPDs for both calcium and alkalinity improved during the 14-week weathering period.

RPDs for the following analytes increased significantly during the 14-week weathering period (see Table 4.7c):

- **Iron (Fe)** − Unweighted and weighted pooled RPDs are 44.8 and 50.9 during the initial flush period, compared to 91.5 and 90.4 during the 14-week weathering.

- **Aluminum (Al)** − Unweighted and weighted pooled RPDs are 37.0 and 38.6 during the initial flush, compared to 76.9 and 72.5 during the 14.week weathering period.

- **Selenium (Se)** − Unweighted and weighted pooled RPDs are 23.5 and 26.2 during the initial flush period, compared to 44.2 and 42.9 during the 14-week weathering.

- **Acidity** − Unweighted and weighted pooled RPDs are 20.0 and 27.0 during the initial flush period, compared to 106 and 99.9 during the 14-week weathering.

comparison of replicate weathering samples: Method precision across laboratories was assessed using weighted results from replicate samples exposed to weathering procedures in multiple laboratories. Weighted results (analyte concentration multiplied by the volume of water collected and divided by total sample weight) were used to mitigate the effects of the weight of individual samples and the volume of water collected when comparing results. Relative standard deviations (RSD) were calculated for replicate sample results prior to weathering (initial flush at Week 0) and as pooled RSDs for all sample weeks beginning with Week 1 and continuing through Week 14 (14-week). Because the differences in water volumes collected and total sample weights used can increase variability greatly across laboratories, RSDs are presented based on weighted results only.

The following results were eliminated from RSD calculations:

- Results associated with analytical QC failures
- Results reported at less than the laboratory MDL
- Results identified as outliers using Grubbs Test for outlying results
- Laboratory 6 did not submit acidity results, and submitted alkalinity results obtained using indicator paper; these results were not comparable to results submitted by other laboratories.
- Laboratory 1 did not include a saturation period during Week 13; results submitted during Weeks 13 and 14 were not comparable to results submitted by other laboratories
- Laboratory 8 reported analytical results for measurement of metals in mg/L. These results were not comparable to the results of the metals laboratory (reported as µg/L) and therefore, were not included in interlaboratory RPD or RSD determinations.
- Analytical results for measurement of alkalinity and acidity in Laboratories 2, 4, 5, 7 and 8, were reported to a laboratory-specific censoring level. For example, Laboratories 2, 4, 7 and 8 reported results of acidity to <10, "negative," <1, and 0, respectively. Laboratories 2, 4, 5 and 7 reported results of alkalinity to <20, <5, 0, and<1, respectively. Although these data were used to determine within laboratory precision (as RPD), the data are not comparable to data results from other laboratories and were not used for evaluations of method performance across laboratories (i.e., pooled RSDs).

Pooled RSDs from replicate samples across laboratories are presented for each analyte in each sample in Table 4.8a; analyte-specific RSDs are presented in Table 4.8b.

Table 4.8a: Pooled interlaboratory RSDs based on analyte concentrations in replicate samples *(Note: Highlighted cells contain RSDs >50.)*

	BCS3-PA		HCS-IN		LKFC-PA		KBF-WV		MKSS-PA	
Analyte	Initial Flush	14-week	Initial Flush	14-week	Initial Flush	14-week	Initial Flush	14-week	Initial Flush	14-week
Fe	130	110	118	150	84.7	80.0	130	86.8	44.3	44.6
Mn	46.0	112	67.5	45.1	36.7	29.3	101	1.4	50.3	59.2
Al	4.3	39.1	87.1	97.6	69.5	37.5	131	–	–	–
Ca	35.5	30.5	56.7	29.0	25.5	30.8	43.8	41.4	39.9	40.8
Mg	31.7	30.9	61.4	35.6	44.4	30.2	45.7	37.4	86.6	31.9
Se	43.4	40.8	47.9	63.0	33.3	27.2	62.6	63.4	41.4	45.9
Zn	131	98.3	85.5	84.7	33.6	63.2	135	85.8	89.9	97.2
Na	39.2	30.2	47.6	39.8	52.9	38.9	53.6	41.9	55.1	59.0
K	40.9	24.1	53.8	57.8	41.0	26.0	53.5	31.7	35.5	30.0
SO_4	35.1	26.0	55.8	51.4	32.1	26.2	45.5	25.8	45.2	56.9
Cond.	25.1	15.0	22.5	48.9	28.6	40.6	20.0	11.3	36.0	11.8
	Standard Deviation									
pH	0.3	0.4	1.0	1.8	0.4	0.5	0.3	0.5	0.3	0.3

Table 4.8b: Overall pooled RSDs based on analyte

(Note: Highlighted cells contain RSDs >50.)

Analyte	Initial Flush	14-week
Fe	109.4	114
Mn	65.4	78.0
Al	78.8	86.0
Ca	41.6	34.1
Mg	52.7	33.5
Se	47.4	48.8
Zn	97.6	85.0
Na	49.3	40.5
K	46.6	36.5
SO_4	43.4	37.2
Conductivity	26.0	39.6
	Standard Deviation	
pH	0.6	0.7

Resulting pooled RSDs across laboratories are consistent with results of the pooled RPDs between duplicate samples. RSDs are largest for iron, zinc, aluminum, and manganese and show only a slight increase during weathering from the variability across initial flush results. Pooled RSD results show a slight decrease in variability during weathering for production of calcium, magnesium, sodium, potassium, and sulfate.

Conclusions Regarding Method Performance

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.

The interlaboratory study presented in this report is one of several studies that have been completed to support development of a standardized and effective test procedure for predicting the quality of mine drainage in mining areas that are otherwise difficult to characterize, and combines the efforts of the U.S. Department of the Interior’s Office of Surface Mining, the U.S. Environmental Protection Agency, the Pennsylvania Department of Environmental Protection, several private laboratories, universities, and consultants. Results of this study will be used to revise the existing draft leaching column method (ADTI-WP2) and to provide performance criteria regarding the RPDs and RSDs that should be expected by laboratories using the method (see Tables 4.9 and 4.10).

RPD results included in Table 4.9 reflect the pooled results of the interlaboratory study, using datasets from seven laboratories evaluating the effects of weathering on samples of Brush Creek shale, Kanawha Black Flint shale, Lower Kittanning shale, Houchin Creek shale, and Middle Kittanning sandstone. These results will be included in the draft test method as precision criteria that can be expected from duplicate samples run in a single laboratory.

Table 4.9: Expected method precision (as RPDs) based on Interlaboratory Study Results

Analyte	14-week RPD	Initial Flush RPD	Weathering Test RPD (Difference between 14-week and initial flush RPD)
Fe	90.4	50.9	**39.5**
Mn	52.5	44.1	**8.4**
Al	72.5	38.6	**33.9**
Ca	21.9	38.8	**(16.9)**
Mg	21.4	16.4	**5.0**
Se	42.9	26.2	**16.7**
Zn	60.2	52.0	**8.2**
Na	25.1	21.1	**4.0**
K	23.7	21.5	**2.2**
SO_4	27.5	20.4	**7.1**
Alkalinity	28.7	35.2	**(6.5)**
Acidity	99.9	27.0	**72.0**
Conductivity	13.2	11.1	**2.1**
	Mean absolute difference		
pH	0.2	0.2	**0**

RSD results included in Table 4.10 reflect the pooled results of the interlaboratory study, using datasets from seven laboratories evaluating the effects of weathering on samples of Brush Creek shale, Kanawha Black Flint shale, Lower Kittanning shale, Houchin Creek shale, and Middle Kittanning sandstone.

Table 4.10: Overall pooled RSDs based on Analyte

Analyte	14-week	Initial Flush	Weathering Test RSD (Difference between 14-week and initial flush RSD)
Fe	114	109.4	**4.6**
Mn	78.0	65.4	**12.6**
Al	86.0	78.8	**7.2**
Ca	34.1	41.6	**(7.5)**
Mg	33.5	52.7	**(19.2)**
Se	48.8	47.4	**1.4**
Zn	85.0	97.6	**(12.6)**
Na	40.5	49.3	**(8.8)**
K	36.5	46.6	**(10.1)**
SO_4	37.2	43.4	**(6.2)**
Conductivity	39.6	26.0	**13.6**
	Standard Deviation		
pH	0.7	0.6	**0.1**

Based on results of the study, several general patterns also are apparent as to the effectiveness of the draft weathering procedures in producing valid and verifiable results for prediction of mine drainage water quality.

- The variability between duplicate samples during the initial flush period can provide an indication of variability that will occur during weathering. The lower the variability (as RPD) during the initial flush, the more likely the samples being evaluated are indeed duplicates. All precautions should be taken during sample construction, to ensure duplicate samples are identical as possible (e.g., identical column construction; identical sample weight and particle-size distribution, and the addition and collection of identical volumes of water).

- In terms of the results of dissolved metals, overall variability in all four shale samples and the single sandstone sample, was greatest in results of iron, aluminum, manganese, and zinc and lowest in calcium, magnesium, sodium and potassium. These results are consistent with the concentration levels of these analytes in the water samples (i.e., variability is high across low-level samples and low across high-level samples).

- Variability was greatest in iron and acidity results, and this variability increased with weathering.

- Much of the variability (measured as RPD and RSD) between within-laboratory duplicate samples and inter-laboratory replicate samples can be attributed to the differences in the sample masses used and the water volumes collected from each sample. Because attempts to normalize results to compensate for sample masses and leachate volumes did not significantly affect RPD results, it is likely that additional factors (e.g., sample density, column construction, gas and water introduction) affected sample exposure to weathering conditions.

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MS1-Kincom

Chapter 5: Characterization of rock samples and mineralogical controls on leachates

By Jane M. Hammarstrom, Charles A. Cravotta III, Daniel Galeone, John J. Jackson, and Frank Dulong

Introduction

Rocks associated with coal beds typically include shale, sandstone, and (or) limestone. In addition to common rock-forming minerals, all of these rock types may contain sulfide and sulfate minerals, various carbonate minerals, and organic material. These different minerals have inherently different solubility characteristics, as well as different acid-generating or acid-neutralizing potentials. The abundance and composition of sulfur- and carbonate-bearing minerals are of particular interest in interpreting the leaching column data because (1) pyrite and carbonate minerals are the primary controls on the acid-base account of a sample, (2) these minerals incorporate trace metals that can be released during weathering, and (3) these minerals readily react during weathering due to mineral dissolution and oxidation of iron.

Rock samples were collected by the Pennsylvania Department of Environmental Protection (PaDEP) from five different sites to assess the draft standardized leaching column method (ADTI-WP2) for the prediction of weathering rates and water quality at coal mines. Samples were sent to USGS laboratories for mineralogical characterization and to ActLabs for chemical analysis. The samples represent a variety of rock types (shales, sandstones, and coal refuse) that are typical of coal overburden in the eastern United States. These particular samples were chosen for testing the weathering protocols because they represent a range of geochemical and lithologic characteristics, sulfur contents, and acid-base accounting characteristics (Hornberger et al., 2003). The rocks contain variable amounts of pyrite and carbonate minerals and vary in texture.

This chapter 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). We also characterize some of the post-weathering rock samples, report trace-element content in leachate, and discuss mineralogical controls on leachate quality based on data from one of the participating laboratories. Table 5.1 lists the samples described in this chapter, the sample numbers, and comments on the characteristics of each lithology. Sample locations are plotted in Figure 5.1. Chapters 2 and 3 describe the sample locations, sample preparation protocols, ABA characteristics, and rationale for selection of rock samples for testing. Microprobe data for pyrite and carbonate minerals are tabulated in Appendix 5.1. Leachate data, along with a series of graphs showing concentration and cumulative transport trends, for the laboratory data discussed in this chapter are included as Excel spreadsheets in Appendices 5.2 and 5.3. Leach column data for the interlaboratory study are evaluated and interpreted in Chapters 7 -11.

Table 5.1. Rock samples.

Sample	Lithology	Comment
HCS-IN	Houchin Creek Shale	• Low NP • High S • Produces alkaline mine discharge
LKFC-PA	Lower Kittanning Shale	• Low NP • Produces alkaline mine discharge
KBF-WV	Kanawha Black Flint Shale	• Low NP • Low S • Selenium problem area
BCS3-PA	Brush Creek Shale	• Moderate NP • Moderately high S • Produces alkaline mine discharge
MKSS	Middle Kittanning Sandstone	• Low NP • Low S • Low target analytes (“blank”)
Wadesville #29	Wadesville Sandstone	• High NP • Low S • Produces alkaline mine drainage
LRBT#2	Leechburg Coal Refuse	• High S • High acidity end-member

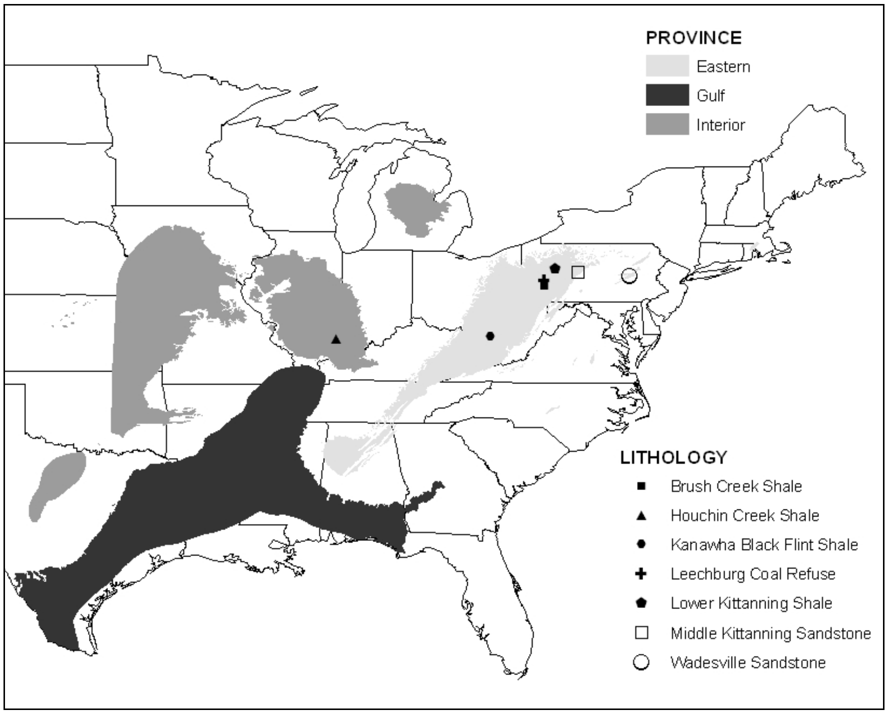

Figure 5.1 Sample location and major coal provinces of the eastern United States. .

Methods

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.

Splits of each rock sample were submitted to ActLabs for chemical analysis of major and trace elements using whole rock fusion ICP analysis (FUS-ICP), total digestion ICP analysis (TD-ICP), multi-element instrumental neutron activation analysis (MULTI-INAA), and high-temperature (>750 ^oC) loss-on-ignition (LOI). Mercury was determined by atomic absorption using a flow injection technique (FIMS); CO_2 was determined by coulometry (COUL). At the completion of the Phase 3 leaching column tests, one of the laboratories recovered the solid sample residue and supplied a split for testing. We sent a split of leach column residue (LCR) to ActLabs for carbon and sulfur analysis; another split was micronized for powder XRD for comparison with the mineralogy of the starting material. Leach column residues were analyzed for carbon and sulfur using automated analyzers (infrared detector). CO_2 was determined by treating a split with 25% HCl; graphitic carbon was determined by heating to 600 ^oC to drive off CO_2 and organic carbon. The difference between total carbon and the organic + CO_2 carbon fractions is reported as graphitic carbon. Details of analytical methods are available at the ActLabs website: http://www.actlabs.com/methods_usa.htm

Samples for mineralogical studies consisted of fresh splits (75 to 100 g) of the five particle size composites used for the phase 3 column experiments, plus unsized Wadesville sandstone and Leechburg Coal refuse (Table 5.1). The composites were split in the Reston laboratory by the cone and quarter method. Half of the sample was retained as an archive sample and half was split for XRD and other mineralogical studies (OMS split). The XRD split was subsampled, micronized in alcohol in a McCrone[1] mill equipped with agate grinding pellets to reduce average particle size to 1 to 5 micrometers, air dried, and analyzed as a powder XRD mount. Polished thin sections were prepared from rock chips (at least five 1-cm size chips per sample) selected from the OMS split.

Powder patterns were collected on a Scintag X1 automated diffractometer equipped with a Peltier detector using CuKa radiation. Patterns were interpreted with the aid of Scintag and MDI Applications JADE search/match software and compared with reference patterns in the Powder Diffraction File (ICDD, 2002). The relative amounts of different minerals were estimated by quantitative phase analysis using the Siroquant computer program (Taylor and Clapp, 1992). Siroquant utilizes the full XRD profile in a Rietveld refinement to estimate the weight percentages of different minerals in the mixture, based on a rigorous identification of minerals present prior to the refinement. Raudsepp and Pani (2003) summarized applications of Rietveld analysis for environmental studies of mine wastes. Small amounts (<5 weight percent) of a mineral are not always detectable by XRD. XRD cannot uniquely determine mineral composition; thus we report plagioclase, which may be calcic or sodic. Although we report both muscovite and phengite and illite micas, absolute concentrations of minerals are not reliable by

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[1] Any use of trade, product, or firm names is for descriptive purposes only and does not imply endorsement by the U.S. Government.

these methods. The relative differences among mineral groups (micas, chlorite, quartz, carbonates, pyrite, and sulfates) are plotted because these are more reliable estimates of the mineralogical variation among the samples. Overlapping peaks of the many rock-forming minerals present in shales complicate mineral identification. Also, most rock-forming minerals form solid solutions so compositions may differ from the minerals in reference databases used to interpret XRD patterns. Uncertainties in XRD interpretation were resolved by optical and electron microscopy on thin sections, where possible.

Polished thin sections were prepared for each rock by mounting 6 to 12 fragments in colorless epoxy, affixing the cemented fragments to a glass slide, and grinding to a thickness of 30 micrometers. Polished sections were examined with a Nikon petrographic microscope equipped with both transmitted and reflected light. Sections were scanned and photographed to document grain size and texture and to provide reference maps for detailed microbeam analyses. Rock fragments in each polished section were assigned letter labels (A, B, C, etc.) for reference. Sections were coated with carbon and examined with a JEOL JSM-840 scanning electron microscope (SEM) equipped with a back-scattered electron (BSE) detector, a secondary electron (SE) detector, and a PGT x-ray energy-dispersive system (EDS). In BSE images, grayscale colors reflect average atomic number contrasts of minerals. Heavy minerals, such as pyrite or zircon, appear bright or white. Organic material appears black because it is mainly composed of the light element carbon. Other minerals appear in varying shades of gray. EDS spectra were collected to obtain qualitative analysis of mineral compositions to refine XRD identifications and choose appropriate starting minerals from the Siroquant mineral library for Rietveld refinement. The SEM typically was operated at an accelerating voltage of 15 kV and a specimen current of 1 to 2 nA. A JEOL electron microprobe (EMP) was used to analyze pyrite and carbonate minerals. For pyrites, the microprobe was operated at 20kV with a beam current of 30 nanoamps, using a focused beam and natural and synthetic sulfide minerals as standards. Long (60 second) count times were used to optimize detection limits for trace elements in pyrite (Se, Ni, As, Co, Mn, Cu, Zn, Cd). Detection limits for these elements are on the order of 100 parts per million (ppm). For carbonates, the microprobe was operated at 15kV with a beam current of 10 nanoamps, and a slightly defocused (5-micrometer) beam to minimize sample damage; natural and synthetic carbonate minerals were used as standards. The EPMA technique cannot determine carbon, water, or oxidation states of elements. Therefore, carbon dioxide contents for carbonate minerals are calculated based on stoichiometry.

Petrographic observations and SEM analyses showed that some samples contain organic matter. Non-crystalline (amorphous) materials are non-diffracting by powder x-ray analysis. We addressed the issue of non-diffracting material in two ways. We reran the XRD patterns after adding 15 weight percent corundum as an internal standard. This allowed us to use Siroquant to estimate the amount of non-diffracting material in each sample. The non-diffracting (amorphous) material includes organic material, poorly crystalline ferrihydrite or aluminum oxyhydroxide minerals, and any material rendered amorphous during sample preparation. We also subjected 1 gram powdered sample splits to a low-temperature ash (LTA) procedure to estimate the amount of non-mineral matter. The LTA analyses were done in USGS laboratories by radio-frequency plasma-ashing (Pontolillo and Stanton, 1994; Rao and Gluskoter, 1973; Mitchell and Gluskoter, 1976; Pearson and Kwong, 1979). XRD patterns for the LTA residues were analyzed using Siroquant to estimate mineral abundances for comparison with the pre-ash data.

The target analytes for the interlaboratory leach column tests were iron, manganese, aluminum, calcium, magnesium sodium, potassium, zinc, selenium, and sulfate (Chapter 8; Appendix 5.2). Leaching column effluent from the last two weeks of the 14-week weathering test at West Virginia University was submitted to ActLabs by Dr. Louis MacDonald for analysis of additional trace elements that might be released during weathering. The trace-element leachates were analyzed for 76 elements by ICP-MS, ICP-OES, and FIMS for mercury.

Results

Samples characterized in this study include four shales, two sandstones, and coal refuse (Table 5.1). The Wadesville Sandstone and Brush Creek Shale were used in phase 1 studies in 2002. The Brush Creek Shale and Leechburg Coal Refuse were used in phase 2 leaching column studies conducted in 2003 (Hornberger et al., 2004). The Brush Creek Shale and rocks from the Middle Kittanning Sandstone were used in phase 3 tests in 2006. The samples exhibit a wide range of geochemical characteristics in terms of percent total sulfur and neutralization potential, as described in previous publications (Hornberger et al, 2003, 2004; Hornberger and Brady, 1998, Brady et al, 1998). Acid-base accounting data are discussed in detail in Chapter 9.

Whole-rock chemistry

Geochemical data for the unweathered whole-rock samples are reported in Table 5.2, along with carbon and sulfur analyses obtained for weathered leach column residue from one laboratory. The chemistry of the leachate may not directly mimic the chemistry of the rocks because of differences in the solubilities and rates of reaction of various solid phases that contain the analytes. Variations in major rock constituents are illustrated in Figure 5.2*A*. The wide range in loss-on-ignition (<5 to 60 weight percent LOI) reflects the variable content of organic material and other volatiles. The Wadesville Sandstone contained significantly more calcium (11.23 weight percent CaO) and manganese than any of the other samples (Table 5.2). Total sulfur concentrations are negligible in the sandstones (<0.1 weight percent) and range from 0.2 to 4.3 weight percent in the shales. The coal refuse analyzed for this study contains over 5 weight percent sulfur (Table 5.2). Total sulfur does not correlate with total iron concentrations in the rocks. Sulfur concentrations overlap those reported in the separate ABA determinations (Chapter 9). The carbon dioxide (CO_2) content of the rocks indicates the carbonate mineral content. The shales contain 1 to 3 weight percent carbon dioxide; whereas, the Wadesville Sandstone contained 16.2 weight percent carbon dioxide. As discussed in more detail below, the Wadesville Sandstone had a substantially greater percentage of carbonate minerals than the other rocks. Concentrations of selected trace elements of potential environmental concern are plotted in Figure 5.2*B* on a log scale to facilitate comparison of samples. Relative to the other shales and sandstones, the Houchin Creek shale contains the highest concentrations of base metals (mostly zinc), arsenic, selenium, and mercury. The Leechburg coal refuse contains the highest concentration of mercury (952 parts per billion) detected in any of the samples.

Post-leaching carbon and sulfur data (Table 5.2) show that neither component was exhausted during the leaching study.

Table 5.2. Geochemical data for rock samples.
[Total iron reported as Fe_2O_3; n.d., not determined]

Lithology				Shale				Sandstone		Coal refuse
Sample				HCS-IN	LKFC-PA	KBF-WV	BCS3-PA	MKSS	Wadesville #29	LRBT #2
Element	Units	Detection Limit	Method							
				Major elements as oxides						
SiO_2	%	0.01	FUS-ICP	38.27	50.44	57.44	47.59	75.36	49.43	19.01
Al_2O_3	%	0.01	FUS-ICP	12.59	17.77	16.04	20.45	11.12	9.08	9.28
Fe_2O_3(T)	%	0.01	FUS-ICP	9.09	11.07	8.77	9.52	3.22	6.83	7.55
MnO	%	0.01	FUS-ICP	0.05	0.23	0.13	0.13	0.06	0.37	0.01
MgO	%	0.01	FUS-ICP	1.61	1.88	1.81	2.41	0.89	3.84	0.38
CaO	%	0.01	FUS-ICP	2.25	0.87	1.03	2.25	1.81	11.23	0.12
Na_2O	%	0.01	FUS-ICP	0.5	0.21	0.74	0.25	0.14	0.36	0.12
K_2O	%	0.01	FUS-ICP	2.75	3.68	3.44	3.51	2.4	1.5	1.04
TiO_2	%	0.005	FUS-ICP	0.574	0.861	0.884	0.848	0.653	0.526	0.498
P_2O_5	%	0.01	FUS-ICP	0.35	0.42	0.22	0.3	0.08	0.12	0.01
LOI	%	0.01	FUS-ICP	31.84	12.26	8.86	11.93	4.58	16.58	59.97
Total	%	0.01	FUS-ICP	99.89	99.69	99.37	99.19	100.3	99.86	98
				Trace elements						
Ag	ppm	0.5	INAA	1.2	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5
As	ppm	2	INAA	48	22	8	30	4	4	56
Au	ppb	5	INAA	< 5	< 5	< 5	< 5	< 5	< 5	< 5
Ba	ppm	3	INAA	307	476	580	676	313	309	138
Be	ppm	1	FUS-ICP	4	4	3	4	2	2	2
Bi	ppm	2	TD-ICP	< 2	< 2	< 2	< 2	< 2	< 2	3
Br	ppm	1	INAA	< 1	< 1	< 1	< 1	< 1	< 1	6
Cd	ppm	0.5	TD-ICP	20	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5
Ce	ppm	3	INAA	59	103	90	93	57	61	51
Co	ppm	1	INAA	19	24	16	23	11	15	5
Cr	ppm	1	INAA	179	88	77	101	87	45	51
Cs	ppm	0.5	INAA	6.6	6.6	4.6	8.2	1.9	1.1	4.3
Cu	ppm	1	TD-ICP	117	32	27	77	12	15	28
Eu	ppm	0.1	INAA	1.3	2.1	1.8	1.5	1.1	1	0.7
Hf	ppm	0.5	INAA	2.1	4.8	5.9	2.9	4.4	4.4	2.3
Hg	ppm	1	INAA	< 1	< 1	< 1	< 1	< 1	< 1	1
Hg	ppb	5	FIMS	227	63	11	65	11	< 5	952
Ir	ppb	5	INAA	< 5	< 5	< 5	< 5	< 5	< 5	< 5
La	ppm	0.2	INAA	35.4	53.2	52.6	52.7	31.7	35	25.5
Lu	ppm	0.05	INAA	0.36	0.63	0.6	0.53	0.36	0.34	0.3
Mo	ppm	5	INAA	165	< 5	< 5	< 5	< 5	< 5	< 5
Nd	ppm	5	INAA	26	38	43	40	24	28	18
Ni	ppm	1	TD-ICP	235	64	38	83	23	18	22
Pb	ppm	5	TD-ICP	27	24	22	46	20	15	22
Rb	ppm	20	INAA	80	100	110	120	70	70	50
Sb	ppm	0.2	INAA	13.2	0.9	0.5	0.9	0.4	< 0.2	0.8
Sc	ppm	0.1	INAA	11.9	18.5	15.1	19.4	8.8	9.3	9.9
Se	ppm	3	INAA	81	< 3	< 3	< 3	< 3	< 3	13
Sm	ppm	0.1	INAA	6	10.4	9.2	8.4	5.2	6.1	4
Sr	ppm	2	FUS-ICP	118	108	122	163	66	113	112
Ta	ppm	1	INAA	< 1	< 1	< 1	1	< 1	< 1	< 1
Tb	ppm	0.5	INAA	< 0.5	< 0.5	1.1	0.9	< 0.5	< 0.5	< 0.5

Table 5.2.—Continued.

Lithology				Shale				Sandstone		Coal refuse
Sample				HCS-IN	LKFC-PA	KBF-WV	BCS3-PA	MKSS	Wadesville #29	LRBT #2
Th	ppm	0.5	INAA	5.7	8.8	8.9	9.7	5.3	4.6	5.4
U	ppm	0.5	INAA	37.7	3.5	3	4.3	1.7	1.3	2.2
V	ppm	5	FUS-ICP	695	157	114	218	66	64	64
W	ppm	3	INAA	< 3	< 3	< 3	< 3	< 3	< 3	< 3
Y	ppm	1	FUS-ICP	31	43	39	33	21	25	14
Yb	ppm	0.1	INAA	2.3	3.8	4.1	3.3	2.3	2.7	1.8
Zn	ppm	1	TD-ICP	456	151	126	171	86	50	33
Zr	ppm	2	FUS-ICP	92	182	248	132	199	183	67
CO_2	%	0.01	COUL	1.06	3.13	1.94	2.03	1.93	16.2	1.06
S	%	0.001	TD-ICP	4.33	0.815	0.207	0.538	0.089	0.017	5.54
			Carbon and sulfur analyses on leach column residues							
C_{Total}	%	0.01	IR	18.1	2.53	1.07	1.69	0.79	n.d.	n.d.
$C_{Graphite}$	%	0.05	IR	4.32	0.47	0.19	0.43	< 0.05	n.d.	n.d.
$C_{Organic}$	%	0.05	IR	13.7	1.15	0.52	0.65	0.06	n.d.	n.d.
CO_2	%	0.01	COUL	0.41	3.34	1.3	2.24	2.52	n.d.	n.d.
S	%	0.01	IR	4.88	0.98	0.19	0.55	0.09	n.d.	n.d.
SO_4	%	0.1	IR	1.4	0.4	0.5	1	0.2	n.d.	n.d.

Rock Descriptions: Textures and Mineralogy

Mineralogical data are discussed by rock type. Mineralogy and rock textures for each lithology are illustrated by a series of photomicrographs and SEM images of polished thin sections. Shales and sandstones incorporate a variety of minerals, including different varieties of mineral groups (clays, feldspars). Ankerite, for example, is an iron-bearing variety of dolomite. The term ankerite is used for dolomite-group minerals that have $Fe^{2+}/(Mg+Fe^{2+}) \geq 0.2$. Table 5.3 lists nominal minerals compositions; however, many common rock-forming minerals such as feldspars and micas have variable compositions because they form solid solutions. Also, individual crystals of a single mineral may be compositionally zoned.

Pyrite occurs mainly as framboids in the samples. The term framboid (from the French “framboise”) refers to the raspberry-like texture of the pyrite. Framboids are spherical structures made up of equant microcrystals of pyrite.

Estimated mineral abundances for the raw leach column starting material as determined by Siroquant are summarized in Table 5.4, along with data for samples after the low-temperature ash (LTA), leach column residues, estimated amorphous content and measured % LTA. Some trace minerals identified by SEM were not identified by XRD because of their low modal abundance. Estimates of low concentrations (<5 weight percent) of minerals by XRD are not very reliable; errors on individual minerals are on the order of ± 1 weight percent.

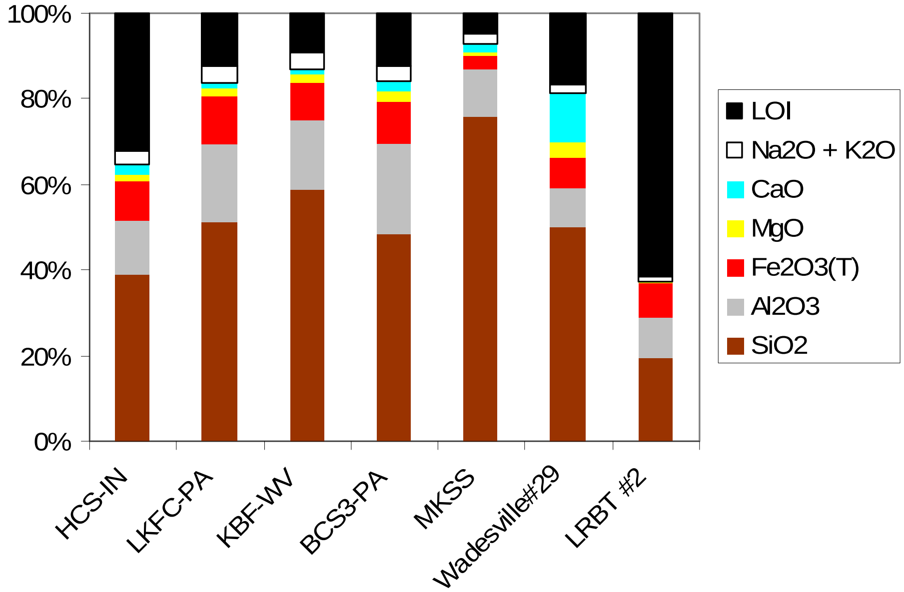


Figure 5.2*A*. Bar chart showing relative proportions of major elements as oxides and loss on ignition (LOI) based on whole-rock geochemical data for unweathered rocks (Table 5.2). Fe_2O_3(T) represents total iron reported as ferric iron.

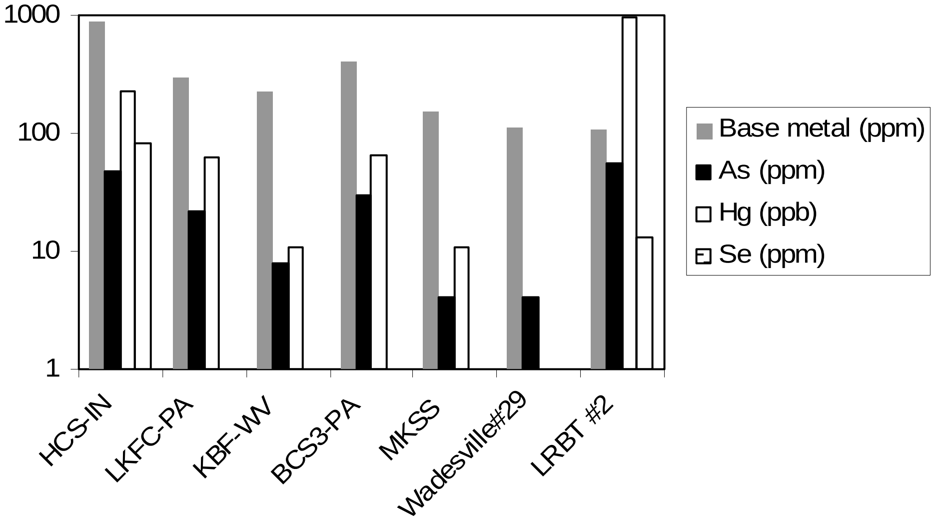


Figure 5.2*B*. Bar chart showing concentrations of selected trace-elements based on whole-rock geochemical data for unweathered rocks (Table 5.2). Base metals = Copper + lead + zinc+ cobalt + cadmium + nickel. Note that the data are plotted on a logarithmic scale. Selenium is below detection limits for all samples except HCS-IN and LRBT#2. Mercury is below detection limits for Wadesville #29.

Table 5.3. Minerals.

[Weathering behavior comments based on Goldrich's (1938) mineral-stability series in weathering and Sverdrup's (1990) relative reactivity of monomineralic samples; NP classes based on Jambor et al. (2002)]

Mineral	Ideal formula	Weathering behavior	NP<0	Inert	NP>0
Quartz	SiO_2	Inert		X	
Chlorite	$(Mg,Fe)_5Al(Si_3Al)O_{10}(OH)_8$	Intermediate weathering			X
Micas and clays					
Muscovite	$KAl_2(AlSi_3O_{10})(OH)_2$	Very slow weathering		X	
Phengite	Series between muscovite and $K(Mg,Fe^{2+})(Al,Fe^{3+})Si_4O_{10}(OH)_2$			X	
Biotite	$K(Mg,Fe)_3(AlSi_3O_{10})(OH)_2$	Intermediate weathering			X
Illite	$K_{0.65}Al_2(Al_{0.65}Si_{3.35}O_{10})(OH)_2$	Very slow weathering			
Kaolinite	$Al_2Si_2O_5(OH)_4$	Slow weathering		X	
Feldspars					
Albite	$NaAlSi_3O_8$	Slow weathering		X	
Anorthite	$CaAl_2Si_2O_8$	Fast weathering		X	X
Potassium feldspar	$KAl_2(AlSi_3O_{10})(OH)_2$	Very slow weathering		X	
Accessory minerals					
Apatite	$Ca_5(PO_4)_3(OH,F,Cl)$	Fast weathering			X
Zircon	$ZrSiO_4$	Inert		X	
Rutile	TiO_2	Inert		X	
Sulfate minerals					
Gypsum	$CaSO_4 \bullet 2H_2O$			X	
Barite	$BaSO_4$	Insoluble		X	
Sulfide minerals					
Pyrite	FeS_2		X		
Carbonate minerals					
Calcite	$CaCO_3$	Dissolving			X
Siderite	$FeCO_3$	Dissolving	X		X
Ankerite	$Ca\,(Fe,Mg,Mn)(CO_3)_2$	Dissolving	X		X

Houchin Creek Shale (Sample HCS-IN). The Houchin Creek Shale was selected for weathering experiments because of its high total sulfur content and low NP values (Table 5.1). In thin section, the shale is a black, very fine-grained homogeneous rock; one of the eight fragments contained clots and veinlets of coarse-grained calcite (Figure 5.3). The shale contains significant amounts of organic material, as indicated by thin section and SEM observations (Figure 5.4) and the low-temperature ash measurement of 79 weight percent. Sample HCS-IN also had the highest LOI of all the shales. The post-leach residue contained 18.1% total carbon, most of which is organic (Table 5.2). The crystalline part of the shale was composed of ~32% quartz, 26% micas and clay minerals, 5% chlorite, 17% pyrite, 6% feldspar, ~ 3% carbonate minerals, gypsum, and accessory minerals (Table 5.4). The XRD-based estimate of amorphous content of the shale was 67 weight percent (Table 5.4). Pyrite is scattered throughout the shale as single grains or as clusters of framboids (Figure 5.3*D*). Most of the minerals were so fine-grained that they cannot be readily identified by optical microscopy. SEM images showed that the quartz was present as rounded grains on the order of 5 to 10 micrometers in diameter in a matrix of micas, clays, and other minerals (Figure 5.4).

Table 5.4. Mineralogy determined by XRD.

[Raw, raw sample of leach column starting material; LTA, sample after low-temperature ash to remove organic material; LCR, leach column residue after 16 weeks leaching. Data reported as weight percent of crystalline part of the rock. For each mineral, the error of the fit is on the order of ± 1 weight percent or less. Amorphous content estimated by Rietveld refinement on corundum-spiked samples. '-', not included in refinement

	HCS-IN			LKFC-PA			KBF-WV			BCS3-PA		
	Raw	LTA	LCR	Raw	LTA	LCR	Raw	LTA	LCR	Raw	LTA	LCR
Chi^{2*}	3.68	3.13	3.3	3.53	3.29	3.47	4.03	3.34	2.9	3.79	3.6	3.49
Mineral												
Quartz	32.4	30.7	34.3	37.1	36.8	40.0	42.0	42.2	39.7	34.4	32.2	33.7
Chlorite	5.0	4.2	4.6	9.9	9.0	8.9	6.2	8.9	6.3	10.9	11.4	7.2
Muscovite	7.8	14.2	8.4	16.4	17.1	12.0	15.7	15.3	15.2	16.8	19.8	18.0
Phengite	4.6	4.4	5.7	3.7	11.3	11.5	10.3	12.9	16.0	6.8	10.5	20.1
Biotite	-	-	-	-	-	-	0.1	0.8	1.7	-	-	-
Illite	11.6	7.7	12.9	9.5	4.6	8.4	2.3	1.6	2.7	8.6	8.4	6.5
Kaolinite	2.4	3.2	3.4	4.6	3.7	5.9	5.4	3.5	4.3	5.2	5.6	3.8
Micas & clay	26.4	29.5	30.4	34.2	36.7	37.8	33.8	34.1	39.9	37.4	44.3	48.4
Albite	4.5	4.3	4.4	0.0	0.0	0.0	9.3	6.2	3.5	0.0	0.0	0.0
Anorthite	0.9	2.5	0.6	1.6	0.1	0.1	0.8	0.1	0.1	0.2	0.1	0.1
Potassium feldspar	0.3	0.8	0.0	1.4	0.0	0.0	1.2	0.0	1.4	1.6	0.8	0.0
Feldspars	5.7	7.6	5	3	0.1	0.1	11.3	6.3	5	1.8	0.9	0.1
Apatite	3.3	6.4	3.5	1.5	2.4	0.1	0.4	1.5	0.9	0.0	0.2	2.2
Zircon	0.6	0.5	0.5	0.5	0.1	0.6	0.0	0.2	0.4	0.9	0.4	0.5
Rutile	0.0	0.5	0.3	0.7	0.4	0.6	0.8	1.1	0.4	0.7	0.9	1.3
Accessory minerals	3.9	7.4	4.3	2.7	2.9	1.3	1.2	2.8	1.7	1.6	1.5	4
Gypsum	6.4	0.0	9.1	0.0	0.0	0.6	0.0	0.0	0.4	0.0	0.0	0.0
Barite	0.0	0.0	0.1	0.2	0.0	0.1	0.7	0.2	0.0	0.9	0.3	0.0
Pyrite	17.5	17.3	11.2	7.5	7.9	2.4	0.8	1.3	0.9	3.0	3.4	3.0
Calcite	0.6	0.6	0.1	0.0	0.7	0.0	0.4	0.9	0.7	2.9	2.0	1.7
Siderite	0.0	0.3	0.0	5.0	4.8	8.4	3.1	1.8	5.2	4.7	3.9	1.5
Ankerite	2.1	2.7	0.9	0.3	1.1	0.2	0.7	1.6	0.3	2.4	0.0	0.4
Carbonate minerals	2.7	3.5	1	5.3	6.6	8.6	4.2	4.3	6.2	10.0	5.9	3.6
Amorphous content	69%			53%			51%			57%		
Low temperature ash (LTA)		79%			99%			99%			100%	
% Mass lost by LTA		21%			1%			1%			0%	
%LOI (chemistry)	32%			12%			9%			12%		

* Chi^2 is a computed statistical residual, which is used as a measure of the fit of the refinement of the XRD pattern. $Chi^2=1$ for a perfect correspondence between the least-squares model and the observed data. In complex rocks, ideal values are almost never observed due to systematic errors and imperfect physical corrections. Values less than 5 are considered reasonable fits for these rocks.

Table 5.4—Continued.

	MKSS			Wadesville #29		LRBT	
	Raw	LTA	LCR	Raw	LTA	Raw	LTA
Chi^{2*}	3.7	3.97	3.03	3.51	3.5	4.2	3.68
Quartz	64.5	58.9	61.7	41.62	41.7	22.98	23.16
Chlorite	4.3	6.0	5.4	3.73	3.24	2.13	1.77
Muscovite	13.8	8.3	13.6	2.54	6.79	7.27	8.3
Phengite	2.2	4.6	3.3	2.65	2.46	0.55	0.55
Biotite	-	-	-	-	-	-	-
Illite	0.5	3.6	3.7	1.7	1.4	14.91	13.68
Kaolinite	1.8	2.3	3.2	1.87	0.28	10.41	13.02
Micas & clay	18.3	18.8	23.8	8.76	10.93	33.14	35.55
Albite	0.3	1.4	0.5	2.6	0.87	0.01	0.02
Anorthite	1.5	2.0	0.0	0.5	1.11	4.35	3.01
Potassium feldspar	0.4	1.0	0.5	0.78	0.94	0.02	0.02
Feldspars	2.2	4.4	1	3.88	2.92	4.38	3.05
Apatite	0.6	1.2	0.9	1.89	0.7	3.89	2.9
Zircon	0.5	0.9	0.2	0.3	0.13	0.65	1.28
Rutile	1.0	1.2	0.9	1.04	0.52	0.63	1.23
Accessory minerals	2.1	3.3	2	3.23	1.35	5.17	5.41
Gypsum	0.0	0.0	0.0	0	0	0.5	0.88
Barite	0.4	0.5	0.5	0.01	0.11	0.62	0.02
Pyrite	0.4	0.7	0.5	0.91	0.53	29.08	29.02
Calcite	3.8	3.1	3.8	1.39	1.02	0.76	0.03
Siderite	2.5	2.9	1.2	0.3	0.06	0.02	0.2
Ankerite	1.6	1.5	0.2	36.1	38.1	1.21	0.88
Carbonate minerals	7.9	7.5	5.2	38	39	2.0	1.1
Amorphous content	37%			15%		77%	
Low temperature ash (LTA)		91%		100%		45%	
% Mass lost by LTA		9%		0%		55%	
%LOI (chemistry)	5%			17%		60%	

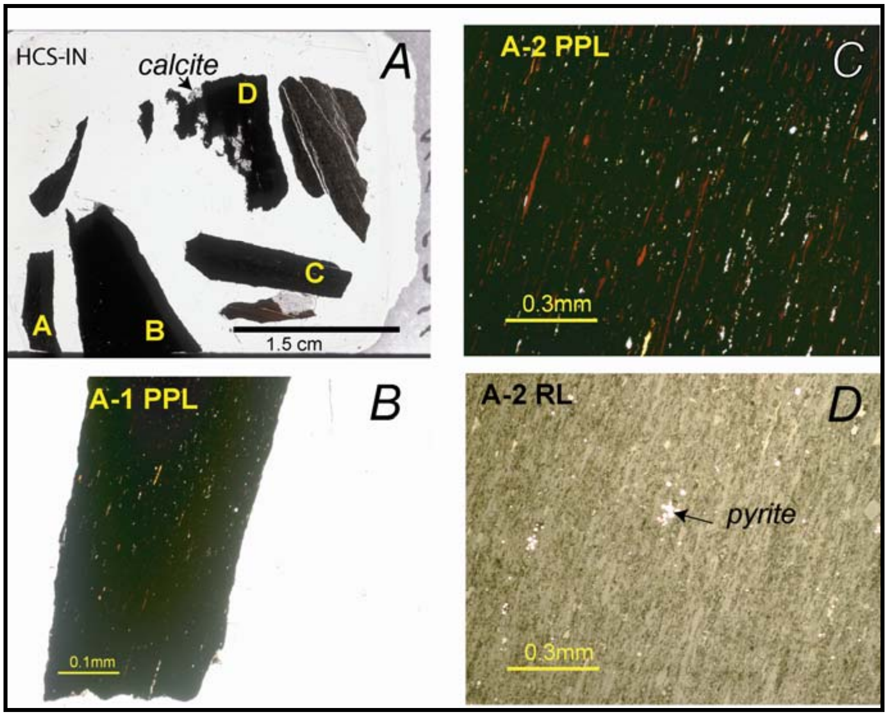


Figure 5.3. Houchin Creek Shale (Sample HCS-IN). *A*, Scanned image of polished thin section. Colorless patches on the edges of rock chip D are inclusions of calcite. *B***,** Photomicrograph of rock chip A in plane-polarized light (PPL) showing the very fine-grained texture of the shale. *C*, Rock chip A at higher magnification. *D*, Same view of rock chip A as shown in *C* in reflected light (RL) shows clusters of pyrite framboids.

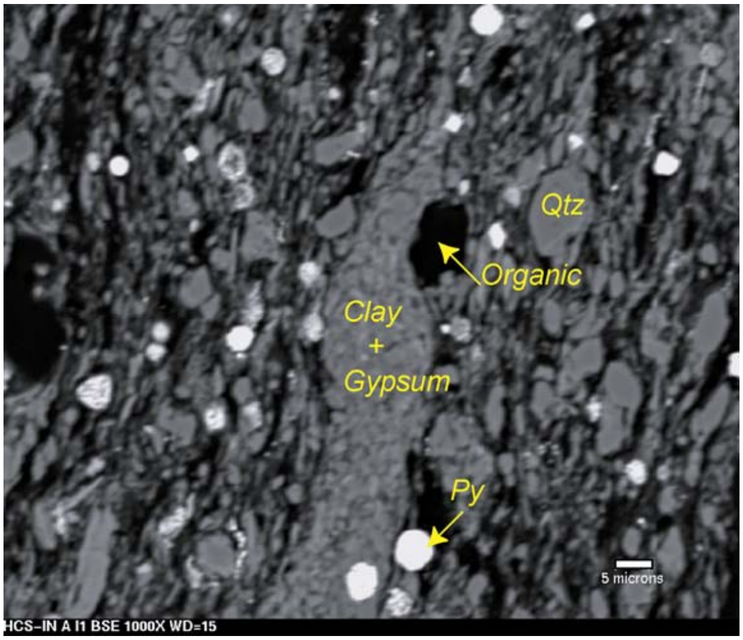


Figure 5.4. Houchin Creek Shale (Sample HCS-IN). SEM image of rock chip A in Figure 5.3 at 1,000X showing pyrite (Py, white) and organic material (black) scattered throughout the shale. BSE (backscatter mode) shows the atomic number contrast of different minerals. Quartz (qtz) appears gray.

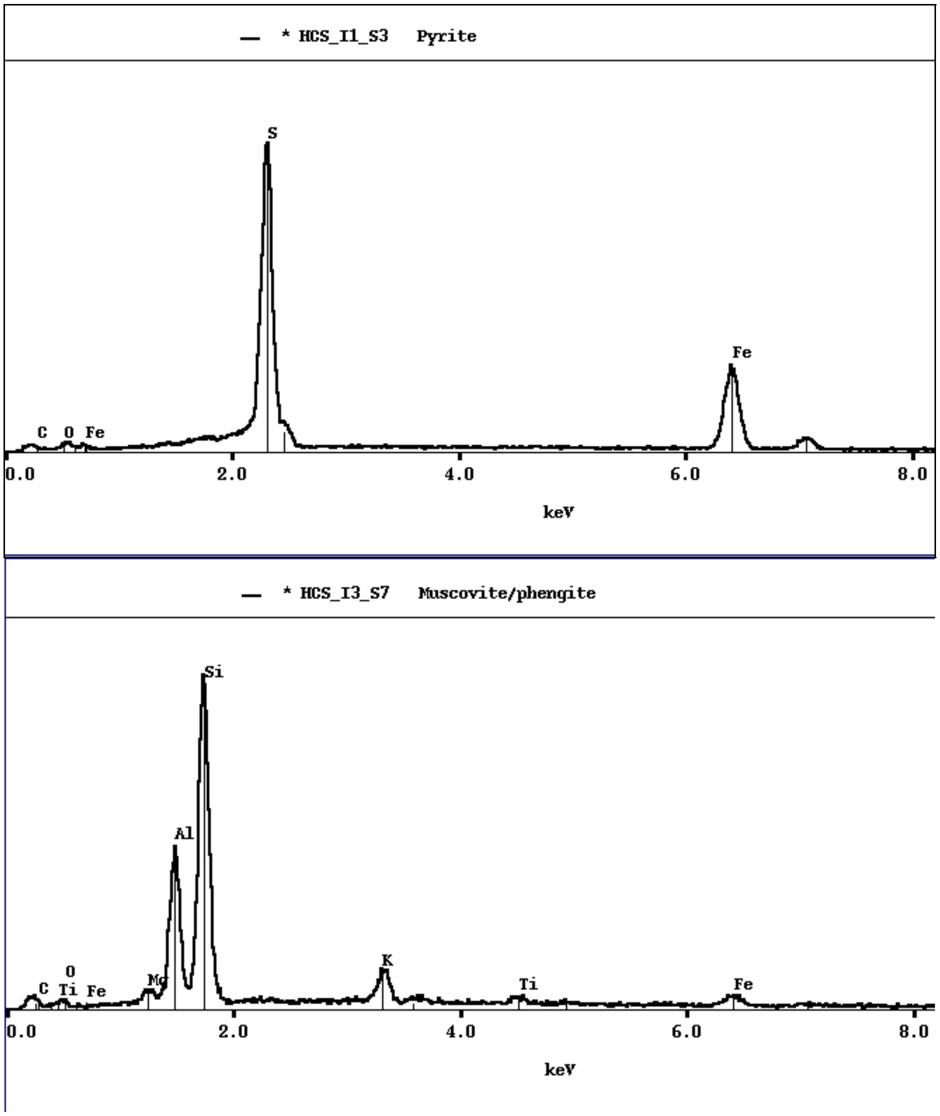


Figure 5.5. Houchin Creek Shale (Sample HCS-IN). EDS spectra for pyrite and muscovite (phengite). The EDS spectra show the elemental compositions at discrete spots in polished thin sections. The vertical bars are the reference positions for characteristic x-ray lines in electronvolts (keV). Pyrite is indicated by iron (Fe) peaks between 6 and 8 keV and sulfur (S) peaks just above 2keV. Muscovite is indicated by peaks for silicon (Si), aluminum (Al), potassium (K) with minor peaks for magnesium (Mg), iron (Fe) and titanium (Ti). Carbon (C) is detected because the samples are carbon-coated for analysis; traces of oxygen (O) are always present.

SEM spectra confirm identification of pyrite and show that some of the muscovite in HCS-IN contains minor amounts of iron and titanium, which agrees with the XRD identification of phengite (Figure 5.5). Carbon-rich organic material contains sulfur. The sulfur may be present as finely disseminated pyrite too small to be resolved by SEM. The SEM study confirmed the presence of gypsum and apatite, and also identified trace amounts of chalcopyrite.

Lower Kittanning Shale (Sample LKFC-PA). The Lower Kittanning Shale sample was collected from the Redbank Creek watershed in Pennsylvania, where overburden produces alkaline drainage although the NP is not very high. Sample LKFC contains about 1 weight percent sulfur and low NP. The Lower Kittanning Shale is coarser grained than the Houchin Creek Shale. Rock chips exhibit a range of textures in thin section. Some rock chips contain quartz grains up to 0.1 millimeters in diameter (Figure 5.6, chips A,B,C,F), some have more uniform, finer-grained , textures, and one chip (G) contained fossils. LKFC has low whole-rock loss-on-ignition and a low-temperature ash concentration of 99 weight percent indicating low total organic content. The XRD-based estimate of amorphous content of the shale is 67 weight percent (Table 5.2). The crystalline part of the shale is composed of the following (in weight percent): ~37 % quartz, 34 % micas and clay minerals, 10% chlorite, 8% pyrite, 3% feldspar, and 5% carbonate minerals (Table 5.4). Pyrite occurs as isolated cubes and as framboids scattered throughout all of the rock chips (Figure 5.7). Accessory minerals include apatite, which accounts for much of the phosphorous and some of the calcium in the rock. Although apatite is an accessory mineral present in low concentrations, apatite has NP>0 and can provide acid neutralization, especially where it is in close proximity to reacting pyrite (Figure 5.8). Framboids occur as rounded clusters of hundreds of discrete grains and as strings of crystals arranged like peas in a pod within organic material (Figure 5.9). These textures indicate an abundance of pyrite surfaces available for oxidation. Siderite is the dominant carbonate mineral identified by XRD. The siderite is not readily identified by optical microscopy because it is so fine-grained. Of the 18 rock chips examined, only chip G contained calcite, which is present as fossil material (Figure 5.10).

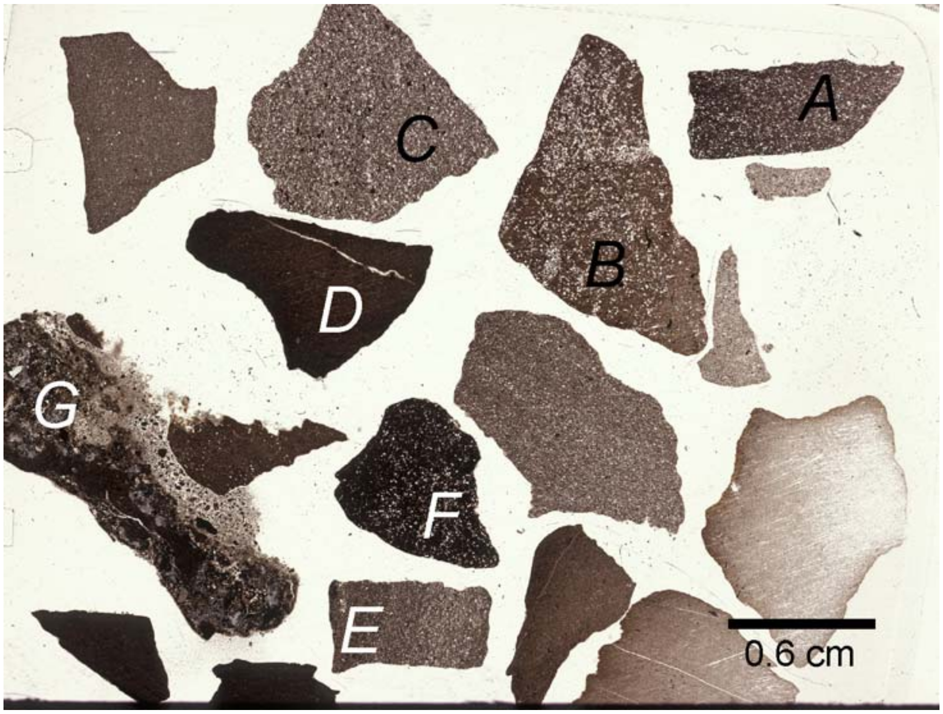


Figure 5.6. Lower Kittanning Shale (Sample LKFC-PA). Scanned image of polished thin section. Note the heterogeneous texture the different chips.

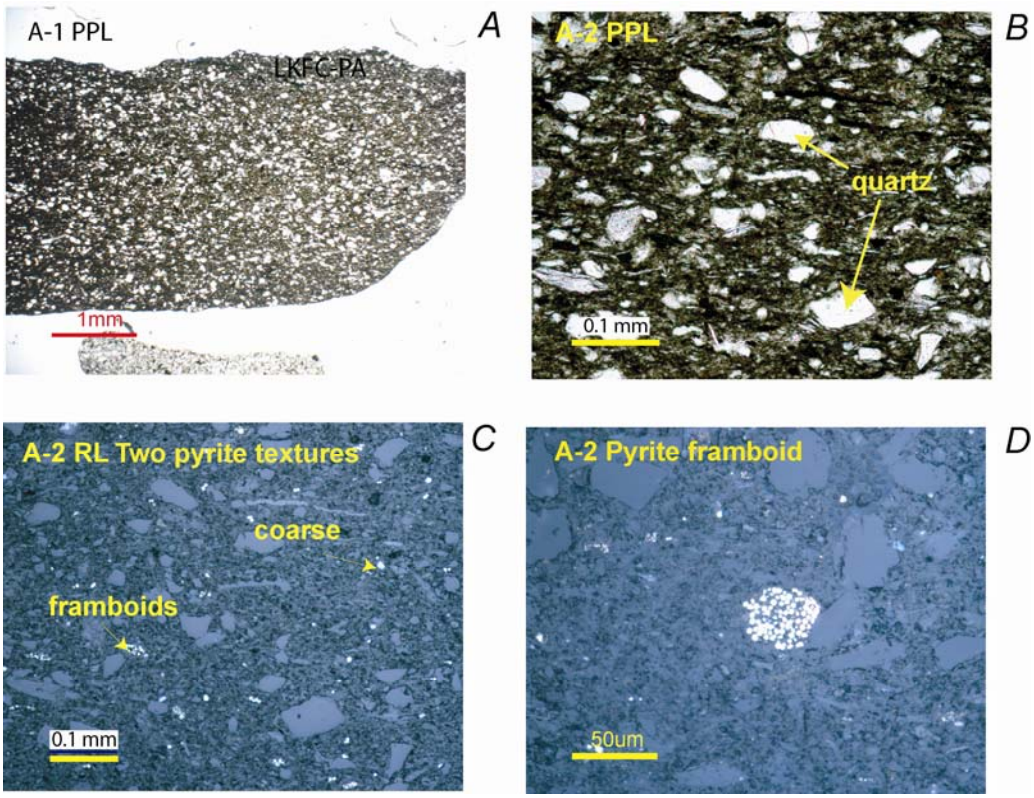


Figure 5.7. Lower Kittanning Shale (Sample LKFC-PA). Photomicrographs. A, Rock chip in plane-polarized light (PPL) at 2.5X. *B,* Subrounded quartz grains (0.1 millimeters across) in a fine-grained matrix mostly composed of mica, chlorite, and clay (20 X, PPL). *C,* Same view as *B*, in reflected light, shows scattered cubes of pyrite as well as framboids. *D,* High-magnification (50X) shows framboid texture, reflected light.

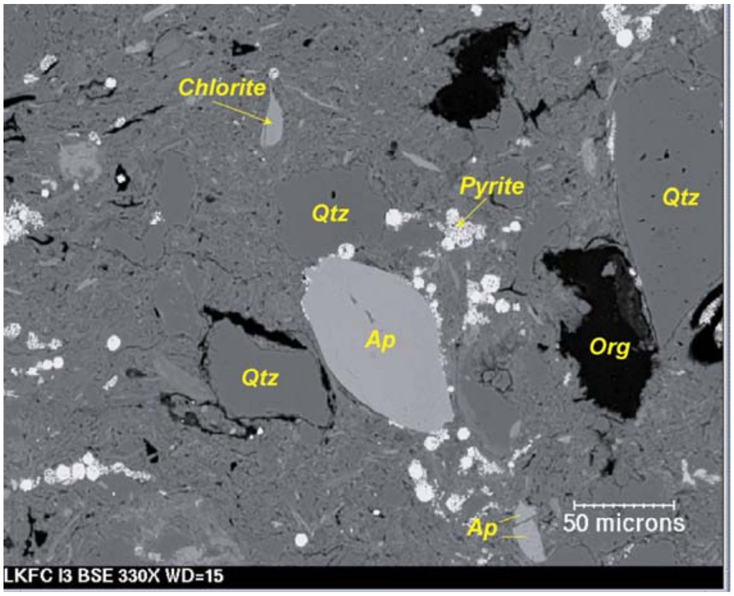


Figure 5.8. Lower Kittanning Shale (Sample LKFC-PA). SEM image showing coarse apatite rimmed by pyrite.

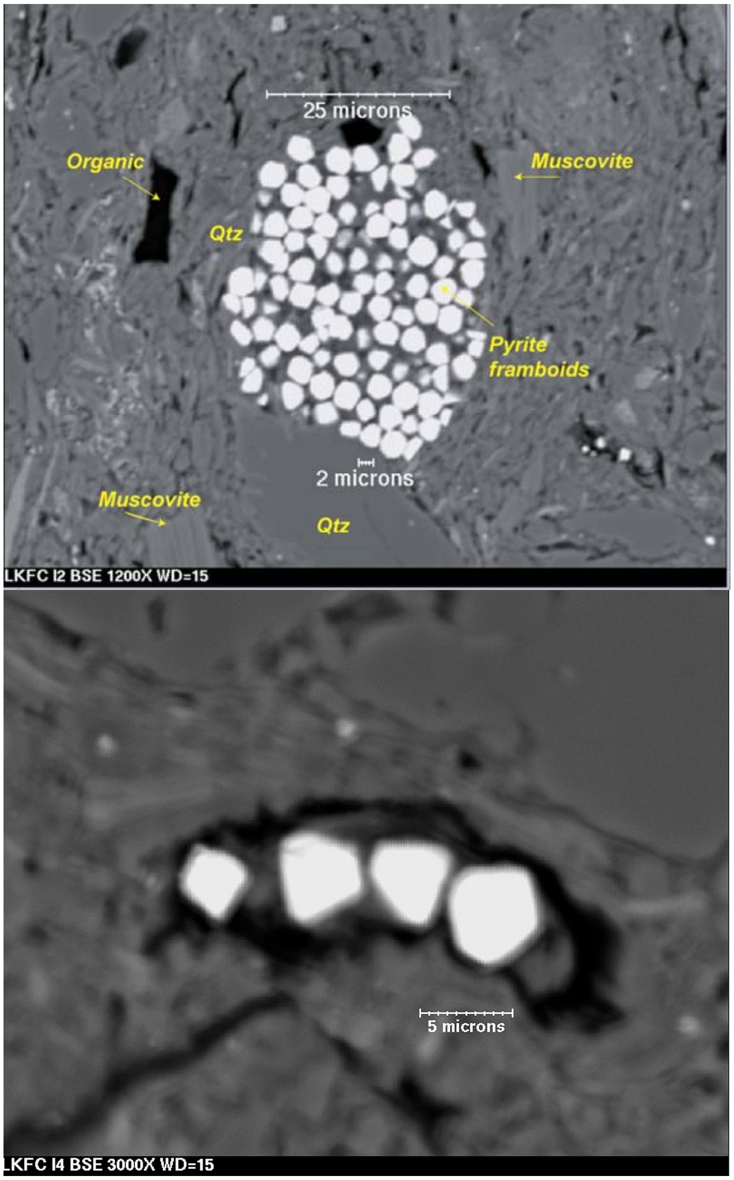


Figure 5.9. Lower Kittanning Shale (Sample LKFC-PA). SEM images of pyrite framboids. Note the large surface area. Rounded clusters on the order of 25 micrometers in diameter may consist of tens to hundreds of individual grains.

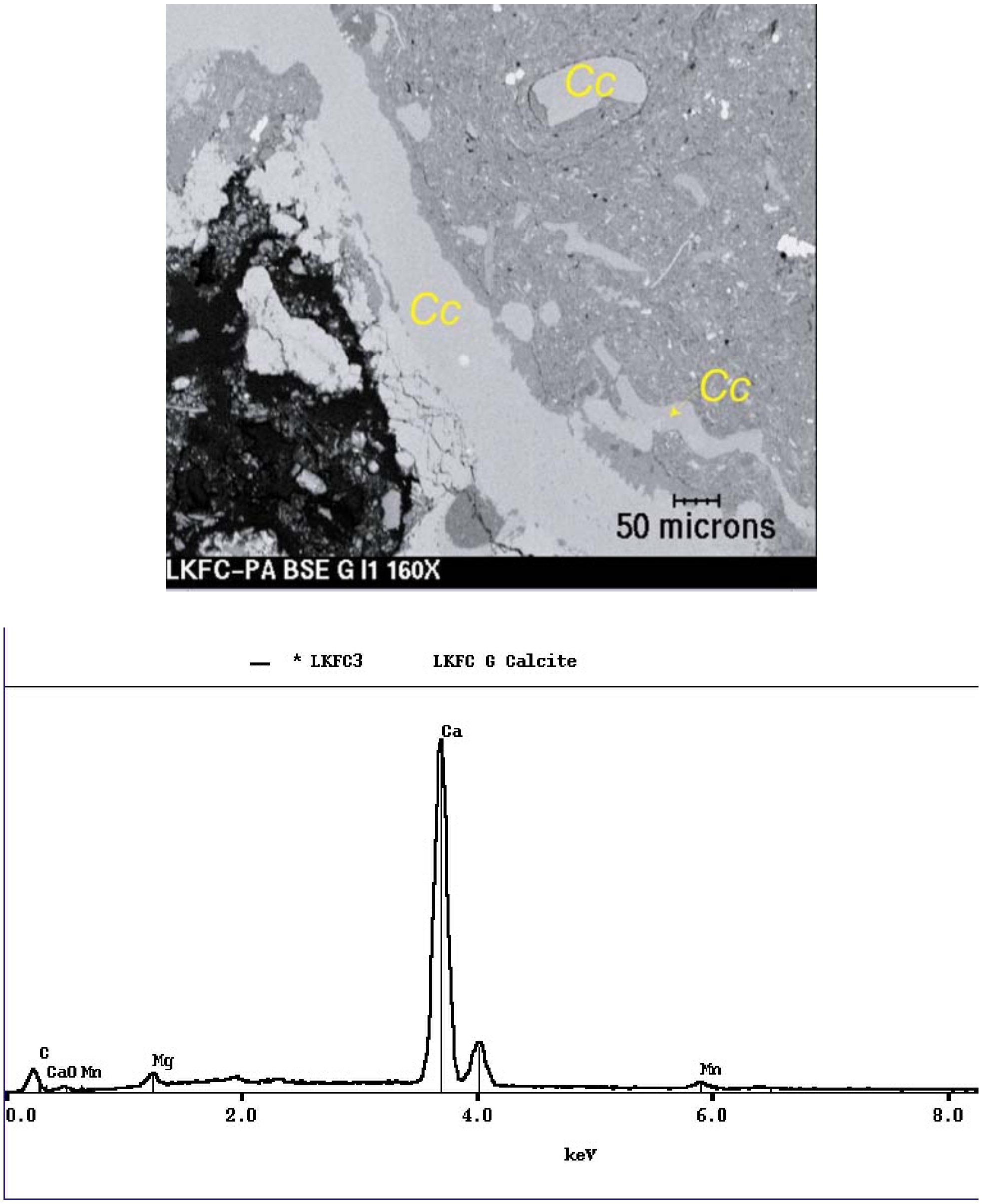


Figure 5.10. Lower Kittanning Shale (Sample LKFC-PA). SEM data showing BSE image of coarse calcite(Cc) in rock chip G. Note that the calcite contains minor amounts of Mg and Mn.

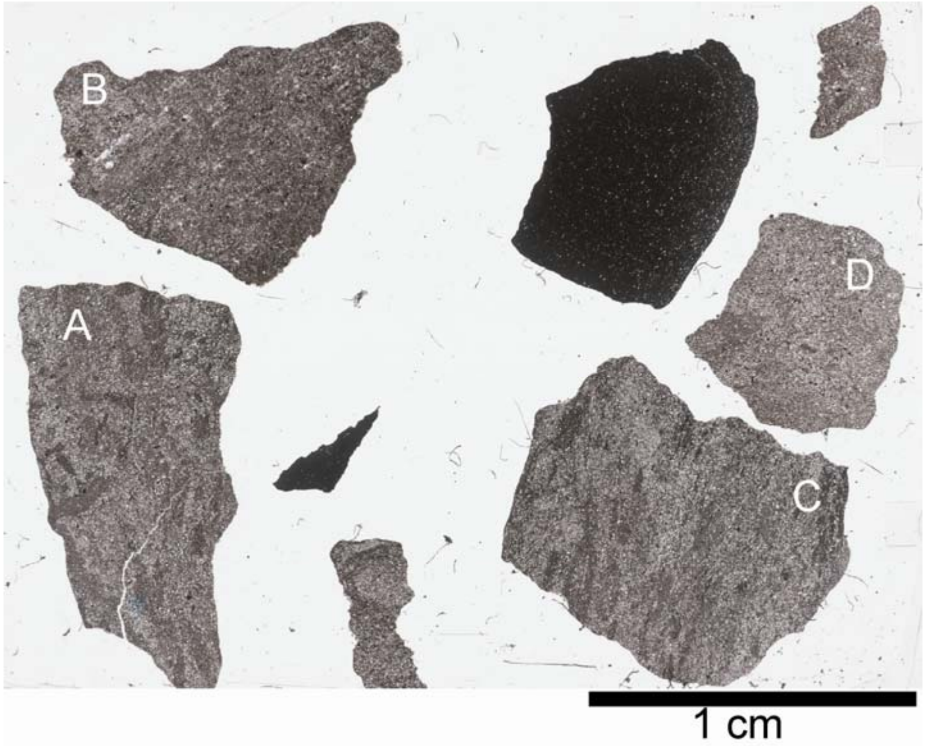


Figure 5.11. Kanawha Black Flint Shale (Sample KBF-WV). Scanned image of polished thin section.

Kanawha Black Flint Shale (Sample KBF-WV). The Kanawha Black Flint Shale was included in the phase 3 tests as a "gray-zone" sample from an area in West Virginia that might contain elevated selenium (Table 5.1). Gray zone samples are those samples for which alkalinity or acidity production is difficult to predict because of moderate amounts of neutralization potential and sulfur. The shale had low NP and contained about 0.2 weight percent sulfur. The selenium content of composite sample analyzed for this studied was below the detection limit (<3 parts per million selenium).

The shale is a patchwork of dark-colored clay-rich areas and coarser-grained quartz-rich areas (Figure 5.11). Low temperature ash (99 weight percent) and a relatively low loss-on-ignition (9 weight percent) indicate a relatively low organic content. XRD analysis estimated the mineralogical composition (in weight percent) as: 42 % quartz, 34% micas and clay minerals, 6% chlorite, <1% pyrite, 11% feldspar, and 4% carbonate minerals (Table 5.4). Laths of colorless muscovite, brown biotite, green chlorite and clots of brownish clay in a carbonate matrix were readily identifiable by optical microscopy (Figure 5.12). Despite the low estimates of organic material and pyrite for the bulk rock, both were present in many of the rock chips. The shale was more sodic (0.74 weight percent Na_2O) than the other samples (Table 5.2). It was also the most feldspathic (Table 5.4). Microprobe analysis confirmed the XRD identification of albite as the major feldspar present. Both Fe-rich carbonate and calcite were identified by SEM (Figure 5.13). Matrix carbonate grains (on the order of 5 micrometers or smaller) were slightly zoned, with iron increasing towards the rim of the grain. Zoned carbonate rimming a sphalerite grain explained the zinc detected in the whole-rock chemistry. Nearly pure calcite fragments (20 micrometers long) are rimed by pyrite (Figure 5-13).

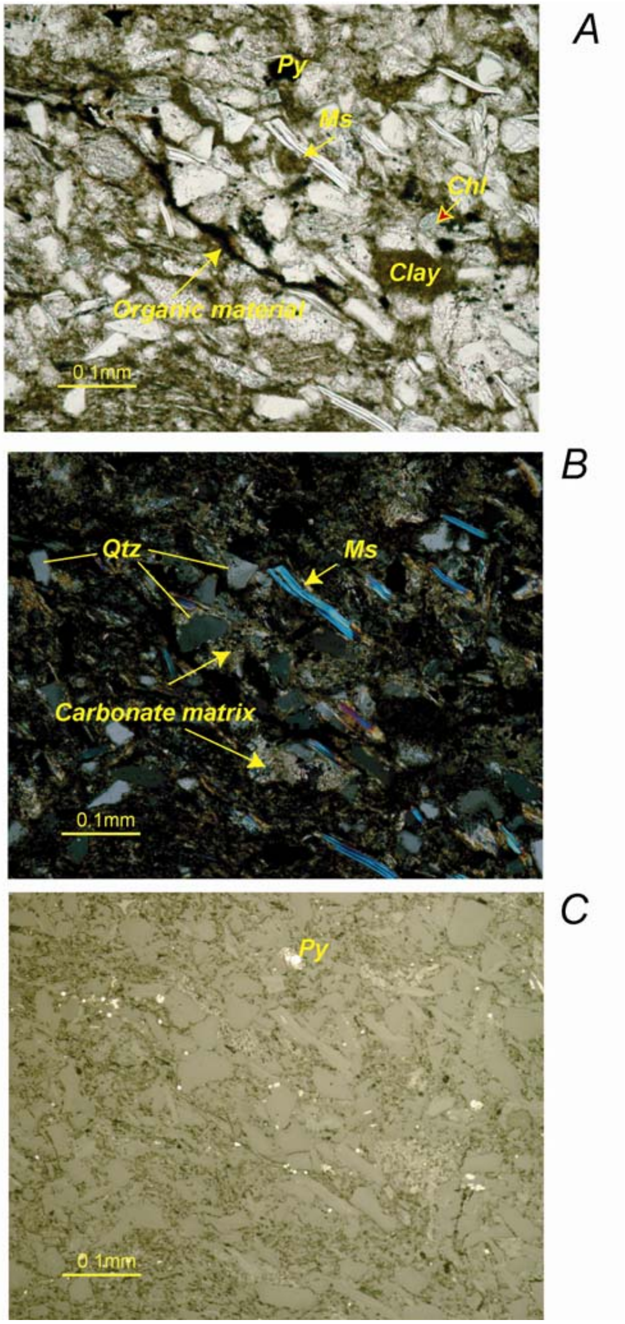
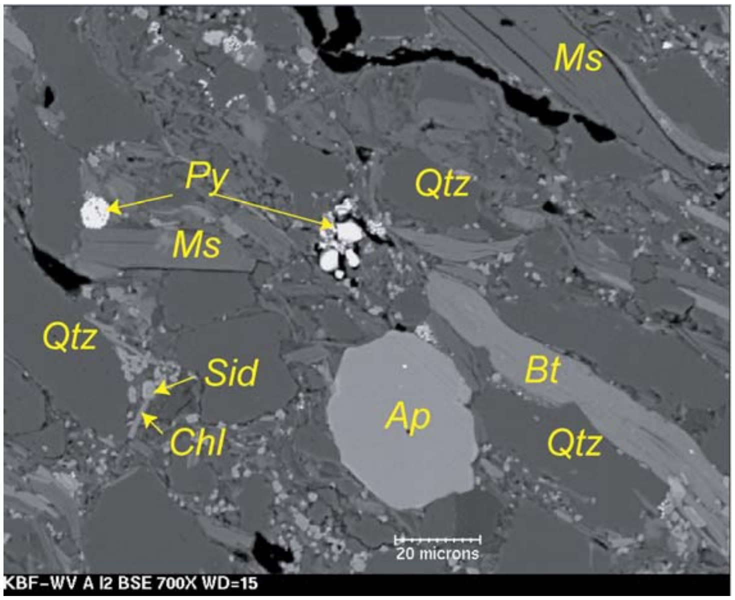


Figure 5.12. Kanawha Black Flint Shale (Sample KBF-WV). Photomicrographs of rock fragment C (Fig. 4). *A*, Quartz grains (Qtz), muscovite laths (Ms), green chlorite (Chl), clots of brown clay, pyrite (Py), and organic material; plane-polarized light. *B*, Same view in crossed nicols shows birefringence of carbonate-rich rock matrix. *C*, Same view in reflected light. All of the white grains are pyrite (Py). Note that both pyrite and organic material appear opaque (black) in transmitted light and some pyrite is enclosed in organic material.

A



B

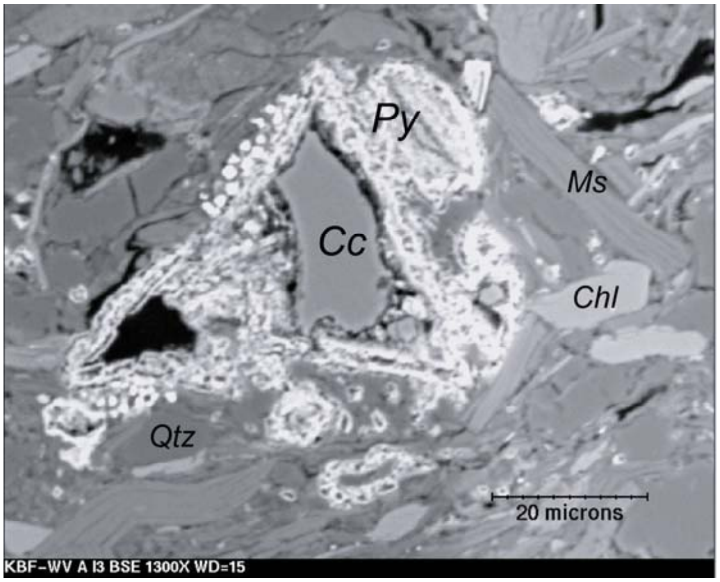


Figure 5.13. Kanawha Black Flint Shale (Sample KBF-WV). Backscattered-electron SEM images showing pyrite textures. *A*, Round pyrite framboid (6 micrometers in diameter) and clot of discrete pyrite grains associated with organic matter. Note large anhedral crystal of apatite (Ap) as well as muscovite (Ms), biotite (Bt), and quartz (Qtz). The finer-grained matrix consists of calcite, siderite (Sid), chlorite (Chl), and clay. *B*, Pyrite crystals (~2 micrometers in diameter) form a 60-micrometer mass rimming calcite (Cc) and organic matter (black). Note cellular structure of pyrite, suggesting that the pyrite has replaced organic matter.

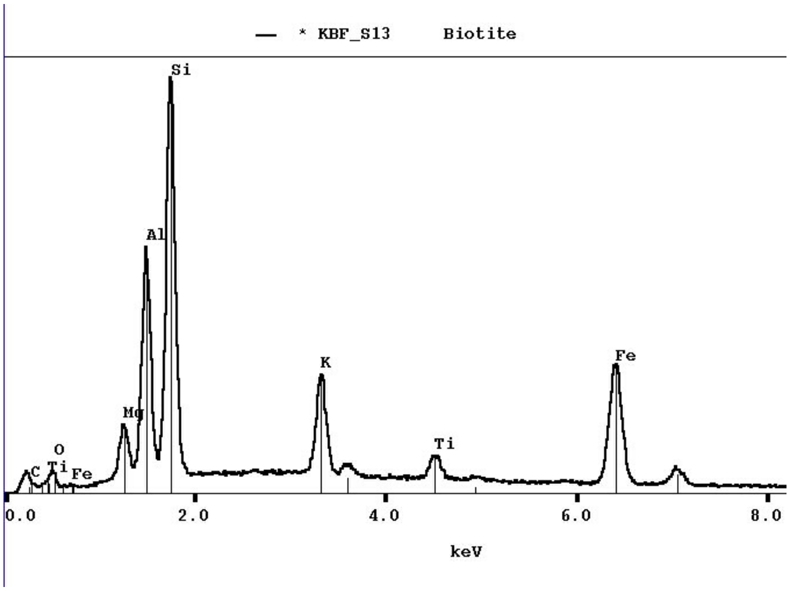


Figure 5.14. Kanawha Black Flint Shale (Sample KBF-WV). The representative EDS spectra show that the biotite is iron-rich, with minor amounts of titanium and magnesium.

Brush Creek Shale (Sample BCS3-PA). The Brush Creek shale is an ADTI reference standard selected as a primary rock sample for weathering experiments (Table 5.1). The shale has moderately high total sulfur (0.90 to 0.93 weight percent) and moderate NP values. Although the shale is classified as a "gray zone" sample for AMD predictions, it is associated with alkaline mine drainage throughout the bituminous coal region of Pennsylvania (Brady et al., 1998).

The Brush Creek Shale sample contained very little organic material based on whole-rock low-temperature ash (100 weight percent) and loss-on-ignition (12 weight percent LOI). Many of the rock chips were fossil-rich; some contain inclusions of calcite or barite (Figures 5.15 and 5.16). Some rock chips show a prominent rock fabric, with elongated mineral grains and black inclusions that contain variable amounts of organic material and pyrite framboids (Figure 5.17). Pyrite framboids had complex internal structures composed of individual pyrite grains ranging from <1 micrometer to 10 micrometers or more (Figure 5.18).

The mineralogical composition of the shale (in weight percent) is: 34 % quartz, 37% micas and clay minerals, 11% chlorite, 2% feldspar, 3% pyrite, and 10% carbonate minerals (Table 5.4). The carbonate minerals include calcite, ankerite, and siderite. Although the carbonate minerals are a minor component of the rock, the XRD pattern for siderite is distinct from that of calcite or ankerite/dolomite. Three separate samples of the composite shale were analyzed by XRD to examine shale heterogeneity and reproducibility of quantitative XRD results. Statistical errors associated with the Rietveld refinement of each pattern are represented by the error of fit (Table 5.5); errors associated with each mineral are ± 1.4 weight percent or less. The spread in estimates indicates sample heterogeneity as well as systematic errors in sample preparation and XRD methodology.

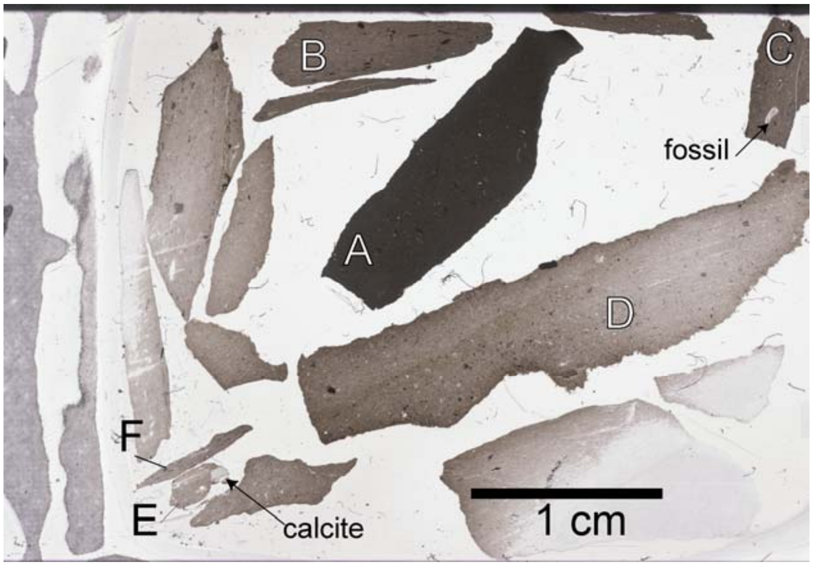


Figure 5.15. Brush Creek Shale (Sample BCS3-PA). Scanned image of polished thin section. Note calcite along the edge of chip E; fossil in chip C.

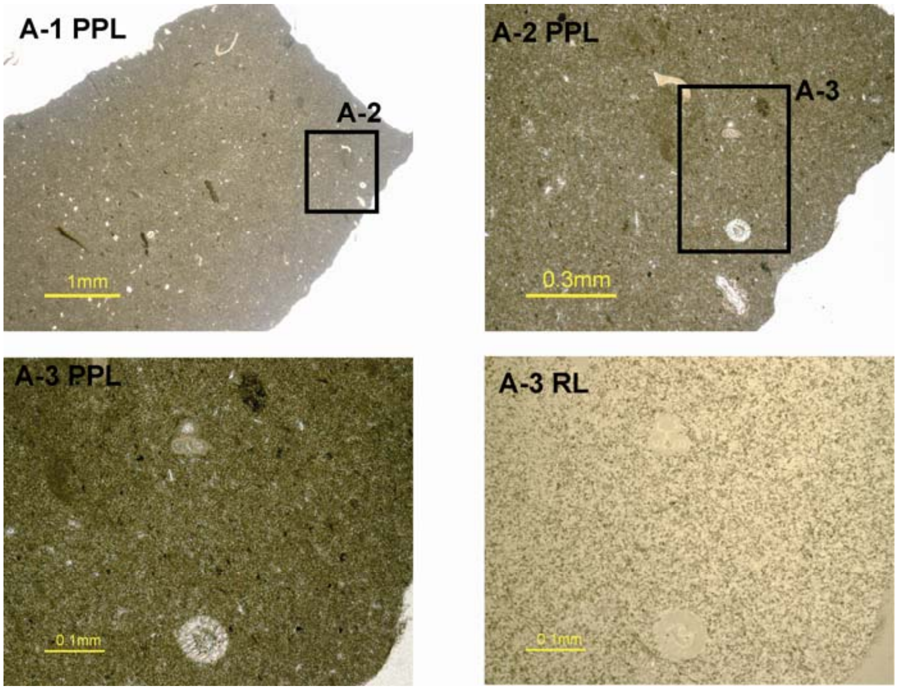


Figure 5.16. Brush Creek Shale (Sample BCS3-PA). Photomicrographs of rock fragment A showing shale textures at successively higher magnification. The shale consists of 0.5 millimeters calcite fossil fragments and elongated dark-colored clots of organic material, pyrite, and clay set in a fine-grained groundmass mainly composed of quartz, chlorite, calcite, siderite, and clay. The groundmass grain size is less than 20 micrometers. PPL, plane-polarized light. RL, reflected light.

Table 5.5. Mineralogy for BCS-3 on replicate splits of raw leach column starting material.

	Split 1		Split 2		Split 3	
Chi^2	3.8		5.5		5.6	
Phase	Weight%	±	Weight%	±	Weight%	±
Quartz	34.4	*1.0*	31.5	*1.0*	30.4	*0.6*
Chlorite	10.9	*0.5*	9.4	*0.5*	9.9	*0.4*
Muscovite	16.8	*0.7*	25.9	*1.4*	21.3	*0.9*
Phengite	6.8	*1.1*	8.3	*1.4*	4.3	*0.5*
Illite	8.6	*0.9*	5.3	*0.8*	10.0	*0.5*
Kaolinite	5.2	*0.4*	6.2	*0.3*	4.0	*0.2*
Micas & clay	37.4		45.7		39.6	
Albite	0.0		0.0		0.0	
Anorthite	0.2	*1.3*	0.4	*1.1*	3.4	*0.9*
Orthoclase	1.6	*0.8*	1.0	*0.7*	0.0	*0.6*
Feldspars	1.8		1.4		3.4	
Apatite	0.0		1.2	*0.6*	2.3	*0.4*
Zircon	0.9	*0.2*	1.0	*0.2*	0.3	*0.1*
Rutile	0.7	*0.3*	1.3	*0.2*	1.4	*0.2*
Accessory minerals	1.6		3.5		4.0	
Gypsum	0.0		0.0		0.0	
Barite	0.9		0.5	*0.2*	0.0	
Pyrite	3.0	*0.3*	3.6	*0.2*	2.7	*0.2*
Calcite	2.9	*0.3*	1.2	*0.1*	2.3	*0.3*
Siderite	4.7	*0.3*	3.3	*0.3*	7.0	*0.5*
Ankerite	2.4	*0.4*	0.0		0.8	*0.3*
Carbonate minerals	10.0		4.5		10.0	

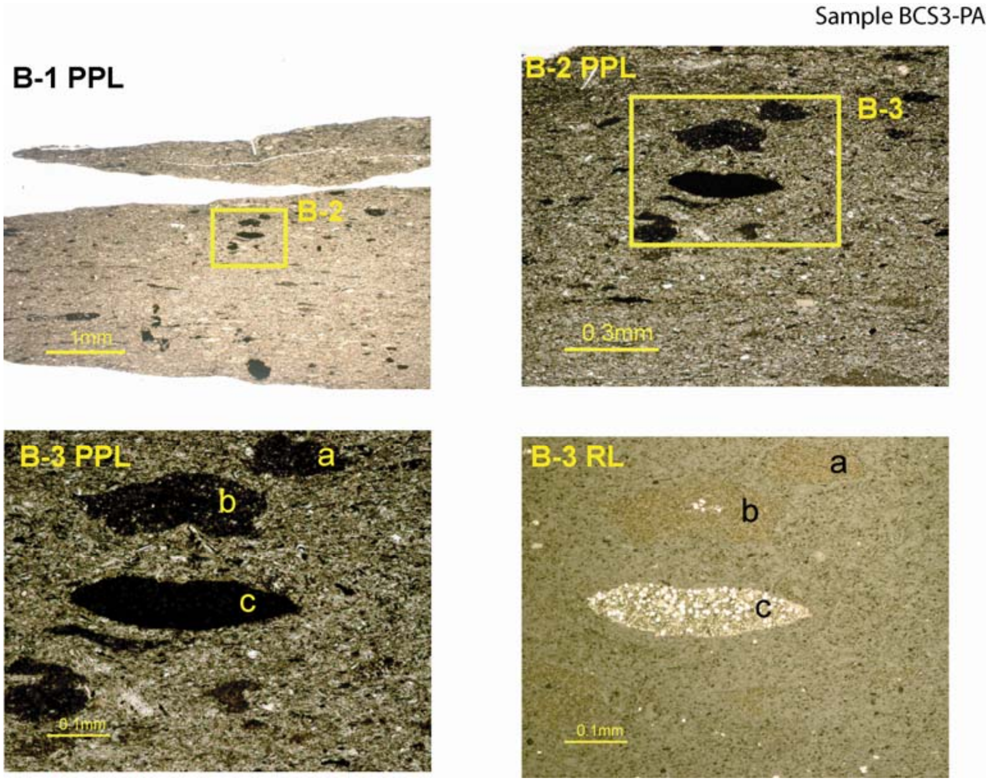


Figure 5.17. Brush Creek Shale (Sample BCS3-PA). Photomicrographs of rock fragment B showing details of elongated, dark brown to black clots. Reflected light (RL) microscopy shows that pyrite (bright white) is present as tiny disseminated grains in the shale matrix and as framboid fillings and cores within the black clots. Comparison of area B-3 at the same magnification in plane and reflected light shows the variation in clot composition from pyrite-free (a), to pyrite-cored (b), to pyrite-filled (c).

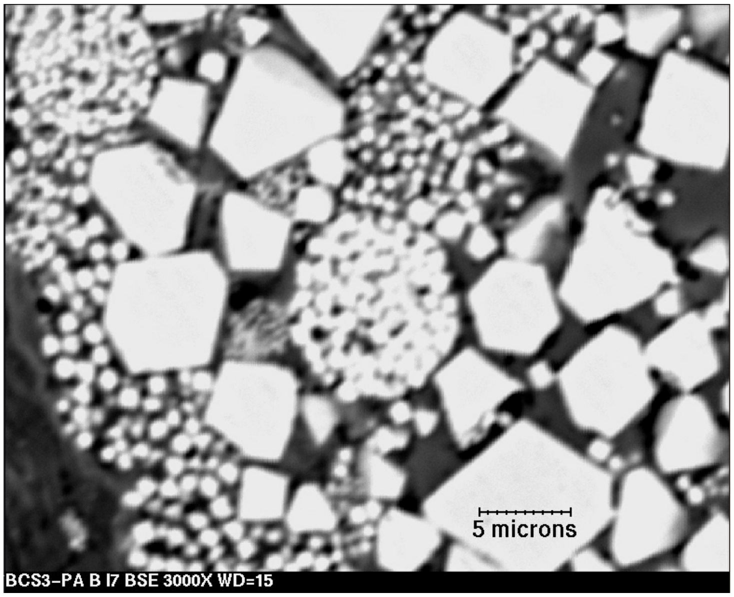


Figure 5.18. Brush Creek Shale (Sample BCS3-PA). SEM image (3,000X) of a pyrite framboid.

SEM data show that fossils are calcite with minor iron and manganese. Groundmass carbonates are zoned with calcic cores and more iron-rich rims. The zoning is apparent in backscattered SEM images because the iron-rims appear brighter due to average atomic number contrasts with more calcic cores (Figure 5.19).

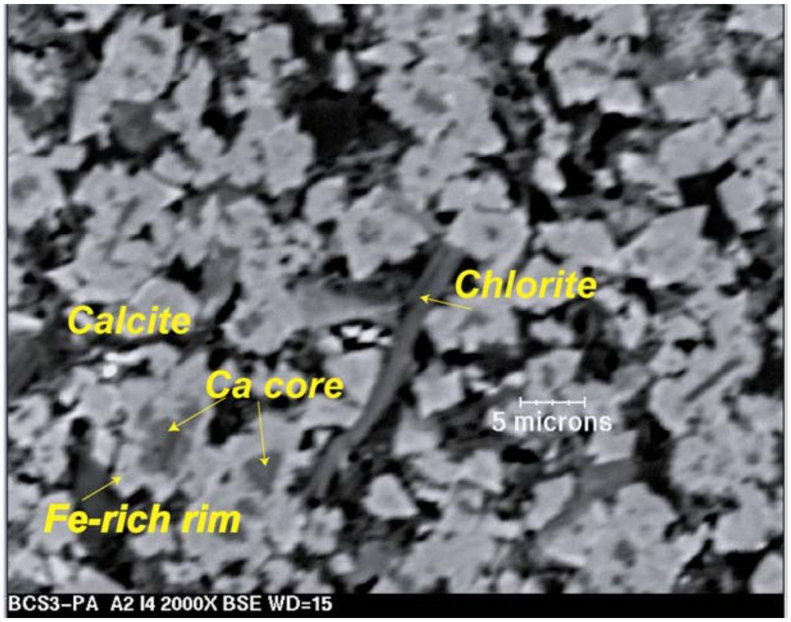


Figure 5.19. Brush Creek Shale (Sample BCS3-PA). SEM image (2,000X) of a groundmass carbonates. Much of the calcite is zoned, with calcium-rich cores (dark gray) surrounded by iron-rich rims (whiter areas).

Middle Kittanning Sandstone (Sample MKSS). The Middle Kittanning Sandstone sample was collected from Hawbaker quarry in Clearfield County, PA. The sandstone has low NP and low total sulfur (0.09 weight percent). MKSS was included as a relatively inert sample and was expected to behave as a minimal contributor of target analytes in the leaching study. Sample MKSS had a low temperature ash measurement of 91 weight percent and a loss-on-ignition of 5 weight percent. MKSS is a homogeneous, quartzose sandstone having an equigranular texture (Figure 5.20). Angular to subrounded 0.3 millimeter quartz grains are cemented by a fine-grained groundmass of mica, chlorite, clay and carbonate (Figure 5.21). XRD analysis estimated the mineralogical composition (in weight percent) as: 65 % quartz, 18% micas and clay minerals, 4% chlorite, 2% feldspar, <1% pyrite, and 8% carbonate minerals (Table 5.4). The accessory minerals zircon, rutile, monazite, and apatite were all confirmed by SEM. MKSS contains zoned carbonate (Figure 5.21) as well as discrete, adjacent grains of calcite and siderite (Figure 5.22) near pyrite framboids. SEM analyses confirm the XRD analysis of kaolin.

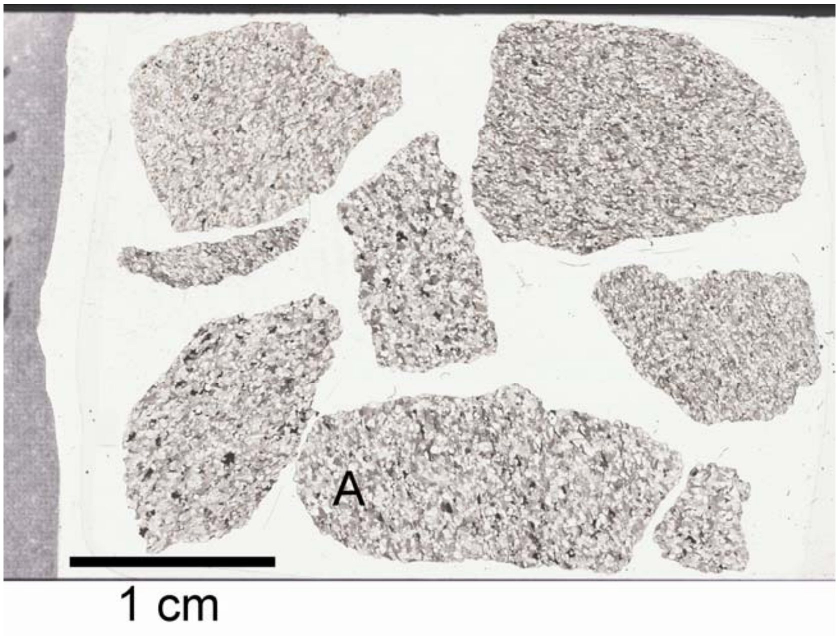


Figure 5.20. Middle Kittanning Sandstone (Sample MKSS). Scanned image of polished thin section. Note homogeneous texture of this rock.

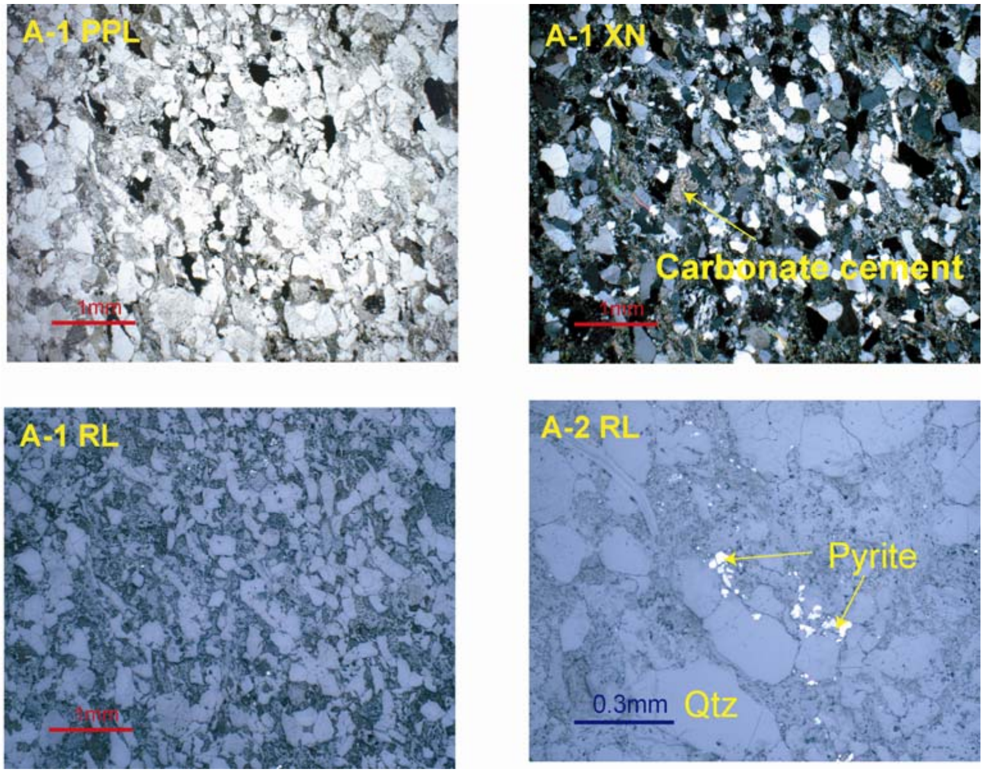


Figure 5.21. Middle Kittanning Sandstone (Sample MKSS). Photomicrographs of rock fragment A in plane light (PPL), crossed nicols (XN) view shows carbonate cementing millimeters-size quartz grains. Reflected light (RL) microscopy of same view (RL). A-2 RL, at higher magnification shows pyrite.

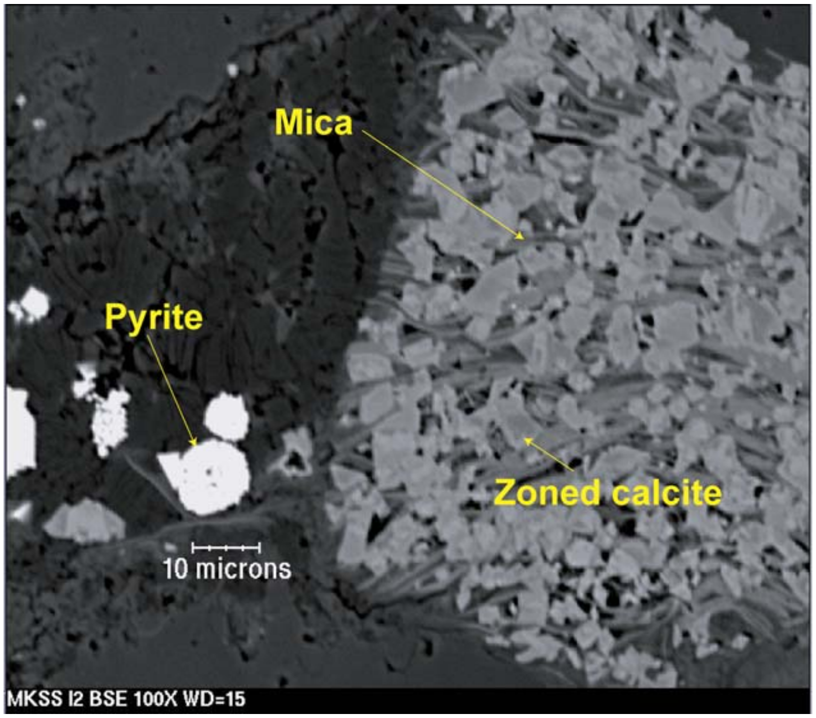


Figure 5.22. Middle Kittanning Sandstone (Sample MKSS). SEM image shows round clusters of pyrite framboids (bright white) and a large inclusion of zoned calcite and mica.

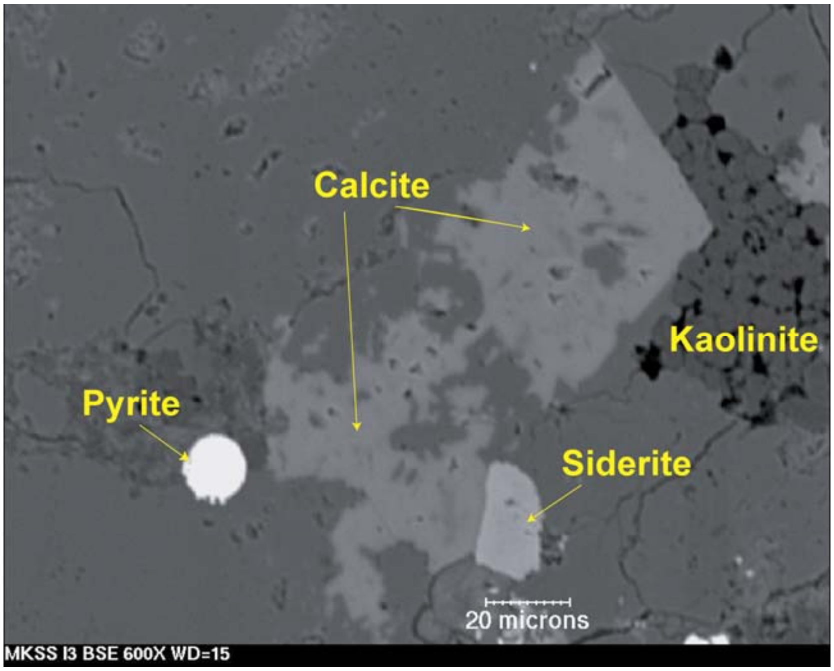


Figure 5.23. Middle Kittanning Sandstone (Sample MKSS). SEM image shows adjacent calcite and siderite near a round pyrite framboid and a clot of kaolinite.

Wadesville Sandstone (Sample Wadesville #29). Wadesville sandstone was selected as a secondary protocol standard because it has physical and chemical characteristics in marked contrast to the primary standard, the friable "gray-zone" Brush Creek Shale. The Wadesville is a calcareous sandstone that forms a hard lithologic unit (Hornberger et al., 2003). The sample was collected from a large open-pit surface anthracite mine in Schuylkill County, PA, where the mine pool discharge is one of the most alkaline natural discharges in the state of Pennsylvania (alkalinity >400 mg/L). The sample had negligible total sulfur (<0.1 weight percent) and significant NP (255 to 282 ppt). The Wadesville contained significantly more calcium (11.23 weight percent CaO), more carbon dioxide (16.2 weight percent CO_2), and less total sulfur (<0.02 weight percent) than any of the other samples included in this study (Table 5.2). In thin section, the sandstone was homogeneous from chip to chip (Figure 5.24). Coarse-grained carbonate cemented quartz grains; pyrite was sparse (Figure 5.25). XRD analysis estimated the mineralogical composition (in weight percent) as: 42 % quartz, 9% micas and clay minerals, 4% chlorite, 4% feldspar, <1% pyrite, and 38% carbonate minerals (Table 5.4).The low temperature ash treatment produced no mass loss. The sandstone also had the lowest estimated content of amorphous material (15 weight percent). No organic material was observed. SEM images and compositions confirm that the dominant carbonate mineral in the sample is zoned ankerite (Figure 5.26), in agreement with the XRD data. The outermost rims of each carbonate grain are iron-rich relative to the interior parts of the grain.

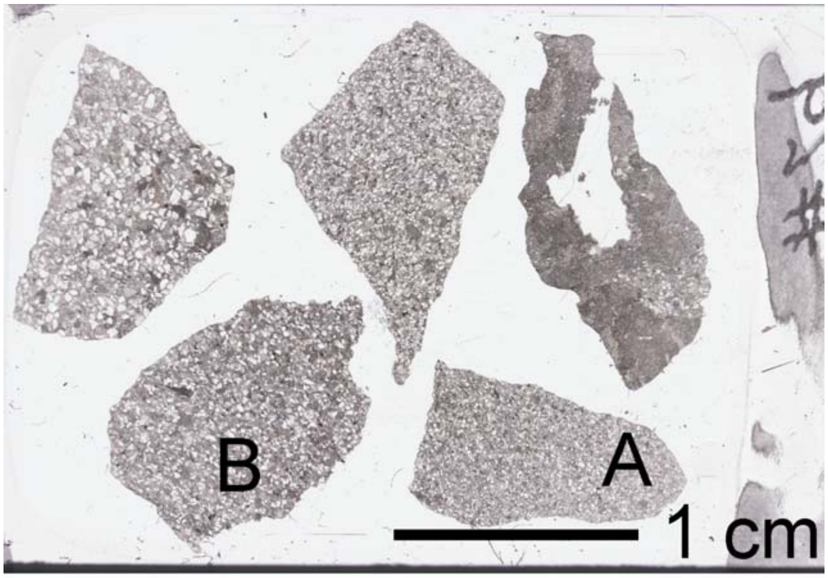


Figure 5.24. Wadesville Sandstone. Scanned image of polished thin section. Note homogeneous texture of this rock.

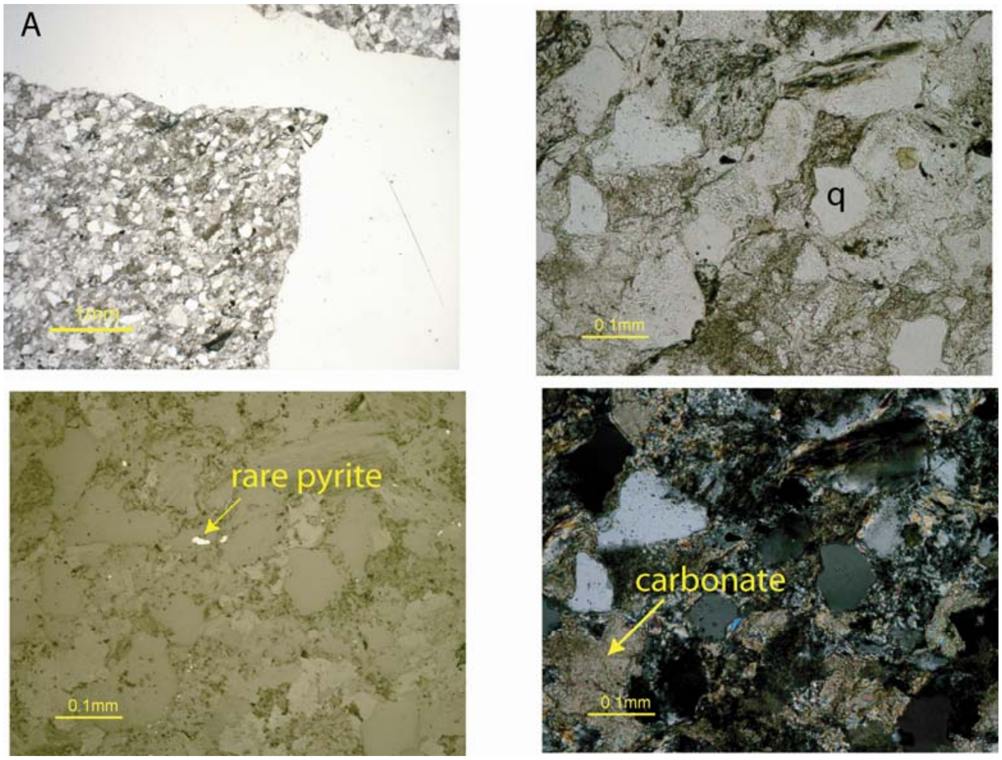


Figure 5.25. Wadesville Sandstone. Photomicrographs of rock fragment A in plane light (PPL) at low magnification (upper left). At higher magnification in plane, reflected light, and crossed nicols show quartz (q), rare pyrite, and the carbonate matrix (same view for all 3 photos).

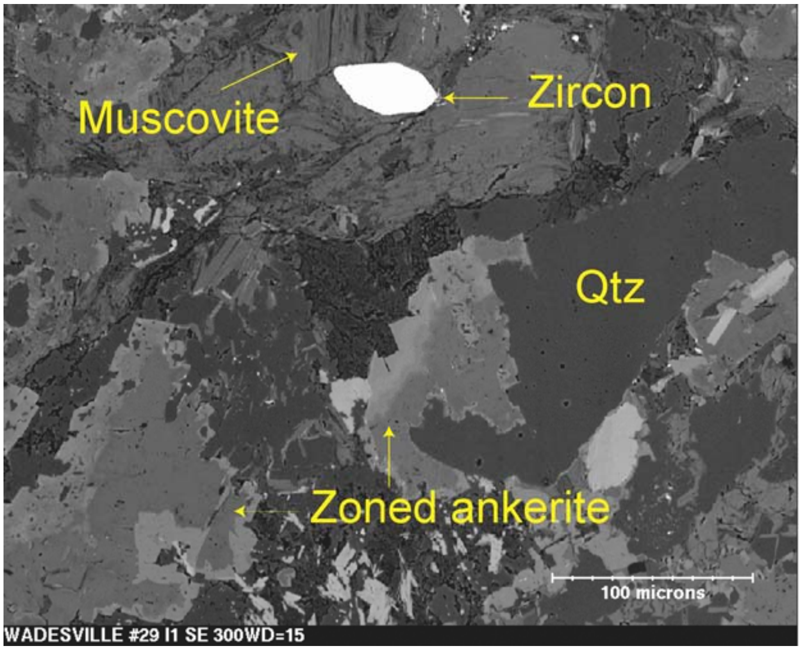


Figure 5.26. Wadesville Sandstone. SEM image of zoned carbonate cement in rock chip A. Note large zircon crystal in field of view.

Leechburg Coal Refuse (Sample LRBT#2). The Leechburg coal refuse deposits in Armstrong County, PA are associated with mines developed on the Lower Kittanning coal (Hornberger et al., 2005). The coal refuse was used in 2002 and 2003 weathering tests because of its high total sulfur content and low NP. The sample provided for characterization contains significant amounts of organic material, as indicated by the low-temperature ash determination (45 weight percent), significant amorphous content (77 weight percent), and significant volatile content (LOI 60 weight percent). The sample analyzed for geochemistry contained 5.5 weight percent total sulfur, 56 parts per million arsenic, and 952 parts per billion mercury (Table 5.2). XRD analysis estimated the mineralogical composition of the crystalline part of the material (in weight percent) as: 23 % quartz, 33% micas and clay minerals, 2% chlorite, 4% feldspar, 29% pyrite, and 2% carbonate minerals (Table 5.4). The sample was difficult to polish due to the high organic content, resulting in a smeared thin section (Figure 5.27). SEM images showed that the quartz grains were on the order of 5 micrometers in diameter. Although the pyrites were readily identifiable by SEM due to atomic number contrast with the quartz and organic material, they were too small to work with for determining mineral composition (Figure 5.28).

Figure 5.27. Leechburg Coal Refuse (Sample LRBT#2). Scanned image of a polished thin section. The sample is of organic material which complicated sample preparation and resulted in a thin, smeared mount.

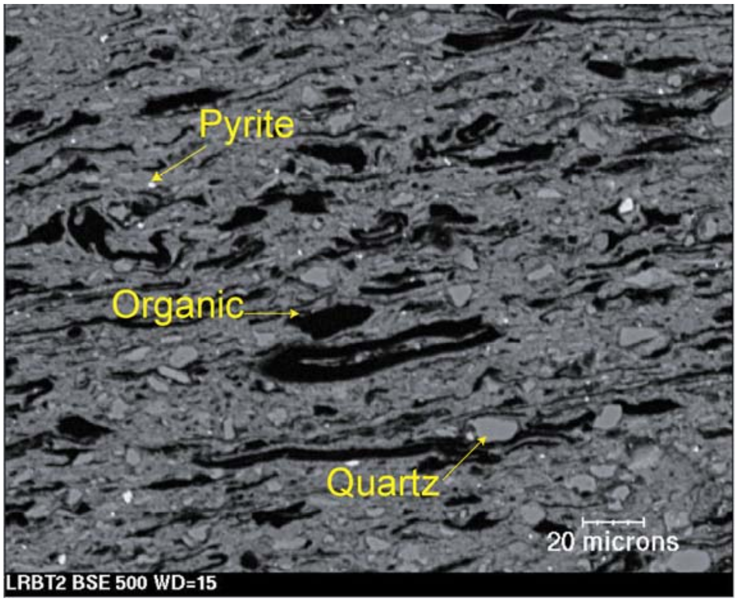


Figure 5.28. Leechburg Coal Refuse (Sample LRBT#2). SEM image showing fine-grained texture. The black material is organic; the bright white pinpoints are pyrite.

Mineral chemistry

Electron microprobe analytical data for pyrite and carbonate minerals are tabulated in Appendix 5.1, along with detection limits and statistics for each sample. Both mineral groups posed analytical challenges due to the fine grain size of the minerals. Ideally, mineral compositions total 100 (98 to 102) weight percent and computed atomic ratios match the expected mineral formulas. For pyrite, FeS_2, this means 2 atoms of sulfur for every atom of iron. Because the electron beam activates a volume of material at the mineral surface, uneven surfaces, holes, and the tiny grain size of individual pyrite grains in framboids produce low element totals. The atomic ratios, however, are appropriate for pyrite.

Pyrite. Pyrite was analyzed for iron, sulfur, selenium, nickel, arsenic, manganese, zinc, cadmium, cobalt, and copper. Trace element concentrations in pyrite varied within each sample; however, a few trends in the data are apparent (Figure 5.29). HCS-IN and Wadesville #29 were the only samples that contained selenium above detection limits; some pyrite in these samples contain over 1 weight percent manganese. Some pyrite grains in each sample contained arsenic above detection limits. Concentrations of other metals that typically occur in pyrite were at or below detection limits. Mercury was analyzed for in some samples, but none was detected. The trace elements are not evenly distributed throughout individual crystals in framboids, as shown by element maps (Figure 5.30). On these maps, the hotter colors indicate higher concentrations of an element. Note that the pyrite is outlined by high concentrations of iron, sulfur, arsenic, manganese, and selenium. The distribution of the trace elements is uneven across the pyrite crystals suggesting some zoning, even though spot analyses for selenium in pyrites in LKFC-WV are all below detection limits (Appendix 5.1) and the selenium concentrations in the bulk rock was <3 parts per million (Table 5.2). Sample HCS-IN has the highest whole-rock selenium content (81 parts per million; selenium was detected in 13 of the 17 pyrites analyzed from HCS-IN (Appendix 5.1).

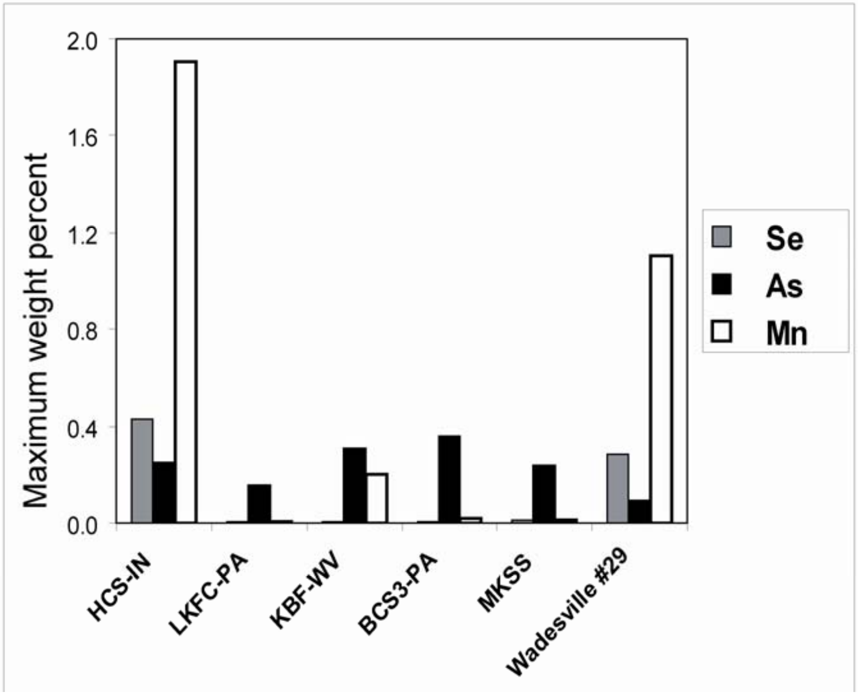


Figure 5.29. Trace elements in pyrite. The bar chart shows the maximum concentration of arsenic, selenium, and manganese detected in pyrite in each sample (Appendix 5.1)

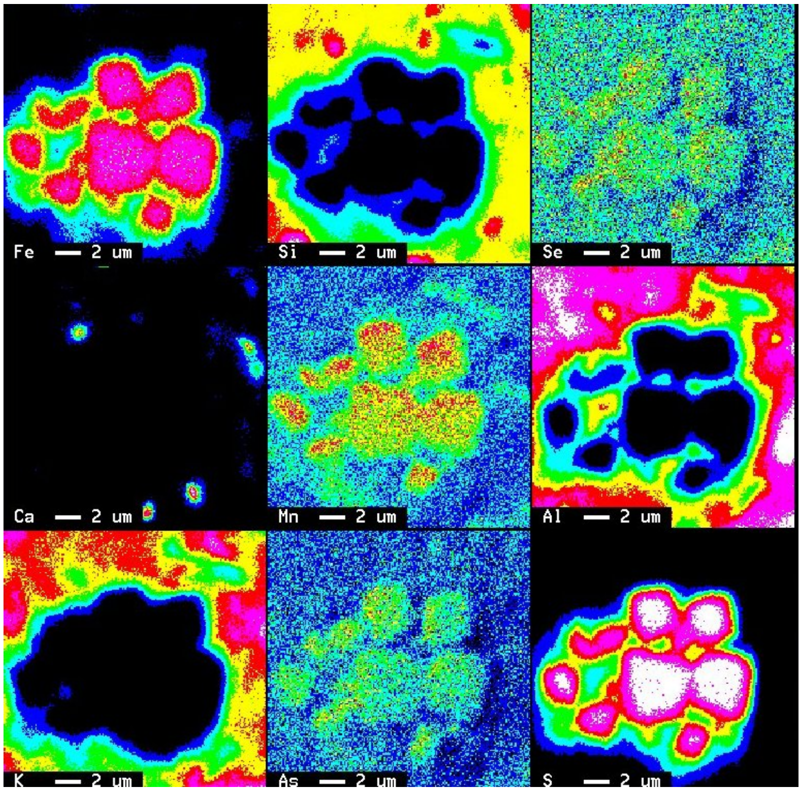


Figure 5.30. Trace elements in pyrite. The map shows the distribution of nine elements in and around a pyrite framboid in sample LKFC-PA.

Carbonate Minerals. Carbonate minerals are an analytical challenge because they tend to "cook" when exposed to an electron beam and because carbon is not analyzed. Typically, carbonates are analyzed by EPMA using a defocused (wide) electron beam. However, because of the zoning observed in carbonates in the SEM studies and the small grain size of minerals in shales, a focused beam was used for the analyses of both standards and unknowns. The elements calcium, magnesium, manganese, iron, and strontium were analyzed using carbonate minerals as standards, and the CO_2 content is calculated based on mineral stoichiometry ($CaCO_3$ for calcite, $FeCO_3$ for siderite, and $CaMg(CO_3)_2$ for dolomite group minerals. Silicon, aluminum, sodium, and potassium were analyzed as part of the carbonate mineral analysis package to screen for contaminants. Carbonate mineral analyses are tabulated in Appendix 5.1 by lithology, along with calculated CO_2 content and mineral formulas. Molar compositions are plotted in Figure 5.31, which is intended to illustrate the range of observed compositions of carbonate group minerals in the samples. Carbonate minerals in the leach column starting materials include calcite, siderite, and ankerite (ferroan dolomite). No pure dolomite compositions were observed (Figure 5.31). Quantitative XRD mineralogy for Houchin Creek Shale estimated about 3 weight percent carbonate minerals (Table 5.4). Localized patches of calcite in one of the rock chips (Figure 5.3A) were the only carbonate minerals observed in the thin section. The calcite contains about 0.5 weight percent MgO, 1.5 to weight percent MnO, and <1 weight percent FeO, and plots near the calcite apex on Figure 5.31. The Lower Kittanning Shale contains magnesian calcite in fossil fragments (Figure 5.10) and siderite in groundmass carbonate. The carbonate in Kanawha Black Flint Shale includes iron-rich ankerite and siderite with variable manganese (up to 6 weight percent MnO); calcite was also identified by SEM in contact with pyrite (Figure 5.13). In Brush Creek Shale, calcite occurs in shell fragments (Figure 5.16) and as zoned calcite in groundmass (Figure 5.19). Calcite cores are nearly pure; rims contain up to about 8 weight percent MnO + MgO + FeO. The Brush Creek calcite contains up to 0.5 weight percent SrO. Middle Kittanning Sandstone contains both siderite and calcite (Figures 5.22 and 5.23). Most of the microprobe data indicate magnesian siderite (up to 10 weight percent MgO, 1-2 weight percent MnO, <2 weight percent CaO); one analysis plotted in the ankerite field and three analyses indicate calcite with ~1 weight percent FeO, as much as 2 weight percent MnO, and traces of MgO. No siderite was detected in Wadesville Sandstone; all of the carbonate analyzed as ankerite or calcite (Figure 5.31).

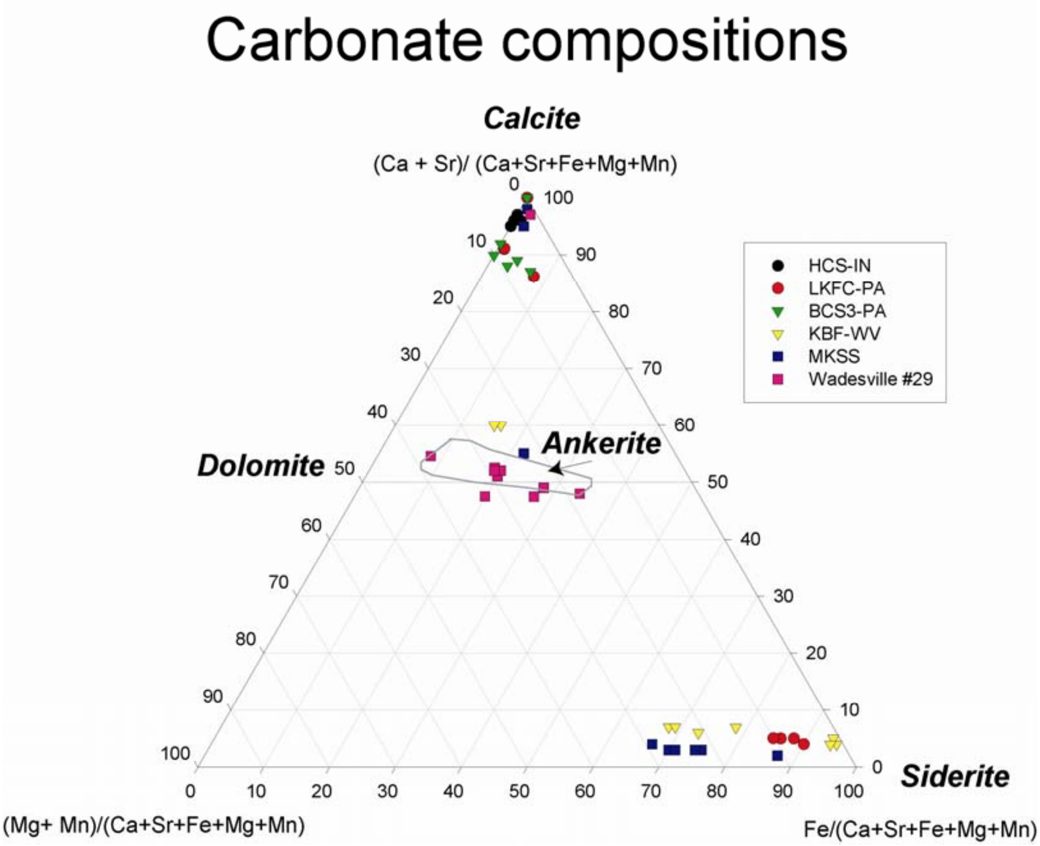


Figure 5.31. Carbonate mineral compositions. Molar cation ratios based on data in Appendix 5.1. The ankerite field is based on the compositional ranges for ankerites cited by Chang et al. (1996).

Leach column residues

Several months elapsed between the end of the leaching experiments and opening the columns. Thus, any minerals that were near-saturation in the final water column may have evaporated and precipitated, which complicates interpretation of weathering products. Residues differ in color from the starting material. The raw Houchin Creek Shale, for example, is black but the leach column residue material has a brownish-orange caste and some rock chips were partially coated with iron precipitates (Figure 5.32).

Carbon and sulfur analyses for leach column residues are listed in Table 5.2. Pre-and post leach total sulfur analyses are generally comparable or indicate an increase, and might reflect sample heterogeneity or analytical error. Quantitative XRD analyses of the leach column residues for HCS-IN (see LCR columns in Table 5.4) suggest that gypsum may have precipitated. The raw and LCR gypsum estimates for HCS-IN are 6.4 and 9.1 weight percent, respectively. The carbon species were determined for the LCR samples; these data indicate that CO_2 apparently decreased for HCS-IN and KBF-WV, but increased for the other samples. All of the shales contain graphite and organic carbon in the leach column residue. Carbon species were not determined for the raw material. The “before leaching” (raw and LTA) and “post-leaching” (LCR) XRD data suggest an apparent decrease in carbonate minerals for samples HCS-IN and BCS-3 and an apparent decrease in pyrite for samples HCS-IN and LKFC-PA. Paste pH measurements on leach column residues indicated that although the effluents from all columns at week 16 were near-neutral, acid-generating weathering products accumulated in the columns for Houchin Creek Shale and possibly, for Lower Kittanning Shale (Figure 5.32*B*).

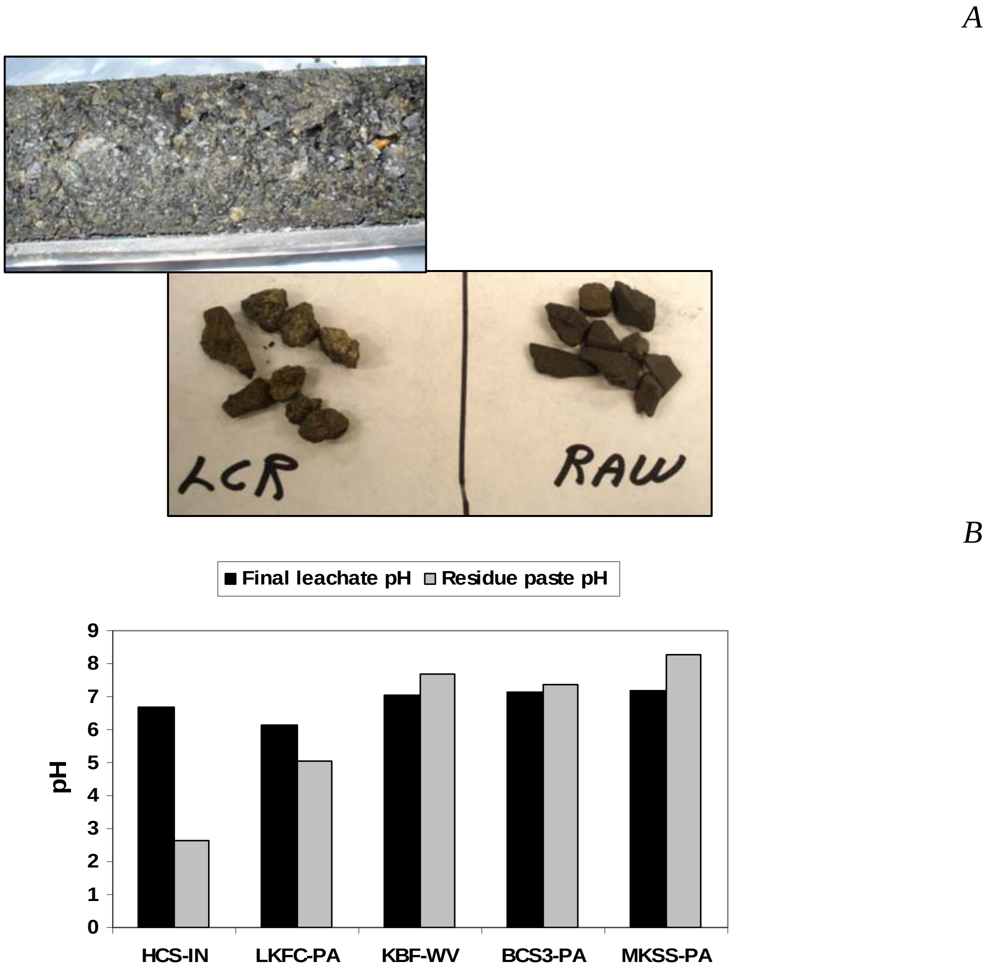


Figure 5.32. Leach columns were opened several months after the 16-week leach study was completed. *A*, Photographs of one of the Houchin Creek Shale columns. Rock chips from the leach column residue (LCR) show iron oxide coatings and precipitates that were not present in the black starting material (RAW). *B*, Comparison of final column effluent pH and paste pH on column residue material. Acid-generating weathering products accumulated in the HCS-IN column after the experiment ended.

Target analytes in leachates

In addition to monitoring pH, conductivity, alkalinity, and acidity, the laboratories that participated in this study analyzed dissolved concentrations of aluminum, calcium, iron, manganese, potassium, magnesium, selenium, zinc, and sulfate in column leachates. Data, evaluation, interpretation of results of the interlaboratory leaching study, effects of particle size, kinetic data, and implications for long-term weathering behavior are addressed elsewhere in this report. In this chapter, we include a series of graphs of data from one of the participating laboratories (USGS) as Appendices 5.2 and 5.3 as a framework for discussing mineralogical controls on leachate quality. Figures 5.33 through and 5.35 illustrate selected data from Appendices 5.2 and 5.3.

Despite an acid-base account based on total sulfur and neutralization potential that indicated potential for acidic effluent for two of the four shales, effluents from all of the columns were net alkaline with near-neutral pH at the end of the experiments. Figure 5.33 indicates that after the initial flush, leachate from all five rock samples was net alkaline based on hot acidity. The initial flush dissolved any weathering products that accumulated in the samples prior to onset of the weathering experiment. After the initial flush, alkalinity, pH, and calcium concentrations remained relatively stable. Figure 5.34 shows leachate concentrations for dissolved sulfate, calcium, iron, and aluminum over the course of the leaching study. Sulfate and calcium were detected in column effluent throughout the experiment; sulfate generally declines with time whereas calcium was relatively constant. After the first three weeks, iron and aluminum dropped off. The likely explanation for this behavior is the precipitation of iron and aluminum oxyhydroxide minerals due to hydrolysis reactions. Weathering of pyrite, siderite, or other iron-bearing minerals in the columns releases ferrous iron, which was readily oxidized to ferric iron under the oxidizing conditions of the experiment (effluent ORP $\geq$ 150 millivolts for all columns). For example, consider the reaction:

$$Fe^{3+}_{(\text{dissolved})} + 3\ H_2O \rightarrow Fe(OH)_{3\ (\text{Solid precipitate})} + 3H^+$$

These precipitates coated and cemented rock fragments in the leach column residue (Figure 5.32). Although the hydrolysis reactions generate acidity, sufficient alkalinity was present in the leach column material during the course of the experiment to consume the acid because the effluents remained net alkaline (Figure 5.33). See Appendix 5.2 for addition time-series data (concentration and cumulative transport graphs). Computations of saturation indices based on effluent chemistry using WATEQ4F (Ball and Nordstrom, 1991) indicate that with the exception of the initial flush, the effluents from all columns except those containing Lower Kittanning Shale (sample LKFC) were saturated or nearly saturated with calcite throughout the experiment (Figure 5.35A). Effluents from the Indiana shale HCS-IN were saturated or supersaturated with gypsum (Figure 5.35B), which is consistent with the apparent increase in gypsum detected by XRD for the leach column residue (Table 5.4). Precipitation of gypsum can potentially inhibit calcite dissolution. See Appendix 5.3 for computation of saturation indices.

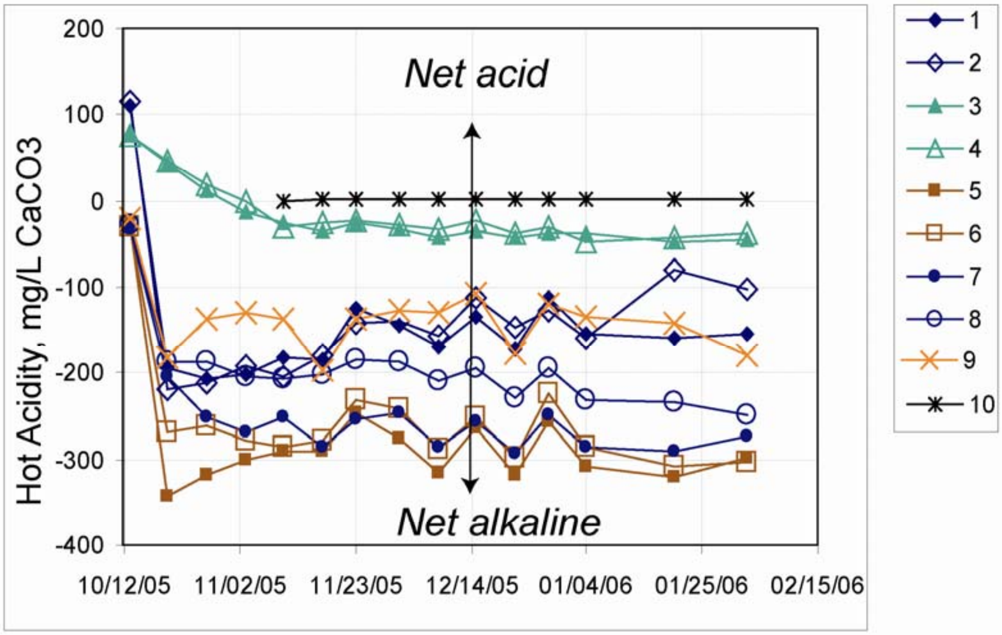


Figure 5.33. Hot acidity concentrations in leachates as a function of time for duplicate leach columns of Houchin Creek Shale (1 and 2), Lower Kittanning Shale (3 and 4), Kanawha Black Flint Shale (5 and 6), Brush Creek Shale (7 and 8), a single column of Middle Kittanning Sandstone (9), and deioinzed water (10). Hot acidity concentrations >0 indicate net acidity; hot acidity concentrations <0 indicate net alkalinity.

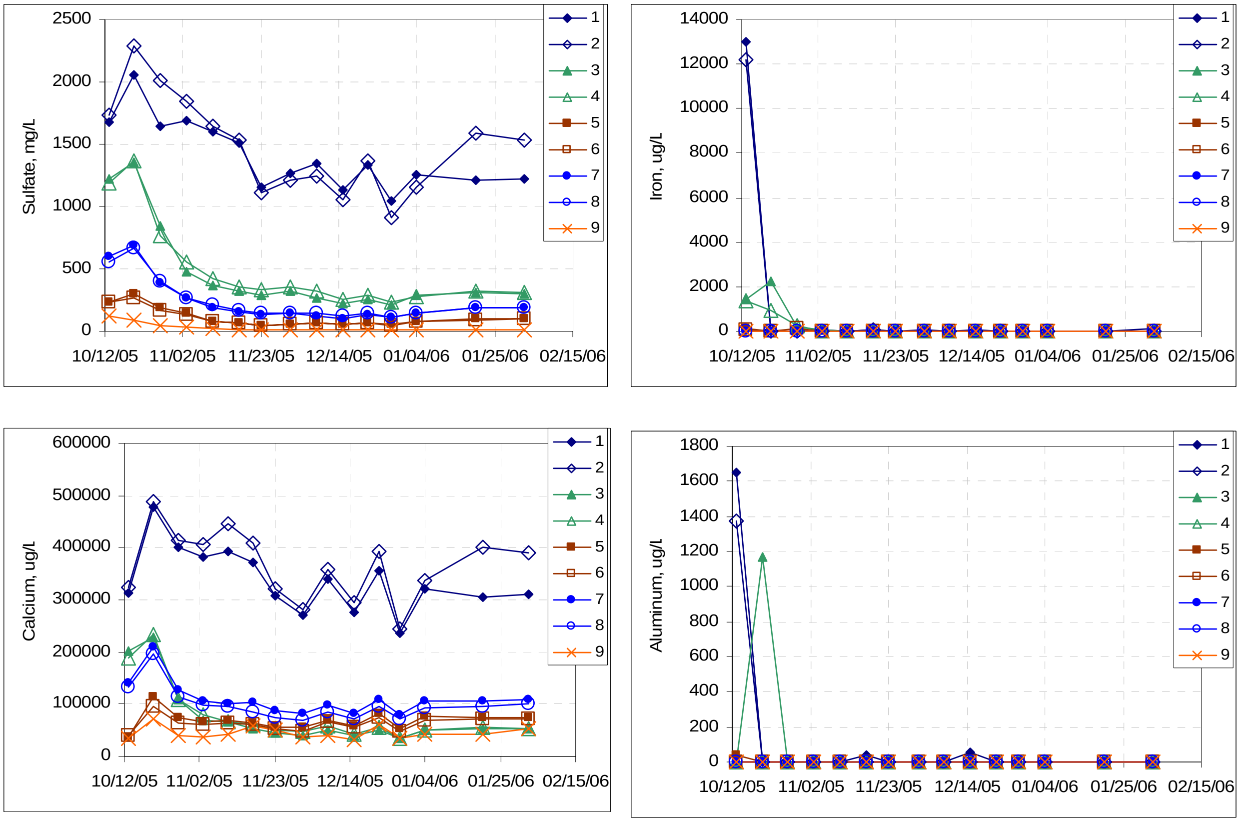


Figure 5.34. Concentrations of target analytes in leachates as a function of time for duplicate leach columns of Houchin Creek Shale (1 and 2), Lower Kittanning Shale (3 and 4), Kanawha Black Flint Shale (5 and 6), Brush Creek Shale (7 and 8), and a single column of Middle Kittanning Sandstone (9).

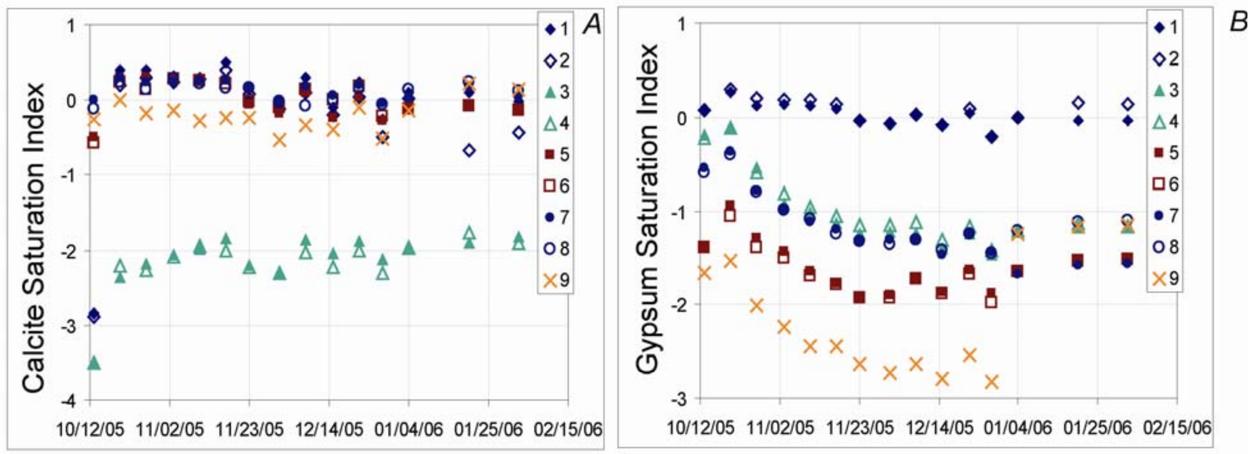


Figure 5.35. Effluent saturation indices for calcite (A) and gypsum (B). Saturation indices (log IAP/K) >0 indicate saturation or supersaturation of the solid phase. See Appendix 5.3 for details and references. Same sample key as Figure 5.34.

Trace elements in leachate

Rocks associated with coal beds may contain a variety of trace elements. The target analytes for the interlaboratory leachate tests included selenium and zinc. Because the geochemical data for the unweathered rocks in Table 5.2 showed variable concentrations of some other trace elements of potential environmental concern, we acquired a comprehensive element suite for the final leachates from one of the participating labs (Table 5.6). Effluent from duplicate columns was analyzed for all samples except KBF-WV; effluent from one column was analyzed for KBF-WV.

Zinc was the dominant base-metal in leachates (Table 5.6). Comparison of total base-metal concentrations in starting materials and leachates (Figure 5.36) indicates that the (1) duplicate columns produced similar base-metal leachate concentrations, (2) total base-metal concentration in leachates were < 10 mg/L for all samples, (3) Houchin Creek shale produced the highest concentrations of base metals in leachate. Although cadmium was below detection limits (0.5 parts per million) in the starting materials, the leachate data show that cadmium concentrations increase linearly with increasing effluent zinc (Figure 5.37). None of the effluents contained mercury above detection levels (6 nanograms per liter). Selenium was detected in concentrations of >5 micrograms per liter in effluent from the Houchin Creek, Lower Kittanning, and Brush Creek shales whereas the Kanawha Black Flint shale from West Virginia had the lowest selenium leachate concentration of all the samples (Figure 5.38). Other elements that can be released upon weathering of pyrite include arsenic and thallium, both of which were detected in all of the leachates.

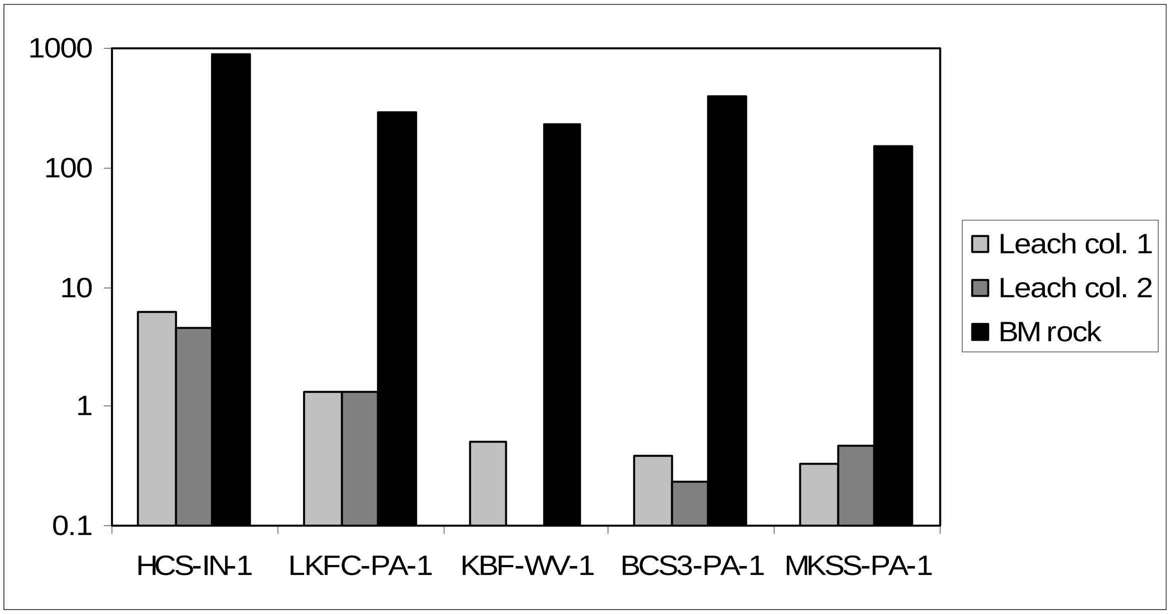


Figure 5.36. Base-metal concentrations in starting materials (BM rock) and leachates in parts per million and mg/L, respectively.

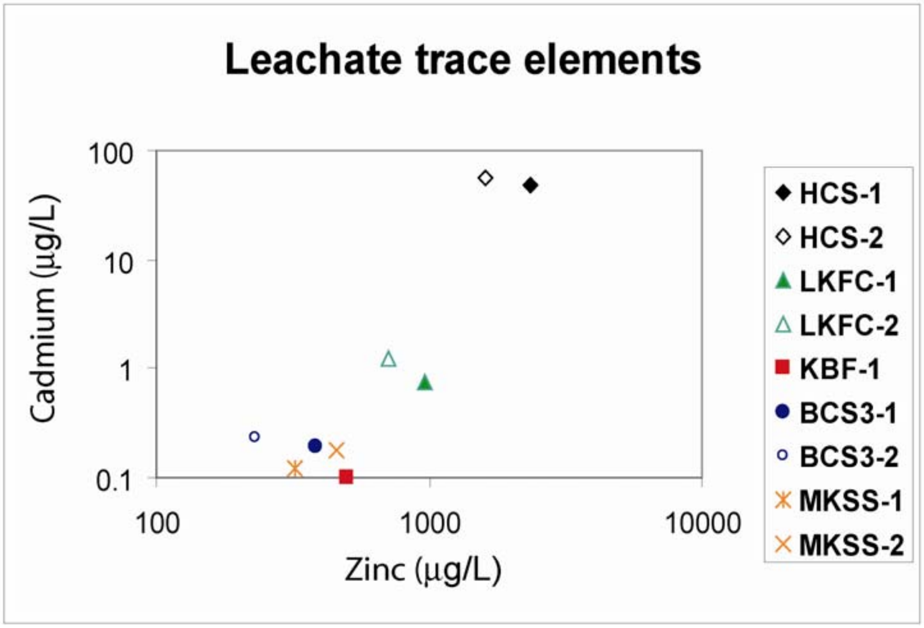


Figure 5.37. Cadmium and zinc in leach column effluent. Duplicate columns (1 and 2).

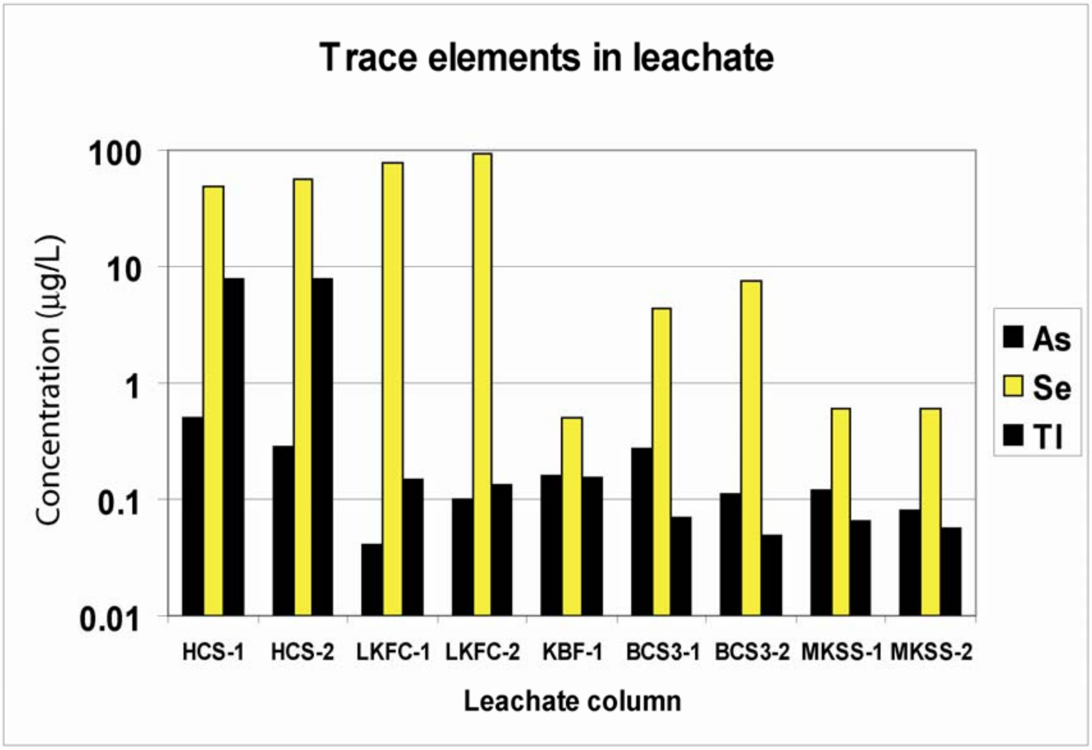


Figure 5.38. Trace elements in leachates.

Table 5.6. Trace elements in final leach column effluent from one laboratory.
[1 and 2 represent duplicate columns. Methods: MS, ICP-MS; OES, ICP-OES used when ICP-MS concentrations exceed upper limits of the method; FIMS for mercury. Element concentrations are reported in micrograms per liter (µg/L), milligrams per liter (mg/L), and (or) nanograms per liter (ng/L)]

Element		D.L.	Method	HCS-IN		LKFC-PA		KBF-WV	BCS3-PA		MKSS	
	units			1	2	1	2	1	1	2	1	2
Ag	µg/L	0.2	MS	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2
Al	µg/L	2	MS	3	7	2	3	< 2	9	5	8	11
As	µg/L	0.03	MS	0.5	0.28	0.04	0.1	0.16	0.27	0.11	0.12	0.08
Au	µg/L	0.002	MS	0.003	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002
Ba	µg/L	0.1	MS	25.7	26.6	54	68.5	106	70.8	65.5	66.4	75.3
Be	µg/L	0.1	MS	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
Bi	µg/L	0.3	MS	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3
Br	µg/L	3	MS	192	190	230	228	235	202	132	168	162
Ca	µg/L	700	MS	> 20000	> 20000	> 20000	> 20000	> 20000	> 20000	> 20000	> 20000	> 20000
Ca	mg/L	0.1	OES	628	580	171	218	205	320	196	89.6	111
Cd	µg/L	0.01	MS	48.1	56.1	0.73	1.24	0.1	0.19	0.23	0.12	0.18
Ce	µg/L	0.001	MS	0.266	0.269	0.235	1.49	0.019	0.036	0.037	0.029	0.009
Co	µg/L	0.005	MS	> 200	194	70.8	122	0.277	1.43	0.048	1.41	1.79
Co	µg/L	2	OES	207	--	--	--	--	--	--	--	--
Cr	µg/L	0.5	MS	< 0.5	< 0.5	< 0.5	< 0.5	1.5	1.2	< 0.5	< 0.5	< 0.5
Cs	µg/L	0.001	MS	0.201	0.169	0.068	0.096	0.129	0.045	0.032	0.059	0.047
Cu	µg/L	0.2	MS	0.7	3.4	1.5	1.7	< 0.2	< 0.2	0.5	1.3	1.7
Dy	µg/L	0.001	MS	0.069	0.033	0.017	0.131	0.003	0.008	0.004	0.004	< 0.001
Er	µg/L	0.001	MS	0.048	0.019	0.01	0.061	0.003	0.007	0.002	0.003	0.001
Eu	µg/L	0.001	MS	0.009	0.005	0.006	0.03	0.01	0.006	0.003	0.006	0.003
Fe	µg/L	10	MS	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	10
Ga	µg/L	0.01	MS	0.14	0.16	0.47	0.62	< 0.01	0.04	< 0.01	0.03	0.03
Gd	µg/L	0.001	MS	0.063	0.04	0.021	0.211	0.004	0.007	0.004	0.005	0.001
Ge	µg/L	0.01	MS	0.26	0.28	0.31	0.37	0.03	0.03	0.05	0.04	0.02
Hf	µg/L	0.001	MS	0.002	0.003	< 0.001	0.002	0.007	0.006	< 0.001	0.002	< 0.001
Hg	µg/L	0.2	MS	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2
Hg	ng/L	6	FIMS	< 6	< 6	< 6	< 6	< 6	< 6	< 6	< 6	< 6
Ho	µg/L	0.001	MS	0.017	0.009	0.003	0.029	< 0.001	0.002	0.001	< 0.001	< 0.001
I	µg/L	1	MS	41	81	68	99	17	31	10	130	18
In	µg/L	0.001	MS	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001
K	µg/L	30	MS	5000	4780	9690	10800	18400	8000	6350	9120	7990
La	µg/L	0.001	MS	0.162	0.241	0.229	1.07	0.016	0.021	0.021	0.034	0.009
Li	µg/L	1	MS	131	140	57	76	59	24	16	11	11
Lu	µg/L	0.001	MS	0.005	0.001	< 0.001	0.003	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001
Mg	µg/L	1	MS	> 20000	> 20000	> 20000	> 20000	> 20000	> 20000	> 20000	> 20000	> 20000
Mg	mg/L	0.1	OES	192	228	133	173	124	106	96.5	18.9	23.9
Mn	µg/L	0.1	MS	> 10000	> 10000	> 10000	> 10000	150	2500	8.6	1320	1410
Mn	mg/L	0.01	OES	11.6	10.6	42.8	43	--	--	--	--	--
Mo	µg/L	0.1	MS	101	54.5	0.1	0.3	0.2	0.6	0.9	0.4	0.4
Na	µg/L	5	MS	19400	21700	4810	6420	2200	8030	8290	1280	1520
Nb	µg/L	0.005	MS	0.015	0.011	< 0.005	< 0.005	0.007	0.015	0.006	< 0.005	< 0.005
Nd	µg/L	0.001	MS	0.164	0.111	0.068	0.52	0.009	0.022	0.013	0.028	0.006

				HCS-IN		LKFC-PA		KBF-WV	BCS3-PA		MKSS	
Ni	µg/L	0.3	MS	> 1000	> 1000	256	485	3.2	4.5	1.4	2.8	5.6
Ni	µg/L	5	OES	3550	2710	--	--	--	--	--	--	--
Os	µg/L	0.002	MS	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002
Pb	µg/L	0.01	MS	0.91	4.33	0.22	0.33	0.27	0.17	0.51	0.3	0.3
Pd	µg/L	0.01	MS	< 0.01	< 0.01	0.03	0.02	0.03	0.13	0.03	0.02	0.01
Pr	µg/L	0.001	MS	0.035	0.027	0.017	0.13	0.003	0.005	0.004	0.006	< 0.001
Pt	µg/L	0.3	MS	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3
Rb	µg/L	0.005	MS	12.2	11.2	13.7	15.1	30.8	5.12	4	6.75	6.35
Re	µg/L	0.001	MS	0.331	0.263	0.002	0.002	0.004	0.004	0.002	0.004	0.004
Ru	µg/L	0.01	MS	0.03	0.02	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Sb	µg/L	0.01	MS	1.19	0.73	0.1	0.18	0.1	0.19	0.24	0.24	0.28
Sc	µg/L	1	MS	1	< 1	< 1	< 1	3	2	< 1	< 1	< 1
Se	µg/L	0.2	MS	48.8	56.9	79.1	93.1	0.5	4.3	7.6	0.6	0.6
Si	µg/L	200	MS	5300	3100	1900	2000	9400	7000	2100	1700	1300
Sm	µg/L	0.001	MS	0.035	0.017	0.009	0.103	0.003	0.002	0.002	0.004	< 0.001
Sn	µg/L	0.1	MS	0.7	2.1	0.8	2.8	1.2	2.1	6	3.6	1.8
Sr	µg/L	0.04	MS	> 200	> 200	> 200	> 200	> 200	> 200	> 200	129	149
Sr	µg/L	10	OES	1040	1080	450	550	2380	990	690	--	--
Ta	µg/L	0.001	MS	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001
Tb	µg/L	0.001	MS	0.011	0.005	0.003	0.027	< 0.001	0.001	< 0.001	< 0.001	< 0.001
Te	µg/L	0.1	MS	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
Th	µg/L	0.001	MS	0.002	0.002	< 0.001	< 0.001	0.002	0.001	0.001	< 0.001	< 0.001
Ti	µg/L	0.1	MS	0.6	0.4	0.2	0.2	0.8	0.5	0.2	0.1	< 0.1
Tl	µg/L	0.001	MS	7.81	7.67	0.148	0.135	0.153	0.069	0.048	0.064	0.057
Tm	µg/L	0.001	MS	0.005	0.001	< 0.001	0.005	< 0.001	0.001	< 0.001	< 0.001	< 0.001
U	µg/L	0.001	MS	> 200	41.3	0.148	0.1	2.26	5.47	3.91	1.75	1.9
U	mg/L	0.05	OES	0.23	--	--	--	--	--	--	--	--
V	µg/L	0.1	MS	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
W	µg/L	0.02	MS	0.12	0.07	0.12	0.04	< 0.02	0.03	0.03	0.08	0.05
Y	µg/L	0.003	MS	1.51	1.02	0.44	2.76	0.05	0.117	0.041	0.054	0.019
Yb	µg/L	0.001	MS	0.035	0.01	0.006	0.024	0.005	0.008	0.002	0.003	0.002
Zn	µg/L	0.5	MS	> 250	> 250	> 250	> 250	> 250	> 250	231	> 250	> 250
Zn	µg/L	5	OES	2350	1610	969	712	496	386	--	323	460
Zr	µg/L	0.01	MS	0.13	0.14	0.03	0.03	0.38	0.24	0.06	0.07	0.07

Mineralogical sources of leachate target analytes

The rock characterization study demonstrates the chemical variability of the starting materials and the mineralogical source of leaching analytes. 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

Iron is not likely to be a good indicator of pyrite weathering progress because of the variable iron content of the carbonate minerals. Both pyrite and carbonates contribute iron to the leachates. During rock weathering, the best predictor of potential acid production is the carbonate content (Perry, 1998; Brady et al., 2004; Jambor et al., 2005). Once the available carbonate in the rock is exhausted or unavailable for NP generation due to inhibition by armoring, then the “runaway” acid-generation condition can develop. The nature of the carbonate mineral is important because not all carbonates produce alkalinity. It is well-known that siderite, for example, overestimates alkalinity determined by acid-base accounting because the ferrous iron released from the dissolving carbonate is oxidized to ferric iron which undergoes hydrolysis and precipitation (Skousen et al., 1997). Differences in carbonate mineral composition among samples, as well as carbonate mineral abundances and textures, will affect the weathering behavior of these rocks. Pyrite is present as framboids in all of the samples. The framboids form clusters of extremely fine-grained individual crystals with lots of surface area, and therefore are likely to be highly reactive. Some pyrite is in contact with calcite which provides inherent NP. Although apatite is a minor component of these rocks, it occurs in contact with pyrite in some places, and provided NP. Manganese is present in pyrite as well as in carbonate minerals.

The major minerals present in the shales are quartz, muscovite/illite, chlorite; the amounts of pyrite and carbonate minerals vary. XRD patterns for the raw shale samples are shown in Figure 5.39, along with the reference patterns for quartz, pyrite, chlorite, and muscovite. Relative amounts of different minerals, and relative amounts of different carbonate minerals, in each sample are plotted as bar charts in Figure 5.40. Accessory minerals include apatite, zircon, and rutile. Siderite and ankerite are less soluble than calcite. Furthermore, the zoning of some carbonates suggests that leachate chemistry could change as weathering proceeds and carbonate is consumed. In addition to carbonate minerals and apatite, some silicate minerals provide long-term NP that may be a factor in natural weathering, but probably does not occur on the time scales of the leaching tests. The silicate minerals in the shales that may contribute NP are chlorite and biotite. Although calcic feldspars are known to contribute NP, the feldspars identified in these rocks are mainly sodic. Quartz is inert. Jambor et al's (2002) static NP determinations on individual minerals show that most rock-forming silicate and aluminosilicate minerals provide insufficient NP to produce a threshold NP of 20 kg $CaCO_3$ equivalent. Ideal formulas for minerals identified in the ADTI samples are listed in Table 5.3, along with comments on weathering behavior (based on Goldrich, 1938) and potential acid-neutralizing capacity of individual minerals based on relative reactivities of monomineralic samples at pH5 (Sverdrup, 1990) and NP determinations for monomineralic samples (Jambor et al., 2002). Relative dissolution rates for calcite in laboratory experiments at pH5 are several orders of magnitude faster than dissolution rates for any of the silicate minerals such as biotite or chlorite (Jambor, 2003; Kowalewski and Rimstidt, 2003). Textural relations, such as pyrite in contact with calcite as shown in Figure 5.13, demonstrate inherent neutralization for oxidative weathering of pyrite. Although none of the leach effluents in the USGS experiments were net acidic after the 16 weeks of the experiment, the relative rates of exhaustion of pyrite versus calcite determine long-term weathering behavior of the samples. Leachate experiments on Houchin Creek Shale from some of the other laboratories did go acidic during the final weeks of the experiments. See Chapter 8 for evaluation of weathering rates and predictions of the long-term weathering behavior of the samples based on the complete interlaboratory data set.

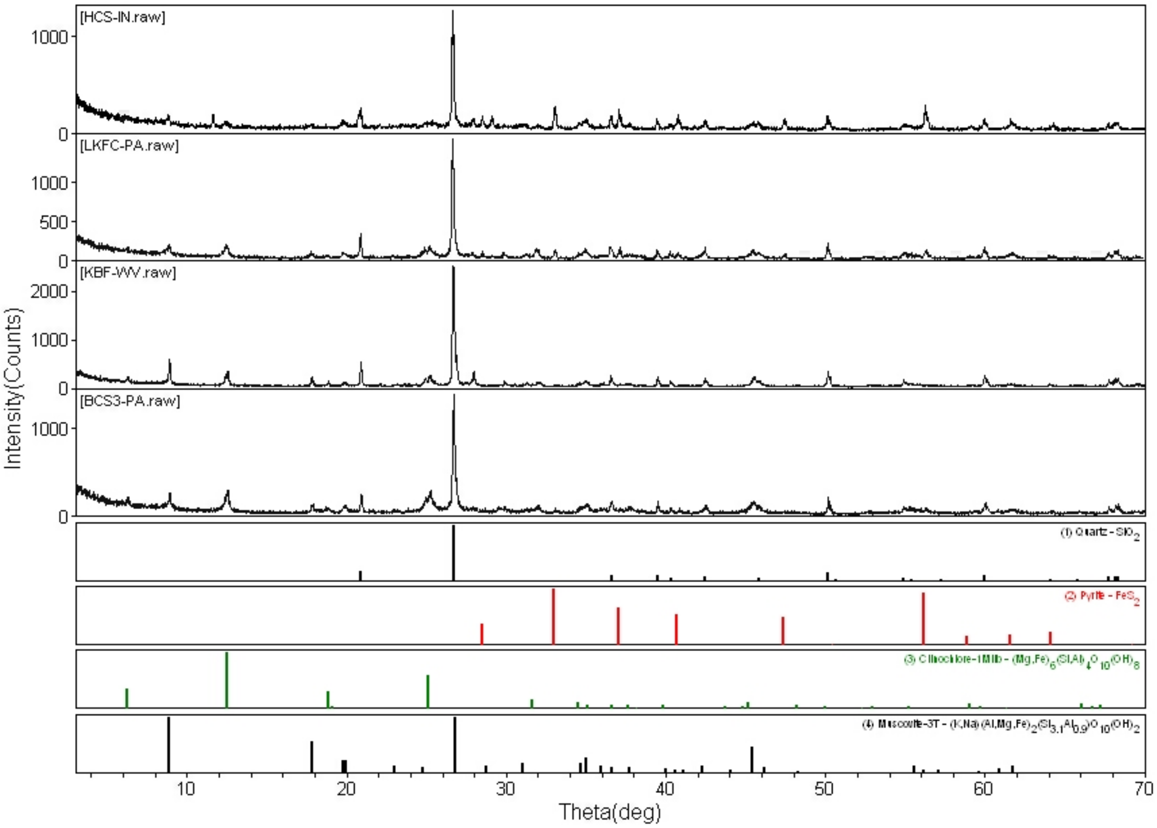
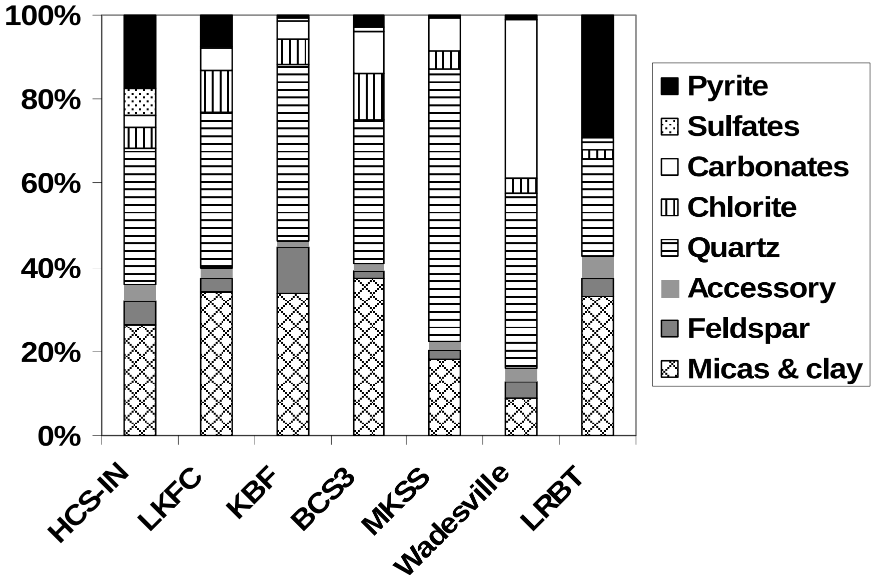


Figure 5.39. XRD patterns for shales and peak locations for standard reference patterns for quartz, pyrite, chlorite (clinochlore variety), and muscovite. Note that the strongest peak in each XRD pattern is the most intense quartz peak at 26.6 degrees.

Low-temperature ash determinations as well as optical and scanning-electron microscopy show that organic material is a significant component of the Houchin Creek Shale and the Leechburg Coal Refuse. Minor amounts of organic material are observed in other samples. The



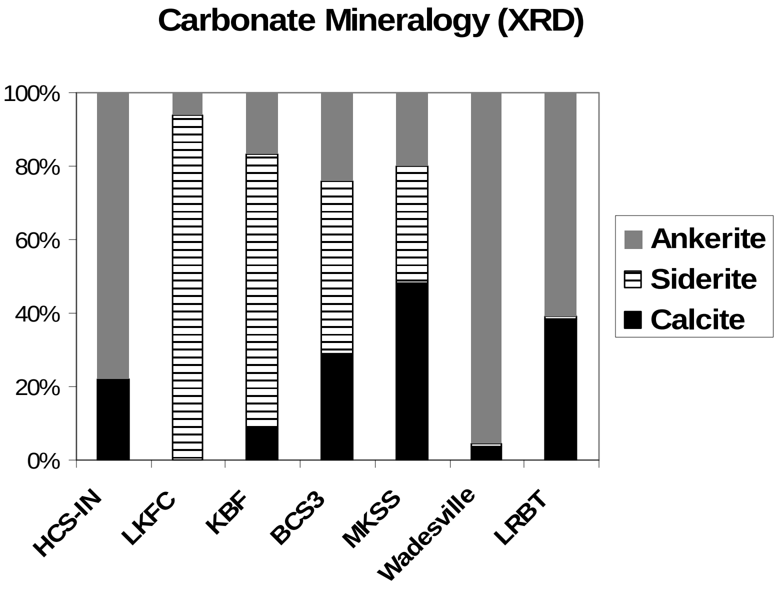


Figure 5.40. Bar charts showing relative percentages of different minerals in the crystalline parts of the samples based on quantitative x-ray powder diffraction (XRD). The bottom chart shows the relative percentages of different carbonate minerals. For example, the Houchin Creek Shale (HCS-IN) has only 3 weight percent total carbonate minerals. The carbonate mineral makeup of that 3 weight per cent is: 0% siderite, 78% ankerite, and 22% calcite.

presence of organic material may affect the production and (or) transport of carbon dioxide in leaching columns. The organic matter could decompose generating carbon dioxide, or it could sorb carbon dioxide generated by acid reaction with carbonate minerals or introduced with compressed air.

Mineralogical Controls on Leachate Quality

Differences in mineralogy among the five lithologies tested are reflected in leach column effluents. We examined mineralogical controls on leachate quality by comparing the cumulative sulfate–sulfur, calcium, and alkalinity leached from the samples during the 16 weeks of the experiment with bulk rock total sulfur, total calcium (as CaO), and estimated abundances of pyrite and carbonate minerals in starting materials. We also computed the percentage of initial sulfur leached during the course of the experiment. These calculations are based on total sulfur in the rock (Table 5.2) and leach column effluent data from the USGS laboratory; data and calculations are given in Appendix 5.2.

The cumulative amount of sulfate leached from the rocks at the end of 16 weeks is consistent with the relative abundance of pyrite (and total sulfur) in the starting material, but does not correlate directly with initial sulfur concentrations measured by TD-ICP (Figure 5-41*A)*. The Houchin Creek Shale contains an estimated 17 weight percent pyrite[2] (4.33 weight percent initial sulfur). The Middle Kittanning Sandstone contains 0.4 weight percent pyrite (<0.1 weight percent total initial sulfur). Less than 10 percent of the initial sulfur present in any of the samples was leached during the experiment (Figure 41*B*). Although the Lower Kittanning Shale contains much less pyrite (8 weight percent) and total sulfur (<1 weight percent) than the Houchin Creek Shale, the percentage of total sulfur leached from the Lower Kittanning sample after 16 weeks was three times as great. The Houchin Creek Shale is a finer-grained rock than the Lower Kittanning Shale. The Houchin Creek Shale contains a significant amount of organic material; carbonate minerals include calcite and ankerite. The Lower Kittanning Shale contains very little organic material, the dominant carbonate mineral is siderite, and both coarse and framboidal pyrite are observed. These differences may affect the kinetics of pyrite weathering in the two shales.

The cumulative alkalinity in leach column effluent and the initial carbonate mineral content of the starting materials are not closely related (Figure 5.42). Although the Brush Creek Shale, with an estimated 10 weight percent total carbonate minerals, generated the highest cumulative alkalinity, the Kanawha Black Flint Shale, with only 4 weight percent total carbonate minerals generated greater cumulative alkalinity than the Middle Kittanning Sandstone, with 8 weight percent total carbonates. The Brush Creek Shale and the Houchin Creek Shale both contain 2.25 weight percent CaO (Table 5.2), yet they the generated different amounts of alkalinity during the course of the experiment. The Brush Creek and Houchin Creek shales contain an estimated 2.9 and 0.6 weight percent calcite, respectively. The Brush Creek shale contains siderite as well as calcite (Ca-rich cores and Fe-rich rims). No siderite was observed in Houchin Creek Shale. Although it contained 5 weight percent total carbonates, the Lower Kittanning Shale generated the least alkalinity during the weathering experiment (Figure 5.42). Siderite is the dominant carbonate minerals in the Lower Kittanning Shale; calcite was only observed within a fossil-rich clast. The presence of calcite appears to exert a strong control on alkalinity in column effluent. Although the quantitative XRD data are uncertain for low concentrations of minerals in complex

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[2] Mineral percentages based on crystalline component

rocks such as these, the data suggest that the nature of the carbonate mineral as well as the amount of carbonate minerals affects leachate quality. The occurrence of a variety of different carbonate minerals, including siderite and zoned carbonate minerals, may explain some of the complications associated with NP determinations in acid-base accounting that lead to uncertainties in mine drainage prediction.

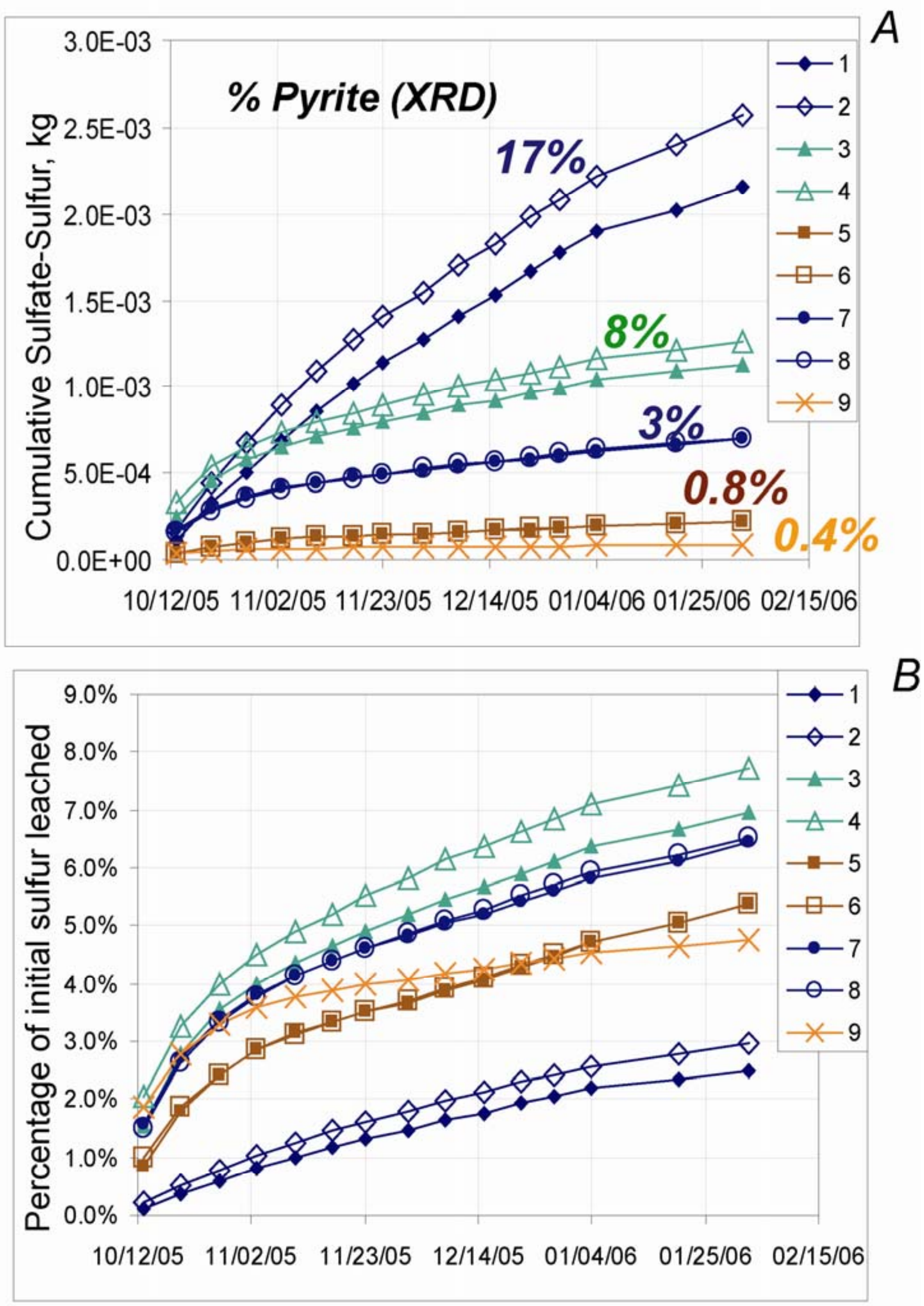

Figure 5.41. Sulfur in leach column effluent as a function of time for duplicate columns of Houchin Creek Shale (1 and 2), Lower Kittanning Shale (3 and 4), Kanawha Black Flint Shale (5 and 6), Brush Creek Shale (7 and 8), and a single column of Middle Kittanning Sandstone (9). *A*, Cumulative sulfate-sulfur. Curves are labeled with the weight percent pyrite determined by XRD (Table 5.4). *B*, Percentage of initial sulfur leached. Initial sulfur based on chemical analyses by TD-ICP reported in Table5.2. See Appendix 5.2 for leachate data and calculations.

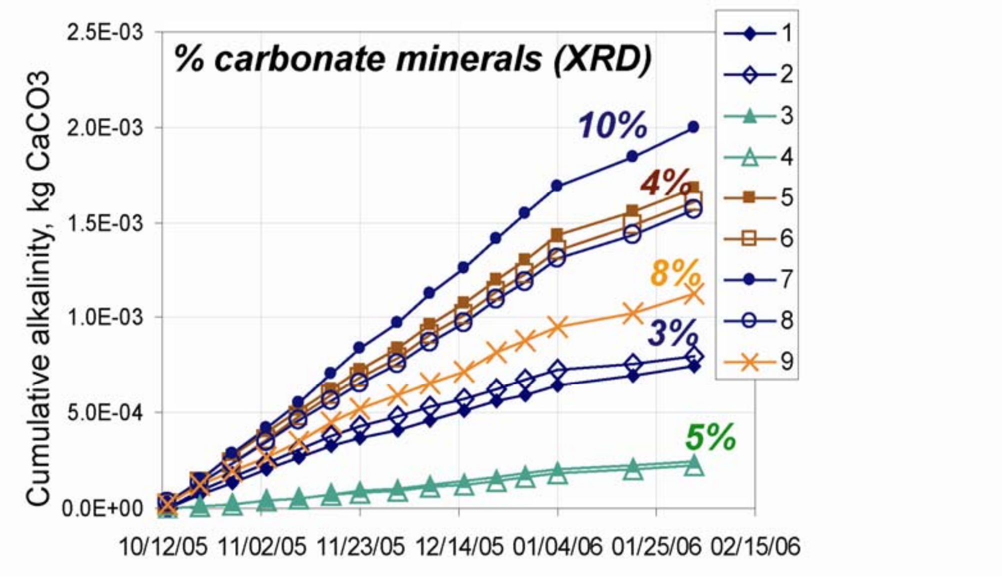

Figure 5.42. Cumulative alkalinity in column effluent as a function of time for duplicate columns of Houchin Creek Shale (1 and 2), Lower Kittanning Shale (3 and 4), Kanawha Black Flint Shale (5 and 6), Brush Creek Shale (7 and 8), and a single column of Middle Kittanning Sandstone (9). Curves are labeled with the weight percent total carbonate minerals determined by XRD (Table 5.4). See Appendix 5.2 for data and calculations.

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Chapter 6. Evaluation of Particle Size and Surface Area Effects

Barry E. Scheetz, William B. White, Daniel Shollenberger and Roger J. Hornberger

Introduction

Hornberger and Brady (1998) surveyed some 90 different leach protocols that have been applied to AMD overburden rock analyses for which a prescription is usually presented on the geometry, frequency of sample collection, and amount of material to be leached, but no detailed accounting was made of these parameters nor was the data utilized in any analytical sense. In order to provide a common basis for comparison between different leach experiments following a protocol, account of the exposed surface of the solids to the solvent needs to be addressed. Otherwise the cross-laboratory experiments, although individually correct, cannot be compared with other results in the literature, and cannot be used to extract quantitative rate constants. The observed leach rates would be an accurate result of the individual experiment, but meaningless as a fundamental property of the material itself.

Conceptual Background

Effects of Surface Area

On an atomistic level, dissolution of solid materials involves the interaction of water molecules with the surface atoms of the solid. Ion-dipole attractions from water molecules break the bonds holding the surface ion in the solid which then move to the solvent. Solvation of these ions occurs in the solvent as water molecules attach themselves to the ions and the complex diffuses out into the solvent. Fundamentally, the more bonds that need to be broken, the slower a material is to dissolve. Conversely, the more bonds exposed to the interaction with water, the more ions will be taken into solution. We are all familiar with the dissolution behavior of sugar in iced-tea: sugar cubes, granular sugar and powdered sugar can easily be ranked by their exposed surface area.

Effect of Leachate Volume

In a similar analogy, the volume of the iced-tea to which the powdered sugar is added will impact the rate of the dissolution of sugar. A small amount of solids will readily dissolve in a large volume of solvent; where as a large amount of solid will only slowly dissolve in the same large volume of solvent as saturation is approached. Figure 6.1 is a typical leach behavior which depicts rapid dissolution at short times resulting in low but steadily increasing concentration. As the concentration approaches the solubility controlling limit the early stage rapid dissolution rate decreases to the steady state condition at saturation.

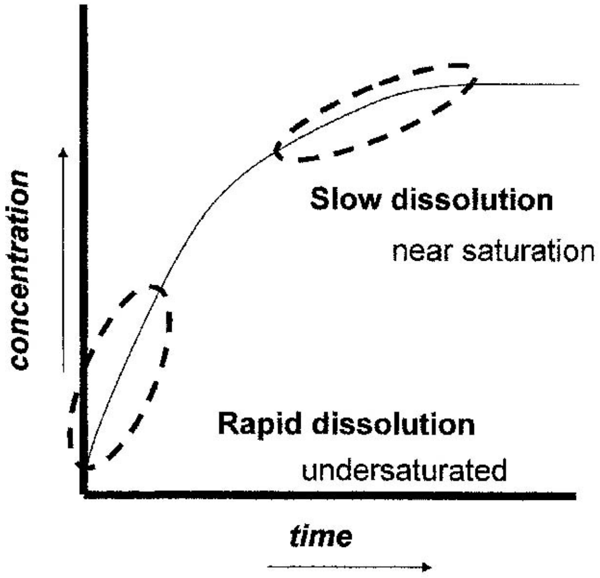


Figure 6.1. Schematic representation of dissolution as a function of time.

Machiels and Pescatore (1983) illustrate this effect of surface area to volume ratio with both laboratory leach data and computational modeling of the leach data; presented here in Fig. 6.2. In this example of the leaching of a borosilicate glass analog of a nuclear wasteform, the glass dissolution, as represented by a normalized mass loss, is an order of magnitude less in leaching solutions with a high SA/V versus a low SA/V.

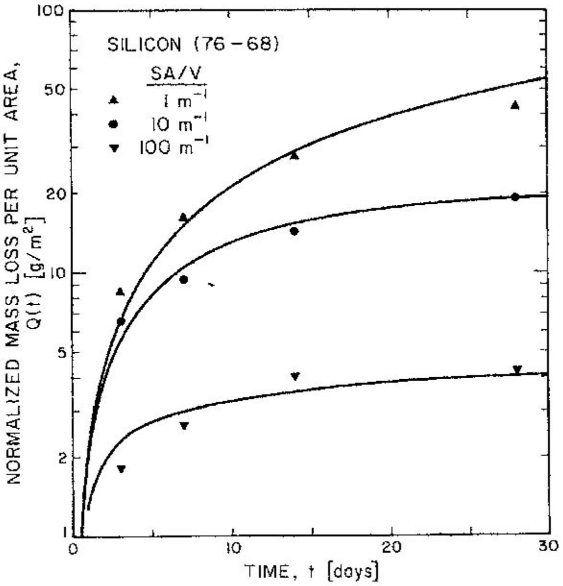


Figure 6.2. Effect of SA/V ratio on the release of silicon to leaching solutions for a borosilicate glass. [Machiels and Pescatore, 1983]

This concept was more widely recognized by researchers [e.g. Ethridge et al., (1979); Hench et al., (1980); Buckwalter et al., (1982); Oversby (1982); Pederson et al., (1983); Machiels and Pescatore (1983)] that the particle size of the leached materials and the volume of fluid that was available for the leaching process had a significant impact on the experimental results. Figure 6.3 demonstrates this dependence. Shown is the release of silica form a nuclear waste form as a function of time with control of the surface area to volume ratio.

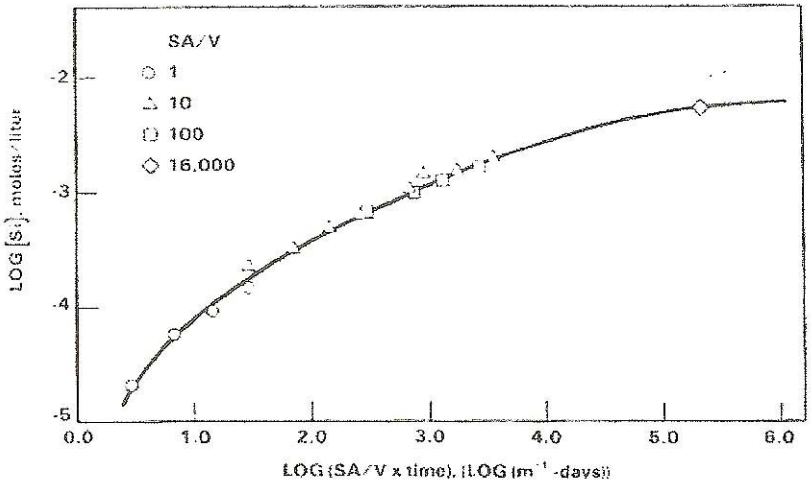


Figure 6.3. Log [Si] vs Log SA/V x t for a glassy nuclear waste form (after Pederson et al., 1983).

What is important in this figure is that by specifically including the surface area/volume parameter, leaching rates varying over 3 orders of magnitude can be scaled onto the same plot.

Measurement of Surface Area

The well established method for determining the surface area of a solid material is BET [Brunauer et al., (1938); Yates (1992)]. This method is a routine analytical approach to measure the accessible surface of the rock to N_2 gas molecules. In the analytical procedure, the rock specimen is heated to degas the surface in a heated vacuum cell. This step is followed by the introduction of gas back into the cell. The final step is to drive off the newly adsorbed gas and measure the quantity released. Knowing the volume of the gas and the molecular diameter of the particular gas, an accurate surface area can be calculated. Gases other than N_2 can be used but they would possess a different molecular size and thus a different quantity of gas would be needed to cover the same surface area. Therefore, it becomes necessary to specify the gas used in the measurement. Additional discussion of surface area measurements and their relationships to porosity and reaction kinetics is given by Brantley and Mellott (2000).

Although the technique is well established, instrumentation may not be readily available to most laboratories. To address this issue, some researchers have used a geometric surface area in place of the BET surface. If the solid materials being tested are glass, this approach may be acceptable, however, if the materials are rocks with irregular surface areas, this approach will significantly under estimate the areas.

Machiels and Pescatore (1983) also illustrated this phenomenon by taking a glass and polishing its surface to roughness of 7 microns. They used this surface roughness as a reference to which they compared the enhanced roughness of the same material polished to a 600 and 100 grit finish (Fig. 6.4).

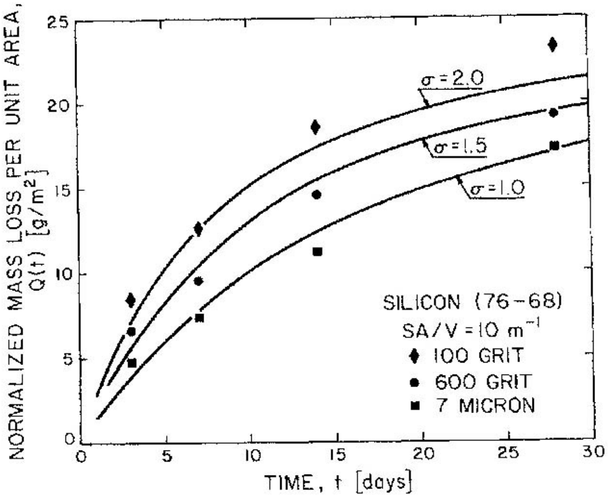


Figure 6.4. Comparison of the normalized release of silicon from a borosilicate glass as a function of surface roughness. [Machiels and Pescatore, 1983]

Results

Measurement Method for Surface Area of Column Materials

Surface areas were measured on the sieve fractions of starting material. At the completion of the testing; the contents of the columns were 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 above, multiplying each mass by the surface area (SA), and combining their fractional percent of the total as a weighted linear average:

$$A \times SA_{sieve1} + B \times SA_{sieve2} + C \times SA_{sieve3} + \quad = \quad SA_{bulk}$$

Where: $A + B + C = 1$
A = fraction of total sieve 1 size
B = fraction of total sieve 2 size
C = fraction of total sieve 3 size

Surface Area Data

Duplicate leaching columns were run for each of the shales in this study and only a single column for the sandstone. Tables 6.1 through 6.5 summarize the surface area data. Each contains the weight fraction of retained on the individual sieves, the BET surface area for each fraction and the modeled ‘effective’ surface area for the materials before the testing protocol.

Table 6.1 Surface area measurements, sieve analysis and calculation of effective surface areas before and after weathering testing in duplicate for the Kawanaha Black Flint Shale.

Kawanwha Black Flint Shale

	surface area	% retained	normalized surface area
3/8	8.94		0
#4	7.5	0.4	3
#10	12.98	0.25	3.2
#16	9.8	0.1	1
#40	9.91	0.1	1
#60	10.68	0.05	0.5
pan	7.61	0.1	0.8
			9.5 m^2/g

Kawanwha Black Flint Shale

	column 3 surface area	% retained	normalized surface area
3/8	8.32		0
#4	9.31	0.4	3.72
#16	8.34	0.35	2.92
#40	10.17	0.1	1.02
#60	10.1	0.05	0.51
pan	9.57	0.1	0.96
			9.12 m^2/g

	column 4 surface area	% retained	normalized surface area
3/8	10.76		0
#4	7.9	0.4	3.2
#16	9.69	0.35	3.4
#40	10.59	0.1	1.1
#60	13.65	0.05	0.7
pan	7.73	0.1	0.8
			9.07 m^2/g

Table 6.2. Surface area measurements, sieve analysis and calculation of effective surface areas before and after weathering testing in duplicate for the lower Kittanning Shale.

Lower Kittanning Shale

	surface area	% retained	normalized surface area
3/8			0
#4	11.71	0.4	4.7
#10	12.78	0.25	3.2
#16	12.78	0.1	1.3
#40	14.71	0.1	1.5
#60	13.68	0.05	0.7
pan	10.63	0.1	1.1

12.4
m^2/g

Lower Kittanning Shale

	column 7		
	surface area	% retained	normalized surface area
3/8			0
#4	13.44	0.4	5.38
#16	14.04	0.35	4.91
#40	15.95	0.1	1.6
#60	12.3	0.05	0.62
pan	15.54	0.1	1.55

14.05
m^2/g

	column 8		
	surface area	% retained	normalized surface area
3/8	11.71		0
#4	13.44	0.4	5.38
#16	12.83	0.35	4.49
#40	15.67	0.1	1.57
#60	16.15	0.05	0.81
pan	15.36	0.1	1.54

13.78
m^2/g

Table 6.3. Surface area measurements, sieve analysis and calculation of effective surface areas before and after weathering testing in duplicate for the Houchin Creek Shale.

Houchin Creek Shale

	surface area	% retained	normalized surface area
3/8	13.03		0
#4	15.77	0.4	6.3
#10	12.15	0.25	3
#16	17.8	0.1	1.8
#40	18.5	0.1	1.9
#60	17.06	0.05	0.9
pan	11.39	0.1	1.1
			15 m^2/g

Houchin Creek Shale

column 5			
	surface area	% retained	normalized surface area
3/8	13.09		0
#4	10.98	0.4	4.39
#16	13.78	0.35	4.82
#40	14.02	0.1	1.4
#60	16.58	0.05	0.83
pan	12.75	0.1	1.28
			12.72 m^2/g

column 6			
	surface area	% retained	normalized surface area
3/8	11.59		0
#4	10.31	0.4	4.12
#16	8.68	0.35	3.04
#40	9.08	0.1	0.91
#60	11.55	0.05	0.58
pan	12.2	0.1	1.22
			9.87 m^2/g

Table 6.4. Surface area measurements, sieve analysis and calculation of effective surface areas before and after weathering testing in duplicate for the Middle Kittanning Sandstone.

Middle Kittanning Sandstone

	surface area	% retained	normalized surface area
3/8	2.65		0
#4	2.55	0.4	1
#10	2.79	0.25	0.7
#16	2.82	0.1	0.3
#40	2.79	0.1	0.3
#60	2.69	0.05	0.1
pan	3.23	0.1	0.3
			2.7 m^2/g

Middle Kittanning Sandstone

	surface area	% retained	normalized surface area
3/8	2.7		0
#4	2.74	0.4	1.1
#16	3.05	0.35	1.07
#40	2.91	0.1	0.29
#60	2.53	0.05	0.13
pan	2.91	0.1	0.29
			2.87 m^2/g

Table 6.5. Surface area measurements, sieve analysis and calculation of effective surface areas before and after weathering testing in duplicate for the Brush Creek Shale.

Brush Creek Shale

	surface area	% retained	normalized surface area
3/8	20.43		0
#4	9.59	0.4	3.8
#10	13.06	0.25	3.3
#16	11.77	0.1	1.2
#40	11.76	0.1	1.2
#60	11.49	0.05	0.6
pan	11.02	0.1	1.1
			11.1 m^2/g

Brush Creek Shale

	column 1		
	surface area	% retained	normalized surface area
3/8			0
#4	17.45	0.4	6.98
#16	17.79	0.35	6.23
#40	18.73	0.1	1.87
#60	18.61	0.05	0.93
pan	11.41	0.1	1.14
			17.15 m^2/g

	column 2		
	surface area	% retained	normalized surface area
3/8	15.67		
#4	17.98	0.4	7.19
#16	16.4	0.35	5.74
#40	18.42	0.1	1.84
#60	17.77	0.05	0.89
pan	17.78	0.1	1.78
			17.44 m^2/g

Unlike the Hornberger (2003) study, two of the shales exhibited an increase in surface area after the leaching experiment and two show a reduction as would be anticipated by the preferential dissolution of small high surface energy particles. These data are summarized in Table 6.6.

Table 6.6 Summary of the before and after changes in the observed BET surfaces areas.

	starting surface area	post leaching A	surface area B	percent change
Kawanwha Black Flint Shale	9.5	9.12	9.07	-4.3
Lower Kittanning Shale	12.4	14.05	13.78	12.2
Houchin Creek Shale	15	12.72	9.87	-24.7
Middle Kittanning Sandstone	2.7	2.87		6.3
Brush Creek Shale	11.1	17.15	17.44	55.8

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 themeasured BET surface area which is about a factor of 3 to 10 times larger than limestone or sandstone. Because of the variability in the mineralogical composition of the shales in general, a wider variability in BET surface areas would be anticipated. Shales that have more soluble, fine-grained components will in general present a larger measured surface area after leaching primarily because of the layered structure of the phyllosilicates. In contrast, both sandstone and limestone are more nearly monomineraloic, quartz or dolomite/calcite, respectively. Neither of these minerals have structures that contribute to enhanced surface area.

Previous phases of this program (Hornberger et al., 2003) have looked at other rock types. Figure 6.5 summarized the BET surface areas of all of the rock types tested to date.

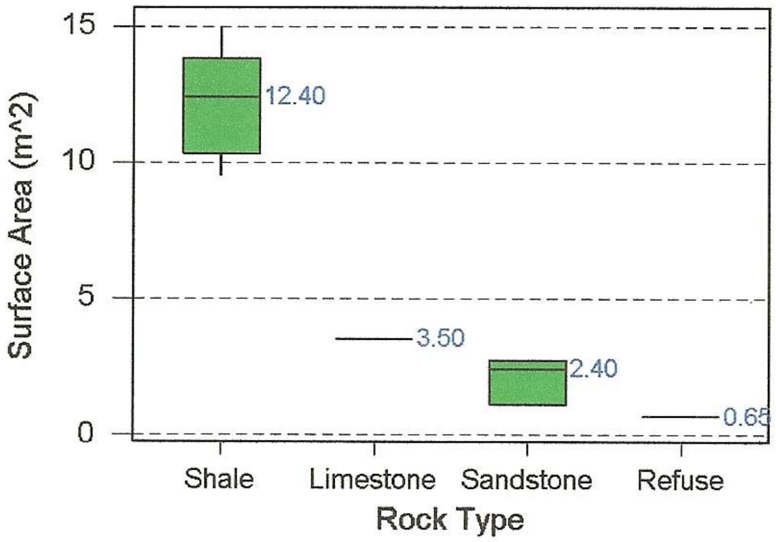


Figure 6.5. Box and whisker plot for BET of different rock types used in this program to date. [Brady, personnel communication]

Calculation of Surface Area to Volume Ratios

The design of the leaching column experiments allows a direct calculation of the surface area to volume ratio. The surface area for the reconstituted rock mass in the column is calculated as shown in the equation for SA_{bulk} shown above. This quantity is then scaled to the total rock mass in the column. The volume is simply the volume of water drained from the column after each weekly 24-hour fill-and-drain cycle.

$$\frac{SA}{V} = \frac{1000\ m\ SA_{bulk}}{V}$$

Where: SA/V = surface area to volume ratio (meters $^{-1}$)
m = mass of solids inn column (grams)
SA_{bulk} = BET surface area of solids (meter-squared/gram)
V = volume of leachate from each drain cycle (liters)

Using this formula, the range of SA/V for the shale samples is $36.1 \times 10.^{6}$ m $^{-1}$ to 41.8×10^{6} m $^{-1}$ and the sandstone is $10.4 \times 10\text{-}^{6}$ m $^{-1}$. Hence, the SA/V for the shales is about 3 to 4 times greater than the sandstone. On Figure 6.5 there is a similar difference between surface areas of shales and sandstones, wherein the median shale of 12.4 is about 5 time greater than the median sandstone. The greater numbers for the shale is probably attributed to the number of bedding plans and the friability of these types of rocks. Figure 6.5 and Tables 6.1 through 6.6 show that the variation between rock types is greater than the variations within a rock type.

According to Pederson et al., (1982) "Thus, short-term tests at a high SA/V value can be used to predict leachate solution concentrations for long-term tests at lower values of SA/V."

The surface area data have been very useful in this study, however, it is not likely that most of the commercial labs using the leaching column method will have the BET surface area measuring equipment. However, the labs will have the sieves to do the particle size distributions, and some of that data can be related to the surface area data. Ideally the surface area data should be gathered on a greater range of rock types and more rock samples of each type. Then, some positive statements of surface area, given a certain rock type, could be made.

The range of concentrations of alkalinity, acidity, sulfates and metals in the present study are representative of the concentrations of those analytes found in the mine environment. Therefore, the writers believe that the SA/V ratios for the ADTI-WP2 leaching column method are appropriate for future use.

Implementation of Surface Area to Volume Ratio

A way of quantifying the release of ions into a leaching solvent is to represent it as a *normalized elemental mass loss* (ASTM C 1220, (1998)). The normalized mass loss $[NL]_i$ for an element is determined by:

$[NL]_i = C_{ij} \text{ x } V_j/[f_i \text{ x } SA]$

Where: $[NL]_i$ = normalized mass loss of element ***i***

C_{ij} = concentration of element ***i*** in specimen ***j*** leachate that was filtered through a 0.45 micron filter

V_j = the initial volume of leachate containing specimen ***j***

f_i = the mass fraction of element ***i*** in the unleached specimen

SA = specimen surface area.

The observant reader will recognize that the normalized mass loss actually normalizes against only the quantity of materials that has been removed from the specimen; effectively compensating for the intrinsic solubility of that element in the solid materials being investigated. Just because an element may be present in a leach specimen, doesn’t mean that it is labile.

Conclusions

If a useful leaching protocol is to be implemented which can be used to compare samples for a wide range of laboratories and a range of potential lithologies and ultimately will be used to predict long-term performance, then more of a realistic surface area than a geometric surface area needs to be utilized. Hornberger et al., (2003) illustrated this point by showing that the shale overburden in that study had a ten-fold larger surface area than a sandstone overburden.

For a leaching protocol to realistically represent the release of constituents from a solid into solution during dissolution, the methodology must take into account the entire surface of the materials to be tested. Determination of the surface areas of four shales and a sand stone using the nitrogen sorption pioneered by Brunauer et al., (1938) and now standardized as the BET method showed that the measured surface of the test shales is about a factor of five greater than rock which are composed of non-phyllosilicate mineral. Further, before and after comparison of the surface areas of the shales varied in response to their bulk mineralogy.

Chapter 7. Column Leaching Tests: The Underlying Physical Chemistry

William B. White, Keith B.C. Brady, Roger J. Hornberger and Barry E. Scheetz

Introduction

The ADTI-WP2 column leaching tests are intended to produce empirical results of practical value in a reproducible manner. If the designated protocols are followed, any laboratory should be able to estimate the acid-producing properties of any rock or waste material. Underlying the practical leach test, however, is the basic physical chemistry of the dissolution process. The chapter that follows is an attempt to extract as much of the underlying science as possible.

Conceptual Models for Dissolution Kinetics

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 which measuring reaction kinetics in such heterogeneous materials as crushed rock or coal waste samples. For a comprehensive discussion of chemical kinetics in geochemistry see Lasaga (1998).

As background for discussion of the column experiments, it is useful to consider various possible cases and the dependence of dissolution rate on time that might be expected. For earlier related discussions see White (1986; 1992).

There are several experimental approaches to the determination of dissolution kinetics. The most direct is to place a known mass of material with a known surface area in a known volume of solvent and then monitor the uptake of dissolved elements in solution (Fig. 7.1). In Case 1, the material has a low solubility and dissolves congruently. The concentration in solution will at first rise rapidly until concentrations reach values where back reactions become important. The rate then slows and the concentration gradually approaches the saturation concentration determined by thermodynamic equilibrium. The dissolution process can often be described by a rate equation of the form

$$\frac{dC}{dt} = \frac{S}{V}\left(1 - \frac{C}{C_S}\right)^n \qquad (7.1)$$

In this equation, C is the instantaneous concentration, C_S is the saturation concentration, S is the surface area, V is the volume of solution and n is the reaction order. If the equilibrium solubility is low, the surface area can be treated as a constant. In contrast, Case 2 (Fig. 7.2) describes the dissolution of a more soluble material of limited mass. Dissolution takes place rapidly and continues until the material is entirely dissolved. In Case 2, the surface area does not remain constant so the rate equation (7.1) must be modified to take account of the (generally unknown) time dependence of the surface area, S(t). When the soluble material is completely dissolved, of course, the accumulated concentration in solution becomes constant and the rate drops to zero. With respect to minerals that might be expected in spoil materials, calcite would behave as Case 1; gypsum as Case 2.

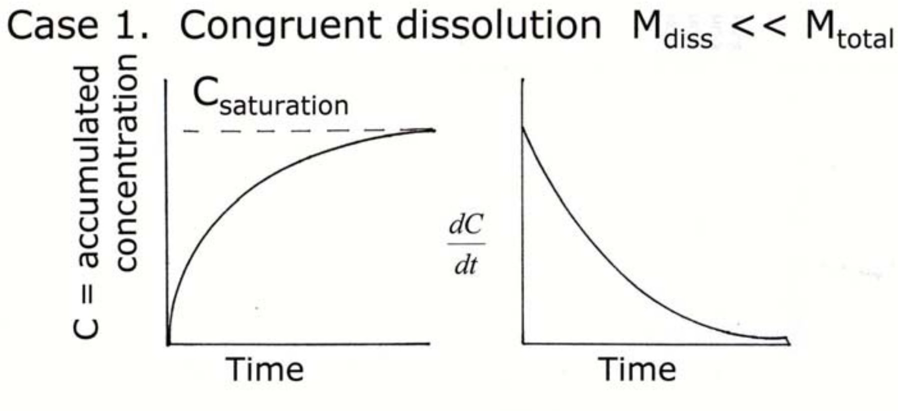


Figure 7.1. Schematic dissolution curve for a congruently dissolving solid of low equilibrium solubility.

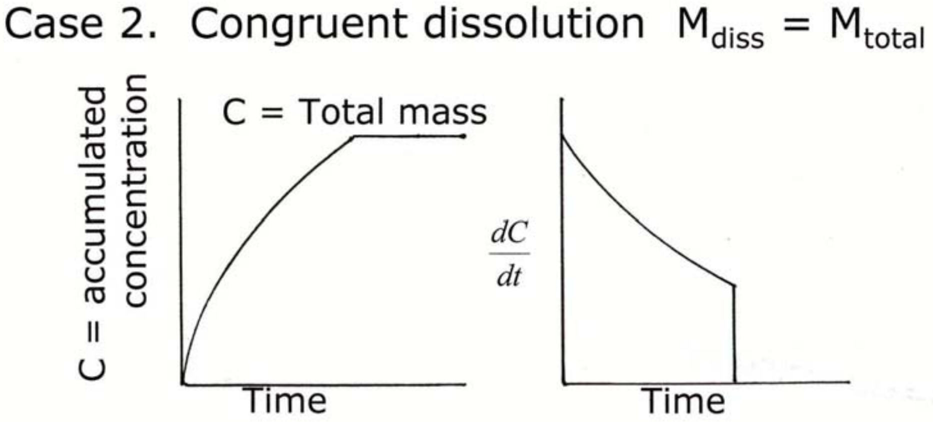


Figure 7.2. Schematic dissolution curve for a congruently dissolving solid of high solubility and limited mass.

Most minerals, however, do not dissolve by simple congruent dissociation into component ions but instead dissolve by chemical reaction with water or hydrogen ions as illustrated in

Case 3. The result will be that some components of the mineral will be taken into solution leaving other components as a solid reaction product. If the solid reaction products form a barrier layer, the rate of reaction will be controlled by diffusion of reactants through the barrier layer. Control by the rate of chemical reaction at the mineral surface will usually produce a linear dependence of concentration on time if the reaction is first order (n = 1 in equation 7.1). Control by diffusion typically produces a square root of time dependence (Fig. 7.3).

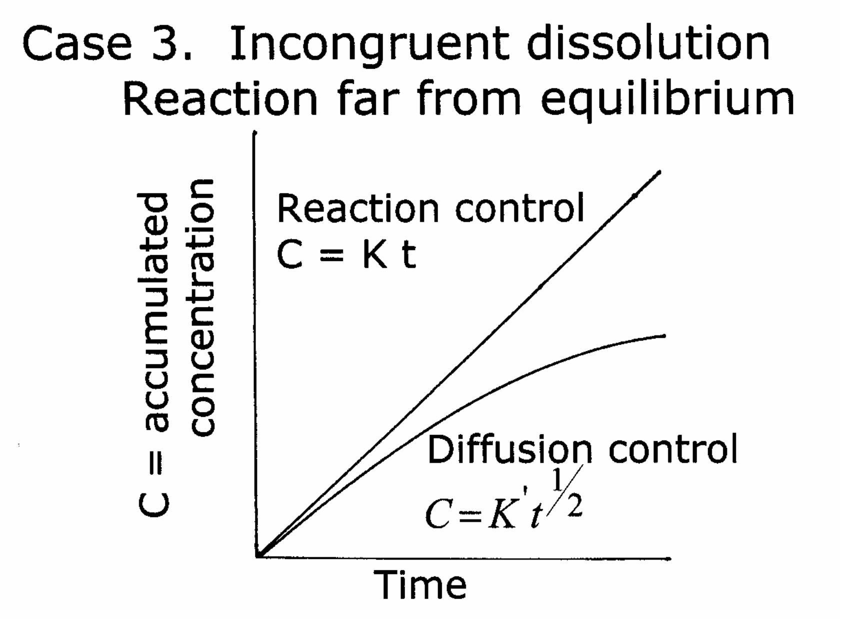


Figure 7.3 Schematic dissolution curves for materials dissolving by chemical reaction with the solvent.

Either of these mechanisms describes the dissolution of a single phase. In a heterogeneous material such a rock or mine spoil, there may be multiple phases, each releasing the same element but dissolving at different rates. The bulk rate curves for heterogeneous mineral assemblages does not lend themselves to easy mathematical analysis.

Alternative approaches to geochemical kinetics are various forms of flow-through experiments. These may be designed so that the material to be dissolved is continuously bathed in fresh solution. In flow-through experiments, the dissolving mineral never reaches equilibrium with the solution. The rate is given by the initial slope of the concentration/time curve and thus is usually the fastest rate. Instead of a continuous flow of solvent, the reaction vessels can be drained at periodic intervals and replaced with fresh solution. The column experiments are a variant of this experimental arrangement.

The materials in ADTI-WP2 leach columns, following an initial flush, undergo a 6-day weathering period as wet rock in contact with a flowing, CO_2-containing atmosphere. This is followed by a 1-day soak period in deionized water after which the water is rapidly drained for analysis and a subsequent weathering period begins. The release of leach elements from the test column is, therefore, episodic.

Each flush begins with fresh water so that the initial concentration is supposed to be zero. However, considerable water remains on mineral surfaces so that there is some, unknown, initial concentration. Concentrations rise rapidly as the weathering products accumulated from the previous six-day weathering cycle are dissolved and extracted (Fig. 7.4). Only the final concentrations, obtained when the columns are drained, were analyzed so the shapes of the curves in Figure 7.4 are completely schematic.

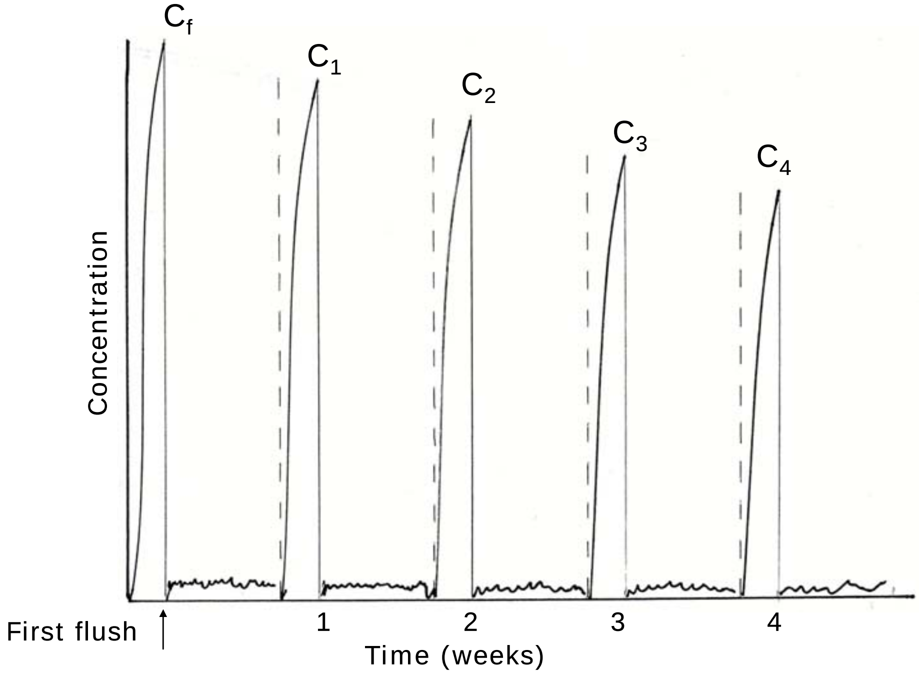


Figure 7.4. Schematic drawing of expected leaching curves from the experimental columns. The peak values, C_f to C_4 would be the instantaneous weekly concentrations which would be added to construct the cumulative curves.

Overview of Column Leach Analytical Data

The input for further analysis is the collected analytical data from the participating laboratories for the five rock types. This section examines several aspects of variations in the leaching column data from the 9 leaching columns in each of the eight participating laboratories, wherein 5 different rock sample types were tested for fourteen parameters of leachate chemistry on a weekly basis for 14 weeks. The chemical parameters are: pH, specific conductance, acidity, alkalinity, sulfate and nine metals: iron (Fe), manganese (Mn), aluminum (Al), calcium (Ca), magnesium (Mg), sodium (Na), potassium (K), selenium (Se)and zinc (Zn). Each of the eight labs conducted weekly chemical analyses of pH, conductivity, alkalinity and acidity, and were instructed to maintain daily records of room temperature, rate of gas flow through the columns, and carbon dioxide content of the gas exiting from the leaching columns. The chemical analyses of the 9 metals and sulfate for 7 of the labs were conducted by Prochem Analytical, an EPA contractor, on leachate aliquots sent to Prochem by each of the 7 labs.

The metals data from Lab 8 were not comparable to data from the other 7 labs, hence the raw data concentration plots of metals in this section do not include data from Lab 8.

Many factors control the leaching behavior of rock samples in leaching column tests as described in Geidel et al., (2000), Hornberger and Brady (1998), Bradham and Carruccio (1995) and numerous other references. The method specifications for this interlaboratory study required maintaining a constant temperature of 25° C, a CO_2 content of 10% in the gas mixture within the columns and an airflow rate of 1.0 liters per minute through the columns. The eight participating labs were not consistent in their adherence to these specifications. The records for Lab 1 and Lab 8 were incomplete; the other six labs maintained the daily log sheet provided for these records. The log sheets were developed to facilitate daily checks of the leaching environment for every day of the month, except weekends and holidays.

The monthly median temperatures and ranges of temperature are shown in Table 7.1. Lab 3 exhibited the best temperature control of the participating labs. Most of the labs were a few degrees cooler than the 25° C target value and most exhibited a few degrees of variation throughout each month. Lab 4 reported the temperatures in Fahrenheit and had the greatest variations in temperature, as shown in Table 7.1; in a three day period in March the temperature in the lab varied by 19° (i.e. March 8= 61° F, March 9= 70° F, March 10= 80° F).

Table 7.1. Median monthly temperatures and differences.

		Lab 2	Lab 3	* Lab 4	Lab 5	Lab 6	Lab 7
Jan	Median	22.3	25.0	68.0	23.4	21.0	20.0
	Difference	3.0	0.1	10.0	3.0	4.0	0.0
Feb	Median	22.2	25.0	65.0	23.9	21.0	19.0
	Difference	2.6	2.0	13.0	2.8	4.0	3.0
March	Median	23.3	25.8	70.0	23.3	22.0	20.0
	Difference	4.0	1.0	19.0	4.9	3.0	3.0
April	Median	23.0	26.0	72.5	23.1	22.5	21.0
	Difference	3.6	3.5	10.0	4.9	2.0	3.0

* Note: Lab 4 reported temperatures in Fahrenheit all others in Centigrade.

The carbon dioxide content or partial pressure of CO_2 in the leaching columns is a very important factor in how much alkalinity is generated from carbonate mineral dissolution as shown in Figure 1.1 (from White, 1988). The amount of carbon dioxide in the gas exiting the leaching columns was measured by a portable CO_2 meter, and the monthly median CO_2 values for Labs 2 through 7 are shown in Table 7.2.

Lab 5 did the best job of consistently maintaining the 10.0% CO_2 in the leaching columns for all 5 rock types as shown in Table 7.2. Labs 2, 4, 6 and 7 usually measured CO_2 amounts far less than the 10% target value as shown by the monthly median values in Table 7.2. Lab 3 frequently exceeded the 10% CO_2 target gas mixture, which could result in higher alkalinity concentrations in laboratory leaching than the actual mine environment. Labs 2 and 7 occasionally met the 10% CO_2 target.

Table 7.2. Median CO_2 content in leaching columns (percent).

		Lab 2		Lab 3		Lab 4		Lab 5		Lab 6		Lab 7	
		C1	C2	C1	C2	C1	C2	C1	C2	C1	C2	C1	C2
HCS-IN	Jan.	7.5	8.5	11.7	13.8	5.3	5.8	10.5	10.5	-	-	7.0	7.0
	Feb.	4.0	4.0	12.0	12.0	5.0	5.0	10.5	10.5	2.5	2.0	7.0	6.5
	Mar.	5.5	4.0	6.0	10.0	5.0	5.0	10.3	10.6	2.5	2.3	6.0	6.0
	Apr.	4.0	4.0	9.0	8.0	5.3	5.0	10.5	10.3	2.8	3.0	5.5	5.3
LKFC-PA	Jan.	7.5	5.3	12.9	14.1	6.0	5.75	10.5	10.5	-	-	7.0	7.0
	Feb.	3.5	3.0	11.0	11.0	5.5	5.0	10.5	10.3	2.0	2.0	7.5	6.5
	Mar.	3.0	3.5	10.0	10.0	5.0	5.0	10.0	10.0	1.8	2.0	6.0	6.5
	Apr.	3.0	2.5	9.0	9.3	5.3	5.3	10.3	10.0	2.8	3.0	5.5	5.5
KBF-WV	Jan.	7.5	7.5	16.2	13.7	6.0	5.8	9.5	8.0	-	-	7.0	7.0
	Feb.	5.0	4.0	11.5	12.5	5.0	5.0	10.5	9.0	3.0	3.5	7.0	7.8
	Mar.	3.5	3.5	10.0	10.0	5.0	5.0	10.3	8.5	1.5	1.0	5.0	5.5
	Apr.	3.0	3.0	9.0	10.0	5.0	5.0	10.2	9.5	2.5	1.5	5.0	5.5
BCS_3-PA	Jan.	8.3	8.0	8.3	12.2	5.5	5.5	8.5	7.0	-	-	6.0	6.5
	Feb.	5.0	3.5	11.0	12.0	5.0	5.0	9.8	7.5	3.5	3.5	6.0	6.5
	Mar.	4.0	3.5	10.0	10.0	5.0	5.0	9.5	8.0	2.5	2.3	6.0	6.0
	Apr.	3.0	3.5	9.0	10.0	5.0	5.0	9.8	8.5	3.3	3.0	6.0	6.0
MKSS-PA	Jan.	6.0		12.3		4.8		9.0		-		7.5	
	Feb.	4.0		12.0		4.0		9.5		2.5		7.0	
	Mar.	3.0		10.0		4.0		9.0		2.5		5.5	
	Apr.	4.0		10.0		4.3		9.0		4.0		5.5	

The variations in CO_2 values within and between labs are shown in boxplots in Figure 7.5. The boxplots show that Labs 3 and 5 did the best job of controlling the CO_2 near to the 10% target value. Lab 3 had a median CO_2 content of 10.0%, but the spread from the median to the upper quartile is from 10 to 12%, and there are a few CO_2 values greater than 12%. Lab 5 had a median of 9%, and the interquartile range is smaller than Lab 3, with fewer values exceeding the target of 10%.

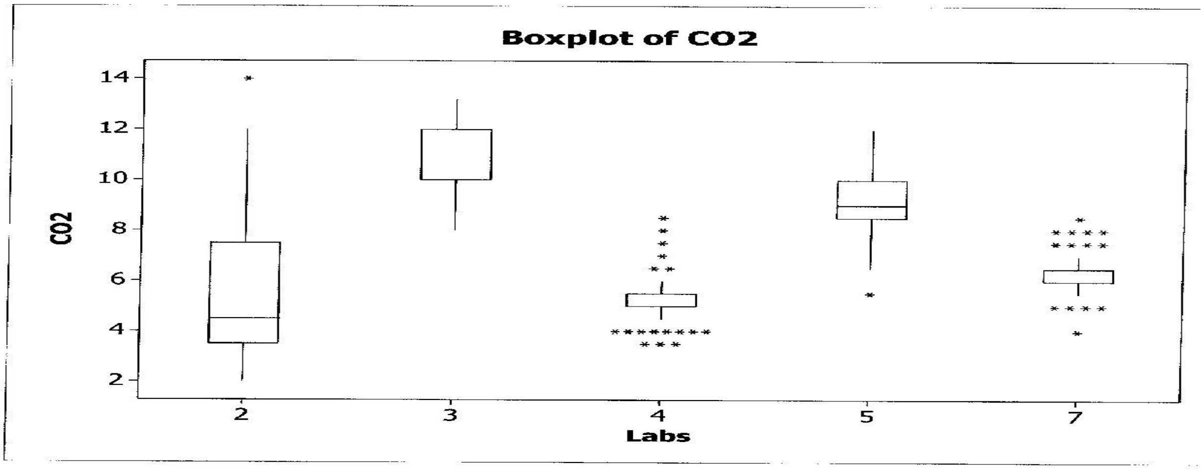


Figure 7.5. Range in CO_2 content of leach column atmosphere between laboratories. CO_2 concentration given in percent by volume.

A plot of CO_2 versus alkalinity is shown in Figure 7.6. This plot shows no distinct linear relationship with alkalinity in leaching column effluent as the dependent variable, and carbon dioxide content (i.e. CO_2%, partial pressure) as the independent variable. Theoretically, alkalinity produced from weathering this calcareous shale sample should increase in proportion to increasing CO_2 content within the leaching column (see Figure 1.1), but that relationship is not evident in this data set. However, several patterns of variation are evident in this bivariate plot. Lab 2 exhibited the greatest scatter of points, having the largest range in CO_2 and alkalinity. Labs 4 and 5 showed the least scatter of data points. Curiously, the range in alkalinity concentrations for Lab 5 is between 500 and 600 mg/l over a CO_2 range of 6.2 to 11%; for Lab 4 the range in alkalinity is 400 to 500 mg/l over a CO_2 range of 3.8 to 7.8%. This implies that relatively high alkalinity concentrations can be produced in leaching columns having far less than the 10% target value. The most unusual bivariate relationship is in the data from Lab 3 where there is a cluster of data points with relatively high alkalinity concentrations and a second cluster of four data points where relatively low (i.e. 50 to 100 mg/l) alkalinity is produced over a CO_2 range of 8.5 to 13 percent.

The gas flow rate of the gas mixture entering the leaching columns was controlled by Rotometers, which were intended to promote consistency in meeting the target 10% CO_2 value in each of the 9 leaching columns in each lab. Labs 4 and 5 very consistently maintained a gas flow rate of 1.0 liters per minute (lpm). Lab 2 typically reported gas flow rates of 0.2 to 0.35 lpm; Lab 3 was consistently at 0.35 or 0.45 lpm; while Labs 6 and 7 were typically higher than 1.0 lpm, with median values of 1.9 lpm in numerous cases. The gas flow rate is probably not independent of the method of gas mixing employed in the leaching test and the partial pressure of CO_2 in the columns. The three methods that may be used are: (1) a single tank of gas containing 10% CO_2, 10% oxygen and 80% nitrogen, (2) a tank of CO_2 mixed with a second tank of compressed air, or (3) a tank of CO_2 mixed with the "house air" line in the laboratory.

Lab 1 is the only lab which used the single tank mixture, which ensured attaining the 10% CO_2 target. Most other labs used the "house air" option, of which it appears that Labs 4 and 5 did the best job of controlling the rate of gas flow.

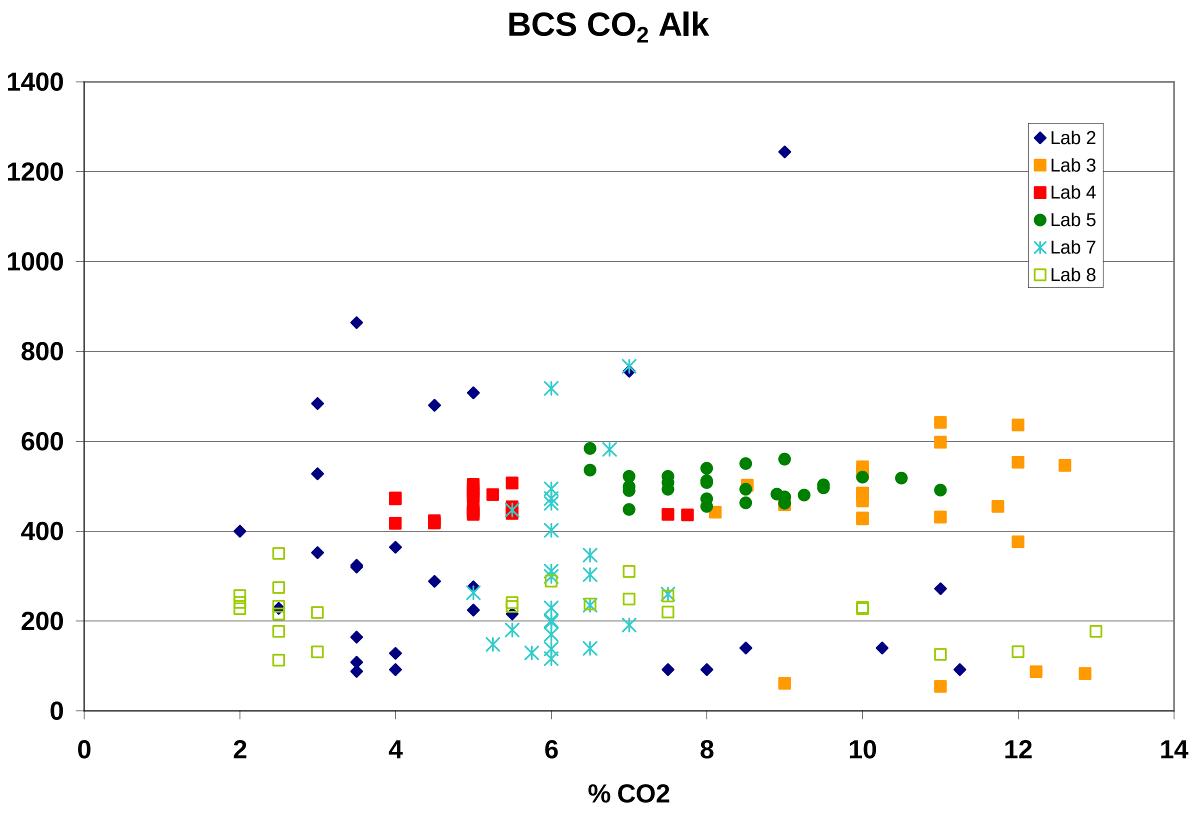


Figure 7.6. Alkalinity vs Carbon Dioxide for BCS shale in mg/L.

The volume of leachate drained out of the leaching columns on a weekly basis is summarized by lab and rock type in Table 7.3, which contains the minimum and maximum values, the range differences and the median for each leaching column. The volume of leachate drained out of a leaching column should be related to the amount of pore spaces within the column, the porosity of the particles of the lithologic unit, the surface area and the degree of packing of the rock particles. The difference in the water volume of duplicate columns within labs is much less than the differences in volume among labs in Table 7.3, which may be related to differences in the packing and volume of rock samples used between labs. There also appears to be subtle differences between the volume of leachate drained and lithology, with the sandstone sample columns having greater intergranular porosity. In cases where the differences in the volume of leachate are great, it may be necessary to normalize the data before attempting to interpret and analyze the results.

Table 7.3. Volume of leachate drained out of columns in mL.

Rock Type		Lab 1		Lab 2		Lab 3		Lab 4		Lab 5		Lab 6		Lab 7		Lab 8	
		C1	C2	C1	C2	C1	C2	C1	C2	C1	C2	C1	C2	C1	C2	C1	C2
HCS	min	304	338	190	200	171	166	350	340	225	170	315	270	196	220	164	124
-IN	max	323	360	380	365	362	443	440	420	259	305	430	385	365	420	274	280
	range	19	22	190	165	191	277	90	80	34	135	115	115	169	200	110	156
	med	315	351	285	295	246	254	370	363	245	261	373	313	268	250	200	198
LKFC	min	443	440	200	285	244	242	350	350	235	238	160	285	120	140	118	117
-PA	max	459	457	375	405	367	401	395	410	300	314	305	350	245	340	220	245
	range	16	17	175	120	123	159	45	60	65	76	145	65	125	200	102	128
	med	453	449	283	325	314	316	365	355	267	252	240	310	190	210	171	199
KBF	min	387	409	235	245	267	262	330	345	227	244	90	135	085	120		
-WV	max	408	422	385	370	370	370	405	410	249	269	295	275	155	155	230	
	range	21	13	150	125	103	108	75	65	22	25	205	140	155	70	110	
	med	402	420	300	300	305	326	340	360	239	260	228	178	96	140	195	
BCS3	min	516	462	325	315	313	245	385	340	260	265	240	240	350	260	116	161
-PA	max	565	559	490	500	420	412	460	440	340	315	330	385	530	430	274	250
	range	49	97	65	185	107	167	75	100	80	50	90	145	180	170	158	89
	med	523	522	398	385	347	312	410	350	282	299	283	308	400	288	193	208
MKSS	min	515		355		302		330		277		165		145		156	148
-PA	max	544		485		370		450		353		345		520		236	261
	range	29		130		68		60		76		180		105		80	113
	med	536		413		330		430		324		260		450		200	191

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. A simple plot of a water quality parameter (e.g. sulfate) through time, using the raw data (i.e. not weighted, not transformed), is often useful to explore patterns of variation or trends, and get a feel for the data prior to more complex analyses of the data. In this study, 14 water quality analytes were determined for 5 rock types which yields more than 70 plots if all of the analytes are plotted for each rock type and additional plots are delineated to compare rock types. This section includes some examples of these time plots. In these data plots week 1 is the "initial flush" and weeks 2 through 15 are the 14 weekly leaching episodes.

pH, Conductivity and Sulfate

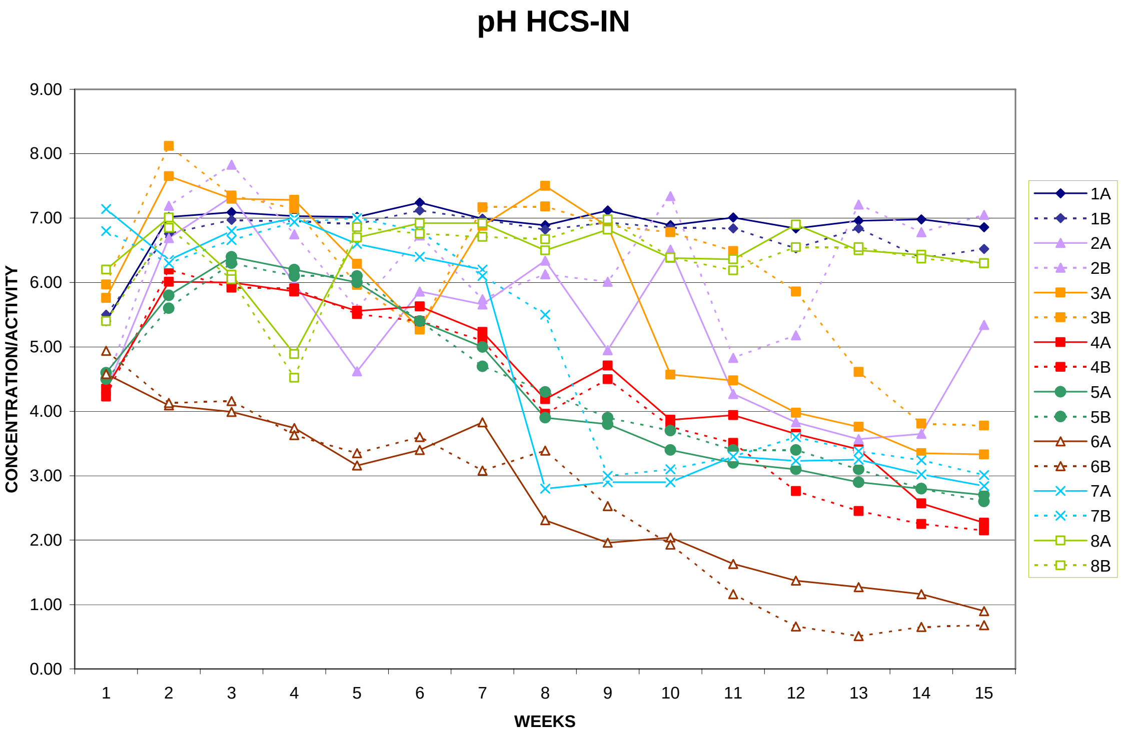


Figure 7.7. pH variations of the Houchin Creek Shale leachate.

The pH of leachate from the leaching columns containing the Houchin Creek shale from Indiana is shown in Figure 7.7. The median pH of the sixteen leaching columns ranged from 2.18 to 7.00. Figure 7.5a shows considerable variation in pH behavior among labs. The pH in Lab 1 remained constantly near 7.0 throughout the 14 week leaching period and there is a close alignment of the duplicate columns. Lab 8 exhibited pH behavior in a manner similar to Lab 1. In Lab 6 there was a steady decline in pH from pH 5 at the start of the weathering test, to a pH below 1.0 in both duplicates by week 14. Labs 2, 3, 4 and 5 also showed a decline in pH throughout the test period, but generally were above pH 5.0 for the first seven weeks of the test period, and then declined to the pH 2 to pH 3 range by the end of the weathering test. Extremely high acidity values of 16,000 mg/l and 12,000 mg/l were produced in week 14 in Lab 4, and corresponding sulfate values of 8,130 and 5,630 mg/l in Lab 4, and 20,600 mg/l in Lab 6, week 14.

The plot of sulfate in Figure 7.8 gives the appearance that some carbonate minerals were present in the leaching column for the first seven weeks of the weathering test, but became overwhelmed by acidity production from the high sulfur content and took off for the remainder of the weathering period in three of the labs (Labs 4, 5 & 6).

It appears that there were microenvironments favorable to acidity production in the columns of these labs, that were absent from Lab 1 and some of the other labs as shown on Figure 7.7 and 7.8.

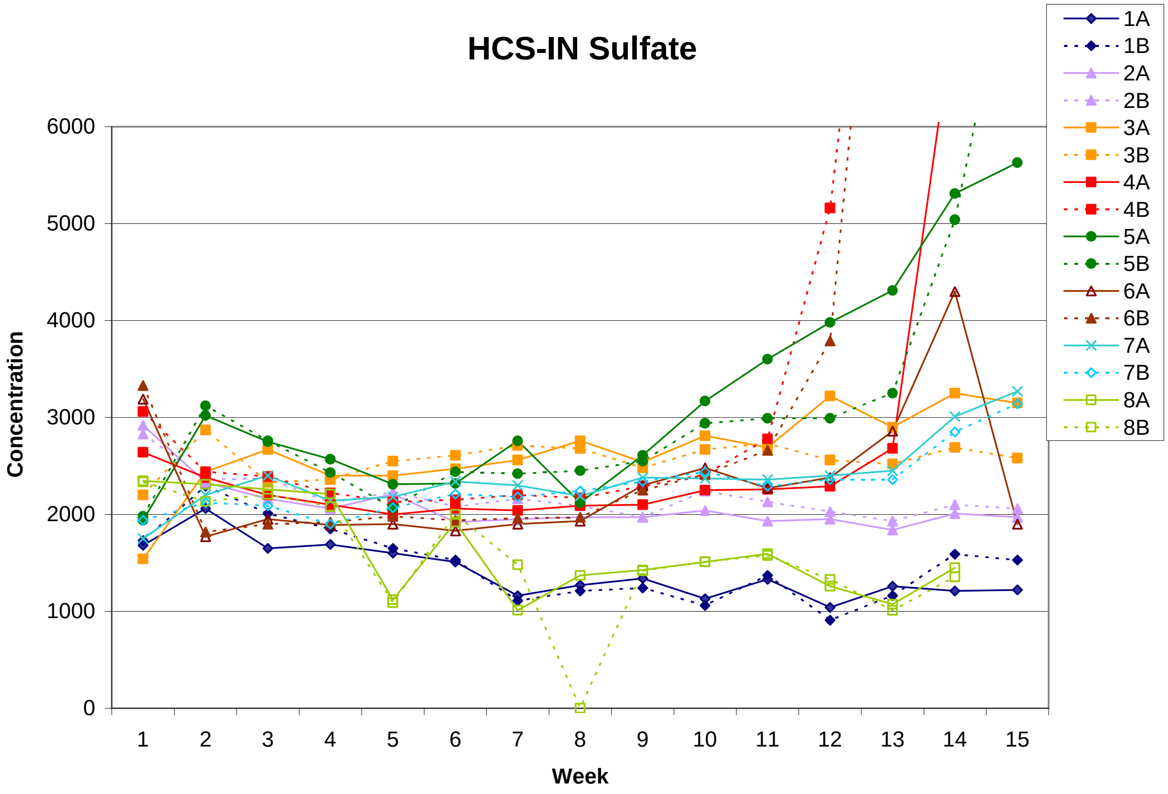


Figure 7.8. Sulfate in effluent from duplicate columns of Houchin Creek Shale.

The conductivity of the leachate is an excellent indicator of the amount of dissolved ionic species in the leaching column effluent. Figure 7.9 shows the conductivity of the 8 labs for the LKFC-PA sample. Week 1 consistently had the highest conductivity of the series after which the values gradually decreased through the 14 week period. Lab 7 had much higher conductivity values than the other seven labs. The pattern of variation for these seven labs is very similar, and the duplicate samples of each of the labs are close together. The pattern of variation for sulfate shown in Figure 7.10 is very similar to that described for conductivity above. A large part of the reasons for that similarity in conductivity and sulfate from the LKFC-PA rock sample is that sulfate is the dominant anion in the leachate.

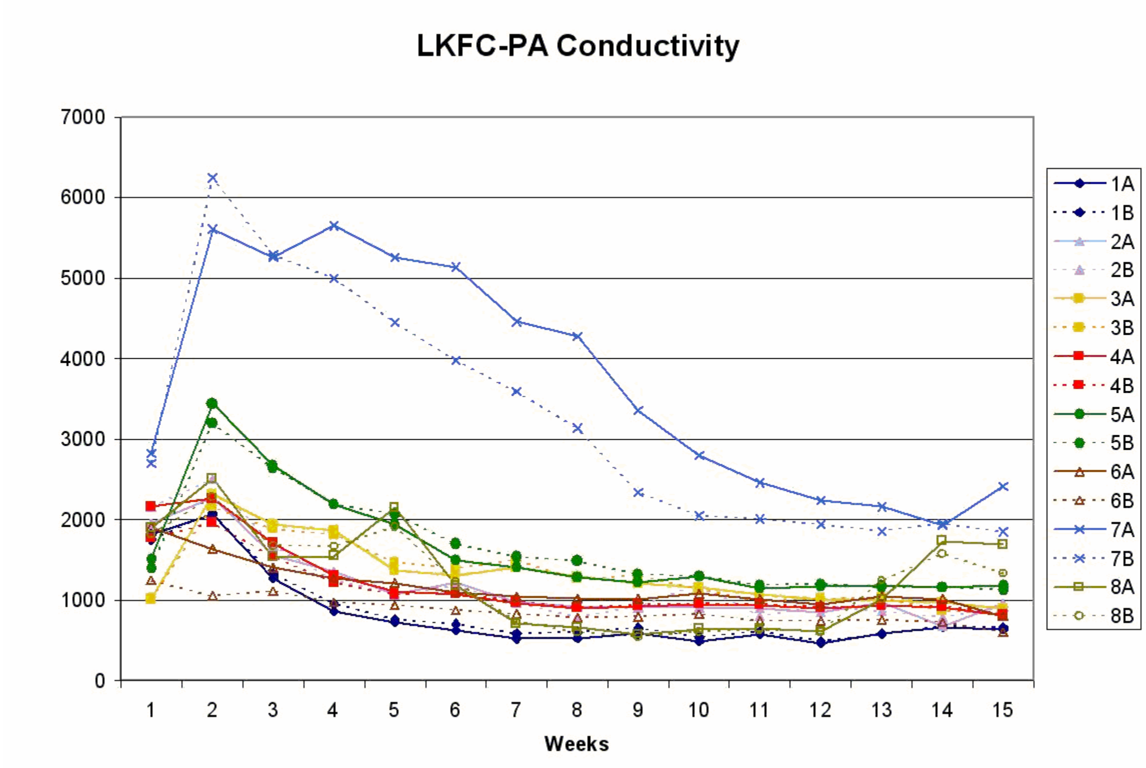


Figure 7.9. Patterns of variation of conductivity (microsiemens) from duplicate columns.

Alkalinity

The Brush Creek Shale produced significant alkalinity concentrations in Phase 1 (see Hornberger et al., 2003) and Phase 2 (see Brady et al., 2004) of this method development project. Most labs reported alkalinity values of several hundred mg/L throughout the 14 week leaching period for the Brush Creek Shale, but there was some scattering of values as shown on Figure 7.11. When the data are plotted for Labs 4 and 5 only, the scatter disappears and the duplicate samples are very consistent, as shown on Figure 7.12. The configuration of this plot is indicative of attaining calcite solubility control as described in Brady et al., (2004).

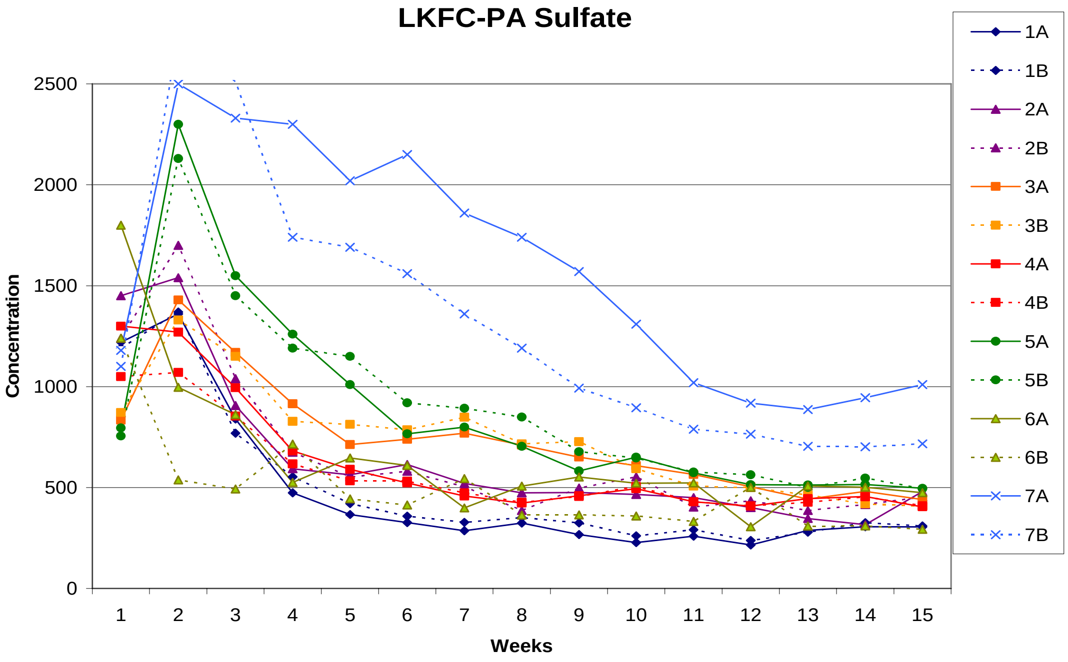


Figure 7.10. Patterns of variation of sulfate concentration in mg/L.

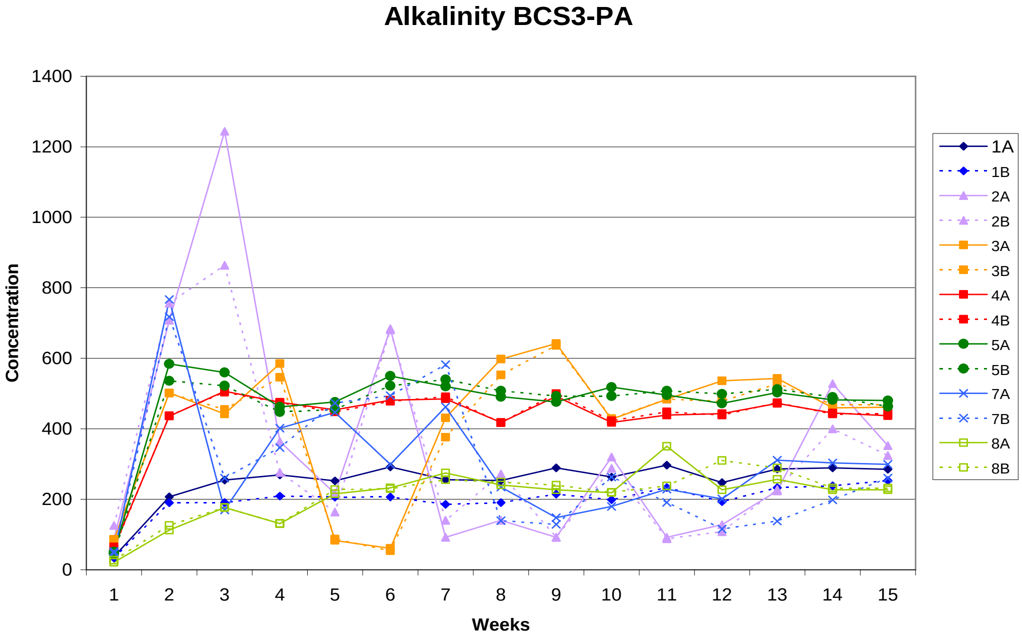


Figure 7.11. Alkalinity variations (mg/L) in duplicate leaching columns.

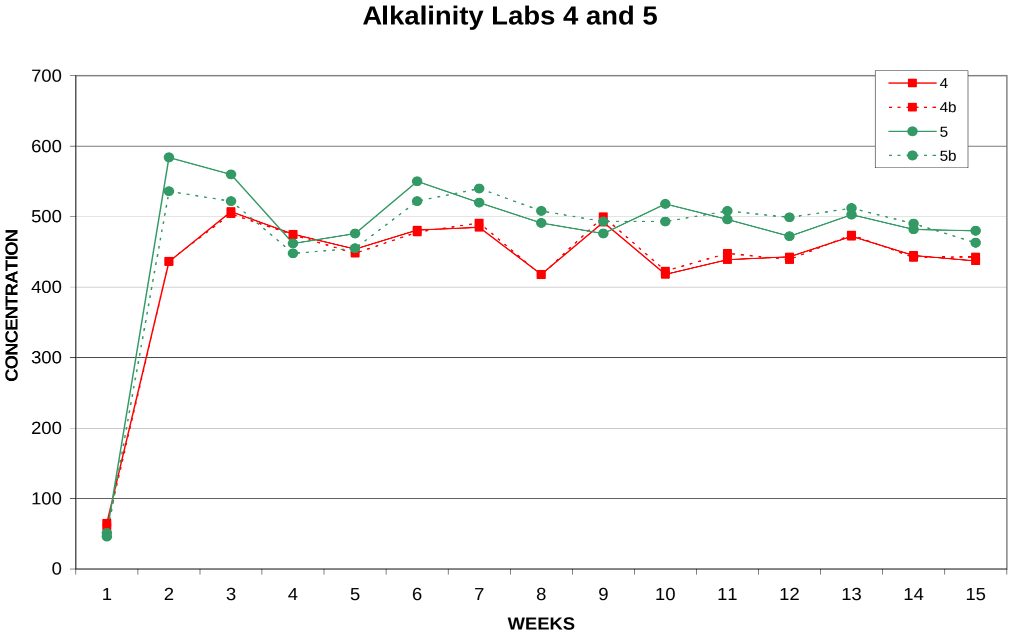


Figure 7.12. Alkalinity concentrations (mg/L) for duplicate Brush Creek Shale columns in Labs 4 and 5.

The relatively low NP values of the Lower Kittanning Falls Creek Shale do not make it a typical “gray zone” sample (NP 12.41 to 16.47), but its leaching behavior is remarkable in terms of alkalinity production. The alkalinity plot for seven of the labs exhibits considerable scattering of the data, as shown in Figure 7.13, but when the data from only Labs 3, 4 and 5 are plotted in Figure 7.14, there is a trend of increasing alkalinity through time.

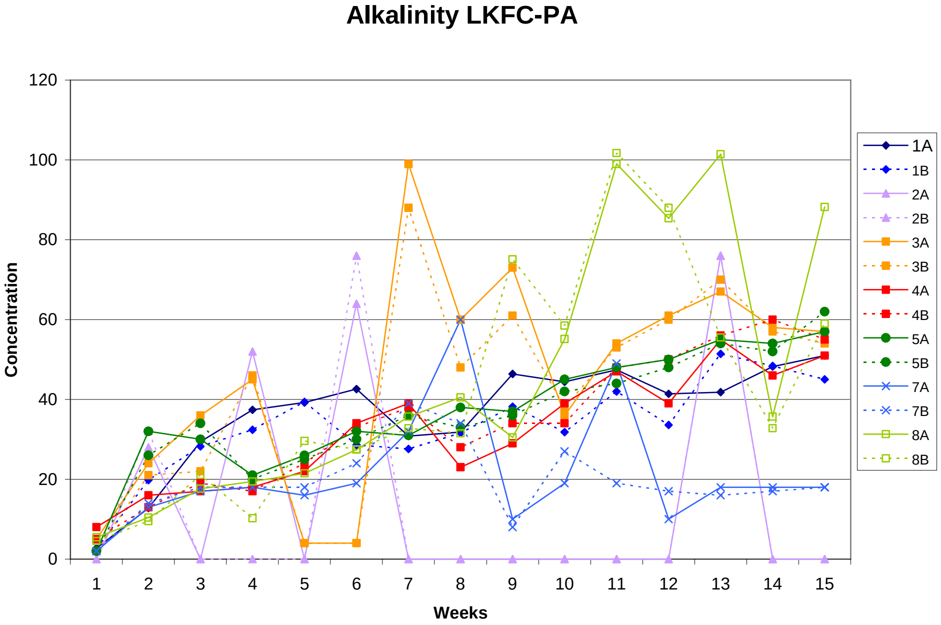


Figure 7.13. Alkalinity concentrations (mg/L) of Lower Kittanning Shale duplicate columns.

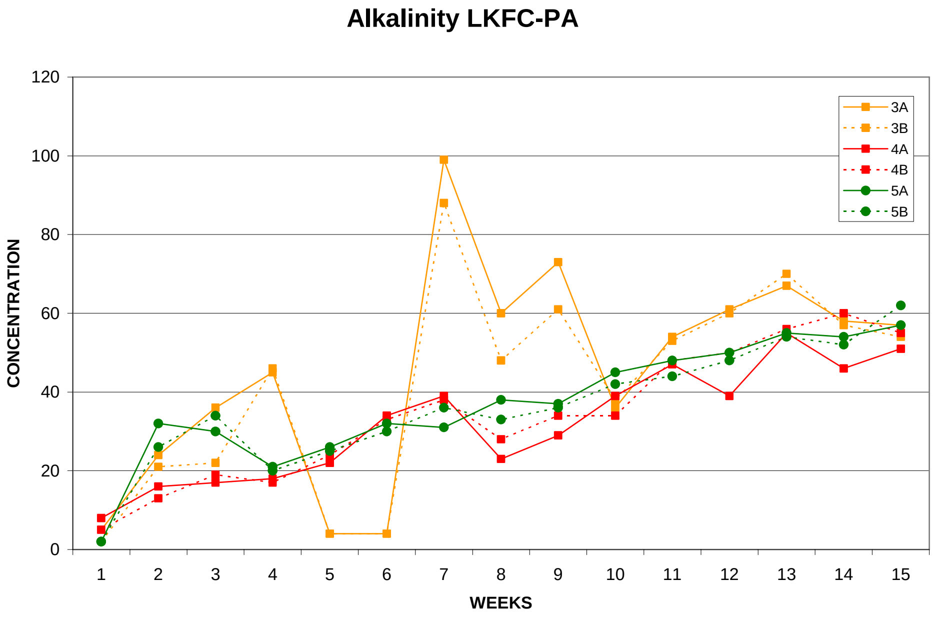


Figure 7.14. Increase in alkalinity concentrations (mg/l) in duplicate at Labs 3, 4, and 5.

Detection and Quantification Limits

The raw data tables from the arrays of leaching columns of the 8 participating labs that are discussed in this section of the report, are contained in Tables 2A through 2N of Appendix E. The "less than" values (e.g. <20) in Tables 2N and 2M on acidity and alkalinity, respectively, are related to detection limits. To report acidity values as <20, for example, is to indicate that the detection limit used in the laboratory titration for acidity is 20 mg/L and any values less than that are not significantly different than zero, and should be interpreted as negligible. In the following discussion of iron and other metals, the use of Method Detection Limits (MDL) and Minimum Levels (ML) will be reported in the data tables and used in the interpretation of the data. The MDL is defined as the lowest value of a determinative signal that shows a constituent of interest to be greater than zero. The ML is defined as the lowest value on a calibration curve, or the lowest point of quantification. (A MDL of 0.1 and a ML and 1.0 were used in the determination and quantification of sulfate values but all of the sulfate values for all five rock types were greater than 1.0 mg/L) The MDL's and ML's will become more meaningful in the following discussion of iron and other metals. In the data tables in Appendix E, analytical results below the ML but above the MDL are shaded in light gray and analytical results below the MDL are shaded in dark gray.

The metals analytical results are expressed in micrograms per liter (parts per billion) as is typically done with mine drainage, surface-water and ground-water data because some of the water quality parameters of interest, such as selenium, are present at very low levels. Some very high concentrations of iron are present in the leachate from the HCS-IN shale samples in Labs 4 and 6, which initially appeared to be unlikely or impossible values.

However, if these results are expressed as parts per million or parts per thousand they become more plausible. For example the HCS-IN sample in Lab 6, Column 6, week 14 produced 6,700,000 parts per billion, which equals 6,700 parts per million, or 6.7 parts per thousand or 0.67 percent.

The rationale for obtaining very high concentration results can also be explained in terms of laboratory instrumentation and operational procedures. Sample results that are significantly higher than the documented calibration range of the method and instrument used to analyze samples are typically obtained using sample dilution or a decreased sample volume. If a sample contains an analyte concentration that is outside (higher than) the calibration range of the analytical method or instrument, the analyst can dilute the sample, analyze the diluted sample, and multiply the result by the dilution factor. Alternatively, the analyst can use a decreased sample size, analyze the decreased volume, and multiply the result to compensate for the decreased volume.

Iron (Fe)

The overall range in reported iron concentrations for all five rock types is 0 µg/L to 6,700,000 µg/L (HCS-IN). The MDL for iron is 9.9 µg/L, so all 0 values were replaced with half of the MDL (4.95) for plotting purposes. (The ML is 50 µg/L.) The extreme range of the iron data makes meaningful plotting of the data very difficult, as there are many low values mixed with extreme peaks. Figure 7.15 shows the iron data plotted in a logarithmic scale, which makes the individual data points discernable, but there is considerable scatter among the data points. On Figure 7.15 for the HCS-IN shale, a trend of increasing iron concentrations is evident for the last seven weeks of the weathering period, especially in Labs 4, 5 and 6. This trend is consistent with the great increase in conductivity and sulfates discussed previously for the HCS-IN shale.

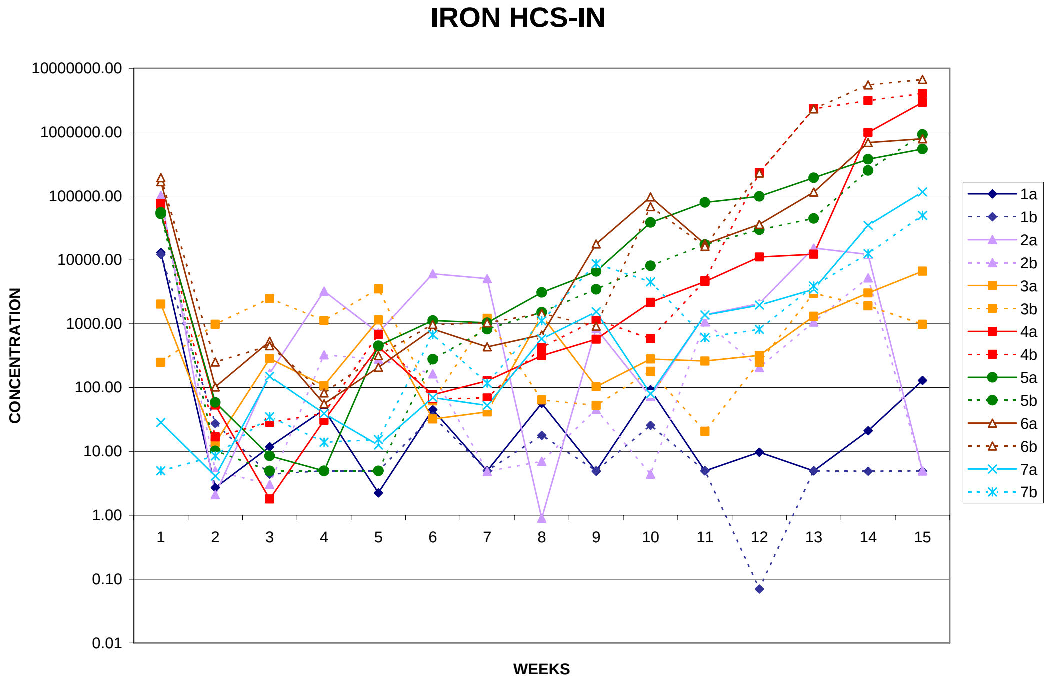


Figure 7.15. Range of iron concentrations (ug/l) of Houchin Creek Shale on a log scale.

Manganese (Mn)

The concentrations of manganese in the leachate for the LKFC-PA shale follow a consistent pattern on Figure 7.16, wherein the highest Mn values are consistently the first week after the initial flush, followed by a steady decline throughout the 14 week weathering period. The duplicate columns exhibited very similar behavior in all 7 labs. The manganese concentrations from the HCS-IN sample (shown in Figure 7.17) exhibit a very different pattern wherein after week 7 the concentrations in all labs except Lab 1 increase, often dramatically, for the remaining 7 weeks of the leaching test. The MDL for manganese is 0.12 µg/L and the ML is 2 µg/L.

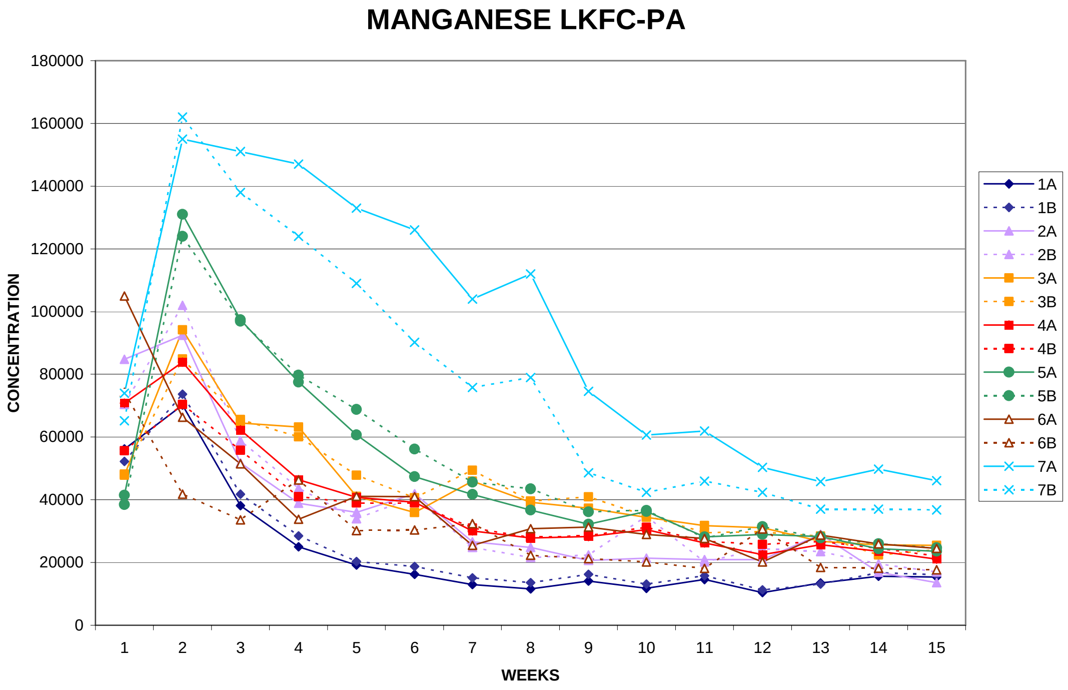


Figure 7.16. Pattern of variation of manganese concentration (ug/l) for Lower Kittanning Shale.

Calcium (Ca)

The plot of the calcium concentrations of the BCS3-PA shale shown in Figure 7.18 exhibits wide variations for Labs 2 and 7; whereas there is close agreement between duplicates and less variation for Labs 1, 4, 5 and 6. When the data are plotted for Labs 4, 5 and 6 only (Figure 7.19), there are some typical peaks in the first weeks of leaching followed by a gradual decline until week 7, after which the data from all three labs are stable at approximately 150 micrograms of calcium for the remaining seven weeks. This trend corresponds with attaining saturation with respect to calcite solubility. The MDL for calcium is 11.8 µg/L and the ML is 50 µg/L.

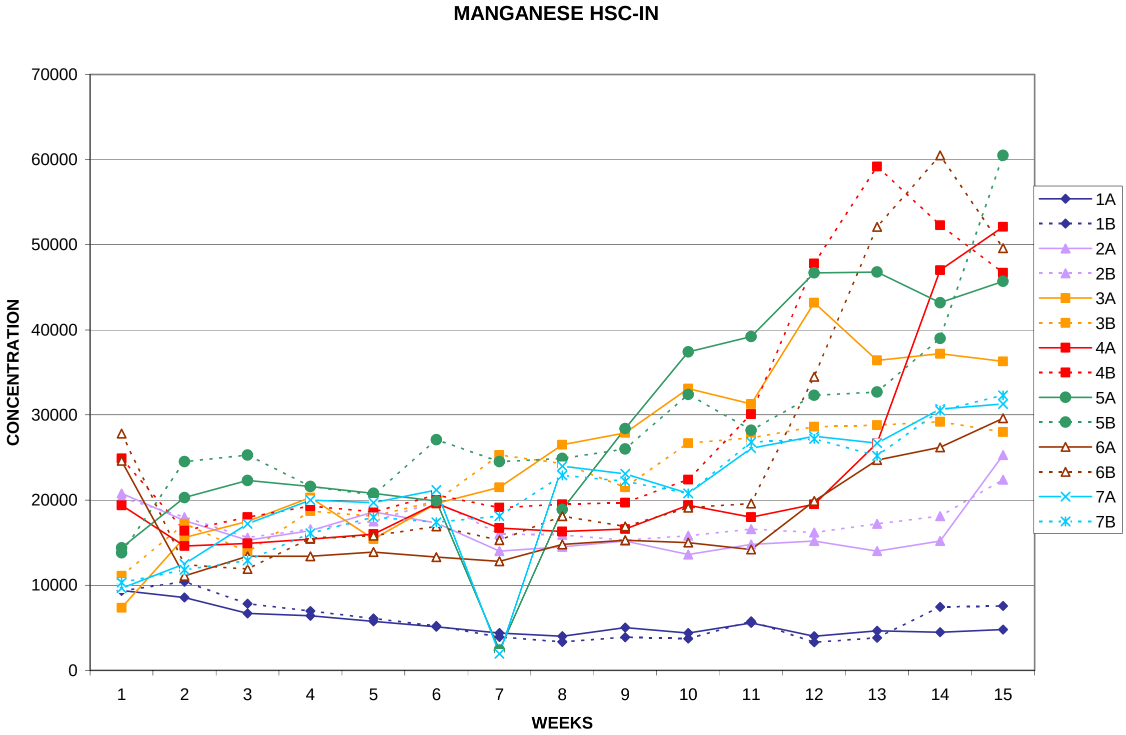


Figure 7.17. Range of manganese concentrations (μg/L) of Houchin Creek Shale .

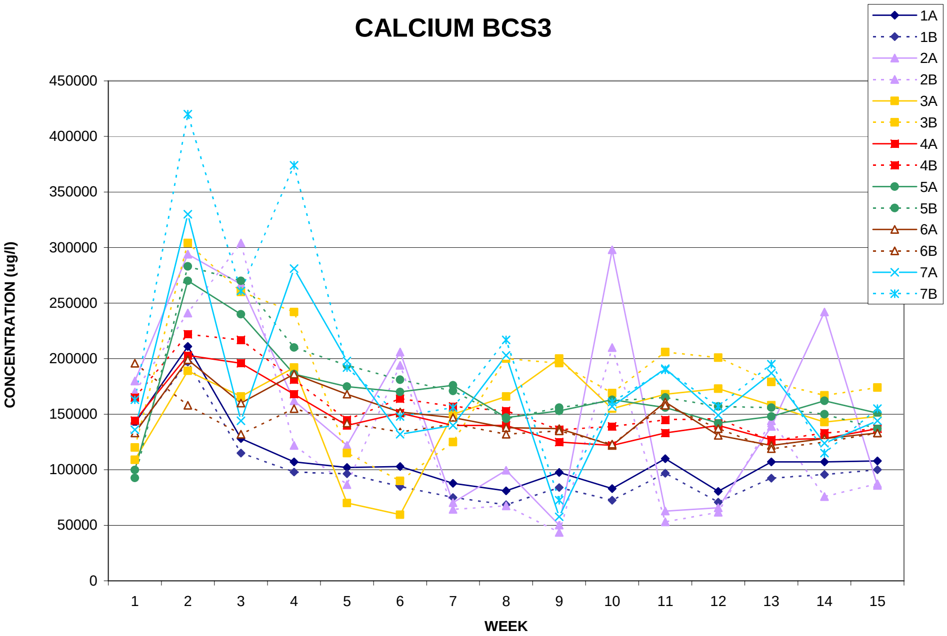


Figure 7.18. Calcium concentrations (μg/L) of Brush Creek Shale duplicate columns.

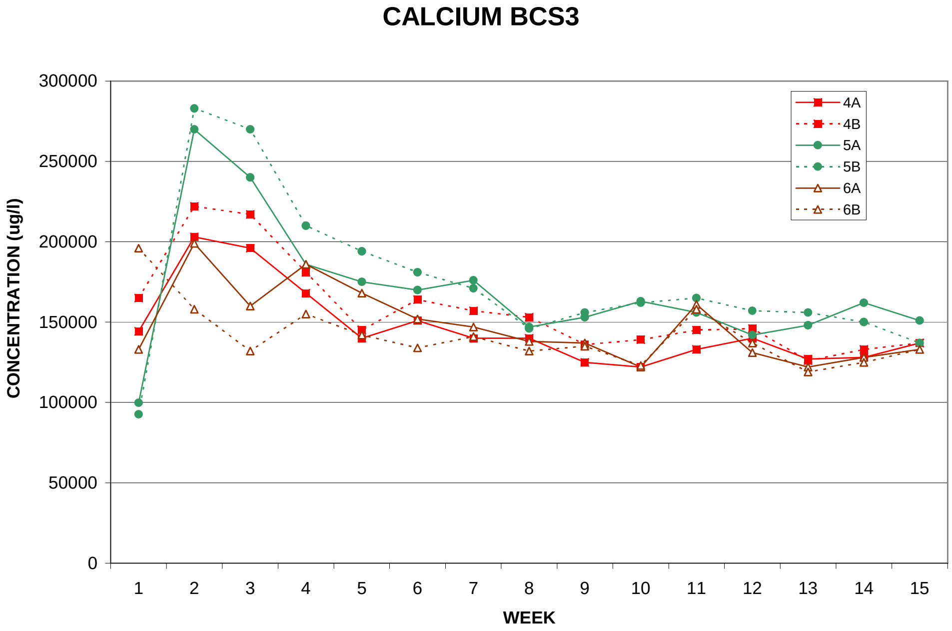


Figure 7.19. Similarity of variations of calcium concentrations (ug/l) in leachate at Labs 4, 5, and 6.

Variations in Leaching Behavior Between All Rock Types

The sulfate leached from all five rock types is shown on Figure 7.20 using data only from Lab 5. This data set shows very close agreement of duplicate columns for the four rock types having duplicate leaching columns. When the sulfate data are plotted on a log scale in Figure 7.20, the five rock types are neatly arranged in the increasing order of sulfate (and acidity) production that would be expected from the acid/base accounting data with the MKSS-PA sandstone the lowest to the HCS-IN shale the highest sulfate.

The alkalinity data shown in Figure 7.21 contains numerous findings that were not evident from the acid/base accounting data, and therefore illustrates the value of the leaching column method for mine drainage prediction. The Brush Creek shale produces 500 to 600 mg/L alkalinity throughout the weathering period as seen in Phase 1 and Phase 2 of the project, and as expected herein. However, the KBF-WV shale and the MKSS-PA sandstone both produce far greater alkalinity than expected from the relatively low NP values. Also, two more subtle types of weathering behavior are seen in Figure 7.21. First, the HSC-IN shale has appreciable alkalinity for the first few weeks of the weathering period, and then declines and is depleted by week 8. The second subtle pattern of weathering in Figure 7.21 is the LKFC-PA shale which starts with the lowest alkalinity of the five rock types, but gradually increases to an appreciable amount by the end of the weathering period. These two types of weathering behavior were not found in Phases 1 and 2 of this study. The succeeding sections of this chapter contain discussion that the leaching column effluents from the BCS3-PA shale, the KBF-WV shale and the MKSS-PA sandstone are saturated with respect to calcite.

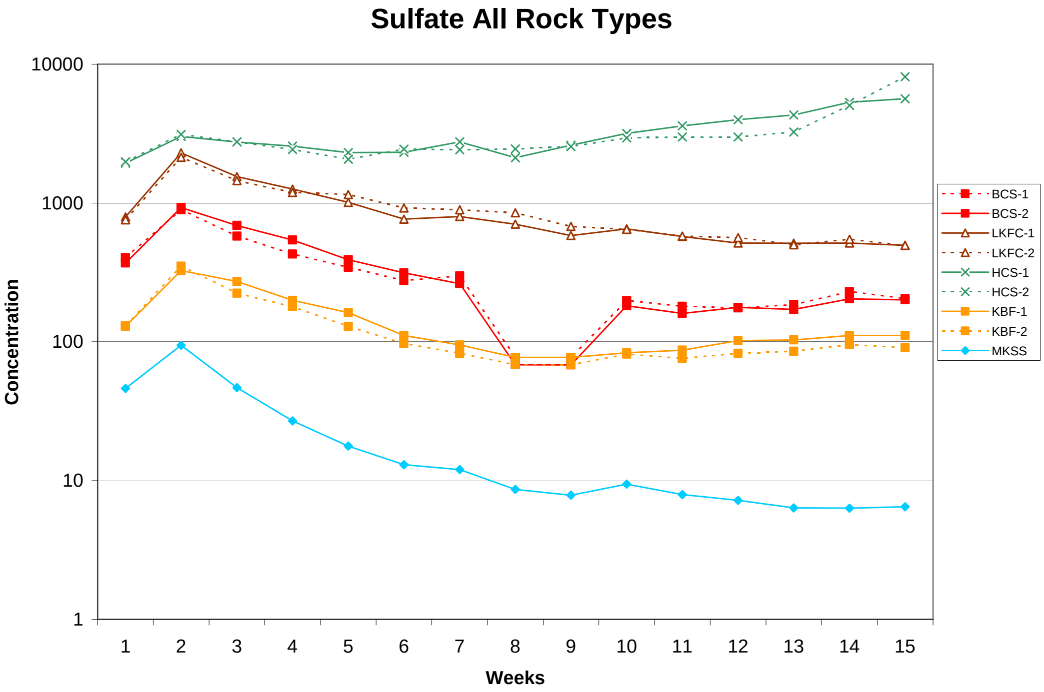


Figure 7.20. Sulfate concentrations (mg/L) in effluent from leaching columns of all rock types.

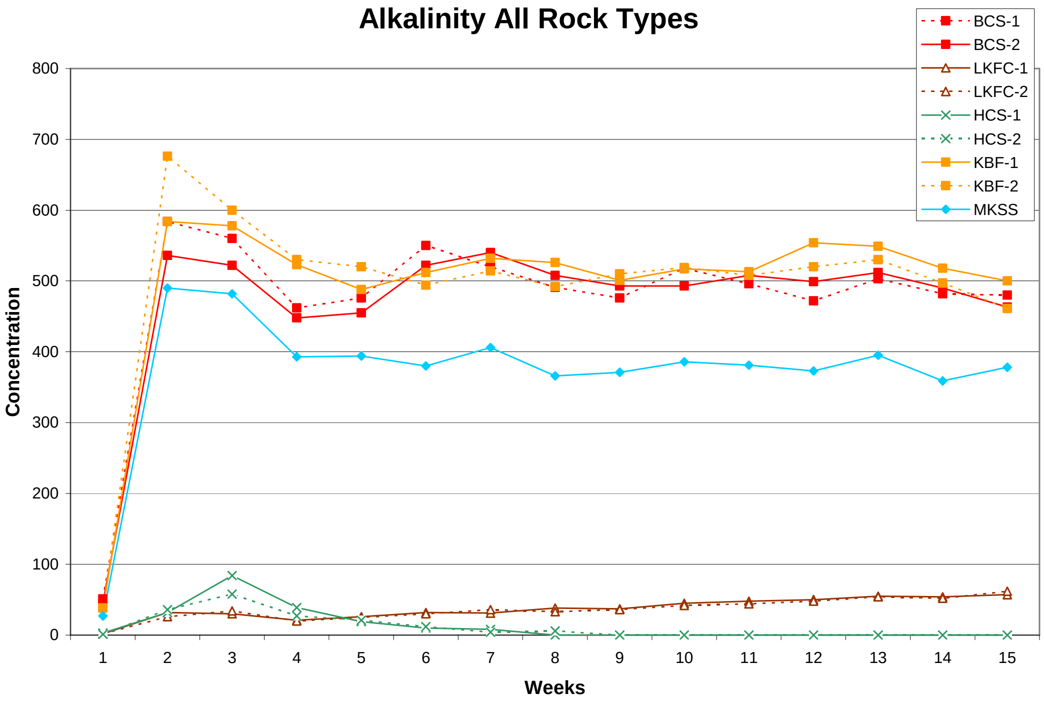


Figure 7.21. Differences in alkalinity concentrations (mg/L) of leachate from the five rock types.

Sulfur Leaching from Shales

Data Processing

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. Data for four of the laboratories, numbers 1, 3, 4, and 5 were used for the analysis. The data processing was as follows:

Sulfate concentrations, as given by the analytical laboratories were multiplied by the "water-out" (mL) to give sulfate concentration as the mass released each week.

The above number was divided by 3 to convert the sulfate mass to sulfur mass (the molecular weight ratio is 96/32) and the resultant masses converted to grams.

The rock weight in each column was multiplied by the percent sulfur as determined by chemical analysis of the rock.

The grams of sulfur in the leachate for each week was divided by the total grams of sulfur in the column to give a "weekly percent of total sulfur leached".

These weekly sulfur releases were summed to give a cumulative release of sulfur. These numbers are plotted in figures 7.22 to 7.25. These plots then formed the basin for further discussion and regression analysis.

Results and Interpretation

Plots of cumulative sulfur leaching from the four shale samples show that the data are best described by a power function of the form

$$C = A t^{n} \qquad (7.2)$$

In equation 7.2, C = cumulative concentration of leached sulfur expressed as a percentage of the sulfur loading in the original rock, A = coefficient determined by curve fitting, t = time in units of weeks, and n = the exponent of the power function to be determined by curve fitting.

The fitting parameters for the four shale samples are listed in Table 7.4. The regression coefficient, r^2, is a measure of the goodness of fit and is generally excellent for the four laboratories and four samples. The leaching curves for the four laboratories for any given sample have similar shapes but do not completely overlap. The fit with the calculated regression curves, as shown on the figures, is also very good.

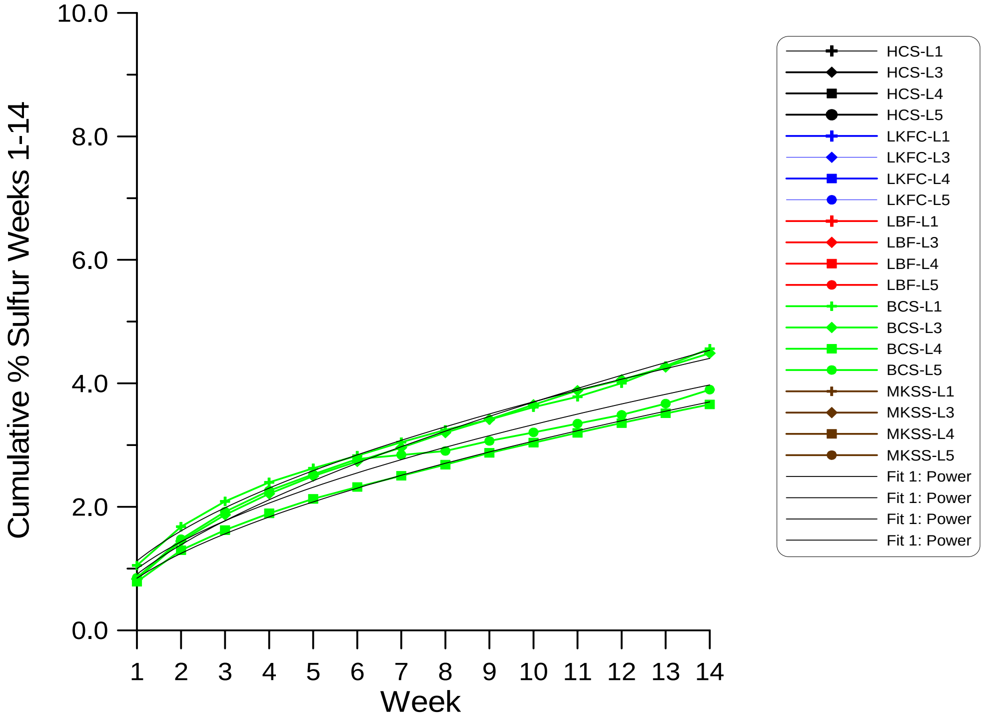


Figure 7.22. Sulfur leaching from BCS3-PA, the Brush Creek Shale.

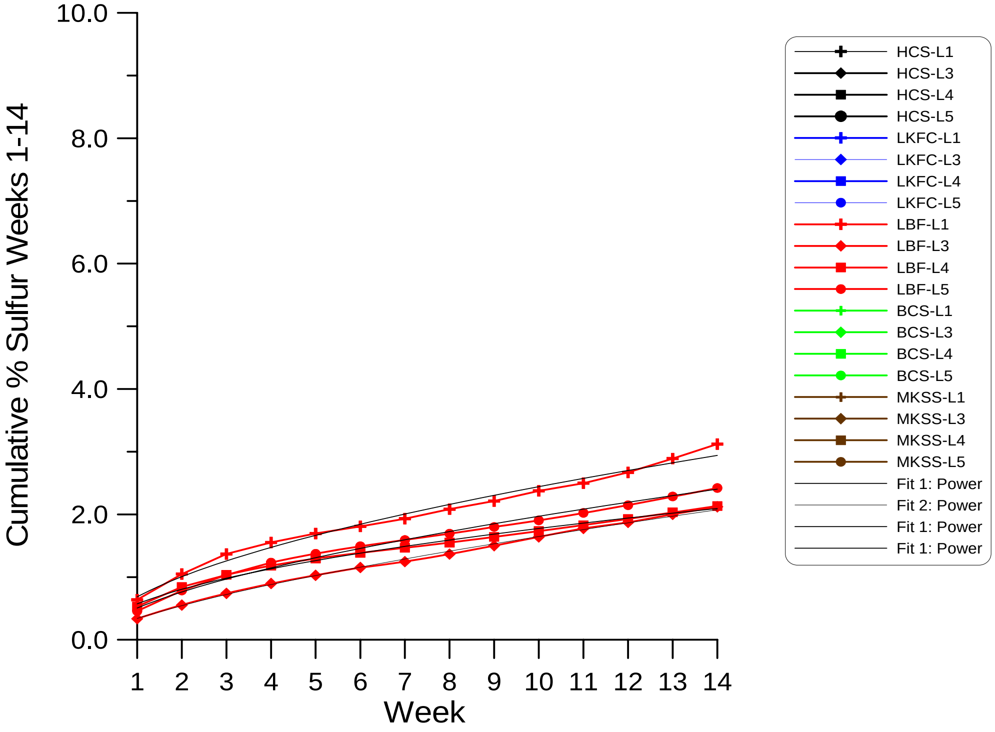


Figure 7.23 Sulfur leaching from KBF-WV, the Kanawha black flint shale.

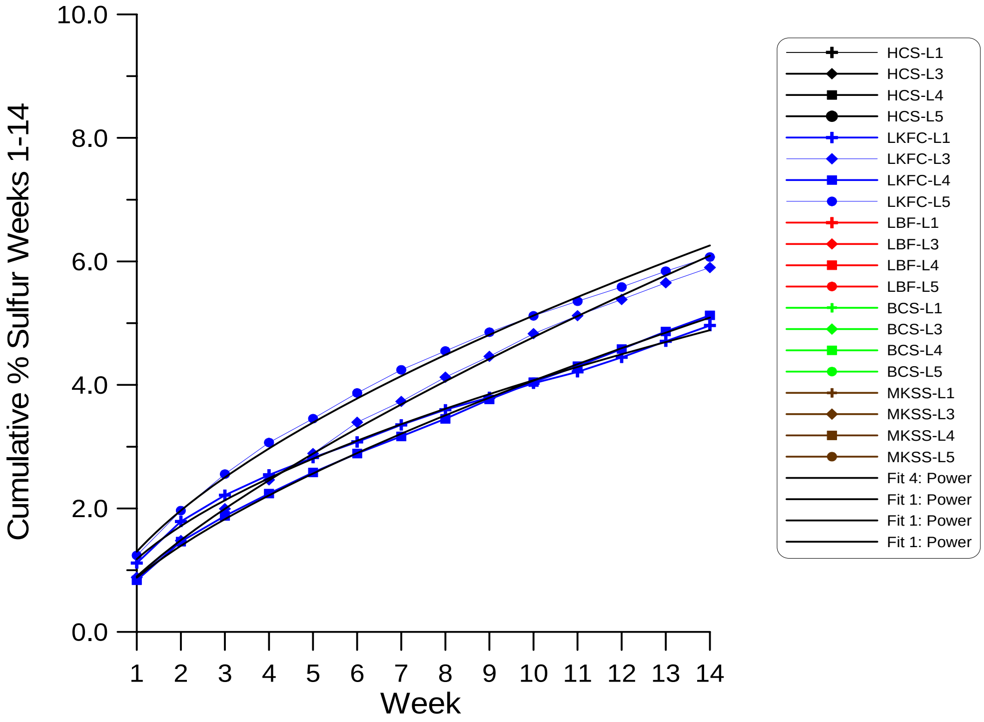


Figure 7.24. Sulfur leaching from LKFC-PA, the Lower Kittanning Shale.

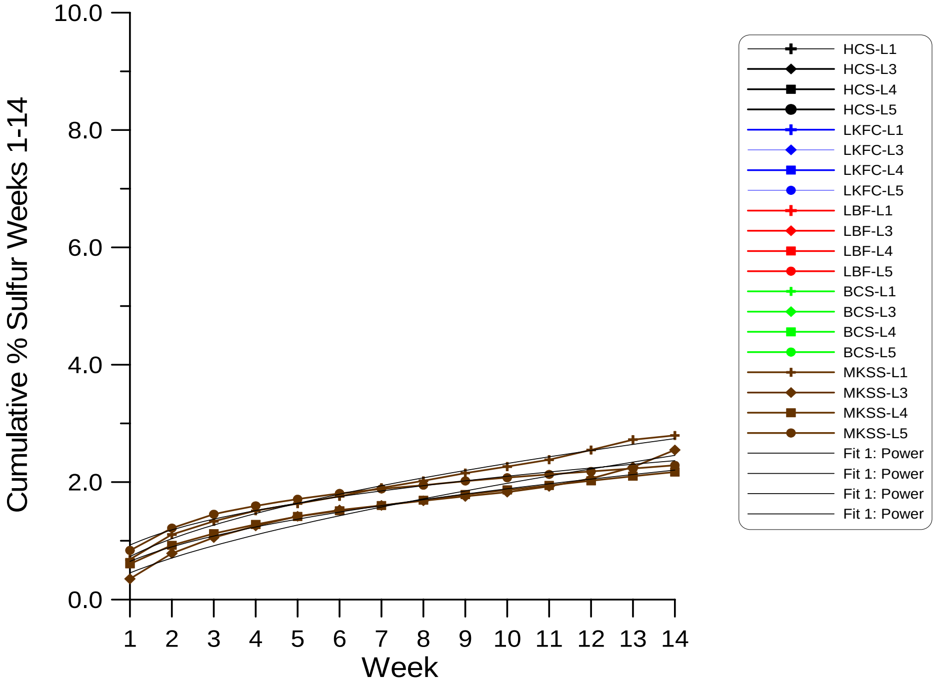


Figure 7.25. Sulfur leaching from MKSS-PA, the Middle Kittanning Sandstone.

Table 7.4 Fitting parameters for sulfur release shown in Figures 7.22 – 7.25.

Sample	A	n	R^2
BCS3-PA			
L1	1.124	0.517	0.993
L3	0.908	0.609	0.994
L4	0.845	0.559	0.995
L5	0.998	0.524	0.970
KBF-WV			
L1	0.686	0.551	0.988
L3	0.340	0.685	0.998
L4	0.573	0.491	0.991
L5	0.506	0.590	0.990
LKFC-PA			
L1	1.180	0.536	0.966
L3	0.899	0.725	0.999
L4	0.879	0.666	0.998
L5	1.301	0.595	0.997
MKSS-PA			
L1	0.732	0.500	0.992
L3	0.454	0.640	0.953
L4	0.651	0.462	0.994
L5	0.927	0.355	0.976

The exception to expected leaching pattern was HCS-IN, the Houchins Creek Shale (Fig. 7.26). Instead of leaching rates decreasing with increasing time, in this specimen, the leaching rates increased through the end of the 14-week experimental period. The HCS-IN leaching can be approximated with an exponential function with a positive coefficient.

The rapid increase in rate at the end of the experimental sequence was observed in the leaching of some other elements from the Houchins Creek Shale. The exponential form does not make theoretical sense, because it would imply a runaway process that turns on late in the experimental sequence. Clearly, these curves cannot be sustained and must eventually bend over as the sulfur in the shale is completely extracted.

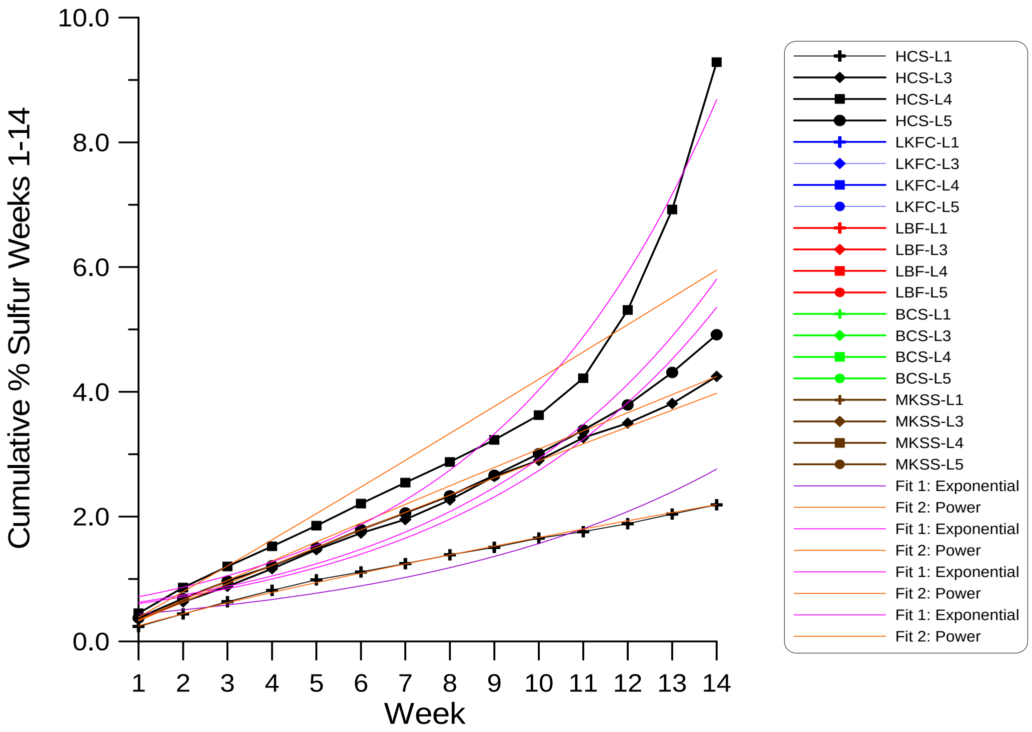


Figure 7.26. Sulfur leaching from HCS-IN, the Houchins Creek Shale. Both power law and exponential fitting curves are shown.

Carbonate Leaching

Determining Carbonate Dissolution Rates

There are two ways to calculate carbonate dissolution rates, the “cation” approach and the “anion” approach. The rate of reaction can be determined from the amount of material that is weathered each week as a portion (or percentage) of the total of that material that is in the rock. Neutralization potential was determined two ways, the traditional Sobek et al,. (1978) method and the modified Skousen et al., (1997) method that takes steps to reduce the effects of siderite interference. Hydrogen peroxide is added in order to oxidize and precipitate iron. Siderite ($FeCO_3$), a non-alkalinity generating carbonate can give falsely high NP readings if the water is not oxidized (Skousen et al., 1997; Rose and Cravotta, 1998). The Skousen method NP results are about half the Sobek method results (Table 7.5). This is consistent with the mineralogic analyses performed by Hammarstrom et al., (this volume, Table 5.4), where about half the carbonates in the Brush Creek shale are siderite. The Skousen method NP numbers were used to determine the average NP, and the calcium carbonate content, for the all rocks in this study.

Although NP does not in and of itself specify the forms of carbonate, with the improved NP method of Skousen et al., it is reasonable to assume that most of the NP is from alkaline earth carbonates. For simplicity and accuracy, results are expressed as calcium carbonate equivalent.

Table 7.5. Acid-Base Accounting data for the Brush Creek Shale.

NP Sobek	NP Skousen	%S
96.97	49.68	0.59
96.96	49.31	0.59
96.98	47.61	0.56
96.97	47.07	0.59
Ave 96.97	**Ave 48.42**	**Ave. 0.58**

The following steps illustrate how carbonate dissolution rates were determined.

Step 1. Determine the amount of calcium carbonate (equivalent) in the column.

Using the Average NP number (Table 7.5) and the known mass of sample in a column, the amount of calcium carbonate equivalent can be computed for the material in that column. For example, Lab 5's Brush Creek Shale, Column 1 contained 1879.2 grams of material. The units for NP are tons/1000 tons $CaCO_3$ equivalent. The amount of calcium carbonate equivalent contained in the column can be computed as follows:

$$1879.2 \text{ grams} \times (48.42/1000) = 91.0 \text{ grams } CaCO_3 \text{ equivalent.}$$

Thus, this column contains the carbonate equivalent of 91 grams $CaCO_3$. This number will be used later to determine weathering rate.

Step 2. Determine the amount of calcium carbonate weathered each week. This is done by determining the mass of the weathering products produced each week in the leachate. There are two ways this can be done, the "cation approach" and the "anion approach" discussed below.

Step 2a. *The "Cation" Approach*

The Cation Approach involves computations using the two cations that are commonly associated with acid-neutralizing carbonates, namely calcium and magnesium. These are evaluated in terms of calcium carbonate equivalent by summing Ca as $CaCO_3$ and Mg as $CaCO_3$. Three assumptions are made:

(1) all Ca and Mg in solution are derived from carbonate dissolution,
(2) Ca and Mg have not been lost from the solution and retained in the column, and
(3) gypsum is not present in the material being leached.

If gypsum is present, then there is calcite from a source that is not directly related to carbonate dissolution. Thus, the calcium carbonate dissolution rate can not be accurately determined, unless one determines the amount calcium from gypsum dissolving per week and subtracts this portion.

Assumption 1. 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. There is more discussion on this topic below.

Assumption 2. Gypsum and calcite are the most common calcium-bearing minerals that are likely to precipitate from solution. It is recommended that gysum and calcite solubility be calculated to determine whether the solutions are saturated or under- or over-saturated with these minerals. If gypsum or calcite are precipitating then some of the calcium that has dissolved will not be measured in the leachate, but in fact is being retained in the column.

Assumption 3. The presence of gypsum in a sample can be determined through hand sample observation, X-ray diffraction or other mineral determining techniques.

The mass of Ca and Mg leached each week is determined from the mg/L of Ca and Mg leach multiplied by the volume of leachate.

$$Analyte,\ mg = \left(\frac{mg}{L}\right) \times \left(Leachate\ Volume\ Out,\ L\right)$$

The examples used below are of actual leachate obtained from the same column during the same week. That is, all data are all from the same sample event.

Calculating $CaCO_3$ from Ca The mass of calcium carbonate (equivalent) can easily be determined from the mass of calcium. The atomic weight of Ca is 40, and the molecular weight of $CaCO_3$ is 100. Thus, $CaCO_3$ is 2.5 times the weight of Ca alone, and 40 grams of Ca converted to calcium carbonate equivalent is 100 grams of $CaCO_3$. For example, a sample leaches 176 mg/L Ca and the volume drained from the column is 279 mL.

$$\left(176.0\frac{mg}{L}\right) \times \left(0.279\ L\right) = 49.1\ mg\ Ca$$

and

$$49.1\ mg\ Ca \times 2.5 = 122.8\ mg\ as\ CaCO_3$$

Therefore, during this sample event 122.8 mg of $CaCO_3$ equivalent weathered from the rock.

Calculating $CaCO_3$ from Mg The conversion of Mg to $CaCO_3$ is the same process as that for calcium. The atomic weight of Mg is 24.3. Dividing the molecular weight of $CaCO_3$ of 100 by 24.3 gives a conversion factor of 4.1.

$$\left(83.1\,\frac{mg}{L}\right)\times\left(0.279\ L\right)=23.2\ mg\ Mg$$

and

$$23.2\ mg\ Mg\times 4.1=95.0\ mg\ as\ CaCO_3$$

Calculating $CaCO_3$ equivalent from Ca + Mg The next step is to simply sum the calcium carbonate equivalents calculated above:

$$122.8\ mg\ Ca+95.0\ mg\ Mg=217.8\ mg\ as\ CaCO_3$$

Therefore, during the course of the previous week, 217.8 mg of carbonates, measured as $CaCO_3$ equivalent, were dissolved.

Step 2b. *The "Anion" Approach*

The Anion Approach involves determining excess alkalinity and neutralized alkalinity produced by evaluating two anions that are commonly associated with neutralized mine drainage, bicarbonate and sulfate. The sulfate part of the equation is not necessarily intuitive and requires some explanation. This approach only works where the water is alkaline. It will not work for acidic samples. Again, assumptions are made: (1) sulfate has not been lost from the solution and retained in the column, and (2) gypsum is not contributing to the sulfate load.

Assumption 1. The most common sulfate-bearing mineral that is likely to precipitate from solution is gypsum. If gypsum is precipitating then some of the sulfate that has dissolved will not be measured in the leachate, but in fact is being retained in the column.

Assumption 2. The presence of gypsum can be determined through hand sample observation or X-ray diffraction or other mineral determining techniques.

Bicarbonate alkalinity. Bicarbonate alkalinity is generally reported as $CaCO_3$ equivalent, so no conversion is necessary. If it is not reported as $CaCO_3$ equivalent, HCO_3 can be converted to $CaCO_3$ using the following equation:

$$\text{mg/L } HCO_3 \times 0.8202 = \text{mg/L } CaCO_3$$

Determining milligrams of $CaCO_3$ is performed using the same process as that for calcium and magnesium discussed above, except no conversion is typically necessary to obtain calcium carbonate equivalent. Using the same sample event as the examples above, the concentration of alkalinity as $CaCO_3$ was 520 mg/L.

$$\left(520\,\frac{mg}{L}\right)\times\left(0.279\ L\right)=145.1\ mg\ CaCO_3$$

Thus, the alkalinity times the volume of leachate represents 145.1 mg of dissolved $CaCO_3$.

Alkalinity Neutralized The alkalinity measured in a mine water is the "excess" alkalinity that has been produced. For samples with pyrite oxidation occurring (indicated by elevated sulfate), some alkalinity has been neutralized by the acid. The amount of acidity that has been produced can be calculated based on the following stoichiometry:

$$FeS_2 + 3.25\ O_2 + 3.5\ H_2O = Fe(OH)_3 + 2\ SO_4^{2-} + 4\ H^+$$

For every mole of pyrite oxidized there are 2 moles of sulfate produced and 4 moles of H^+. It takes 2 moles of $CaCO_3$ to neutralize 4 H^+. This relationship can be written as:

$$\frac{4 \text{ mol } H^+}{2 \text{ mol } SO_4^{2-}} = \frac{2 \text{ mol } CaCO_3}{2 \text{ mol } SO_4^{2-}} = \frac{200 \text{ g } CaCO_3}{192 \text{ g } SO_4^{2-}}$$

Therefore, for every 1 mg/L (or gram) of sulfate, 1.04 mg/L (or gram) of acidity, as $CaCO_3$, are produced.

Therefore, if a sample is net alkaline, the neutralized alkalinity can be calculated from sulfate, by using the following equation:

$$\text{mg/L } SO_4 \times 1.04 = \text{mg/L } CaCO_3$$

Using a sulfate value of 298 mg/L, we get:

$$\left(298\,\frac{mg}{L}\times 1.04\right)\times(0.279\ L) = 86.5\ mg\ neutralized\ alkalinity\ as\ CaCO_3$$

<u>*Calculating $CaCO_3$ from Alkalinity + Sulfate*</u> The next step is to simply sum the calcium carbonate equivalents calculated above:

$$141.1\ mg\ Alkalinity\ CaCO_3 + 86.5\ mg\ neutralized\ alkalinity = 227.6\ mg\ as\ CaCO_3$$

Therefore, during the course of the previous week, 227.6 mg of carbonates, measured as $CaCO_3$ equivalent, were dissolved. We had calculated earlier that there is a total of 91.0 grams of $CaCO_3$ equivalent in the column. Thus, during this one week

$$\left(\frac{0.2276\ g}{91.0\ g}\right)\times 100 = 0.25\%\ CaCO_3\ weathered$$

That is, one-quarter of one percent of the total $CaCO_3$ dissolved during that week.

Step 2 c. Compare the anion derived numbers to the cation derived numbers.

Cumulative Weathering Rates

The above calculations were performed for each week, for each column and for each laboratory. The only reasonable way to do the multiple calculations was to use a spreadsheet. The types of calculations presented in spreadsheet format are displayed in Table 7.6. The percentage weathered each week can be added cumulatively to determine the amount of carbonate (or sulfur) weathered through the duration of the test. This also allows for the evaluation of whether or not the rate of weathering changes throughout the course of the test. Figures 7.27 through 7.32 show cumulative weathering plots for calcium carbonate weathering rates calculated using the cation and anion approaches. The carbonate weathering results for the Brush Creek Shale and the Lower Kittanning FC shale are illustrated below.

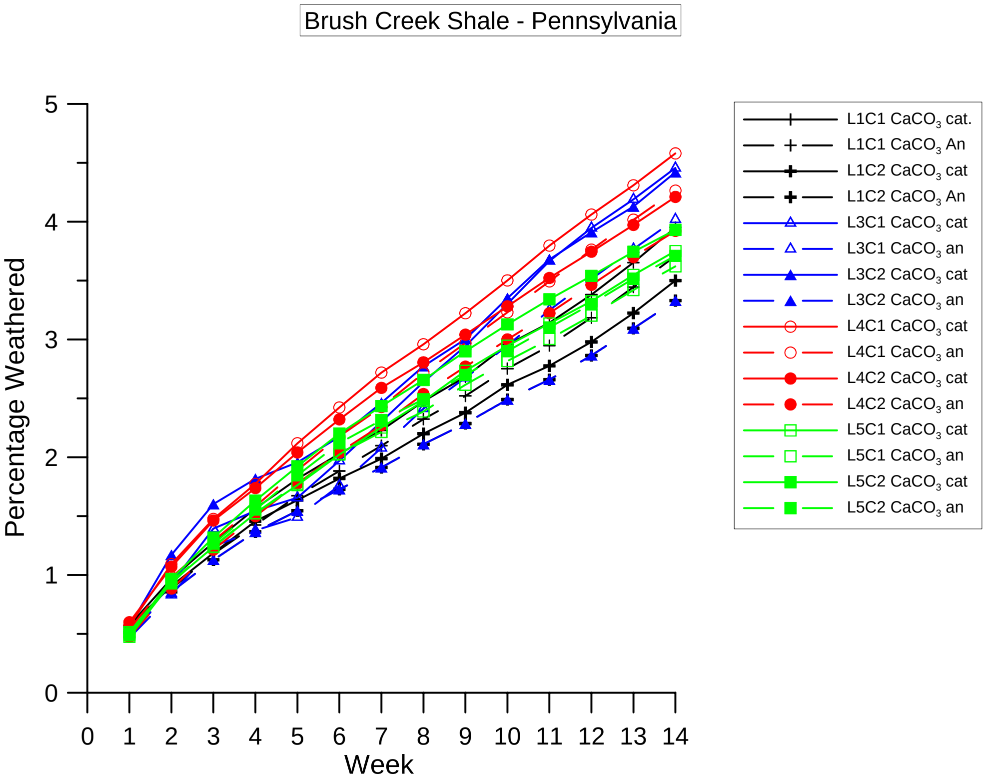


Figure 7.27. Cumulative carbonate dissolution rate determined using cations and anions for the Brush Creek Shale. Data are for laboratories 1, 3, 4 and 5.

Table 7.6. Example table of the computational steps to determine CaCO3 weathering rate. Column 1 identifies the week that was leached. Week “0” is the initial flush. Weeks 1 through 14 are the actual weeks that the sample is weathered. Column 2 is the leachate volume collected. Column 3 is mg/L calcium. Column 4 is the mg calcium computed from columns 2 and 3. Column 5 is the mg calcium displayed cumulatively. Column 6 is calcium displayed as calcium carbonate. Columns 7 through 10 are the same as those described above, but for manganese. Column 11 is the sum of columns 6 and 10. Column 12 is column 11 divided by the total mass of calcium carbonate equivalent in the column, expressed in percent.

1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**
Week	VolOut mL	mg/L Ca	mg Ca	cumulative mg Ca	cumulative mg Ca as CaCO3	mg/L Mg	mg Mg	cumulative mg Mg	Cumulative mg Mg as CaCO3	Cumulative Ca + Mg as CaCO3	% CaCO3 weathered each week from 91.0 g
0	1356	99.8	135.33	135.33	338.32	57.1	91.83	91.8	377.90	716.22	0.79
1	310	270.0	83.70	219.03	547.57	148.0	54.41	146.24	601.82	1149.39	1.26
2	340	240.0	81.60	300.63	751.57	131.0	52.82	199.07	819.20	1570.77	1.73
3	295	186.0	54.87	355.50	888.75	93.3	32.64	231.71	953.53	1842.28	2.02
4	309	175.0	54.08	409.57	1023.93	82.7	30.31	262.02	1078.25	2102.19	2.31
5	270	170.0	45.90	455.47	1138.68	78.8	25.23	287.25	1182.09	2320.78	2.55
6	279	176.0	49.10	504.58	1261.44	83.7	27.70	314.95	1296.07	2557.51	2.81
7	296	147.0	43.51	548.09	1370.22	68.7	24.12	339.06	1395.32	2765.54	3.04
8	285	153.0	43.61	591.69	1479.24	68.4	23.12	362.18	1490.46	2969.70	3.26
9	285	163.0	46.46	638.15	1595.37	84.3	28.49	390.68	1607.72	3203.09	3.52
10	268	156.0	41.81	679.96	1699.89	68.6	21.80	412.48	1697.45	3397.34	3.73
11	260	142.0	36.92	716.88	1792.19	62.7	19.33	431.82	1777.01	3569.21	3.92
12	260	148.0	38.48	755.36	1888.39	59.8	18.44	450.26	1852.90	3741.29	4.11
13	274	162.0	44.39	799.75	1999.36	68.7	22.33	472.58	1944.77	3944.13	4.33
14	264	151.0	39.86	839.61	2099.02	66.4	20.79	493.37	2030.32	4129.35	4.54

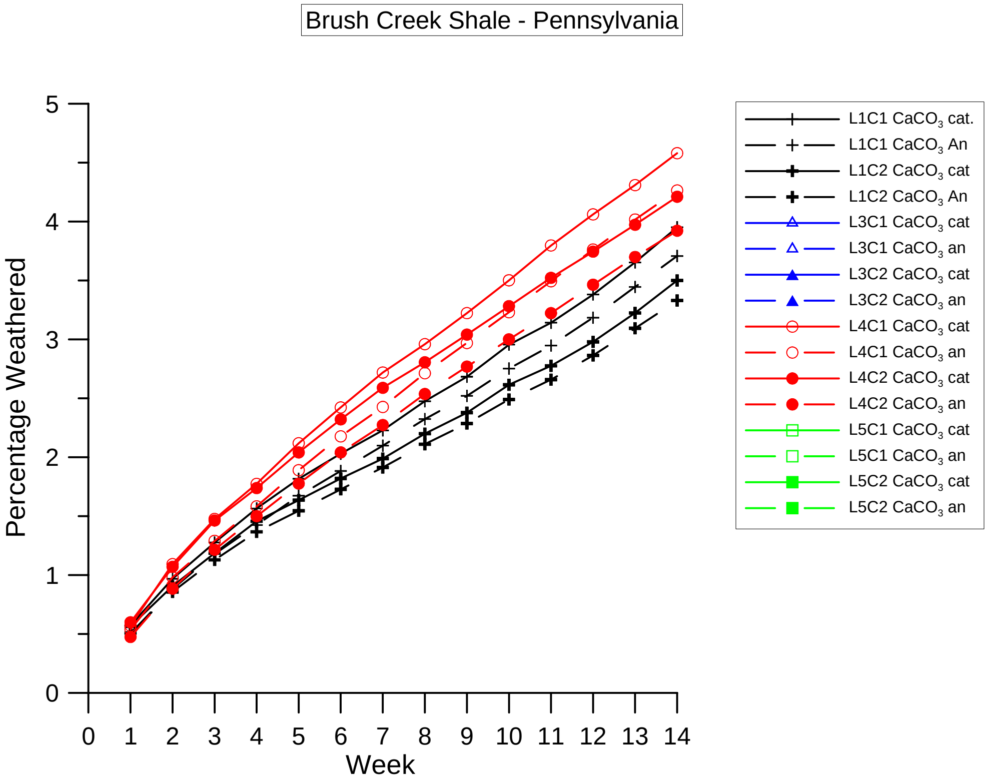


Figure 7.28. Same data as in Figure 7.27, but showing only Labs 1 and 4.

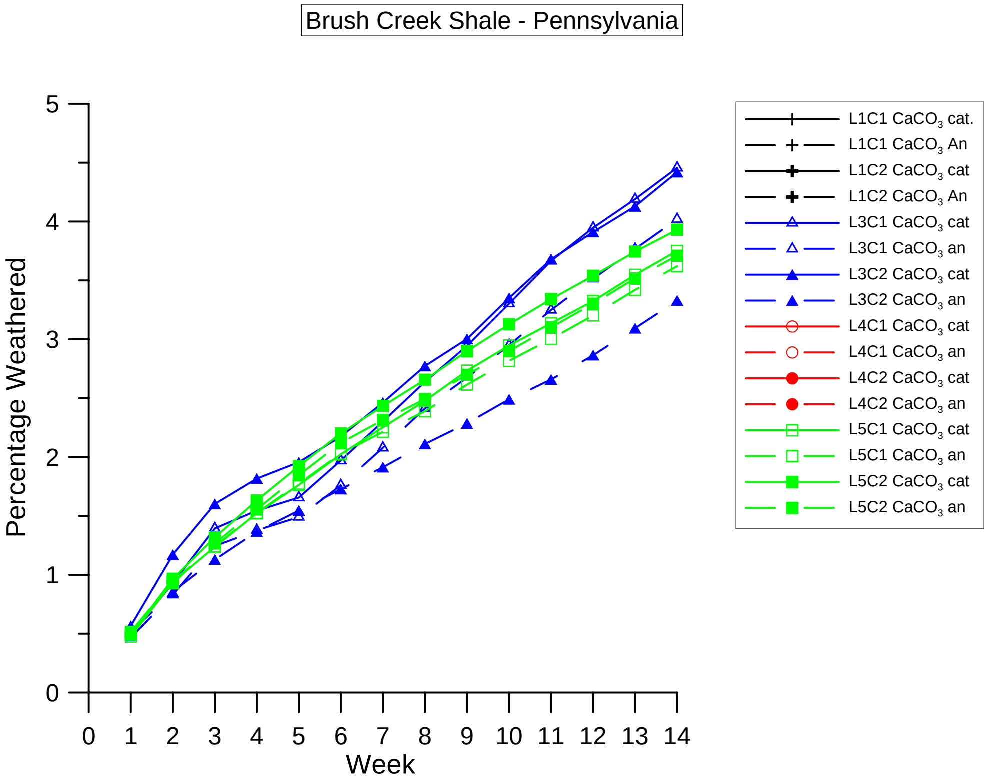


Figure 7.29. Same data as in Figure 7.27, but showing only Labs 3 and 5.

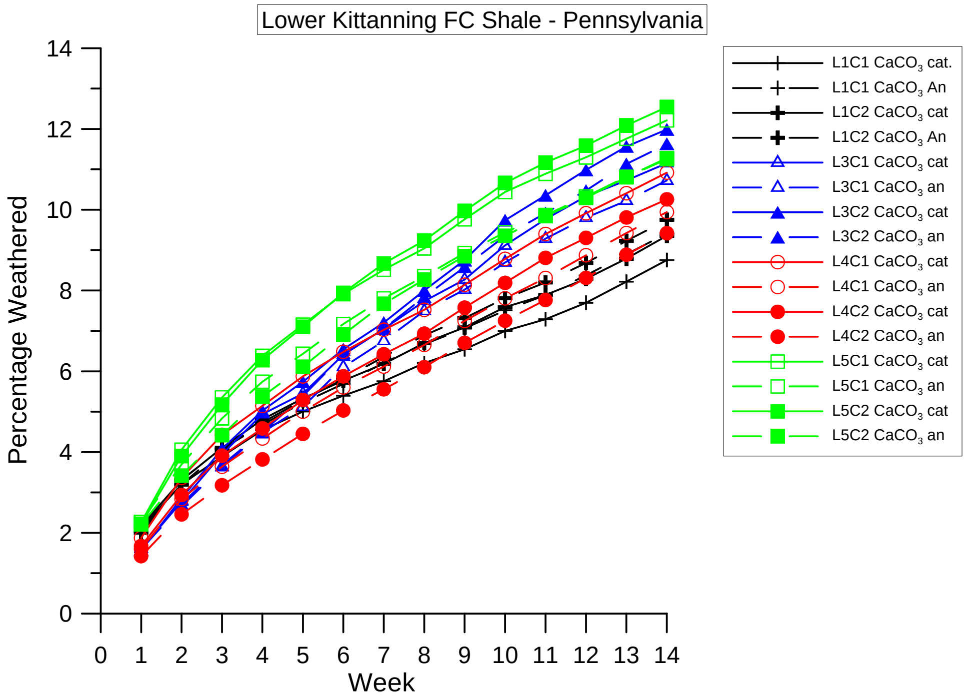


Figure 7.30. Cumulative carbonate dissolution rate determined using cations and anions for the Lower Kittanning FC Shale. Data are for laboratories 1, 3, 4 and 5.

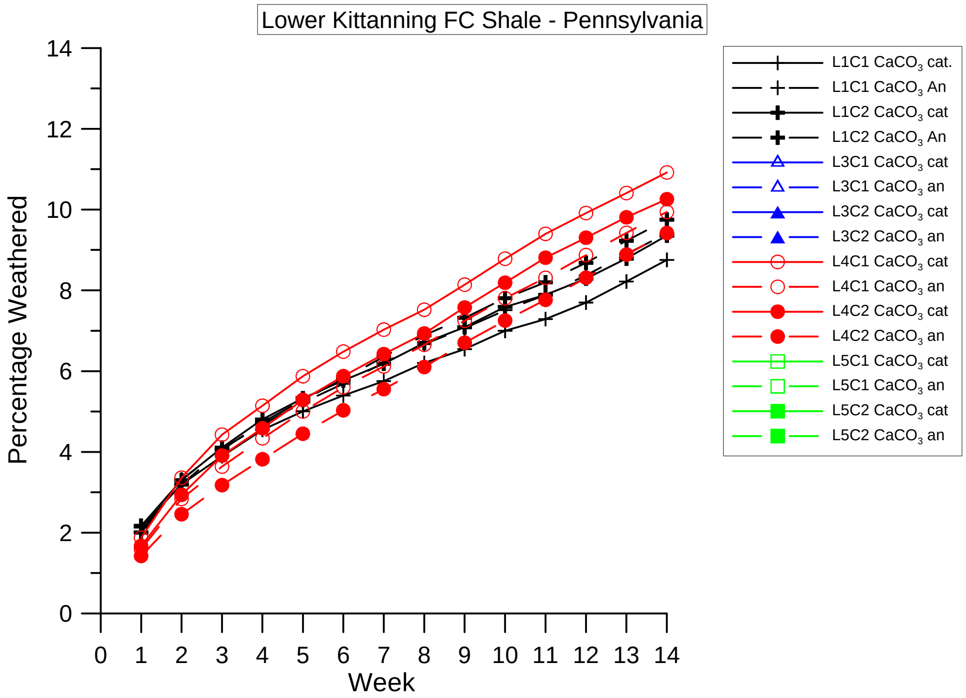


Figure 7.31. Same data as in Figure 7.30, but showing only Labs 1 and 4.

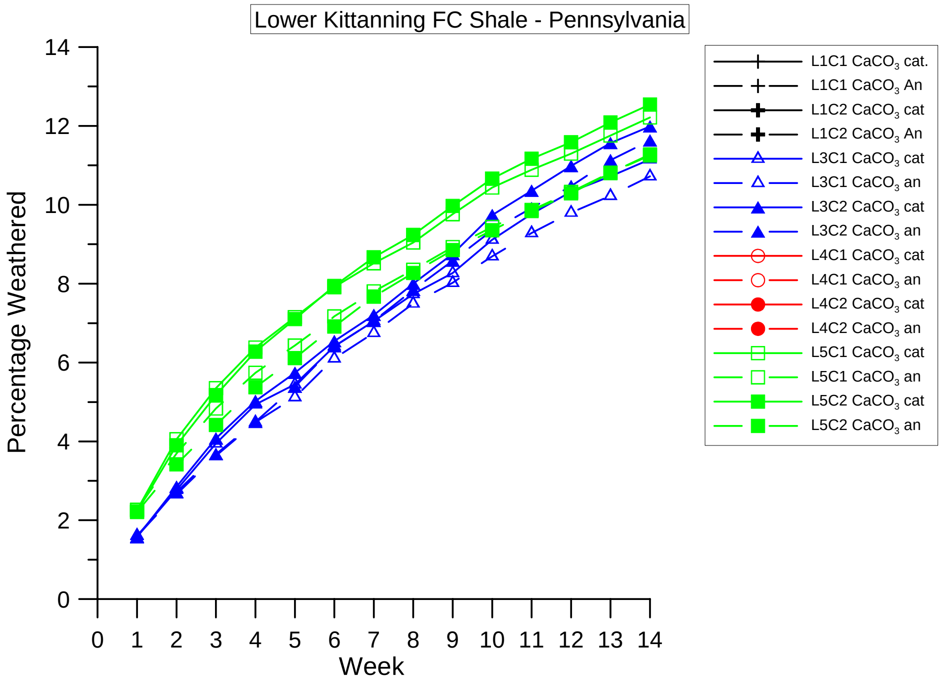


Figure 7.32. Same data as in Figure 7.30, but showing only Labs 3 and 5.

Figures 7.27 through 7.32 show that the weathering rates determined by the cation and anion approaches result in very similar values. This close relationship is also evident in Figure 7.34. The similar results of the cation and anion approaches instill confidence that the numbers from both approaches are accurate. There is generally a slightly larger percentage weathered for the cation computation. This may be due to Mg (in particular) being present in rocks other than carbonates.

Hammarstrom (Chapter 5) identified the mineralogy of the rocks used in the leaching study. Table 7.7 identifies calcium and magnesium minerals that can contribute these cations to solution. Quite a number of Mg-bearing minerals are present in these rocks. Although present, their contribution, compared to carbonate minerals, is likely minor. Figure 7.33 shows relative dissolution rates for a variety of minerals. As can be seen, most minerals are orders of magnitude less reactive than carbonates, especially under neutral pH conditions. Although chlorite is not shown on the graph, its dissolution rate is also orders of magnitude less than calcite, and in fact less than that of biotite (Freyssinet and Farah, 2000).

Table 7.8 shows the percentages of calcium, magnesium, CO_2, calcite, ankerite and chlorite. Chlorite is included because it was fairly abundant in all rock types studied and could contribute magnesium to the solutions. (Data from Hammarstrom, Chapter 5)

Table 7.7. Calcium- and magnesium-bearing minerals in rocks used for the leaching study. Formulas are simple basic formulas. Minerals are those identified by Hammarstom (Chapter 5).

Mineral	Composition	Comments
Ankerite	$Ca(Mg,Fe)(CO3)_2$	Present in all samples
Anorthite	$CaAl_2Si_2O_8$	<1% in all samples except MKSS
Apatite	$Ca_5(F,Cl,OH)(PO_4)_3$	Less than 2% except in HCS-IN (>3%)
Biotite	$K(Mg,Fe)_3(AlSi_3O_{10})(OH)_2$	Only identified in KBF-WV & <1%
Calcite	$CaCO_3$	Present in all samples
Chlorite	$Mg_3(Si_4O_{10})(OH)_2$-$Mg_3(OH)_6$	Present in all samples (see Table 7.6)
Phengite	$K(AlMg)_2(OH)_2(SiAl)_4O_{10}$	Present in all samples

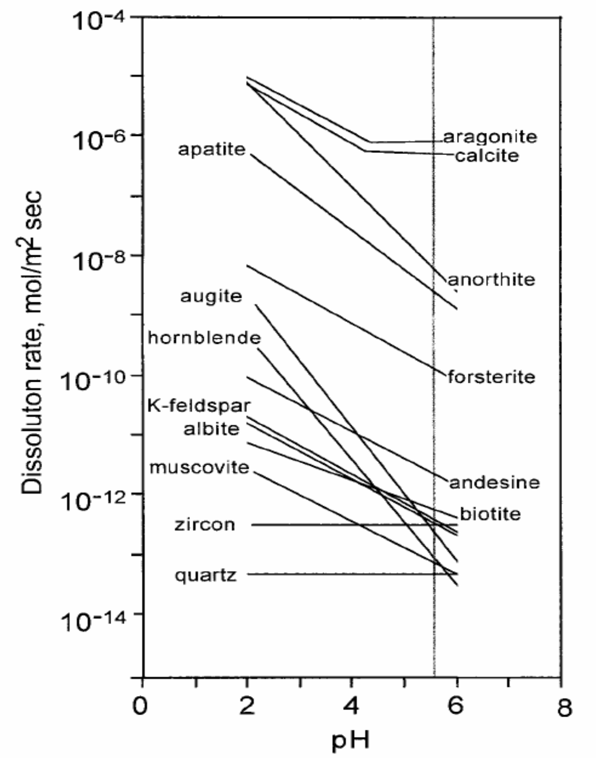


Figure 7.33. Relative dissolution rates of minerals. From Kowalewski & Rimstidt (2003).

Table 7.8. Elements and minerals relevant to Ca and Mg concentrations.

Rock Type	%Ca	%Mg	%CO2	%Calcite	%Ankerite	%Chlorite
HCS-IN	2.25	1.61	1.06	0.60	2.40	4.60
LKFC-PA	0.87	1.88	3.13	0.35	0.70	9.45
KBF-WV	1.03	1.81	1.94	0.65	1.15	7.55
MKSS-PA	1.81	0.89	1.93	3.45	1.55	5.15
BCS-PA	2.25	2.41	2.03	2.45	1.20	11.15
BCS-PA2				2.13	1.10	10.10
BCS Weighted Ave.				2.26	1.14	10.52

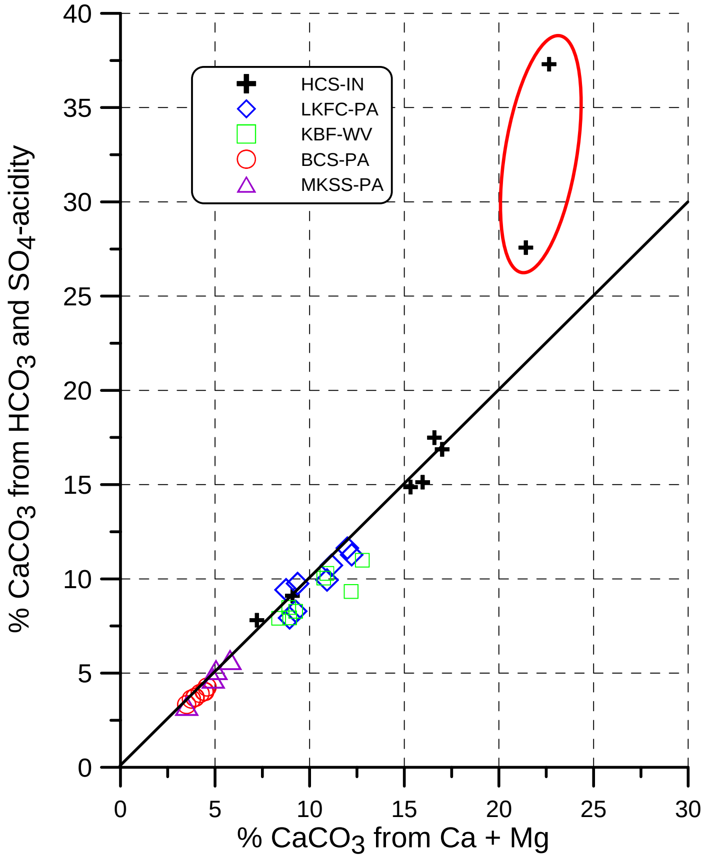


Figure 7.34. Comparison of the "anion" and "cation" methods of determining carbonate dissolution. The cumulative value at the end of 14 weeks leaching was used to construct this plot. As can be seen, most data fall on or near the diagonal line, which represents where data would fall if both methods produce the same answer. The circled values indicate columns that became acidic.

<u>The Race to the Finish</u>

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 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 sulfur in the rock is determined during acid-base accounting. The examples below are analyses of the Brush Creek Shale and are for the same leaching event used above for the carbonates. The average sulfur shown in Table 7.5 was used for these calculations.

Step 1. Determine the amount of sulfur in the column from the average of the samples analyzed.

Using the average percent sulfur value (Table 7.5) and the known mass of sample in a column, the amount of calcium carbonate equivalent can be computed for the material in that column. That is, what is being computed is the amount of calcium carbonate that would be needed to neutralize the acid generated from the oxidation of the pyrite in this rock. For example, Lab 5's Column 1 contained 1879.2 grams of material. The amount of sulfur contained in the column can be computed as follows:

$$1879.2 \text{ grams} \times (.0058) = 10.9 \text{ grams Sulfur.}$$

For the purposes of this study we used total sulfur values. This approach probably slightly overestimates the amount of pyrite present, but likely less than 10% (Brady and Smith, 1988). Forms of sulfur determinations are not used because of the plethora of analytical and other problems associated with determinations of forms of sulfur in coal overburden samples (Brady and Smith, 1988). Pyrite is 53.45% sulfur, so if one wanted to determine the amount of pyrite in a rock the percent sulfur can be multiplied by 1.873:

$$0.58\% \text{ S} \times 1.873 = 1.09\% \text{ pyrite}$$

Step 2. Determine the sulfur oxidation rate.

Sulfur has an atomic weight of 32. Sulfate (SO_4) has an ionic weight of 96 (32 + (16 x 4) = 96). Thus, sulfur comprises one-third the weight of sulfate. To calculate the amount of sulfur leached each week use the following equation:

$$\frac{298\ mg/L\ SO_4}{3} \times 0.279\ L = 27.7\ mg\ S\ weathered$$

The percentage of the available sulfur that was weathered during this time period can be determined using the following equation:

$$\left(\frac{0.0277\ g}{10.9\ g}\right) \times 100 = .25\%\ S\ weathered$$

The percent sulfur that has weathered can be compared to the percent carbonate that has weathered. Figures 7.35 and 7.36 show comparisons of these two types of data for the LKFC-PA and the BCS-PA shales. The LKFC-PA (Figure 7.35) has distinctly different rates of weathering for carbonates compared to sulfides, with the carbonates weathering faster than the sulfides. The weathering rates of the two mineral groups are similar for the BCS-PA (Figure 7.36).

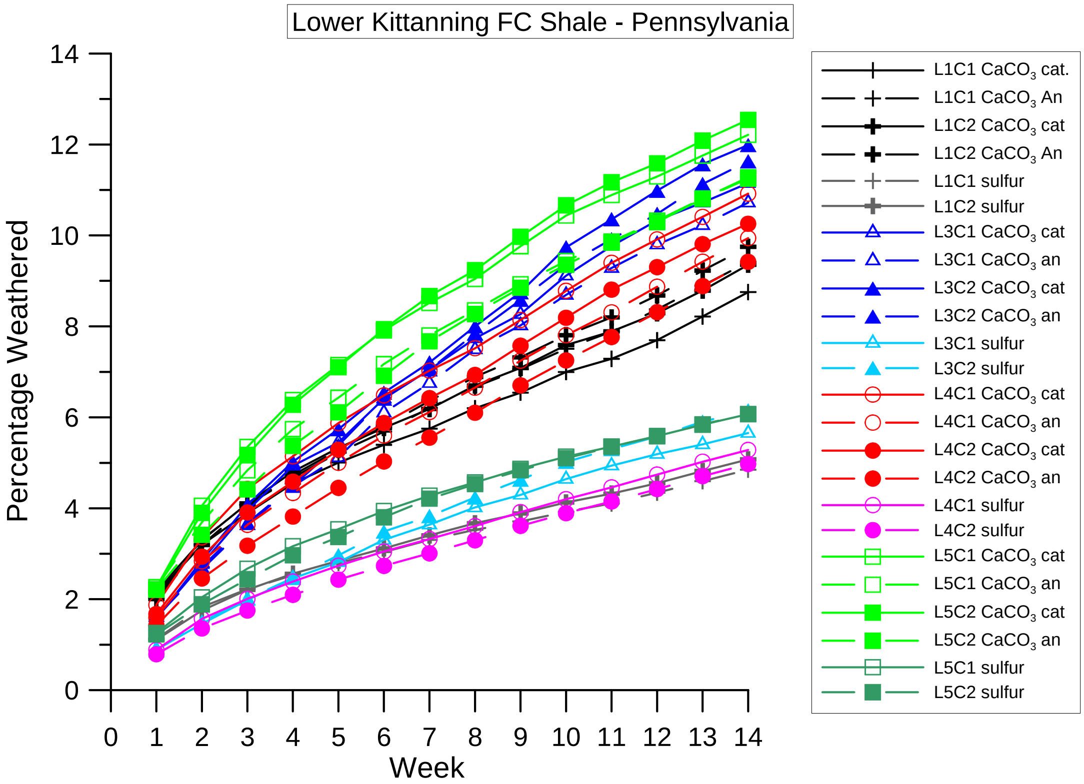


Figure 7.35. Weathering rates through time for carbonates and sulfur for the LKFC shale. The weathering rates for the two mineral groups form two distinct groups, with the sulfur weathering at a slower rate than the carbonate minerals.

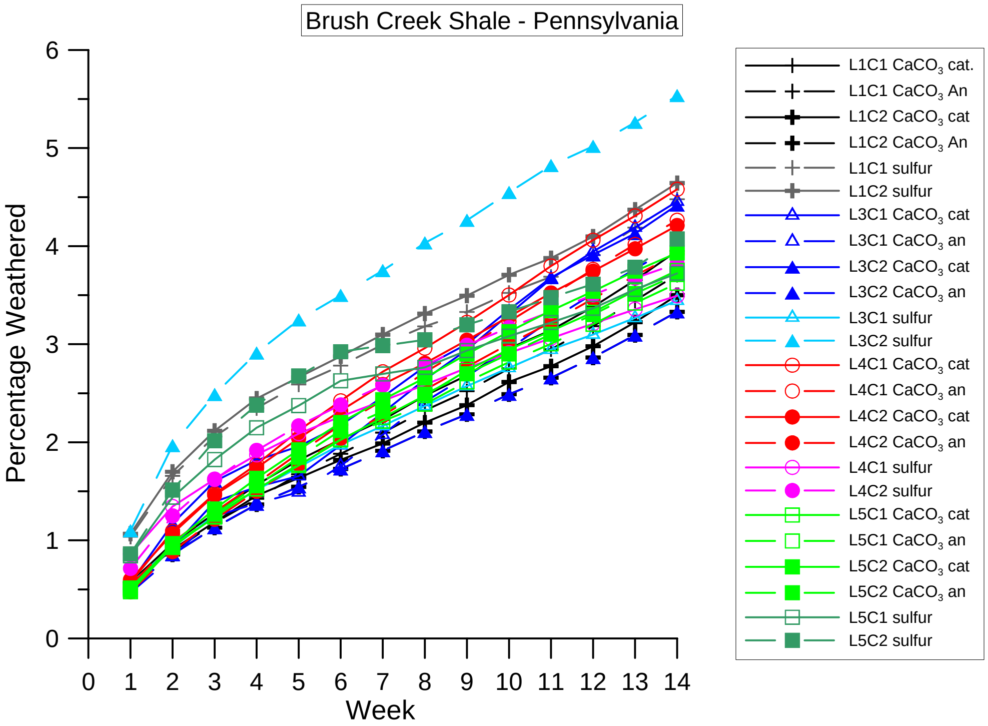


Figure 7.36. Weathering rates through time for carbonates and sulfur for theBCS shale. The weathering rates for the two mineral groups overlap, with the sulfur weathering at more or less the same rate as the carbonate minerals.

Figure 7.37 shows the cumulative percent sulfur and carbonates weathered at the end of 14 weeks of leaching for the five rocks examined in this study. The plot represents data from four labs, and the duplicate columns. Other than the Brush Creek Shale all the samples at the end of 14 weeks had weathered more calcite than pyrite. The Brush Creek seems to have carbonate and pyrite weathering at about the same rate.

The diagonal black line on Figure 7.37 is drawn where carbonate weathering equals pyrite weathering. Even though there were weathering rate differences among the labs, the sample results for a given rock type cluster together. That is, the differences among labs are less than the differences between rock types. The one sample that displays extreme scatter is the LKFC-PA shale, which in some labs remained alkaline, while in others, by the end of the test, the water was acidic. Thus there were big differences in the rate of weathering among the labs for this sample. Figure 7.37 illustrates that the laboratories produced very similar results with similar predictions for a given rock type.

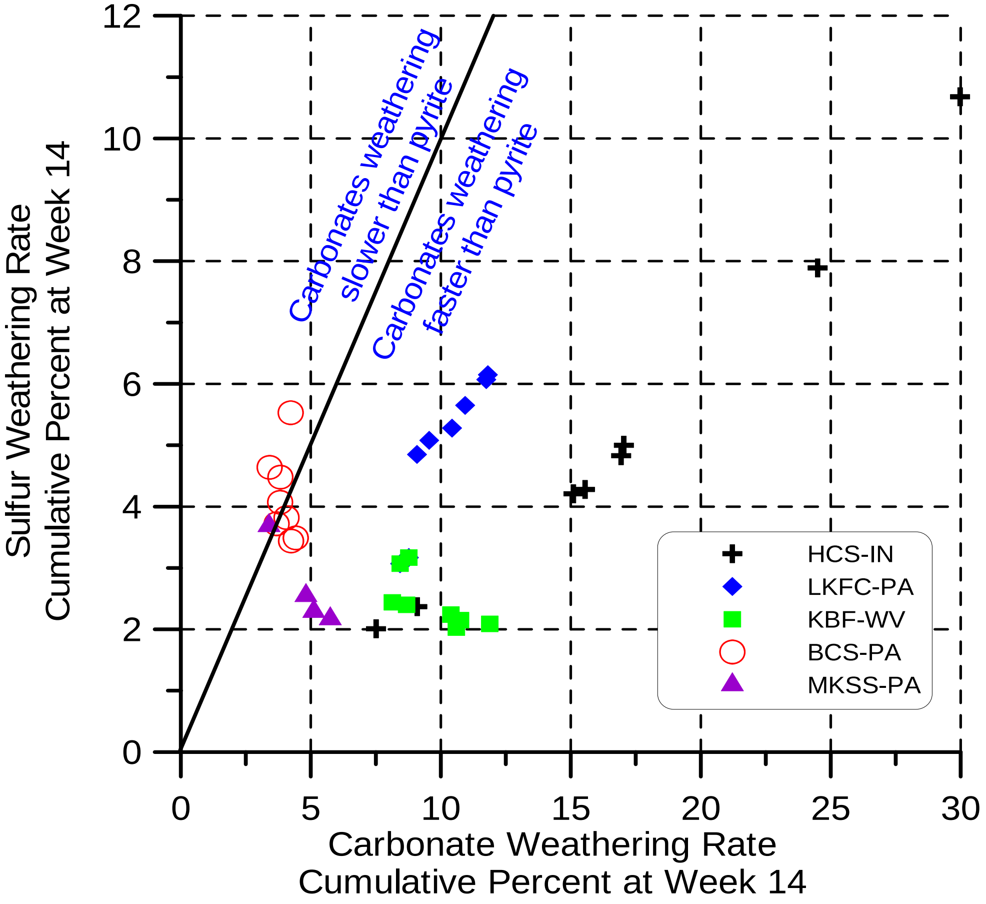


Figure 7.37. Comparison of weathering rates for pyrite and carbonates for five rock types by four laboratories. Most rock types are represented by eight points (two columns each lab), the exception being the MKSS-PA, where there was a single column in each lab.

Leaching of Minor Elements

Data Analysis

The overall objective of this study was to determine inter-laboratory reproducibility of the leach data. As indicated earlier in this report, the inter-laboratory variability was considerable. Rather than attempt to interpret the laboratory results individually or weight one laboratory against another, the seven laboratories' results were averaged over the seven data sets for each species of interest and each rock type. Tables of means were constructed for each species and each sample. A second set of tables was then constructed for the accumulated extraction of the given species from the given sample. Both tables were then plotted against time. The plots of accumulated release give the best indication of the overall kinetics of the column leaching experiments. The tables of accumulated release were than fitted to a power function by regression analysis and the fitting parameters of equation 7.2 were extracted. The first flush is included at time = zero in the data plots. For this reason, most of the plots do not go through zero at time = zero. The time = zero point was excluded from the regressions but the accumulative concentrations include material released on the first flush.

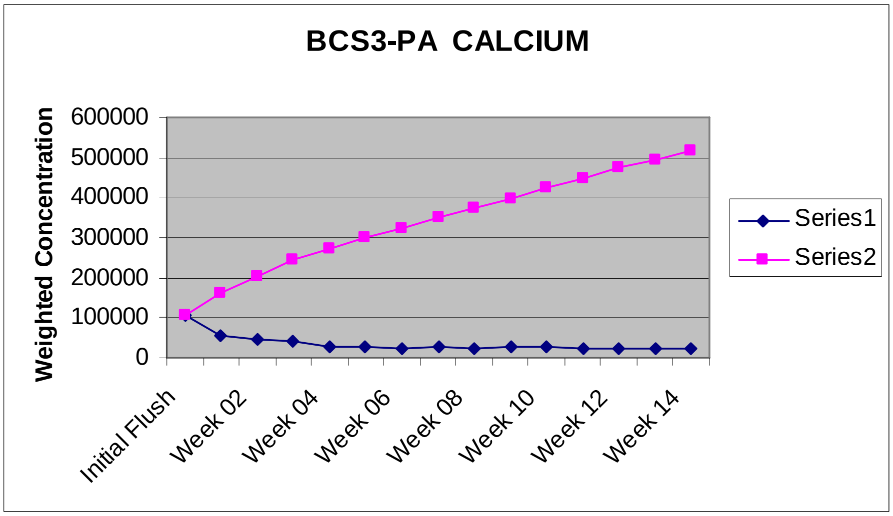
The experimental columns were loaded with a known mass of rock sample and filled with a known volume of water. These numbers varied somewhat from experiment to experiment and were determined by direct measurement for each experiment. Two data sets were then available – the raw concentrations as reported by the analytical laboratory and a weighted concentration that takes account of the specific weight of sample and volume of solution for each experiment. Numerically, the weighted concentrations would be

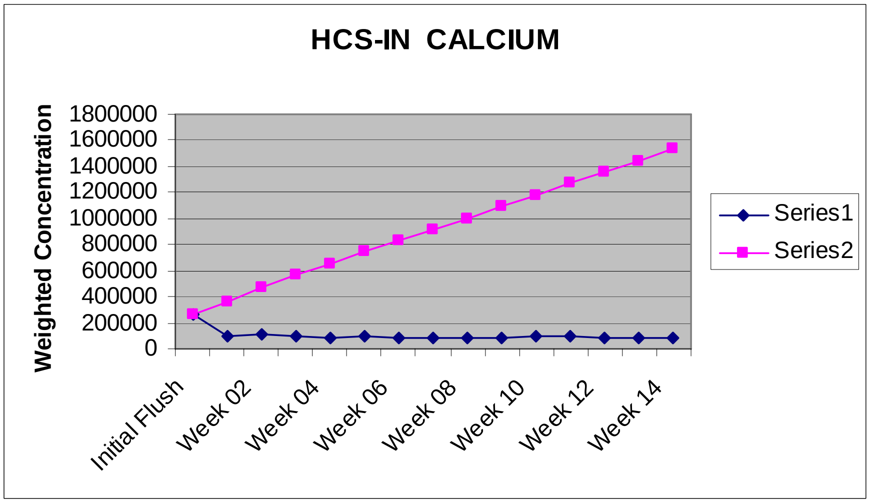
$$Weighted\ Concentration \quad = \quad \frac{Concentration\ (\mu g\,/\,L)\ x\ Volume\ (mL)}{Sample\ Mass\ (g)}$$

Combining units, the weighted concentration has units of µg/kg of solid.

Major Cations: Calcium, Magnesium, and Potassium

Individual plots showing the cumulative leaching of the three major cations from each rock type are given in Figure 7.38. Averaging the results from all of the laboratories has the effect of smoothing the data. The cumulative leaching curves are all rather similar. There is a slight flattening with increasing time but no indication that the sources of these elements are reaching depletion at the end of the 14-week experiment.


BCS3-PA CALCIUM
Weighted Concentration
600000
500000
400000
300000
200000
100000
0
Initial Flush
Week 02
Week 04
Week 06
Week 08
Week 10
Week 12
Week 14
Series1
Series2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Weighted Concentration
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1400000
1200000
1000000
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0
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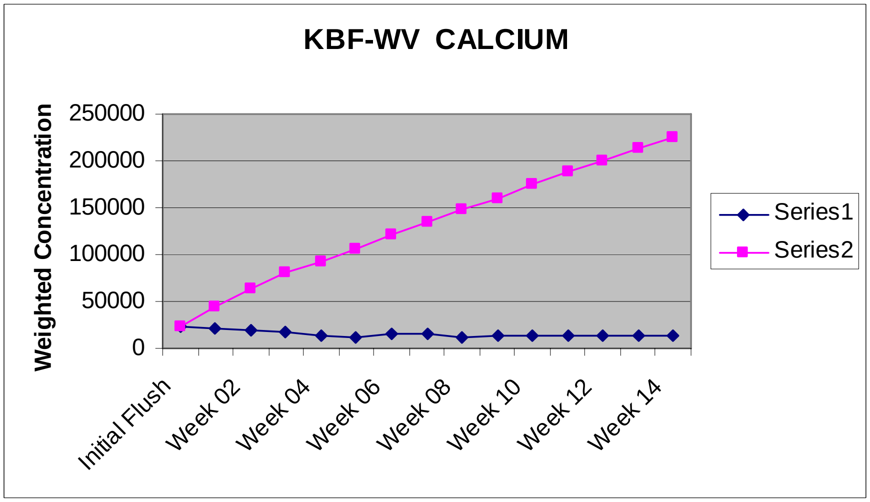
Week 04
Week 06
Week 08
Week 10
Week 12
Week 14
Series1
Series2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Weighted Concentration
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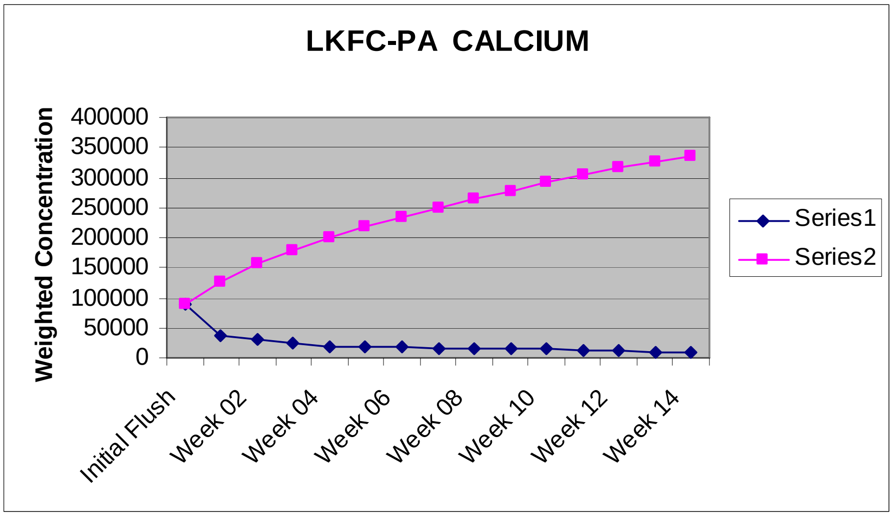
100000
50000
0
Initial Flush
Week 02
Week 04
Week 06
Week 08
Week 10
Week 12
Week 14
Series1
Series2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Weighted Concentration
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200000
150000
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Initial Flush
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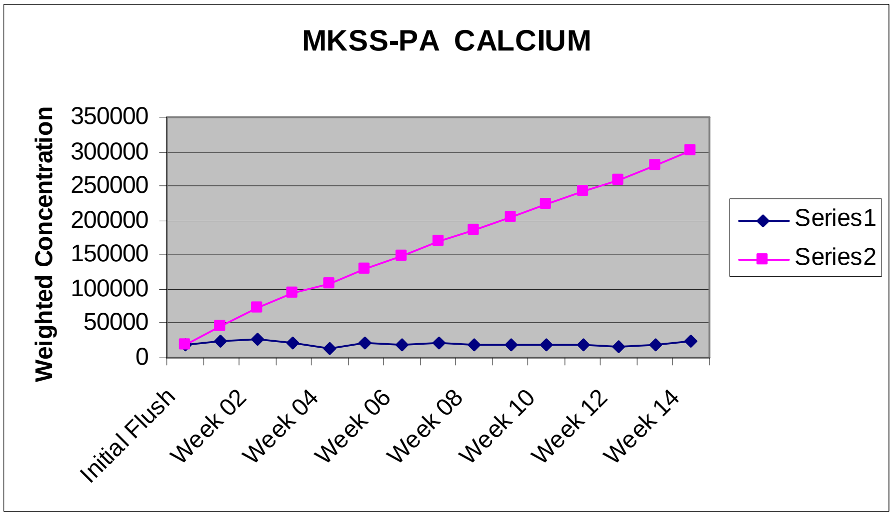
Week 10
Week 12
Week 14
Series1
Series2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Week 04
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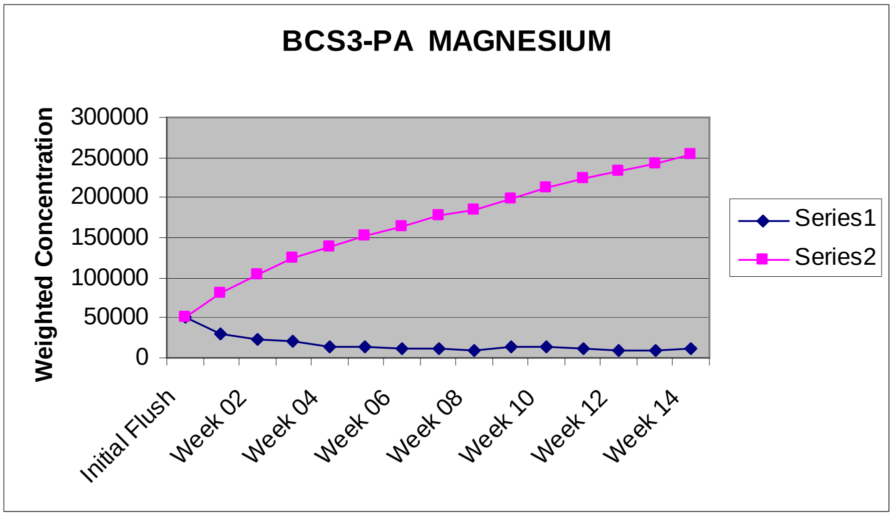
Week 10
Week 12
Week 14
Series1
Series2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Weighted Concentration
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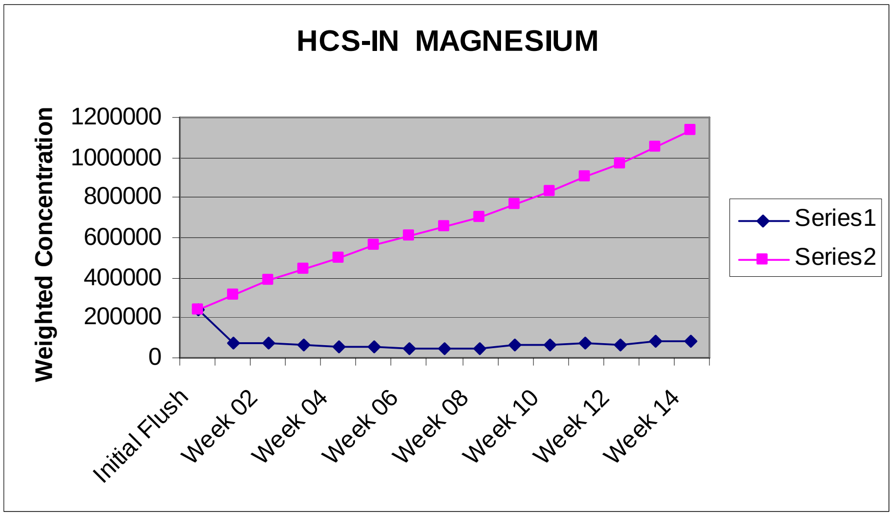
150000
100000
50000
0
Initial Flush
Week 02
Week 04
Week 06
Week 08
Week 10
Week 12
Week 14
Series1
Series2


HCS-IN MAGNESIUM
Weighted Concentration
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0
Initial Flush
Week 02
Week 04
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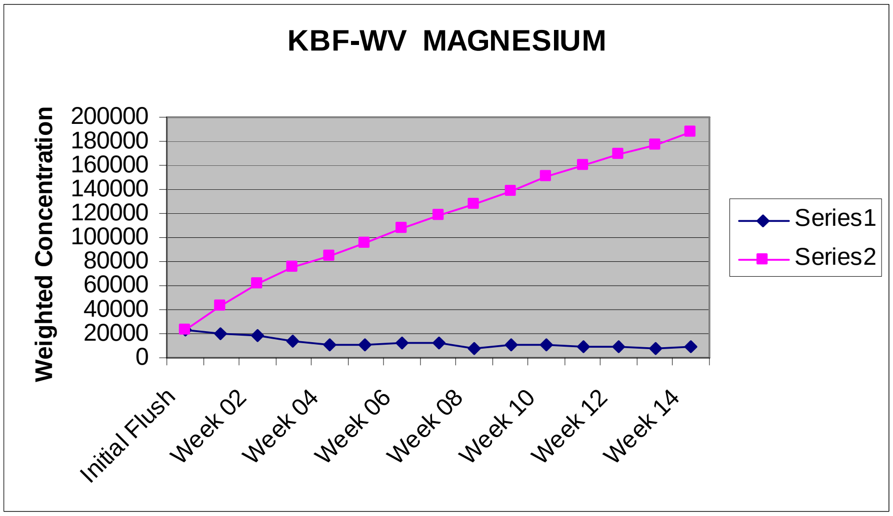
Week 10
Week 12
Week 14
Series1
Series2


KBF-WV MAGNESIUM
Weighted Concentration
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180000
160000
140000
120000
100000
80000
60000
40000
20000
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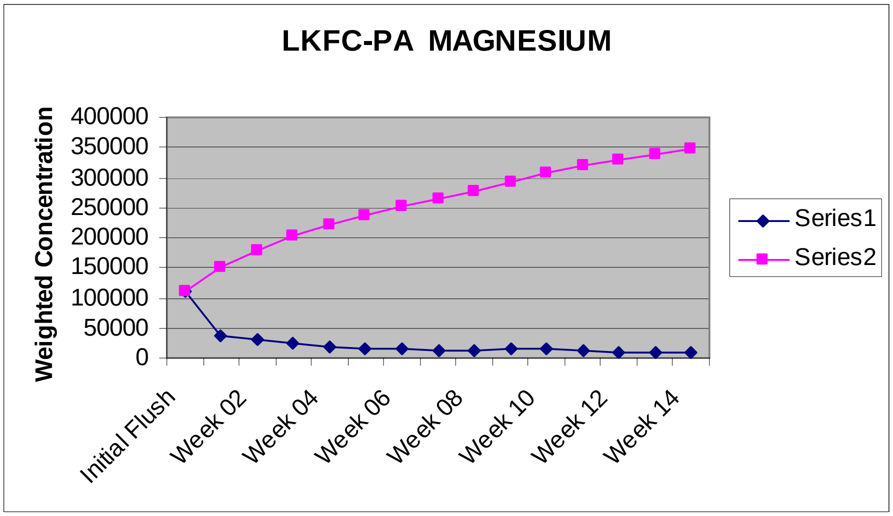
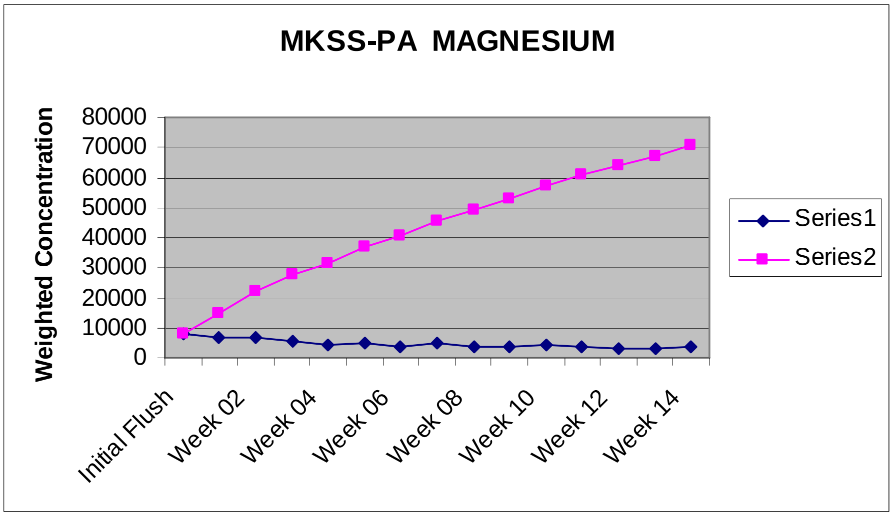
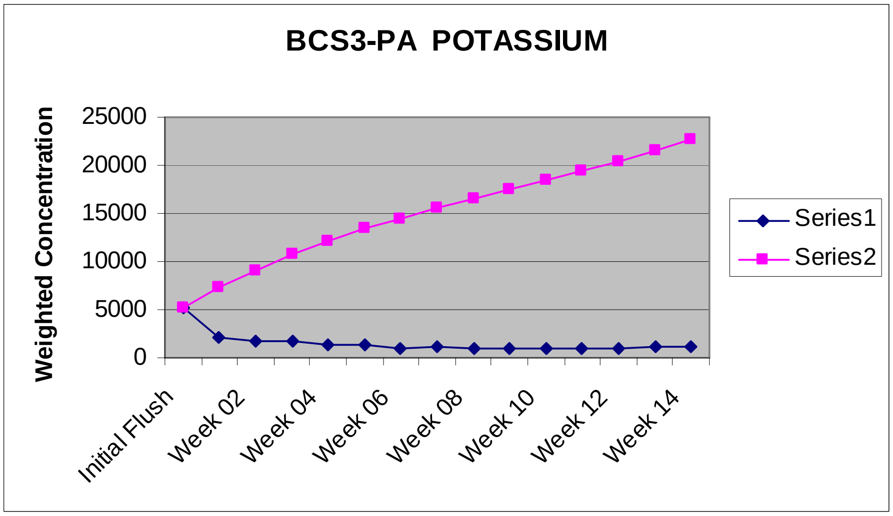
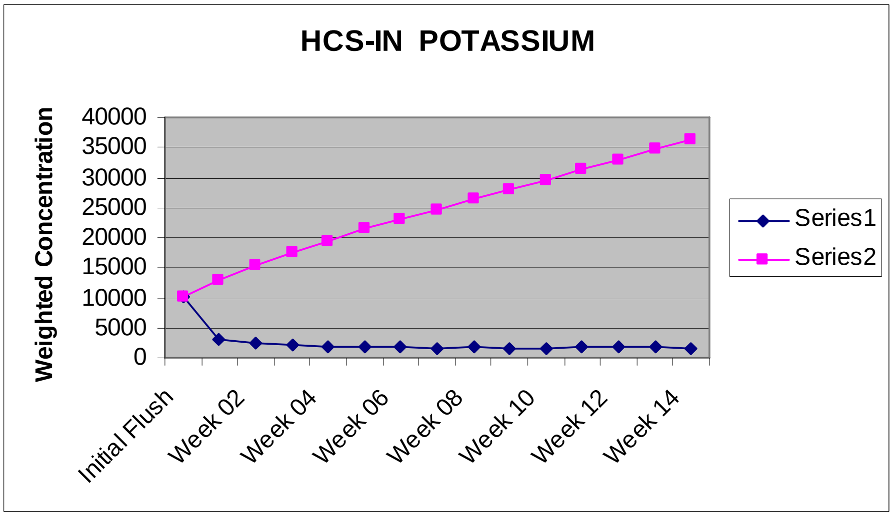
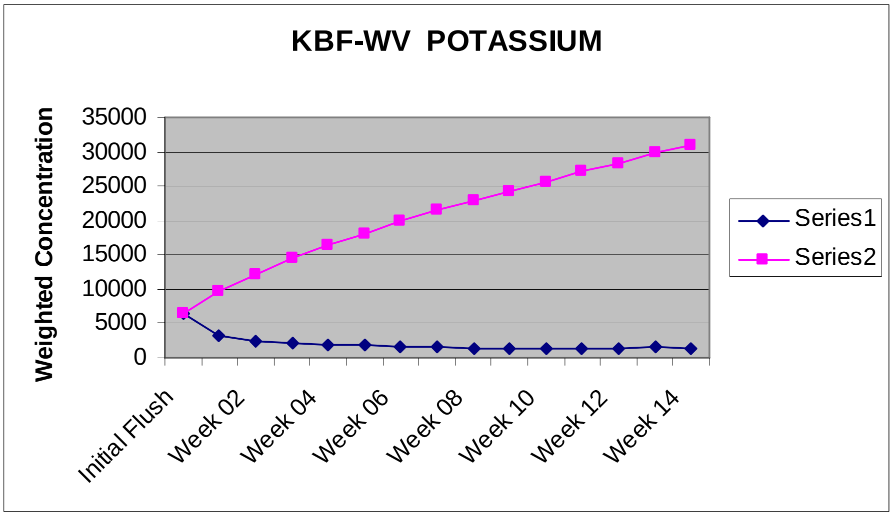
Initial Flush
Week 02
Week 04
Week 06
Week 08
Week 10
Week 12
Week 14
Series1
Series2

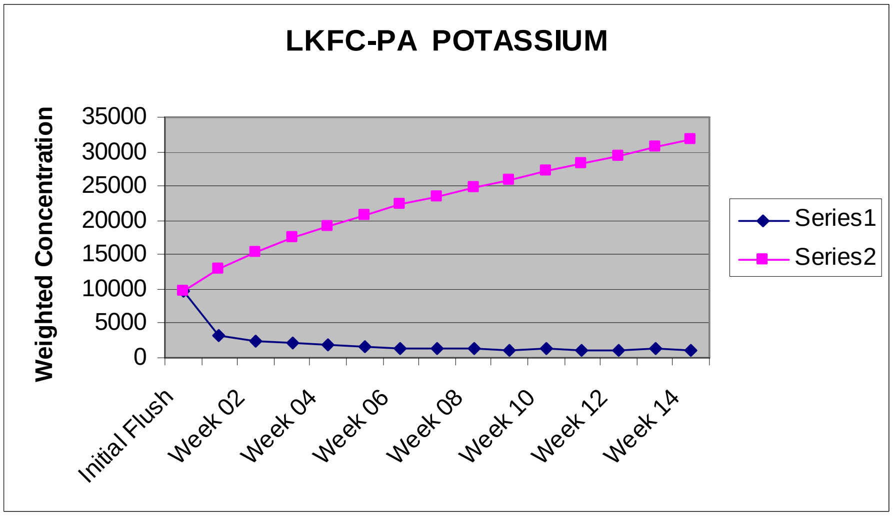

LKFC-PA MAGNESIUM
Weighted Concentration
400000
350000
300000
250000
200000
150000
100000
50000
0
Initial Flush
Week 02
Week 04
Week 06
Week 08
Week 10
Week 12
Week 14
Series1
Series2


MKSS-PA MAGNESIUM
Weighted Concentration
80000
70000
60000
50000
40000
30000
20000
10000
0
Initial Flush
Week 02
Week 04
Week 06
Week 08
Week 10
Week 12
Week 14
Series1
Series2


BCS3-PA POTASSIUM
Weighted Concentration
25000
20000
15000
10000
5000
0
Initial Flush
Week 02
Week 04
Week 06
Week 08
Week 10
Week 12
Week 14
Series1
Series2


HCS-IN POTASSIUM
Weighted Concentration
40000
35000
30000
25000
20000
15000
10000
5000
0
Initial Flush
Week 02
Week 04
Week 06
Week 08
Week 10
Week 12
Week 14
Series1
Series2





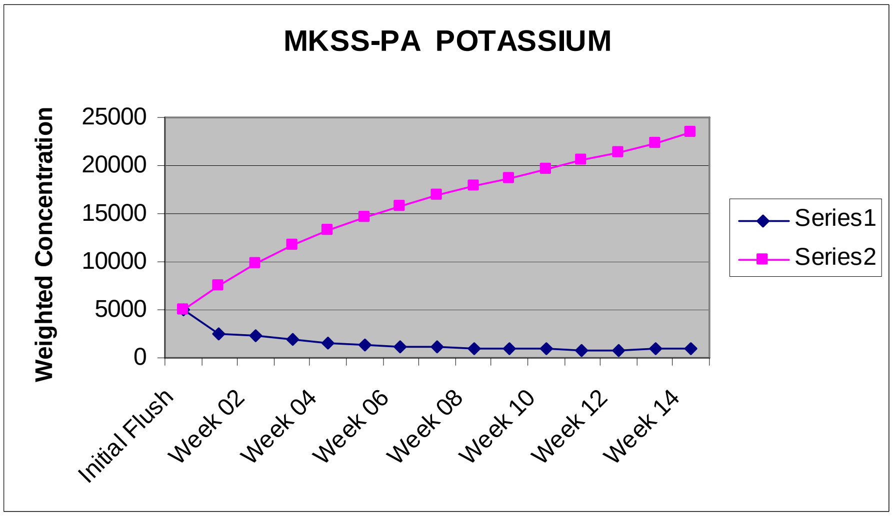
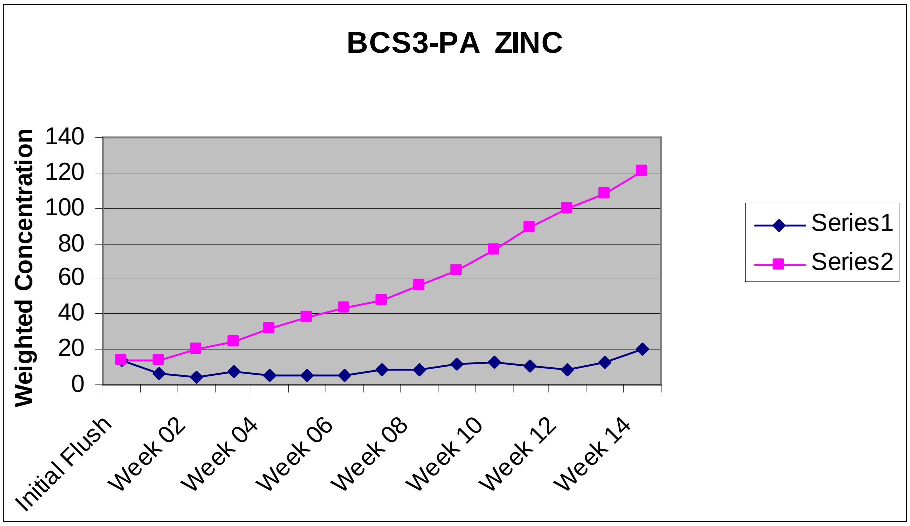
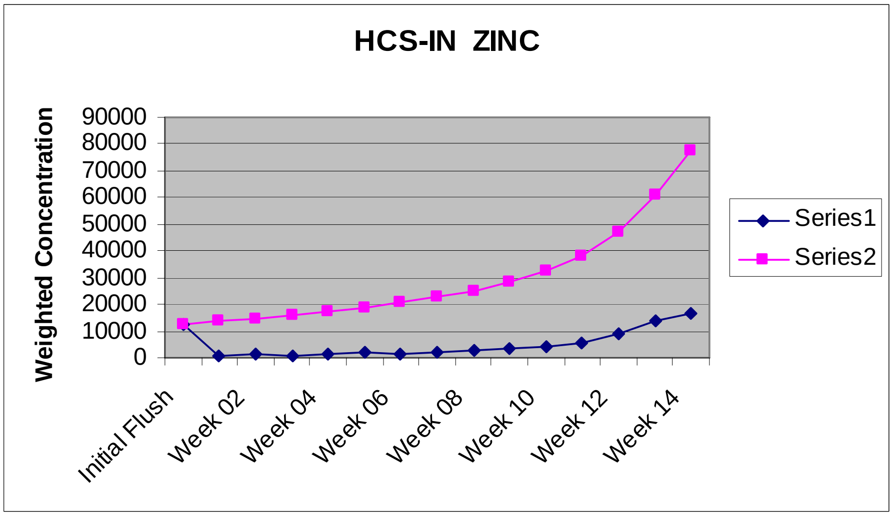


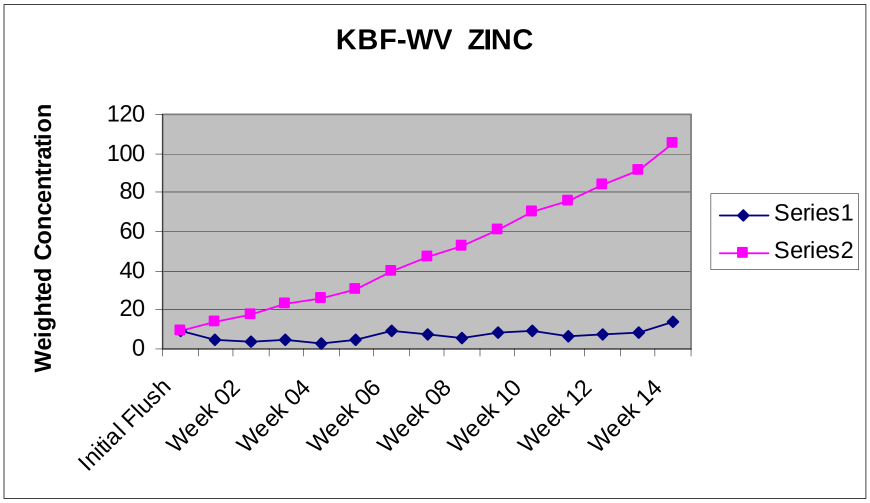
Figure 7.38. Plots of week-by-week release (series 1) and cumulative release including the first flush (series 2) of calcium, magnesium, and potassium.

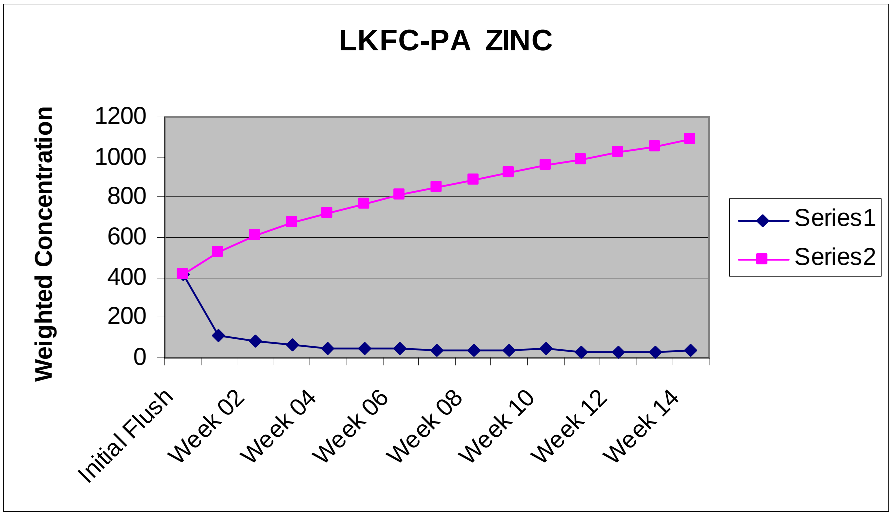
Zinc

Of the various transition metals that occur in minor amounts in the reference rock samples, zinc is leached in sufficient quantities to justify examining the rate of release. Even so, the concentrations are low and some scatter in the data is to be expected. The zinc release data are shown in Figure 7.39. The shapes of the cumulative zinc release curves vary considerably from one rock sample to another. In particular, the zinc release from the Houchins Creek Shale increases rapidly during the last several weeks of the experiment.









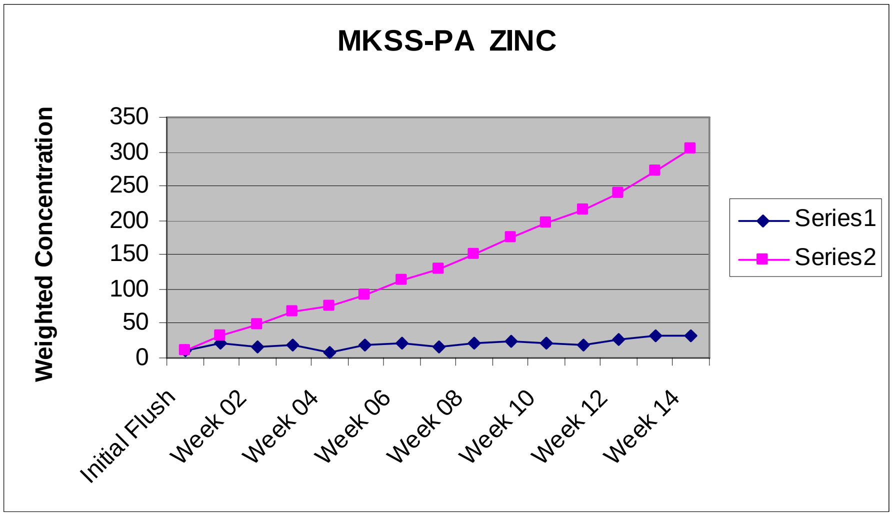
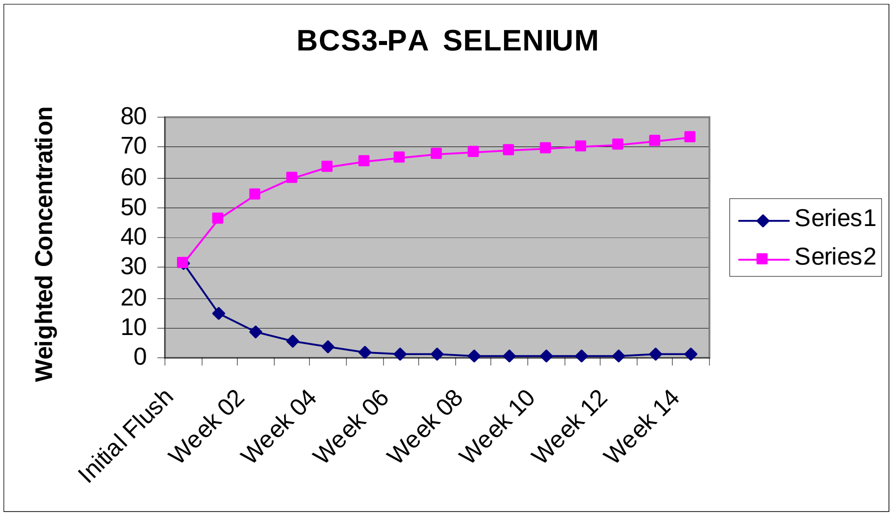
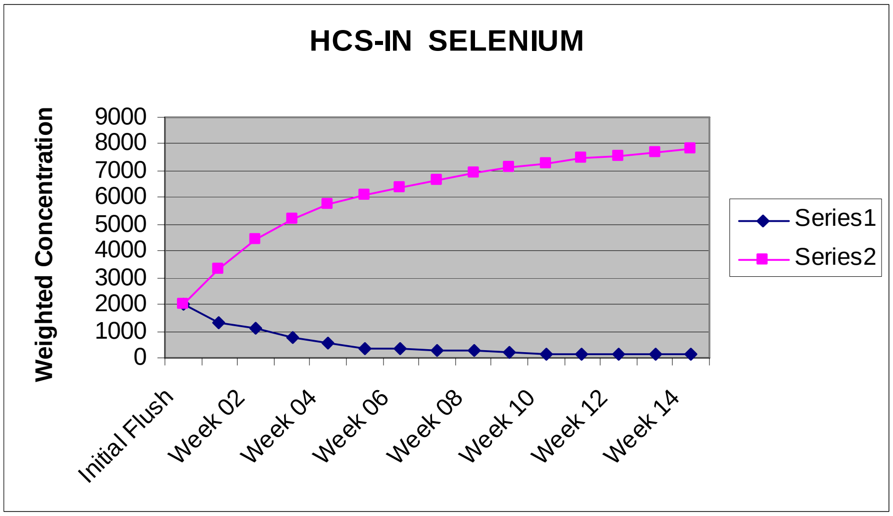


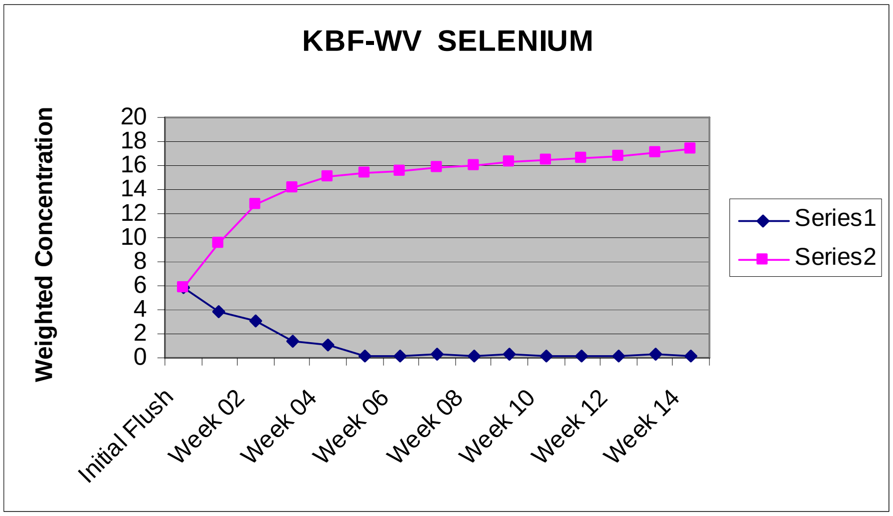
Figure 7.39. Plots of week-by-week (Series 1) and cumulative (Series 2) release of zinc.

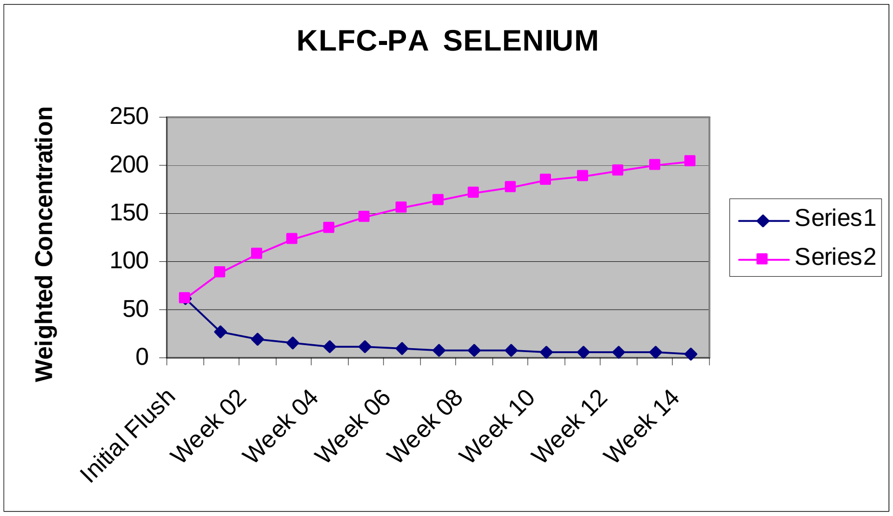
Selenium

Selenium is an element of concern. Release of selenium is described in Figure 7.40. Many of the samples show rapid initial release of selenium followed by a flattening of the rate curves although the curves never become completely horizontal.









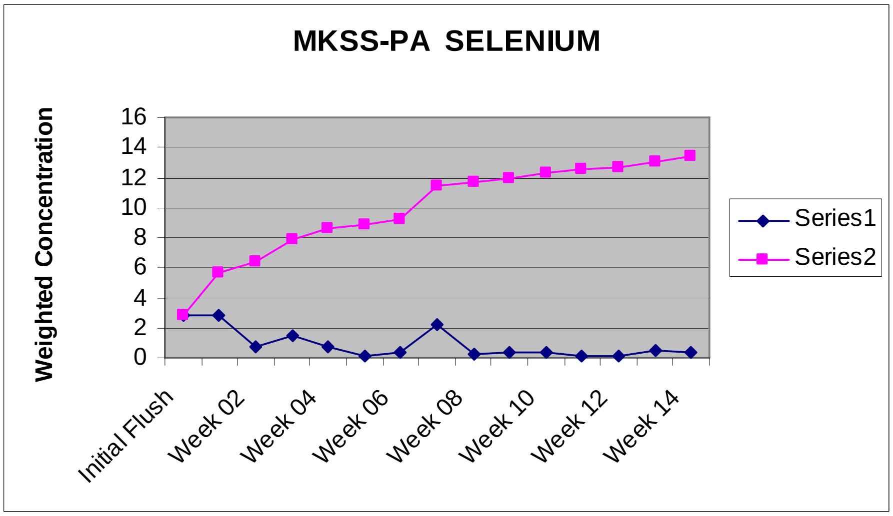
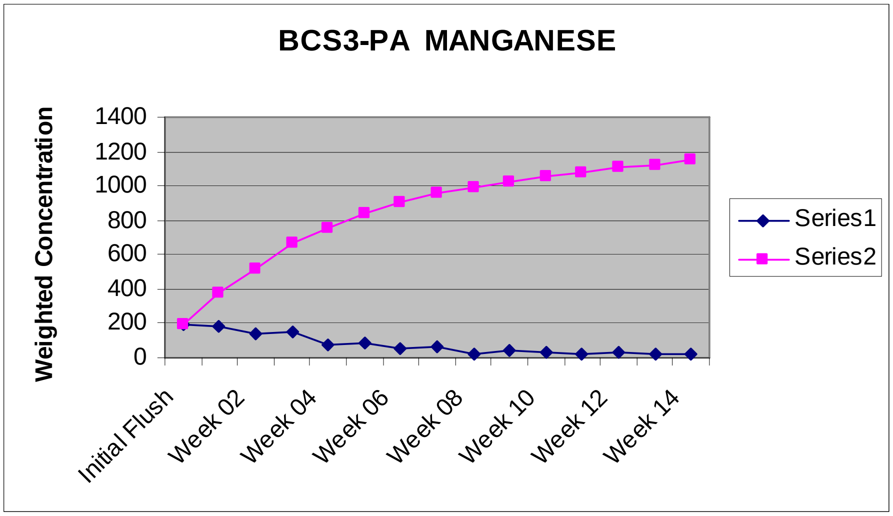
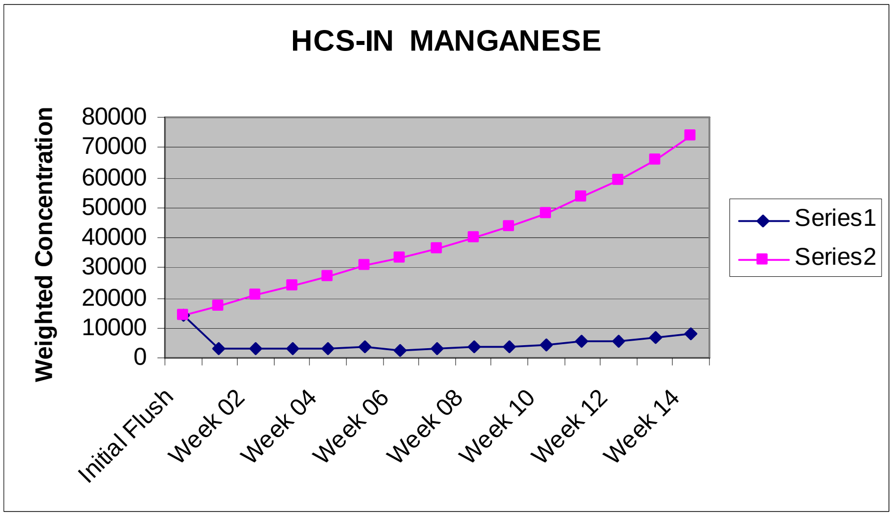


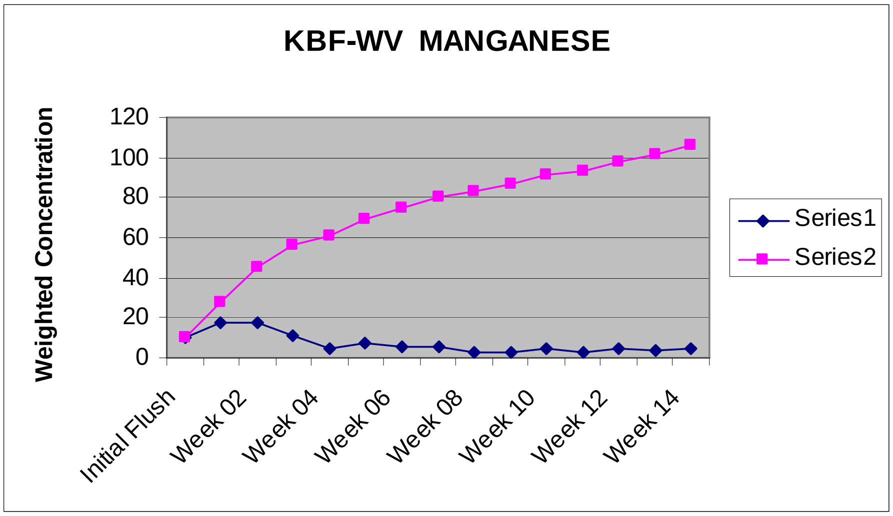
Figure 7.40. Plots of week-by-week release (Series 1) and cumulative release (Series 2) of selenium.

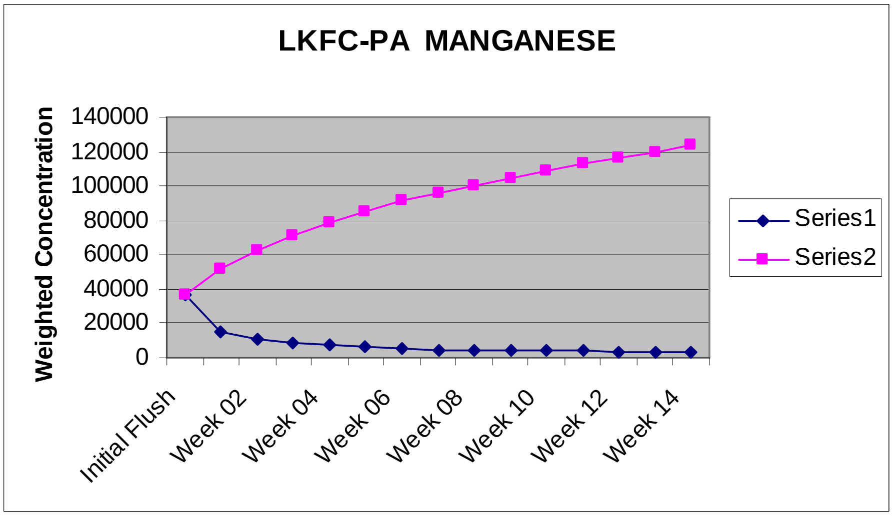
Manganese, Iron and Aluminum

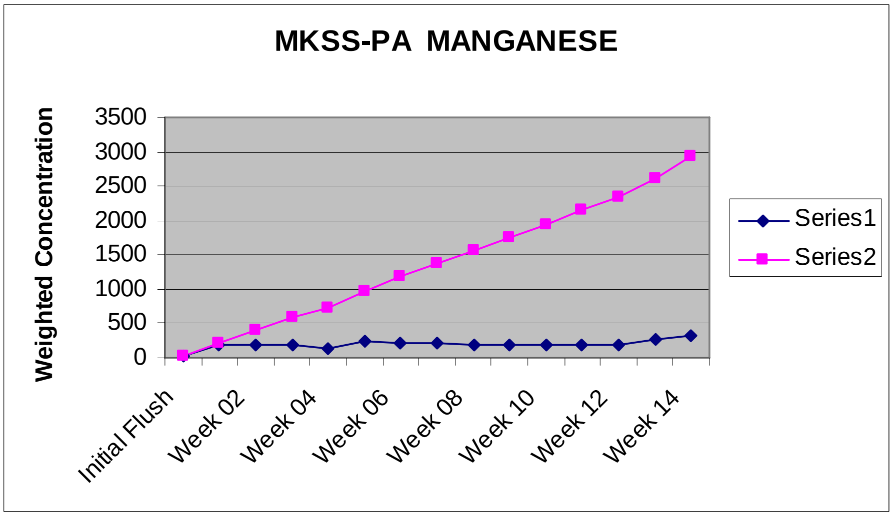
Manganese, iron, and aluminum are common constituents of most rocks. Manganese and iron are highly insoluble in neutral to alkaline environments but can be leached by low pH waters and, as such, are of concern when there is production of acid. Manganese was extracted from the columns in sufficient quantity to produce smooth leach curves. Iron concentrations were lower and so the plots are more erratic. Aluminum was mostly below the detection limit in the analyses, and is not further discussed in this section. The leach curves for manganese and iron are shown in Figure 7.41.

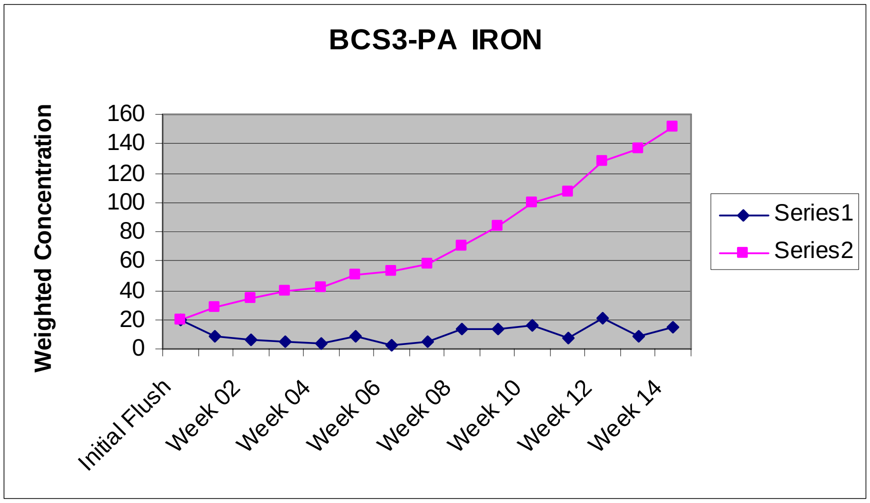


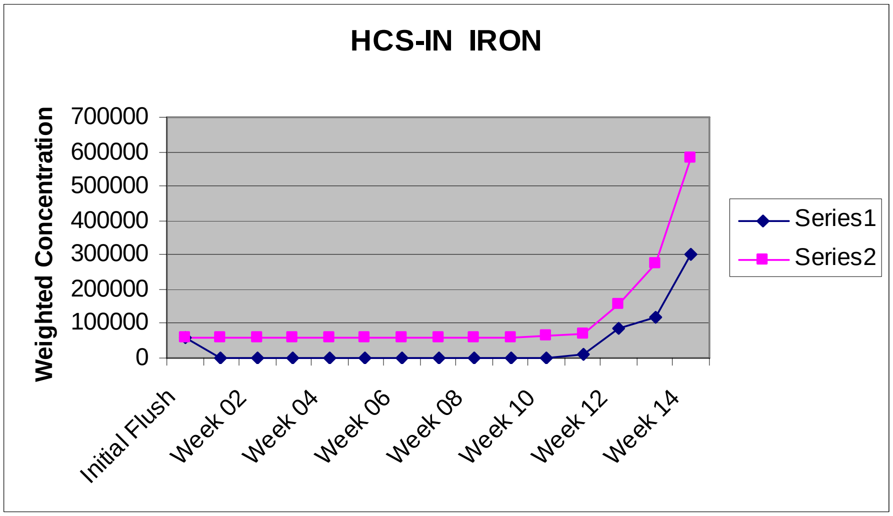


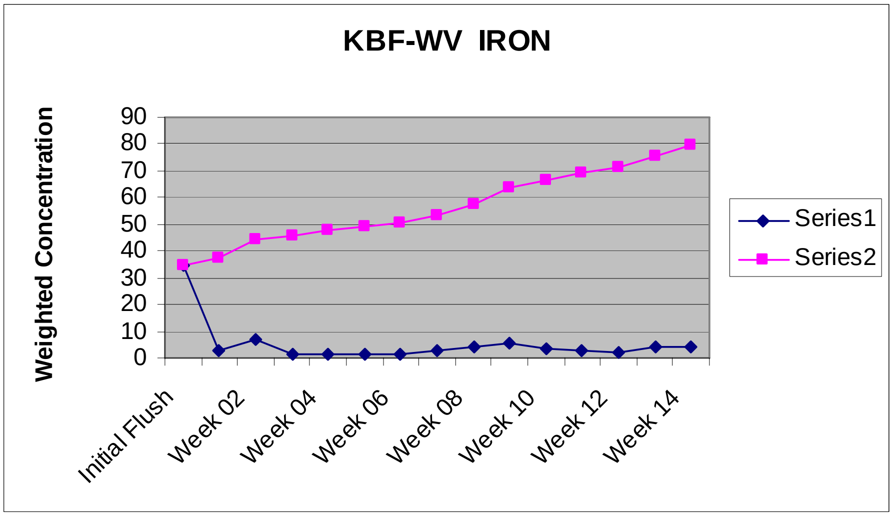

KBF-WV MANGANESE
Weighted Concentration
120
100
80
60
40
20
0
Initial Flush
Week 02
Week 04
Week 06
Week 08
Week 10
Week 12
Week 14
Series1
Series2


LKFC-PA MANGANESE
Weighted Concentration
140000
120000
100000
80000
60000
40000
20000
0
Initial Flush
Week 02
Week 04
Week 06
Week 08
Week 10
Week 12
Week 14
Series1
Series2


MKSS-PA MANGANESE
Weighted Concentration
3500
3000
2500
2000
1500
1000
500
0
Initial Flush
Week 02
Week 04
Week 06
Week 08
Week 10
Week 12
Week 14
Series1
Series2


BCS3-PA IRON
Weighted Concentration
160
140
120
100
80
60
40
20
0
Initial Flush
Week 02
Week 04
Week 06
Week 08
Week 10
Week 12
Week 14
Series1
Series2


HCS-IN IRON
Weighted Concentration
700000
600000
500000
400000
300000
200000
100000
0
Initial Flush
Week 02
Week 04
Week 06
Week 08
Week 10
Week 12
Week 14
Series1
Series2


KBF-WV IRON
Weighted Concentration
90
80
70
60
50
40
30
20
10
0
Initial Flush
Week 02
Week 04
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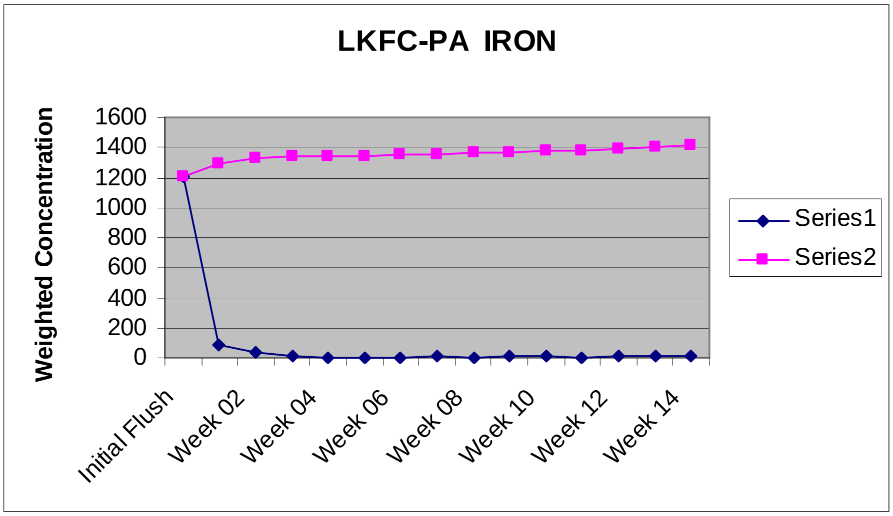
Week 08
Week 10
Week 12
Week 14
Series1
Series2



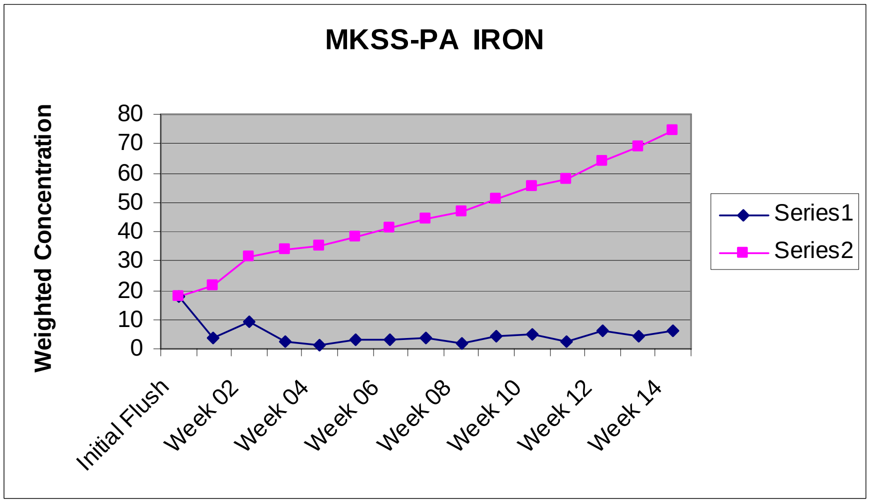


Figure 7.41. Leach curves for manganese and iron.

Discussion and Conclusions Concerning Minor Elements

Considering the inter-laboratory variations, the averaged data give remarkably smooth rate curves for the cumulative release of various minor elements. Regressions based on a power law fit (equation 7.2) were calculated for each of the cumulative release curves (Table 9).

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 – a 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.

Table 7.9 Fitting parameters for power law regression of minor element data.

	BCS3-PA	HCS-IN	KBF-WV	LKFC-PA	MKSS-PA
CALCIUM					
A	150276	320331	40638	120685	42966
n	0.451	0.564	0.630	0.381	0.715
R^2	0.988	0.978	0.991	0.995	0.992
MAGNESIUM					
A	78068	272488	40836	143448	14330
n	0.432	0.490	0.561	0.326	0.597
R^2	0.993	0.944	0.992	0.993	0.998
POTASSIUM					
A	6879	11790	9030	12212	7391
n	0.431	0.400	0.453	0.346	0.427
R^2	0.989	0.974	0.993	0.988	0.998
ZINC					
A	10.7	8988	10.3	504	26.0
n	0.849	0.604	0.812	0.279	0.872
R^2	0.937	0.634	0.943	0.988	0.962
SELENIUM					
A	48.7	3556	10.8	86.9	5.3
n	0.160	0.313	0.192	0.324	0.354
R^2	0.956	0.982	0.907	0.999	0.970
IRON					
A	20.4	32987	34.2	1288	20.7
n	0.663	0.518	0.279	0.031	0.432
R^2	0.854	0.144	0.893	0.920	0.923
MANGANESE					
A	406	13979	31.4	50388	209
n	0.413	0.548	0.468	0.334	0.973
R^2	0.971	0.897	0.989	0.998	0.994

The cumulative rate data for zinc give relative good fits for all samples except the Houchins Creek Shale. Because of the low concentration of zinc in the leachate, the data points have somewhat larger scatter then do the points for calcium, magnesium, and potassium but the R^2 values remain in the range of 0.94 to 0.98. The fit for the Houchins Creek Shale is 0.634 in spite of the data fitting a very smooth curve. Normally, an R^2 this low would imply a tremendous scatter in the data. The explanation is that the plot curves upward at long times, a shape that is not compatible with the power function rate equation. It shows that the release of zinc from the Houchins Creek Shale involves a more rapid rate process that is activated after the experiments are well underway.

The behavior of selenium is unique among the elements examined. The initial release is very rapid, followed by a flattening of the rate curves are long times. The fits are reasonably good – $R^2 = 0.90$ to 0.999 – but the exponents are in the range of 0.16 to 0.35, well outside of expected values for a diffusion controlled process. Again, the hypothesis is that there is more than one process involved. It appears possible that selenium occurs in several of the phases in the spoil sample. One dissolves rapidly giving the initial burst o selenium. The later release of selenium is due to a second phase that dissolves for slowly after the first phase is completely dissolved.

Manganese produces smooth rate curves with good fitting values. The only value of R^2 below 0.97 is the Houchins Creek Shale and the value there is 0.897. Three of the exponents are in the range expected for diffusion-controlled processes. However, the Lower Kittanning Shale has $n = 0.334$ which is somewhat outside the expected range. In contrast, the Middle Kittanning Sandstone has $n = 0.973$, almost linear behavior.

Iron is present in the leachates only a low concentration. The fitting parameters for the average cumulative release curves are highly erratic. It does not seem useful to attempt any interpretation.

Chapter 8: Leaching Behavior of Elements

Eric F. Perry

Nine elements and four general chemistry parameters exhibited distinctive behavior during the 14 week test among the five rocks and seven laboratories. The test successfully distinguished weathering characteristics of the five rocks on concentration, flux and leachate composition bases. 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. Pyrite content, as represented by sulfur measurements and mineralogical studies described in chapter 5, was one of the most important influences on leachate chemistry. Pore gas composition, including the partial pressure of carbon dioxide (CO_2), strongly influenced the observed solution alkalinity concentrations and carbonate mineral dissolution.

Chemical Concentration

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. Iron and aluminum, although major components in the rocks, were present at detections levels or ug/L, for most of the leaching cycle in four rocks. The low concentrations reflect pH and redox solubility controls on these metals. Sample HCS-IN, which produced acidic leachate during the test, leached significant quantities of iron and aluminum.

The rocks leached varying concentrations of the major constituents, and were generally consistent with minerlogical compostion. Figure 8-1 shows the concentration distribution at weeks 1 and 14 for calcium, magnesium, sodium, potassium, and alkalinity in the five rocks. Other data for weeks 1 and 14 include sulfate concentration and specific conductance (Figure 8-2), selenium and zinc (figure 8-3), and iron, aluminum and manganese (Figure 8-4).

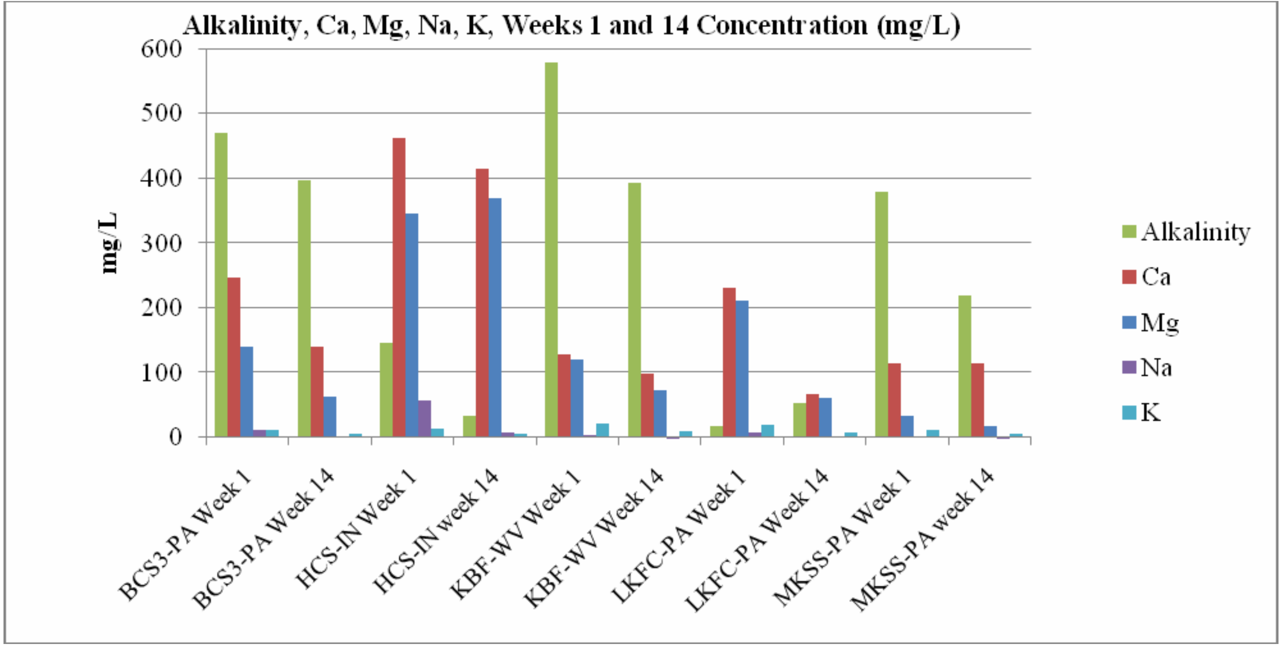


Figure 8-1. Alkalinity, Calcium, Magnesium, Sodium and Potassium Concentrations at Weeks 1 and 14 for 5 Rocks. Values are medians of all labs in mg/L.

Samples BCS3-PA and HCS-IN, which contain the most carbonate, also produced the highest calcium and magnesium leachate concentrations. HCS-IN which generated acidic leachate consumed carbonate and/or other minerals most aggressively. It produced the highest concentration data for most chemical parameters. The “blank” sample MKSS-PA generallly produced low concentrations of major and minor constituents, and KBF-WV and LKFC-PA leachate concentrations were intermediate between the end members.

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 rock types and sulfate values were 60 to 88% lower (Figure 8-1 and 8-2). The single exception was sample HCS-IN where magnesium and sulfate concentrations actually increased through the test, indicating that mineral weathering and leaching intensified as conditions became acidic. Alkalinity concentration declined the least (about 16%) in sample BCS3-PA and the most in HCS-IN as that sample consumed its’ neutralizers. One sample, LKFC-PA, had higher alkalinity at the week 14 than at week 1. The reason for this increase or slower release of alkalinity during the test is not clear. The trace element selenium declined in concentration about 90 to 95% from week 1 to week 14 in all 5 rocks (Figure 8-3). The rapid decrease suggests that selenium leaching might be a short term event.

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. Under atmospheric conditions, calcium carbonate dissolution can only produce about 60 mg/L alkalinity, yet mine waters frequently contain carbonate alkalinity well in excess of that, and measured or calculated pCO_2 is above atmospheric conditions. Cravotta (2008b) in a detailed study of 140 mine discharges in Appalachia, USA, reported a mean pCO_2 of about 0.1 atmospheres; the same condition specified for the test columns. Alkalinity, carbonate solubility and pCO_2 relationships are discussed under “Solubility Controls” later in this chapter.

Specific conductance data in figure 8-2 are a surrogate measure of the dissolved solids content. They are consistent with the elemental analyses, and show a decline in dissolved solids content for 4 samples through the test period, and an increase in the acid weathering HCS-IN sample. The “blank” sample MKSS-PA had the lowest dissolved solids content as would be expected based on its’ mineral composition, which includes a high percentage of quartz. The highest chemical concentrations are typically observed during initial weathering and leaching, followed by gradual declines through time. Younger (1997) describes an early flush of weathering products from flooded underground mines in Britain, followed by a decline in pollutant concentrations. After 10 to 20 years, the curves become asymptotic or nearly so. Similar behavior has been described for coal mines in Appalachia (Perry and Rauch, 2006). The increasing specific conductance in HCS-IN from week 1 to 14 reflects two phases of weathering; the first with circumneutral leachate as alkalinity is generated; and the second, an acidification phase as pyrite oxidation dominates. The solubility of many minerals and elements increases at low pH, and this is reflected by the higher conductance readings at week 14.

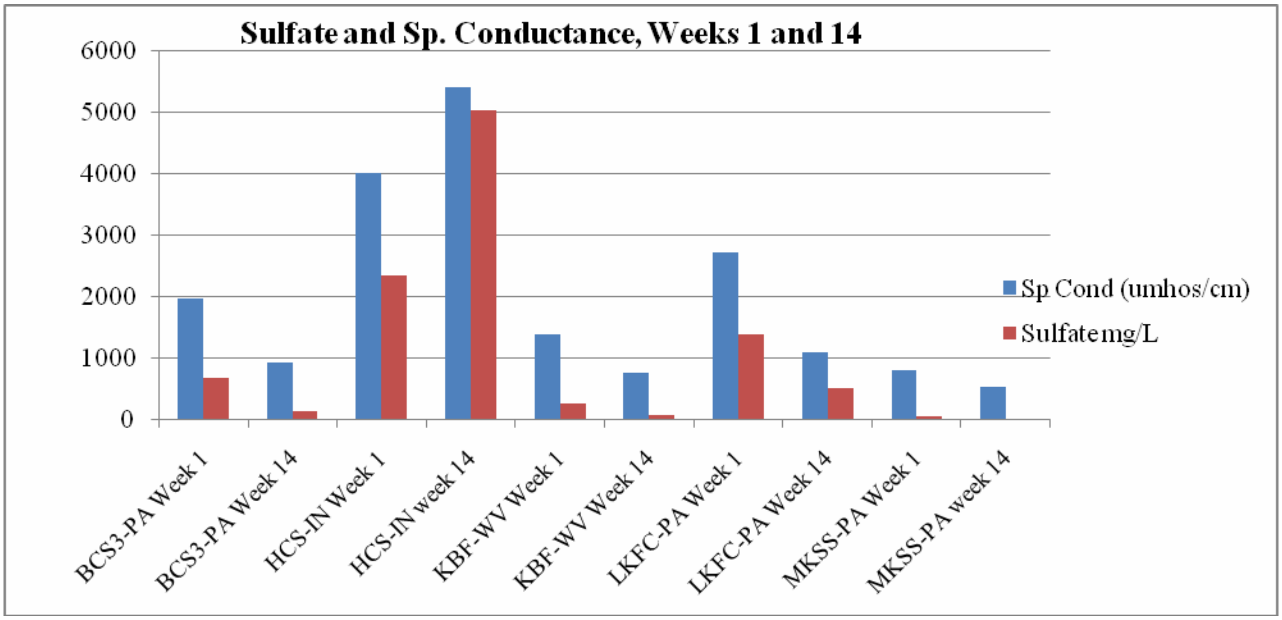


Figure 8-2. Sulfate and Specific Conductance, Weeks 1 and 14 For 5 Rocks. Sulfate in mg/L, Specific Conductance in umhos/cm. Values are medians of all labs.

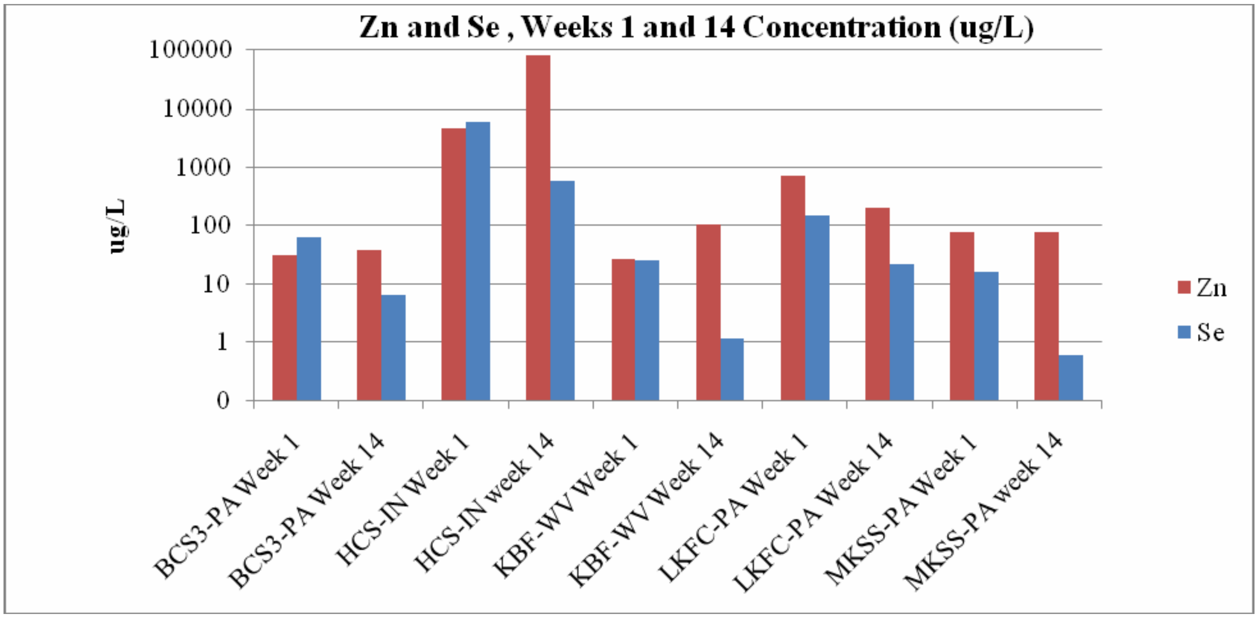


Figure 8-3. Selenium and Zinc Concentration, Weeks 1 and 14 for 5 Rocks. Data are median values of all labs. Concentration is ug/L, log scale. Values are medians of all labs.

Figure 8-3 shows weeks 1 and 14 zinc and selenium concentration data. Four rocks leached these elements at concentrations of a few ug/L, and concentrations declined during the test. Sample HCS-IN produced the highest leachate concentrations and zinc actually increased from week 1 to 14 as the sample acidified. Selenium concentration declined about 90 to 95% for all five rocks from week 1 to week 14. Sample KBF-WV was collected from a mining area in

West Virginia where selenium has been identified as mostly closely associated with coal and carbon rich shales in parts of the Kanawha formation in West Virginia (Vesper et al, 2008). This sample leached negligible quantities of selenium.

Figure 8-4 shows weeks 1 and 14 concentration data for the mine water metals iron, aluminum and manganese. Most leachate analyses were at or near detection levels for iron and aluminum, so few trends are evident. The low concentrations are consistent with the test protocol, and geochemical behavior of these elements. The column is a strongly oxidizing environment, with oxygenated air continually passing through the apparatus. Under strongly oxidizing conditions, conversion of Fe(II) to Fe(III) is favored, and occurs as:

$$Fe^{2+} \quad + \quad 0.25\ O_2 \quad + H^+ \rightarrow Fe^{+3} \quad + \quad 0.5\ H_2O$$

At circumneutral pH, the conversion can progress rapidly, followed by formation of solid phase Fe(III) oxyhydroxide minerals (Langmuir, 1997). Aluminum solubility is strongly pH dependent, with a minimum concentration at circumneutral pH leachates such as those produced in four of the rocks. Only the acidic HCS-IN leachates contained appreciable soluble aluminum and iron. Manganese, which is soluble over a wide range of pH and redox conditions, is present in small to moderate amounts in all samples.

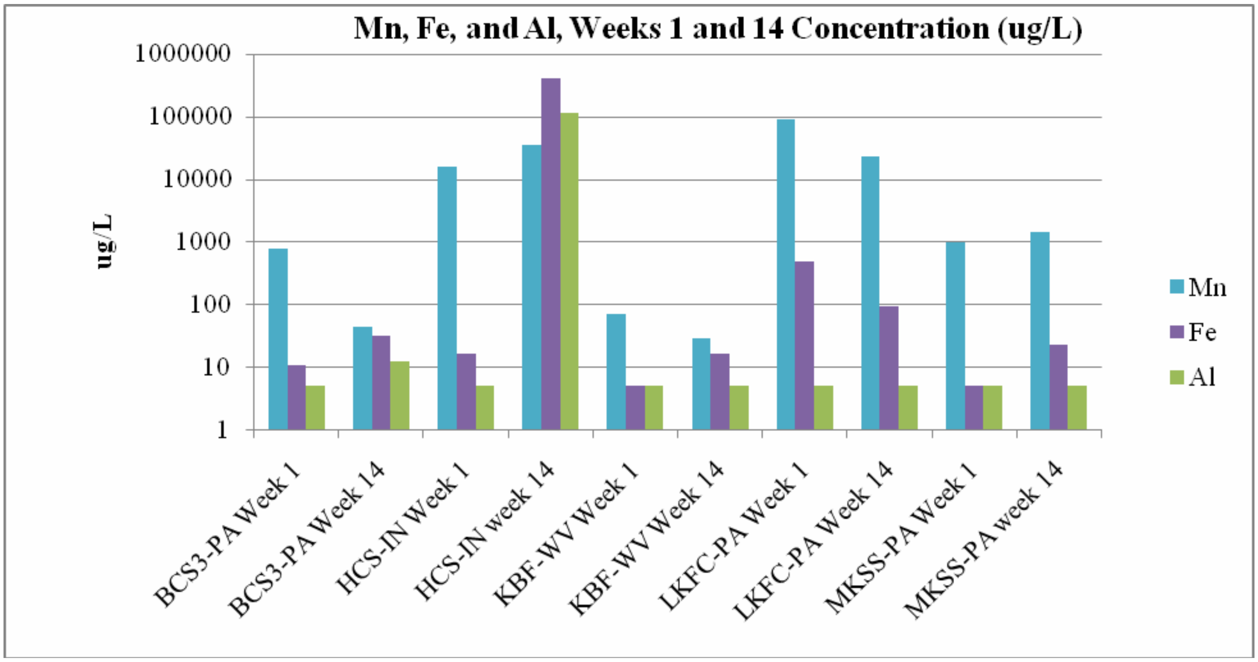


Figure 8-4. Iron, Manganese and Aluminum Concentration, Weeks 1 and 14 For 5 Rocks. Values are medians of all labs. Concentration is ug/L, log scale.

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 and as shown in the cumulative weathering graphs in Chapter 7. Iron and aluminum were largely removed from solution by the formation of new minerals in four samples, rather than being leached from the columns.

Mineral solubility, pH and redox controls on elements leaching are discussed in the section "Solubility Controls" later in this chapter.

Leachate Composition

The five rocks produced water of various compositions. Figure 8-5 is a Durov plot, a graphical display of week 1 and week 14 leachates, based on dominant cations and anions expressed in percentage milliequivalents. The plot also displays pH and dissolved solids content (estimated from specific conductance). The cation fraction is dominated by calcium and magnesium, while sulfate and bicarbonate are the principal anions. These findings are summarized in table 8-1. The chemical signature for four of the five rocks did not change overall from week 1 to week 14; indicating weathering reactions were consistent throughout the test. Sample BCS3-PA shifted from a sulfate-bicarbonate water at week 1, to a bicarbonate-sulfate type water at week 14. This suggests a gradual depletion of pyrite weathering products, and continued alkalinity production from carbonates. Two samples, HCS-IN, and LKFC-PA produce sulfate dominated water. These two rocks have the highest sulfur contents. The other three rocks produce bicarbonate dominated leachate and have low sulfur contents. Three samples are approximately saturated for the mineral calcite. These waters have dissolved all of the calcium carbonate they can hold, and calcium and bicarbonate concentrations are at a maximum for the conditions in the column.

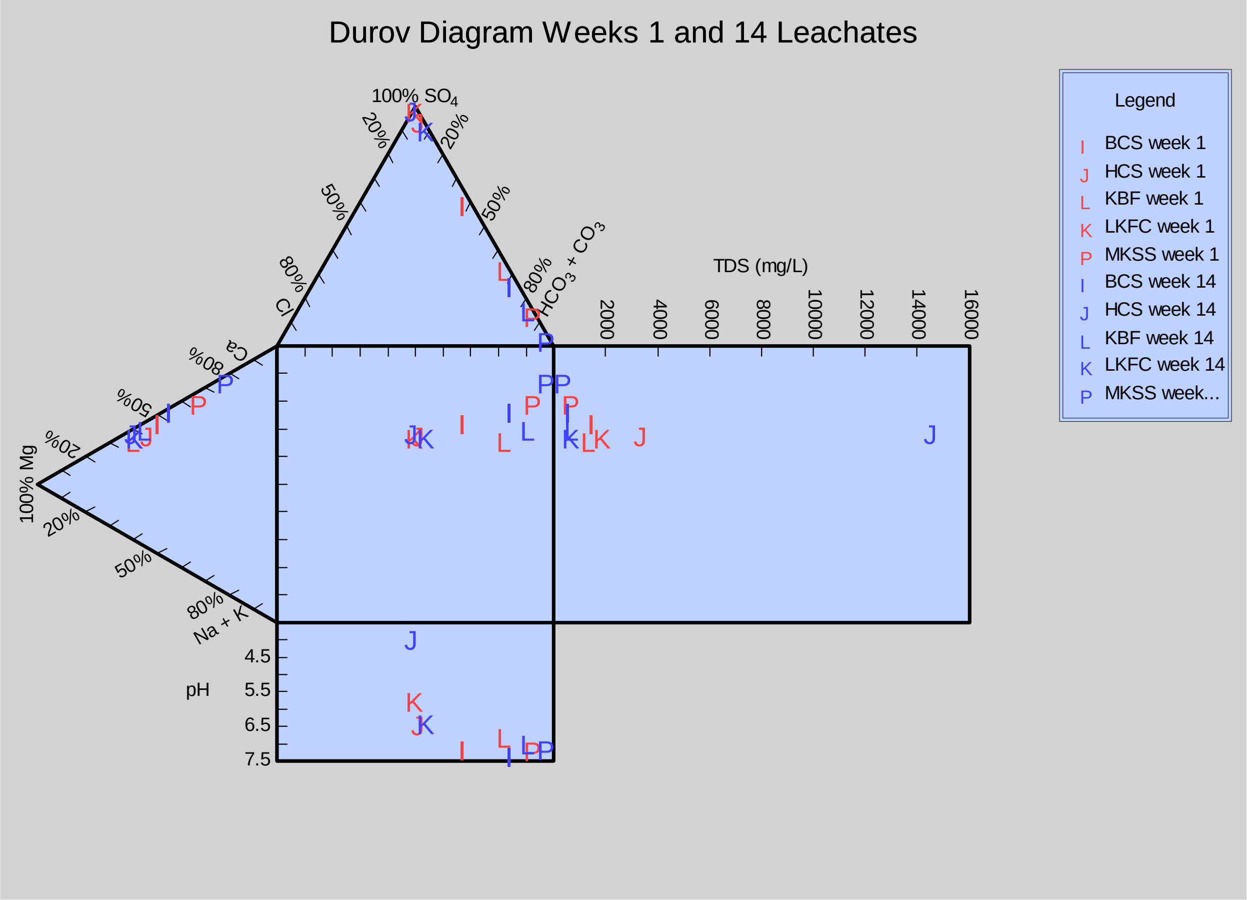


Figure 8-5. Durov (Composition) Plot of Weeks 1 and 14 Leachates. Values are medians of all labs.

Table 8-1
Leachate Water Type at Weeks 1 and 14

Sample	BCS3-PA	HCS-IN	KBF-WV	LKFC-PA	MKSS-PA
Week 1 Water Type	Ca-Mg- SO_4 - HCO_3	Mg-Ca - SO_4	Mg-Ca - HCO_3	Mg-Ca - SO_4	Ca -Mg- HCO_3
Week 14 Water Type	Ca-Mg- HCO_3- SO_4	Mg-Ca - SO_4	Mg-Ca - HCO_3	Mg-Ca - SO_4	Ca -Mg- HCO_3
Calcite Saturated	Yes	No	Yes	No	Yes

The column leaching waters have compositions characteristic of mine waters. Cravotta (2008a, 2008b) sampled about 140 surface and underground mine discharges in Appalachia, including strata that is similar to some of the study samples. Cravotta's data when replotted to show cation/anion composition, shows water much like those in Figure 8-5.

The test produced leachates of different chemical composition as shown by comparing mean (average) leachate composition for the five rocks over the 14 week test. These data are summarized in Table 8-2 for the major elements, pH and specific conductance. Chemical concentrations were compared using analysis of variance techniques (ANOVA). The test compares the mean values of 14 weeks of data among the different rocks. Statistically significant differences occur for each chemical parameter. The ANOVA F-test showed that that the differences are not likely due to chance. Alkalinity concentrations were distinct for each rock, and specific conductance values were divided among four categories. Calcium and magnesium concentration also shows distinct difference, with the BCS3-PA and HCS-IN leaching the highest concentrations of these two elements. These rocks contained the most carbonates. Sulfate concentrations were also divided among several categories and generally follow the total sulfur content of the rocks. Table 8-2 shows that the test produces waters of different composition from both geochemical and statistical bases, and has value for discriminating among the weathering behavior of rocks. Leaching of the trace element zinc was distinct only for the HCS-IN.

Table 8-2
Mean Leachate Composition for Five Rocks(1)

Sample	**pH**	**Alkalinity (mg/L)**	**Specific Conductance**	**Calcium (mg/L)**	**Magnesium (mg/L)**	**Sulfate (mg/L)**	**Zinc (ug/L)**
BCS3-PA	7.23*	368****	1131**	157**	75**	220*	35.2*
HCS-IN	5.12***	76**	3851****	458***	337***	2609***	19862**
KBF-WV	6.99*	427*****	958**	99*	83**	592**	44*
LKFC-PA	6.10**	38*	1464***	109*	100**	95*	283*
MKSS-PA	7.14*	250***	604*	102*	22*	17*	74*

(1) Values followed by the same number of asterisks (*) are **not** statistically significantly different at a probability level of p=0.05. Values with differing number of asterisks **are** statistically significantly different. Means computed from week 1 to week 14 data inclusive. F-test indicates ANOVA model is statistically significant.

Chemical Flux (Load)

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.

Fraction Leached

Table 8-3 shows the total elemental content and fraction leached for the five rocks. These data represent only the elemental fraction removed completely from the column. It does not account for materials that weathered and were retained in the column by the formation of other minerals, adsorption or exchange reactions. Four of five rocks leached about 0.001% or less of the Fe and Al present. Only the acidic leachate from sample HCS-IN contained appreciable quantities of Fe and Al. Less than 1% of total Mn was leached, except in sample HCS-IN where nearly 18% of Mn was removed. Between about 3 to almost 9% of total Ca was removed during the test and about 1 to 2 % of Mg was leached. For sulfur, initially present mostly as sulfides, about 2 to 4.5 % of total sulfur was removed during leaching. The trace element Se is in low concentrations (<3 ppm) in four of the five rocks, and less than one to about 7% of the total was removed during the test.

The rocks were ranked from most (1), to least (5) based on the fraction leached from the original content for each element. An overall average rank was computed from all parameters, and is shown in table 8-3. 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.

Table 8-3Total Elemental Content and Relative Fraction Leached(1)

Sample	BCS3-PA		HCS-IN		KBF-WV		LKFC-PA		MKSS-PA	
Element	Total(2) (%)	Leached Fraction	Total (%)	Leached Fraction	Total (%)	Leached Fraction	Total (%)	Leached Fraction	Total (%)	Leached Fraction
Fe	6.66	$< 10^{-5}$	6.36	0.0015	6.14	$< 10^{-5}$	7.74	10^{-5}	2.25	$<10^{-5}$
Mn	0.10	0.0009	0.04	0.18	0.10	0.0001	0.18	0.07	0.05	0.006
Al	10.83	$< 10^{-5}$	6.66	3×10^{-4}	8.49	$<10^{-5}$	9.41	9×10^{-5}	5.89	3×10^{-5}
Ca	1.61	0.033	1.61	0.089	0.74	0.027	0.62	0.052	1.29	0.023
Mg	1.45	0.018	0.97	0.11	1.09	0.015	1.13	0.018	0.54	0.008
Na	0.18	0.012	0.37	0.032	0.55	0.0009	0.16	0.008	0.10	0.003
K	2.91	0.0007	2.28	0.0012	2.85	0.001	3.05	0.0009	1.99	0.001
S	0.53	0.035	5.54	0.045	0.20	0.024	0.81	0.043	0.09	0.021
Se	<3	0.021	81	0.11	<3	0.004	<3	0.068	<3	0.002
Zn	171	0.0055	456	0.088	126	0.0006	151	0.007	86	0.002
pH Week 1	7.12		6.61		7.19		5.45		7.20	
pH Week 14	7.14		3.24		7.18		6.27		7.16	
Average Rank	3.4		1		4.2		2.3		4.0	

(1) Median values of all columns, all labs.

(2) Se and Zn total concentrations are in ppm.

Table 8-4 summarizes elemental leaching on an absolute basis, in cumulative mg of element leached per Kg of sample during the 14 week test. The trends are similar to the relative fraction data in table 8-3. Sample HCS-IN leached about 4 times as much sulfur as the next most active sample, LKFC-PA. The blank sample MKSS-PA leached the least. BCS3-PA leached more calcium than four other rocks and has the largest neutralization potential values. The rocks were also ranked from most (1), to least (5) based on the total leached for each element, and an overall average rank computed.

Table 8-4
Total Element Content and Absolute Amount Leached

Sample	BCS3-PA		HCS-IN		KBF-WV		LKFC-PA		MKSS-PA	
Element	Total(2) (%)	Leached(3) (mg/Kg)	Total (%)	Leached (mg/Kg)	Total (%)	Leached (mg/Kg)	Total (%)	Leached (mg/Kg)	Total (%)	Leached (mg/Kg)
Fe	6.66	0.73	6.36	96.1	6.14	0.32	7.74	0.946	2.25	0.069
Mn	0.10	0.996	0.04	68.5	0.10	0.102	0.18	127	0.05	3.12
Al	10.83	0.032	6.66	20.8	8.49	0.015	9.41	0.086	5.89	0.018
Ca	1.61	543	1.61	1443	0.74	205	0.62	323	1.29	300
Mg	1.45	268	0.97	1123	1.09	191	1.13	371	0.54	70.9
Na	0.18	22.9	0.37	119	0.55	5.4	0.16	12.7	0.10	3.33
K	2.91	1.07	2.28	1.24	2.85	1.25	3.05	1.07	1.99	0.093
S	0.53	1066	5.54	8576	0.20	299	0.81	2187	0.09	111
Se	<3	0.065	81	8.97	<3	0.013	<3	0.204	<3	0.014
Zn	171	0.095	456	.043	126	0.084	151	1.13	86	0.188
pH Week 1	7.12		6.61		7.19		5.45		7.20	
pH Week 14	7.14		3.24		7.18		6.27		7.16	
Average Rank	2.7		1.5		3.7		1.8		3.7	

(1) Median values of all columns, all labs.
(2) Se and Zn total concentrations are in ppm.
(3) Leached fraction calculated as cumulative total mass of element in leachate / Kg of sample.

The acid forming shale HCS-IN leached the greatest elemental fraction and absolute amounts for most parameters in tables 8-3 and 8-4. The samples rank for overall weathering intensity and element leaching as follows, using either relative or absolute amount leached:

HCS-IN(%S=5.15) > LKFC-PA(%S=0.91) > BCS3-PA(%S=0.59) >
KBF-WV(%S=0.31) ≈ MKSS-PA(%S=0.04)

Weathering intensity follows the same ranking order as the original sulfur content of the rocks. Pyrite content indicates in general terms, how intensely the rock will weather.

Solubility Controls

The leaching behavior of elements, and interpretation of leaching test results, is influenced by mineral solubility, oxidation-reduction state, and for carbonate minerals, the partial pressure of carbon dioxide. A proper interpretation of column leaching results and estimation of field performance requires consideration of solubility controls imposed on elements.

Carbonates, Alkalinity and Carbon Dioxide Partial Pressure

The aqueous carbonate system is described by a series of equilibrium equations including carbon dioxide gas as follows:

$$CO_{2\,(g)} + H_2O \leftrightarrow H_2CO_3$$

$$H_2CO_3 \leftrightarrow H^+ + HCO_3^-$$

$$HCO_3^- \leftrightarrow H^+ + CO_3^{2-}$$

and the dissolution of carbonate minerals, such as calcite as:

$$CaCO_3 \leftrightarrow Ca^{2+} + CO_3^{2-}$$

These reactions collectively determine the amount of carbonate that dissolves and the subsequent alkalinity concentrations. Figure 8-6 illustrates the effects of carbon dioxide pressure on pH and alkalinity when dissolving calcium carbonate in pure water. At normal atmospheric conditions, solution pH is about 8.3 and calcite solubility produces around 60 mg/L alkalinity. At the column test condition of 10% CO_2, or pCO_2 of 0.1, calcite solubility is increased to produce alkalinity approaching 350 mg/L. The use of 10% CO_2 for the test protocol had a significant effect on carbonate weathering and alkalinity concentrations.

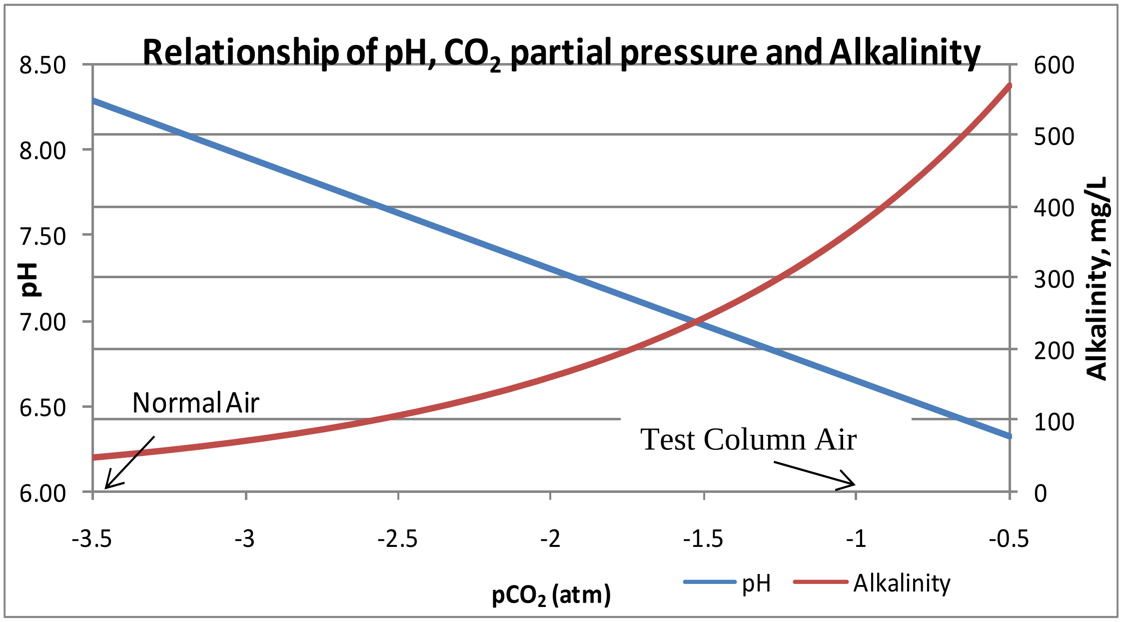


Figure 8-6. Effect of pCO2 on Alkalinity, pH and Calcium Carbonate Dissolution.

Figure 8-7 shows median alkalinity concentrations for the five samples over the 14 week test period. Three rocks BCS3-PA, KBF-WV and MKSS-PA produced significant alkalinity, with concentrations ranging from about 200 to 400 mg/L from weeks 4 to 14. These three rocks also produced leachates that were at saturation for the mineral calcite throughout the 14 week test (Figure 8-6). These samples were able to continuously dissolve the maximum amount of calcite that the water could hold during the test and are significant sources of acid neutralization in the test. The saturation index calculations are based on chemical equilibrium concepts, and are described in Appendix B of Draft Method 1627 document (2008). The computer code PHREEQCI (Parkhurst and Appelo, 1999) was used to calculate calcite and other mineral

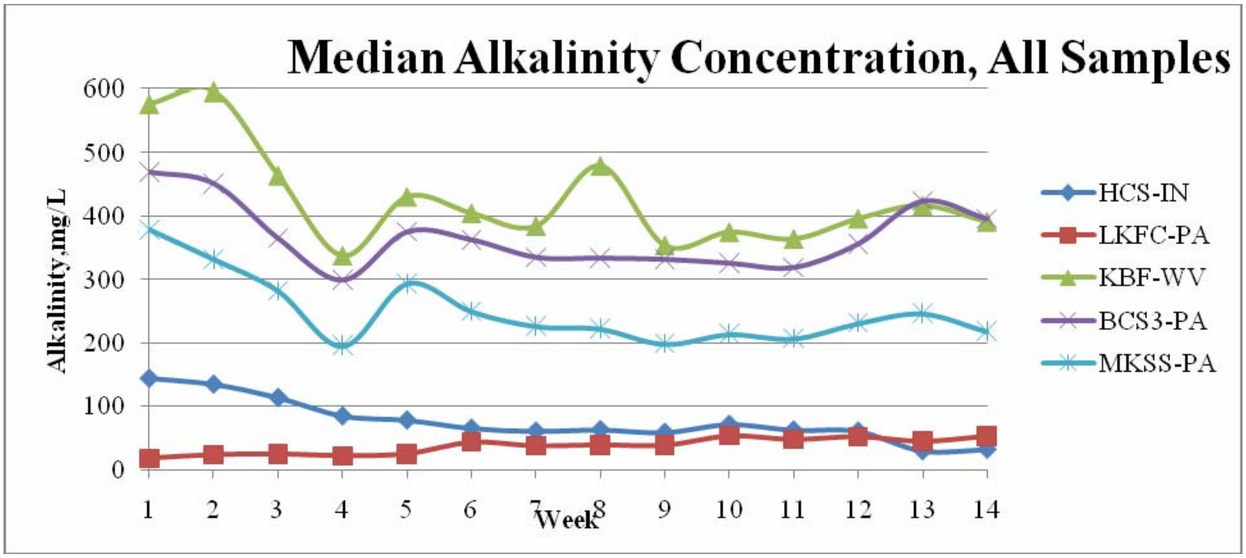


Figure 8-7. Alkalinity Concentration Weeks 1 to 14 for Five Rocks. Values are medians of all labs.

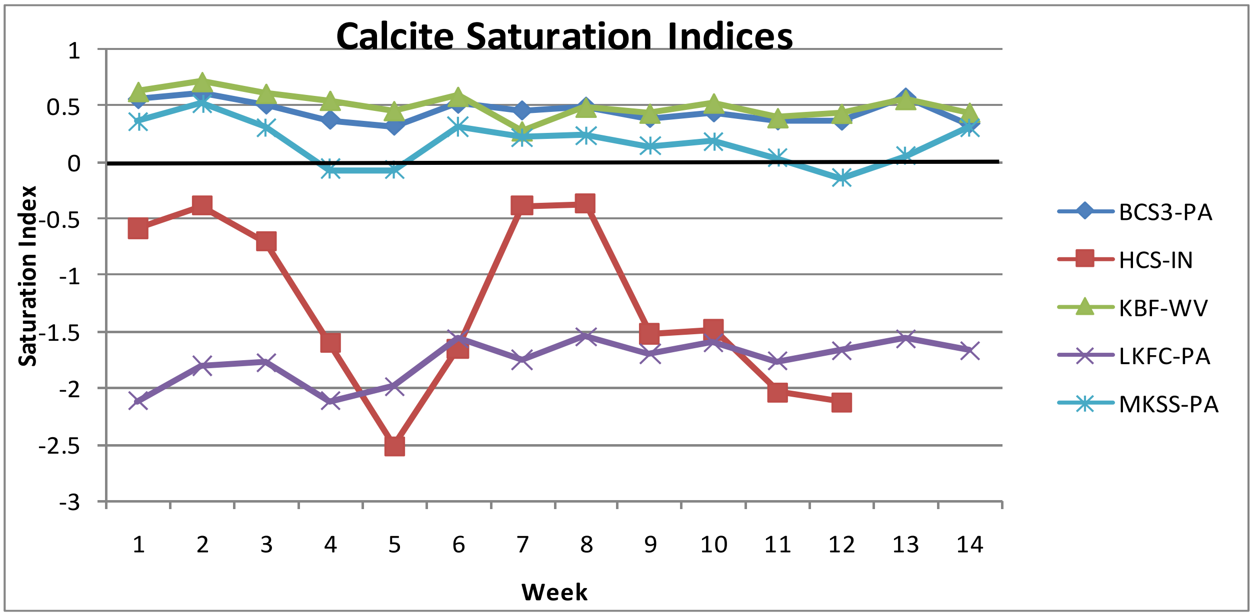


Figure 8-8. Calcite Saturation Indices Weeks 1 to 14 for Five Rocks. Values are medians of four labs.

saturation indices. Leachates with a saturation index value greater than zero are over-saturated and cannot dissolve more of that mineral. Leachates with saturation index less than zero are under-saturated and the mineral, if present, can dissolve, because the solution is holding less than the maximum. HCS-IN and LKFC-PA produced leachates that were under-saturated for calcite. These rocks have less significant sources of neutralization.

Sulfate Minerals

Gypsum ($CaSO_4$*2 H_2O) and other sulfate bearing minerals could influence the amount of sulfate in leachates. Gypsum was identified in sample HCS-IN (chapter 5). Gypsum saturation indices, calculated using PHREEQCI, are shown in figure 8-9. Sample HCS-IN is at approximate equilibrium for gypsum, indicating solubility of that mineral is likely controlling the amount of sulfate in solution. The other four rocks are under-saturated for gypsum, and have no gypsum solubility limitations on their leachate composition.

Sulfate concentration is often used as a surrogate estimate of acid production from pyrite. For samples like HCS-IN, where sulfate concentration may be limited by solubility controls, actual acid production may be greater than estimated. Other metal-sulfate minerals such as schwertmannite, the jarosite series, and jurbanite could also control the solution concentrations of sulfate and various metals. Mineral solubility constraints should be part of the evaluation scheme for leachate interpretation.

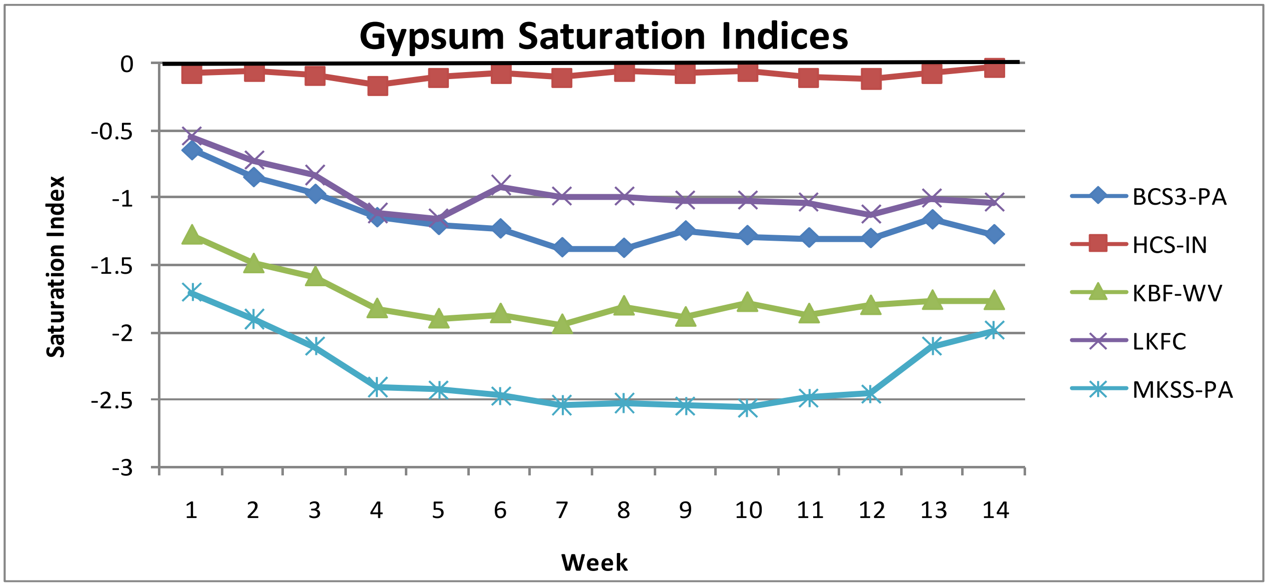


Figure 8-9. Gypsum Saturation Indices for Five Rocks. Values are medians of four labs.

Oxidation-Reduction

Oxidation reduction reactions can exert a strong influence on elements with more than one possible valence state. More than one potential valence state is possible for the elements iron(+2,+3), manganese(+2,+3,+6,-7) and selenium(-2,+4,+6). Their behavior can be estimated from the use of equilibrium calculations and graphically illustrated in Eh/pH diagrams. One laboratory measured the Eh, or oxidation reduction status of the weekly leachate samples, even though this was not a requirement of the test protocol. These data confirmed that oxidizing conditions existed, and allow equilibrium calculation of leachate speciation.

Figure 8-10 shows the distribution of iron species of week 14 leachates for the 5 rocks. Four of the five samples are in the stability field for the solid, poorly crystalline Iron Hydroxide, $FeOH)_3$(ppd). This is consistent with very low leachate iron concentrations, oxidizing conditions, generally low solubility of Fe (III) at circumneutral pH, and post leaching observations discussed in chapter 5. Soluble forms of iron are the preferred state for the acidic HCS-IN leachate. Cravotta (2008b) found that iron concentration in many mine waters is controlled by iron oxyhydroxides or hydroxysulfate minerals.

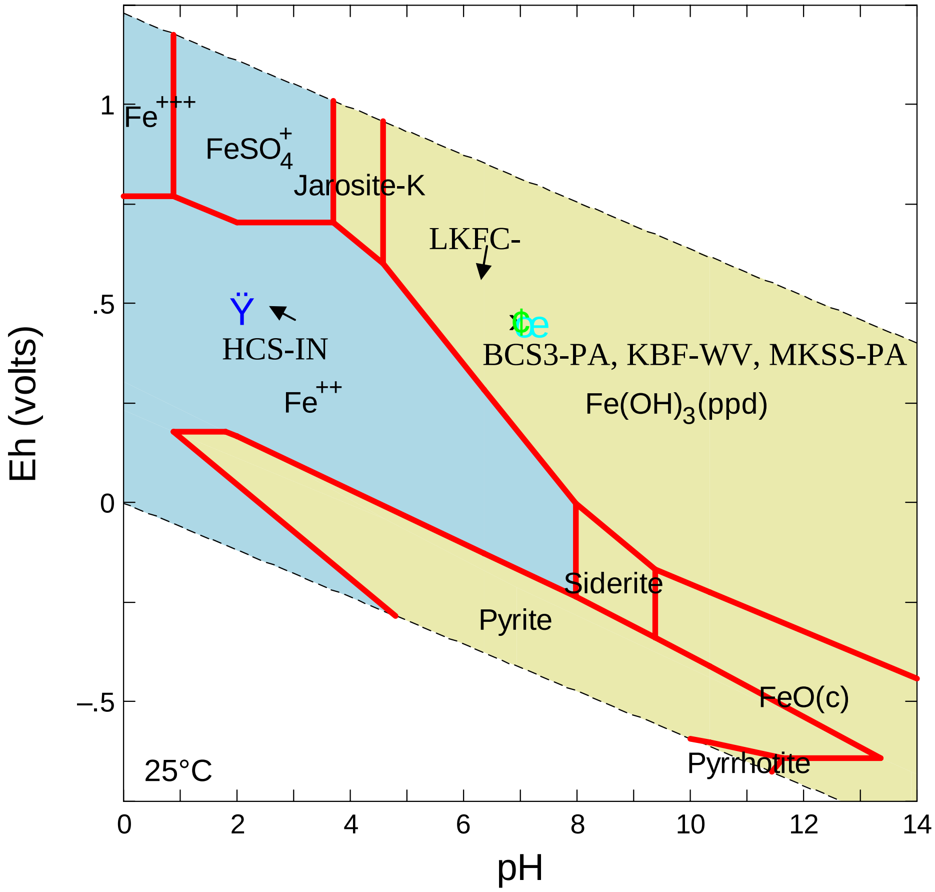


Figure 8-10. Eh/pH Plot of Selected Iron Minerals and Week 14 Leachates.

pH

pH is the principal solubility control for aluminum, and strongly influences the behavior of iron and other elements. Figure 8-11 shows aluminum solubility for leachates containing sulfate, potassium and silica at chemical activities representative of week 14 conditions. Aluminum solubility is at a minimum at about pH 6, and increases rapidly at pH conditions less than about 5. Aluminum solubility is controlled by alumino-silicates such as the clay mineral kaolinite, sulfate minerals such as alunite or others at low pH, and oxyhydroxides such as $Al(OH)_3$. Four of the five rocks produced leachates with pH between 6.1 and 7.2 and all contain kaolinite in the clay fraction. Aluminum concentrations were at or near detection for these rocks. The acidic conditions in HCS-IN leachate allow much higher concentration of soluble aluminum.

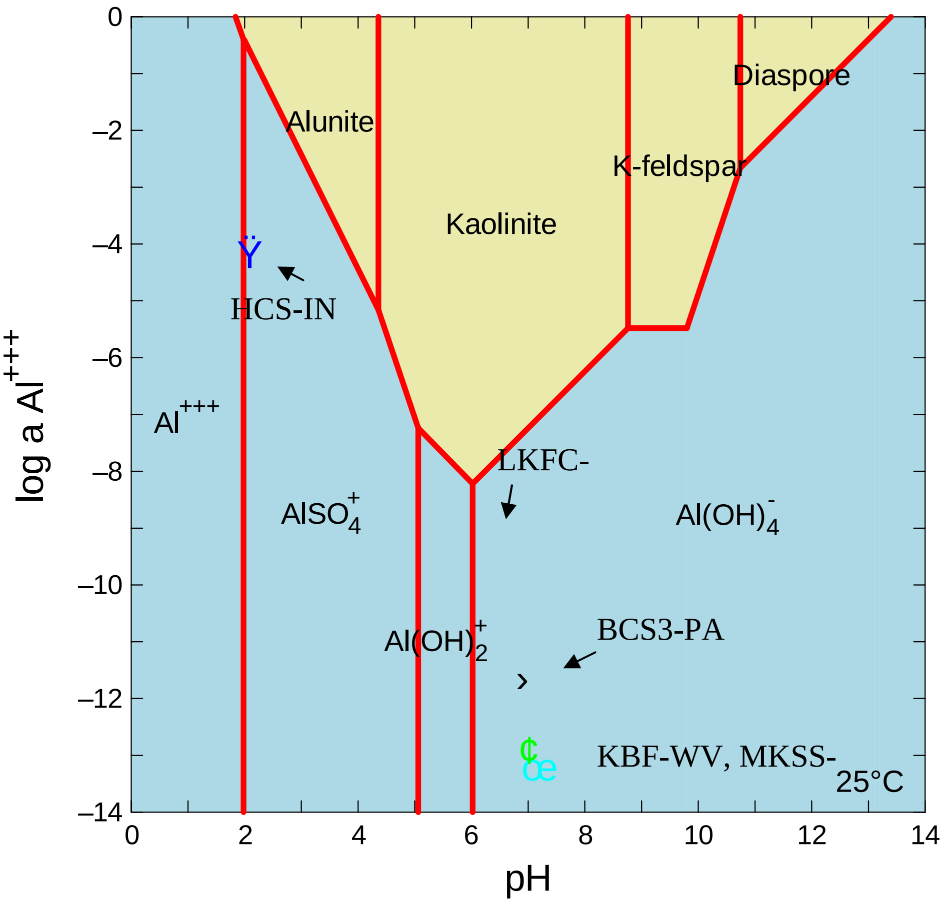


Figure 8-11. Aluminum Solubility as a Function of pH for selected Sulfate and Clay Minerals. Aluminum activity (y-axis) on log scale.

Weathering Rates

Chemical Concentration

Time series plots of chemical concentrations in the columns often exhibited curvilinear behavior. This behavior, which is observed in many chemical and biological systems, has been described using an exponential decay function of the general form:

$$C_t \;=\; C_o \text{ x } e^{-kt}$$

where: C_t = concentration at time t
C_o = concentration at time zero
e = base e, approximate value of 2.718
k = decay constant, rate of concentration change per unit time
= t t ime

The exponential changes with time in mine water chemistry are not, strictly speaking, decay processes, but are a rate of change with a mathematical description. The term decay is used for convenience in this chapter in the context of describing rate of change in column leachate chemical concentration. For chemical processes that follow a decay function, it is possible to estimate concentration values at different times, and provide some insight into longer term leachate composition. The decay function implicitly assumes constant conditions, and does not account for variations such as change in pCO_2 or other test variables.

Decay constants were calculated by plotting the ratio $\ln(C_t/ C_o)$ versus time. The slope of that plot, determined by linear regression, gives an estimate of k, the decay constant. Estimated k values for concentration change are shown in table 8-5, for calcium, sulfate, alkalinity, specific conductance as a surrogate for dissolved solids, and selenium, along with their R^2 values. The R^2 indicates the percentage of variation explained by the regression, and is shown in parentheses in Table 8-5. R^2 values approaching 100% show a strong relationship for estimating decay constants, while lesser values indicate a weaker association.

Calcium concentration decay was statistically insignificant for two rocks; HCS-IN and MKSS-PA. Both rocks have calcium solubility constraints; gypsum for HCS-IN, and calcite for MKSS-PA. For these two rocks, mineral dissolution was rapid enough to prevent significant change in calcium concentration during the 14 weeks of leaching. The remaining 3 rocks differ by about a factor of 4, with the slowest rate of calcium change in BCS3-PA. This rock had the largest carbonate content.

Table 8-5
Estimated Decay Constants for Calcium, Sulfate,
Alkalinity and Selenium Concentration, and Specific Conductance

Sample	Calcium(1)	Sulfate(1)	Alkalinity(1)	Specific Conductance(1)	Selenium(1)
BCS3-PA	-4.2×10^{-3}	-1.5×10^{-2}	-3.4×10^{-3}	-6.2×10^{-3}	-4.1×10^{-2}
	(48.3%)(2)	(73 %)	(41.4%)	(57%)	(89.6%)
HCS-IN	N.S. (3)	$+6.4 \times 10^{-3}$	-1.3×10^{-2}	$+ 1.0 \times 10^{-2}$	-2.4×10^{-2}
		(52.4%)	(82%)	(91%)	(94.5%)
KBF-WV	-1.7×10^{-2}	-3.7×10^{-2}	-4.8×10^{-3}	-5.5×10^{-3}	-5.0×10^{-2}
	(39%)	(89.4%)	(42.7%)	(66.6%)	(77.1%)
LKFC-PA	-1.0×10^{-2}	-1.2×10^{-2}	$+1.1 \times 10^{-2}$	-9.7×10^{-3}	-1.6×10^{-2}
	(75%)	(71.6%)	(83%)	(83.9%)	(91.6%)
MKSS-PA	N.S.	-2.0×10^{-2}	-6.2×10^{-3}	N.S.	-
		(78%)	(55%)		

(1) Constant in $^{-\text{day}}$. Calcium, Sulfate in mg/L. Alkalinity as $CaCO_3$Eq. Specific Conductance data in µmhos/cm. Selenium in µg/L.
(2) Values in parentheses are R^2 values, or percentage of variation explained by the regression
(3) N.S. = not significant.

Sulfate decay, like calcium, is on the order of 10^{-2}/day for 4 rocks. The larger R^2 values indicate a stronger relationship to the decay function for sulfate than calcium. The sulfate values are closely spaced within a factor of about 2.5, indicating very similar sulfate leaching behavior.

The + value for HCS-IN shows that sulfate concentration increased in this leachate, rather than decreased.

Alkalinity concentration decay is about 4 to 5 times less than for sulfate for 3 rocks (BCS3-PA, KBF-WV and MKSS-PA), suggesting that carbonate neutralization may persist longer than acid generation for these samples. Alkalinity decayed most rapidly in HCS-IN, as that sample ultimately produced acidic leachate. The + value for LKFC-PA reflects the increase in alkalinity in this leachate through time. The lowest R^2 values are associated with rocks whose leachates are at saturation for calcite, and may therefore not completely follow a simple time-concentration decay function.

Specific conductance values, representing dissolved solids concentration, are grouped within a factor of about 1.5 for three rocks. This suggests consistent leaching behavior, and the potential to estimate dissolved solids behavior for rocks with similar mineralogical composition. The “blank” sample, MKSS-PA, showed no significant decay in dissolved solids. This rock has the lowest specific conductance, and the highest content of quartz and other weathering resistant minerals. The + value for HCS-IN shows that dissolved solids concentration increased in this leachate through time.

Selenium decay values are within a factor of about 3, and had the highest R^2 values of any parameter in table 8-5. Like the conductance data, selenium decay suggests consistent and predictable behavior for this parameter. Decay was not estimated for MKSS-PA because of the number of non-detect readings.

Gzyl and Banks (2007) estimated decay constants to describe the rate of change in pH and sulfate concentration in flooding underground coal mines in Poland. They reported decay constants on the order of 3 to 5 x 10^{-3} per day, or about an order of magnitude slower than the column tests. Underground mine flooding is a different hydrologic regimen than the weekly flushing cycle of the column test protocol. However, the two data sets suggest that the column test does provide an accelerated chemical weathering cycle that represents field behavior on the order of at least a few years. The leaching column is intended to simulate surface mine conditions, however no comparable published decay constant values were found for surface mine-spoil.

Chemical Flux

Chemical flux or load leached each week was greatest during the first five weeks of weathering for most parameters. Thereafter, weekly flux declined slowly or remained near constant. Figure 8-12, weekly sulfate flux for sample BCS3-PA is typical of the observed leaching behavior. Week 1 flux exceeds 140 mg/Kg, but rapidly declined to about 40 mg/Kg by week 5, and to about 25 mg/Kg by the last week. The first five weeks may represent a rapid initial weathering and flush, followed by slower leaching, more representative of long term chemical weathering. Other major and trace elements generally displayed similar behavior. The rapid initial flux, followed by a slow decline is consistent with the authors’ unpublished data and collective experience with mine discharge behavior in the Appalachian region. The column leaching mimics field behavior.

The data plotted in Figure 8-12 exhibit a curvilinear behavior, suggesting that some type of log or exponential function can be fitted. Cumulative flux data were plotted and found to fit either a power or natural log functions of the general forms:

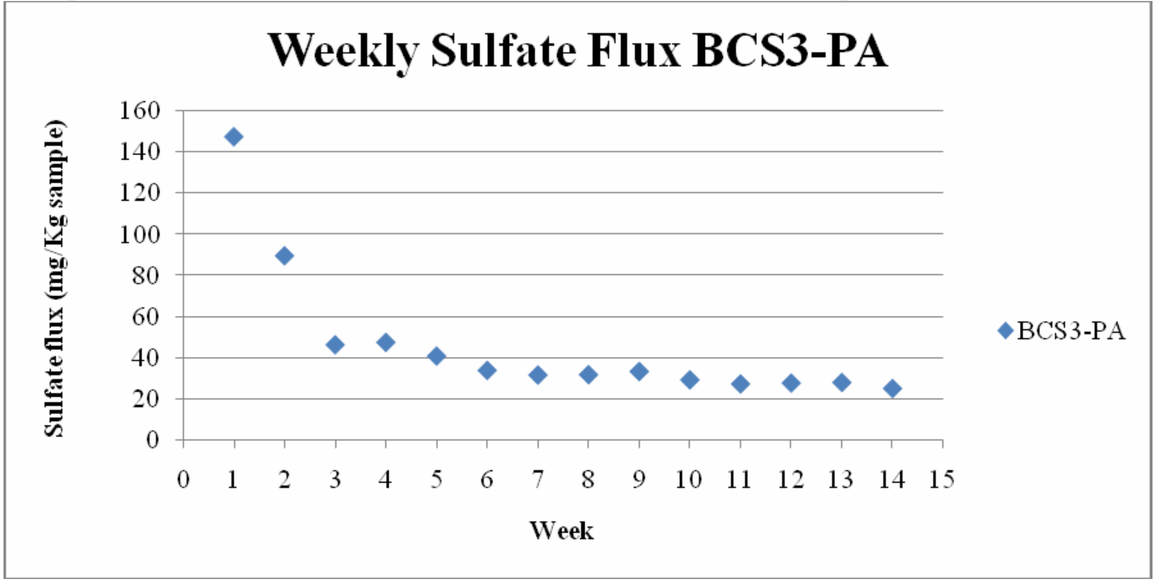


Figure 8-12. Weekly Sulfate Flux (mg/Kg sample) for BCS3-PA. Values are medians of all labs.

$$y = bx^{m} \qquad \text{(power)}$$
$$y = m*\ln(x) + b \qquad \text{(natural log)}$$

Figure 8-13 shows sulfate flux data for BCS-PA (same as figure 8-12) plotted on a cumulative basis with a fitted power function. Other samples and element flux data showed behavior similar to figures 8-12 and 8-13, and generally fit either a power or natural log function. The fit of these functions shows that element flux can be estimated; if leaching conditions are constant and mineral solubility influences are absent.

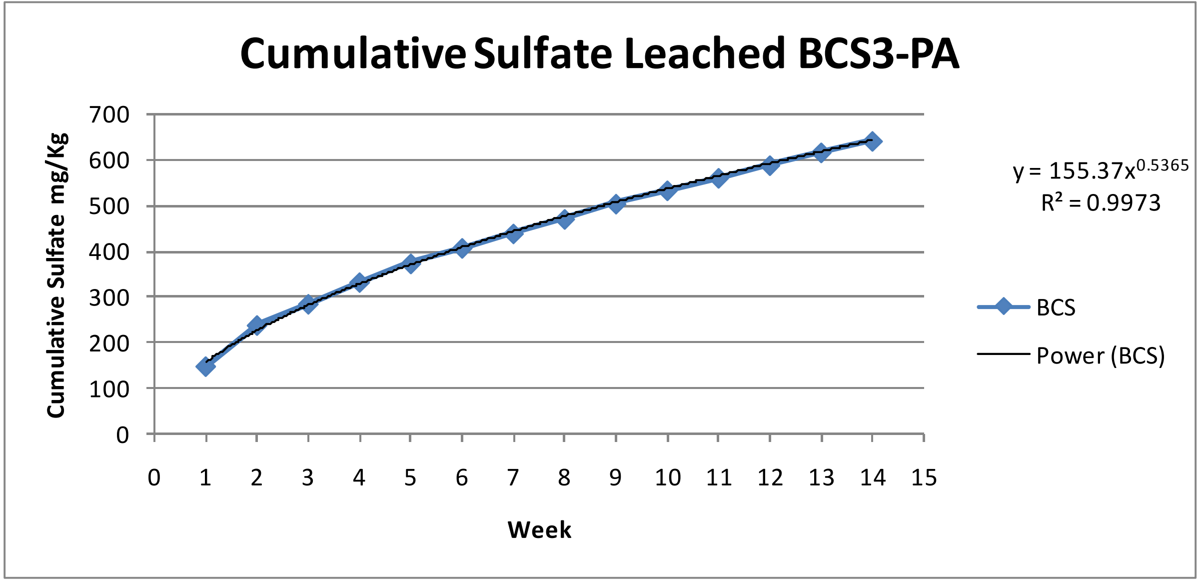


Figure 8-13. Cumulative Sulfate Leaching (mg/Kg sample), BCS3-PA. Values are medians of all labs.

Calcium flux data displayed a linear trend for four rocks (BCS3-PA, HCS-IN, KBF-WV, and MKSS-PA) that produced leachates saturated for calcite or gypsum. Only LKFC-PA, which was under-saturated for both calcite and gypsum, produced a log fit plot. Figure 8-14a and b shows the two types of cumulative plots. The linear plots exemplified by Figure 8-14a show that these rocks dissolve minerals containing the constituent element and leach at a constant rate. Elemental flux is constrained by mineral solubility. The curvilinear log or power function plots are typical of "shrinking core" models of rock weathering, where diffusion is an important leaching control. Plots of cumulative flux can provide insight into leaching mechanisms and constraints.

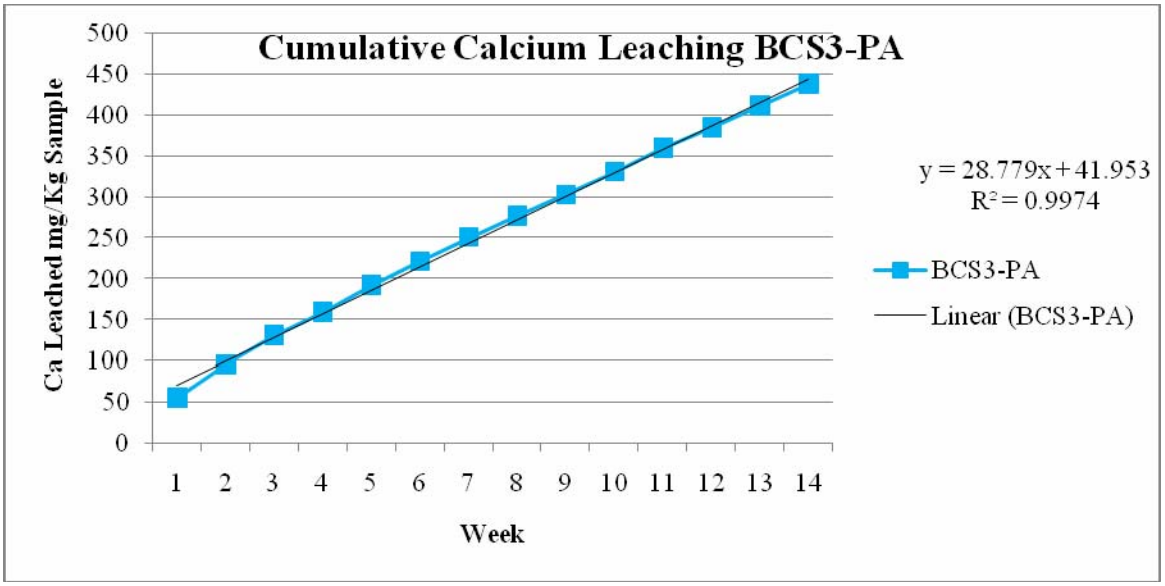


Figure 8-14a. Calcium Flux(mg/Kg sample), BCS3-PA with linear trend. Leachate is Calcite Saturated.

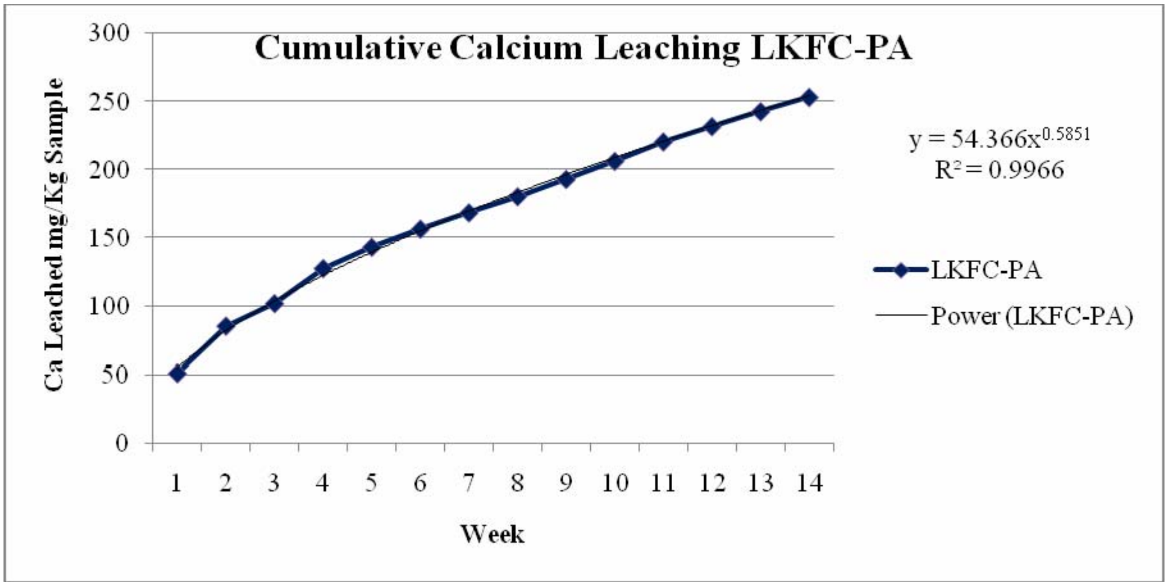


Figure 8-14b. Calcium Flux(mg/Kg sample), LKFC-PA. Leachate is Under-Saturated for Calcite.

Chapter Summary

The inter-laboratory study produced a large body of elemental leaching data that demonstrated the utility of the column leaching test. The five rocks produced leachates that:

- Had distinct chemical composition. The test discriminates among rocks of differing mineralogical make-up. Calcium and magnesium were the dominant cations, while sulfate and bicarbonate were the principal anions. The different leachate chemistries can be distinguished by graphical techniques like Durov, Stiff or trilinear (Piper) plots, or statistical methods.
- Weathered at different intensities on both a relative and absolute basis. Weathering intensity paralleled sulfur content. High sulfur rocks weathered most aggressively, while low sulfur rocks leached the least.
- Had significant alkalinity concentrations. The inclusion of pCO_2 of 0.1 atmospheres produced leachates more like that observed in field collected samples. One rock consumed all its alkalinity during the test and produced acidic leachate by week 14. Rocks with limited self neutralization capacity may be identified with the test. pCO_2 is a critical variable for simulating field conditions for alkalinity concentration.
- Had declining concentrations through time. Only HCS-IN concentrations increased during the test, after the sample began producing acidic leachate. Time dependent concentration trends were approximated by a natural log decay function for most elements. The decay equation, or other appropriate models, can be useful for estimating leachate chemical concentration chemistry through time. Alkalinity decay was slower than sulfate for most rocks, suggesting it will persist over acid generation in those samples. Laboratory decay values were about an order of magnitude greater than reported for flooding underground mines, suggesting that the column test does accelerate weathering over field conditions. No comparable decay data for surface mines was found.
- Leaching of minor and trace elements like zinc and selenium was similar to the major elements. Selenium behavior closely followed the natural log decay function, and concentrations declined significantly during the 14 week test.
- Produced the largest chemical fluxes in the first few weeks of the test. Thereafter, fluxes decreased slowly. Time dependent fluxes were well described by power function or natural log regression models. Chemical flux behavior can be estimated through time. The curvilinear models are similar to the behavior expected from “shrinking core” weathering models where diffusion controls leaching.

Cumulative calcium chemical fluxes, unlike most other parameters, produced linear time dependent plots. This behavior is attributable to soluble calcite and gypsum maintaining solution concentrations of calcium. The shape of the plot can give insight into the mechanisms influencing leachate chemistry.

Four of five rocks produced circumnutral pH leachates with very low concentrations of soluble aluminum and iron. The results are consistent with pH and redox behavior of the elements. Only the acidic HCS-IN leachate contained appreciable iron and aluminum. The lack of soluble metals does not necessarily indicate non-weathering of iron and aluminum bearing minerals. Information in Chapter 5 showed the formation of secondary minerals within the columns. Calcite, gypsum, other metal sulfates and metal oxyhydroxides may influence the leachate behavior of various elements. Mineral and element solubility properties should be part of any interpretive scheme for leaching test data.

MS1-Kincom2

Chapter 9. Strengths and Weaknesses of Acid-Base Accounting Data

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

History and Development of the Acid-Base Accounting (ABA) Technique

Much has been written in the past 30 years on the development, applications and interpretation of the ABA method of mine drainage prediction, but for purposes of this report, most of it can be summarized from several chapters by Kania (1998a), Perry (1998) and Skousen et al., (2000) in two familiar books on mine drainage prediction, while additional information on the relationship of ABA to other prediction techniques is also found in chapters by Kania (1998b) and Perry (2000) in the same books.

Acid-Base Accounting was developed at West Virginia University by Richard M. Smith and co-workers (Skousen et al., 1990). The approach grew from early attempts at classifying mine spoils for revegetation potential, based principally on acidity or alkalinity, and rock type. From these broad classifications, the need for lime and suitability for plant species could be assessed. For example, the Neutralization Potential (NP) component of ABA was adapted from the work of M.L. Jackson (1958) as a measure of lime requirements for soil chemical analysis and plant growth.

According to Kania (1998, p. 6-1):

> Laboratory methods for performing acid-base accounting overburden analysis (ABA) have been thoroughly detailed in previous publications. Sobek et al., (1978) formally presented a step-by-step laboratory protocol for performing ABA on mine overburden and is frequently cited as the source document. However, earlier publications described the application of ABA principles to mine overburden testing (West Virginia University, 1971; Grube et al., 1973; Smith et al., 1974; Smith et al., 1976).… ABA is based on the premise that the propensity for a site to produce acid mine drainage can be predicted by quantitatively determining the total amount of acidity and alkalinity the strata on a site can potentially produce.

ABA, as originally developed, consists of measuring the acid generating and acid neutralizing potentials of a rock sample. These measurements of Maximum Potential Acidity (MPA) and Neutralization Potential (NP) are subtracted to obtain a Net Neutralization Potential (NNP), or net Acid-Base balance for the rock as follows in equation 9.1:

$$\text{Net Neutralization Potential (NNP)} = NP - MPA \qquad (9.1)$$

The results are customarily reported in tons per thousand tons of overburden or parts per thousand…

The measurements and calculations of NP, MPA, and NNP are based on the following assumed stoichiometry (Cravotta et al., 1990):

$FeS_2 + 2CaCO_3 + 3.75O_2 + 1.5H_2O \rightarrow$ (9.2)
$2SO_4^{2-} + Fe(OH)_3 + 2Ca^{2+} + 2CO_2$

For each mole of pyrite that is oxidized, two moles of calcite are required for acid neutralization. On a mass ratio basis, for each gram of sulfur present, 3.125 grams of calcite are required for acid neutralization. When expressed in parts per thousand of overburden, for each 10 ppt of sulfur (equal to 1 percent sulfur content) present, 31.25 ppt of calcite is required for acid neutralization.

Cravotta et al., (1990) noted that the stoichiometry in Equation 9.2 is based on the exsolving of carbon dioxide gas out of the spoil system. They suggested that in a closed spoil system, carbon dioxide is not exsolved, and additional acidity from carbonic acid is generated. Cravotta et al., (1990) proposed that up to four moles of calcite might be needed for acid neutralization as follows:

$FeS_2 + 4CaCO_3 + 3.75O_2 + 3.5H_2O \rightarrow$ (9.3)
$2SO_4^{2-} + Fe(OH)_3 + 4Ca^{2+} + 4HCO_3$

The stoichiometry of Equation 9.3 shows that twice as much calcite would be required for acid neutralization. On a mass basis, for each 10 ppt of sulfur present, 62.5 tons of calcite is needed for acid neutralization in one thousand tons of overburden. (from Perry (1998) p. 11-2).

Some problems with the literal interpretation of some ABA results are described in Perry (1998) and Hornberger and Brady (1998). For example, the MPA is a surrogate measure of potential acidity based on total sulfur present, rather than an actual acidity concentration, and the NP test is a surrogate measure of potential alkalinity, based upon estimated calcium carbonate content, rather than an actual alkalinity concentration. Therefore, there may be some missing elements in the direct comparison of potential acidity and potential alkalinity, including kinetic factors in the mine drainage chemistry.

Modifications and Improvements to Acid-Base Accounting Procedures

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 potential for the presence of the carbonate mineral siderite to produce misleading alkalinity predictions in mine drainage has been recognized for about 40 years in a series of publications including Barnes and Romberger (1967), Meek (1981) and Morrison et al., (1990).

According to Skousen et al., (2000, p. 82):

> Siderite ($FeCO_3$), when present in the overburden, reacts quickly with HCI in the standard NP procedure in ABA and falsely indicates that the rock will behave as a net alkaline contributor after weathering (Cargeid, 1981; Morrison et al., 1990; Wiram, 1991). Continued weathering of $FeCO_3$ actually produces a neutral (Meek, 1981; Shelton et al., 1984) to slightly acid solution (Cravotta, 1991; Doolittle et al., 1992; Frisbee and Hossner, 1989). If insufficient time is allowed for complete iron oxidation and precipitation of ferric hydroxide during back titration, erroneously high NP values can be generated on samples containing $FeCO_3$, yielding misleading NP information. Such an analytical oversight can lead to incorrect post-mining water quality predictions and produce costly, long-term reclamation liabilities (Wiram, 1992).
>
> Meek (1981) and Morrison et al., (1990) suggested adding a small quantity of 30% H_2O_2 to the filtrate of an overburden sample to oxidize ferrous iron to ferric iron before back-titration is initiated. Leavitt et al., (1995) proposed a modified NP procedure that includes boiling a 2-gram overburden sample for 5 minutes after the acid is added, filtering the suspension, and adding 5 ml of 30% H_2O_2, then boiling for an additional 5 minutes. Significant reductions in NP values were found for $FeCO_3$ samples using the modified NP method compared to the standard Sobek et al., (1978) method (Table 4.4, Skousen et al., 1997). Variations in NP determinations among laboratories were also dramatically reduced by using this modified method compared to the standard NP method on $FeCO_3$ samples (Table 4.5) (p. 83).

Magnitude of the siderite effect on NP is strongly influenced by mineralogy. Skousen et al., (1997) classified their samples as Fe rich, Ca rich, S rich and Si rich rocks. The Fe rich rocks had the largest change in NP when siderite was accounted for by modified test methods. The sulfur rich rocks also showed a significant decline in NP when analyzed by modified test methods. This may result from more complete oxidation of soluble Fe in the modified test. High grade limestones (Ca rich group) showed little change in NP, since their neutralizing value is derived mainly from calcite. Si rich rocks with a high proportion of clay mineral and quartz showed some decline in NP when subjected to the modified test method.

Skousen et al., (1997) essentially solved the siderite interference problem. It is unfortunate that many commercial laboratories do not use the improved NP procedures, because they are either unaware of the modification, or they have not received technical guidance or requirements from regulatory agencies to implement the modified 1997 NP method. Concerning the problems with fizz ratings, Skousen et al., (2000, p. 84) state:

> Fizz ratings are done to asses the relative amount of carbonate present in a rock sample, which are then used to determine the amount and strength of acid to use in the NP digestion process. Conflicting NP values were found when overburden samples were assigned different fizz ratings and thereby

> digested in different amounts of acid (Table 4.6) [Skousen et al., 1997, Table 4.6]. At higher fizz ratings (more acid added), the NP values increased substantially. Since the subjective fizz rating was not found to be repeatable among laboratories and not reflective of the carbonate content of a rock, a quantitative and repeatable method to determine carbonate content was proposed (Skousen et al., 1997). The method uses the percent insoluble residue after acid digestion to assign a carbonate rating (Table 4.7) [Skousen et al., 1997, Table 4.7], and has been found to accurately determine the amount and strength of acid to add for NP determination.

The fizz rating problems described in Skousen (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 insoluble residue/carbonate rating step in the revised NP method described in Skousen et al., (1997, 2000) would essentially resolve these fizz rating problems. It is unfortunate that most commercial laboratories doing ABA work have not adopted this NP method improvement, reportedly due to cost increases in conducting the ABA test methods. The cost increases are no doubt a real factor which can be quantified, but the relative costs to the mining industry and regulatory agencies in using inaccurate and imprecise NP data cannot be underestimated or overlooked.

Basic Usefulness of ABA Data in Typical Mine Drainage Prediction Work

ABA is the most commonly used mine drainage prediction method used in Pennsylvania, West Virginia and other states in surface mining permit reviews, and ABA or some use of its components (i.e. NP) has worked relatively well in correctly predicting mine drainage quality. ABA and mine drainage quality relationships have been evaluated in Pennsylvania and northern Appalachia in studies by Brady et al., (1994), Perry and Brady (1995) and diPretoro and Rauch (1998) which are all summarized in Perry (1998). Skousen et al., (2002) also reported a comparison of ABA and water quality data for mines in West Virginia.

In addition, a detailed evaluation of mining permitting from 1987 to 1996 in Pennsylvania was performed as a post mortem study of permits resulting in acid mine drainage. It is contained in Smith et al., (2000) and a PA DEP report by the same title, dated March 1999. That study showed that only one percent of the 1,699 permits issued in that 10 year period resulted in post-mining water quality problems precluding bond release. The high level of success in preventing AMD was attributed to advances in the science of prevention and prediction, which included the use of ABA data. However, of the 50 sites where detailed post mortem reviews were performed, 17 sites had post-mining AMD liability. This was attributed to:

- inadequate information in the permit application on which to make a sound judgment and;
- interpretation error in issuing the permit if viewed in the context of the state of improved prediction knowledge at the time of the post mortem study.

While ABA data have been found to be very useful in mine drainage prediction work in many cases, as described above, a major problem occurs in what is referred to as the “gray zone” or the “uncertain zone” as shown on Figure 9.1 and in Geidel et al., (2000). In comparing NP values to

MPA values in this figure and the accompany text, Geidel et al., (2000) use this concept as some criteria for determining whether to conduct kinetic testing. Nevertheless, ABA should still be used as a primary mine drainage prediction tool, and as a companion, screen or precursor to kinetic tests like the ADTI-WP2 Leaching Column Method.

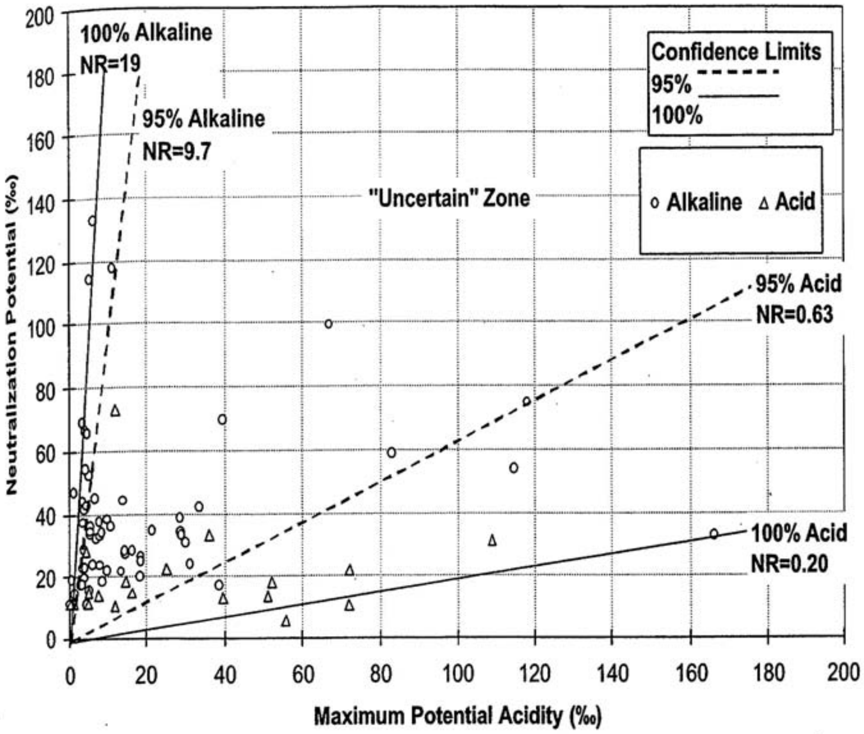


Figure 9.1 The “Gray Zone” of NP and MPA (from Geidel et al., 2000)

Problems with the Neutralization Potential and Total Sulfur Data used in the Interlaboratory Study

The five rock samples used in the ADTI-WP2 interlaboratory validation study have been described in preceding chapters of this report. The total sulfur and neutralization potential data for the original rock splits used to confirm homogenization of the large sample volumes were generated by a single laboratory using the standard and modified method for NP. Subsequently, splits were sent to the eight participating laboratories. The initial characterization and splits analyses are summarized in Tables 9.1 through 9.4 and Tables 9.8 through 9.12. Some significant and troubling variation in results were observed. These problems do not imply that this overall study of leaching column performance and related mineralogical and kinetic interpretations is seriously flawed. However, these data tables demonstrate that there may be significant accuracy and precision problems with conventional ABA data that are used in many mining permit applications. These findings lead to legitimate questions on the usefulness of some portion of conventional (i.e. 1978) ABA method data in routine mine permitting, and also strongly encourage the full implementation of the improved 1997 NP method, and perhaps further improvements in ABA testing procedures.

Summary ABA data for the Brush Creek Shale samples are shown in Table 9.1. Detailed data for all splits and replicates are included in Table 9.8.

Brush Creek Shale

The summary test results for the Brush Creek shale are shown in Table 9.1 and the raw data are in Table 9.8. The first four splits (i.e. 2, 6, 10 & 15) are the original randomly selected splits tested on July 14, 2005 to confirm the homogenization of the large volume of rock sample, which totaled about 25 buckets of five-gallon size. These four splits are very consistent in percent total sulfur, NP by the original 1978 method and by the revised 1997 method. The most remarkable observation of these original splits is that the NP values by the revised method are approximately half the magnitude of the 1978 method, presumably due to siderite interference or other factors related to the carbonate mineralogy. The big problems with this data set come in the subsequent testing and retesting of the splits sent to the participating labs. For example, original split 15 was sent to Lab 2 where the unweathered sample tested on January 19, 2005 had an NP of only 37.7 and the weathered material from the end of the leaching test had NP's of 91.09 and 96.47 from the two columns.

Table 9.1 Brush Creek Shale Summary ABA Data

Sample Treatment		N	%S			NP		
			Min	Mean	Max	Min	Mean	Max
BCS3-PA	Initial Standard NP	4	0.56	0.58	0.59	96.96	96.97	96.98
BCS3-PA	Initial Modified NP	4	0.56	0.58	0.59	47.07	48.42	49.68
BCS3-PA	Splits Before Leaching	6	0.59	0.63	0.75	21.13	44.66	89.30
BCS3-PA	Splits After Leaching	25	0.44	0.59	1.09	3.99	57.43	106.05

Overall the total sulfur percentages in the splits at the various labs are much more consistent than the NP values, but some unweathered splits have greater sulfur content than the weathered samples (i.e. Labs 3, 5 and 7) as would be expected, but some weathered material had higher sulfur values than the unweathered sample (i.e. Lab 2). Some differences in sulfur content by particle size were also observed with the fines having the higher sulfur values, as expected, at Lab 1 and in Column 1 at Lab 6.

The most troubling aspect of this Brush Creek data set is the tremendous variation in NP values, (as shown in Table 9.8), which appears to be related to differences in fizz ratings on the splits of the same homogenous sample, tested on different dates, and maybe not by the same lab analyst. The unweathered splits at the participating labs range from 21.13 (Lab 5) to 89.30 (Lab 4) and the fizz ratings of the entire Brush Creek data set range from 0 to 3. There is no consistency to the unweathered and weathered sample fizz ratings, for example in Labs 3 and 4, where the unweathered samples have lower fizz ratings than the weathered samples. In summary, no lab shows weathered NP values consistently lower than the unweathered sample, as would have been expected.

Houchin Creek Shale

Of the four shale samples used in the study, the Houchin Creek shale has the highest sulfur content. This shale sample was collected from a surface mine in Indiana by OSM staff from the Mid Continent office. The summary ABA data are contained in Table 9.2 and the raw data are found in Table 9.9. The first four samples in Table 9.9 are the original splits from the homogenization of the large sample volume. The sulfur and NP values for these four samples are consistent, but with two curiosities: Split 16 has a sulfur content about a half a percent less than the other three splits, and three of the four NP values from the revised 1997 method are slightly higher than those for the original method. In most of the labs, except Lab 2, the weathered samples from the columns have less sulfur than the unweathered samples, as would be expected. There is also a large variation in sulfur content by particle size classes in Lab 6, with the fines having the highest sulfur, as reported in previous studies.

The unweatherd NP values of the splits sent to the participating labs are only about half the magnitude of the original splits, and all of these fizz ratings are 0. The most encouraging element of this NP data is that the weathered NP values are substantially less than their unweathered counterparts, reflecting a loss of NP due to the weathering of the samples during the leaching column study.

Table 9.2 Houchin Creek Shale Summary ABA Data

Sample Treatment		N	%S			NP		
			Min	Mean	Max	Min	Mean	Max
HCS-IN	Initial Standard NP	4	4.73	5.08	5.27	41.29	44.14	47.53
HCS-IN	Initial Modified NP	4	4.73	5.08	5.27	41.05	45.54	48.27
HCS-IN	Splits Before Leaching	6	4.93	5.25	5.53	19.61	23.52	26.53
HSC-IN	Splits After Leaching	25	2.99	4.70	5.98	-17.82	13.96	34.69

Kanawha Black Flint Shale

The Kanawha Black Flint shale sample was collected from a roadcut near Charleston, WV in a terrain where selenium concentrations were a concern. However, this rock sample has relatively low total sulfur content and relatively low NP, as shown in Tables 9.3 and 9.10. These types of ABA analyses are sometimes difficult to interpret. The original splits from the homogenization of the sample, tested on June 24, 2005 have relatively consistent sulfur contents and NP values, as shown in Table 9.10, except for the 0.21 percent sulfur in Split 11. The NP values by the 1997 method are slightly lower than the 1978 method values in these 4 splits, as might be expected. The original Split 4 was used by Lab 4 in the weathering study and was retested to have 0.11% less sulfur than the original. Original Split 11 was sent to Lab 2 for the weathering study, and upon retesting the unweathered split is only 0.03% different from the original test value. However, the sulfur contents of the weathered material from both leaching columns had higher sulfur contents than the unweathered sample as shown in Table 9.10. It is curious that the sulfur contents of all of the particle size classes from the two columns at Lab 6 are only about one third to one half of the sulfur contents of the original splits, indicating a greater degree of weathering than at most of the other labs.

With this rock sample, there are again numerous inconsistencies and questions about the NP values and fizz ratings. Many of the unweathered and weathered samples from the participating labs are considerably higher to several times higher than the original homogenization splits. Also, there is one anomalous weathered sample from Lab 5 with an NP of 315.62 and a fizz rating of 2. The other fizz ratings in Table 9.10 are about evenly divided as 0 or 1.

Finally, one observation of the NP values is that the weathered NP values for numerous labs (Labs 3, 4, 7 and 8) especially Lab 4, are considerably less than the unweathered samples from these labs.

Table 9.3 Kanawha Black Flint Shale Summary ABA Data

Sample Treatment		N	%S			NP		
			Min	Mean	Max	Min	Mean	Max
KBF-WV	Initial Standard NP	4	0.21	0.30	0.35	15.17	16.95	18.69
KBF-WV	Initial Modified NP	4	0.21	0.30	0.35	13.17	13.61	14.26
KBF-WV	Splits Before Leaching	6	0.24	0.27	0.39	14.05	18.56	21.49
KBF-WV	Splits After Leaching	24	0.05	0.17	0.31	10.62	37.77	315.62

Lower Kittanning Shale (LKFC-PA)

The Lower Kittanning shale from the Falls Creek site exhibits consistency in the sulfur and NP values of the original homogenization splits in Tables 9.4 and 9.11, however, 3 of the 4 NP values from the 1997 method are slightly higher than those from the 1978 method. Split 3 from the original July 14, 2005 tests was weathered in Lab 4, and the retested unweathered sample had an almost identical sulfur content, but a slightly higher NP. The unweathered sulfur contents for Labs 3, 4, 5, 7 and 8 were higher than the weathered samples from the leaching columns, as would be expected, especially in the samples from Lab 7. However in the particle size classes shown for the two columns at Lab 6, the highest sulfur contents are not in the fines.

This Lower Kittanning shale sample has the most consistent and reasonable NP values of the five rock samples shown in Tables 9.8 through 9.12. For example, the weathered NP samples from the columns at Labs 3 and 4 are less than the unweathered sample NP values, especially at Lab 4. The fizz ratings are also consistent, as they are all 0, even within the different particle size classes.

Table 9.4 Lower Kittanning Shale Summary ABA Data

Sample Treatment		N	%S			NP		
			Min	Mean	Max	Min	Mean	Max
LKFC-PA	Initial Standard NP	4	0.89	0.91	0.93	12.41	13.54	16.47
LKFC-PA	Initial Modified NP	4	0.89	0.91	0.93	15.63	15.93	16.36
LKFC-PA	Splits Before Leaching	6	0.88	0.98	1.13	9.58	12.84	17.20
LKFC-PA	Splits After Leaching	25	0.63	0.84	1.17	4.83	12.94	17.18

This Lower Kittanning shale sample was collected from an active surface mine highwall in the Redbank Creek Watershed in Jefferson County, Pennsylvania. ABA data are available in the DEP public files for this site and adjacent sites in the watershed. Fortunately (through the assistance of Joe Tarantino and Tim Gillen from the DEP Knox Office), the overburden analysis data was compiled and some field water quality data were available to compare to the ABA and leaching test data from this project. In one overburden drill hole for the Falls Creek mine site the total sulfur of the shale overlying the coal as 0.93% with an NP of 9.70 which is very similar to the data in Tables 9.4 and 9.11. In another drill hole from this mine site the overlying shale had sulfur contents of 4.32, 1.84 and 1.10% with NP values of 1.0, 3.75 and 4.75 respectively. In overburden drill holes from adjacent mine sites the Lower Kittanning shale had total sulfur of 1.70% (NP = 17.15) and 0.95% (NP = 12.64), as shown in Table 9.5.

Table 9.5
Sulfur and NP Content of Lower Kittanning Shale Field Site

Location	%S	NP
Falls Creek Mine	0.93	9.7
Falls Creek Mine	4.32	1.0
Falls Creek Mine	1.84	3.75
Falls Creek Mine	1.10	4.75
Adjacent Mining	1.70	17.15
Adjacent Mining	0.95	12.64

Some field water quality data was also available in the public file and is summarized in Table 9.6. The mine site named the “Roy Mine” is the Falls Creek Energy Co., Inc. permit where our LKFC-PA shale sample was collected. An Original Fuels, Inc. site located 3,000 feet north of the Roy Mine has a post-mining discharge from the toe of spoil. The discharge monitoring data from 19 water samples collected from December 1999 to May 2006 are summarized in Table 9.6. Alkalinity exceeded acidity in all 19 samples and the median alkalinity is 108 mg/l while the median acidity is 11 mg/l. The spoil discharge quality in Table 9.6 is a product of leaching the Lower Kittanning shale and other rocks disturbed by mining. However, the overall field water quality displays characteristics similar to the column leach results, with the exception of iron. The field concentrations of Fe are greater than in the leach column.

Table 9.6 Postmining Spoil Water Quality From the Lower Kittanning Shale Sample Site(1)

Sample	Flow (gpm)	pH	Acidity	Alkalinity	Iron	Manganese	Aluminum
Post mining Minimum	0.3	5.7	0	62	6.99	22.6	<0.5
Post mining Maximum	0.8	6.8	89	258	24.3	52.9	0.66
Post mining Median			11	108			

(1) pH in S.U, Acidity and Alkalinity in mg/L $CaCO_3$ Eq, all others in mg/L.

Middle Kittanning Sandstone

The Middle Kittanning sandstone was known to have negligible sulfur content and relatively low NP, and hence was selected to serve as a “blank” in this interlaboratory study. The summary ABA data are contained in Table 9.7 and the raw data are found in Table 9.12. The first four splits in Table 9.12 were from the homogenization of the sample tested on January 16, 2003, and are relatively consistent in sulfur percent and NP. The highest sulfur content in Tables 9.7 and 9.12 is 0.15 and many of the unweathered and weathered samples are less than 0.10 percent. The only odd observation of the sulfur contents is in Lab 2 where the weathered sample had 0.15 percent, which is greater than the unweathered sample at 0.05 percent, and not plausible. In most cases there was little difference between the sulfur contents of the unweathered and weathered samples, or the different particle size classes. However, in Lab 7 the unweathered sample had 0.11 percent and the weathered sample had only 0.06 percent sulfur, indicating that about half of the sulfur was removed by weathering in the leaching column. The modified NP test was not done on these sample splits.

Table 9.7 Middle Kittanning Sandstone Summary ABA Data

Sample Treatment		N	%S			NP		
			Min	Mean	Max	Min	Mean	Max
MKSS-PA	Initial Standard NP	4	0.03	0.07	0.11	14.30	19.37	24.58
MKSS-PA	Splits Before Leaching	6	0.05	0.09	0.11	8.10	22.55	44.52
MKSS-PA	Splits After Leaching	16	0.02	0.09	0.15	0.00	31.30	72.25

The NP and fizz ratings for this relatively inert sandstone are very inconsistent and vary in ways that are not readily explainable. For example, original Split 2 was used in Lab 8 and when retested, the unweathered sample had less than half the NP of the original split. The fizz ratings range from 0 to 2, and the highest NP for the coarse size class at Lab 1 is 72.25, with a fizz rating of 1. The samples from Lab 5 show the biggest rational difference of NP depletion due to weathering, where the unweathered sample has an NP of 44.52 and the weathered sample has a NP of 12.77, but the NP of that unweathered sample is more than twice the magnitude of the original homogenization splits. Conversely, the unweathered sample used in Lab 3 had an unweathered NP of 8.10 when tested on January 24, 2006, and a weathered NP of 26.85 at the conclusion of the leaching column study when tested on May 4, 2006.

Summary and Conclusions

The ABA data discussed in this chapter show major differences in the total sulfur content and neutralization potential (NP) of the five rock samples used in the interlaboratory validation study of the ADTI-WP2 leaching column method. However, the problems with the NP and fizz rating data, in particular, and some of the total sulfur data demonstrate:

- the use of the conventional ABA method is not an exact science, and interpretive skills are still necessary to utilize ABA data for prediction,
- that the improved NP method should be fully implemented including the use of the insoluble residue test in place of the subjective fizz ratings,
- and that static test methods (e.g. ABA) need to be augmented by kinetic test methods in some cases to get better measures of expected acidity, alkalinity and metals concentrations and fluxes, and other relevant mine drainage data.

The difficulties noted with obtaining reproducible NP analysis are serous enough to affect the reliability of mine drainage quality prediction.

Supplemental Raw Data Tables

The raw data used in constructing Tables 9.1, 9.2, 9.3, 9.4 and 9.7 are contained in the following tables.

Table 9.8 Test results for Brush Creek Shale.

Rock Samples for ADTI-WP2 Interlaboratory Study							
Rock ID	**Split**	**Lab No. / Col No.**	**Total Sulfur %**	**NP (1978)**	**NP (1997)**	**Test date**	**Partical Size/ notes**
BCS3-PA	2		0.59	96.97	49.68	7/14/2005	original splits
BCS3-PA	6		0.59	96.96	49.31	7/14/2005	original splits
BCS3-PA	10		0.56	96.98	47.61	7/14/2005	original splits
BSC3-PA	15		0.59	96.97	47.07	7/14/2005	original splits
BSC3-PA		1 - unw					
BCS3-PA		1	0.64	78.67		6/30/2006	composite fizz 2
BCS3-PA		1	0.68	106.05		6/30/2006	3/8 to #4 fizz 2
BSC3-PA		1	1.09	55.03		6/30/2006	<#60 fizz 2
BCS3-PA	15	2 - unw	0.59	37.7		1/19/2006	
BCS3-PA	15	2 - 1	0.64	91.09		4/27/2006	fizz 3
BCS3-PA	15	2 - 2	0.61	96.47		4/27/2006	fizz 3
BCS3-PA	9	3 - unw	0.75	35.62		1/24/2006	fizz 1
BCS3-PA	9	3 - 1	0.67	48.64		5/4/2006	fizz 3
BCS3-PA	9	3 - 2	0.67	88.81		5/4/2006	fizz 3
BCS3-PA	14	4 - unw	0.60	89.30		1/6/2006	fizz 2
BCS3-PA	14	4 - 1	0.61	92.70		4/26/2006	fizz 3
BCS3-PA	14	4 - 2	0.57	67.98		4/26/2006	fizz 3
BCS3-PA	3	5 - unw	0.61	21.13		1/30/2006	fizz 0
BCS3-PA	3	5 - 1	0.48	29.03		6/7/2006	fizz 1
BCS3-PA	3	5 - 2	0.44	3.99		6/7/2006	fizz 1
BCS3-PA		6 - unw					
BCS3-PA		6 - 1	0.48	51.04		6/8/2006	#4 fizz 1
BCS3-PA		6 - 1	0.47	40.17		6/8/2006	#16 fizz 1
BCS3-PA		6 - 1	0.48	36.55		6/8/2006	#40 fizz 1
BCS3-PA		6 - 1	0.58	66.25		6/8/2006	#60 fizz 2
BCS3-PA		6 - 1	0.63	56.77		6/8/2006	<#60 fizz 2
BCS3-PA		6 - 2	0.48	44.51		6/8/2006	#4 fizz 1
BCS3-PA		6 - 2	0.46	42.89		6/8/2006	#16 fizz 1
BCS3-PA		6 - 2	0.51	39.54		6/8/2006	#40 fizz 1
BCS3-PA		6 - 2	0.63	42.27		6/8/2006	#60 fizz 1
BCS3-PA		6 - 2	0.56	38.24		6/8/2006	<#60 fizz 1
BSC3-PA	17	7 - unw	0.61	42.76		1/12/2006	fizz 1
BCS3-PA	17	7 - 1	0.52	51.02		6/9/2006	fizz 1
BCS3-PA	17	7 - 2	0.50	51.02		6/9/2006	fizz 1
BCS3-PA	12	8 - unw	0.63	41.43		1/12/2006	
BCS3-PA	12	8 - 1	0.63	64.51		6/26/2006	fizz 2
BCS3-PA	12	8 - 2	0.64	52.49		6/26/2006	fizz 2

Table 9.9. Test results for Houchin Creek Shale.

Rock Samples for ADTI-WP2 Interlaboratory Study							
Rock ID	**Split**	**Lab No. / Col No.**	**Total Sulfur %**	**NP (1978)**	**NP (1997)**	**Test date**	**Partical Size/ notes**
HCS-IN	5		5.27	41.85	41.05	7/14/2005	
HCS-IN	9		5.21	41.29	45.27	7/14/2005	
HCS-IN	16		4.73	45.87	47.55	7/14/2005	
HSC-IN	23		5.10	47.53	48.27	7/14/2005	
HSC-IN		1 - unw					
HCS-IN		1	5.74	34.69		6/30/2006	composite
HCS-IN		1	4.16	27.10		6/30/2006	3/8 to #4
HCS-IN		1	4.64	27.16		6/30/2006	< #60
HCS-IN	2	2 - unw	4.93	19.61		1/19/2006	
HCS-IN	2	2 - 1	5.38	9.92		4/27/2006	fizz 0
HCS-IN	2	2 -2	5.01	6.90		4/27/2006	fizz 0
HCS-IN	4	3 - unw	5.19	24.73		1/24/2006	
HCS-IN	4	3 - 1	5.31	2.30		5/4/2006	fizz 0
HCS-IN	4	3 - 2	5.09	5.32		5/4/2006	fizz 0
HCS-IN	1	4 - unw	5.38	22.20		1/6/2006	
HCS-IN	1	4 - 1	4.83	-8.06		4/26/2006	fizz 0
HCS-IN	1	4 - 2	4.87	-17.82		4/26/2006	fizz 0
HCS-IN	5	5 - unw	5.35	22.59		1/30/2006	
HCS-IN	5	5 - 5	5.00	-12.35		6/7/2006	fizz 0
HCS-IN	5	5 - 6	4.69	-13.46		6/7/2006	fizz 0
HCS-IN		6 - unw					
HCS-IN		6 - 5	5.05	15.60		6/8/2006	#4 fizz 0
HCS-IN		6 - 5	3.56	1.95		6/8/2006	#16
HCS-IN		6 - 5	3.37	-1.65		6/8/2006	#40
HCS-IN		6 - 5	4.12	-3.37		6/8/2006	#60
HCS-IN		6 - 5	5.81	-8.95		6/8/2006	<#60 fizz 0
HCS-IN		6 - 6	5.04	-7.07		6/8/2006	#4 fizz 0
HCS-IN		6 - 6	3.71	1.69		6/8/2006	#16 fizz 0
HCS-IN		6 - 6	2.99	-6.50		6/8/2006	#40 fizz 0
HCS-IN		6 - 6	3.53	-6.84		6/8/2006	#60 fizz 0
HCS-IN		6 - 6	5.98	-12.44		6/8/2006	<#60 fizz 0
HCS-IN	3	7 - unw	5.53	25.43		1/12/2006	
HCS-IN	3	7 - 5	4.88	13.03		6/9/2006	fizz 0
HCS-IN	3	7 - 6	4.61	17.65		6/9/2006	fizz 0
HCS-IN	15	8 - unw	5.14	26.53		1/12/2006	
HCS-IN	15	8 - 1	5.12	16.63		6/26/2006	fizz 0
HCS-IN	15	8 - 2	4.92	15.44		6/26/2006	fizz 0

Table 9.10 Test results for Kanawha Black Flint Shale.

Rock Samples for ADTI-WP2 Interlaboratory Study							
Rock ID	**Split**	**Lab No. / Col No.**	**Total Sulfur %**	**NP (1978)**	**NP (1997)**	**Test date**	**Partical Size/ notes**
KBF-WV	4		0.35	15.17	13.17	6/24/2005	
KBF-WV	7		0.30	16.76	13.34	6/24/2005	
KBF-WV	11		0.21	17.17	13.65	6/24/2005	
KBF-WV	14		0.32	18.69	14.26	6/24/2005	
KBF-WV		1 - unw					
KBF-WV		1	0.24	36.32		6/30/2006	composite fizz 1
KBF-WV		1	0.21	43.91		6/30/2006	3/8 to #4 fizz 1
KBF-WV		1	0.24	29.39		6/30/2006	< #60 fizz 1
KBF-WV	11	2 - unw	0.24	14.05		1/19/2006	
KBF-WV	11	2 - 1	0.31	14.85		4/27/2006	fizz 0
KBF-WV	11	2 - 2	0.29	10.62		4/27/2006	fizz 0
KBF-WV	6	3 - unw	0.39	17.28		1/24/2006	
KBF-WV	6	3 - 1	0.26	15.01		5/4/2006	fizz 0
KBF-WV	6	3 - 2	0.30	12.76		5/4/2006	fizz 0
KBF-WV	4	4 - unw	0.24	21.05		1/6/2006	
KBF-WV	4	4 - 1	0.24	12.14		4/26/2006	fizz 0
KBF-WV	4	4 - 2	0.26	11.44		4/26/2006	fizz 0
KBF-WV	10	5 - unw	0.27	16.09		1/30/2006	
KBF-WV	10	5 - 3	0.05	-39.21		6/7/2006	fizz 0
KBF-WV	10	5 - 4	0.08	315.62		6/7/2006	fizz 2
KBF-WV		6 - unw					
KBF-WV		6 - 3	0.12	32.23		6/8/2006	#4 fizz 1
KBF-WV		6 - 3	0.12	22.17		6/8/2006	#16 fizz 0
KBF-WV		6 - 3	0.10	20.43		6/8/2006	#40 fizz 0
KBF-WV		6 - 3	0.13	23.36		6/8/2006	#60 fizz 0
KBF-WV		6 - 3	0.11	20.16		6/8/2006	<#60 fizz 0
KBF-WV		6 - 4	0.13	54.35		6/8/2006	#4 fizz 1
KBF-WV		6 - 4	0.13	37.39		6/8/2006	#16 fizz 1
KBF-WV		6 - 4	0.10	34.00		6/8/2006	#40 fizz 1
KBF-WV		6 - 4	0.10	34.07		6/8/2006	#60 fizz 1
KBF-WV		6 - 4	0.13	32.45		6/8/2006	<#60 fizz 1
KBF-WV	12	7-unw	0.24	21.49		1/12/2006	
KBF-WV	12	7 - 3	0.12	19.87		6/9/2006	fizz 0
KBF-WV	12	7 - 4	0.16	19.99		6/9/2006	fizz 0
KBF-WV	9	8 - unw	0.25	21.39		1/12/2006	
KBF-WV	9	8 - 1	0.25	16.23		6/26/2006	fizz 0

Table 9.11 Test results for the Lower Kittanning Shale.

Rock Samples for ADTI-WP2 Interlaboratory Study							
Rock ID	Split	Lab No. / Col No.	Total Sulfur %	NP (1978)	NP (1997)	Test date	Partical Size/ notes
LKFC-PA	3		0.93	12.71	15.63	7/14/2005	
LKFC-PA	8		0.90	16.47	16.36	7/14/2005	
LKFC-PA	11		0.89	12.57	15.65	7/14/2005	
LKFC-PA	16		0.92	12.41	16.06	7/14/2005	
LKFC-PA		1 -unw					
LKFC-PA		1	1.04	16.15		6/30/2006	composite
LKFC-PA		1	1.17	16.59		6/30/2006	3/8 to #4
LKFC-PA		1	0.89	14.97		6/30/2006	< #60
LKFC-PA	14	2 - unw	0.88	12.86		1/19/2006	
LKFC-PA	14	2 - 1	0.96	17.18		4/27/2006	fizz 0
LKFC-PA	14	2 - 2	1.12	8.29		4/27/2006	fizz 0
LKFC-PA	2	3 - unw	1.00	9.74		1/24/2006	
LKFC-PA	2	3 - 1	0.99	5.84		5/4/2006	fizz 0
LKFC-PA	2	3 - 2	0.91	7.26		5/4/2006	fizz 0
LKFC-PA	3	4 - unw	0.94	17.20		1/16/2006	
LKFC-PA	3	4 - 1	0.85	4.83		4/26/2006	fizz 0
LKFC-PA	3	4 - 2	0.89	7.13		4/26/2006	fizz 0
LKFC-PA	13	5 - unw	0.97	9.58		1/30/2006	
LKFC-PA	13	5 - 7	0.74	16.87		6/7/2006	fizz 0
LKFC-PA	13	5 - 8	0.77	5.19		6/7/2006	fizz 0
LKFC-PA		6 - unw					
LKFC-PA		6 - 7	0.81	15.62		6/8/2006	#4 fizz 0
LKFC-PA		6 - 7	0.79	15.77		6/8/2006	#16 fizz 0
LKFC-PA		6 - 7	0.71	12.72		6/8/2006	#40 fizz 0
LKFC-PA		6 - 7	0.69	15.08		6/8/2006	#60 fizz 0
LKFC-PA		6 - 7	0.68	13.91		6/8/2006	<#60 fizz 0
LKFC-PA		6 - 8	0.81	16.50		6/8/2006	#4 fizz 0
LKFC-PA		6 - 8	0.75	14.14		6/8/2006	#16 fizz 0
LKFC-PA		6 - 8	0.69	14.81		6/8/2006	#40 fizz 0
LKFC-PA		6 - 8	0.70	15.90		6/8/2006	#60 fizz 0
LKFC-PA		6 - 8	0.63	13.36		6/8/2006	<#60 fizz 0
LKFC-PA	7	7 - unw	1.13	14.41		1/12/2006	
LKFC-PA	7	7 - 7	0.85	13.80		6/9/2006	fizz 0
LKFC-PA	7	7 - 8	0.70	12.95		6/9/2006	fizz 0
LKFC-PA	6	8 - unw	0.96	13.25		1/12/2006	
LKFC-PA	6	8 - 1	0.91	14.14		6/26/2006	fizz 0
LKFC-PA	6	8 - 2	0.88	14.37		6/26/2006	fizz 0

Table 9.12. Test results for the Middle Kittanning Sandstone.

Rock Samples for ADTI-WP2 Interlaboratory Study							
Rock ID	Split	Lab No. / Col No.	Total Sulfur %	NP (1978)	NP (1997)	Test date	Partical Size/ notes
MKSS-PA	2		0.08	20.90		1/16/2003	
MKSS-PA	8		0.04	17.70		1/16/2003	
MKSS-PA	12		0.03	14.30		1/16/2003	
MKSS-PA	6		0.11	24.58		1/6/2006	
MKSS-PA		1 - unw					
MKSS-PA		1	0.07	47.30		6/30/2006	composite fizz 1
MKSS-PA		1	0.10	72.25		6/30/2006	3/8 to #4 fizz 1
MKSS-PA		1	0.12	38.84		6/30/2006	< #60 fizz 1
MKSS-PA	4	2 - unw	0.05	26.76		1/19/2006	
MKSS-PA	4	2 - 1	0.15	28.45		4/27/2006	fizz 2
MKSS-PA	7	3 - unw	0.11	8.10		1/24/2006	
MKSS-PA	7	3 - 1	0.09	26.85		5/4/2006	fizz 2
MKSS-PA	6	4 - unw	0.11	24.58		1/16/2006	
MKSS-PA	6	4 - 1	0.11	28.85		4/26/2006	fizz 2
MKSS-PA	3	5 - unw	0.07	44.52		1/30/2006	
MKSS-PA	3	5 - 9	0.08	12.77		6/7/2006	fizz 1
MKSS-PA		6 -unw					
MKSS-PA		6 - 9	0.05	0.00		6/8/2006	3/8 no fizz/no NP?
MKSS-PA		6 - 9	0.05	41.76		6/8/2006	#4 fizz 1
MKSS-PA		6 - 9	0.06	27.99		6/8/2006	#16 fizz 1
MKSS-PA		6 - 9	0.00	39.00		6/8/2006	#40 fizz 2
MKSS-PA		6 - 9	0.14	35.33		6/8/2006	#60 fizz 1
MKSS-PA		6 - 9	0.02	33.18		6/8/2006	<#60 fizz 1
MKSS-PA	1	7 - unw	0.11	21.18		1/12/2006	
MKSS-PA	1	7 - 9	0.06	26.40		6/9/2006	fizz 1
MKSS-PA	2	8 - unw	0.10	10.13		1/12/2006	
MKSS-PA	2	8 - 1	0.09	-0.19		6/26/2006	fizz 0
MKSS-PA	2	8 - 2	0.08	10.50		6/26/2006	fizz 0

Chapter 10. Summary, Conclusions and Applications

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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.

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Method 1627: Kinetic Test Method for the Prediction of Mine Drainage Quality

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Disclaimer

This Method has been reviewed and approved for publication by the Statistics and Analytical Support Branch within EPA’s Engineering and Analysis Division. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

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METHOD 1627

Kinetic Test Procedure for the Prediction of Mine Drainage Quality

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1.0 Scope and Application

The U.S. Environmental Protection Agency's Clean Water Act (CWA) and U.S. Department of Interior's Office of Surface Mining (OSMRE) Surface Mining Control and Reclamation Act (SMCRA) establish requirements intended to minimize material damage beyond mine sites, including impacts to water quality. Since enactment of these regulations, the incomplete ability to reliably predict and, therefore, prevent acid mine drainage (AMD) has hampered the environmental protection intended by the Act.

Acid-base accounting is a widely used method for coal mine drainage prediction, however, its applicability is limited to strata that have an appreciable net acid-base balance. Mines with near equal amounts of acid and alkaline production potential fall into a "gray" area that is difficult to predict. This gray area also includes some mines with low amounts of sulfur and carbonates, where it is difficult to predict whether water quality will be alkaline or acidic over time. Method 1627 is a standardized simulated weathering test that provides information that can be used to predict mine drainage quality that may occur from coal mining operations and weathering. The method is intended for use in determining probable hydrologic consequences (PHC) and cumulative hydrologic impact assessment (CHIA) data supporting SMCRA permit application requirements. The method also is intended as a tool for generating data for use in designing and implementing best management practices and treatment processes needed by mining operations to meet U.S. Environmental Protection Agency discharge compliance requirements at 40 CFR Part 434.

The procedures detailed in this method are directed primarily toward the coal mining industry and regulatory agencies. However, the method also may be applicable to highway and other construction involving cut and fill of potentially acid-producing rock. This method originated under the auspices of the Acid Drainage Technology Initiative (ADTI) which is a consortium of scientists from federal research and regulatory agencies, state regulatory agencies, the mining industry and its consultants, and academia, who develop mine drainage technology through consensus building. Accordingly, the method has been referred to generically as the ADTI Weathering Procedure 2 (ADTI-WP2) in other publications. The objectives of the procedures are to predict the water quality characteristics (e.g., pH, acidity, metals) of mine site discharges using observations from sample behavior under simulated and controlled weathering conditions in the laboratory. The method incorporates techniques similar to those already used into reproducible, documented, and validated procedures for widespread use. The method is based on procedures that have been developed and evaluated in single, multiple and interlaboratory method validation studies using up to eight laboratories representing the mining industry, private sector, federal agencies, and academia. Results of these studies are included in References 12.21 - 12.23.

This method is "performance-based." Laboratories are permitted to modify the procedures (with the exception of method requirements indicated as "must") to overcome limitations or lower the cost of measurements if all performance criteria are met. Performance criteria are presented in Section 11, Table 4 are based on method performance in an interlaboratory method validation study, using datasets from seven laboratories, after outlier removal.

2.0 Method Summary

The procedures described in this method include: (a) the collection of representative samples, (b) preparation of samples, (c) controlled simulation of field weathering conditions, and (d) leachate collection and analysis.

Samples are crushed to pass through a 3/8" wire mesh and characterized for neutralization potential,[1] total (percent) sulfur, and particle size distribution. Samples are reconstructed from particle size sieve separations to a specified particle size distribution (by percent weight), exposed to simulated weathering conditions, and periodically leached over time (at least 12 weeks) with CO_2-saturated, deionized reagent water. Throughout method implementation, a CO_2-air mixture is added to the column and to the saturation water (leachate) to maintain a condition that is expected in the field. The leachate is collected and tested for pH, conductivity, net acidity, alkalinity, sulfate, dissolved metals, and (depending on data needs) other analytes.

3.0 Limitations / Interferences

The purpose of this method – to characterize the water quality of mine site drainage – is limited primarily by the extent to which the sample and simulated weathering conditions approximate actual site conditions. The degree of representation is highly dependent on sample collection, storage, and preparation (crushing and particle size distribution) and on simulated weathering conditions (e.g., water handling, gas mixing, and saturation and drying cycles). This method, therefore, includes procedures needed to produce reliable prediction results under standardized conditions.

When implementing this method and assessing method results, the user should consider sample collection and storage procedures, the changes made to the sample between collection and preparation (e.g., sample crushing and reconstruction), and the similarity of the simulated weathering to actual site conditions (e.g., percent humidity, partial pressures of gases, and saturation/drying cycles). It is not possible to collect a sample from the field for evaluation in the laboratory without disrupting the *in-situ* particle size distribution through collection mechanisms and crushing. This method contains requirements to ensure that results represent standardized sample structure and weathering conditions.

3.1 Surface Area to Volume Ratio– The ratio of the total surface area of the sample to the volume of water that is added and collected during each saturation cycle can determine the extent to which water comes into contact with the sample.

3.1.1 In general, the column diameter should be a minimum of four times the diameter of the largest particle (References 12.4 and 12.16). This ratio is recommended for samples with grain sizes exceeding 0.5 cm (0.2 inches). For smaller particles, a factor greater than four should be used. Scaling factors that consider the ratio of column dimensions and particle size are presented in Murr *et al*. 1977. This method specifies a maximum sample particle size of 3/8-inch (see Table 2 in Section 8.1.3) and uses 2-inch diameter columns.

3.1.2 This method contains a requirement and procedures for reconstructing samples from sieved sample portions using a specific particle size distribution (by weight percent) in the reconstructed samples. Reconstructed sample particle size distribution is provided in Table 2.

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[1] Sobek, A.A.,W.A. Shuller, J.R. Freeman and R.M. Smith. 1978. “Field and Laboratory Methods Applicable to Overburden and Minesoils.” U.S.EPA Report EPA-600/2-78-054 / Skousen, J., J. Renton, H. Brown, P. Evans, B. Leavitt, K. Brady, L. Cohen and P. Ziemkiewicz. 1997. “Neutralization potential of overburden samples containing siderite.” Journal of Environmental Quality. Vol. 26, pp. 673-681

3.2 Surface Area – Although particle size distribution can be used to calculate surface area of a given sample, it often fails to indicate the total surface area that is, or can be, contacted by water in the column (i.e., soil particle surfaces can contain pores and other surface characteristics that are not recognized by sieve measurements). If equipment is available, the analyst may want to consider performing an assessment of particle surface area (e.g., BET gas sorption analysis[2]). This assessment provides information for determining rates in terms of mg/surface area/day (see Section 10.4.2).

3.3 Sample Characterization and Leachate Analysis

3.3.1 Given adequate carbonate minerals in the sample and sufficient contact time, the water in the columns may reach saturation with respect to calcite at conditions appropriate for 10% CO_2. When the leachate is being drained, it will evolve toward equilibrium with the air outside the column. This results in a degassing of CO_2 from the leachate and an increase in pH. If the water was at or near calcite saturation while in the column, degassing of CO_2 during collection of the leachate may result in supersaturation of calcite in the leachate. This process is explained in Hornberger et al. (2003). This method describes procedures for collection of leachate to minimize CO_2 degassing (see Section 8.5.1).

3.3.2 Additional potential interferences that may be encountered during leachate analyses are specific to the analytical methods used to characterize the leachate. These interferences and procedures for overcoming the interferences are discussed in the individual analytical methods listed in Tables 1 and 3.

4.0 Safety

4.1 This Method does not address all safety issues associated with its use. The laboratory is responsible for maintaining a current awareness file of OSHA regulations for the safe handling of the chemicals specified in this method or in the methods used to characterize samples (see Table 1) or analyze leachate (see Table 3).

4.2 Each laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method or in the methods that will be used to characterize samples (see Table 1) or to analyze leachate collected from the kinetic test columns (see Table 3). A reference file of Material Safety Data Sheets (MSDS) should be made available to all personnel involved in the chemical analysis.

4.3 Extreme caution should be taken when handling pressurized gas cylinders and the gas introduction procedures described in this method. Columns should be assembled and maintained in a hood, or otherwise well-vented area to control continuous venting of column off gases.

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[2] (1) Brunauer, S., P.H. Emmett and E. Teller (1938). J. Amer. Chem. Soc. Vol. 60, p. 309 and (2) Yates, D.J.C. (1992) "Physical and chemical adsorption--measurement of solid surface areas. In: Encyclopedia of Materials Characterization: Surfaces, Interfaces, Thin Films." Edited by C.R. Brundle, C.A. Evans Jr. and S. Wilson, Boston, MA: Butterworth- Heineman, pp. 736-744.

5.0 Apparatus and Materials

Columns consist of vertical tubes or cylinders that are constructed to contain a sample of 3/8-inch maximum particle size and to allow for transport and/or holding of gases and water. An example column is presented in Figure 1. Water and/or gases are introduced into and drained from the bottom of the column to eliminate air entrapment, simulate various groundwater conditions, and maximize contact with particle surface area.

5.1 Column Apparatus – The column is constructed of a transparent polycarbonate or polystyrene cylinder with an inner diameter of 2 inches. *Note*: Use of polycarbonate, polystyrene or a similar transparent material is recommended so that sample conditions can be observed during addition of the sample to the column and throughout the weathering and leaching procedures.

5.1.1 Column - 2-inch, clear, rigid, Schedule 40 PVC pipe, U.S. Plastic Part Number 34107, or equivalent.

5.1.2 Column seals - Columns are sealed at the bottom, and include a removable cap that contains a port for measuring and venting gases. 2-inch, clear, rigid, Schedule 40 PVC fittings, Cap Slip, U.S. Plastic Part Number 34296, or equivalent. Used to seal the top and bottom of the column.

5.1.3 Column Ports - Ports are inserted into the top and bottom of the column to allow introduction of mixed gases and water, leachate collection, and gas venting.

5.1.3.1 Air/gas introduction and venting ports - Threaded / barbed elbows - Nylon, thread ¼” NPT, Tube ID ¼” (U.S. Plastic Part Number 64301, or equivalent) or polypropylene, thread ¼” NPT, Tube ID ¼” (U.S. Plastic Part Number 64482, or equivalent)

5.1.3.2 Leachate drainage port - Nylon, threaded ¼” NPT, Tube ID 3/8” (U.S. Plastic Part Number 64794, or equivalent)

5.1.4 Column Tubing and Clamps - Column ports are connected to tubing that is oriented to allow gravity flow of water into the column, drainage of water from the column, and introduction and venting of gases (see Figure 1). Clean flexible tubing should be used to provide greater control of water and gas flow. Recommended tubing sizes are 0.25” (gas mixture) and 0.5” (reagent water). Tubing should be tied to the column port using a hose clamp or equivalent.

5.1.4.1 Vinyl tubing - Used for tubing that will not require clamping (e.g., manifold, gas lines, tubing from gas source to humidified gas reservoir). ¼-inch ID and 3/8-inch OD, 1/16-inch wall thickness (Fisher Scientific Part Number 141697C, or equivalent)

5.1.4.2 Rubber tubing - Used for tubing that will require clamping (e.g., water introduction and drainage tubing, tubing from humidified gas reservoir to column). Thick wall, rubber latex tubing. ¼-inch ID, 7/16-inch OD, 3/32-inch wall thickness (Fisher Scientific Part Number 14-178-5D, or equivalent)

5.1.4.3 Plastic tubing clamps - Used on latex tubing for quick, total shut off of gases or fluids. Fits 1/8- to ½-inch tubing. (Fisher Scientific Part

Number 5869, or equivalent) OR Thermo pinch tight tube clamps (McMaster-Carr Part Number 5031K13, or equivalent)

5.1.4.4 Fixed jaw clamps - Used on latex tubing to adjust gas flow (Fisher Scientific Part Number 05870A, or equivalent)

5.1.4.5 Nylon Tees - Used to connect tubing. Tube ID ½-inch and ¼-inch (U.S. Plastic Part Numbers 64349 and 64346, or equivalent)

5.1.4.6 Couplers - Used to connect tubing. Tube ID ¼-inch, nylon or PVDF (U.S. Plastic Part Numbers 64322 and 64437, or equivalent). Tube ID ½-inch, nylon (U.S. Plastic Part Number 64325, or equivalent)

5.1.5 Column Lining - To allow uniform introduction of both water and gases into the column, the bottom (up to approximately 5% of the total column height) contains several layers of filter and support materials (refer to Figure 1). Reagent water and gas mixtures are introduced through the plates, beads, and filter material and into the sample via ports in the bottom of the column. These layers consist of 2 PVC/ polypropylene perforated plates, three layers of filter material (aquarium filter media, and a 1.5-inch layer of 5/16-inch diameter acrylic or glass beads. The layers should be added as presented in Figure 1 and are intended to trap the smallest sample particle size, but not result in clogging.

[*Note*: Glass wool has been shown to neutralize acid and elevate pH in experimental work at both the Minnesota Department of Natural Resources and the US Bureau of Mines. It should not be used in this type of testing unless it is tested and shown to be unreactive.]

5.1.5.1 Perforated Sheets - Polypropylene, Natural, 3/16-inch thickness, 3/16-inch hole diameter, staggered rows (U.S. Plastic Part Number 42562, or equivalent) OR PVC Perforated Sheets same thickness, diameter, staggered rows (U.S. Plastic Part Number 42562, or equivalent)

5.1.5.2 Plastic Beads - Polypropylene, ½-inch diameter (U.S. Plastic Part Number 91539, or equivalent) or HDPE, 5/16-inch diameter (U.S. Plastic Part Number 91547, or equivalent)

5.1.5.3 Filter Pads - Marineland Bonded Filter Pads, 312 square inches. Cut into circles to provide three filter pads to line column (Petco, Part Number SKU:237531, or equivalent)

5.2 Gas Mixture – Gases are mixed to a ratio of 90% air to 10% CO_2 using either a certified gas mixture, two-stage gas cylinder regulators, flow meters, mixing valves (gas proportioners), or flow valves. (Also see Section 6.1.)

5.2.1 Gas introduction – Once mixed, gases are introduced into the reagent water in the reagent water reservoir (Section 5.2.2) through a bubbler or porous stone below the water surface. The humidified gas mixture is maintained at the same temperature as the column (i.e., 20 - 25°C ∀3°C, see Section 8.2.3) and is introduced continuously through the column at a ratio of 9:1 (Air:CO_2). See Figure 2.

5.2.1.1 Gas monitoring - Gas flow must be introduced continuously to maintain constant positive pressure, and must be monitored daily using flow meters, gas meters, or tube indicators (e.g., Draeger tubes) to ensure positive flow and to ensure that the concentration of CO_2 in the outflow gas is at least 10%. (Bacharach Model No. 10-5000, with a tolerance of ±0.5% or equivalent.)

5.2.1.2 Tubing clamps - Fisher #05-871A (swivel jaw) or #05-870A (fixed jaw), or equivalent, are used to control gas flow through the tubing into the columns. Use of a flow regulator and meter is recommended to maintain a flow rate of approximately 1 L/minute of the mixed humidified gas into the column (e.g., Omega Model #FL3817-V Rotameter or equivalent).

5.2.1.3 Rotameters - Capable of controlling the flow at approximately 1 liter/minute. Rotameters should be used between the gas source and the reagent water reservoir, and between the reagent water reservoir and each column. (TC-OMEGA Part Numbers FL-817-V or FL-815-V, or equivalent.)

5.2.1.4 Tubing connectors - Threaded, barbed elbows, 0.12 x 0.25-inch, used to connect rotameters to inlet and outlet tubing. (U.S. Plastic Part Number 64758, or equivalent.)

5.2.2 Reagent Water Reservoir – A water bottle or carboy is half filled with reagent water (Section 6.2). The bottle is sealed with a rubber stopper containing inlet and outlet ports for the introduction and release of the mixed gases (see Figure 2).

5.2.2.1 Carboy - 2.5-Gallon carboy. Carboys with handles provide support for bungee cords needed to hold the stopper in place. (U.S. Plastic Part Number 75029, or equivalent.)

5.2.2.2 Rubber stopper - 2-hole, with third hole drilled into stopper at a distance sufficient to allow bungee cord to secure stopper in place once tubing is inserted. (Thomas Scientific Part Number 8742S20, or equivalent.)

5.2.2.3 Ridged tubing - 5/16-inch ID extruded ridged tubing, inserted into holes in stopper to provide support for flexible tubing. Inlet and outlet tubing is attached to ridged tubing. (U.S. Plastic Part Number 44018, or equivalent.)

5.2.2.4 Gas outlet port – Tubing is fitted through and just below the rubber stopper into the headspace remaining in the reservoir.

6.0 Reagents

6.1 Gas Mixture – A mixture of humidified air and CO_2 at a ratio of 9:1. This mixture is introduced continuously into the column (also see Section 5.2).

6.1.1 Carbon dioxide (CO_2) – Industrial grade. Gas cylinders or liquid CO_2 (i.e., Dewars) may be used.

6.1.2 Air – Industrial grade compressed air at approximately 21% O_2, 78 % N_2. Alternatively, house air may be used. Caution: The introduction of oil contaminants into weathering columns can significantly affect the results of this method. If house air is used, it must be run through an in-line filter to ensure that all oil is removed.

6.1.3 An industrial grade premixed compressed gas cylinder containing O_2:CO_2:N_2 at a ratio of 1:1:8 may be used as an alternative to combining the gases in Sections 6.1.1 and 6.1.2.

6.2 Reagent Water - Reagent water is prepared by distillation, deionization, reverse osmosis, or other technique that removes potential interferences (e.g., metals and organics).

6.3 Reagents for Sample Characterization and Leachate Analysis – Reagents required for sample characterization and leachate analyses are specific to the analytical methods used, and are provided in the individual analytical methods listed in Tables 1 and 3.

7.0 Sample Collection, Preservation, and Handling

7.1 Sample Collection - Collect representative bulk samples using air-rotary drilling, core drilling, or extraction from highwall, roadcut, or outcrop exposures. Collect samples using standard procedures described in Sobek *et al*., 1978; Block *et al.*, 2000; Griffiths, 1967; and Tarantino and Shaffer, 1998. Approximately 2000g of sample is needed to fill a single column as described in this method.

7.2 Documentation – Record the location, date, time, and amount of sample collected.

7.3 Sample Crushing and Splitting – Prior to method implementation, bulk samples must be crushed to a maximum particle size of 3/8 inch. To demonstrate the accuracy of results, it is recommended that at least two identical homogeneous sample aliquots are prepared from each bulk sample (see Section 8.1.3). Crush bulk samples into 3/8 inch size fractions using a jaw crusher. (The first portion of sample that is crushed should be run through a screen or sieve to ensure the crusher is set to the appropriate size.) After the entire sample is crushed, it is riffled through a bulk splitter with openings set to approximately 1.5 inches, and split using a riffle splitter or other similar piece of equipment to get identical representative splits of the total sample volume. These procedures are described in ASTM C-702-98 and Noll *et al*., 1988.

7.4 Sample Shipment, Storage, and Preservation – From the time of sample collection until method implementation, some oxidation of pyrite can occur, resulting in soluble acid-sulfate salts. Prior to method implementation, samples should be stored in sealed, HDPE containers, or some other airtight container, under dark, dry, and cool conditions. For small sample sizes, opaque Nalgene bottles may be used. Crushed samples should not be stored for longer than six weeks. Sample shipment, storage, and preservation procedures are described in ASTM D5079.

8.0 Procedure

8.1 Sample Preparation

8.1.1 Sample Sizing – Pass the sample through a 3/8-inch mesh to ensure that no particle sizes greater than 3/8 inch are added to the column (see Section 7.3). Following this sizing, determine the particle size distribution of the sample using at least five dry sieves (i.e., sieves No. 4, 10, 16, 35, 60).[3] For analysis of particle size distribution, use U.S. sieves or sieves of equivalent mesh size (e.g., U.S. #16 = Tyler #14). Approximately 2 kg is needed for each column.

8.1.2 Sample Characterization – Prior to method implementation, samples should be analyzed for neutralization potential (NP) and percent total sulfur. Methods for analysis of these parameters are included in Table 1. 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. [Note: Additional parameters may be measured if required or requested by the data user.]

Table 1: Sample Characterization and Appropriate Methods

(Note: Any approved ASTM, USGS, EPA, Association of Official Analytical Chemists (AOAC), or Standard Methods analytical method may be used for sample characterization)

Characteristic	**Method**
Neutralization Potential	Sobek, 1978 (EPA-600/2-78-054); Skousen *et al.*, 1997
Total Sulfur	ASTM D3177, ASTM D4239, ASTM D2492

8.1.3 Sample reconstruction - Once samples have been collected and crushed, sample particle size distribution that occurred in the field is lost. The distribution provided in Table 2 is intended to provide standardized conditions and to facilitate uniform exposure of samples to weathering conditions and collection of leachate. Using the sieved sample portions (see Section 8.1.1), reconstruct samples into particle size distribution portions according to the weight percentages specified in Table 2.

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[3] If additional information is needed to determine surface area or if method results will be used to determine reaction rates in mg/surface area/day, the analyst may want to consider using additional sieves, Malvern system of laser diffraction, or assessment of particle surface area (e.g., BET gas sorption analysis).

Table 2: Particle size distribution of reconstructed samples

U.S Sieve # (or equivalent mesh size)	Percent of Sample (by weight)
3/8" to 4	40
4 - 10	25
10 - 16	15
16 - 35	10
35 - 60	5
Less than 60	5
Total	**100**

8.2 Column Preparation

8.2.1 Filling the Column – Uniform exposure of the sample to weathering conditions is critical to method performance. Using a standardized rock density table (e.g., Blaster's Guide), determine the approximate total weight of sample needed to fill the column to 4 inches below the top. Approximately 1800-2000 grams should be sufficient to fill a column that is 2.5-feet in height and 2-inches in diameter.

8.2.2 Using a wide-bore or powder funnel, add approximately 2,000 grams of the reconstructed sample to the column, being careful to ensure uniform distribution with little to no packing. (*Note*: The top of the sample should be at least 4 inches below the top of the column to prevent loss of sample or leachate water during test implementation.) Weigh the sample before adding it to the column.

Note: The total weight of the sample added to the column must be recorded to the nearest 1.0 gram, for use in results calculations.

8.3 Column Maintenance

8.3.1 Maintain the column at a temperature between 20 - 25°C ∀3°C (e.g., 22°C ∀3°C).

8.3.2 Check the column daily to ensure temperature and gas flow are maintained. An example daily reporting sheet is provided in Section 13, Form 1.

8.3.2.1 The temperature must be recorded at least daily and remain constant. If data will be used for assessment of reaction kinetics or gas mixture partial pressure assessments, the data should be adjusted for temperatures outside the range of 20 - 25°C.

8.3.2.2 Using a portable CO_2 meter (Section 5.2.1.1) capable of measuring CO_2 to 10% (within +/- 0.5%), take daily readings of the CO_2 released from the column exhaust.

8.4 Simulated Weathering Procedure – The simulated weathering procedures described in this section consist of alternating cycles of saturation and humidified gas mixture. These procedures are recommended for evaluation of overburden in non-arid regions or areas where there may be variably saturated conditions. Alternative procedures may be used, provided they are designed to assess site conditions and meet the reproducibility performance standards included in Section 11.

8.4.1 Initial Column Flush - Once the column has been filled with sample, reagent water is introduced through the water inlet port (refer to Figure 1) until the column is full and all visible pore spaces are saturated. Gently tap the column to fill any visible air pockets with water. Alternatively, a thin wire may be inserted into the column to adjust the sample and ensure saturation. Allow the reagent water to sit in the column for approximately 1 hour prior to collecting and analyzing the initial flush water for conductivity. Continue to add, drain, and analyze reagent water in this manner until the conductivity of the water stabilizes (relative standard deviation between conductivity measurements ≤20%). Composite the collected flush water into a single composite water sample, and analyze using the same procedures used to analyze the water samples collected following each 24-hour saturation period (see Section 8.5).

[Note: The volume of water added to and collected from the column should be recorded with each flush. These volumes also should be recorded during each weekly saturation period.]

8.4.2 Humidified Air Cycles – Once the column has been drained of the final initial flush sample, the humidified gas mixture (see Section 5.2) is introduced continuously through the gas inlet port at the bottom of the column (see Figures 1 and 2). The column is allowed to sit for a period of 6 days during the humidified air cycle. This cycle is repeated after each saturation cycle (Section 8.4.3).

8.4.3 Saturation Cycles - Following each humidified air cycle, reagent water is introduced through the water inlet port to just above the sample surface. If necessary, gently tap the column to fill any visible air pockets with water. The volume of water added must be recorded. If the introduction of water into the column through the bottom port is difficult or slow, a pipette bulb can be used to create a vacuum to pull water up and into the column. Once water has been added, clamp the water inlet tube shut, as close as possible to the column, to ensure that the water collected at the end of the saturation period has been in sufficient contact with the sample. Record the volume of water added to the column.

8.4.3.1 Gas Introduction – Once the column has been saturated according to procedures in Section 8.4.3, introduce the gas mixture into the sample through the gas inlet port at the bottom of the column until a slight positive pressure is reached (i.e., a small outflow is produced through the air vent in the top of the column). Gas flow can be controlled and maintained at approximately 1.0 L/minute using a combined flow regulator and meter (e.g., Omega FL-3817-V Series Rotameter or equivalent).

[Note: Care should be taken to avoid displacing the water during gas introduction. Gas should be introduced slowly until slight positive pressure is reached.]

8.4.3.2 Leaching - Allow the column to sit for a period of 24 hours in this saturated condition. Following this 24-hour period, drain the column and collect the leachate (see Section 8.5.1), then repeat the humidified air cycle in Section 8.4.2). The saturation cycle is repeated every week until method implementation is complete (for up to a minimum of 12 weeks).

8.5 Leachate Collection and Analysis

8.5.1 Leachate Collection – Following each 24-hour saturation cycle, the water/leachate is drained from the column and collected for analysis (Section 8.4.3.2). Leachate is drained from the column through the water inlet tubing by disconnecting the tubing from the water source.

Note: The procedure used to collect leachate *must* minimize carbon dioxide degassing (e.g., insert the drainage tube into the bottom of the sample collection container throughout collection; seal the container immediately following sample collection; refrigerate the sample if analysis is not performed immediately; keep sample container submerged in ice if collection drainage is slow).

8.5.1.1 The total volume added to and collected from each column must be measured and recorded prior to water analysis. An example weekly reporting sheet is provided in Section 13, Form 2.

8.5.1.2 Analyze the leachate immediately for determination of pH and conductivity, and prepare additional aliquots for further analysis. If the leachate will be analyzed for dissolved parameters (SO_4^{-2}, metals), the leachate must be filtered through a 0.45 µm filter prior to analysis.

8.5.2 Leachate Analysis – The leachate is analyzed for target parameters using approved methods. Recommended analytical methods are listed in Table 3. Specific conductance (conductivity), alkalinity, and pH are analyzed as soon as possible after collection. Leachate that will not be analyzed immediately for measurement of other parameters (e.g., metals, sulfate) must be preserved and stored according to the requirements specified in the analytical method(s) to be used.

Table 3: Analytes and Appropriate Methods

(Note: Any Approved ASTM, USGS, EPA, AOAC, or Standard Methods analytical method may be used for leachate analysis)

Analyte	Method
pH	EPA 150.1; Std. Methods 4500-H; ASTM D1293; USGS I-1586
Dissolved Metals ** (e.g., Fe, Mn, Al, Mg, Ca, Se)	EPA 200.7, 236.1, 236.2; Std. Method 3111, 3113, 3120; ASTM D1068; USGS I-3381
Sulfate	EPA 375.1, 375.2, 375.4; Std. Methods 4500
Alkalinity (to pH 4.5)	EPA 310.1, 310.2; Std. Methods 2320B; ASTM D1067; USGS I-1030, I-2030
Acidity / Net Acidity (to pH 8.2)	EPA 305.1; Std. Methods 2310; ASTM D1067
Specific Conductance	EPA 120.1; Std. Methods 2510B; ASTM D1125; USGS I-1780

** The analytes measured will depend on specific permit needs or other intended uses of the data

9.0 Quality Control

9.1 All quality control measures described in the referenced analytical methods for leachate analysis (Table 3) and sample characterization (Table 1) should be used.

9.2 Blanks - Inert material (e.g., clean, well characterized quartz chips or sand of requisite particle size) is run along with samples to check for unexpected contributions from the test apparatus and reagents.

9.3 Duplicate Samples – Duplicate samples are prepared according to procedures in Section 8. Identical sample masses and leaching volumes are used, and samples are exposed to identical simulated weathering conditions.

9.3.1 At a minimum, at least one sample from each mine site must be run in duplicate. If there are more than ten samples per site, then 10 percent of the total number of samples must be run in duplicate.

9.3.2 If necessary, the leachate from duplicate samples can be analyzed using a staggered approach. In this case, pH and conductivity are measured weekly from both the primary and duplicate column. Analytes not requiring immediate measurement (e.g., metals), are measured weekly in leachate from the primary column, but every other week in leachate from the duplicate column.

9.3.3 Analysis of these samples gives a measure of the precision (relative percent difference, RPD) associated with sample preparation and with laboratory procedures. RPDs between results of duplicate samples are calculated for each analyte (using Equation 1) and should not exceed the RPDs listed in Table 4.

Equation 1: Relative Percent Difference between Duplicate Samples

$$RPD = \frac{|C1 - C2|}{(C1 + C2)/2} * 100\%$$

Where:

$C1$ = concentration in primary sample
$C2$ = concentration in duplicate sample

10.0 Calculations / Results

10.1 Analytical data should be reported initially in units of mg/L for aqueous (leachate) samples and mg/kg or percent for solid (overburden characterization) samples. Results also may be reported in parts per thousand (ppt).

10.2 Report total sample weight (Section 8.2.1) and leachate volume (Section 8.4.1).

10.3 The mass of each analyte weathered from the sample each week can be calculated using Equation 2.

Equation 2: Analyte Concentration in Samples

$$Analyte,\ mg = \left(\frac{mg}{L}\right) \times \left(Leachate\ Volume\ Out,\ L\right)$$

10.4 Acid production or metals release per weight of sample also can be determined by dividing the result in Section 10.3 by the weight of the sample exposed to weathering conditions.

10.5 Evaluation of the weathering data can be performed to support permitting decisions and developing special handling plans for selected overburden strata. These data can be used alone or in combination with data resulting from other mine drainage prediction tools (e.g. Acid/Base Accounting, X-Ray diffraction). Typically, Acid/Base Accounting (ABA) (i.e., total sulfur and neutralization potential) would be performed on all overburden samples, and the weathering test described in this method would be performed on selected samples where the ABA was inconclusive.

10.5.1 For permitting decisions the method can be used to determine whether inconclusive samples have alkalinity exceeding acidity. This is the most fundamental question in evaluating overburden analysis data. Using ABA, a rock sample with a total sulfur content of 1% would have a Maximum Potential Acidity (MPA) of 31.25; if the rock sample had a NP of 31.25, it would be interpreted that the acidity and alkalinity would be equal or 0. The total sulfur content is a surrogate measurement of the potential acidity and the NP is a surrogate of actual alkalinity. The kinetic test method produces a leachate that can be analyzed for the actual acidity and alkalinity produced by the sample.

10.5.2 Using ABA, it is not possible to obtain any measurement or accurate estimate of the potential for production of iron, manganese, aluminum or other metal of concern. The kinetic test method produces a leachate that can be analyzed for any metal concentration. However, the user of the method should consider the iron concentration, for example, to be an accuarate and precise measurement of the iron in the leachate, and not necessarily an accurate measurement of the effluent from a mine site. In this respect, the iron concentration can be used to indicate which rock samples may cause an iron problem on the mine site, and not a number that should be compared to the effluent limitations for compliance purposes.

10.5.3 Since the weathering test is conducted for at least 12 weeks (see Section 2.0) or longer if appropriate, a simple time plot should be constructed to determine if there are any trends in the data. For example, plots of acidity and sulfate should be made to determine if there is an increase through time that would indicate that acid mine drainage is likely to be produced from that lithologic unit. In addition, time plots of alkalinity and calcium should be constructed to determine if there are trends in the alkalinity or calcium data that would indicate that alkalinity production or calcite dissolution is occurring from selected rock samples.

10.5.4 Understanding the reaction kinetics of the rock samples weathering within the leaching columns (and in the mine environment) is the ultimate goal of this method. For example, if the sample is a shale from a marine paleoenvironment with a pyritic sulfur content of 0.8% and a NP of 80 tons per thousand tons of calcium carbonate equivalents, does the weathering pattern have the characteristic shape of a diffusion-controlled process (i.e., plot is the square root of time)? Can we predict that the rate of pyrite oxidation will be offset by the rate of calcite dissolution, and will the pyrite be depleted before the calcite? (See References 12.3, 12.11, 12.12 and 12.24 and Appendices A and B).

11.0 Method Performance

RPD results listed in Table 4 reflect the pooled results of the interlaboratory study, using datasets from seven laboratories evaluating the effects of weathering on samples of Brush Creek shale, Kanawha Black Flint shale, Lower Kittanning shale, Houchin Creek shale, and Middle Kittanning sandstone. Method precision was assessed using results of duplicate samples exposed to identical weathering procedures. RPDs were pooled for leachate samples collected over a 14-week period.

Table 4: Expected method precision (as RPDs) based on Interlaboratory Study Results

Analyte	14-week RPD	Initial Flush RPD	Weathering Test RPD (Difference between 14-week and initial flush RPD)
Fe	90.4	50.9	**39.5**
Mn	52.5	44.1	**8.4**
Al	72.5	38.6	**33.9**
Ca	21.9	38.8	**(16.9) ***
Mg	21.4	16.4	**5.0**
Se	42.9	26.2	**16.7**
Zn	60.2	52.0	**8.2**
Na	25.1	21.1	**4.0**
K	23.7	21.5	**2.2**
SO_4	27.5	20.4	**7.1**
Alkalinity	28.7	35.2	**(6.5) ***
Acidity	99.9	27.0	**72.0**
Conductivity	13.2	11.1	**2.1**
	Mean absolute difference		
pH	0.2	0.2	**0**

* Relative percent difference between analyses were greater between samples collected during initial flush than between weekly samples.

12.0 References

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13.0 Forms and Figures

Form 1:
Example Daily Monitoring Reporting Form

Sample ID:						
		Column 1		**Column 2**		
Date / Time	**Temp. ^oC**	**Flow (Lpm)**	**% CO_2 (in exhaust)**	**Flow (Lpm)**	**% CO_2 (in exhaust)**	**Notes**

Form 2:
Example Weekly Monitoring Reporting Form

Sample ID:							
Date / Time	**Week #**	**Water In (mLs)**	**Water Out (mLs)**	**pH**	**Conductivity (umhos/cm)**	**Alkalinity (to pH 4.5) mg/L as CaCO3**	**Acidity (to pH 8.2) mg/L as CaCO3**
	Initial Flush						
	Week-1						▨
	Week-1	▨					
	Week-2						▨
	Week-2	▨					
	Week-3						▨
	Week-3	▨					
	Week-4						▨
	Week-4	▨					
	Week-5						▨
	Week-5	▨					
	Week-6						▨
	Week-6	▨					
	Week-7						▨
	Week-7	▨					
	Week-8						▨
	Week-8	▨					
	Week-9						▨
	Week-9	▨					
	Week-10						▨
	Week-10	▨					

Figure 1: Leaching Column

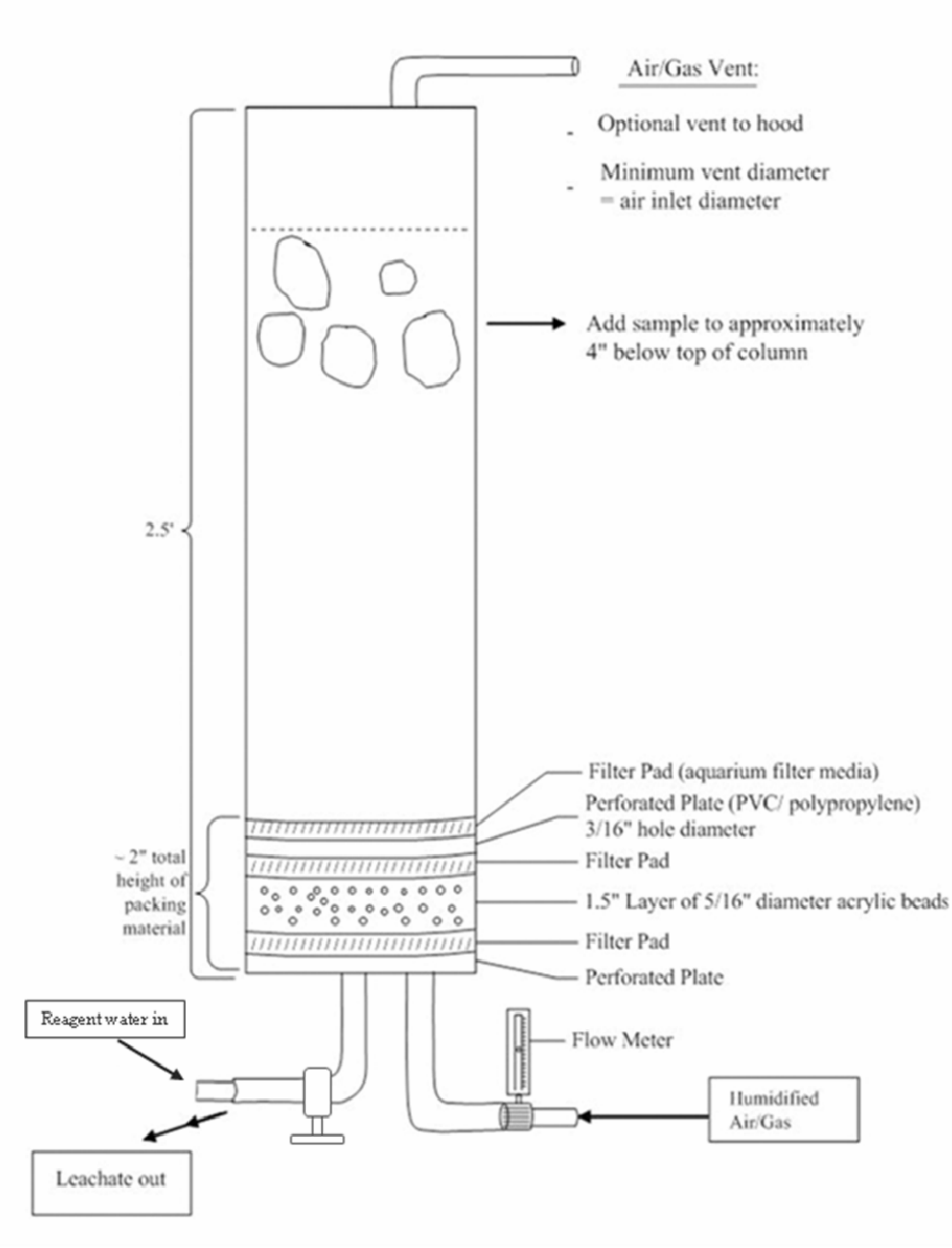
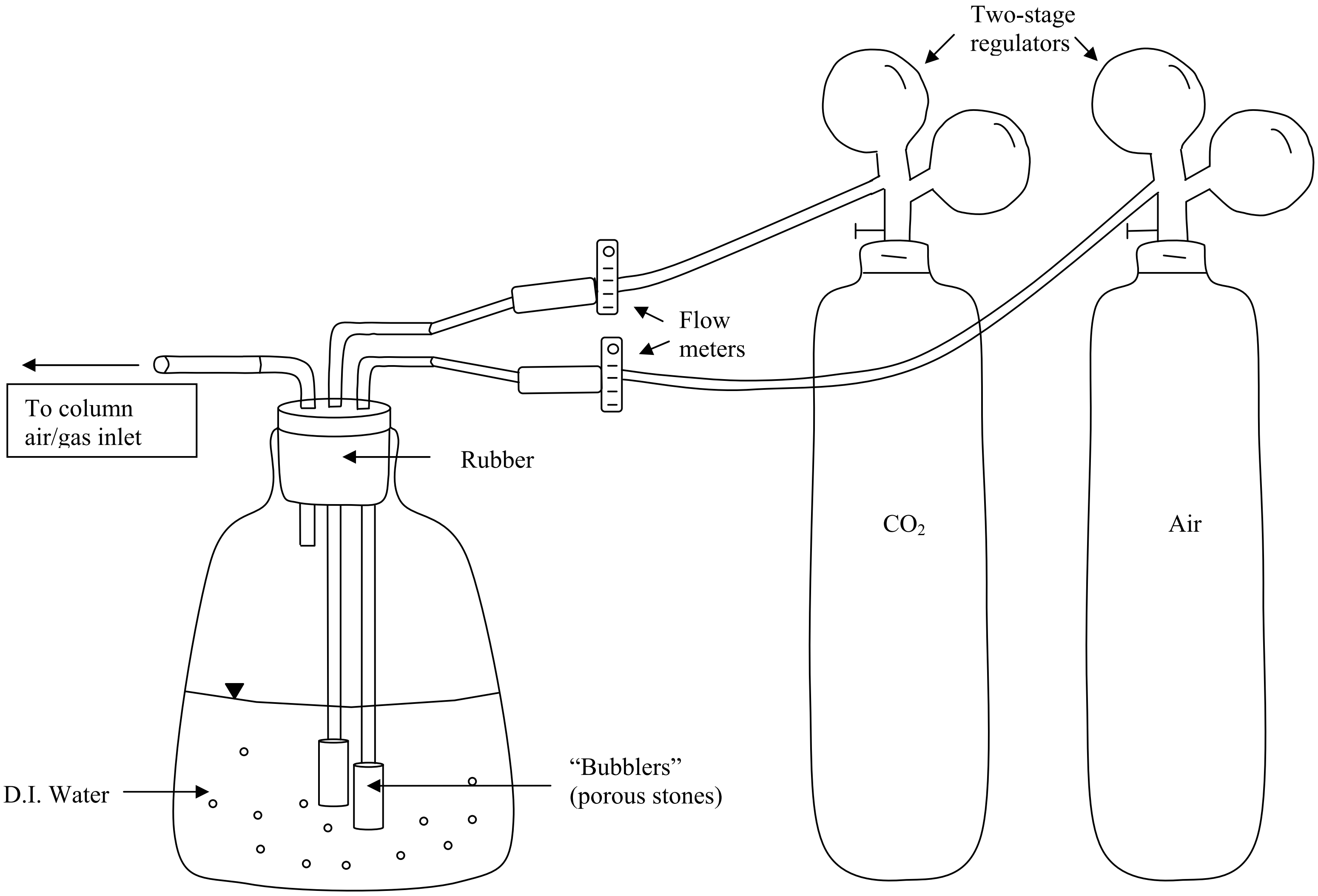


FIGURE 2: HUMIDIFIED AIR/GAS



Appendix A: Example calculations for determining carbonate dissolution and pyrite oxidation rates

Determining Carbonate Dissolution Rate

There are two ways to calculate carbonate dissolution. Ultimately the rate of reaction is determined from the amount of material that is weathered each week as a portion (or percentage) of the total of that material that is in the rock. The examples below used acid-base accounting analyses of the Brush Creek Shale (Table A-1). Material was obtained from four 5-gallon buckets of crushed, but not yet pulverized rock. Neutralization potential (NP) was determined two ways, the traditional Sobek et al. (1978) method and the modified Skousen et al. (1997) method that takes steps to reduce the effects of siderite interferience. Siderite, a non-alkalinity generating carbonate can give falsely high NP readings if the sample is not oxidized (Skousen et al., 1997; Cravotta and Rose, 1998). The Skousen method NP results are about half the Sobek method results. Field observations and mineralogy work performed by Hammarstrom et al. indicate that the Brush Creek shale contains appreciable siderite. The Skousen method NP numbers were used to determine the average NP for the Brush Creek Shale.

Table A-1. Acid-Base Accounting data for the Brush Creek Shale.

NP Sobek	NP Skousen	%S
96.97	49.68	0.59
96.96	49.31	0.59
96.98	47.61	0.56
96.97	47.07	0.59
Avg 96.97	**Avg 48.42**	**Avg 0.58**

Although NP does not in and of itself specify the forms of carbonate, with the improved NP method of Skousen et al. it is reasonable to assume that most of the NP is from carbonates that contribute to neutralization. For simplicity and accuracy, results are expressed as calcium carbonate equivalent.

Step 1. Determine the amount of calcium carbonate (equivalent) in the column.

Using the Average NP number (Table A-1) and the known mass of sample in a column, the amount of calcium carbonate equivalent can be computed for the material in that column. For example, Lab 5's Column 1 contained 1879.2 grams of material. The units for NP are tons/1000 tons $CaCO_3$ equivalent. The amount of calcium carbonate equivalent contained in the column can be computed as follows:

$$1879.2 \text{ grams} \times (48.42/1000) = 91.0 \text{ grams } CaCO_3 \text{ equivalents}$$

This number will be used to determine weathering rate.

Step 2. Determine the amount of calcium carbonate weathered each week. This is done by determining the mass of the weathering products produced each week in the leachate. There are two ways this can be done, the "cation approach" and the "anion approach" discussed below.

Step 2a. *The "Cation" Approach*

The Cation Approach involves computations using the two cations that are commonly associated with acid-neutralizing carbonates, namely calcium and magnesium. These are evaluated in terms of calcium carbonate equivalent by summing Ca as $CaCO_3$ and Mg as $CaCO_3$. Three assumptions are made:

(1) all Ca and Mg in solution are derived from carbonate dissolution,

(2) that Ca and Mg have not been lost from the solution and retained in the column, and

(3) gypsum is not present in the material being leached.

If gypsum is present, then there is sulfate from a source that is not directly related to pyrite oxidation. Thus, pyrite oxidation rate can not be accurately determined, unless one determines the amount of gypsum dissolution per week and subtracts this portion.

- Assumption 1. By far the most common and most soluble mineral containing calcium on mine sites is calcite. Other common sources of calcium are other carbonate minerals such as dolomite and ankerite. Magnesium is another common carbonate ion. Although there are other sources of Mg, the carbonates are by far the most soluble sources of Mg found in overburden rocks.

- Assumption 2. The most common calcium-bearing mineral that is likely to precipitate from solution is gypsum. Gypsum solubility can be determined as shown in Appendix B. If gypsum is precipitating then some of the calcium that has dissolved will not be measured in the leachate, but in fact is being retained in the column.

- Assumption 3. The presence of gypsum can be determined through hand sample observation, X-ray diffraction or other mineral determining techniques.

The mass of Ca and Mg leached each week can be determined from the mg/L of Ca and Mg leach multiplied by the volume of leachate.

$$Analyte,\ mg = \left(\frac{mg}{L}\right) \times \left(Leachate\ Volume\ Out,\ L\right)$$

The examples used below are of actual leachate obtained from the same column during the same week. That is, all data are all from the same sample event.

Calculating $CaCO_3$ from Ca The mass of calcium carbonate (equivalent) can easily be determined from the mass of calcium. The atomic weight of Ca is 40, and the molecular weight of $CaCO_3$ is 100. Thus, $CaCO_3$ is 2.5 times the weight of Ca alone, and 40 grams of Ca converted to calcium carbonate equivalent is 100 grams of $CaCO_3$. For example, a sample leaches 168 mg/L Ca and the volume drained from the column is 385 mL.

$$\left(176.0\frac{mg}{L}\right) \times \left(0.279\ L\right) = 49.1\ mg\ Ca$$

and

$$49.1\ mg\ Ca \times 2.5 = 122.8\ mg\ as\ CaCO_3$$

Therefore, during this sample event 122.8 mg of $CaCO_3$ equivalent weathered from the rock.

Calculating $CaCO_3$ from Mg The conversion of Mg to $CaCO_3$ is the same process as that for calcium. The atomic weight of Mg is 24.3. Dividing the molecular weight of $CaCO_3$ of 100 by 24.3 gives a conversion factor of 4.1.

$$\left(83.1\,\frac{mg}{L}\right)\times\left(0.279\ L\right)=23.2\ mg\ Mg$$

and

$$23.2\ mg\ Mg\times 4.1=95.0\ mg\ as\ CaCO_3$$

Calculating CaCO3 from Ca + Mg The next step is to simply combine the calcium carbonate equivalents calculated above:

$$122.8\ mg\ Ca+95.0\ mg\ Mg=217.8\ mg\ as\ CaCO_3$$

Therefore, during the course of the previous week, 217.8 mg of carbonates, measured as $CaCO_3$ equivalent, were dissolved.

Step 2b. *The "Anion" Approach*

The Anion Approach involves determining excess alkalinity and neutralized alkalinity produced by evaluating two anions that are commonly associated with neutralized mine drainage, bicarbonate and sulfate. The sulfate part of the equation, is not necessarily intuitive and requires some explanation. This approach only works where a water is net alkaline. It will not work for acidic samples. Again, assumptions are made: (1) sulfate has not been lost from the solution and retained in the column, and (2) gypsum is not present in the rock.

- Assumption 1. The most common sulfate-bearing mineral that is likely to precipitate from solution is gypsum. Gypsum solubility can be determined as shown in Appendix B. If gypsum is precipitating then some of the sulfate that has dissolved will not be measured in the leachate, but in fact is being retained in the column.

- Assumption 2. The presence of gypsum can be determined through hand sample observation or X-ray diffraction or other mineral determining techniques.

Bicarbonate alkalinity. Bicarbonate alkalinity is generally reported as $CaCO_3$ equivalent, so no conversion is necessary. If it is not reported as $CaCO_3$ equivalent, HCO_3 can be converted to $CaCO_3$ using the following equation:

$$\text{mg/L } HCO_3 \times 0.8202 = \text{mg/L } CaCO_3$$

Determining milligrams of $CaCO_3$ is performed using the same process as that for calcium and magnesium discussed above, except no conversion is typically necessary to obtain calcium carbonate equivalent. Using the same sample event as the examples above, the concentration of alkalinity as $CaCO_3$ was 520 mg/L.

$$\left(520\ \frac{mg}{L}\right)\times\left(0.279\ L\right)=145.1\ mg\ CaCO_3$$

Alkalinity Neutralized The alkalinity measured in a mine water is the “excess” alkalinity that has been produced. In samples with pyrite oxidation occurring, some alkalinity has been neutralized by the acid. The amount of acidity that has been produced can be calculated based on the following stoichiometry:

$$FeS_2 + 3.25\ O_2 + 3.5\ H_2O = Fe(OH)_3 + 2\ SO_4^{2-} + 4\ H^+$$

For every mole of pyrite oxidized there are 2 moles of sulfate produced and 4 moles of H^+. It takes 2 moles of $CaCO_3$ to neutralize 4 H^+. This relationship can be written as:

$$\frac{4\text{ mol }H^+}{2\text{ mol }SO_4^{2-}} = \frac{2\text{ mol }CaCO_3}{2\text{ mol }SO_4^{2-}} = \frac{200\text{ g }CaCO_3}{192\text{ g }SO_4^{2-}}$$

Therefore, for every 1 mg/L (or gram) of sulfate, 1.04 mg/L (or gram) of acidity, as $CaCO_3$, are produced.

Therefore, if a sample is net alkaline, the neutralized alkalinity can be calculated from sulfate, by using the following equation:

$$\text{mg/L }SO_4 \times 1.04 = \text{mg/L }CaCO_3$$

Using a sulfate value of 235 mg/L, we get:

$$\left(298\ \frac{mg}{L}\times 1.04\right)\times\left(0.279\ L\right)=86.5\ mg\ neutralized\ alkalinity\ as\ CaCO_3$$

<u>*Calculating $CaCO_3$ from Alkalinity + Sulfate*</u> The next step is to simply combine the calcium carbonate equivalents calculated above:

$$141.1\ mg\ Alkalinity\ CaCO_3 + 86.5\ mg\ neutralized\ alkalinity = 227.6\ mg\ as\ CaCO_3$$

Therefore, during the course of the previous week, 227.6 mg of carbonates (measured as $CaCO_3$ equivalents), were dissolved. We had calculated earlier that there is a total of 91.0 grams of $CaCO_3$ equivalent in the column. Thus, during this one week:

$$\left(\frac{0.2276\ g}{91.0\ g}\right)\times 100 = 0.25\%\ CaCO_3\ weathered$$

Step 2 c. Compare the two methods. Figure A-1 compares the percentage $CaCO_3$ equivalent leached at the end of 14 weeks for data from four of the laboratories used in this study. The two methods compare favorably in all cases except for the HCS-IN sample after it went acidic. When a sample goes acidic only the "cation" approach is appropriate because the acidity (measured from sulfate) has not all been neutralized.

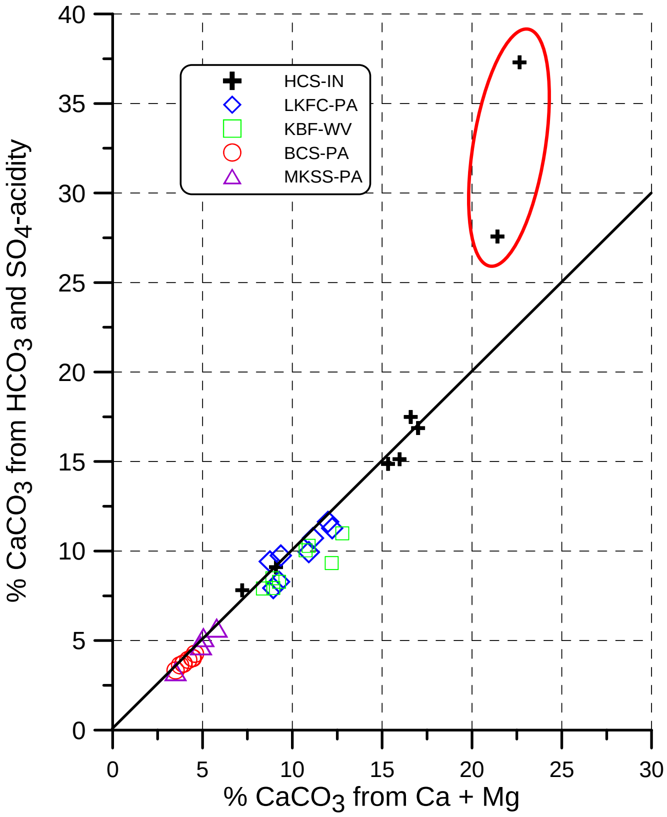


Figure A-1. Comparison of the "anion" and "cation" methods of determining carbonate dissolution. The cumulative value at the end of 14 weeks leaching was used to construct this plot. As can be seen, most data fall on or near the diagonal line, which represents where data would fall if both methods produce the same answer. The circled values indicate columns that became acidic.

Determining Pyrite Oxidation Rate

Pyrite oxidation rate is determined from the amount of sulfur weathered each week. This is then compared to the mass of sulfur in the rock. The sulfur in the rock is determined during acid-base accounting. The examples below are analyses of the Brush Creek Shale and are for the same leaching event used above. The average sulfur shown in Table A-1 was used for calculations.

Step 1. Determine the amount of sulfur in the column from the average of the samples analyzed.

Using the average percent sulfur value (Table A-1) and the known mass of sample in a column, the amount of calcium carbonate equivalent can be computed for the material in that column. For example, Lab 5's Column 1 contained 1879.2 grams of material. The amount of sulfur contained in the column can be computed as follows:

1879.2 grams x (.0058) = 10.9 grams sulfur

For the purposes of this study we used total sulfur values. There are multiple known problems with using forms of sulfur (Brady and Smith, 1990) for coal overburden samples. Pyrite is 53.45% sulfur, so to determine the amount of pyrite in a rock the percent sulfur can be multiplied by 1.873:

$$0.58\%\ \mathrm{S} \times 1.873 = 1.09\%\ \mathrm{pyrite}$$

Step 2. Determine the sulfur oxidation rate.

Sulfur has an atomic weight of 32. Sulfate has an ionic weight of 96 (32 + (16 x 4) = 96). Thus, sulfur comprises one-third the weight of sulfate. To calculate the amount of sulfur leached each week use the following equation:

$$\frac{298\ mg/L\ SO_4}{3} \times 0.279\ L = 27.7\ mg\ S\ weathered$$

To determine the percentage of the available sulfur that was weathered during this time period use the following equation:

$$\left(\frac{0.0277\ g}{10.9\ g}\right) \times 100 = 0.25\%\ S\ weathered$$

Thus the weathering rate of the pyrite is similar to that for the carbonates during this particular weathering cycle.

Cumulative Weathering Rate

The above calculations are done for each week. The only reasonable way to do the multiple calculations for each column and for each week is to us a spreadsheet. The types of calculations presented in spreadsheet format are displayed in Table A-2. The percentage weathered each week can be added cumulatively to determine the amount of carbonate or sulfur weathered through the duration of the test. This also allows for the evaluation of whether or not the rate of weathering changes throughout the course of the test. If a rate is beginning to dramatically accelerate, the test should probably be extended in duration. The graphs that follow are from Table A-2 data.

Comparisons of cumulative weathering rates can show which suite of minerals is weathering faster, the carbonates or the sulfides. Best-fit lines can be fitted to the data to predict weathering into the future. If the sulfides are exhausted before the carbonates, the rock will likely produce excess alkalinity well into the future. If carbonate minerals are exhausted first, especially if this happens quickly, the rock will likely go acidic with time.

Table A-2. Example table of the computational steps to determine $CaCO_3$ weathering rate. Column 1 identifies the week that was leached. Week "0" is the initial flush. Weeks 1 through 14 are the actual weeks that the sample is weathered. Column 2 is the leachate volume collected. Column 3 is mg/L calcium. Column 4 is the mg calcium computed from columns 2 and 3. Column 5 is the mg calcium displayed cumulatively. Column 6 is calcium displayed as calcium carbonate. Columns 7 through 10 are the same as those described above, but for magnesium. Column 11 is the sum of columns 6 and 10. Column 12 is column 11 divided by the total mass of calcium carbonate equivalent in the column, expressed in percent.

1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**
Week	**VolOut mL**	**mg/L Ca**	**mg Ca**	**Cumulative mg Ca**	**Cumulative mg Ca as CaCO3**	**mg/L Mg**	**mg Mg**	**Cumulative mg Mg**	**Cumulative mg Mg as CaCO3**	**Cumulative Ca + Mg as CaCO3**	**% CaCO3 weathered each week from 91.0 g**
0	1356	99.8	135.33	135.33	338.32	57.1	91.83	91.8	377.90	716.22	0.79
1	310	270.0	83.70	219.03	547.57	148.0	54.41	146.24	601.82	1149.39	1.26
2	340	240.0	81.60	300.63	751.57	131.0	52.82	199.07	819.20	1570.77	1.73
3	295	186.0	54.87	355.50	888.75	93.3	32.64	231.71	953.53	1842.28	2.02
4	309	175.0	54.08	409.57	1023.93	82.7	30.31	262.02	1078.25	2102.19	2.31
5	270	170.0	45.90	455.47	1138.68	78.8	25.23	287.25	1182.09	2320.78	2.55
6	279	176.0	49.10	504.58	1261.44	83.7	27.70	314.95	1296.07	2557.51	2.81
7	296	147.0	43.51	548.09	1370.22	68.7	24.12	339.06	1395.32	2765.54	3.04
8	285	153.0	43.61	591.69	1479.24	68.4	23.12	362.18	1490.46	2969.70	3.26
9	285	163.0	46.46	638.15	1595.37	84.3	28.49	390.68	1607.72	3203.09	3.52
10	268	156.0	41.81	679.96	1699.89	68.6	21.80	412.48	1697.45	3397.34	3.73
11	260	142.0	36.92	716.88	1792.19	62.7	19.33	431.82	1777.01	3569.21	3.92
12	260	148.0	38.48	755.36	1888.39	59.8	18.44	450.26	1852.90	3741.29	4.11
13	274	162.0	44.39	799.75	1999.36	68.7	22.33	472.58	1944.77	3944.13	4.33
14	264	151.0	39.86	839.61	2099.02	66.4	20.79	493.37	2030.32	4129.35	4.54

Graphing the Data

The first thing that one should do with the data is graph the concentrations. This will allow one to spot obvious trends and errant values. Figures A-2 through A-6 shows actual data and calculated values from one of the columns from one of the laboratories used in the interlaboratory method evaluation study (Method 1627 Reference 12.23).

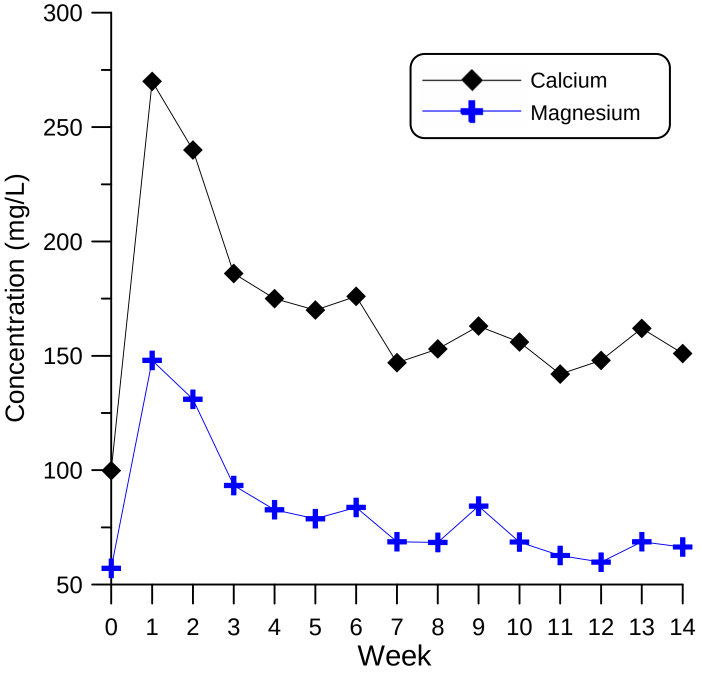


Figure A-2. Concentration of calcium and magnesium through the “initial flush” (week 0) to week 14.

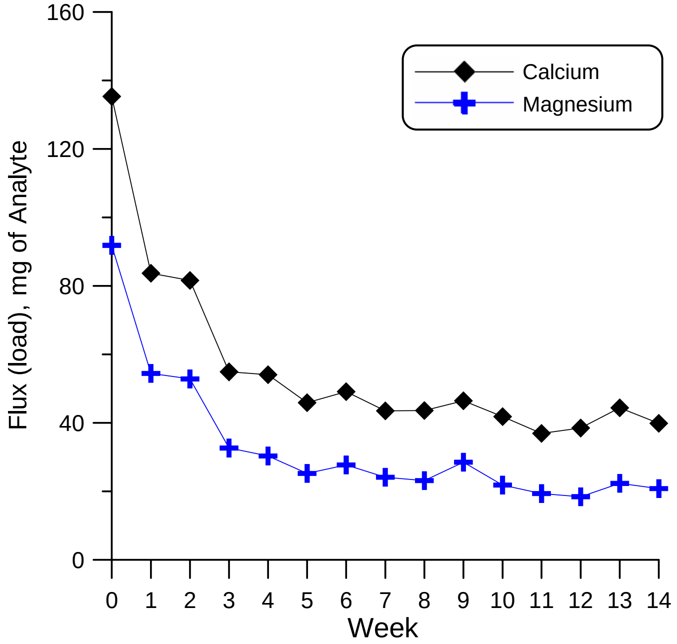


Figure A-3. Flux (load) of analyte.

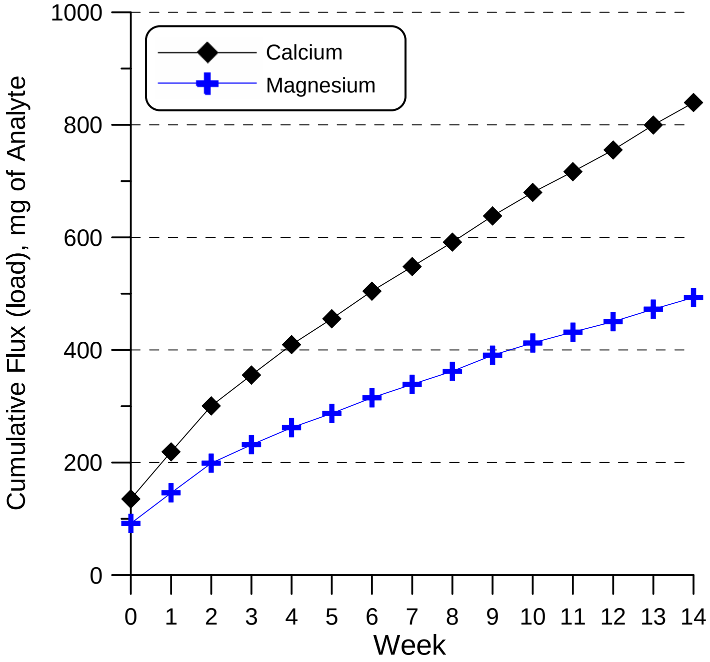


Figure A-4. Cumulative flux (load) of analyte over the 14 week period.

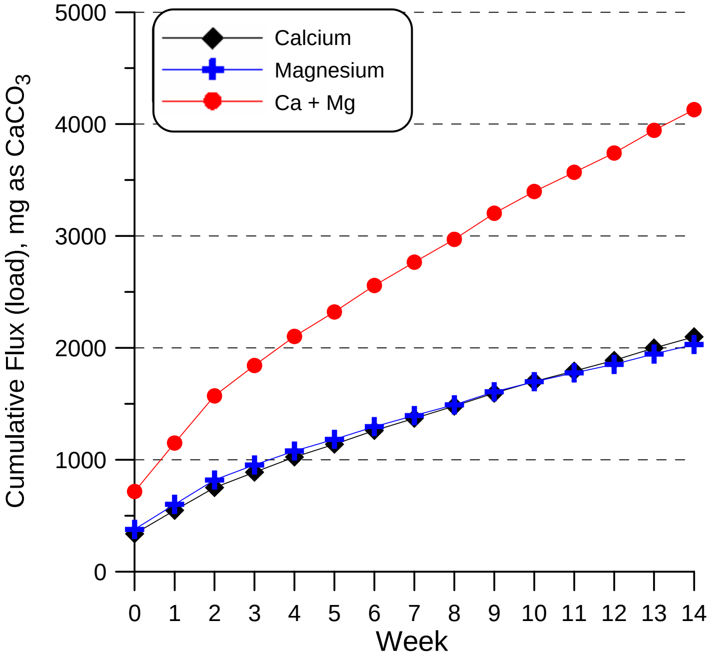


Figure A-5. Cumulative flux of calcium and magnesium expressed as calcium carbonate. Also plotted is the flux of total calcium carbonate equivalent (Ca + Mg).

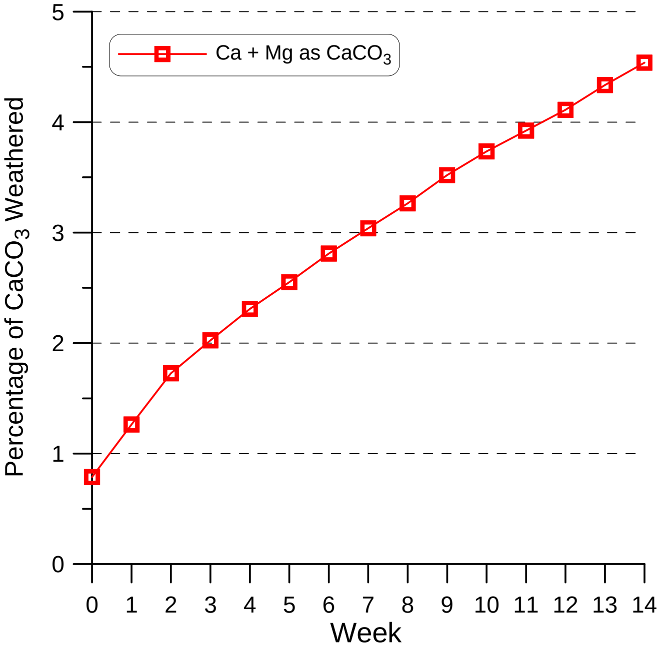


Figure A-6. Percentage of calcium carbonate equivalent weathered through the course of the leaching test. In this instance, approximately 4.5% of the calcium carbonate (equivalent) was removed from the column during the weathering test.

Appendix A References

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Sobek, A., W. Schuller, J. R. Freeman, and R. M. Smith, 1978. Field and Laboratory Methods Applicable to Overburdens and Minesoils. Prepared for U.S. Environmental Protection Agency, Cincinnati, Ohio. EPA-600/2-78-054, 203 p.

Appendix B: Example calculations for estimating mineral solubility of calcite and gypsum

Mineral Solubility

Given sufficient time and stable conditions, a mineral will dissolve in water, up to the point where the water cannot "hold" any more of that mineral's constituents. This characteristic solubility relation for a mineral can be evaluated by an equilibrium equation and constant, assuming the system is at or near chemical equilibrium. For many rock-water reactions, the equilibrium assumption is reasonable. A precipitation / dissolution reaction can be written into a chemical reaction expression as follows:

$$wA + xB \longleftrightarrow yC + zD$$

Where: A, B, C and D are products and reactants, and w, x, y and z are stoichiometric coefficients. Gypsum and calcite dissolution/precipitation reactions are:

$$CaSO_4 * 2\,H_2O \longleftrightarrow Ca^{2+} + SO_4^{2-} + 2\,H_2O$$

$$CaCO_3 \longleftrightarrow Ca^{2+} + CO_3^{2-}$$

The chemical reaction can be formulated into a mathematical expression as follows:

$$\frac{[C]^y \times [D]^z}{[A]^w \times [B]^x} = K^o$$

Where: the brackets represent chemical activity in moles/L, and K^o is an equilibrium constant characteristic for the reaction. Values for equilibrium constants are experimentally determined at specific temperatures, usually 25°C. The van't Hoff equation is used to correct the value of K^o at temperatures other than 25°C.

At equilibrium, gypsum and calcite solubility are represented as:

$$\frac{\left[Ca^{2+}\right]^1 \times \left[SO_4{}^{2-}\right] \times \left[H_2O\right]^2}{CaSO_4 * 2H_2O} = K^o \qquad \log K^o \approx -4.58$$

and

$$\frac{\left[Ca^{2+}\right] \times \left[CO_3{}^{2-}\right]}{\left[CaCO_3\right]} = K^o \qquad \log K^o \approx -8.48$$

The product of the left side of the above two equations is called an ion activity product (IAP), and is calculated using results of leachate analysis (see Section 8.5 of Method 1627). The IAP is compared to the equilibrium constant K^o to calculate a saturation index S.I. as follows:

$$S.I. = \log_{10} \frac{IAP}{K^o}$$

Because the ion activities are expressed in moles per liter, it is mathematically convenient to calculate $S.I.$ in log base 10.

The computed saturation index S.I. is interpreted as follows:

- S.I. less than zero(0), indicates the water is under-saturated for the mineral, or is holding less than the maximum it can contain of that mineral's constituents. The mineral cannot precipitate from the water. If the mineral is present in the rock, it could dissolve into the water.
- S.I equal zero(0), indicates the water is saturated for that mineral. The water has dissolved all of that mineral's constituents that it can hold, and is at equilibrium for that mineral.
- S.I. greater than zero(0) indicates the water is over-saturated for that mineral. The water has more of the mineral's constituents than it can hold, and the solid mineral should precipitate.

The equilibrium constant K^o is usually determined on mineral phases that are pure, or of known composition. Some minerals such as calcite may have other elements substituted in the crystal lattice. Calcite can contain a few percent magnesium, iron, strontium or other elements in place of calcium. Solubility of these mixed phases can be different than the pure mineral. Even for pure mineral phases, reported equilibrium constants often have a range of experimental uncertainty.

The products and reactants in solubility calculations are expressed as chemical activities or "effective concentration." In very dilute waters, activity and total concentration are nearly the same. However, as ionic strength of a water increases, charged ions interact and the effective and total concentrations diverge. The difference between chemical activity or "effective concentration," and total concentration depends on ionic strength. The chemical activity is calculated from estimates of ionic strength, ion size and charge and total concentration in several steps.

The first step is calculating ionic strength, which is a measure of the electrical charge present in solution. It is calculated as:

$$I = 0.5 \times \sum m_i {z_i}^2$$

Where: m_i is molar concentration, and z_i is charge on the ion. The charge is summed for each measured cation and anion.

It is possible to estimate ionic strength from specific conductance measurements; however, those estimates can be less precise.

The second step is to calculate an activity coefficient using either the Debye-Huckel or Davies equations.

$$\log \gamma_i = -A{z_i}^2\sqrt{I} \quad \text{(Debye-Huckel)}$$

$$\log \gamma_i = \frac{-A{z_i}^2\sqrt{I}}{1+\sqrt{I}} - 0.3 \times I \quad \text{(Davies)}$$

Where: A is a constant, I is ionic strength, and γ_i is the activity coefficient. The Davies equation is considered accurate up to ionic strengths of about 0.5 molar.

Chemical activity and total concentration are related to each other by the activity coefficient γ_i as follows:

$$\text{Activity Coefficient } (\gamma_i) = (\text{Chemical Activity / Concentration})$$

Activity coefficients are usually less than one, and chemical activity and total concentration are expressed in mol/L. The coefficient permits conversion of the total concentration values into activity units needed for solubility calculations. The activity of a solid in the calcite and gypsum reactions is defined as 1, and the amount of water involved in reaction is small relative to the bulk solution, that the activity of water is also 1 or nearly so. Mineral solubility concepts are described in more detail in the references listed at the end of this appendix.

Software for Calculating Gypsum and Calcite Solubility

Saturation indices for calcite and gypsum can be calculated using the US EPA geochemical code, MINTEQA2, or the US Geological Survey software, PHREEQCI. These software are equilibrium speciation models that calculate the composition of dilute aqueous solutions in laboratory, surface or ground water systems, including the distribution among dissolved, adsorbed, and solid phases under specified gas composition. This software includes a choice of several comprehensive data bases for modeling, and both models solve iteratively for equilibrium composition to a specified level of precision. Commercial software, such as Geochemist Workbench, is also capable of performing these calculations. The model computations follow the techniques for chemical activities and equilibrium constants described in the first section of this appendix.

- MINTEQA2 and corresponding documentation can be obtained at EPA's Center for Exposure Assessment Modeling, Multimedia Models, at: http://www.epa.gov/ceampubl

- PHREEQCI and corresponding documentation can be obtained from the USGS Water Resources Division, Geochemical Software at: http://water.usgs.gov/software/lists/geochemical

The recommended parameters for calculating gypsum and calcite solubility are: pH, alkalinity, temperature, calcium, sulfate, magnesium, sodium, potassium, iron, aluminum, manganese. Magnesium, sodium, potassium, iron, aluminum or manganese can be omitted if these parameters are known to be present only in small concentrations (< about 10 percent of the total cation charge).

Mineral solubility can also be computed in spreadsheets.

Example Calculation of Gypsum and Calcite Solubility

Gypsum and calcite solubility were calculated for the five standard rock samples using PHREEQC and MINTEQA2. The two software produce near identical results with only very minor differences due to rounding and significant figures. Table B-1 shows the leachate composition data and computed saturation indices for sample BCS3-PA from one lab. Gypsum and calcite saturation indices were calculated for each weekly sample, and results are plotted in Figure B-1 for 12 weeks.

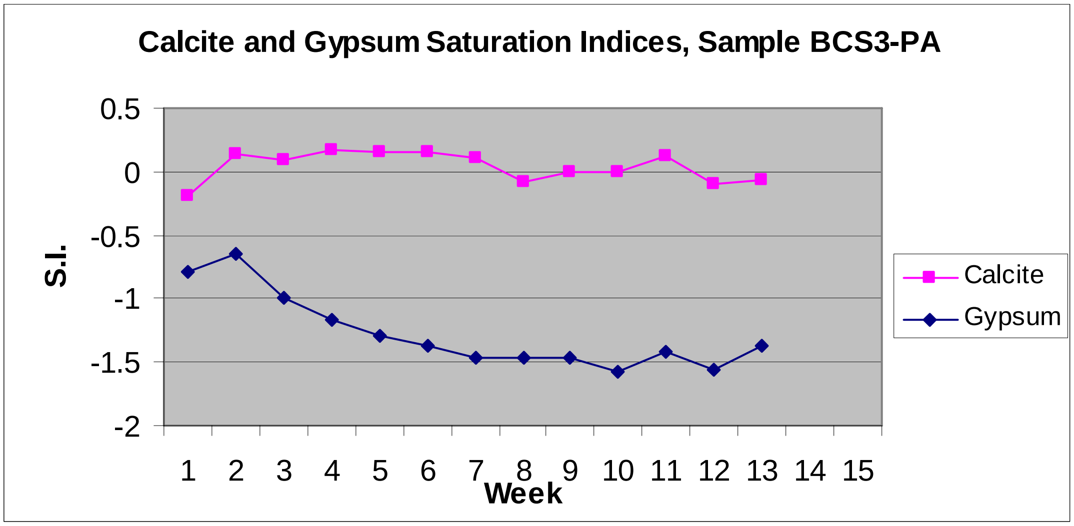

Figure B-1. Calcite and Gypsum Saturation Indices, Sample BCS3-PA

This rock is approximately at equilibrium for calcite throughout the test period. Calcite is dissolving into the leach water up to the maximum amount of carbonate alkalinity and calcium that the water can"hold." The aqueous concentrations of these two parameters are constrained by the solubility of calcite.

The leachate samples are under-saturated for gypsum throughout the entire test period. The mineral gypsum cannot form a solid precipitate from these waters. The aqueous concentrations of calcium and sulfate are not constrained by gypsum solubility. Because the saturation index is in log base 10, the plot shows that after week two, the water is under-saturated for gypsum by a factor of greater than 10. If gypsum is present in the rock, it could dissolve into solution.

Table B-1: Leachate Composition for Sample BCS3-PA for 12 weekly samples (1)

Week	pH	Alkalinity	Temperature	Ca	Mg	Sulfate	Na	K	Calcite S.I.	Gypsum S.I.
1	7.20	198.5	20.8	204	103.8	678	11.3	6.1	0.13	-0.65
2	7.24	222.7	21.8	121.5	68.6	392	6.9	6.5	0.09	-0.99
3	7.33	239.2	21.5	102.5	57.6	270	5.0	5.7	0.17	-1.17
4	7.32	229.1	22.4	99.2	53.8	203	2.8	4.4	0.16	-1.29
5	7.29	249.3	21.9	93.9	38.1	162	2.4	4.3	0.16	-1.37
6	7.34	220.5	21.5	81.4	33.2	135	1.4	4.3	0.11	-1.47
7	7.18	221.9	22	74.7	31.8	147	2.3	3.2	-0.08	-1.47
8	7.14	252	21.1	90.8	40.7	133	2.4	3.9	0.00	-1.46
9	7.23	230.9	20.4	77.8	33.6	110	1.7	3.9	-0.01	-1.57
10	7.18	264.9	21.9	103.4	44.7	137	1.7	3.5	0.12	-1.41
11	7.15	220.3	22	75.7	27	112	1.5	3.4	-0.09	-1.56
12	7.02	259.3	22.2	99.7	33.5	148	1.5	2.2	-0.06	-1.37

(1) pH in S.U., alkalinity in mg/L $CaCO_3$,temperature in C°; Ca, Mg, sulfate, Na and K in mg/L, calcite and gypsum indices are dimensionless.

S.I. is saturation index

References

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APPENDIX B

RESPONSE TO PEER REVIEW COMMENTS ON DRAFT KINETIC TEST PROCEDURE

* Note: The version of the test method used for peer review preceded the Final Draft version;. Comments from this peer review were considered and incorporated in revisions to the draft method where appropriate.

Pages 279-301

RESPONSE TO PEER REVIEW COMMENTS
ON DRAFT KINETIC TEST PROCEDURE

In late January 2003, the draft Kinetic Test Procedure was sent to six reviewers identified by the project team as experts in the fields of either kinetic test procedures, the mining industry, or geochemisty.

REVIEWERS

Arthur W. Rose, P.G.	Penn State University
Kim Lapakko	MN Department of Natural Resources
WW. White, P.G.	U.S. Bureau of Land Management
Robert Kleinman	Department of Energy
Terry Brown	Western Research Institute
Gwen Geidel	University of S. Carolina (review comments not yet received)

To date, comments have been received from 5 of the six reviewers and are summarized below. In addition to asking reviewers to provide general comments, the Project Team asked that reviewers consider and address the following specific aspects of the draft method:

1) Document's Scientific Merit: Reviewers are asked to comment on the scientific soundness of the draft method.
    a. The method contains procedures for assembling samples based on particle size distribution, including removal of small particle-size portions. These procedures are intended to provide results that can be interpreted against a standard, and to eliminate or reduce channeling and exposure variability. Do you have any comments related to this aspect of the method?
    b. Are the parameters for water (alkalinity, acidity, dissolved metals (iron, manganese, aluminum, magnesium, calcium), sulfate and conductivity) and soil characteristics (percent sulfur, neutralization potential, and particle size distribution) sufficient to provide useful information regarding mine drainage quality? Are any of these parameters unnecessary, or are there additional parameters that should be tested?
    c. Do the weathering procedures described in the method provide a useful standardized assessment of sample exposure?
    d. Section 10 includes information regarding the method performance (relative percent difference, RPD, between duplicate samples) that can be expected by laboratories using duplicate samples. This information also is intended to provide quality control specifications that can be applied for verification of data. Do you believe that the RPD between duplicate samples exposed to identical weathering procedures is sufficient for evaluating method performance. Can you recommend any additional or alternative cost effective and feasible quality control procedures?

2) Document Quality and Clarity: Peer reviewers are asked to critique the document for its clarity given its potential scientific and technical applications. More specifically, reviewers are asked to address the following questions:
    a. Are sufficient details provided for setting up and implementing the method procedures?
    b. Are data equations presented in a technically clear and appropriate manner?
    c. Does the method accurately present the equations necessary to obtain useable data results?

3) Do you believe that this draft method has the potential to serve as an effective and standardized tool in predicting the quality of mine drainage? Do you have recommendations that may enhance method procedures towards obtaining this goal?

4) Do you believe that the draft method has sufficient detail to allow its application in laboratories that typically perform mine drainage analyses? Do you believe that the detail provided allows sufficient

flexibility for method users to adjust for cost and laboratory conditions, while still meeting the method performance criteria?

5) What, in your opinion, are the most influential variables in creating the results that are obtained using the weathering procedures in this draft method?

1. Scientific Merit:

a. The method contains procedures for assembling samples based on particle size distribution, including removal of small particle-size portions. These procedures are intended to provide results that can be interpreted against a standard, and to eliminate or reduce channeling and exposure variability. Do you have any comments related to this aspect of the method?

1a.1	**Comment:** The removal of the small fraction could and probably will significantly affect the acid forming potential of some materials. For example, I have studied materials containing acid forming materials almost entirely in the small particle-size fractions. How does this method account for that? Acid-Base Accounting? ***Response***: *We agree and have extensively considered the fact that removal of the small fraction particle size will affect the acid forming potential of certain rock material. To perform laboratory-scale kinetic leaching evaluations of these materials, however, it is not possible to completely represent field conditions. For example, rocks are crushed in order to fit rock samples into the leaching columns, resulting in an increase in the percentage of fine particles. In addition, method development activities demonstrated numerous problems caused by fine particles in terms of gas/water introduction and leachate collection from the columns over time. To address these practical concerns and provide a standardized procedure, the method specifies a particle size distribution for all samples. Text has been added (Section 8.1.3 of revised method) to acknowledge that "Once samples have been collected and crushed, sample particle size distribution that occurred in the field is lost. This distribution is intended to provide standardized conditions and collection of leachate."*
1a.2	**Comment:** Section 3.1.1 What column size is used for particles <0.5 cm? If particles are crushed to <3/8", why not just specify this size? Or give a minimum typical size based on 3/8" material? If the material is smaller, does it make any difference if the column is this large? Do you need to mix units here (cm vs. in)? ***Response:*** *This section also states that "For smaller particles, a factor greater than four should be used. Scaling factors that consider the ratio of column dimensions and particle size are presented in Murr et al. 1977." For clarification, the following sentence has been added: "This method specifies a maximum sample particle size of 3/8-inch (see Table 2 in Section 8.13) and uses 2-inch diameter columns."*
1a.3	**Comment:** Section 7.1.5--last sentence seems to give guidance and doesn't. We know that small particles might have a significant impact--telling the user to further evaluate it without giving guidance on how to do it is not fair--the method created the problem and has to resolve it. ***Response:*** *This section has been removed from the method. Section 8.1.2 (Section 7.1.2 of the method reviewed by the commenter) covers this concern, stating that "Samples should be analyzed for neutralization potential and percent total sulfur. Methods for analysis of these parameters are included in Table q. If the overall change in particle size, NP, percent sulfur, or other parameters will be determined, there analyses also may be performed on the sample after the last leachate has been collected and the sample removed from the column." Please also see response Comment 1a.1.*
1a.4	**Comment:** Section 7.2 Why are fines eliminated from testing? This fraction of the sample will generally have the highest specific surface area and the largest extent of iron sulfide and carbonate mineral liberation. Consequently, this fraction may have the largest impact on drainage quality and should be subjected to testing. Alternatively, the rationale for excluding this fraction must be clearly stated. ***Response:*** *See response to Comment 1a.1.*

1a.5	**Comment:** Part 7.1.5 – I am not sure I understand the basis for this determination. The leaching method is needed because acid-base accounting doesn't provide results that will describe results in the field. Yet, the evaluation of the fine fraction (the most reactive component) should be evaluated using acid-base accounting before consideration for additional evaluation. In addition, the products from the fine fraction may interact with the products from the coarse fraction. If the fine fraction is removed from the system, how do you account for any interactions? ***Response:*** *See response to Comments 1a.1 and 1a.3.*
1a.6	**Comment:** Section 6.1.3 I am skeptical of this reconstruction step. If the sample crushes easily and most pyrite is in the fines, then the test results may be much lower than in nature. I think you have to put the whole sample into the column, in its natural particle sizes. Otherwise, the result can be markedly different from nature. ***Response:*** *See response to Comment 1a.1.*
1a.7	**Comment:** Section 6.1.5 The fines are not added to the column? Again, I don't like this. ***Response:*** *See response to Comment 1a.1.*
1a.8	**Comment:** Part 7.1.4 – The exclusion of the < 35 mesh size fraction from the column is a concern. Both potential acidity and neutralization potential associated with the fine size fractions are eliminated. Since the smaller size fractions can be considered more reactive (more soluble, etc.), the removal of this material from leaching column may impact the resulting leachate chemistry. In addition, the interaction of the large and small size fractions will not be evaluated by the weathering process. ***Response****:* *See response to Comment 1a.1.*
1a.9	**Comment:** In terms of technical merit, I am particularly unhappy with the procedure of removing the fines, and making an arbitrary mix of the coarser fractions. This has got to result in acidity, etc. that are not representative of the field material, in some cases. I can see that doing a size analysis can allow you to estimate an approximate surface area, and that you might have some problems with clogging by fines, but the procedure seems very artificial and perhaps misleading in some of the most critical cases, where lots of fines are present in nature, or the rock is very inhomogenous physically. ***Response:*** *See response to Comments 1a.1 and 1a.3.*

b. Are the parameters for water (alkalinity, acidity, dissolved metals (iron, manganese, aluminum, magnesium, calcium), sulfate and conductivity) and soil characteristics (percent sulfur, neutralization potential, and particle size distribution) sufficient to provide useful information regarding mine drainage quality? Are any of these parameters unnecessary, or are there additional parameters that should be tested?

1b.1	**Comment:** Section 6.3.1.2 If the leachate is filtered, CO_2 will be lost. The procedure in this section needs more work. Probably the leachate should be stirred gently, its pH and conductivity measured, then part put into a cooled container, and the rest filtered. Preferably the alkalinity should be measured immediately. ***Response:*** *The following note is included in the method (at Section 8.5, Leachate Collection): "The procedure used to collect leachate must minimize carbon dioxide degassing (e.g., insert the drainage tube into the bottom of the sample collection container throughout collection; seal the container immediately following collection; refrigerate the sample if analysis is not performed immediately; keep sample container submerged in ice if collection drainage is slow)." Instructions to filter the leachate to remove fine particles have been removed. Instead, the leachate is analyzed immediately for determination of pH and conductivity, and additional aliquots are prepared for further analysis. Aliquots are filtered only if they are to be analyzed for dissolved parameters (method Section 8.5.1.2).*

1b.2	**Comment:** Table 2. What does “Alkalinity 2030” mean? The procedures list seems to end with an imcomplete method (I-). ***Response:*** *Thank you. “2030” has been removed, and replaced with “(to pH 4.5)”. Additionally, the USGS Method cited has been revised to I-2030.*
1b.3	**Comment:** Section 2.0 Production of metals was mentioned in section 1, paragraph 2, sentence 3. Consequently, methods for determining solid-phase metal concentrations should be included. ***Response:*** *Table 1 provides a list of methods that can be used to determine the neutralization potential and total sulfur content of soil samples, both of which are to be determined during initial sample characterization (see method Section 8.1.2). Analytical procedures for determining metal concentrations in soil samples are outside the scope of this method.*
1b.4	**Comment:** Section 3.0 The purpose of the method is to characterize water quality. What aspects of water quality are of interest, pH, acidity, metals, other? ***Response:*** *Recommended target analytes, along with appropriate corresponding analytical methods, are listed in Table 3 of the method (Analytes and Appropriate Methods). Note, this is Table 2 in the method reviewed by the commenter. Additionally, Section 8.5.2 (Section 7.4.2 of reviewed method) notes that leachate is analyzed immediately upon collection for specific conductance, alkalinity, and pH.*
1b.5	**Comment:** Section 7.3.1 “...until the conductivity of the flush water stabilizes...” Guidance should be supplied as to what constitutes stabilization. For example “...until the conductivity of the flush water changes by no more than XX ΦS...” ***Response:*** *This sentence has been revised to: “Continue to add, drain, and analyze reagent water in this manner until the conductivity of the water stabilizes (relative standard deviation between conductivity measurements ≤ 20%).”*
1b.6	**Comment:** Section 7.4.1.2 In concert with the following comment, is there certainty that solids in the leachate sample do not include precipitates? Although I lack experience with the method, given the large size of particles in the column it seems unlikely that they would be lost during leachate collection. ***Response:*** *Appendices addressing carbonate dissolution, pyrite oxidation, and mineral solubility of calcite and gypsum have been added to the method.*
1b.7	**Comment:** Section 7.4.1.3 What is the degree of certainty that this method of collection eliminates precipitation of calcite? That is, has this aspect been evaluated empirically? ***Response:*** *See response to Comment 1b.6.*
1b.8	**Comment:** Table 3 Why is pH excluded from results? Is this controlled by the gas mixture rather than mineral dissolution reactions? ***Response:*** *pH quality control results were determined during the multi-laboratory study and are provided in Table 4 of the September 2008 method revision.*
1b.9	**Comment:** The parameters for water and soil characteristics appear to be sufficient. However, HCO_3^{-1} might be included since this constituent maybe important in certain situations. ***Response:*** *Alkalinity accounts for the bicarbonate anions in a sample. Alkalinity can be converted to bicarbonate by dividing alkalinity by 0.8202 (see Study and Interpretation of the Chemical Characteristics of Natural Water, US Geol. Survey Water-Supply Paper 2254, p. 57)*

1b.10	**Comment:** Section 3.2 Can gas sorption determinations of surface area be conducted on particle sizes this large? ***Response:*** *Yes. These determinations were performed by the Materials Research Laboratory at Penn State University during development and validation of this method.*
1b.11	**Comment:** Section 3.2 The total surface area determination described applies to the entire solid matrix. With respect to pyrite and carbonate mineral reactions, the surface areas of these minerals is of importance. It is unlikely the total surface area will accurately reflect the surface areas of these minerals. Consequently, the merits of conducting gas sorption analysis on the solids matrix for the purpose of normalizing rates for surface area are unclear. ***Response:*** *Gas sorption analysis is optional.*
1b.12	**Comment:** Section 3.2 Determining the extent of carbonate and iron sulfide mineral liberation may be more appropriate for normalizing dissolution rates of these minerals. ***Response:*** *Appendices have been added to the method to provide example calculations for determining carbonate dissolution rates, pyrite oxidation rates, and mineral solubility of calcite and gypsum.*
1b.13	**Comment:** Section 6.1 Should lithologic logs be retained to document the representativeness of samples? ***Response:*** *Yes, lithologic logs are routinely retained by regulatory agencies and permittees as part of regulatory requirements.*
1b.14	**Comment:** Section 9.4.2 As mentioned previously, expression of results in terms of total surface area may be misleading because this does not necessarily reflect the available mineral surface areas that contribute to reactions of interest. ***Response:*** *This equation has been removed from the method. Instead, results are calculated in units of mass weathered per week and mass produced per sample weight. Method appendices also have been added to provide example calculations for determining carbonate dissolution rates, pyrite oxidation rates, and mineral solubility of calcite and gypsum.*
1b.15	**Comment:** Part 7.1.2 – Total S may be an appropriate parameter for calculating potential acidity for eastern mines. However, many sites/materials contain SO_4^{-2} and SO_4^{-2} minerals in addition to pyrite. In such cases pyrite levels should be determined and used in lieu of total S. ***Response:*** *Appendices have been added to the method to provide example calculations for determining carbonate dissolution rates, pyrite oxidation rates, and mineral solubility of calcite and gypsum.*
1b.16	**Comment:** The use of total S levels to calculate acid potential may work for some mines but many of the mines in the west and some in the east contain significant SO_4^{-2}'s, SO_4^{-2} minerals etc. Pyrite determinations are needed to calculate potential acidity at some mine sites/materials. ***Response:*** *See response to Comment 1b.15.*
1b.17	**Comment:** Section 9.1 Will NP be presented in units of mg/kg or percent, or as more commonly presented in units of parts per thousand? ***Response:*** *The units reported for NP of the rock sample will depend on the reporting requirements specified by the data user. A footnote also has been added to provide a reference for procedures that can be used to determine NP. (See method Section 2.0.)*

1b.18	**Comment:** Section 9.3 May also want to record cumulative mass release for critical analytes ***Response:*** *The equations reviewed by the commenter have been removed from the method. Instead, results are calculated in units of mass weathered per week and mass produced per sample weight.*
1b.19	**Comment:** Part 7.4.2 – Sample solution for SO_4^{-2} determinations should be filtered using a 0.45 :m filter. ***Response:*** *This sentence has been revised to state that: "If the leachate will be analyzed for dissolved parameters (SO_4^{-2}, metals), the leachate must be filtered through a 0.45 µm filter prior to analysis." (See method Section 8.5.1.2.)*
1b.20	**Comment:** Section 7.1.2 The sample characterization is extremely limited, and additional analyses should be considered. To conduct a 16-week test on a sample on which so little is known limits the value of the results. It is possible that there is substantial data on specific strata to counter this deficiency to some degree. If so, the rationale for such limited solid-phase characterization should be stated. For example, if metal release is of interest, determination of metal concentrations in the initial sample would be beneficial. Whole rock and trace metal chemistry analyses can be conducted for less than $100 per sample. The mineral phases in which carbonate occurs may also prove to be valuable. ***Response:*** *A note has been added to this section, stating that additional parameters may be measured if required or requested by the data user.*
1b.21	**Comment:** All the test parameters are needed (alkalinity, acidity, pH, conductivity, Fe, Mn, Al, Ca, Mg, SO4). Also should specify the temperature and the amounts of sample and solution. ***Response:*** *We agree that the test parameters listed (see method Table 3) are needed. Specific requirements regarding sample preservation (e.g., temperature) and volumes are noted in the analytical method selected for measuring each parameter, and are not within the scope of this method. Section 9.1 (Section 8.1 of the method reviewed) also states that "All quality control measures described in the reference analytical methods for leachate analysis (Table 3) and sample characterization (Table 1) should be used.*
1b.22	**Comment:** Section 2.2 You need to clearly present this as two alternative methods for surface area: 1) Calculation from particle size, 2) Gas adsorption. I don't see any description in the procedure for getting the surface area from the size distribution. ***Response:*** *A footnote has been added to this section, to provide two references to procedures that can be used to determine particle surface area using gas adsorption. (See method Section 3.2.)*
1b.23	**Comment:** Section 7.1.2 What grain size sample is submitted for NP and S determinations? This seems to require a grinding step. ***Response:*** *Grain size specifications are provided in the methods listed for determination of these parameters (see Method Table 1). Typically, a split of the sample is ground to -60 mesh.*

c. Do the weathering procedures described in the method provide a useful standardized assessment of sample exposure?

1c.1	**Comment:** Section 2.0 Why is the 8 to 16 week period selected? Is this duration adequate to empirically determine if coal mine wastes will produce acid? ***Response:*** *This sentence has been revised to state that the sample are exposed to simulated weathering conditions over a period of at least 12 weeks. During method development and validation in several laboratories, soils, and studies, it was determined that analyte production typically peaked at approximately 10 –12 weeks.*
1c.2	Section 6.3 Appropriate ranges should be provided for "…dry, and cool conditions." ***Response****: The last sentence of this Section states that "Sample shipment, storage, and preservation procedures are described in ASTM D5079."*
1c.3	**Comment:** The weathering procedures described may provide a useful standardization assessment for a single sample exposure if the weathering procedure is written specifying specific procedures. Seemingly, simple changes in the procedure will result in significant differences in results. After spending three (3) years with OSM attempting to develop QA/QC programs for laboratories in the Western United States, I found that laboratory evaluations of pH, EC etc. from a saturated paste or 1:1 mixture were often different likely as a result of equilibration time (12 to 24 hours), extraction method (differences in vacuum, etc.); all seemingly insignificant differences in method. ***Response:*** *We agree. The quality control specifications provided in Section 11.0 (Method Performance) of the method were generated from pooled data generated in seven laboratories performing the method on replicate soil samples. These specifications reflect the variability that should be expected across and within laboratories.*
1c.4	**Comment:** Part 9.4.2 – Surface area determinations may be difficult to duplicate. QA/QC would be a large problem between laboratories. I am not sure how important it is to show the data on a surface area basis. ***Response:*** *Surface area determinations are optional.*
1c.5	**Comment:** Part 7.2.2 – Any type of filling and packing (tapping) will cause differential compaction and particle size segregation. ***Response:*** *We agree. This section (Section 8.2.2 in September 2008 revision) has been modified to state "Using a wide-bore or powder funnel, add approximately 2,000 grams of the reconstructed sample to the column, being careful to ensure uniform distribution with little to no packing."*
1c.6	**Comment:** Sections 7.3.2 and 7.3.3.2 Does the column sit unsaturated for 7 days or 6 days? Logically, it is the latter. ***Response:*** *This section (Section 8.4.2 in September 2008 revision) has been modified to clarify that the column is allowed to sit for a period of 6 days during the humidified air cycle.*

1c.7	**Comment:** Section 3.2 Not clear. It appears that the gas mixture is used in 2 ways: 1) bubbled into reagent water reservoir, and 2) bubbled into column. Is the 10% CO_2 defined by the gas mixer or by the outflow gas composition? If the flow rate is appreciable, I would think that inflow composition would be OK, since the amt. Of water is finite. Does one need a gas analyzer to measure the outflow gas composition? Specifications on instrument and allowable error in percentage? ***Response:*** *Section 4.2.1.1 (Section 5.2.1.1 of September 2008 revision) provides instructions for monitoring gas flow, including daily monitoring using flow meter, gas meters, or tube indicators) to ensure that the* CO_2 *in the outflow is at least 10%. A requirement to use a portable* CO_2 *meter, capable of measuring* CO_2 *to 10% (within ± 0.5%), to take daily readings of the* CO_2 *released from each column also has been added (see method Section 8.3.2.2).*
1c.8	**Comment:** Section 4.2.1.2 Tubing clamps seem pretty crude for controlling flow. What flow rate is desired? Why not a flow meter (bubbler)? ***Response:*** *This section (Section 5.1.4 of September 2008 revision) has been modified to include details regarding tubing and clamps that are recommended for controlling flow. Information also has been provided regarding recommended flow meters (rotometers) capable of controlling flow at approximately 1 L/minute. (See method Section 5.2.1.3.)*
1c.9	**Comment:** Section 4.1.2 It is not clear that glass beads of the size indicated would produce "uniform introduction of both water and gases." For example, the criterion stated could result in glass beads of 1-inch diameter in a 2-inch diameter column. I have no data or literature to cite that would indicate this would not produce uniform flow, but intuition suggests that it will be of little benefit. Please provide a citation regarding this criterion. ***Response:*** *Specifications for plastic (polypropylene) beads of ½-inch diameter or HDPE 5/16-inch diameter, have been included. (See method Section 5.1.5.2.)*
1c.10	**Comment:** Glass wool is suggested as a possible filter media. USBM initially used glass wool as filter media in its first humidity-cell tests of metal-mine waste rock. Unfortunately, after 25 weeks of testing it was discovered that glass wool contributed alkalinity to the effluent (an increase of at least 2 pH units). After considerable leach testing of various filter media material, we found that polypropylene felt was non-reactive and provided a very satisfactory filter material. The polypropylene product we used was purchased from National Filter Media Corp. (NFMC) and the product serial number is S/226 075 020 (my NFMC contact in Salt Lake City is Mark Rydalch 2 801-363-6736). Also see my comments on Section 8.4. ***Response:*** *Thank you. In response to this and other comments, a note has been added to Section 5 of the method to state that "Glass wool has been shown to neutralize acid and elevate pH in experimental work at both the Minnesota Department of Natural Resources and the US Bureau of Mines. It should not be used in this type of testing unless it is tested and shown to be unreactive. Aquarium filter media is provided as an alternative liner material.*
1c.11	**Comment:** Glass wool has been shown to neutralize acid and elevate pH in experimental work at both the Minnesota Department of Natural Resources and the US Bureau of Mines. It should not be used in this type of testing (ASTM 2000, note 5, p. 259) unless it is tested and shown to be unreactive. ***Response:*** *See response to Comment 1c.10.*

1c.12	**Comment:** Section 4.2 It appears that maintaining the appropriate gas mixture may be important for obtaining reproducible results. Values presented in Table 3 indicate that RPD for air-CO_2 mixtures is always greater than that for air-only. One very plausible explanation for this is that the air-CO_2 mixture is not effectively controlled. ***Response:*** *We agree that maintenance of gas flow and mixture components is important for obtaining reproducible results. The method performance specifications provided in Section 11.0 of the September 2008 revision are based on data generated in seven laboratories, and consider the variability that can occur within and between laboratories. Section 4.2.1.1 (Section 5.2.1.1 of September 2008 revision) provides instructions for monitoring gas flow, including daily monitoring using flow meter, gas meters, or tube indicators) to ensure that the* CO_2 *in the outflow is at least 10%. A requirement to use a portable* CO_2 *meter, capable of measuring* CO_2 *to 10% (within ± 0.5%), to take daily readings of the* CO_2 *released from each column also has been added (see method Section 8.3.2.2).*
1c.13	**Comment:** If variation in the air-CO_2 mixture affects results, the use of a certified gas mixture appears to be a reasonable approach to eliminating this problem. I am not familiar with the other methods of maintaining a constant ratio of air to CO_2. If their use is to be permitted, testing of the control method (if not done already) would be prudent. ***Response:*** *See response to Comment 1c.12.*
1c.14	**Comment:** Section 4.2.1.2 The MN DNR experienced problems maintaining constant flow with tubing clamps. The ability of these clamps to maintain adequately constant flow for this method should be checked if this has not been done already. ***Response:*** *See response to Comment 1c.12.*
1c.15	**Comment:** The application of humidified air to the ASTM 5744 cell, during the early stages of development, at times resulted in addition of water to the cell if flow rates were excessive. Establishing a range of acceptable gas flow rates into the column would help control this variability. ***Response:*** *See response to Comment 1c.12.*
1c.16	**Comment:** Section 5.0 The gas mixture described in 5.1.1 and 5.1.2 is different than the alternative described in 5.1.3 (approximate O_2:CO_2:N_2 ratios of 2:1:7 vs 1:1:8). Has the influence of this variation been examined? Is there a commercially available mixture that more closely approximates that of 90% air-10%CO_2? Given the variability in results for the air-CO_2 mixture, providing a consistent mixture (applied at a consistent flow to the column) should be considered. ***Response:*** *The primary concern is to provide 10%* CO_2 *to mimic field conditions. Both of the gas mixtures cited will provide 10%* CO_2. *Additionally, either mixture will provide sufficient oxygen for oxidation of pyrite.*
1c.17	**Comment:** Part 7.3.1 – Tapping the column and the use of the wire to adjust saturation will result in differential compaction and particle segregation. I don't think either is needed. ***Response:*** *We agree. Both have been removed from the method. (Also see response to Comment 1c.5.)*

1c.18	**Comment:** Sections 7.2 and 7.3: I am concerned that no specific sample mass or leach volume has been prescribed. I recognize that these would change depending upon the size of column selected (i.e., 2, 4, or 6-inch ID) and target sample masses could be identified/prescribed for each size. If the objective is to completely flush reaction products from the column during each weekly leach so that mass release rates can be determined (especially from replicates of the same lithology having the same percent S and Ca + Mg carbonates) then a fixed mass and volume would prevent adding additional variables into the test. ***Response:*** *The method has been revised to specify a column inner diameter of 2 inches, column height of 2.5 feet, and a sample weight of approximately 1800 – 2000 grams. Instructions to measure and record the volume of water added to and collected from each column, with each weekly saturation/drainage cycle, also have been added. (See method Section 8.5.1.1.)*
1c.19	**Comment:** Section 7.3.2 The extent of water retained may affect dissolution reactions. Can the column be weighed before and after the rinse to determine water retention? Retention can be approximated by the difference of water added and water removed. However, this does not account for potential water addition during the humidified air cycle. Such addition was observed during early developmental stages of the ASTM 5744 Modified Humidity Cell test (also mentioned in comments under section 4.2.1.2; see also 7.4.1.1). If this occurs in the column method, it will affect the accuracy of the approximation mentioned in the third sentence of this comment. ***Response:*** *We agree and acknowledge that it water will be retained during each saturation/leachate collection cycle. Instructions have been added to measure and record the volume of water with each weekly cycle (see method Section 8.5.1.1). An example form for use in recording this and other weekly monitoring information also has been added (see Section 13.0).*
1c.20	**Comment:** Section 7.4.1 The first sentence indicates "...the total volume of water/leacheate is drainage from the column..." To what does "total volume" refer? The amount added? All water in the column? ***Response:*** *The word "total" has been deleted from this sentence. Also see response to Comment 1c.19.*
1c.21	**Comment:** Section 7.4.1: I question that it is possible to recover the total leach volume from the rock column. As much as 150 mL of a 500 mL leach was typically retained in USBM humidity cell tests after each leach cycle. We did notice that recovered leach volumes began to increase after multiple leach cycles as the retained interstitial water volume stabilized over time. However, we never achieved 100% recovery of the 500 mL leach volume (I recall something like 400+mL at best). ***Response:*** *See response to Comment 1c.19.*
1c.22	**Comment:** Section 7.4.1.1 Recommend recording total leach volume minus recovered leach volume. This will help you document volume of interstitial water remaining in the sample at the beginning of the humidified air cycle. Also recommend weighing column at the end of the humidified air cycle. (In the early stages of method development, water addition during the humdified air cycle at times was so great that the bed became saturated and water ponded at the top. As the technique and technicians improved, the water additions during the humidified air cycle were generally less than 5 mL.) ***Response:*** *Instructions to measure and record the volume of water added and leach volume removed with each weekly cycle has been added to the method. (See response to Comment 1c.19.) Although weighing columns before and after leachate collection would provide useful information, it would be impractical and perhaps problematic.*

1c.23	**<u>Comment:</u>** Table 3 As mentioned previously, the greater variability in results using the air-CO_2 mixture may indicate problems in controlling this mixture. The variability of this mixture and its effect on results should be examined, if this has not yet been done. ***<u>Response:</u>*** *The effect of CO_2 was evaluated in two laboratories during initial method development. Results are provided in method Reference 12.21. See response to 1c.12 regarding method requirements for measurement of the CO_2 component in gas mixtures.*
1c.24	**<u>Comment:</u>** The procedure does not indicate how many weeks the test should extend for, and how the results for multi-week tests should be reported. It is common that the first few weeks are much different from later weeks. At least 8 weeks needed? Perhaps the data for the week of maximum acidity and an average of the last few weeks should be reported. ***<u>Response:</u>*** *The method summary has been revised to state that the sample are exposed to simulated weathering conditions over a period of at least 12 weeks. During method development and validation in several laboratories, soils, and studies, it was determined that analyte production typically peaked at approximately 1 –12 weeks. See response to Comment 1c.1.*
1c.25	**<u>Comment:</u>** Section 4.1 Note that using clear columns and storing columns in the light may enhance biological growth, for example, algae. For a 16-week test, this is unlikely to be extensive. For tests of longer duration, algal growth may be of concern. ***<u>Response:</u>*** *Method developers considered this concern, but thought the ability to observe sample conditions throughout the weathering and leaching procedures was more important. See method Section 5.1.*
1c.26	**<u>Comment:</u>** Section 3.1.2 Can introduced gas pass up thru the glass wool, geotextile (size?), etc? I would expect it to be trapped once the system is saturated, and result in a gas bubble underneath that wants to push up. Some of your later discussion implies that this happens. Why not place the gas inflow above the glass wool etc.? ***<u>Response</u>****: Some of the laboratories involved in the method development and validation studies experienced and resolved this problem by controlling the flow of air into the column. As a result, the method text has been revised to clarify that once the column has been saturated, the gas mixture is introduced through the gas inlet port at the bottom of the column until a slight positive pressure is reached (i.e., a small outflow is produced through the air vent in the top of the column). Gas flow can be controlled and maintained at approximately 1.0 L.minute using a combined flow regulator and meter (e.g., Omega FL-3817-V Series Rotometer or equivalent." See method Section 8.4.3.1.*
1c.27	**<u>Comment:</u>** Section 7.3.3.1: It strikes me that it would be difficult to prevent displacing some of the leach water with the gas during its introduction into the column, and consequently having some of it escape from the air exit port (this fluid loss would mess up your mass release calculations). Using the gas-saturated reagent water leach alternative mentioned in the note following this section seems much more simple and trouble free. Suggest replacing the verbiage in Section 7.3.3.1 with the note information. ***<u>Response</u>****: The alternative procedure that was included in the method reviewed by the commenter has been deleted, and the method has been revised to provide a standardized procedure that involves cycles of 24-hour periods of saturation with reagent water, followed by 6-day exposures to a humidified gas mixture. Also, see response to Comment 1c.26.*

1c.28	**Comment:** Section 7.3.3.1 It seems there is a potential for water to be forced through the air/gas vent if gas is introduced to the column when it is filled with water. Given this possibility, it seems that saturating reagent water with the gas mixture prior to flooding the column should be prescribed. Furthermore, sections 4.2 and 4.2.2 leave the impression that gas will be introduced into the reagent water reservoir. Perhaps experience indicates gas can be added to the water-filled column without water loss and, therefore, either alternative is acceptable. ***Response***: *See response to Comments 1c.26 and 1c.27.*
1c.29	**Comment:** Section 3.3.1 Acidification of the entire sample may provide an alternative for dissolving any $CaCO_3$ precipitated during sample collection. How long does sample collection take? Could $CaCO_3$ precipitate during this period even though flow is introduced to the bottom of the collection vessel and the vessel is covered immediately after sample collection? ***Response:*** *Acidification is not necessary. Alkalinity is measured promptly following sample collection, minimizing effects from* $CaCO_3$ *precipitation.*

d. Section 10 includes information regarding the method performance (relative percent difference, RPD, between duplicate samples) that can be expected by laboratories using duplicate samples. This information also is intended to provide quality control specifications that can be applied for verification of data. Do you believe that the RPD between duplicate samples exposed to identical weathering procedures is sufficient for evaluating method performance. Can you recommend any additional or alternative cost effective and feasible quality control procedures?

1d.1	**Comment:** Tables 3 and 4. What is a relative percent difference? Why not just percent difference? Or is this percent difference from the mean or some more complicated statistical function? Need to define this more exactly. ***Response:*** *An equation has been added to the method to define relative percent difference. See Equation 1, Section 9.2.3.*
1d.2	**Comment:** Section 8.3 Replicate Samples: Recommend including statement or note emphasizing importance of using same sample mass and leach volume for each replicate to avoid introducing additional variables into the test. ***Response:*** *This section (Section 9.2 of the September 2008 revision) has been modified to clarify that duplicate samples are run using identical sample masses and leaching volumes.*
1d.3	**Comment:** Title of Table 4 (which needs to be renumbered) Highest resulting percent difference (RPD) between duplicate samples during method validation in two laboratories also, i would argue again that what has been done so far has not been validation--testing would better describe it. ***Response:*** *Since receipt of this comment, the method has been validated in a multi-laboratory study involving eight laboratories; the table has been updated to reflect results in seven laboratories that did not submit outlying results. The table has also been renumbered and given the following title: Expected method precision (as RPDs) based on Interlaboratory Study Results.*
1d.4	**Comment:** Part 8.3 – The use of at least triplicate samples rather than duplicate samples is necessary for the method performance determinations. Statistical analysis based on duplicate samples is a stretch. Method performance must be based on triplicate samples at a minimum. If two results differ significantly, what does the statistical result tell you? Not much. You still have no idea about performance. ***Response***: *Duplicate sample are typically used in U.S. EPA and ASTM analytical methods. We agree, however, that the use of triplicate (or four, five….) samples would provide more statistical power. Method users are not limited to use of duplicates.*

1d.5	**Comment:** Part 8.4 – Control Sample – USGS in Denver has developed a hard rock standard sample. It could be done on a regional basis (coal type) with expiration dates. ***Response:*** *The Brush Creek Shale that was used in method development and validation is a control sample that was developed in cooperation with USGS in Denver. Requirements to run a standard material have been removed from the method.*
1d.6	**Comment:** Section 8.2 How will standard reference results be used to "evaluate the validity of field sample results"? ***Response:*** *Use of standard reference materials has been removed from the method. See response to Comment 1d.5.*
1d.7	**Comment:** Section 8.4 Control Sample: Recommend using inert material (e.g., well characterized quartz chips of requisite particle size); this will allow you to check for unexpected contributions from the test apparatus (this is how USBM discovered that glass wool filter media contaminated the humidity-cell effluent with alkalinity and raised pH from 7 to 9+). ***Response:*** *Blanks have been added to the method (see method Section 9.2).*
1d.8	**Comment:** In general, there are difficulties in providing some degree of standardization using performance based criteria. It appears that some standardization (prescription) could be applied that would benefit the reproducibility of results. It appears that additional prescriptive aspects of testing might be provided without placing undue burden on test practitioners. These discussions have probably taken place, and this issue should be addressed again after additional interlaboratory method validation. ***Response:*** *Results and information generated during the interlaboratory method validation study have been used to standardize numerous aspects of the method (see response to Comments 1c.18, 1c.26, and 1c.27, for example). The method's performance-based criteria is consistent with U.S. EPA, ASTM, Environment Canada, and numerous other agencies and organizations approaches to providing standardized methods that allow flexibility for adjusting to costs, product availability, technology improvements, and data user requirements. See http://www.epa.gov/epawaste/hazard/testmethods/pbms.htm for information regarding U.S. EPA's Performance-Based Measurement System.*
1d.9	**Comment:** At this stage of test development it is difficult to assess how effective the "performance-based" criteria will be in providing comparable results within and among testing laboratories. Ultimately this must be assessed in terms of environmental mine waste management decisions made based on test results. For example, drainage pH values predicted by different laboratories may be 2.9 and 3.4. This could be viewed as a large difference. However, if the decision on how the material tested will be handled at the operation is the same, irrespective of the pH difference, then the difference is inconsequential in the practical sense. ***Response****: Laboratory variability, based on results of the interlaboratory method validation study, was assessed and used to establish the method performance criteria that are provided in Table 4 of the method. Also see response to Comment 1d.9.*
1d.10	**Comment:** Section 6.2 How many splits are collected? ***Response:*** *The following sentence has been added: "To demonstrate the accuracy of results, it is recommended that at least two identical homogeneous sample aliquots are prepared from each bulk sample. See method Sections 7.3 and 8.1.3.*
1d.11	**Comment:** Section 10.0 You should not define RPD again and again--you already defined it on the previous page--now just use the acronym, or don't use it at all except in the tables. Last sentence in the text, delete the word "through" ***Response:*** *Thank you. Text has been revised as recommended.*

2. Document Quality and Clarity: Peer reviewers are asked to critique the document for its clarity given its potential scientific and technical applications. More specifically, reviewers are asked to address the following questions:

a. Are sufficient details provided for setting up and implementing the method procedures?

2a.1	**Comment:** I see a lot of features that need to be clarified and tightened up. Has this been read by people from an analytical lab? Some of the lab procedures seem rather crude or potentially unsatisfactory. Also, the authors need to decide if they are specifying a distinct procedure, or just recommending improvements to existing methods. All the qualifications seem to leave a lot of room for individual initiative in the specifics of the method. ***Response:*** *The method has been reviewed by and tested in up to eight individual laboratories; two of these laboratories participated in both the method development and validation studies, and provided significant input regarding method implementation details (e.g., apparatus, materials, reagents, gas mixtures, column preparation, and gas introduction). We are not aware of what existing methods the commenter is referring to in this comment; this method is intended as a stand-alone distinct procedure. However, additional details have been added throughout the method since receipt of reviewers comments and completion of laboratory testing.*
2a.2	**Comment:** Sufficient details are provided to setup and implement the method. However, it is recommended that allowances for manipulating or changing the procedure be limited. ***Response:*** *See response to Comment 1d.9.*
2a.3	**Comment:** Section 4.1.4 Do you really mean natural rubber tubing? I would think plastic tubing would be preferable, such as Tygon. Or is this really a rubber? Does natural mean it comes from rubber trees vs. a chemical plant where most rubber now is made? ***Response:*** *Thick wall, rubber latex tubing is used for tubing that will require clamping. Specifications for this tubing are provided in method Section 5.1.4.2.*
2a.4	**Comment:** Section 4.1.5 It seems like removing the tubing to drain is pretty messy. Why not put in a 3-way stopcock? ***Response:*** *The tubing is disconnected from the water source, but is not removed from the column port. A clamp is used to stop water flow. See method Figure 1.*
2a.5	**Comment:** Section 6.1.1 What do the sieve sizes mean (4,10,16,35,60)? Are these mesh openings/in, or sieve numbers? If the latter, what scale? What size sample should be sieved (lbs)? ***Response:*** *The sieve sizes are listed as "No. 4, 10, 16, etc.", which is standard notation. Table 2 lists these as sieve numbers, and notes that sieves of their equivalent mesh size can be used. The following sentence also has been added to the method: "Approximately 2 kg is needed for each column." See method Section 8.1.1.*
2a.6	**Comment:** Section 7.2.2 Is resolution of the sample weight to 0.05 g necessary? This represents an error of (0.05/1800) = 0.0028%. If weighing to 0.05 g is not a problem, I have nothing against the requirement. However, it is highly unlikely that other measurements in the test will be near this degree of resolution and lesser requirement for weight accuracy could be adopted. ***Response:*** *This sentence has been removed, and a note has been added to state that "The total weight of the sample added to the column must be recorded to the nearest 1.0 gram, for use in results calculations." See text box in method Section 8.2.2.*
2a.7	**Comment:** Section 5.2 Some standards for water purity should be provided, e.g. ASTM 2000. ***Response****: This section has been revised to state that reagent water is prepared by distillation, deionizatin, reverse osmosis, or other technique that removes potential interferences (e.g., metals and organics).*

2a.8	**Comment:** Section 7.1.2 The sample should be dried and weighed following test completion. ***Response:*** *Although we agree that drying and weighing the sample after test completion could provide useful information, it is not considered necessary to produce method results.*
2a.9	**Comment:** Section 7.1.2 Portions of fresh and leached samples should be archived for potential future examination. ***Response:*** *Although we agree that it may be desirable to archive leachate samples for potential future evaluation, it is not considered necessary.*
2a.10	**Comment:** Section 6.1 What is the minimum size of sample (lbs.)? ***Response:*** *The method has been revised to specify a column inner diameter of 2 inches, column height of 2.5 feet, and a sample weight of approximately 1800 – 2000 grams.*

b. Are data equations presented in a technically clear and appropriate manner?

2b.1	**Comment:** Data equations provided are clear. However, there is no advantage in showing acid generation on a particle surface area basis. Surface area is not an easy and/or precise determination. ***Response:*** *This equation has been removed from the method. Instead, results are calculated in units of mass weathered per week and mass produced per sample weight.*
2b.2	**Comment:** Sections 9.3 and 9.4.2--equations have words and unitsallruntogetherlike this, insert spaces. ***Response:*** *Thank you. Equations have been clarified.*

c. Does the method accurately present the equations necessary to obtain useable data results?

2c.1	**Comment:** The equations provide useable data, however I see no advantage in showing the data on a surface area basis. ***Response:*** *This equation has been removed from the method. Instead, results are calculated in units of mass weathered per week and mass produced per sample weight.*
2c.2	**Comment:** Section 8.3.2 This equation is said to be a rate, but it lacks a time input. Why not just include division by days in the equation? ***Response:*** *This equation has been removed from the method. Instead, results are calculated in units of mass weathered per week and mass produced per sample weight.*

3. Do you believe that this draft method has the potential to serve as an effective and standardized tool in predicting the quality of mine drainage? Do you have recommendations that may enhance method procedures towards obtaining this goal?

3.1	**Comment:** Somewhere there needs to be a discussion of how the results of this test are to be used. If the test gives acidity <0 after 8 weeks, is the site ok? How does one use the data on mg/cm^2 and mg/cm^{2}day? ***Response:*** *Section 10.0 of the method has been expanded to include instructions and guidance regarding use of method results. Appendices also have been added to provide example calculations for determining carbonate dissolution and pyrite oxidation rates, and for estimating mineral solubility of calcite and gypsum.*

3.2	**Comment:** How will test data be used for prediction? Will it be assumed that column data will simulate that in the field? Will drainage quality or rates be used in conjunction with modeling? ***Response:*** *See response to Comment 3.1.*
3.3	**Comment:** How is variability in the overburden composition accounted for? Are several samples from each stratum tested? ***Response:*** *The number and location of samples that should be collected will depend on the site and rock structure to be evaluated. Section 7.1 of the method instructs users to "Collect representative bulk samples using air-rotary, drilling, core drilling, or extraction ....." The section also provides several references of standardized sample collection procedures.*

4(a). Do you believe that the draft method has sufficient detail to allow its application in laboratories that typically perform mine drainage analyses?

4a.1	**Comment:** You have made some nice progress in defining a method and I particularly like the fact that you address potential problems in spots, such as the use of the bulb pipette. The description is in general, detailed enough to allow other labs to adopt it. ***Response:*** *Thank you.*
4a.2	**Comment:** The description is in general, detailed enough to allow other labs to adopt it. ***Response:*** *Thank you. Additional detail has been added based on observations and results during the interlaboratory method validation study.*
4a.3	**Comment:** The draft method (without the ability for individual laboratories to modify the method) provides sufficient detail to allow its successful application. ***Response:*** *See response to Comment 1d.9.*

4(b). Do you believe that the detail provided allows sufficient flexibility for method users to adjust for cost and laboratory conditions, while still meeting the method performance criteria?

4b.1	**Comment:** I strongly recommend that a standard method be established with little allowance for deviations. The method must compare "apples with apples" and not "apples with oranges". ***Response:*** *See response to Comment 1d.9.*
4b.2	**Comment:** Few, if any, deviations from the method can be tolerated. Small deviations could result in great differences between laboratories. ***Response:*** *See response to Comment 1d.9.*
4b.3	**Comment:** I do not believe that the flexibility for a laboratory to modify the method will result in meeting the method performance criteria. Each laboratory may reach a high level of precision, but comparison between laboratories will be less than acceptable. ***Response:*** *See response to Comment 1d.9.*
4b.4	**Comment:** Section 7.3 The possibility of multiple T and moisture and timing regimes seems to negate the advantage of a standard procedure. ***Response:*** *See response to Comment 1d.9.*

5. What, in your opinion, are the most influential variables in creating the results that are obtained using the weathering procedures in this draft method?

5.1	**Comment:** The most influential variables in creating the results obtained using the weathering procedures in this draft method are: 1. Particle size – Removing the small particle size may decrease variability but at the same time a significant source of acidity and neutralization potential may be eliminated for some materials/sites. 2. Method flexibility may significantly impact the ability to compare data between laboratories. ***Response:*** *See response to Comments 1a.1 and 1d.9.*

GENERAL

G.1	**Comment:** Another major question is whether this procedure, or any kinetic procedure, really provides results similar to runoff from a field site. This would seem to be another major research project needed before this method can be considered reliable. ***Response:*** *Penn State University's Mineral Research Institute applied this method to rock samples in a highly acidic rock in major highway cut and fill in north central Pennsylvania and demonstrated that the results compared well to the results being produced in the field (see method Reference 12.7). Section 3.0 of the method acknowledges, however, that "the method is limited by the extent to which the sample and simulated weathering conditions approximate actual site conditions." The method further acknowledges that "It is not possible to collect a sample from the field for evaluation in the laboratory without disrupting the in-situ particle size distribution through collection mechanisms and crushing." Because it is not possible to precisely mimic field conditions, particularly weathering conditions over time, the method is designed to generate data based on standardized conditions, and those conditions must be considered by each data user. Section 3.0 also states that when assessing method results, "the user should consider sample collection and storage procedures, the changes made to the sample between collection and preparation (e.g., sample crushing and reconstruction), and the similarity of the simulated weathering to actual site conditions (e.g., percent humidity, partial pressures of gases, and saturation/drying cycles).*
G.2	**Comment:** Section 7.1.2 As a general comment, there are at least two benefits to conducting weathering tests under controlled conditions. First, a body of empirical data will be generated to understand the behavior of particular lithologic units. Second, a scientific foundation for the behavior of lithologic units can be developed. In order for the second benefit to be derived, tests must be conducted on well-characterized samples. Is the level of scientific understanding at a stage where the second benefit is of no value? ***Response****: Section 8.1.2 of the method discusses sample characterization. The extent of characterization is optional and depends on data user needs. The U.S. Geological Survey did extensive characterization of samples that were used in the interlaboratory study during validation of this method. Results were presented at the 2005 Geological Society of America conference in Philadelphia, PA .*

G.3	**<u>Comment:</u>** Part 7.3 – The statement that these procedures are recommended for evaluation of overburden in non-arid regions or areas where there may be variably saturated conditions does not make much sense. Acid mine drainage whether occurring in the east or west have variable saturated conditions. ***<u>Response:</u>*** *We agree that saturation cycles occurs in both arid and non-arid regions of the U.S., however, the statement is intended to distinguish between western arid coal regions and the more humid eastern coal regions where variable saturated conditions are more prevalent.*
G.4	**<u>Comment:</u>** Paragraph 2, sentences 1 and 2. These sentences appear to be at odds with one another. The first says that acid-base accounting (ABA) is applicable "to strata that have an appreciable amount of either pyrite or carbonates." The second indicates that "mines with either a scarcity or an abundance of these materials fall into a "gray" area that is difficult to predict." Thus the first says that ABA is applicable if there is an "appreciable amount" of pyrite or carbonate and the second indicates that an abundance of these materials leads to an inconclusive result. This should be clarified. ***<u>Response</u>****: This paragraph has been revised to clarify that ABA is limited to strata that have an appreciable net acid-base balance, and that mines with near equal amounts of acid and alkaline production potential fall into a gray area that is difficult to predict. See second paragraph of method Section 1.0.*
G.5	**<u>Comment:</u>** I strongly urge the team to consider a field validation test. What you have done so far has not <u>validated</u> the method at all. It doesn't matter if 20 people agree that 2+2=5 if that is not the right answer. Comparing the replicability of the method is a good and necessary step, but so is evaluating whether your improvements in procedures that enhance consistency and reaction rates improve or detract from accurate predictions. Using samples from problematic sites that have already been reclaimed, test the variables (such as adding carbon dioxide, and removing the small particles, both of which could dramatically affect the validity of the prediction) to see if you are making the method more or less useful. If not, in my opinion, you are debating whether it is more appropriate to do a waltz or a highland fling on top of the pin. ***<u>Response:</u>*** *See response to G.1.*
G.6	**<u>Comment:</u>** Tests of this nature include the period between rinses, during which most dissolution occurs, and the rinse phase, during which reaction products are removed. A brief description of the test's intent and rationale regarding these phases may benefit the uninitiated (and assist those reviewing the method). It appears that simulation of field conditions is of interest in order to maintain a reaction environment similar to that in the field. The CO_2-air mixture is added to the column and to the rinse water (leachant) to maintain a condition that is apparently expected in the field. It may be helpful to state this, as well as the reasons gas phase composition is of importance to the reactions of interest. Alternatively, citations addressing this aspect could be provided. It is unclear if the rinse phase is intended to remove the majority of reaction products. Clarification would, once again, be helpful. ***<u>Response</u>****: Although dissolution and chemical reactions that occur in the columns is critical to understanding the geochemistry of samples, particularly when exposed to weathering conditions, such details are outside the scope of the method. However, useful information regarding carbonate dissolution, pyrite oxidation, and the mineral solubility of calcite and gypsum have been added as method appendices. .*

MISCELLANEOUS

M.1	**Comment:** How do you define "mine discharges at a mine site", i.e. does "mine discharges" mean that only the quality of discharge from the adit is being predicted? ***Response:*** *The method is primarily designed to predict mine discharge quality of post mining discharges at surface mines. However, the method could also be applied to active mines, including adit and other active mine discharges.*
M.2	**Comment:** You intersperse metric and standard units. You need to be consistent at least. Given the fact that the method, if adopted, will undoubtedly be used internationally, I would suggest including both (one in parentheses) each time. ***Response:*** *Method developers have intentionally used English units when referring to construction materials, and metric units when referring to laboratory measurements.*
M.3	**Comment:** Para. 2.0 line 4. A bracket appears for no reason, and is not closed. ***Response:*** *Thank you. This has been corrected.*
M.4	**Comment:** Section 1.0, second paragraph, second line Strata that are dominated by either pyrite or... next line substitute both for "those" --same idea--having a scarcity or an abundance of just one is not problematic. ***Response:*** *See response to Comment G.4.*
M.5	**Comment:** lines 9-11--...are needed to predict mine drainage pollution...also have for predicting the efficiencies.... next paragraph--last sentence doesn't make sense as written please rewrite and avoid the phrase method performance--it sounds like a drama lesson. ***Response:*** *The Scope and Application section of the method has been reviewed and revised for clarification. The term "method performance" is used across all program offices with the U.S. Environmental Protection Agency. See response to Comment 1d.8.*
M.6	**Comment:** Section 2.0 Delete described in this Method--The procedures include: ***Response:*** *The commenter's recommended edit has been incorporated.*
M.7	**Comment:** Section 3.0 First paragraph, second sentence: Consider as an alternative, "…quality that will be produced by the weathering of an overburden sample…" ***Response:*** *This sentence has been revised to state that "The purpose of this method – to characterize the water quality of mine site drainage – is limited primarily by the extent to which the sample and simulated weathering conditions approximate actual site conditions.*
M.8	**Comment:** Section 3.1.2 ...requirement for determining the particle size distribution...third line, eliminate first "and" ***Response:*** *Thank you. The correction has been incorporated.*
M.9	**Comment:** Section 3.2 First line, delete determination of; 6th line, to consider assessing the effective.... ***Response****:* *The recommended edit has been incorporated.*
M.10	**Comment:** Section 3.3 Eliminate dash ***Response:*** *Thank you. The dash has been eliminated.*

M.11	**Comment:** Section 4.1, 5th line Transparent material is recommended so that sample conditions can be monitored during.... ***Response:***
M.12	**Comment:** Section 4.2.1 ...and throughout rest of document, eliminate semi-colon after 20-25 degrees C ***Response:*** *The semi-colon is an artifact of different versions of Microsoft Word/Word Perfect, and has been eliminated from the September 2008 pdf version of the method.*
M.13	**Comment:** Section 5.1.2 Insert that in last sentence--to ensure that all oil is removed. ***Response:*** *The commenter's recommended edit has been incorporated.*
M.14	**Comment:** Section 6.1 Insert commas after et al. in both locations ***Response:*** *Commas have been inserted.*
M.15	**Comment:** Section 6.2 Remove comma before et al., 1988 ***Response:*** *Comma has been removed.*
M.16	**Comment:** Section 7.1.1 ...to ensure that no particles are sized greater than....Also, insert space between No. and 4 ***Response:*** *The commenter's recommended edits have been incorporated.*
M.17	**Comment:** Section 7.1.2 It looks like there is an unnecessary space before Sample; 3rd line, delete "an assessment of"; 5th line--on the sample after the last leachate sample.... ***Response:*** *The commenter's recommended edits have been incorporated.*
M.18	**Comment:** Table 1 Note Should Approved be capitalized? ***Response:*** *Approved has been revised to lower case in the title of this table.*
M.19	**Comment:** Section 7.1.2 Last sentence. Consider as alternative wording, "...performed on the sample following the test (i.e., the..." ***Response:*** *This sentence has been revised to state that "...these analyses also may be performed on the sample after the last leachate sample has been collected and the sample has been removed from the column."*
M.20	**Comment:** Section 7.1.3 ....portions, separate samples... ***Response:*** *Thank you. Correction has been incorporated. (See method Section 8.1.3.)*
M.21	**Comment:** Section 7.1.4 table referred to is untitled and unnumbered--it should be Table 2 ands referred to as such. ***Response:*** *The edit recommended by the commenter has been incorporated. (See Table 2, method Section 8.1.3.)*
M.22	**Comment:** Section 7.2.3 Remove semi-colons ***Response:*** *Semi-colons have been removed.*
M.23	**Comment:** Section 7.4.1.3 For the last sentence consider, "...in ice if drainage is slow.) ***Response:*** *The edit recommended by the commenter has been incorporated. (See method Section 8.5.1.)*

M.24	**Comment:** Section 7.4.1.3: Redundant - this is the same verbiage as the Note in Section 7.4.1. Recommend eliminating one or the other. ***Response:*** *The redundant text has been removed from this section, and is provided only as a note. See method Section 8.5.1.*
M.25	**Comment:** Section 7.3.3.2 A sentence needs to be inserted after the first sentence saying that the columns should be drained and then allowed to remain undisturbed for 6 (or 7) days. ***Response:*** *This section (method Section 8.4.3) has been revised to state that "Following this 24-hour saturation period, drain the column and collect the leachate, then repeat the humidified air cycle (Section 8.4.2). Section 8.4.2 explains that "The column is allowed to sit for a period of 6 days during the humidified air cycle. This cycle is repeated after each saturation cycle (Section 8.4.3)."*
M.26	**Comment:** Section 7.4.2 Looks like an unnecessary space before Recommended. Reference to Table 2 should now be Table 3. ***Response:*** *Thank you. Corrections have been incorporated.*
M.27	**Comment:** Table 4 Should the gas mix for the coal refuse be "Saturated air" rather than "Saturate H_2O"? ***Response:*** *This table has been removed from the method; it has been replaced with information based on inter-laboratory study data.*
M.28	**Comment:** Many of the references are incomplete. ***Response:*** *Method reference citations have been completed, where information is available.*
M.29	**Comment:** References: ASTM. 2000. D5744-96, Standard test method for accelerated weathering of solid materials using a modified humidity cell. *In* Annual book of ASTM Standards, 11.04. American Society for Testing and Materials, West Conschohocken, PA (257-269). ***Response:*** *This reference is provided as indicated by the commenter.*