APPENDIX A. CONSIDERATIONS FOR CHEMICAL MONITORING AT COAL MINES

by

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INTRODUCTION

Ground water and drainage from coal mines range in quality from strongly acidic (pH <4.5) to near neutral, or *alkaline* (alkalinity > acidity; pH $\geq$ 6) (Cravotta et al., 1999). Acidic mine drainage (AMD) commonly has elevated concentrations of sulfate (SO_4^{2-}), iron (Fe), manganese (Mn^{2+}), aluminum (Al^{3+}), and other solutes that result from the oxidation of pyrite (FeS_2) and the dissolution of carbonate, oxide, and aluminosilicate minerals (Cravotta, 1994; Rose and Cravotta, 1998). Predicting the potential for AMD formation requires a detailed evaluation of the geologic and hydrologic systems at a proposed mine site. A significant amount of qualitative information (such as lithology, drainage characteristics, presence/absence of seeps, etc.) can be obtained through observations by trained professionals. However, for confident predictions of post-mining water quality, water and, in many instances, rock must be sampled for analysis. The samples must be collected and analyzed under controlled conditions using standard measures to assure reliable data.

The goal of AMD prediction is to evaluate a planned physical and chemical alteration of a particular site (i.e. a proposed mining operation as described by the permit application) and determine as accurately as possible whether, and to what extent, water quality will be affected. To accomplish this, it is necessary to: 1) establish data collection points that are representative of the physical and chemical systems associated with the subject site; 2) collect, preserve, and transport samples from the field site to the testing laboratory in a manner that minimizes physical and chemical changes in the sample; and 3) perform laboratory procedures that accurately characterize the samples and yield useful results.

Water samples are collected to establish a pre-mining baseline and to aid in prediction, by characterizing pre-mining water quality on site and post-mining water quality at adjacent mines. However, it is important to note that even if a prediction is qualitatively accurate, the absolute quantities and rates of production of acidity, alkalinity, and other constituents in the discharge water are difficult to determine on the basis of laboratory tests. For example, overburden evaluation may accurately predict alkaline water; however, the alkaline water can have concentrations of metals and sulfate that exceed regulatory requirements for mine discharges. The uncertainty in post-mining water quality prediction is most commonly attributed to spatial variability of lithology and associated issues associated with rock sampling, analysis, and interpretation. Nevertheless, spatial and temporal variability in the hydrology and water quality at a mine also can be significant sources of error in the evaluation of predicted and measured water quality at coal mines.

Comprehensive reviews and data have been published recently on the chemistry of mine drainage (Nordstrom and Alpers, 1999; Rose and Cravotta, 1998). This chapter summarizes major factors that apply to collecting and analyzing samples for the prediction of pH, alkalinity, acidity, and associated constituents of coal mine drainage. Methods for water sampling and characterization are described to ensure that useful data for prediction and evaluation of post-mining water quality are collected. Other aspects, such as overburden sampling, have already been covered elsewhere in this book, and are therefore addressed in less detail.

HYDROGEOCHEMISTRY OF COAL MINE DRAINAGE

Pyrite oxidation takes place primarily in the unsaturated zone and at the land surface, where oxygen (O_2) and moisture are available and where acid (H^+) and other oxidation products tend to concentrate in fluids and solids. For example, secondary sulfate minerals can form as intermediate oxidation products on pyrite and other sulfide minerals and can precipitate from evaporating sulfate-rich solutions (Nordstrom and Alpers, 1999). Secondary sulfate minerals are important as both sinks and sources of AMD, storing H^+, Fe, and SO_4^{2-} in a solid phase during dry periods and releasing the solutes when dissolved by runoff, recharge, or rising ground water (Cravotta, 1994; Olyphant et al., 1991). Consequently, concentrations of acid and dissolved solutes in mine discharges can increase with increasing flow rates, particularly when recharge first occurs after sustained dry conditions (Hornberger et al., 1990).

In contrast with SO_4^{2-}, which is transported primarily as a dissolved ion, iron can be transported as ferrous (Fe^{2+}) and ferric (Fe^{3+}) ions and as suspended Fe(III) solids. At pH >3, concentrations of dissolved Fe^{3+} are limited by the formation of Fe(III) oxyhydroxides and related solids (Bigham et al., 1996). However, at nea-neutral pH and under anoxic conditions, concentrations of Fe^{2+} can be elevated due to the relatively high solubility of Fe(II) oxyhydroxides and carbonates. Aeration of water containing Fe^{2+} and Mn^{2+} promotes their oxidation and hydrolysis, producing Fe(III) and Mn(III-IV) oxyhydroxides and 2 moles H^+ for each mole Fe^{2+} or Mn^{2+} (Cravotta et al., 1999; Rose and Cravotta, 1998). As explained in more detail below, the potential for the production of H^+ (or consumption of OH^-) by hydrolysis reactions involving Fe, Mn, Al, and other metal ions is measured as acidity.

Neutral or alkaline mine drainage (NAMD) has alkalinity that exceeds acidity, but also can have elevated concentrations of SO_4^{2-}, Fe^{2+}, Mn^{2+}, and other solutes (Rose and Cravotta, 1998). NAMD commonly originates as AMD that has been neutralized by reactions with carbonate, oxide, and aluminosilicate minerals composing the overburden (Blowes and Ptacek, 1994; Cravotta et al., 1999). If present in sufficient quantities along downgradient paths, dissolution of calcite ($CaCO_3$), dolomite [$CaMg(CO_3)_2$], and other calcium or magnesium bearing carbonate minerals neutralizes acid and produces alkalinity ($[OH^-] + [HCO_3^-] + 2[CO_3^{2-}]$). By definition, alkalinity = 0 for $pH < 4.5$ (Greenberg et al., 1992). Generally, the rate of dissolution of carbonates decreases with increasing pH, alkalinity, and Ca^{2+} concentrations, and decreasing concentrations of dissolved carbon dioxide and carbonic acid ($H_2CO_3^*$) (Plummer et al., 1979; Stumm and Morgan, 1996). The neutralization of AMD generally does not affect SO_4 concentrations; however, if present upgradient from pyrite, the calcareous minerals can buffer the initial pH to be near neutral, which can slow or inhibit pyrite oxidation and the production of SO_4 (McKibben and Barnes, 1986; Moses et al., 1991).

Strongly acidic waters are capable of reacting with aluminosilicate minerals, such as kaolinite, illite, chlorite, mica, and feldspar. Although pH can be increased by the dissolution of aluminosilicates, the subsequent hydrolysis of Al^{3+} ions will generate acid. Ion-exchange reactions involving clay minerals derived from weathered claystone or shale strata also can be important. These reactions, which typically take place in the saturated zone, can remove H^+, dissolved metals, and other contaminants from mine drainage (Winters et al., 1999; Lambert et al., 1999). Calcium ion exchange for sodium ($2Na^+$ = Ca-EX) can increase alkalinity by promoting dissolution of calcium carbonate, if present (Cravotta et al., 1994a).

WATER QUALITY MONITORING AND EVALUATION

Ground water at a coal mine commonly varies in quality both spatially and temporally because of variations in physical and chemical conditions in spoil and surrounding zones. Hence, for water quality prediction and evaluation, the median net alkalinity and other constituents for samples from a mine or wells can be useful as representative of site water quality conditions (Chapter 3, Brady et al., 1994). This assumes that the discharge or ground water sample integrates spatial variations in the spoil and that a sufficient number of samples has been collected to identify the median temporal condition; however, it fails to consider how accurately the water sampled at a mine represents the overall range of site conditions.

Figure 1 shows that despite wide variations in the net-alkalinity concentrations for monthly samples from three monitoring wells completed through spoil, the median monthly net alkalinity and net neutralization potential (NNP) for spoil cuttings from the boreholes were positively related. This correlation between NNP and median net alkalinity indicates that spatial variability in ground water quality within the spoil is controlled locally by the ABA. However, the temporal variability in net alkalinities for each of the wells indicates significant effects from dynamic factors including variations in recharge, reaction rates, and solute transport. Furthermore, despite potential for acidic conditions, water from the unmined bedrock was alkaline, indicating mining was necessary to accelerate the oxidation of pyrite. Thus, while the overburden data from the bedrock borehole would have accurately indicated potential for acidic ground water in the mine spoil, the actual water quality in the spoil was more closely related to conditions in the vicinity of the well.

Figure 2 shows that at a mine, or at single ground water sampling location, the net alkalinity can alternate from alkaline to acidic. At this mine, recharge had a pronounced effect because pyritic materials had been selectively placed in compacted pods above the water table. Negative values of NNP were computed on the basis of cuttings from boreholes for each of these wells, ranging from -33 to -0.5 g/kg $CaCO_3$ (Cravotta et al., 1994b), indicating the potential for acidic conditions for this site. Nevertheless, depending on when and where samples were collected, the corresponding water quality data were not always in agreement with this prediction. Although selective handling isolated pyritic strata from ground water, concentrations of metals in ground water were still elevated because the oxidation of pyrite and dissolution of siderite were not abated (Cravotta et al., 1994a).

Data for the pH of ground water and associated discharge samples from four surface mines in the bituminous coalfield of Pennsylvania, when combined so that each mine is represented equally (total frequency of 25% for each mine), show a bimodal frequency distribution (Figure 3a). Most samples are either near neutral (pH 6-7) or distinctly acidic (pH 2.5-4), with few samples having pH 4.5-5.5. This bimodal distribution is consistent with regional data for the northern Appalachians and reflects buffering in the near-neutral and acidic pH ranges (Cravotta et al., 1999). Nevertheless, the pH of the ground water at each mine commonly ranges over several units, mainly caused by spatial variability or heterogeneity. Although acidic and near-neutral waters were sampled at three of the four mines, individual wells or discharges generally reflected locally acidic or near-neutral conditions. A few wells in mixed pyritic and calcareous spoil had water quality that varied temporally between acidic and alkaline (e.g. Figure 2).

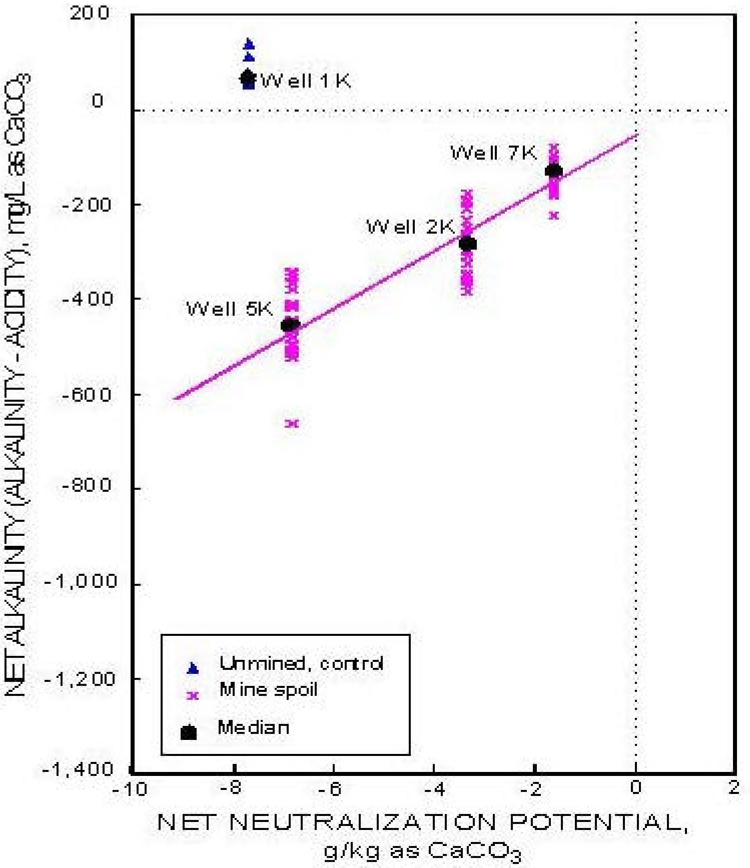

Figure 1. Acid-base accounting and water chemistry data for boreholes installed through the same coal bearing horizon at a coal mine after reclamation (adapted from Cravotta, 1998). NNP is the weighted average of the difference between NP and MPA for rock cuttings from the borehole. Negative values indicate the potential for acidic conditions. Net alkalinity is presented for monthly water samples from the borehole; negative values indicate acidic conditions. The median net alkalinity, indicated separately, is related to NNP.

The pH, alkalinity, and acidity of mine water samples are related, as illustrated in Figure 3b. In general, mine water samples that have pH$\geq$ 6.0-6.5 can be classified as NAMD or alkaline (alkalinity > acidity). The pH of the NAMD samples generally will be buffered by carbonates and hence will not decrease substantially as oxidation and hydrolysis reactions occur. In contrast, mine water samples that have pH < 5 generally can be classified as AMD, or acidic (alkalinity < acidity). These samples commonly contain Fe, Mn, and Al ions; hence, the pH typically will decrease as oxidation and hydrolysis reactions occur. Mine water samples with an intermediate pH of 5-6.5 may or may not have elevated concentrations of Fe^{2+} and Mn^{2+}. As these cations undergo oxidation and hydrolysis, the pH values of acidic samples in this intermediate pH range ultimately will decrease to $pH < 4.5$; however, an ultimate $pH > 4.5$ is likely for alkaline samples.

Measurement of pH, Alkalinity, and Acidity

The pH of a solution is a measure of the effective hydrogen-ion (H^+) concentration or, more accurately, is the negative logarithm of the H^+ activity in moles per liter ($pH = -\log aH^+$) (Nordstrom et al., 2000). The pH of water samples is controlled by reactions that produce or consume H^+, incluuding hydrolysis and dissociation of acids and bases (Wood, 1976). Samples with identical pH can have widely variable alkalinities and/or acidities depending on the concentrations of solute species. Accurate values of pH normally must be measured in the field because the pH can be affected by changes in ionic speciation owing to gas-exchange reactions, such as the exsolution of CO_2, and to mineral-precipitation reactions, such as the formation of carbonate and hydroxide compounds (Wilde et al., 1976; Wood, 1998). Consequently, laboratory pH values for mine drainage can differ from field pH values by several units (Wood, 1996).

Alkalinity is the capacity for a solution to neutralize acid, or H^+, ions (Greenberg et al., 1992; Hem, 1985; Stumm and Morgan, 1996). In practice, alkalinity indicates the potential for the pH of a water sample to change with the addition of moderate amounts of acid. Although a number of solutes, including carbonate, hydroxide, sulfide, phosphate, borate, silicate, ammonia, and organic bases can contribute to alkalinity, the inorganic carbon species, HCO_3^- and CO_3^{2-}, are the predominant sources of alkalinity in most natural water samples (Hem, 1985).

Standard methods to determine alkalinity involve titration with a standard concentration of sulfuric acid (H_2SO_4) (Wood, 1976; Greenberg et al., 1992; Fishman and Friedman, 1989; Wilde et al., 1998). The primary difference among the methods involves the selection of the titration endpoint as a fixed pH value or a variable pH value. The current standard recommends only the pH 4.5 end point (Fishman and Friedman, 1986; Greenberg et al., 1992).

Owing to the potential for CO_2 exsolution and pH changes, alkalinity commonly is indicated as an unstable constituent requiring field measurement (e.g. Wood, 1976; Wilde et al., 1998). In practice, the exsolution of CO_2 will increase pH; however, the alkalinity will be conserved by this process, as indicated by:

$$HCO_3^- = CO_2\ (gas) + OH^-$$

where the reactant HCO_3^- and product OH^- are stoichiometrically balanced and have identical acid-neutralizing capacity. In contrast, the in-bottle precipitation or accidental introduction of hydroxide or carbonate minerals can affect the acid neutralizing capacity of a sample. For example, $CaCO_3$ or $Fe(OH)_3$ will dissolve as H_2SO_4 is titrated into the sample, adding to alkalinity. If these particles formed after sampling and are thoroughly mixed and completely redissolved during titration, then the alkalinity will be unaffected. However, if the solids adhere to the bottle or were introduced accidentally, then alkalinity can be reduced or increased, respectively. If alkalinity is to be measured in the laboratory, water samples should be recently collected, completely filled,sealed and chilled.

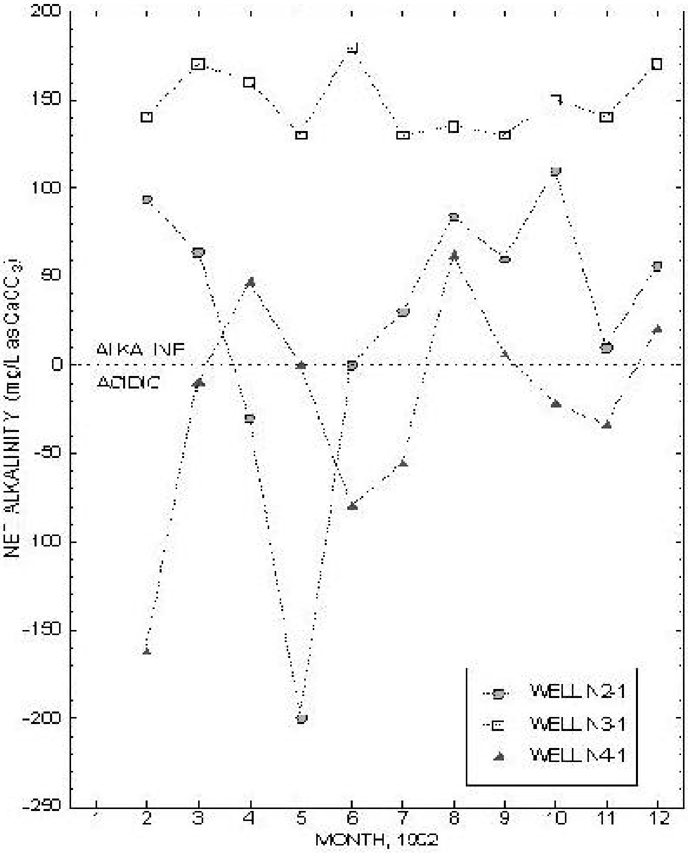

Figure 2. Temporal variations in net alkalinity data for ground water samples from monitoring wells screened through reclaimed spoil at a surface coal mine in Pennsylvania (adapted from Rose and Cravotta, 1998).

Acidity is defined as the capacity for a water sample to react with strong base, or OH^-, to a designated pH (Greenberg et al., 1992). In practice, acidity indicates the potential for mine drainage pH to decrease owing to the hydrolysis of Fe, Al, Mn, and other cations (Payne and Yeates, 1970; Ott, 1986, 1988; Cravotta and Rose, 1998). The acidity of mine water commonly is measured by one of three titration methods: hot acidity with the addition of hydrogen peroxide (Greenberg et al., 1992), cold acidity with the addition of hydrogen peroxide (Fishman and Friedman, 1989), and cold acidity without hydrogen peroxide (Ott, 1986, 1988). All the methods involve titration with a standard concentration of sodium hydroxide (NaOH) to a pH 8.3 endpoint. The addition of hydrogen peroxide (H_2O_2, 30%) promotes oxidation of reduced forms of polyvalent cations, such as Fe^{2+} and Mn^{2+}. Boiling the sample for the hot acidity method accelerates hydrolysis of the cations, improving method precision; however, because Mg^{2+} produces positive interference with hot acidity, the measured hot acidity could be excessive (Payne and Yeates, 1970). Expressed as equivalents, Mg^{2+} is among the predominant cations in mine drainage (Cravotta and Rose, 1998). Thus, acidity values obtained by cold acidity methods tend to be lower, and may be more meaningful, than those determined by hot acidity (Ott, 1986; 1988), particularly if Mg^{2+} is a predominant cation and if samples, after being boiled, are not cooled sufficiently before completing the hot acidity titration.

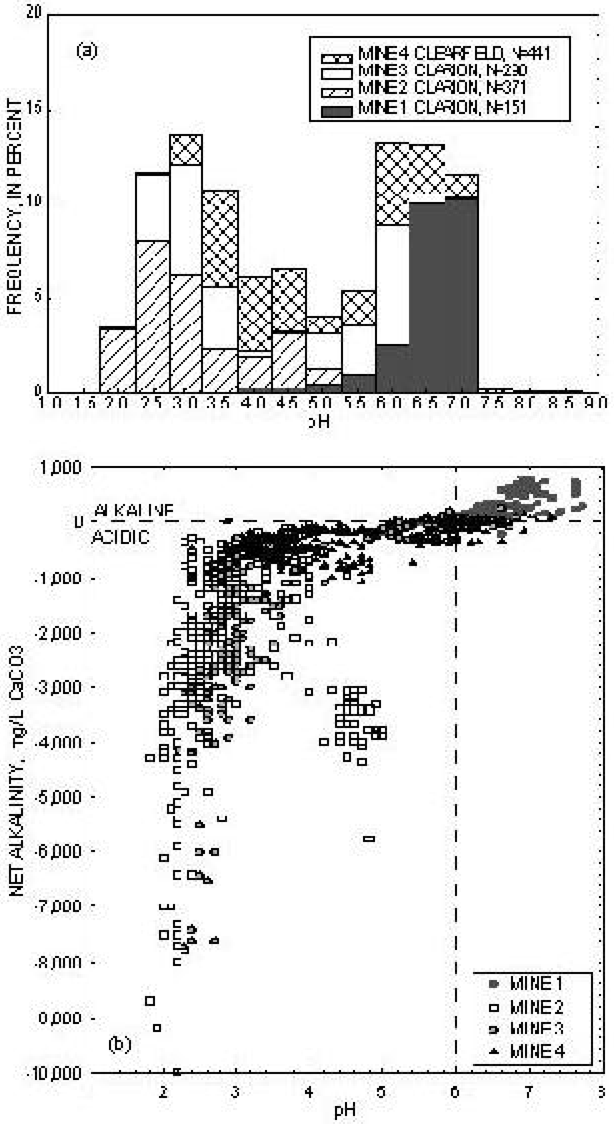

Figure 3. Acidity, alkalinity, and pH data for water samples from four mines in Pennsylvania (adapted from Rose and Cravotta, 1998): a). frequency data for pH showing bimodal distribution; b). net alkalinity relative to pH. Alkalinity and acidity are capacity properties of a solution to neutralize base or acid, respectively. Both properties may be imparted by several different solute species, and both are evaluated by acid-base titration to appropriate pH end points (Hem, 1985). Acidity and alkalinity are expressed as equivalents, or as $CaCO_3$, enabling comparison with one another and with stoichiometric reactions involving carbonate species.

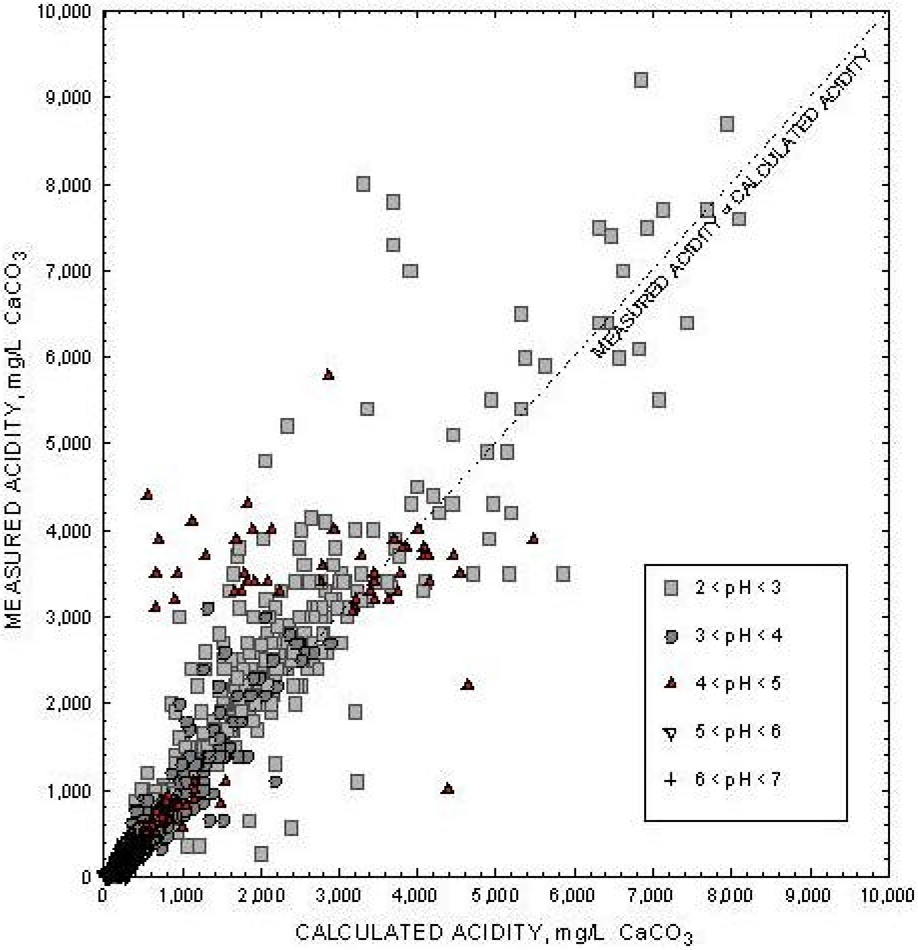

Figure 4. Comparison of measured and calculated acidity (adapted from Rose and Cravotta, 1998).

The acidity of mine water can be estimated as the sum of the equivalents of H^+, Fe^{2+}, Fe^{3+}, Al^{3+}, and Mn^{2+} multiplied by 50:

$$\text{Acidity(mg/L CaCO}_3\text{)} = 50*\{10^{(3\text{-pH})}+[(3C_{Fe3+}+2C_{Fe2+})/56]+[(3C_{Al3+})/27]+[(2C_{Mn2+})/55]\}$$

where C is the concentration in mg/L, the multiplication factor is the charge, and the divisor is the molecular weight of the subscripted species. On the basis of the above equation, calculated acidities generally are comparable to measured acidities (Figure 4); however, discrepencies exceeding 10% are apparent. Probable causes for discrepencies include exsolution of CO_2 and H_2S, ion complexation by H^+ and OH^- (e.g. HSO_4^-, $FeOH^{2+}$), and the inclusion of Mg^{2+} in the hot acidity measurement (Payne and Yeates, 1970; Cravotta and Rose, 1998).

GROUND WATER MONITORING CONSIDERATIONS

Coal-bearing rocks consist of multiple layers, or strata, of different compositions. Before mining, the relative abundance and vertical distribution of pyritic, acid-forming lithologies and calcareous, neutralizing lithologies can be evaluated to indicate the potential for AMD formation and to develop a mine plan or overburden handling plan. As discussed in Chapter 2, acid-forming and neutralizing materials tend to be more abundant for a given stratum at depth, where they have been protected from weathering, because rain water infiltration commonly has depleted the pyrite and calcareous minerals near the surface. Although different methods of mining, overburden handling, water management, and reclamation can affect spoil properties, mining typically produces spoil that consists of a mixture of acid-producing and neutralizing materials, is inverted stratigraphically, and has higher permeability and porosity than the unmined rock (Cravotta et al., 1994a,b). Because of the increased permeability of the spoil, inflow rates of oxygenated air and water are higher and the water table within spoil tends to be deeper than in unmined rock (Guo et al., 1994; Jaynes et al., 1984a,b; Rose and Cravotta, 1998). Hence, pyrite oxidation and associated reactions are facilitated in spoil by the exposure of previously deep-lying unweathered strata to O_2 and circulating water. Additionally, deep burial and inundation of previously shallow-lying, weathered strata facilitates reductive-dissolution of Fe- and Mn-oxyhydroxide minerals and the subsequent release of metals associated with these compounds (Francis et al., 1989, 1990). These processes can be rapid and can produce significant and prolonged effects on the water quality at a mine and downgradient locations.

Monitoring designs to evaluate pre-mining conditions and effects of mining and remediation on the chemistry of ground water need to consider and produce site-specific information on the hydrology at the mine, the chemistry of water from unsaturated and saturated zones, and the relative abundance and distribution of acid-forming and alkaline-producing minerals along flow paths. As discussed in Chapters 2 and 3, water quality and quantity will vary spatially and temporally at a mine, particularly during active mining, but also for years after reclamation and during the reestablishment of the zone of saturation and hydrologic equilibrium (recharge/discharge). The ability to evaluate such variability and hence, to minimize the uncertainty of AMD prediction, requires the installation of sampling points along potential flow paths and the monitoring of water quality and quantity for sufficient duration and frequency to characterize seasonal and long-term trends. Monitoring sites should be established at locations within the mine area and at one or more upgradient and downgradient locations for surface and ground water. Monitoring points alont two or more transects and at two or more depth intervals will be needed to assess complex spatial trends. Periodic monitoring (monthly or quarterly) over several annual cycles is needed to indicate seasonal trends. Long-term trends may be revealed by quarterly monitoring that is sustained for years to decades. Supplemental information is available on local rainfall and air temperature (e.g. National Oceanic and Atmospheric Administration climatic data) and local streamflow and ground water stage (e.g. USGS hydrologic data records), which can help one evaluate seasonal and longer term trends in water quality and quantity.

Although mine discharges routinely are sampled under regulatory programs, the water at a discharge point(s) may not be representative of the site conditions as a whole, particularly where flow rates are substantially smaller or larger than the estimated inflow volume from recharge at a mine. Hence, site characterization can be enhanced through the use of selectively placed monitoring wells and lysimeters and, for some special circumstances, gas samplers (Figure 5). These devices can be used to evaluate spatial and temporal variations in the hydrogeology and water quality at a mine that could result from environmental factors and from different mining and reclamation practices. Drill cuttings from monitoring boreholes can be logged and characterized for major minerals and sulfur and carbonate contents. These data can be compared directly with water-quality data from the boreholes and with pre-mining rock samples. Samples of pore water and pore gas from the unsaturated zone, along with temperature, can indicate geochemically active zones, because the oxidation of pyrite generates heat and consumes oxygen, even when solutes are stored as secondary solids. Pressure-vacuum lysimeters and open tubing installed to various depths in the spoil are useful for collection of unsaturated-zone water and gas (O_2, CO_2) data, respectively. These data will indicate chemical changes as water infiltrates the spoil and can be useful for evaluating the effectiveness of covers in modifying the chemistry of recharge (Cravotta, 1998) or the effectiveness of spoil handling methods for minimizing pyrite oxidation (Cravotta et al., 1994a,b; Guo and Cravotta, 1996). Ground water measurements from properly constructed wells into spoil and underlying bedrock can be used to evaluate the chemistry, origin, and potential for movement of ground water in the spoil and surrounding rock (Cravotta, 1994). By deepening the spoil wells slightly into the underclay, a sump is created, which facilitates water sampling.

QUALITY ASSURANCE/QUALITY CONTROL

Quality Assurance (QA) is a management system for assessing the qualitative and quantitative reliability of field and laboratory data, and ensuring that all information and data are technically sound and properly documented. **Quality Control (QC)** refers to a set of measurements that assures that the analytical results are accurate and precise. QC procedures commonly used include duplicate analyses and comparison testing using known standards, blanks, and spiked samples. QA is essentially an audit function to ensure that QC work is being completed satisfactorily. A suitable QA/QC program will add costs to the permitting effort, but will increase the degree of confidence of the regulatory personnel in the data being being reviewed. This will ultimately increase the the probability of timely permit decisions and decrease the chance of unexpected AMD problems resulting from predictions based on flawed data.

Any project that is based on the evaluation of data gained from the collection and subsequent laboratory analysis of field samples should be subject to some degree of QA/QC, and thus have a QA/QC plan. A basic QA/QC plan ensures that the data generated are indicative of the study site characteristics and its potential to produce AMD. The need and ability to assess the quality of analytical data is typically proportional to the degree of confidence required.. The extent to which QA/QC is implemented should be based on the acceptable level of uncertainty or confidence of results needed to answer specific question(s). The costs involved in site-specific hydrologic and overburden studies will increase as the need for confidence in the data increases. Under certain circumstances, the need for high-confidence data becomes very important. If expensive mangement options are to be decided on based on the analytical data (such as the potential for perpetual treatment from a large mine complex), a higher degree of confidence should be required. Data that will be used to assess human health risks (not normally the case in a mining scenario) or data that will or could be used in litigation should also be subjected to more extensive QA/QC.

At a minimum, the QA/QC plan should assess: field sampling procedures (including sample collection, preservation, storage, and transportation); measurement of field parameters; field notes/documentation; sample custody procedures; selection of laboratory and analytical procedures; laboratory sample analysis and QA/QC; and specific routine procedures to assess data. The QA/QC plan should be developed and maintained by the personnel performing the field investigation and analyzing the laboratory data. Although the QA/QC plan of the investigating entity should address laboratory procedures to some extent (i.e. constituents to be tested and analytical methods to be used), the analytical laboratory should have an internal QA/QC plan that addresses all aspects of laboratory operation.

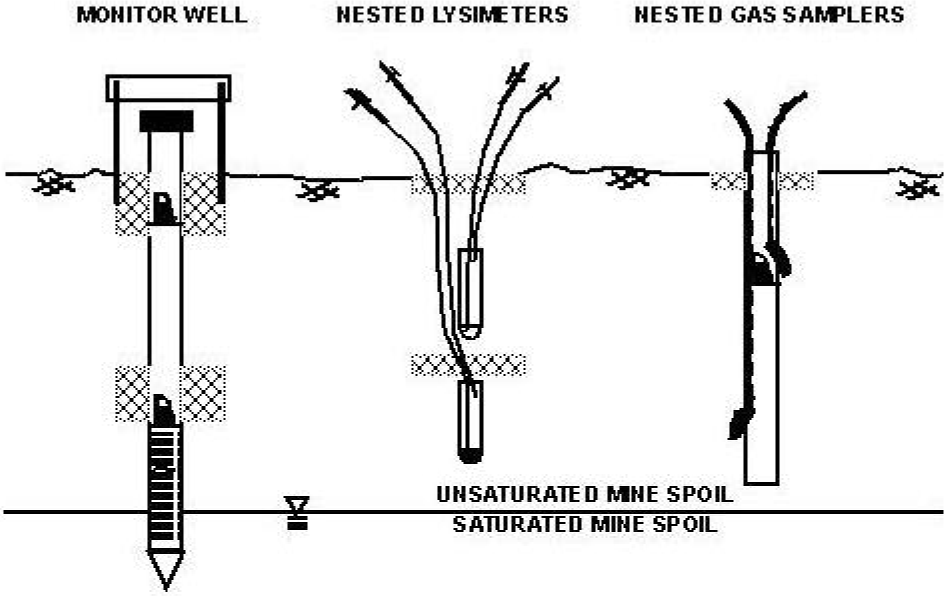

Figure 5. Schematic diagram showing nested monitoring design for evaluation of subsurface chemistry in mine spoil (adapted from Cravotta et al., 1994).

FIELD SAMPLING PROCEDURES

General sampling procedures have been discussed in other chapters of this document. It must be emphasized, however, that sampling should be conducted carefully so that the sampled media (water, soil, or rock) approximates actual field conditions as closely as possible. Generating quality data representative of field conditions requires that the condition of the media sampled is not significantly altered by the introduction of contaminants or the occurrence of natural chemical processes during sampling, storage, and transportation to the laboratory.

The primary concern with soil and overburden samples is to ensure that contamination from outside sources (i.e. cross-contamination from other sampling locations via drilling equipment or sampling scoops) does not occur. Soil samples and drill cuttings collected at specified intervals should be stored in individual sample bags or containers labeled with the sample site and location, depth interval, and date. Continuous rock cores are generally placed in core boxes by the driller for transportation to the facility where detailed logging and sample extraction will be performed. However, field personnel should work with the driller to ensure that any intervals not placed in the core boxes due to loss during core recovery or removal for testing by other parties (i.e. coal seams removed for proximate analysis) are identified and clearly marked. In all cases, field samplers should use the sample containers and storage/transportation methods specified in the QA/QC plan. These elements may vary depending on the required test parameters for each sample. Sample containers should be labeled at a minimum with the project location, sample point number, sample depth, and date. During storage, the primary concern is to minimize changes in sample properties due to drying and oxidation. Changes in moisture can be measured by weighing fresh samples, and then reweighting them after oven or freeze drying. Freeze drying is appropriate for preserving the original mineralogy and forms of sulfur.

Water sampling typically requires a greater degree of care than soil and rock. Water samples for analysis of inorganic chemical constituents, including acidity, alkalinity, sulfate, and metals, should be collected and stored in polyethylene bottles (Wilde et al., 1998). During surface water sampling, care should be taken to minimize the disturbance of bottom sediments that could be incorporated into the sample. Introduction of such sediments during sampling produces elevated levels of suspended solids, and depending on the chemistry of the disturbed sediments, could increase levels of Fe, Al, and possibly Mn (e.g. Horowitz, 1991). Ground water sampling at wells should be conducted only after the appropriate volume of water (specified in the QA/QC plan) has been purged from the well (e.g. Claassen et al., 1982; Wilde et al., 1998). The samples should be processed (filtered, preserved) and stored at the appropriate temperature specified in the QA/QC plan, and delivered to the laboratory as soon as possible after the completion of sampling. Samples for laboratory analysis of alkalinity, acidity, and specific conductance (SC) should be filled completely to displace any air. Samples for analysis of dissolved constituents can be filtered through 0.45-micrometer or smaller porosity filters. Samples for analysis of dissolved and suspended metals should be stored in acid-rinsed bottles and acidified with concentrated nitric or hydrochloric acid as specified in the QA/QC plan. Samples that are not preserved should be refrigerated or stored on ice until analyzed.

Sample bottles should be labeled with a station identification number and coded to identify the sample preservation. The date and time of sample collection should be recorded on the label and the corresponding analytical services request forms at the time of sample collection. Analytical services request forms should include station identification, date and time of sample collection, a code to identify the preservation technique, an analysis code to designate the specific laboratory analyses to be performed, and the name of the person who collected the sample as well as other pertinent information, such as project name and contact information. As specified in the QA/QC plan for chain of custody, one copy of the form should be submitted with each sample to the laboratory; a duplicate copy should be retained by the investigator until laboratory results are received and data are entered into the appropriate data base.

Field Measurement of Unstable Water-Quality Constituents

Data for flow rate, ground water head, temperature, dissolved oxygen (DO), pH, and redox potential (Eh), and to a lesser extent, SC, alkalinity, and acidity, should be measured in the field at the time of sample collection because these characteristics are likely to change once the water sample has been extracted from its natural environment (Wood, 1976). The measurement of these unstable characteristics should be conducted using field-calibrated instruments (Rantz et al., 1982a,b; Wilde et al., 1998). From a QA/QC standpoint, it is important that the field equipment be calibrated periodically according to the manufacturers' specifications and/or the QA/QC plan. Generally, field equipment should be calibrated, at a minimum, at the beginning of each sampling day and checked periodically. Depending on the length of the sampling event and the number of measurements to be made, recalibration and periodic checks in appropriate standards should be conducted during the day.

The measurement of flow at surface streams and ground water discharge points, and water level in monitoring wells, is critical to address the permit application questions regarding existing water quantity and the potential for change. Accurate flow measurements are becoming increasingly important, particularly where the determination of daily loadings of a given contaminant is required. The QA/QC plan should assure that the methods used to measure flow and water levels are acceptable. Current meters can be used to measure flow rate (e.g. Rantz et al., 1982a,b). This method typically involves measurement of the cross-sectional channel area in square feet (ft^2) and average water velocity in feet per second (ft/s) to obtain discharge in cubic feet per second (cfs). Where flow rates are too small (<0.01 cfs) or too diffuse for current meters, volumetric methods using calibrated containers and timing devices can be used to determine flow rate. Generally, smaller flows can be collected by routing them through a small diameter plastic pipe, and using a stopwatch to measure the time required to fill a container of known volume to obtain discharge in gallons per minute or liters per minute. Other accurate methods of surface flow measurement (e.g. weirs, flumes, staff gages) are available (Rantz et al., 1982a,b), but are less portable and/or require installation and maintenance of permanent equipment. Regardless of method, flows should be measured as accurately as possible—visual estimates, other than staff gage values, are rarely, if ever, adequate.

Static water level in wells should be measured as specified in the QA/QC plan. The most common methods use a chalked steel measuring tape or an electronic water level (conductivity sensing) probe with a visual or audible indicator attached to a graduated wire cord. Results can be expressed in distance below a particular datum (i.e. top of casing, ground level, etc.), or can be converted to a static water level if the elevation of the wellhead is known. Reference points for water level measurements needs to be consistent and stable. A reference point can be surveyed relative to one or more stable, marked reference points nearby.

Because temperature, pH, Eh, and DO can be affected by interaction with the atmosphere and gas exchange during sample processing and storage, in situ (downhole, instream) measurements or on-site measurements using flow-through cells that minimize atmospheric contact with the water are appropriate. Although SC, alkalinity, and acidity are suggested field measurements (Wilde et al., 1998), comparable data for these constituents can be obtained for fresh, completely filled, sealed, and chilled samples with short holding times in the laboratory. Nevertheless, because of possible effects from aeration, gas exchange, and hydrolysis of ions, data for some samples that are analyzed in the field and laboratory or analyzed repeatedly through time should be evaluated to determine if sample storage and laboratory testing leads to unacceptable errors. Field pH and SC data may also provide data quality checkpoints because they can be measured in subsequent laboratory analyses.

Field measurements of temperature, SC, DO, and/or pH in water should be conducted serially before and during purging and sampling to assure that water processed for laboratory analysis is representative of the ground water and surface water systems. Final field data should be recorded and samples should be collected only after stable, steady-state conditions are indicated.

FIELD NOTES/DOCUMENTATION

A detailed record of field activities and site-specific conditions that may affect the samples should be documented in a field notebook. The type of information and degree of detail may vary according to the complexity of the study. For a typical mining water quality study, the following information should be recorded: 1) Name of sample collector(s); 2) Project name, location, and date of sampling; 3) Field conditions: weather, hydrologic conditions (baseflow, runoff), description of sample site, and documentation of any unique conditions that may affect sampling activity or sample quality; 4) Specific field book entry for each sample point, including site description, time of sample collection, and record of point-specific measurements (flow/water level, temperature, pH, SC, etc.); 5) if wells are sampled, there should be a record of static water level before sampling, documentation of purging times and volumes, water level after purging, actual sample collection time, and field measurements of pH, temperature, and SC before and after purging.

Although all notes and observations of field conditions and the recording of field measurements are important, it is essential that the field sampler document any unique and/or temporary conditions that may alter the permanent hydrologic regime of the sample point. This is especially true if these conditions are affecting the physical or chemical characteristics of the sample at the time of sampling or have the potential to do so in the future. For example, if a small stream that has always been clear during the baseline monitoring program is found to be highly turbid due to activities upstream from the monitoring point, laboratory analyses of the sample could indicate anomalously high levels of suspended solids, Fe, and Al. If this condition or other similar events that may affect water quality are not documented by the field sampler, the resulting water quality anomalies may be unexplained or misinterpreted by persons not familiar with the project area. Documentation is particularly important in areas of previous/existing mining where hydrologic studies may be designed to predict the consequences of future mining by assessing the impacts of past mining. Any sources of water quality fluctuations should be documented as completely as possible to differentiate actual mining impacts from those stemming from other activities.

Field notes for soil/rock sampling activities should include: 1) Name of sample collector(s) performing sample collection; 2) Project name, location, and date of sampling; 3) Field conditions: weather; description of sample site; documentation of any unique conditions that may affect sampling activity or sample quality; 4) Specific field book entry for each sample point, including description (such as drill hole, soil pit, highwall exposure, etc.); time of sample collection; log of individual sample characteristics (depth interval, color, texture, lithology or soil classification, etc.); and percent recovery. Standardized classifications for color (Munsell Color Charts) and texture (Universal Soil Classification System) should be used to the fullest extent possible to minimize personal biases. Rock classification systems are not as standardized as those for soils, and lithologic determinations should be made by a trained individual. Field guides such as the *AGI Data Sheets* published by the American Geological Institute may be useful for rock identification.

Field notes for soil/rock sample collection by drilling should also document any observations that may indicate the subsurface geologic or hydrologic conditions present at the site. These may include, but are not limited to, drilling advance rates, water levels, loss of air circulation, loss of cuttings, water yield or loss during drilling at different depths, and caving/hole stability.

SAMPLE CUSTODY PROCEDURES

An acceptable QA/QC program in AMD prediction studies requires that the complete history of every sample be recorded (Downing and Mills, 1998). The chain of custody begins with the person(s) collecting the sample in the field and is transferred to each subsequent person or entity that handles the sample. Such a history will include:

- The date, time and sampling protocol for the original sample;
- The method, duration, and location of any sample storage;
- A detailed record of any physical or chemical treatment of the sample, including drying, crushing, grinding, screening, splitting, and washing;
- A record of everyone who has handled the sample, including time and place; and
- Records of disposal of any sample components, fractions, and splits.

This cradle to grave record for a sample constitutes the chain of custody. Any engineer or geoscientist evaluating AMD test work results may need to follow the chain of custody backwards in order to investigate unusual or unexpected results. In addition to its necessity for scientific investigation, chain of custody has important legal ramifications. All events related to the collection, transfer, analysis, and ultimate disposal of samples should be recorded using a chain-of-custody form. This information will be recorded on the analytical services request forms or a related document specified in the QA/QC program that will be transmitted with samples on each step from the field collection through laboratory analysis.

SELECTION OF LABORATORY AND ANALYTICAL PROCEDURES

Regulations governing prediction of hydrologic consequences specify minimal testing parameters prior to issuance of a mining permit. These can include typical baseline constituents associated with AMD (pH, acidity/alkalinity, iron, manganese, aluminum, sulfate, dissolved solids and/or SC) for water samples, and ABA for the overburden. Most laboratories that serve the mining industry can perform these tests. However, more rigorous testing may be required for a specific site. For example, where applications of fly ash or biosolids are proposed for use during reclamation, regulatory agencies may require toxicity testing on such materials and monitoring for heavy metals. Reviewers may require additional testing for prediction studies in sensitive watersheds, such as kinetic testing using humidity cells or leaching columns. Such procedures may require specialized equipment and technical expertise not available at all laboratories, and require more stringent QA/QC because the implementation of additional regulatory requirements is usually coupled with a higher degree of scrutiny by the regulatory agency.

The selection of a laboratory to perform sample testing is an integral part of generating reliable data to predict mining consequences. It is important to ensure that the laboratory can perform all testing required for the prediction study, and document QA/QC procedures used to maximize data confidence. Not all laboratories are equal in terms of equipment, facilities, trained personnel, etc. Some laboratories have a long-standing reputation for generating high-quality data with few errors; others may be capable but may not have yet established a proven track record; still others may have a reputation for providing fast, low-cost analyses with questionable QC procedures. The sheer number of testing laboratories present near some metropolitan areas may make laboratory selection a difficult task. However, the effort expended in designing a hydrologic monitoring program and careful field sample collection and handling may go for naught if the samples are submitted to a laboratory that is not capable of providing analytical results that are representative of the delivered sample. Therefore, developing a working relationship with a qualified laboratory is a very important part of generating quality data that can be used with confidence for prediction of AMD potential.

Industry members that have extensive monitoring requirements and regulatory agency personnel that review the hydrologic consequence portions of permit applications may be able to recommend reliable laboratories. At a minimum, the selected laboratory should have a comprehensive in-house QA/QC program outlined in a QA/QC manual. The manual should be sufficiently comprehensive to apply to most laboratory operations, and should be subject to periodic review and update. In addition to internal QA/QC, it is also desirable to seek laboratories that are certified for particular types of analytical work by outside agencies such as the U.S. EPA, State Health Department, etc. Certification under such programs usually requires periodic testing of unknown standard samples submitted by the certifying agency to determine the accuracy and reproducibility of laboratory methods.

The cost of laboratory analyses is always an important consideration when developing a project budget. However, selection of an analytical laboratory should never be done solely on a cost basis. Laboratory testing costs can vary depending on the number of samples and analytical schedule. There may be significant differences in pricing for analyses on a per item basis compared to package pricing for a routine suite of constituents.

Laboratory Sample Analysis and QA

Water and overburden samples should be analyzed for physical characteristics and chemical constituents using approved methods (e.g. Fishman and Friedman, 1989; Greenberg et al., 1992; Skousen et al., 1997; Sobek et al., 1978; Wilde et al., 1998). One or more QA samples, including blanks, duplicates, and standards for inorganic constituents, should be analyzed as blind samples with each set of samples to check for contamination, accuracy, and precision of analytical results. On average, approximately 10% of the total samples should be QA samples. When first starting a project and establishing initial data for a site, a greater percentage of samples may be QA samples, and subsequently, upon verification of acceptable results and the availability of site data for comparison with new results, a smaller percentage may be QA samples.

Blanks are used to check for contamination resulting during sample collection and analysis. Laboratory blanks are used to check for contamination from the sample bottle or from laboratory processing of samples, and field blanks are used to check for contamination of samples from exposure to sampling and filtering equipment. Laboratory blank water, which can consist of deionized or distilled water from commercial sources, will be placed with appropriate preservatives in the type of bottle specified for the desired analysis and will not be taken to the field. A field blank will consist of the same type of water and sample bottle used for a laboratory blank; however, the field blank will be processed through the sampling and filtering equipment in the field, after routine cleansing and rinsing of the equipment following water-sample collection.

Duplicate samples should be used to evaluate field and laboratory analytical precision in analysis of overburden chemistry or concentrations of metals and anions in water samples. Samples for analysis of dissolved constituents should be filtered into one container and then split. Preservation and storage of the duplicate samples must be conducted using identical procedures.

The accuracy of field and laboratory measurements should be evaluated using standard reference samples from the National Institute of Standards and Technology, U.S. EPA and USGS, and/or commercial sources, as well as matrix spiked or synthetic samples prepared using certified reagent grade chemicals. Standards are rock or water samples that have known characteristics or concentrations of constituents of concern. Deionized water, the same water source used for laboratory blanks, should be used to prepare any standards from ampouled concentrates. Standards submitted for analysis should be stored in the same type of containers or bottles and transported with the unknown samples for analysis.

Approved techniques for chemical measurements (e.g. Fishman and Friedman, 1989; Greenberg et al., 1992; U.S. EPA, 1983; Wilde at al., 1998) should be used to provide uniform methods for both field and laboratory analysis. Accuracy and precision can be quantified by use of data from duplicate and standard samples as described earlier. During the project, detection limits should be verified, and accuracy and precision of data checked in accordance with the QA/QC Plan.

Common laboratory errors include (Calow, 1991): incorrect identification of samples; contamination; improper or inappropriate sample preparation; inaccuracy of sample weights or volumes; improper or inappropriate sample dissolution/treatment; chemical and physical interference; improper or inappropriate instrumentation, or inaccurate measurement; calculation errors; and incorrect data handling/reporting. In this list, all but chemical and physical interference have a human component. This highlights the importance of QA/QC, which establishes standardized procedures to minimize the potential for error, and checkpoints to provide opportunities to detect and correct errors that do occur.

The laboratory QA/QC process typically begins when the laboratory delivers sample containers and preservatives to the field investigator. After the samples are collected and transported to the laboratory, proper procedures must be followed for chain-of-custody, sample storage and holding time, sample preparation, use of quality-control samples, instrument calibration, sample analysis, laboratory validation, data reporting, and record keeping. This process is outlined below:

1) Samples delivered to laboratory
2) Samples logged in, temperature and pH checked
3) Paperwork (chain-of-custody) checked
4) Samples stored in refrigerators
5) Samples checked out - sample preparation begins
6) Sample extracts and/or digests assigned to analysts
7) Sample analysis by approved methods using calibrated instruments
8) Lab QC samples checked to ensure no contamination during storage, handling, preparation, etc.
9) Data evaluation and reporting
10) Validation by section head/manager (checks calculations, significant figures, etc.)

11) Data package preparation
12) Lab manager approves and signs data package
13) Data package submitted to client

Although a detailed description of the laboratory QA/QC process is beyond the scope of this report, the ultimate goal of performing these procedures is to implement a mechanism by which the qualitative and quantitative reliability of the data can be assessed.

SPECIFIC ROUTINE PROCEDURES TO ASSESS DATA

Quality of analytical measurements can be evaluated by examination of five data quality parameters: precision, accuracy, representativeness, completeness, and comparability. These terms are defined briefly below.

Precision is a measure of the degree of agreement among replicate analyses of a sample. Values should demonstrate the reproducibility of the measurement process. The sample standard deviation and coefficient of variation are commonly used as indicators of precision; smaller values (i.e. less variation about the mean of all analytical results) indicate better precision.

Accuracy is how close the analytical result is to a true or reference value. A true value is one that has a certified concentration based on many analyses, or a sample that has been spiked with a known concentration of a reference material. Accuracy is generally expressed as a percentage of the true value.

Representativeness is the degree to which data can be compared with other results of a large sample accurately represent parameter variations at a sampling point and/or environmental condition. All testing data should reflect, as much as possible, the existing conditions at the time of sampling.

Comparability is the degree of confidence with which one data set can be compared to another. The produced data may be compared to other available data, such as data generated by another laboratory over a specific time period, or data collected from literature or research by others.

Completeness is the measure of the amount of valid data obtained from a study area compared to the amount that was expected to be obtained under normal conditions. Completeness goals should be defined at the beginning of a project to ensure that sufficient data are collected.

Precision and accuracy can ususally be evaluated by examining QA data available on request from the laboratory, and/or submitting duplicate and spiked samples along with the field samples delivered for testing. Representativeness is commonly a function of the location of a sample point within a medium (such as an aquifer or large stream), and a determination whether characterization of that medium can be accomplished by a single sample point or if multiple points are required. From this standpoint, representativeness of data is largely the responsibility of the investigator and/or field sampler. Although water in small small, narrow streams may be well mixed, width- and/or depth-integrated sampling may be appropriate for representative samples where seepage is diffuse, discharges occur along a stream bank, a stream channel is braided or broad, or other scenarios where the water at the sampling site is poorly mixed and could vary in quality. Likewise, the investigator must analyze the purposes of the investigation and supplementary data available from other studies, and ultimately be responsible for evaluating comparability and completeness of data.

When evaluating water-quality data collected for a baseline monitoring program, the investigator should compare the data to previously collected data at each monitoring point for general trends. Analytical results that are substantially greater or less than the previously observed values should be checked to determine if the variations are valid. For example, a sulfate concentration of 150 mg/L at a sample point that has exhibited concentrations between 10-15 mg/ L over the previous 6 months may indicate a simple laboratory dilution or calculation error. Another example is the case of a dramatic increase in iron content at a sample point that has exhibited less than 1 mg/L of iron, which could result from several possible sources. Elevated iron in conjunction with high suspended solids and elevated flow generally indicates turbidity due to increased runoff during rainstorms. If the elevated iron levels are due to runoff caused by rainfall, this occurrence should also be apparent from entries in the field sampler's notes, or in site rainfall data (if available). Elevated iron and suspended solids in absence of increased flow or evidence of runoff could result from in-stream excavation work upstream from the sample point—if this is the cause, it should be noted in the field sampler's notes. It could also result if the field sampler inadvertently disturbed bottom sediments while collecting the sample. Elevated iron without increased flow or suspended solids may be evidence of laboratory error, a contaminated sample container, or contamination of the sample during the transportation, handling, or preparation.

Assuming no sample contamination or laboratory errors, baseline data should be uniform or exhibit trends that can be linked to seasonal flow variations. Sudden dramatic increases in concentrations may be explained by major precipitation events, or unique situations that affect the stream on a short-term basis and should be documented in the field sampler's notes. If dramatic variations cannot be otherwise explained, further evaluation should be conducted to determine the probable cause. If this type of evaluation is performed soon after receipt of the data package from the laboratory, the sample, if retained, can be retested to confirm or rule out the possibility of laboratory error. If there is no laboratory error and the sample was contaminated during some other stage of sample handling or transportation, it may be necessary to resample to obtain valid data.

In addition to the evaluation of results for QA samples, QA checks can be performed on water-quality constituents for unknown samples to check for internal consistency. For example, SC, sulfate, and total dissolved solids generally are correlated (e.g. Hem, 1985; Fishman and Friedman, 1989). Additionally, if major cations and anions are determined, then the chemical ionic balance, or charge balance, can be computed (Fishman and Friedman, 1989). Finally, ABA and water-chemistry data collected during the program can be plotted and/or statistical analysis carried out in order to determine spurious results and confidence of data. For example, as shown in Figures 1 - 4, the pH, alkalinity, acidity, and overburden chemistry commonly will be correlated. Outliers from the general trends will need to be examined to determine if deviation from the main trend is due to sampling and/or analytical errors. Downing and Mills (1998) report several examples of such plots. These include: 1) Inorganic carbonate NP vs. NP to determine whether there is any correlation between carbonate content (carbonate NP) and total NP; 2) Neutralization Potential Ratio (NPR), which is NP divided by MPA against total or pyritic sulfur analysis; and 3) maximum acidity potential (AP), determined from sulfide sulfur analyses plotted against total sulfur analyses.

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