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

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U.S. Environmental Protection Agency
Office of Water
Office of Science and Technology
Engineering and Analysis Division (4303T)
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Washington, DC 20460

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Background

Method 1627 was validated in an interlaboratory study involving laboratories from the federal, state, commercial, mining industry, and academic sectors. The method was peer reviewed by experts from the Minnesota Department of Natural Resources, U.S. Bureau of Land Management, U.S. Department of Energy, Pennsylvania State University, and the Western Research Institute. Other than the dedication below and minor formatting changes, the text of this document is the same as the May 2009 version of the method.

Acknowledgments

Support for the development of Method 1627 was provided by personnel in the U.S. Department of Interior's Office of Surface Mining, the Pennsylvania Department of Environmental Protection, and the Computer Sciences Corporation. Data or other contributions were made by Mahaffey Laboratory, Ltd., Geochemical Testing, Pennsylvania State University, the U.S. Geological Survey, Benchmark Analytical, Consol Energy, ProChem Analytical, Sturm Environmental Services, and West Virginia University.

Dedication

This method is dedicated to the memory of Roger Hornberger, without whom the method and supporting data would not be available. Mr. Hornberger spent most of his life in the Schuylkill Haven area of Pennsylvania, earning a BS in landscape architecture and an MS in geology from Penn State University. He joined the Pennsylvania Department of Environmental Protection in 1978, and became the District Mining Manager in Pottsville, in 1987.

His extensive concern and expertise regarding coal mining, particularly in the Eastern United States, has significantly benefited both the mining industry and the environment. His interest in overburden analysis as a tool that could be applied to predict post-mining water quality began in the early 1980s. The analytical procedures described in this method, and its extensive amount of supporting data, are one of many fruits of Mr. Hornberger's dedication and passion to filling this need. The individuals who knew and worked with Roger are forever appreciative of his enthusiasm, professionalism, extreme expertise, and unique ability to assemble and facilitate teams of experts across multiple agencies, organizations, and disciplines.

Disclaimer

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1.0 Scope and Application

Although acid-base accounting is widely used for coal mine drainage prediction, 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 developing cumulative hydrologic impact assessment (CHIA) data to support Surface Mining Control and Reclamation Act (SMCRA) permit application requirements. The method also can be a tool with which to generate data used to design and implement 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 in this method are directed toward the coal mining industry and regulatory agencies. 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. The method has been referred to generically as the ADTI Weathering Procedure 2 (ADTI-WP2) in other publications. This method may be used in the laboratory 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. The method incorporates techniques similar to those already used into reproducible, documented, and validated procedures for widespread use. The method is based on procedures 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 which means that you may modify the procedures (with the exception of requirements indicated as “must”) to improve performance (e.g., to overcome interferences or improve the accuracy or precision of the results) provided that you meet all performance requirements in this method. Requirements for establishing equivalency of a modification are in Section 11, Table 4, and are based on method performance in an interlaboratory method validation study, using datasets from seven laboratories, after outlier removal. For Clean Water Act (CWA) uses, additional flexibility is described at 40 CFR 136.6. Modifications not in the scope of Part 136.6 or in Section 11 of this method may require prior review and approval.

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.

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,

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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

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.

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.

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[2] 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.

5.1 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 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 2000 g 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

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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).

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.

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 accurate 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 RPD) 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 (µmhos/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

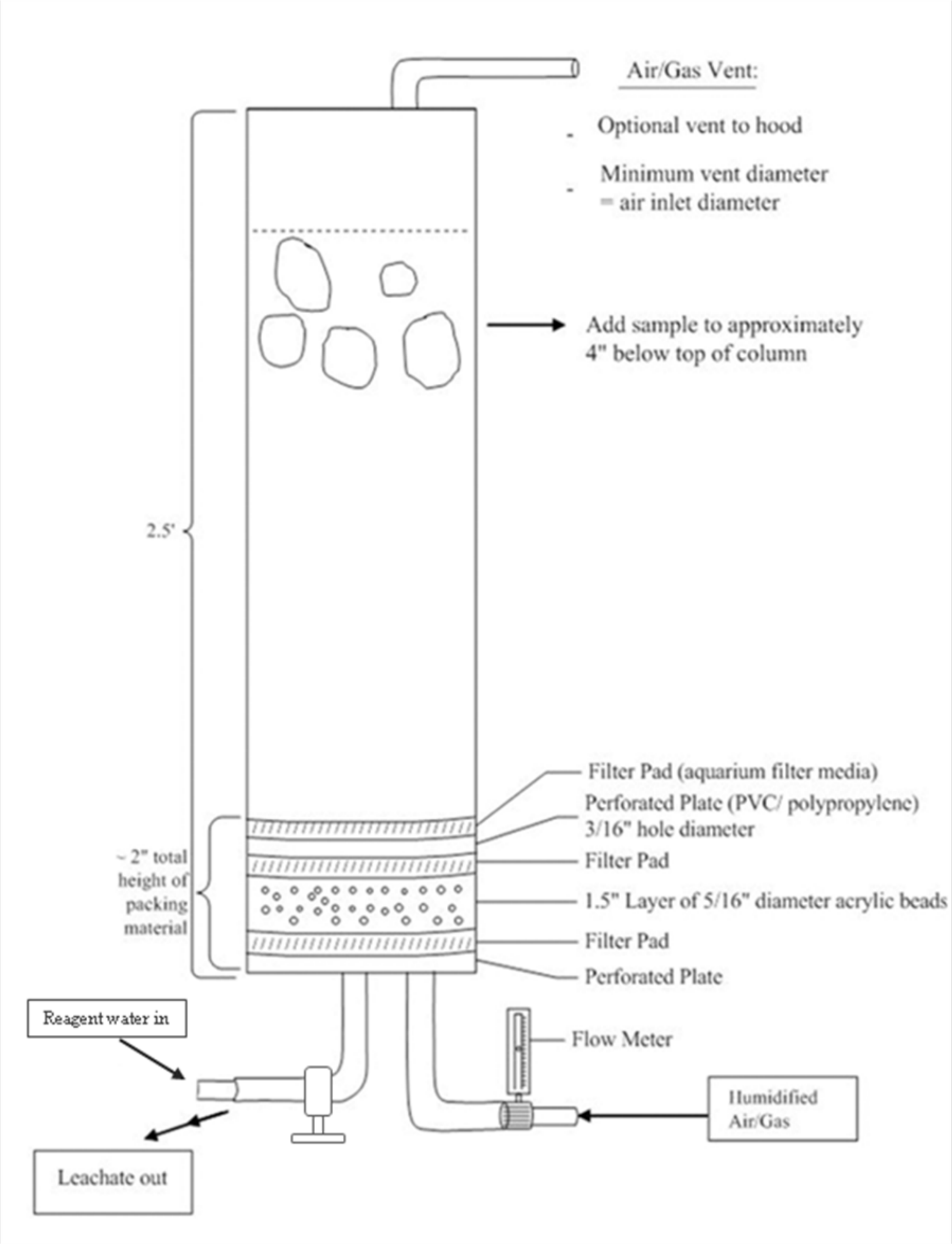
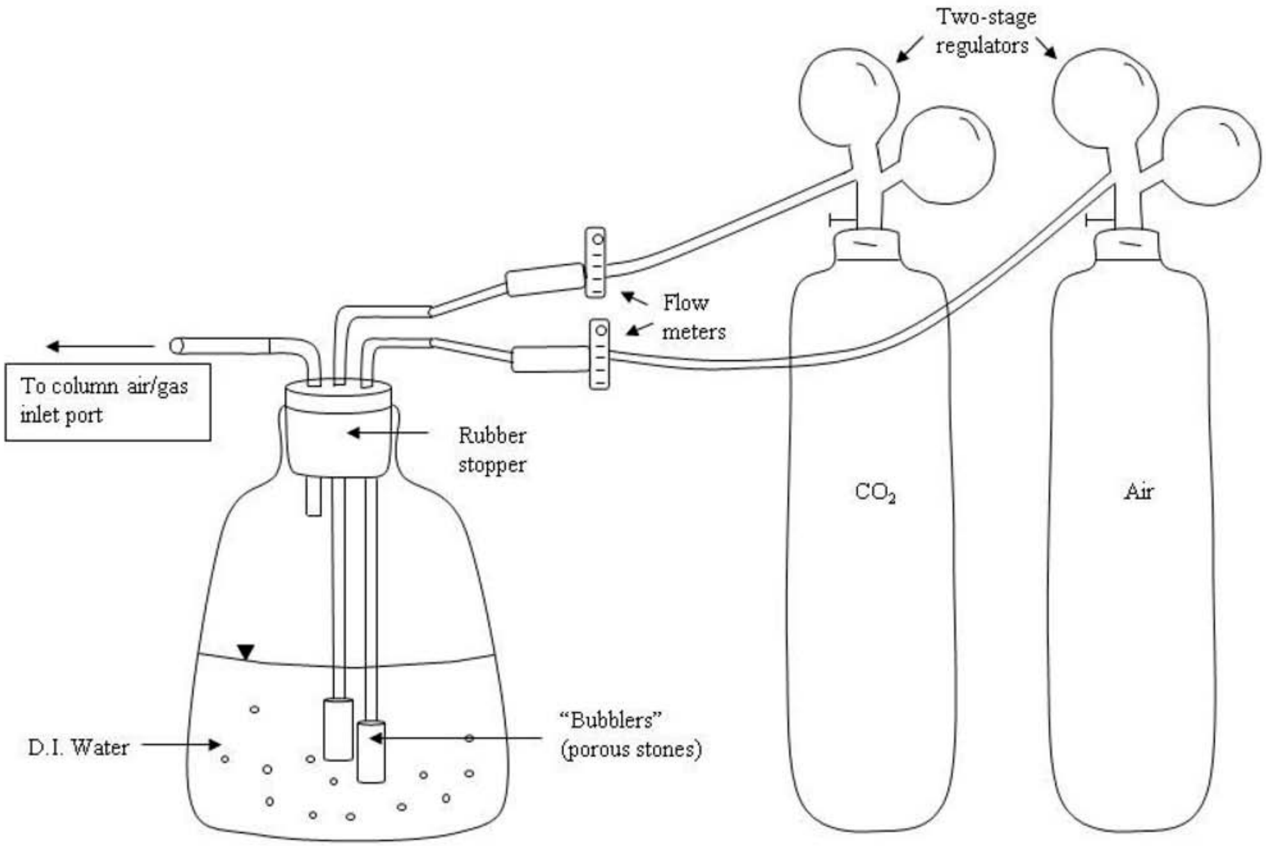


Figure 2: Humidified Air/Gas



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 interference. 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

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

<u>*Calculating CaCO3 from Ca + Mg*</u> 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.

<u>Step 2b</u>. *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.

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

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:

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

Calculating $CaCO_3$ from Alkalinity + Sulfate 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.

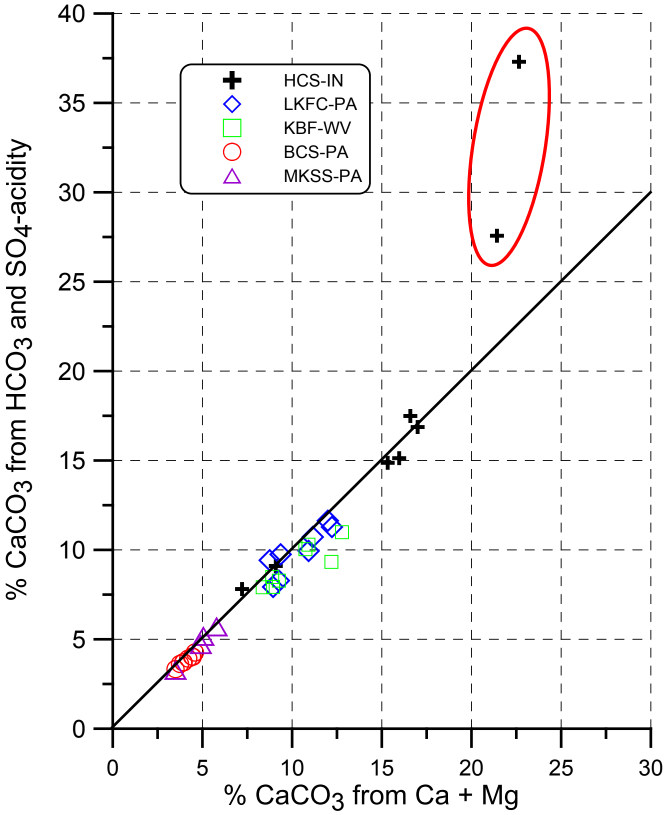


Figure A-1. Comparison of the "anion" and "cation" methods of determining carbonate dissolution. The cumulative value at the end of 14 weeks leaching was used to construct this plot. As can be seen, most data fall on or near the diagonal line, which represents where data would fall if both methods produce 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:

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

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:

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

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	**Vol Out 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).

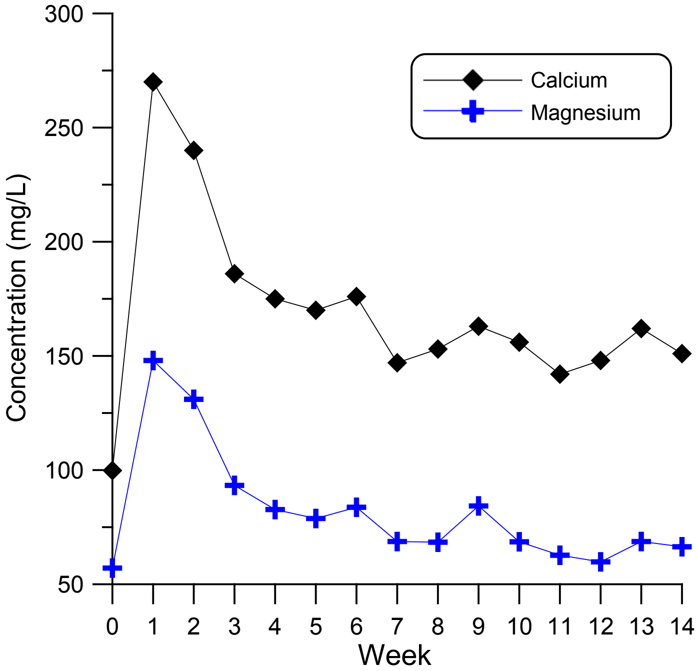


Figure A-2. Concentration of calcium and magnesium through the "initial flush" (week 0) to week 14.

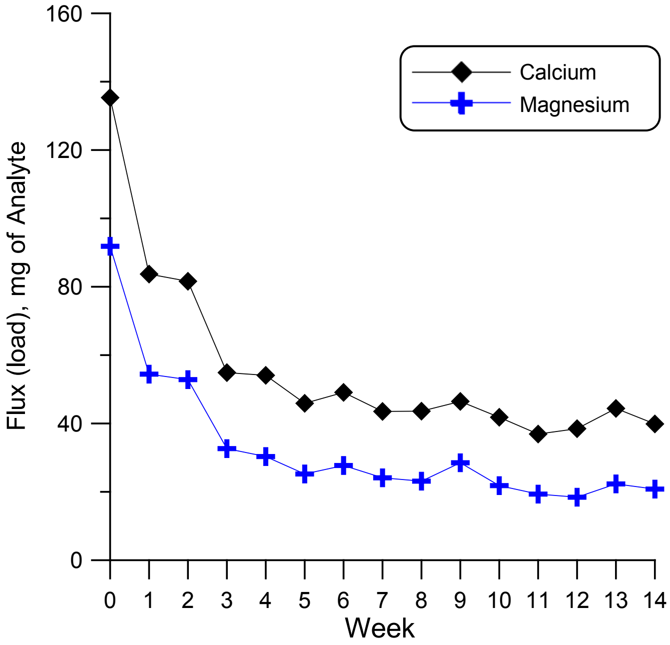


Figure A-3. Flux (load) of analyte.

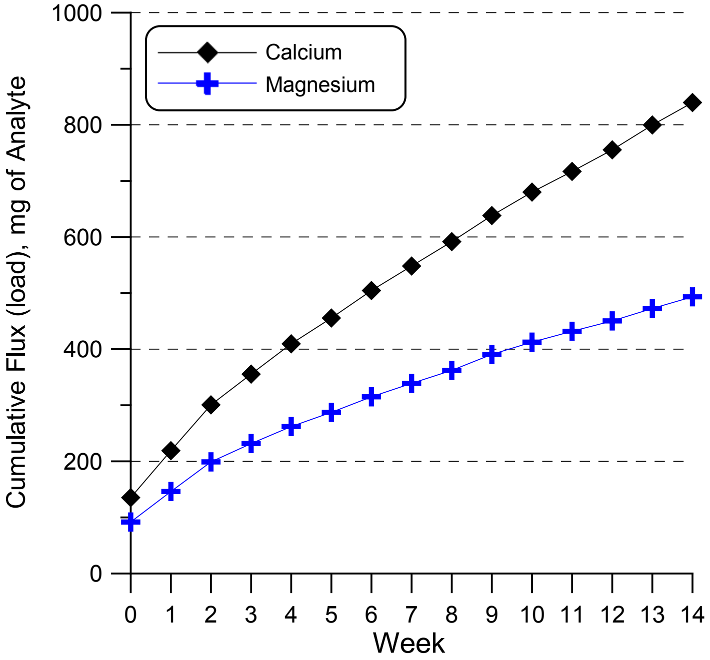


Figure A-4. Cumulative flux (load) of analyte over the 14 week period.

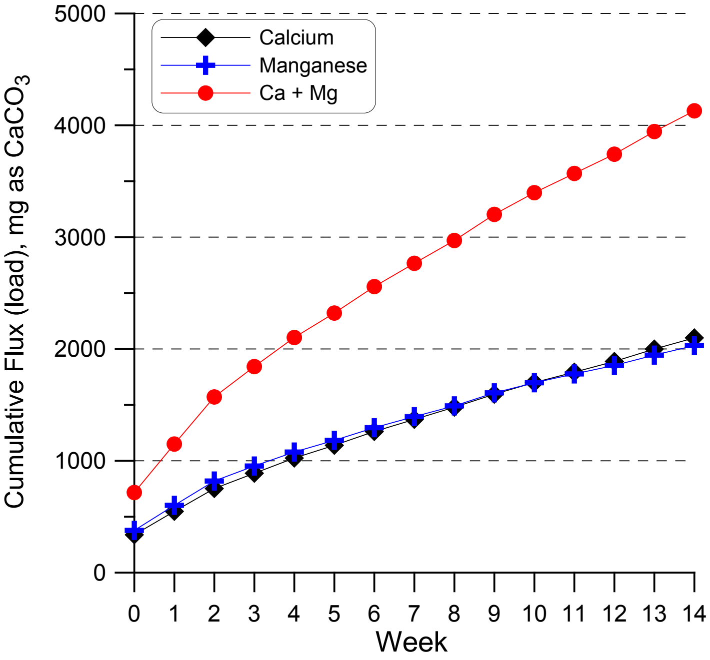


Figure A-5. Cumulative flux of calcium and magnesium expressed as calcium carbonate. Also plotted is the flux of total calcium carbonate equivalent (Ca + Mg).

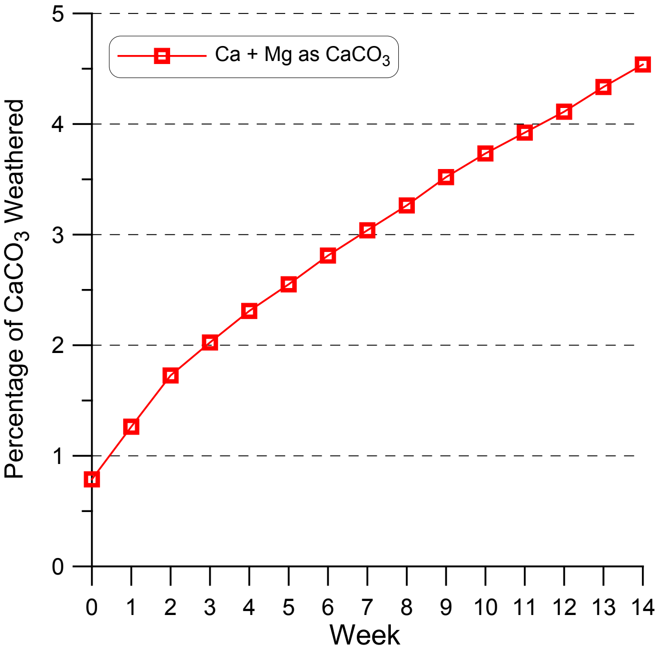


Figure A-6. Percentage of calcium carbonate equivalent weathered through the course of the leaching test. In this instance, approximately 4.5% of the calcium carbonate (equivalent) was removed from the column during the weathering test.

Appendix A References

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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:

$$\frac{[Ca^{2+}]^1 \times [SO_4{}^{2-}] \times [H_2O]^2}{CaSO_4 * 2H_2O} = K^o \qquad \log K^o \approx -4.58$$

and

$$\frac{[Ca^{2+}] \times [CO_3{}^{2-}]}{[CaCO_3]} = K^o \qquad \log K^o \approx -8.48$$

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.

$$\log \gamma_i = -Az_i^{\,2}\sqrt{I} \quad \text{(Debye-Huckel)}$$

$$\log \gamma_i = \frac{-Az_i^{\,2}\sqrt{I}}{1+\sqrt{I}} - 0.3 \times I \quad \text{(Davies)}$$

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:

Activity Coefficient (γ_i) = (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.

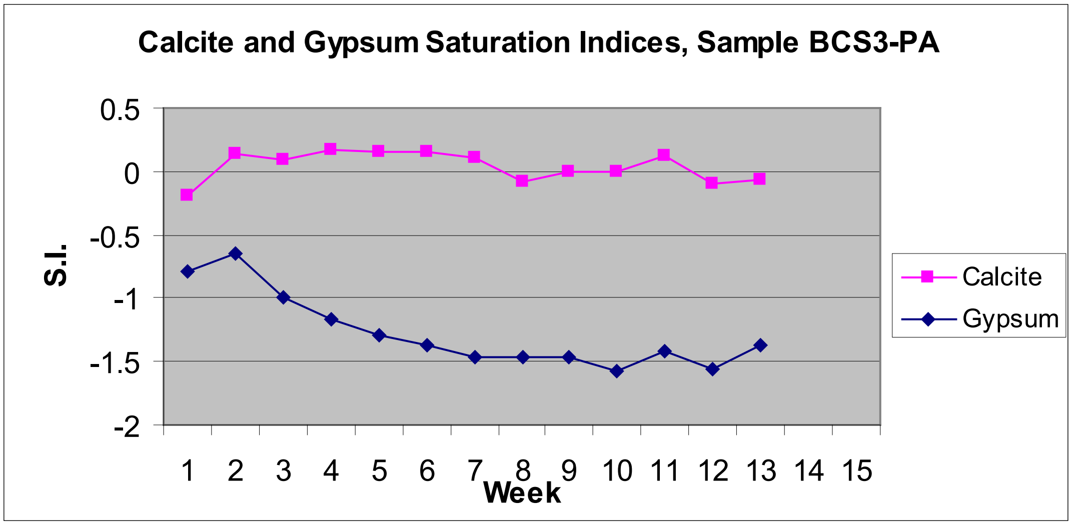

Figure B-1. Calcite and Gypsum Saturation Indices, Sample BCS3-PA

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

Appendix B References

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