Prediction of Water Quality at Surface Coal Mines

Prepared by Members of the Prediction Workgroup
of the
Acid Drainage Technology Initiative (ADTI)

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ADTI is a government/industry joint venture dedicated to the development and use of best science applications to the problem of acid mine drainage.

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Preface

This report presents the principal techniques and methods used to predict the water quality that will result from surface coal mining and reclamation. It has been prepared by a subset of the Coal Sector of the Acid Drainage Technology Initiative (ADTI), which in turn is a coalition of State and Federal agencies, industry, academia, and consulting firms working together to promote communications and technology enhancement in the field of acid drainage. The ADTI Coal Prediction Workgroup was initiated by the Office of Surface Mining (OSM), National Mining Association (NMA), the Interstate Mining Compact Commission (IMCC), and the National Mine Land Reclamation Center (NMLRC), which coordinates and facilitates ADTI activities. The ADTI Coal Prediction Workgroup has had a number of members over the years since it began work in 1996. It is with deep gratitude that the ADTI coal sector acknowledges the voluntary contributions of the authors, researchers, editors, and their employers that have made this document possible. However, in addition, the efforts of all the members of the Workgroup, and the agencies, companies and universities that allowed them to work on ADTI, are gratefully acknowledged:

This report summarizes some of the more recent advances in understanding and experience in the field of mine drainage prediction as well as some previously unpublished experiences in coal mine drainage prediction. It is intended to provide a balanced and moderately detailed overview of coal mine drainage prediction and to serve as a guide to the literature of this rather broad field. Contact information for all of the authors can be found at the end of the book, in Appendix C.

CHAPTER 1: INTRODUCTION AND RECOMMENDATIONS

by

Robert L. P. Kleinmann, Roger Hornberger, Bruce Leavitt, and David M. Hyman

THE NATURE OF THE PROBLEM

Nationwide, over 19,300 km (12,000 miles) of rivers and streams and over 730 km^2 (180,000 acres) of lakes and reservoirs are adversely affected by contaminated water draining from abandoned mines. The vast majority of this problem occurs in the eastern United States; EPA Region 3 (which includes Pennsylvania, West Virginia and Maryland) considers coal mine drainage to be its most significant non-point pollution problem. However, despite the magnitude of the problem, the situation is much better than it was 30 years ago, when the number of stream miles adversely affected was 50% worse. The improvement can be attributed to the reclamation of many abandoned operations, and to the regulatory requirements on coal mining operations, which now must both prevent acid mine drainage (AMD) generation and treat their effluent water during and after mining to meet effluent limits.

The regulatory authorities and the mining industry have worked hard to improve water quality during and after mining. A key component of this activity is predicting the post-reclamation water quality before mining occurs. The regulatory agencies make such predictions to aid in permitting decisions. Generally, where analysis indicates that poor post-reclamation water quality is anticipated, permits to mine are granted with restrictions (requiring the use of special preventive practices, such as alkaline additions, to overcome neutralization deficiencies, or deleting a coal seam or an area from the permit) or are denied altogether. The mining industry is generally required to demonstrate that no pollution will result. Despite these efforts, AMD is common at reclaimed surface mines, in part because the task of predicting post-mining water quality is highly problematic. As a result, the industry spends over a million dollars a day chemically treating contaminated mine water. The industry can only afford the long-term liability of water treatment if it is planned for; unanticipated water treatment that must continue after mining and reclamation has been completed can bankrupt a company.

At surface coal mines where the overburden chemistry is dominated by either calcareous or highly pyritic strata, the prediction of post-reclamation water quality is relatively straightforward. However, at sites where neither clearly predominates, predicting post-reclamation water quality can be complex. Fifteen years ago, researchers found that at these more difficult-to-predict sites, overburden analysis procedures generally used to predict post-reclamation water quality at surface coal mines were no more effective than flipping a coin. Since then, a great deal of effort has gone into improving the procedures. Pennsylvania has compiled statistics indicating that overall, its permitting decisions are now accurate 98% of the time; that is to say, only a small percentage of the mines anticipated to produce neutral or alkaline water produce AMD. (It is not possible to estimate the number of mines not permitted to open in Pennsylvania because of anticipated AMD that, in fact, would have produced acceptable water.) Largely as a result of ADTI, other states are now beginning to similarly assess their permitting practices. However, even without the statistics from other states, it is clear to all of those working in the field that prediction of post-reclamation water quality has improved.

OUR OBJECTIVES

This report provides an overview of techniques, methods, and procedures that are being used to predict the quality of water that will be generated after a site is surface mined for coal, and then reclaimed. It was prepared by a subset (Group 1) of the Acid Drainage Technology Initiative (ADTI), which in turn is a coalition of State and Federal agencies, industry, academia, and consulting firms working together to promote communications and technology enhancement in the field of acid drainage. Group 1 is comprised of about 25 people, who focus on problems associated with predicting water quality, while Group 2 focuses on avoidance and remediation. Group 2 published a handbook in 1998 that should be considered as a companion volume to this one.

The objectives of this report are to provide a summary of the various options available to predict post-reclamation water quality at surface coal mines, including their relative strengths and limitations, and to promote the integrated use of the various methods. Ideally, this report will lead to an increased awareness and consideration of the various options that are available, and encourage both industry and regulatory agencies to use the most appropriate and cost-effective means of accurately predicting post-reclamation water quality. Recommendations are provided at the end of several of the chapters; these are summarized at the end of this chapter.

Currently, although similarities exist, each State's permitting agency has its own mine drainage prediction methodology. The amount and types of data required vary from state to state, including different requirements for documenting pre-mining water quality, overburden lithology and geochemical properties, and the proposed mining and reclamation plans. As a result, the degree of success in preventing AMD on new permits varies. This report incorporates the results of an informal survey of the mine drainage prediction processes and risk reduction techniques used by Alabama, Indiana, Illinois, Kentucky, Maryland, Ohio, Pennsylvania, Tennessee, Virginia, and West Virginia. The objective of this survey was to lay the groundwork for an extensive, long-term post-mortem regional analysis of mine permits relative to predicted post-mining water discharge quality, similar to what Pennsylvania has accomplished. This would allow local and regional variations to be factored into future recommendations. The authors hope that all of the regulatory agency personnel reviewing this document will learn ways in which they can improve the permitting process in their state, in part by incorporating successful techniques being used elsewhere.

It should be noted that this report presents only the components relevant to predicting water quality at surface mines at which coal is being mined. Although the general approach is similar, issues and interpretation of results can be quite different for hard rock operations and underground coal mining. Therefore, a separate volume will soon be produced that will focus on hard rock issues. In the future, a volume to predict the water quality from underground mines is also planned, once we have sufficient field validation of the technology being used.

FORMATION OF ACID MINE DRAINAGE

Acidity at coal mines is principally due to the oxidation of pyrite, FeS_2, which is commonly associated with the coal and surrounding strata. Coal owes its origins to the burial of organic matter in swamps; pyrite also

forms in such environments. Several types of pyrite may be present, and the reactivity of the different forms can be significantly different due to the nature of their formation and the effect that grain size has on surface area.

Mining disrupts the rock strata and exposes the pyrite to air and water, allowing oxidation to take place. Oxidation of the sulfide component of the pyrite to sulfate produces 2 moles of acidity for every mole of pyrite. Sulfur may also be present in the rock as sulfate minerals, such as jarosite ($KFe_3(SO_4)_2(OH)_6$), or as organic sulfur. Some of the sulfate minerals can dissolve and form acid solutions, but the organic sulfur is organically bound with the coal and has little or no effect on acid potential. Acidity is also produced by the oxidation of the iron from Fe^{+2}, ferrous, to Fe^{+3}, ferric iron, and its subsequent hydrolysis. The acid water that results from all of these reactions leads to the dissolution of other common contaminants, such as aluminum and manganese, and occasionally other metals such as copper, zinc, and nickel.

At the same time, the rock strata typically include components that dissolve and produce alkalinity. In coal-bearing strata, alkalinity is principally represented by $CaCO_3$, either as limestone, calcareous cement or calcite, or as $CaMg(CO_3)_2$, dolomite. $FeCO_3$, siderite, is also commonly present but does not contribute alkalinity.

Although these minerals can oxidize and/or dissolve in the absence of mining, the disruption and displacement of the rock strata typically accelerates the processes. Accurately predicting post-reclamation water quality involves understanding how the mineral components will react in the mine environment and how the acid-forming reactions and the acid-neutralizing or alkalinity-generating reactions will balance at a given site. There are many complicating variables. For example, concentrations of pyrite and carbonate minerals vary both horizontally and vertically, so that accurately determining the amount of each at a site can be very difficult. The kinetics of the reactions change as the water quality changes (for example, as pyrite oxidizes and the pH drops). Reaction rates are also affected by such variables as climate, the activity of iron-oxidizing bacteria, the rate of diffusion of oxygen, water infiltration rates, atmospheric chemistry within the mine spoil, the degree of compaction, pyrite and carbonate mineral grain size and morphology, the relative locations of the pyritic and calcareous rocks, and the location of the water table.

Prediction of water quality involves measuring the most important variables, making certain assumptions relative to less-important variables, extrapolating from what has been learned through experience at other sites, and sometimes conducting laboratory simulations to evaluate kinetic aspects. Generally, one attempts to predict whether the site will produce acidic or alkaline drainage, though sites that produce alkaline water may still require chemical treatment or special handling, due to the level of metal contaminants present.

METHODS OF PREDICTION

Most frequently, prediction of post-reclamation water quality at surface coal mines involves analysis of overburden samples. These samples can be analyzed using one of several static tests, which involve determining and comparing the amount of potentially acidic and alkaline constituents in the rock. There are also kinetic tests, which are principally leaching methods in which rock samples from the proposed mine site are subjected to simulated weathering conditions and the leachate is analyzed in a laboratory for mine

drainage quality parameters. These kinetic tests may be conducted in an apparatus in the laboratory or in the field, and the test results may be evaluated independently of static tests or integrated with static test results on the same rock samples. Other methods of prediction include the use of geophysical and/or geochemical procedures.

As an alternative approach, the prediction of drainage quality from the natural background water quality at the site or from the chemistry of water at an adjacent mined site involves scientific inference and common sense. If representative samples of surface and ground water are collected on or near a proposed site, it is reasonable to assume that they should indicate something about the geology of the site and the quality of the mine drainage that will be produced after mining. For example, within areas of the Appalachian Coal basin of the eastern United States where major stratigraphic sections of carbonate rocks are present, surface and ground water will have a relatively high concentration of alkalinity, particularly in the head waters of small tributaries and in springs and ground water seeps. If the springs, seeps and tributary samples on or near a proposed mine site have low buffering capacity, it is less likely that carbonate rock will be present to produce alkaline drainage or to neutralize AMD. However, a major problem in relying solely upon background water quality is that significant sections of potentially acidic strata may be present on site, but not reflected in the pre-mining water quality. This occurs because the high acidity only results after the pyrite or other acid-producing minerals are exposed to increased oxidation and weathering during mining.

The use of mine water quality at nearby sites is a very similar, and generally more useful, technique. Post-mining discharges, highwall seeps, and pit waters at adjacent active, reclaimed, or abandoned sites can provide good indications of whether future mine drainage is likely to be highly alkaline, highly acidic or somewhat neutral, if adequate stratigraphic correlations of coal seams and overburden lithologic units can be made. Discharges from active or abandoned underground mines are of some value, but not as useful as surface mine data. Such data can be compiled from state agency permit files of active or completed sites. At least two major problems may impede the accurate prediction of proposed mine site drainage quality from nearby sites. One is that the proposed mine site may have significantly different overburden chemistry due to facies changes, differences in depths of weathering or other local-scale geologic variations. A second is that the existing water quality may reflect past mining and reclamation practices. For example, the existing reclaimed site may have coal preparation plant refuse or large amounts of alkaline additives, such as flyash, buried in the backfill, both of which will skew the water quality one way or the other. These potential interpretation problems are discussed in more detail in chapter 3.

Static and kinetic tests incorporate chemical analyses performed on rock samples from the actual mine site. A critical point is that these methods are only valid if the rock samples are truly representative of the site where mining is proposed. Rock samples may be collected from exploration boreholes or other sources (e.g. exposed highwalls). Both static and kinetic tests produce site-specific geochemical evaluations of potential acidity or alkalinity, and possibly other parameters of predicted water quality. The major difference between static and kinetic tests is that static tests provide measurements of the amount of selected chemical constituents <u>in</u> the rock sample (e.g. total sulfur, neutralization potential), while kinetic tests provide measurements of the amount of selected chemical constituents that come <u>out</u> of the rock samples in leachate (e.g. acidity and iron concentrations) under specified conditions. The total amount of an element or mineral (e.g. sulfur or pyrite) in the rock sample may not be directly proportional to the amount of the associated

parameter (e.g. sulfate or iron) in the simulated effluent produced in a leaching test or actual mine drainage in the field. This is due to reaction kinetics, mineral solubility controls, crystallinity and morphology of the minerals, and other physical, chemical, and biological factors. However, both static and kinetic tests have potential value, provided that their limitations are recognized when interpreting the results.

In this report, we focus primarily on the static test that is most commonly used to predict mine drainage quality in the eastern United States, namely acid-base accounting (ABA). This method involves a comparison of the maximum potential acidity (MPA), typically calculated from the total sulfur in the sample, to the neutralization potential (NP). Other static tests have been developed and employed for use in coal mine drainage prediction, but ABA is the most routinely used method for coal mine drainage prediction. A recent innovation, Evolved Gas Analysis (EGA), also deserves mention as it has the potential to fill a gap between static and kinetic tests, since it is a static test that provides some information that can be used to factor in reaction kinetics. In addition, geochemical logging techniques adapted from the oil and gas industry can be used to provide an instantaneous analysis that simulates ABA. All of these methods are discussed in Chapter 4.

Kinetic tests are most appropriately used when the results of static tests falls between the regions defined (by practice) as acid or alkaline. The most commonly used kinetic tests for mine drainage prediction involve either leaching columns or humidity cells. These tests have been used, evaluated, and compared in many coal mine drainage prediction studies, but are in fact only occasionally used by the mining industry and state regulatory agencies in the Appalachian Coal Basin. Other kinetic test methods, such as the Soxhlet reactor, have also been used in prediction efforts, but even less frequently than humidity cells and leaching columns. Kinetic test methods are more routinely used by the metal mining industry and regulatory agencies in the western U.S. and Canada. Barriers to their use in the eastern United States include their expense and the time (months) needed to obtain results, as well as the fact that they have not had the widespread field validation that ABA has had.

Kinetic tests incorporate dynamic elements of the physical, chemical, and biological processes involved in the weathering of mine rock, and attempt to simulate the kinetics of the chemical reactions that control the production of acidic or alkaline mine drainage. Factors that may be incorporated include: size, shape and structure of the apparatus; volume and placement of the rock samples in the apparatus; particle size; mineralogy; antecedent storage conditions; interleach storage conditions; rock to water ratio; leaching solution composition; leaching interval; pore gas composition and nature of bacterial populations. If the critical physical, chemical and biological conditions are proportionally representative of the natural environment, the water quality of the leachate may be used to predict or estimate the water quality from the proposed mine site. Unfortunately, kinetic test procedures are necessarily simplifications of the natural environment, and it is easy to be fooled by laboratory procedures that underestimate or overestimate some component of the real world. These issues are addressed in detail in Chapter 5. In addition, the validity of kinetic tests, like static tests, depends on how well the samples represent the site. It is important to remember that despite apparently precise laboratory analyses, test results may not accurately predict mine drainage quality.

To summarize, this report provides information on numerous methods to predict post-reclamation water quality at surface coal mines. The various advantages, disadvantages and assumptions of the principal methods are discussed; these must be understood by anyone selecting or interpreting the results from these techniques. This array of prediction methods is analogous to a collection of tools in a toolbox. The choice of which tool to use is ideally a function of site-specific circumstances, but in the past, the decision has often been dictated more by familiarity with the test and the ability of practitioners to extrapolate the test results to mine scale decisions. In the context of compliance and enforcement, when the only tool in your toolbox is a hammer, everything begins to look like a nail. It is the hope of the ADTI participants that, with sufficient information, practitioners will feel comfortable using tools that are more appropriate, rather than just familiar. Regulatory agencies and the mining industry should both consider and promote the proper use of all mine drainage prediction tools, and to become comfortable using them in concert to optimize the odds of accurately predicting the effects of mining a given site in a particular manner.

RECOMMENDATIONS

The use of ABA for accurate prediction of mine water quality depends on obtaining representative samples of the geologic materials that will be disturbed. Geologic variability within a site must be captured through the use of a sufficient number of samples. The effect of weathering on the sampled strata must be considered; the absence of carbonate minerals or pyrite in the top 20 feet of overburden sampled is likely not representative of the same strata at greater depths. Studies in Pennsylvania have shown that an absolute minimum of three and more typically six or seven holes are needed per 100 acres in order to capture the geologic variability of a site. The collective experience of the ADTI Coal sector underscores Pennsylvania's findings, though of course each site is different and it is hard to generalize. However, Pennsylvania has also found that their sampling requirement can be entirely waived if water quality is good at adjacent mines that have extracted the same coal seam. In fact, they have found that the most effective predictor of AMD potential has been previous mining in the same seam and general location as the proposed operation.

If the strata are adequately sampled, overburden analysis, and in particular, ABA, works well in most overburden. However, an overburden analysis located between analytical results clearly associated with alkaline discharges and those that are clearly associated with acidic discharges is said to fall within a *gray zone*. The uncertainty is caused by variability in rock strata and the ability to adequately represent those strata with a limited volume of sample material, as well as sources of error in the analytical procedures.

For example, the presence of the mineral siderite has long been known to cause false levels of alkalinity to be reported in ABA results. In addition, the subjective fizz test has been shown to result in significant lab-to-lab variability in ABA test results on the same sample. Chapter 4 contains a modification of the ABA procedure that eliminates these two sources of error. The ADTI Coal sector strongly recommends to all operators, researches, and regulators that these ABA modifications be adopted. The authors believe that broad application of this methodology will result in fewer mines that produce acidic discharges, and allow for the safe permitting of mines that would not have been permitted utilizing the old procedure.

It is also necessary to define the gray zone. The ADTI coal sector recommends that strata with a neutralization potential (NP) less than 10 tons/1000 tons or a net neutralization potential (NNP) less than

0 tons/1000 tons be considered potentially acid producing. Strata with an NP greater than 21 tons/1000 tons or an NNP greater than 12 tons/1000 tons can be considered alkaline. The gray zone is the defined region between these values. These values are based on the ABA procedure currently used in the U.S., and their derivation is discussed in chapter 4. As the ABA modifications recommended in this text are applied in the field, it is anticipated that the accuracy of predictions should improve. These values should therefore be re-assessed once the modified test procedures have been adopted. It is anticipated that the elimination of the siderite problem and the elimination of subjectivity in the fizz test should reduce the size of the undecided gray zone, and lower the break points for the generation of an alkaline discharge.

Dynamic or kinetic testing, in which the rock samples are subjected to mild to severe weathering under laboratory conditions, are described in detail in Chapter 5. While kinetic tests have been utilized to make permitting decisions, the time and effort required for such testing have generally limited their applicability. In addition, the lack of standardization has also caused problems. The Chapter 5 recommendations should correct the latter problem; presumably, this will allow kinetic tests to be used when clarification of the likelihood of acid generation for sites in the defined gray zone is necessary.

Finally, it should be emphasized that regardless of whether one is preparing or reviewing a permit, the unique character and condition of each mine site precludes a simple cookbook approach. If site characterization is adequate, it is generally possible to predict post-mining water quality. This evaluation should then be factored into a consideration of whether this predicted water quality is likely to have unacceptable effects on local water quality, and if so, whether anything can be done during mining and reclamation to allow it to proceed without such adverse effects.

CHAPTER 2: HOW GEOLOGY AFFECTS MINE DRAINAGE PREDICTION

by

Keith Brady, Roger Hornberger, William Chisholm, and Gary Sames

INTRODUCTION

Acid mine drainage (AMD) is a major problem in the northern Appalachian Basin, particularly within the Allegheny Group stratigraphic section (Appalachian Regional Commission, 1969; Wetzel and Hoffman, 1989). AMD is much less significant in the midwestern states, and so this chapter and the next emphasize the Appalachian states. Figures 2.1 and 2.2 illustrate the extent of contamination in the northern Appalachian Basin, using data from Wetzel and Hoffman (1983). It should be noted that the distribution of contaminated mine water is not simply a function of the amount of pyrite and limestone in the overburden. For instance, some watersheds are much more intensely mined than other watersheds, and some watersheds on the periphery of the basin may have little or no coal. However, some general statements on the distribution of water quality problems can be made. The West Branch of the Susquehanna River has the highest percentage of streams with pH less than 6.0 (56%). This watershed has a correspondingly high percentage of streams with sulfate above 75 mg/L, indicating that the proportionally low pH is due to mining. The other two watersheds with greater than 35% of the streams having a pH less than 6.0 occur where mining would have encountered the Allegheny Group. Watersheds in southern West Virginia and Kentucky that have sulfate concentrations above 75 mg/L in greater than 35% of the streams illustrate that high sulfate does not necessarily correspond with low pH; none of the sampled streams have a pH less than 6.0.

Although there is a general relationship between geology and mine drainage quality, no comprehensive study relating geology and mine drainage quality has been attempted for the entire Appalachian basin. An examination of geologic studies suggests some significant differences in mineralogy for the southern (Pottsville) and northern (Allegheny through Dunkard) Appalachian strata (e.g., Cecil et al., 1985; Donaldson et al., 1985a). Four principal geologic processes have contributed to the variability of coal properties and the chemistry/mineralogy of the intervening strata. Two of these, paleoclimate and paleodepositional environment, date back hundreds of millions of years to the Pennsylvanian Period. The other two, surface weathering and glaciation (in the northern part of the basin), are more recent, occurring within the past few million years.

The paleoclimatic and paleodepositional environmental influences on rock chemistry in the northern Appalachians resulted in the formation of coal overburden with greatly variable sulfur content (0% to >10% S) and calcareous mineral content (0% to >90% $CaCO_3$). The wide variations in rock chemistry contribute to the wide variations in water quality associated with coal mines.
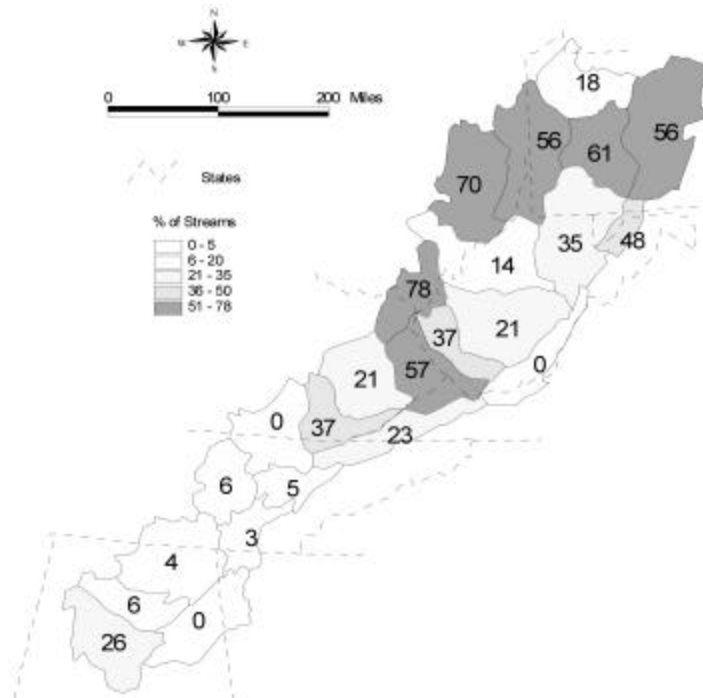
Figure 2.1. Percentage of Streams in the Watersheds with a pH less than 6.0
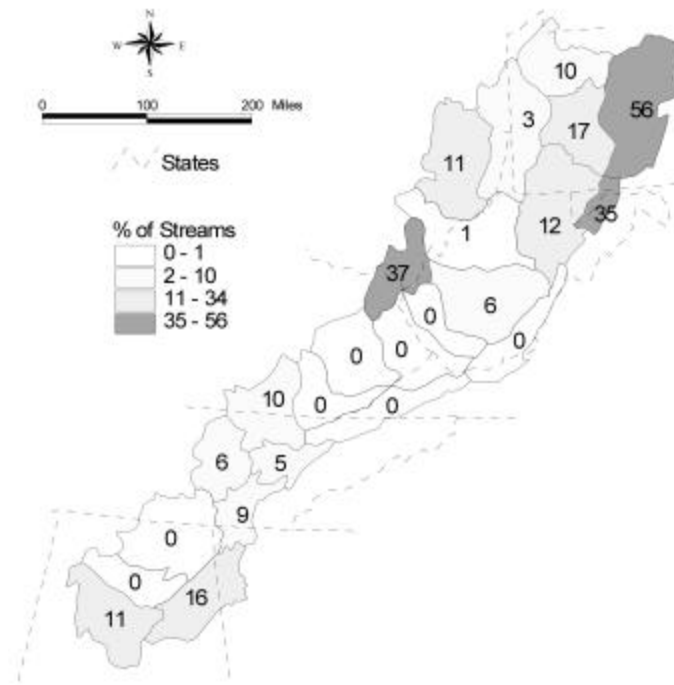
Figure 2.2. Percentage of Streams in the Watersheds With Median Sulfate > 75 mg/l

GEOLOGIC FACTORS

Paleoclimatic Influences

Various attempts have been made to reconstruct the paleoclimate of the northern and central Appalachian Basin during the Pennsylvanian (Cecil et al., 1985; Donaldson et al., 1985a; Phillips et al., 1985; Winston and Stanton, 1989). The models developed in these studies differ as to how wet or dry the upper Pottsville was, but they agree that at the time of deposition of the Allegheny Group, the climate was moderately wet, although drying as the deposition continued. All agree that during deposition of the Conemaugh Group, it was dry. The base of the Monongahela was deposited in a wet period, and the climate probably became drier higher up in the section. Cecil et al. (1985) and Donaldson et al. (1985a) concluded that the period during which the Dunkard was deposited was comparatively dry.

Cecil et al. (1985) suggest that climate affected the shape of the peat deposits, the chemistry of the swamp and ultimately the chemistry of the coals. Periodic dry conditions would allow the surface of the peat to dry, oxidize, and degrade, thus increasing ash content. These conditions, taken together, would result in higher sulfur and ash in the northern Appalachian coals. Cecil et al. believe that this explains why the coals of the southern Appalachian Pottsville Group are lower in sulfur (typically <1% sulfur) and ash (typically lower than 10% ash) than the younger coals of the northern Appalachians (typically >1% sulfur and >10% ash) (Figures 2.3 and 2.4).

As with coal quality, Cecil et al. (1985) and Donaldson et al. (1985a) concluded that overburden strata are also influenced by paleoclimate. The drier conditions during the Upper Pennsylvanian (upper Allegheny and younger strata) resulted in the common occurrence of freshwater limestones, calcareous œments, and calcareous concretions in non-marine sandstones and shales.

A second category of geologic processes that influenced the chemistry and mineralogy of Pennsylvanian Period coal-bearing sediments, including the distribution of calcareous and pyritic rocks, was depositional environment. Typically, within the Pennsylvanian, paleoenvironment is classified as freshwater, brackish and marine (Williams, 1960). These three categories are not evenly distributed geographically or stratigraphically.

Paleoenvironmental Influences

Paleoenvironment is an important control on the distribution of carbonates and pyrite. Marine limestones can have significant alkalinity-generating capability, and mines that encounter these limestones generally produce alkaline drainage. Freshwater limestones are common in the upper Allegheny and Monongahela Groups. Mines that encounter these limestones, likewise, routinely produce alkaline drainage. Brackish environments typically lack calcareous minerals, with siderite being the only carbonate present. Overburden of marine and brackish origin often have much greater thicknesses of high sulfur strata than overburden of freshwater origin. Brackish environments therefore cause strata to be high in sulfur and low in calcareous minerals, which often results in AMD. These paleoenvironmental influences on the distribution of carbonates and sulfur (pyrite) will be examined in more detail below.
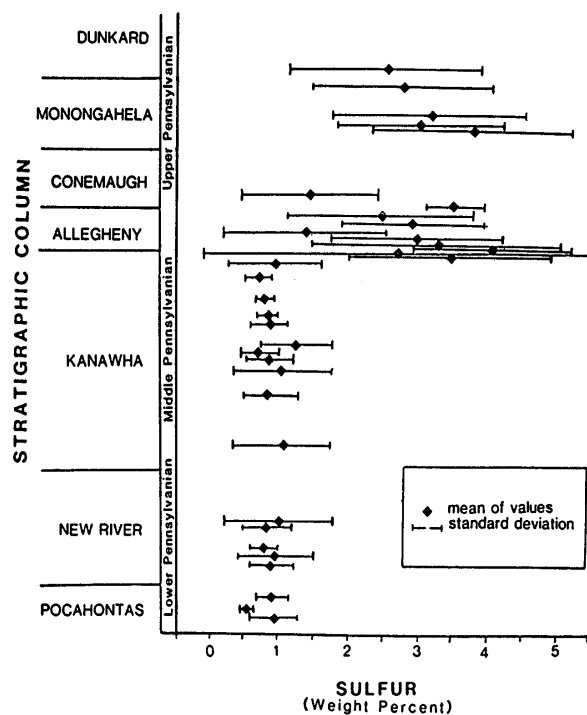
Figure 2.3. Stratigraphic variation of sulfur content for 34 coal beds of the central Appalachians (Cecil et al., 1985).
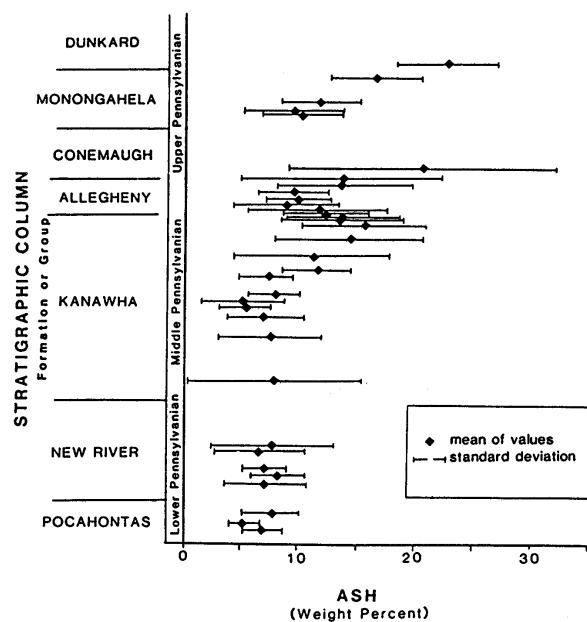
Figure 2.4. Stratigraphic variation of ash content for 34 coal beds of the central Appalachians (Cecil et al., 1985).

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Depositional Environments of Iron Sulfide Minerals

Guber (1972) found that the highest sulfur in rocks overlying the lower Kittanning coal in north-central Pennsylvania was associated with sediments deposited under brackish conditions (Degens et al., 1957; Williams and Keith, 1963). Guber concluded that a brackish environment provides optimum conditions for pyrite formation, with sulfate derived from the brackish water and iron from the nearby terrestrial sources. These sources, coupled with high organic content, provide optimum conditions for pyrite formation: a reducing environment with an ample supply of sulfur and iron.

Relationships between sulfur and depositional environment for coal have also been documented in Texas and Australia. In Texas, Eocene coals deposited in marine and brackish lagoonal environments typically have the highest sulfur (S) concentrations (1.5 to 2%), while alluvial plain coals exhibit the lowest S values (< 1%). Deltaic coals are intermediate in S (1 to 1.5%) (Kaiser 1974, 1978). Permian coals in Australia deposited in lower delta plain facies usually contain > 0.55% S, whereas those associated with braided fluvial facies found further inland, usually on alluvial plains, contain < 0.55% S. Upper delta plain coals, which are located between the lower delta plain and the alluvial plains, are typically of intermediate sulfur (Hunt and Hobday, 1984).

Englund et al. (1986) noted that sulfur in the Pottsville Group Pocahontas No. 3 coal in southern West Virginia and western Virginia was highest at the margins of the deposit (0.9%) and lowest away from the margins (0.4%). Two studies of the Allegheny Group upper Freeport coal in southwestern Pennsylvania show similar trends. Skema et al. (1982) found that coal near the margins contained 4 to 5% sulfur, while coal toward the center of the deposit had 1 to 2% S. Sholes et al. (1979) found that coal near the margins had 5 to 6% S, and 3% or less in the center.

Some of the examples cited above show well-documented relationships between sulfur in coal and paleodepositional environment. However, even where present, the relationships between sulfur and paleodepositional environment are region-specific. For example, the freshwater coals of northern Appalachia are generally higher in sulfur than the marine coals of Texas. Therefore, the use of high and low sulfur as a predictive tool for paleodepositional environment should be used with extreme caution.

Changes in percent sulfur have also been observed at a more local level than discussed above. Studies of the vertical distribution of sulfur in coal have been done for coals around the world, encompassing various geologic periods and coal rank. Increased sulfur at the top and bottom of coal seams appears to be typical. This has also been observed in coal seams of the northern Appalachian basin. Reidenour et al. (1967) found higher sulfur at the top and (sometimes) bottom of Clarion and lower Kittanning coals in Clearfield County that have roof rocks that were deposited in a brackish depositional environment. Appalachian coals interpreted to have been deposited in a freshwater depositional environment also show high sulfur at the top and bottom of the seam (Cheek and Donaldson, 1969; Donaldson et al., 1979; Donaldson et al., 1985b; Hawkins, 1984).

It cannot be assumed that high sulfur in the upper portion of a coal bed, or high sulfur within a coal bed, are evidence of marine influence. Paleoenvironmental interpretations using sulfur alone may not be valid. The

fact that high sulfur is frequently found at the top and bottom of coal seams, regardless of paleoenvironment, is, however, important from a mining standpoint. The top and bottom of a coal seam are the most likely to be left behind on the mine site as pit cleanings because of high sulfur or ash, or as coal that is not recoverable in the mining process. The acid potential from this source must be considered in any evaluation of potential acid-materials problems.

Pyrite and Other Forms of Sulfur

Although pyrite may comprise only a few percent, or even a fraction of a percent, of the overburden rock, its importance to post-mining water quality far outweighs its seemingly minor presence. An overburden that averages just a fraction of a percent sulfur, in the absence of neutralizing rocks, can create significant post-mining water quality or revegetation problems, if not dealt with properly.

Forms of sulfur that occur in coal overburden are sulfide, sulfate and organic. Two iron sulfide minerals occur in the majority of bituminous coal and overburden: pyrite and marcasite. Both have the chemical formula FeS_2 and are 53.4% S, with the remainder being iron, but the two minerals have different crystallinity. For simplicity, we will refer to iron sulfide minerals as pyrite. Excellent explanations of the series of chemical reactions by which AMD is produced from pyrite and other iron sulfide minerals are found in Evangelou (1995), Kleinmann et al. (1981), Lovell (1983), Rose and Cravotta (1998), and Singer and Stumm (1968, 1970). Data and discussion of factors related to pyrite oxidation rates are contained in Braley (1960), Clark (1965), Cravotta (1996), Hammack and Watzlaf (1990), McKibben and Barnes (1986), Moses et al. (1987), Moses and Herman (1991), Nicholson et al. (1988), Rimstidt and Newcomb (1993), Rose and Cravotta (1998), and Watzlaf (1992).

Sulfate minerals are generally secondary weathering products of pyrite oxidation. Nordstrom (1982) shows the sequence by which these minerals can form from pyrite. Many sulfate minerals have been identified in overburden, including those listed in Table 2.1. These minerals (with the exception of barite) are typically very soluble and transient in the humid east. They form during dry periods and then are flushed into the groundwater system during precipitation events. The phases that contain aluminum or iron are essentially stored acidity and will produce acid when dissolved in water. Gypsum, which is not acid forming, is relatively uncommon in Northern Appalachian Basin coal-bearing rocks, whereas other sulfate minerals such as pickeringite and halotrichite occur more commonly. Additional information about these sulfate minerals is found in Cravotta (1994), Lovell (1983), and Rose and Cravotta (1998).

Organic sulfur is sulfur that is tied up in organic molecules. This sulfur can originate by two processes: it can be associated with the original plant material, and it can be complexed with organic molecules during diagenesis. Organic sulfur is not acid forming (Casagrande et al., 1989).

When overburden is analyzed, weight percent total sulfur is generally determined as a means of estimating pyritic sulfur and thus the acid-producing potential of the rock. Because of difficulties with analytical methods, added cost of analysis, and the fact that most sulfur in overburden rock is pyritic, typically only total sulfur is determined. However, when forms of sulfur are determined, organic sulfur estimates are usually determined by difference (Noll et al., 1988); that is, total weight percent sulfur minus pyritic sulfur and

sulfate sulfur. As a result, pyritic or sulfate sulfur are sometimes underestimated during analysis, which causes the organic sulfur fraction to be artificially elevated and apparently acid-forming.

Table 2.1. Secondary sulfate minerals identified in western Pennsylvania mine spoil and overburden. (Minerals from Cravotta (1991, 1994), L. Chubb and R. Smith (PA Geologic Survey, personal communications), and observations by the authors. Mineral chemistries are from Roberts et al. (1990).

<div align="center">

Acid-Producing

</div>

Pickeringite:	$MgAl_2(SO_4)_4 \cdot 22\ H_2O$
Halotrichite:	$Fe^{+2}Al_2(SO_4)_4 \cdot 22\ H_2O$
Alunogen:	$Al_2(SO_4)_3 \cdot 17\ H_2O$
Copiapite:	$Fe^{2+}Fe^{3+}(SO_4)_6(OH)_2 \cdot 20\ H_2O$
Copiapite Group: aluminocopiapite with Mg?	
Coquimbite:	$Fe_2(SO_4)_3 \cdot 9\ H_2O$
Roemerite:	$Fe2+Fe23+(SO_4)_4 \cdot 14\ H2O$
*Jarosite:	$KFe_3^{+3}(SO_4)_2(OH)_6$

<div align="center">

Non-Acid-Producing

</div>

Gypsum:	$Ca(SO_4) \cdot 2\ H_2O$
Epsomite:	$MgSO_4 \cdot 7\ H_2O$
Barite:	$BaSO_4$

[*]Jarosite is less soluble than the other acid-producing sulfate minerals.

Typically, higher sulfur values will be found in marine mudstones than in freshwater mudstones, and carbonaceous rocks will typically contain more pyrite than non-carbonaceous rocks for any given paleoenvironment. A positive linear relationship has been shown between percent organic carbon and percent sulfur for Recent and Pleistocene marine sediments (Goldhaber and Kaplan, 1982; Raiswell and Berner, 1986). The higher the content of organic matter, the darker the rock tends to be. If a mudstone is known to be of marine or brackish origin and it is dark in color, there is a good chance that it is also high in sulfur. Carbonaceous rocks (> 5% organic carbon) may be high in sulfur, at least relative to other rocks, regardless of paleoenvironment. This can be useful in helping to identify potentially high sulfur rocks in the field or in drill cuttings/cores.

Considerable effort has been expended over the years looking at pyrite morphology and attempting to relate this to acid generation. Some of the earliest work is by Caruccio (e.g. 1970); however, numerous other individuals have also examined this issue. Pyrite occurs in several crystal morphologies, ranging from micron-size to millimeter (or larger) crystals and coatings. Pyrite genesis has been suggested as a factor influencing pyrite reactivity. For example, sedimentary pyrite is more reactive than hydrothermal pyrite (Borek, 1994; Hammack et al., 1988). Most pyrite associated with the northern Appalachian Basin is sedimentary in origin.

Morrison (1988) defined nine classes of pyrite morphology, end members being framboidal and euhedral crystal structures. Framboidal pyrite consists of aggregates of very small pyrite crystals (<1 micron in size), while euhedral are generally larger (tens to thousands of microns). Framboidal pyrite therefore has a proportionally larger surface area than euhedral crystals. Classification systems have also been discussed (e.g., Arora et al., 1978; Hawkins, 1984). Caruccio (1970) and Morrison (1988) found a relationship between relative surface area and acid production, with the small particles being more reactive.

Normally, determination of total sulfur will adequately serve as a proxy for acid potential. This is because it includes the sulfur from acid-generating sulfide and sulfate minerals and typically the amount of organic sulfur in overburden rock is insignificant. In locations where gypsum and other sulfur-bearing, non-acid-forming materials are abundant, accurate determination of sulfide sulfur should provide a better prediction of acid potential.

Table 2.2 is included in this section to provide typical and extreme examples of acidity, alkalinity and related water quality parameters in coal mine drainage and nearby well and spring samples. These water samples were compiled from tables contained in Hornberger and Brady (1998) and Brady et al. (1998a) to illustrate mine drainage quality variations in Pennsylvania. Similar variations in mine drainage quality exist in the other states in the Appalachian Basin.

In Pennsylvania coal mine drainage, some of the most extreme concentrations of acidity, iron and sulfate have been found at the Leechburg Mine refuse site in Armstrong County, and at surface mine sites in Centre, Clinton, Clarion and Fayette Counties, as shown in Table 2.2. Acidity concentrations of seeps from Lower Kittanning Coal refuse at the Leechburg site exceed 16,000 mg/L (as $CaCO_3$), while the sulfate concentration of one sample exceeds 18,000 mg/L. At a surface mine on the Clarion Coal in Centre Co., a 35 gpm (132.5 L/min) post-mining discharge had an acidity concentration over 9,700 mg/L with an iron concentration of almost 2,000 mg/L. A water sample from a pit in Fayette County had an acidity concentration greater than 5,900 mg/L and an iron concentration greater than 2,000 mg/L. Schueck et al. (1996) reported on detailed AMD abatement studies conducted at a backfilled surface mine site in Clinton County. A monitoring well there penetrated a pod of buried coal refuse and produced a maximum acidity concentration of 23,900 mg/L and a mean acidity concentration of 21,315 mg/L, based on 13 samples. The maximum concentration of iron was 5,690 mg/L and the maximum sulfate concentration was 25,110 mg/L in the same monitoring well. Toe of spoil seeps at the Clinton County site have acidity and sulfate concentrations greater than 3,500 mg/L and 3,700 mg/L, respectively.

Carbonate Minerals and Their Importance in Mine Drainage Quality

Carbonate minerals form under marine and freshwater environments. Marine limestones, or other calcareous marine rocks, play a significant role in preventing acid drainage in the Appalachian Basin. Marine limestones also significantly contribute to the alkaline water of the Illinois Basin and the Western Interior Coal Province.

Marine rocks in the northern Appalachian Basin occur principally in the lower Allegheny Group and the Glenshaw Formation. The rocks represent open marine to marginal marine (brackish) conditions. The open marine facies are frequently limestone or calcareous shales. Brackish facies often lack

Table 2.2 Water Quality Parameters at Mine Sites in Pennsylvania.

Site Name	County	pH	Alkalinity mg/L	Acidity mg/L	Fe mg/L	Mn mg/L	Al mg/L	SO$_4$ mg/L	Type of Sample
Leechburg	Armstrong	2.4	0.0	16594.0	> 300.0	16.5	> 500.0	11454.0	Seep
Leechburg	Armstrong	2.4	0.0	16718.0	> 300.0	19.3	> 500.0	18328.0	Seep
Leechburg	Armstrong	3.1	0.0	1368.0	> 300.0	13.9	82.3	1896.0	Deep Mine Discharge
Leechburg	Armstrong	2.0	0.0	10383.5	2200.0	3.3	N.D.	14565.2	Diversion Ditch Discharge
Trees Mills	Westmoreland	2.5	0.0	3616.0	190.4	13.5	73.1	1497.8	Deep Mine Discharge
Lawrence	Fayette	2.2	0.0	5938.0	2060.0	73.0	146.0	3600.0	Pit Water
Lawrence	Fayette	2.6	0.0	1840.0	166.0	89.0	85.0	2700.0	Surface Mine Discharge
Blue Lick	Somerset	2.9	0.0	2594.0	> 300.0	35.7	180.0	2701.0	Seep
Stott	Centre	2.7	0.0	9732.0	1959.8	205.3	N.D.	4698.0	Surface Mine Discharge
Stott	Centre	2.8	0.0	4520.0	4880.0	149.5	N.D.	5139.4	Surface Mine Discharge
Orcutt	Jefferson	3.2	0.0	4784.4	6118.4	510.0	N.D.	7500.0	Spoil Piezometer
Orcutt	Jefferson	3.9	0.0	5179.6	2848.0	349.0	N.D.	11120.0	Spoil Piezometer
[†]Fran	Clinton	2.2	0.0	23900.0	5690.0	79.0	2240.0	25110.0	Monitoring Well
[††]Old 40	Clarion	2.2	0.0	10000.0	3200.0	260.0	550.0	14000.0	Monitoring Well
[††]Old 40	Clarion	2.0	0.0	10000.0	44.0	92.0	380.0	10000.0	Monitoring Well
[††]Old 40	Clarion	2.4	0.0	5000.0	700.0	90.0	180.0	3300.0	Spoil Drain
[††]Old 40	Clarion	2.2	0.0	4400.0	1200.0	75.0	250.0	4000.0	Spoil Drain
[††]Old 40	Clarion	3.1	0.0	1100.0	260.0	55.0	26.0	2100.0	Seep
[††]Old 40	Clarion	2.6	0.0	1200.0	1900.0	140.0	58.0	1900.0	Seep
Zacherl	Clarion	2.3	0.0	9870.0	2860.0	136.6	583.0	7600.0	Toe-of-spoil Discharge
Waynesburg	Greene	7.8	379.0	0.0	0.12	0.04	N.D.	165.0	Deep Mine Discharge
Redstone	Fayette	7.4	626.0	0.0	1.65	1.05	< 0.5	1440.0	Spring
Redstone	Westmoreland	8.1	338.0	0.0	0.66	0.33	0.5	181.0	Spring
Blue Lick	Somerset	6.8	166.0	0.0	2.86	0.52	< 0.5	220.0	Pit Sump
Blue Lick	Somerset	7.9	276.0	0.0	< 0.3	< 0.05	< 0.5	436.0	Spring
Blue Lick	Somerset	7.7	138.0	0.0	1.12	0.86	< 0.5	494.0	Stream
Blue Lick	Somerset	6.9	226.0	0.0	0.81	0.83	< 0.5	1102.0	Stream
Vanport	Lawrence	7.5	324.0	< 2	2.10	0.07	N.D.	40.0	Well
Wadesville	Schuylkill	6.7	414.0	0.0	3.61	3.37	< 0.5	1038.0	Deep Mine Pumped Discharge
Wadesville	Schuylkill	6.9	370.0	0.0	1.95	3.42	< 0.5	884.4	Deep Mine Pumped Discharge
Valentine 1	Centre	7.5	226.0	0.0	< 0.01	< 0.01	< 0.135	145.0	Pit Water Outfall
Valentine 2	Centre	7.5	146.0	0.0	0.29	< 0.01	0.4	105.0	Pumped Pit Water
Valentine 3	Centre	7.6	102.0	0.0	2.07	0.05	3.9	44.0	Raw Pit Water
Valentine 4	Centre	8.0	164.0	0.0	0.22	< 0.01	0.59	68.00	Deep Mine Discharge
Ledger	Chester	8.0	284.0	0.0	0.04	0.01	< 0.135	41.0	Pit Sump
Loyalhanna	Westmoreland	7.7	152.0	0.0	< 0.3	< 0.05	< 0.5	143.2	Pit Water

alkalinity-generating calcareous minerals, although siderite ($FeCO_3$) can be abundant. Marine rocks can also be an important component of coal overburden in southern Appalachian (Pottsville) rocks [Alabama -

Horsey (1981), Pody (1987), and Demko and Gastaldo (1996); Tennessee - Dorsey and Kopp (1985); Kentucky - Chestnut (1981); and southern West Virginia - Martino (1994, 1996)].

Freshwater calcareous rocks, including lacustrine limestones, occur in the upper portion of the Allegheny Group and throughout the Conemaugh, Monongahela and Dunkard Groups of the northern Appalachian Basin. The extensive lateral distribution of some of these limestones was discussed in the stratigraphy section of Brady (1998b). These limestones, and other calcareous rocks, are responsible for the alkaline nature of many of the mining-associated discharges within these stratigraphic horizons. Freshwater calcareous rocks also occur in the Conemaugh Group, and are important when they occur above the upper Freeport coal.

In addition to freshwater limestones, the upper Allegheny Group frequently contains an abundance of calcareous claystones, mudstones and siltstones. Much of this interval is distinctly calcareous (>10% $CaCO_3$), but only small portions are limestone (> 50% $CaCO_3$). Additional information on stratigraphic changes in this interval is included in Chapter 3 and in Brady et al. (1988, 1998).

The most common carbonate minerals found in coal mine overburden are listed in Table 2.3. Carbonate minerals are often not "pure" end members, but form solid solution series with cation substitution, and vary with respect to their capacity for acid neutralization. Calcite is more soluble than dolomite although the overall dissolution is similar to that shown for calcite (Geidel, 1982). Both calcite and dolomite will neutralize acid, and potentially inhibit pyrite oxidation. Siderite is less soluble than calcite and dolomite, and does not contribute alkalinity.

Table 2.3. Common carbonate minerals in mine overburden, listed in descending order of their capability to neutralize acid.

Mineral	Chemistry
Calcite	$CaCO_3$
Dolomite	$CaMg(CO_3)_2$
Ankerite	$Ca(Fe,Mg)(CO_3)_2$
Mn-Siderite	$(Fe, Mn)CO_3$
Siderite	$FeCO_3$

Freeze and Cherry (1979) state that the solubility of carbonates is dependent on the partial pressure of carbon dioxide (pCO_2), and show a range of values that are relevant for natural groundwater. They show solubility for calcite in water at 25° C, pH 7, 1 bar total pressure, and a pCO_2 of 10^{-3} bar is 100 mg/L, while the solubility at a pCO_2 of 10^{-1} bar is 500 mg/L, using data from Seidell (1958). However, these relationships may be more complex than they initially appear. According to Rose (personal communication, 1997), the range of bicarbonate concentrations for calcite dissolution in pure water ranges from 83 mg/L at a pCO_2 of 10^{-3} to 370 mg/L at a pCO_2 of 10^{-1}, using the methods (i.e. Case 4) described in Garrels and Christ (1965). Additional discussion of carbon dioxide partial pressures is found in Hornberger and Brady (1998).

Since the alkalinity production process has a dramatically different set of controls, the resultant maximum alkalinity concentrations are typically one or two orders of magnitude less than the maximum acidity concentrations found in mine environments. Examples of relatively high alkalinity concentration in mine drainage, groundwater and surface water associated with surface and underground mines in Pennsylvania bituminous and anthracite coals are shown in Table 2-2. The highest natural alkalinity concentration found in PA DEP mining permit file data (and reported in Table 2.2) is 626 mg/L in a spring located near the cropline of the Redstone Coal in Fayette County. Thick sequences of carbonate strata, including the Redstone Limestone and the Fishpot Limestone, underlie and overlie the Redstone Coal. A curiosity is that some of the highest alkalinity concentrations shown in Table 2.2 are accompanied by equivalent or greater sulfate concentrations, so that bicarbonate may not be the dominant anion in some of these highly alkaline groundwaters.

Carbonate minerals play an extremely important role in determining post-mining water chemistry. They neutralize acidic water created by pyrite oxidation, and there is evidence that they also inhibit pyrite oxidation (Hornberger et al., 1981; Perry and Brady, 1995; Williams et al., 1982). Brady et al. (1994) determined that the presence of as little as 1% to 3% carbonate (on a mass weighted basis) on a mine site can determine whether that mine produces alkaline or acid water. Although pyrite is clearly necessary to form AMD, the relationship between the amount of pyrite present and water quality parameters (e.g., acidity) is only evident where carbonates were absent.

Neutralization potential, a measure primarily of the carbonate content of the overburden, relates positively to the alkalinity of post-mining water. A knowledge of the distribution, amount, and type of carbonates present on a mine site is extremely important in predicting the potential for post-mining problems and in designing prevention plans.

Lithologic and Stratigraphic Factors Affecting Mine Drainage Quality

Lithology is controlled by geologic factors such as paleoclimate and paleodepositional environment. Sandstones are deposited in high-energy environments, whereas shales and siltstone are deposited in quieter environments.

Published studies of Allegheny Group mines with abundant sandstone overburden attest to a problem with water quality. For example, diPretoro (1986) found that all but one mine site within his study area (northern WV) containing greater than 63% sandstone produced net acidic drainage. Sixty-seven percent of sites with less than 30% sandstone had net alkalinity (Figure 2-7). An examination of 41 mine sites in western Pennsylvania by the Department of Environmental Protection (DEP) and the Office of Surface Mining (OSM) also shows relationships between % sandstone and water quality. They found a similar relationship between the % sandstone and acid production for the Allegheny Group. However, in contrast, the sandstones of the Monongahela and Dunkard Groups are typically calcareous (cements) and were found to usually produce alkaline drainage. Both studies show that when there is a low percentage of sandstone, the mine drainage is generally alkaline (Figures 2.5 and 2.6). Although there are certain rules of thumb regarding the relationship between sandstone and mine drainage quality, site-specific information is necessary to accurately predict water quality from a particular mine site.

Brady et al. (1988) looked at the overburden above the upper Kittanning coal in the Stony Fork watershed in Fayette Co., PA. Mine sites with predominantly channel sandstone overburden produced acidic drainage. The sandstone lacked calcareous minerals or cements. Overburden in areas away from the sandstone channels contained calcareous shales and muddy limestone, and mining in these areas resulted in alkaline drainage.
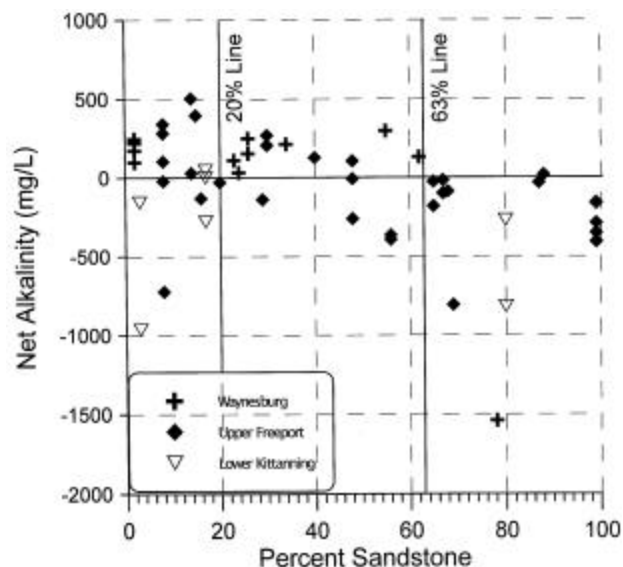
Figure 2.5. Net alkalinity as a function of percent sandstone for surface mines that encountered the Waynesburg, upper Freeport and lower Kittanning coals. Sites are in northern Preston County, WV. Most sites with greater than 63% sandstone are acidic, and most sites with less than 20% sandstone are alkaline (diPretoro, 1986).
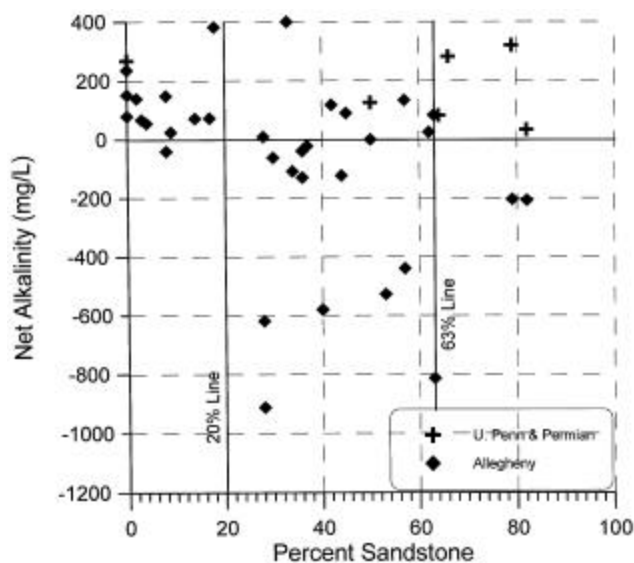
Figure 2.6. Net alkalinity as a function of % sandstone for 41 surface mines in western PA. Mines in the Conemaugh, Monongahela and Dunkard Groups are all alkaline, regardless of % sandstone. Most sites with less than 20% sandstone are alkaline.

Sandstone is typically low in sulfur, even when acid-producing. Channel sands can contain eroded material, including ripped up mats of peat (present day "coal spars") and even fossilized, and often coalified, logs. Individually these coal inclusions can be high in sulfur, but during typical overburden sampling, the inert quartz and other minerals that compose the sandstone dilutes this high sulfur. Thus, such sandstones may contain acid-forming material (coal spars), and yet yield samples that have low overall sulfur concentrations. Occasionally there are pyrite-rich sandstones. Some of these are black and high in organic carbon, while others are light in color, but high in sulfur. The light- colored high-sulfur sandstones seem to occur just above coal or organic-rich shale. Additional discussion is found in Williams et al. (1982) and Brady et al. (1998b).

Frequently, the highest sulfur strata are high-ash coals and other organic-rich rocks. Typically, these organic-rich rocks are immediately above, below or within a coal seam (e.g., a parting) and the shale above the coal is also high in sulfur (Guber, 1972).

As mentioned earlier, calcareous carbonates are more important than pyrite in controlling water quality from surface mines. The presence of only 1 to 3% carbonate minerals can influence whether acidic or alkaline drainage is produced (Brady et al., 1994; Perry and Brady, 1995). The amount of sulfur present is not directly related to acid production except in the absence of calcareous strata.

Carbonate minerals form under both marine and fresh water environments. Marine units contribute significantly to alkaline water in the Illinois Basin and the Western Interior Coal Province, but are also significant in the Appalachian Basin, such as within the lower Allegheny Group. A good example of this is the Vanport horizon, which occurs above the Clarion Coal. In Butler County, Pennsylvania, where the Vanport limestone is thick and in close proximity to the coal, mining of the Clarion coal will result in alkaline drainage. Where the Vanport-equivalent facies are brackish shale and the shale lacks calcareous minerals, such as in Clearfield County, Pennsylvania, the mine water is typically acidic. It should also be noted that in addition to limestones, other marine sediments are often calcareous.

Freshwater calcareous rocks, including lacustrine limestones, are also important. For example, the Monongahela and Dunkard groups have numerous thick, laterally persistent, lacustrine limestones. However, in general, freshwater limestones often contain relatively high concentrations of clay and silt, and can be thin and discontinuous.

State Practices

Alabama, Illinois and Indiana require drill logs with narrative descriptions for any holes drilled on the permit property. Geologic cross sections to assess lateral continuity of the strata and a structure contour map at the bottom of the coalbed are also required using all the available drill hole information. Depositional analysis is not required but permit reviewers are aware of acid-producing units associated with the various coal seams being mined within their state.

Kentucky requires only that the data presented be adequate to describe each aquifer and hydrogeologic regime. A description of the depositional environment is rarely required.

Maryland and Tennessee require a geologic cross section covering the permit area and a descriptive log of any available drill holes. They do not use depositional environment information during the AMD predictive process.

Ohio requires a general description of the geology within the proposed permit area and adjacent areas down to and including the first stratum below the lowest coal seam to be mined or any aquifer below the lowest coal seam that may be adversely affected by mining. The description must include information on the areal and structural geology and any other geologic parameters that may influence required reclamation. A description on how the areal and structural geology may affect the occurrence, availability, movement, quantity, and quality of potentially affected surface water and ground water is also required. Test holes containing lithologic descriptions are required. A description of the depositional environment is not required, but is accepted and reviewed if submitted.

Pennsylvania requires that all drill hole information on a property include narrative logs, and that they be used to build geologic cross sections to assess lateral continuity of the strata, and to construct structure contour map of the bottom of the coalbed. Pennsylvania does not require any depositional analysis by the permit applicants, but does use depositional information internally during review.

Virginia requires a geologic cross section of the permit area from core holes or measured sections of highwalls to assess lateral continuity of the strata. Permit reviewers do not use depositional environment information but are aware of acid-producing units associated with the coalbeds mined within the state.

West Virginia requires drill logs with narrative descriptions for any holes drilled and geologic cross sections to assess lateral continuity of the strata. West Virginia does not use depositional environment information during the AMD predictive process.

State practices for the evaluation of site geology and depositional environment are outlined in Table 2.4.

Effects of Surface Weathering and Glaciation on Mine Drainage Quality

This section will deal with a much more recent geologic process, the physical and chemical weathering of rock, which has occurred within the past million or so years. The significance of this influence on the distribution of carbonate and sulfide minerals (pyrite) can be as great as that which occurred in the more distant past. Weathering results in the near-surface removal of carbonates and sulfide minerals; carbonates by dissolution and sulfides by oxidation. This zone is usually recognizable by the yellow-red hues (indicative of oxidized iron) of the rocks. Generally, in the unglaciated portions of the Appalachian Plateau, the intensely weathered zone extends to 15 to 60 ft (6 to 20 m) below the surface.

Chemical weathering of bedrock is enhanced by physical factors such as stress-relief fracturing on hill slopes and bedding-plane separations due to unloading. Clark and Ciolkosz (1988) have also suggested that periglacial conditions during the Pleistocene contributed to the shattering of near-surface rock, which accelerates weathering by increasing surface area. All of these processes acting together increase the permeability of the weathered zone. The ground water associated with the weathered zone

Table 2.4 State Requirements for Site Geology and Depositional Environment Information

STATE	SITE GEOLOGY	DEPOSITIONAL ENVIRONMENT
AL, IL, IN	Drill logs with narrative descriptions required for any holes drilled on the permit property. Geologic cross sections used to assess lateral continuity of the strata. Requires structural contour map for the bottom of the coalbed using all the available drill hole information.	Does not require any depositional analysis by applicants. Reviewers are familiar with the depositional environment of the coalfields and keep that information in mind during the review process.
KY	The data must be adequate to describe each aquifer and hydrogeologic regime.	A description of the depositional environment is rarely required.
MD	Geologic cross section covering permit area and descriptive log of overburden analysis required.	Does not use any depositional environment information during the predictive process.
OH	Geologic description of the permit area and lithologic description of all test holes are required, along with a discussion of how the surface and ground water might be affected.	A description of the depositional environment is not required, but is accepted and reviewed if submitted.
PA	All drill hole information must include narrative logs. Information is used to build geologic cross sections to assess lateral continuity of the strata and construct a structure contour map of the bottom of the coalbed.	Does not require any depositional analysis by the permit applicants. Uses depositional environment information internally during review, mainly as a regional indicator of AMD potential.
TN	Requires a geologic cross section of the permit area and a descriptive log of any available drill holes.	Does not use any depositional environment information during the predictive process.
VA	Requires a geologic cross section of the permit area from core holes or measured sections of highwalls to assess lateral continuity of the strata.	Reviewers do not formally use depositional environment information, but are aware of acid-producing units associated with the coalbeds.
WV	Requires drill logs with narrative descriptions for any holes drilled and geologic cross sections to assess lateral continuity of the strata.	Does not use any depositional environment information during the predictive process.

is dilute, in terms of dissolved solids, because readily soluble products have been removed by chemical weathering (Brady, 1998b).

Chemical weathering is also influenced by lithology. Coarser, more permeable lithologies may allow oxidation to extend to a greater depth. Kirkaldie (1991) measured the depth of the highly weathered zone. He noted that the maximum thickness of highly weathered rock was 28.9 ft (8.8 m) in sandstone, and only 11 ft (3.3 m) in shale. His observations were based on the physical appearances during drilling and may not directly correlate with chemical weathering. This weathered-rock zone exists throughout the Appalachian Plateau. In spite of this, it has been little studied. Smith and his colleagues (Grube et al., 1972; Smith et al., 1974; and Singh et al., 1982) investigated the effects of weathering on the Mahoning sandstone in northern West Virginia, and noted a "pyrite-free weathered zone approximating 20 feet (6 m) of depth below the

land surface...". Singh et al. (1982), in addition to noting the pyrite-free zone, also noted a loss of "alkaline earth" elements within 20 ft (6 m). Loss of alkaline earth elements (calcium and magnesium) is best explained by a loss of calcareous minerals (calcite and dolomite). Brady et al. (1988; 1996) and Hawkins et al. (1996) all noted similar weathering depths in Appalachian strata.

It is hard to provide rules of thumb for the depth of leaching of carbonates and oxidation of pyrite because these minerals can only occur where they were originally present (before weathering). If no pyrite was ever present within a stratigraphic horizon, its absence is not due to weathering, but to the fact that it was never there in the first place. The same is true for calcareous strata. Brady et al. (1998) concluded that rarely do NPs greater than 3% $CaCO_3$ or S greater than ~0.5% occur within 20 ft (6 m) of the surface in Pennsylvania. A good example of this effect is the Blue Lick coal. Where the coal is under shallow cover, it has less than 0.7% S; however, where the coal occurs under about 60 ft (20 m) of cover, the coal averages over 2% S.

Brady (1998) examined shallow groundwater chemistry from sites in the northern and southern Appalachians. Springs, which would represent water associated with the shallow weathered zone, had low concentrations of ions regardless of geographic location, indicating the widespread presence of a shallow weathered zone.

An accurate knowledge of the extent (depth) of the weathered zone is important from an overburden-sampling standpoint. Overburden sampling should adequately represent the weathered zone and unweathered bedrock. This will entail drilling overburden test holes at maximum cover to be mined and at lesser cover. Drilling only maximum cover or only lower cover overburden holes will probably not adequately define the overburden chemistry of the entire mine.

An understanding of the effects of weathering on the distribution of pyrite, sulfate salts, and carbonates is important in accurately defining their distribution within unmined overburden, designing a mine plan to prevent post-mining problems, and accurately predicting post-mining water quality. An understanding of the weathering profile is just as important as understanding the lateral and vertical distribution of strata and their pyrite and carbonate content, as shown in Figure 2.7.

As with bedrock, the weathering of tills and other glacial sediments results in a change in their effect on water quality. At least 8 tills have been identified in Pennsylvania (White et al., 1969) and in northeastern Ohio (White, 1982). The bedrock in the Lake Erie basin, which was the source for the glacial sediments, consists of a large amount of limestone and dolomite. Therefore, the sediment contained in the glaciers was high in carbonate minerals when it entered Pennsylvania and Ohio.

In the Illinois Basin, most of the coal field is within the glaciated region and the bulk of the tills have carbonate contents greater than 10% in the clay fraction, and up to 64% in the coarse sand fraction (Fleeger, 1980). The presence of glacial deposits is thus more significant for the prevention of AMD in Illinois than in Pennsylvania. Although coal and associated strata in the Illinois Basin are sometimes high in sulfur (Maksimovic and Mowrey, 1993), acid streams (pH< 6) were only identified south of the glacial border (Hoffman and Wetzel, 1993, 1995).
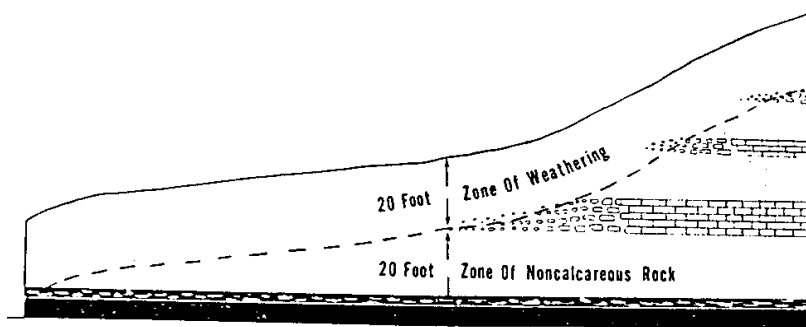
Figure 2.7. Schematic cross-section showing relative positions of high-sulfur strata and calcareous strata (brick pattern). In this example, 40 ft (12 m) or more cover must be mined in order to encounter the alkaline material.

Weathering produces a vertical mineralogical gradation within tills (Leighton and MacClintock, 1930, 1962). Sulfide concentrations are typically negligible, even in unweathered tills, but weathering can remove carbonate minerals that would otherwise be present in significant quantities. In general, the upper portion of the till has lost sulfides and carbonates, while the lower portions retain them. Because a number of factors control the depth of leaching (and other weathering characteristics), the same till may be leached to different depths in different locations. As a rule of thumb, older tills are leached of carbonates to a greater depth than younger tills.

In glaciated areas of Pennsylvania, post-mining water quality is frequently good, presumably due to the carbonate content of glacial sediments. However, not all mines in glacial overburden have alkaline drainage. Older tills, especially in their outcrop area, are low in carbonate and may not provide much neutralization.

In summary, glacial overburden can be beneficial in preventing AMD if it is calcareous. Because of the small grain size, unlithified nature, and the source of carbonates in glacial sediments, the NP determinations of glacial overburden probably more accurately reflect the ability of the glacial sediments to prevent and neutralize acidity than is sometimes the case with bedrock overburden. Site specific data are required to determine the NP of glacial sediments because of their variability in texture and composition due to dilution and weathering.

CONCURRENT RECLAMATION AND SPECIAL HANDLING PRACTICES

Experience indicates that AMD production is strongly influenced by the length of time between mining and reclamation. In theory, leaving a site open accelerates oxidation of the pyritic minerals and subsequently increases acid production. Concurrent reclamation and burial of acidic material can inhibit oxidation and ameliorate AMD formation. The importance of concurrent reclamation is generally accepted.

Special handling of acidic spoil materials, although not well documented in terms of success, is often used to prevent the formation of AMD. ABA data, either as an NP value for a unit or as the percent sulfur

contained, is generally used to determine the need and scope of special material handling to prevent or mitigate AMD.

There are currently two commonly recognized methods of special handling. The first, and most common, is to place the acid-producing material above the highest projected ground water table level: the *high and dry* scenario. This should reduce the formation and mobilization of acid and metals. The second is to place acid-producing material so that it will always be below the water table: the *dark and deep* scenario. The *dark and deep* method controls AMD production by preventing contact between atmospheric oxygen and the pyritic material. In theory, and in laboratory studies, placing the pyrite below the water table should be superior to the *high and dry* placement method. However, maintaining a permanent water table over acid-forming materials can be difficult given the hydrologic conditions at many Appalachian surface mines.

An active surface mine in Clearfield County, Pennsylvania provides an example of how predicting the post-mining water table level can be a problem. The special handling plan at this mine placed acidic material 10 feet above the pit floor to keep it *high and dry* (Hawkins, 1996). However, less than a year after backfilling, ground water levels were at times at least 14 feet above the pit floor, putting the acid-forming materials in the zone of water table fluctuation. While studies indicate that placing acid-forming materials in a fluctuating ground water zone is highly undesirable, Leach and Caruccio (1991) concluded that a reduction in acid load resulted from any time pyrite spent under water. Subaqueous burial of acidic material was advocated by Cederstrom (1971) and is coming back into favor, due to research supported by the Canadian MEND program and work performed by the U.S. Bureau of Mines (USBM) (Watzlaf and Hammack, 1989; Watzlaf, 1992) and others (Leach and Caruccio, 1991). A review of the many studies on special handling of acidic material can be found in Robins and Associates (1982).

Alkaline addition is commonly used to raise the neutralization potential of the mine spoil to prevent or abate the formation of AMD. Limestone and dolostone are the most frequently used materials because of their widespread availability and relatively low cost (Hawkins, 1995). Other materials, such as hydrated lime and alkaline coal combustion wastes, are also used where they are cost effective due to their availability. ABA data, usually the overall NNP value, is generally used to determine the need for alkaline addition and the amount of alkaline material necessary to mitigate AMD formation.

Determining the quantity and placement requirements for the alkaline material are two difficulties associated with alkaline addition. The most common alkaline placement practices include liming the pit floor, blending alkaline materials into the backfill with overburden of lower neutralization potential, and capping the backfill with alkaline material below the soil horizon. Brady and others (1990) conclude that alkaline addition "to prevent AMD from surface coal mines may be effective provided that the alkaline-addition rates are sufficient (to offset negative NNP) and the overburden has relatively low-sulfur content." They also recommend incorporation of the alkaline material concurrently with mining and backfilling, and note that while neutral or alkaline discharges may result, metals concentrations may not be reduced.

State Practices

Current State requirements regarding concurrent reclamation, special handling and alkaline addition are summarized below and in Table 2.5. Given time, some of these requirements may change so if you are with a mining company, you should check to see that the statements are still valid.

Alabama encourages concurrent reclamation, but relies on laws governing and limiting the amount of exposed highwall, spoil, and ungraded acres. Overburden units with an NP deficiency of 5 tons $CaCO_3$ per thousand tons of material or greater are considered acid-producing. Alabama's special handling provision allows only for *high and dry* placement of acidic material. Applicants have the option of overcoming the acidity potential of those units using either alkaline addition or special handling. With respect to alkaline addition, Alabama generally assumes that alkaline drainage will result from overburden with an NNP of 5 tons or greater of excess $CaCO_3$ per thousand tons of material. Overburden with an NNP below -5 tons $CaCO_3$ per thousand tons of material is considered acid-forming, and the applicant is then required to develop a plan to overcome the inherent acidity through any or all of the tools available to them (special handling, alkaline addition, mining methods). Sites with overburden NNP values between -5 and 5 tons $CaCO_3$ per thousand tons of material are considered candidates for alkaline addition if the NNP can be altered to ensure an excess of alkalinity.

Illinois requires concurrent reclamation and regulates the number of open pits, the amount of exposed spoil, and grading activities. Timely burial of high sulfur material is viewed as very important in reducing the risk of AMD. AMD treatment is rarely addressed in permit applications except for the possibility of short term treatment of sedimentation ponds. AMD problems are rare, except in instances where approved reclamation plans are not implemented. Secondary recovery operations (carbon recovery or re-mining) has the greatest potential for exposing large amounts of acid-generating material. The most common special handling methods are blending the acidic material with available alkaline material and adequate cover. *Dark and deep* is the preferred cover option. Alkaline addition is generally limited to surface application of graded spoil in coal refuse disposal areas and locations where acidic material inadvertently ends up on the final graded surface and cannot be adequately covered.

Indiana requires concurrent reclamation and regulates the number of open pits, the amount of exposed spoil, and grading activities. Timely burial of high sulfur material is viewed as very important in reducing the risk of AMD. AMD problems are rare, except in instances where approved reclamation plans are not implemented, and so are rarely addressed in permit applications. Sediment control structures are sometimes used temporarily to meet effluent limits. To insure that water quality problems do not occur, any overburden unit with a calcium carbonate equivalent deficiency of 5 tons $CaCO_3$ per thousand tons of material or greater or a pH less than 4 must be addressed by special handling. Generally, this ranges from less than 5% up to 30% of the overburden. Most commonly, the special handling method used is to blend acidic material with available alkaline material, and then cover. *Dark and deep* is the preferred cover option. Alkaline addition is generally limited to surface application of graded spoil in coal refuse disposal areas and locations where acidic material inadvertently ends up on the final graded surface and cannot be adequately covered.

In practice, Kentucky permit applications do not usually propose special measures to treat or avoid AMD since the applications almost always predict no significant AMD. If problems arise after mining has commenced, treatment is proposed in revisions to the permit. In cases where a permit would otherwise be denied, special handling can change the determination. Typically, special handling includes lime addition, selective spoil handling, and accelerated reclamation.

In Maryland, overburden units with a total sulfur content of 0.3% or greater are considered potentially acid-producing and candidates for special handling. *High and dry* is the preferred method. Material must be placed at least 4 ft above the coalbed floor in backfill that is expected to remain dry, or 10 to 15 ft above the floor if the backfill is expected to hold water.

Ohio requires contemporaneous reclamation, unless a variance is granted (for special circumstances only). Limited amounts of acid-forming and toxic-forming materials are usually handled by all or most of the following practices: they must be kept away from the final highwall, buried above the pit floor and above the predicted reestablished water table elevation (high and dry), away from natural or reconstructed drainage courses (to prevent exposure by erosion) and surrounded by at least four feet of non-toxic material. For larger amounts of toxic-forming material, a more intense waste disposal plan (involving discreet calculations for either neutralization or sealing) must be submitted. This usually is triggered when coal refuse is brought to the site for disposal. Alkaline addition is used in a limited number of cases if other mechanisms for preventing AMD are not practical or are not expected to be successful. Drainage controls, positive drainage, and impermeable bases are required for coal stockpiles.

Pennsylvania requires concurrent reclamation and views quick burial of high sulfur material as very important in reducing the risk of AMD. Overburden units with a total sulfur content of 0.5% or greater are considered acid-producing and candidates for special handling if the units are laterally consistent and recognizable. Miners must be able to handle them with the tools that are available. Special handing (preference for *high and dry* or *dark and deep* was not identified) is generally not requested for any individual rock units if the overburden analyses results in an overall high NNP. If NNP is low, special handling must be combined with alkaline addition.

Tennessee requires concurrent reclamation of every permit applicant. No threshold numbers for identifying acid producing units were cited, but *high and dry* placement in compacted lifts was indicated as the preferred special handling method.

Virginia mostly relies on laws limiting the amount of exposed highwall to drive reclamation, but reserves the right to set specific limits on the time that acidic material can be exposed to the weather. Any overburden units with greater than a 5 ton $CaCO_3$ deficiency per thousand tons of material are required to be addressed with special handling. The most common special handling method identified in Virginia was the blending of acidic material with that of higher NP. *High and dry* handling is also allowed with at least 4 ft between the acid material and the floor and compaction of the enclosing material.

West Virginia has contemporaneous reclamation standards that must be met. Threshold standards for identifying acid units were not cited, but special handling provisions were acknowledged as common and important permit requirements. Applicants must have a storage plan for any acidic

Table 2.5. State Requirements for Concurrent Reclamation, Special Handling and Alkaline Addition.

STATE	CONCURRENT RECLAMATION (CR)	SPECIAL HANDLING AND ALKALINE ADDITION (AA)
AL	CR is encouraged, limiting the amount of exposed highwall, spoil, and ungraded area.	Special handling provisions allow only for *high and dry* placement of overburden with NP deficiency of at least 5 tons $CaCO_3$ per 1000 tons of material. If NNP is <-5, overburden is considered acid-producing and a plan is required to overcome the inherent acidity. If the NNP value is between -5 and 5, the overburden is a candidate for AA.
IL	CR is required.	AMD is rare when approved reclamation plans are implemented. Secondary recovery can cause AMD. *Dark and deep* placement preferred. AA applications are limited.
IN	CR is required.	AMD is rare. Overburden with NP deficiency of at least 5 tons $CaCO_3$ per 1000 tons of material or a pH of 4 requires special handling. *Dark and deep* placement is preferred, along with blending of alkaline and acidic material.
KY	See entry under Special Handling.	Significant AMD problems are rarely predicted before mining. For post-mining AMD problems, permit revisions are used. For otherwise deniable permits, the inclusion of special handling provisions can change the determination. AA should result in an overburden NNP with excess alkalinity.
MD	No CR standards or general requirements.	Overburden with total S$\geq$ 0.3% considered for special handling. *High and dry* is preferred: at least 4 ft above the pit floor if backfill is expected to be dry, or 10-15 ft above the floor if backfill is expected to hold water. AA should result in an overburden NNP with excess alkalinity.
OH	CR required unless variance is granted.	*High and dry* generally required, plus must be away from watercourses and surrounded by at least 4 feet of non-toxic material; more intense waste disposal plan required for coal refuse. AA used when necessary.
PA	CR is required. Quick burial of high S material is viewed as very important.	Overburden with a total S $\geq$ 0.5% considered for special handling if the units are laterally consistent and recognizable. If NNP is low, special handling must be combined with AA, producing an overburden NNP with excess alkalinity.
TN	CR is required.	No threshold numbers for identifying acid producing units. *High and dry* placement in compacted lifts is preferred. AA plans that will result in an overburden NNP with excess alkalinity accepted.
VA	VA reserves right to set limits on the time that acidic material can be exposed to the weather.	Any overburden unit with greater than a 5 ton $CaCO_3$ deficiency per thousand tons of material must be addressed with special handling, most commonly blending of acidic material with that of higher NP. AA that will result in an overburden NNP with excess alkalinity accepted. *High and dry* is also allowed with at least 4 ft between the acid material and the floor, and compaction of the enclosing material.
WV	CR is required; storage plan for any acidic material can't exceed 45 days.	Special handling provisions are common. High and dry isolation is the accepted method. WV will assist in developing a training program to facilitate identification of key overburden units and proper mining techniques. AA plans should result in an overburden NNP with excess alkalinity.

material (that may include covers or other special conditions to reduce exposure to the weather), which cannot exceed 45 days. *High and dry* isolation of acidic material in the backfill is the accepted special handling method. Permit reviewers will meet with applicants and inspectors to assure that special handling

plans are feasible and can be monitored, and will assist in developing a training program for workers to facilitate identification of key overburden units and proper mining techniques.

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CHAPTER 3: HYDROLOGY OF THE APPALACHIAN BITUMINOUS COAL BASIN

by

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INTRODUCTION

The bituminous coal fields of the Appalachian Coal Basin have certain pervasive features that influence hydrology, including discontinuous flat-lying sedimentary rocks of contrasting permeability, incised topography, a shallow weathered rock zone, dendritic stream patterns, and similar patterns of rock fracturing. These features allow for the development of regionally valid conceptual groundwater flow models. Also, the limits of the basin align closely with the margins of the Appalachian Plateaus physiographic province. The province's physical geography permits certain regional generalizations regarding groundwater/surface water interactions. Therefore, local and site-specific hydrologic studies often have basin-wide applicability.

While certain general concepts have been developed, the basin's groundwater hydrology is very complex. This complexity is related to the area's inter-fingering lithologies and to the prevalence of secondary permeability features. On the Plateaus, discrete fractures, partings, or fracture zones can significantly influence groundwater flow within small areas, such as individual coal mining sites. Due to these complicating elements, regional conceptual models, while useful, should not substitute for site-specific hydrologic studies. The following narrative outlines some of the significant groundwater studies within the basin, briefly describes surface water drainage, outlines hydrologic impacts from mining, and emphasizes important basin-wide hydrologic characteristics.

Geologic Setting

The Appalachian Coal Basin follows the spine of the Appalachian Mountains through nine states from Pennsylvania to Alabama, covering an area of approximately 72,000 square miles. It is 175 miles wide at the widest part in Pennsylvania and Ohio, and 35 miles wide at the narrowest part in Tennessee (Figure 3.1). The rocks are predominately flat-lying, consisting of sandstone, conglomerate, siltstone, shale, claystone, limestone and coal (Miller et al., 1968). The bituminous coal seams are contained in relatively flat-lying Pennsylvanian and Permian age clastic strata. The outline of the Pennsylvanian system is approximately co-extensive with the border of the Appalachian Plateau physiographic province. Rocks of Permian age and younger Pennsylvanian rocks of the Monongahela, Conemaugh and Allegheny Groups are confined to an elliptical area in Pennsylvania, Ohio, West Virginia, and Maryland. The oldest Pennsylvania rocks, the Pottsville Group, extend from western Pennsylvania to northern Alabama. Glacial outwash deposits of Pleistocene age occur at the surface in the valleys of northern Pennsylvania, and along the Allegheny and Ohio Rivers.
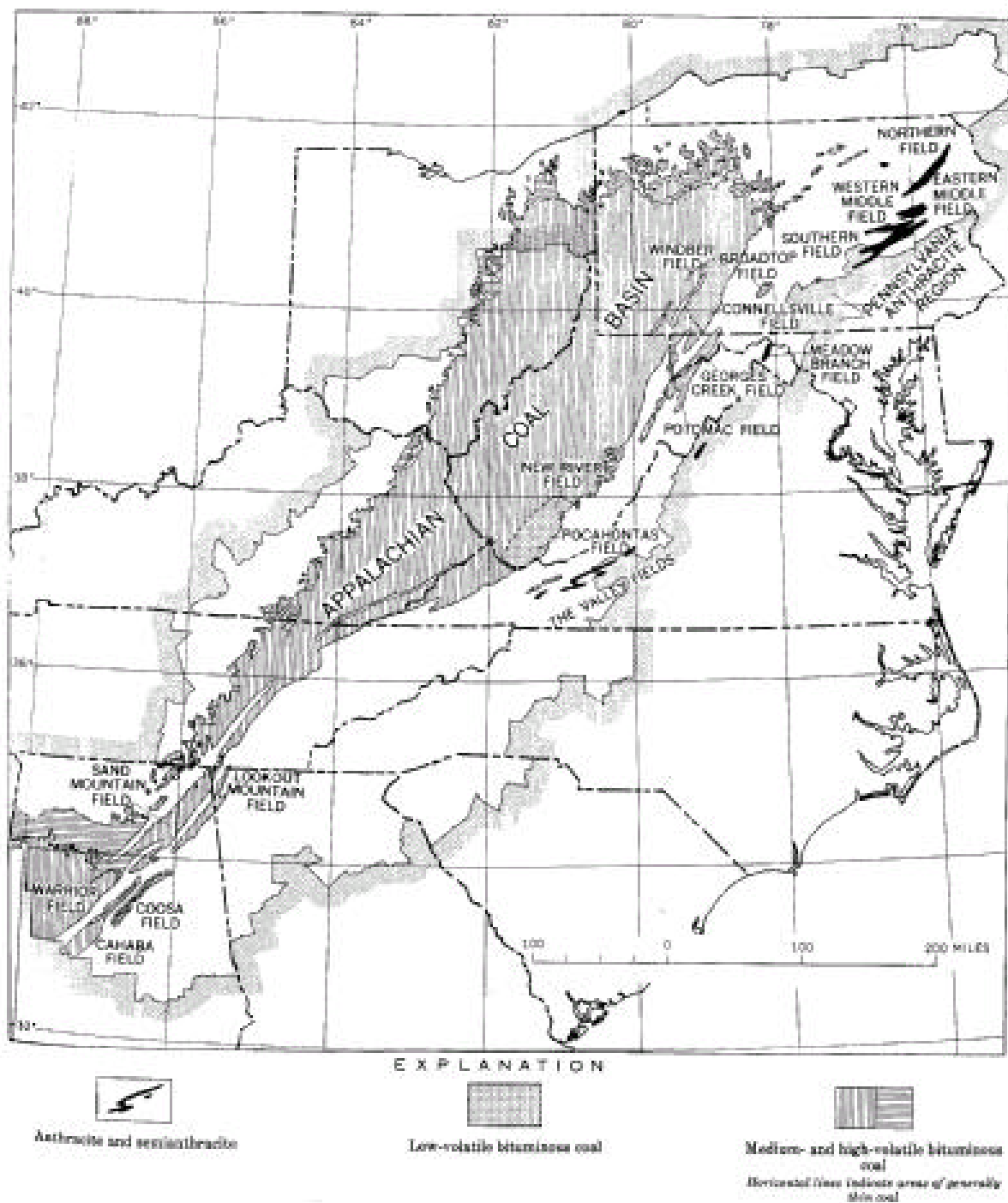
Figure 3.1. The Appalachian Coal Fields

The coal-bearing rocks in the basin are folded into several hundred small subsidiary synclines and anticlines, and, on the eastern edge of the basin, a few coal-bearing synclines are separated structurally from the main part of the basin (Arndt et al., 1968). Hills have been subjected to stress-relief and unloading forces that have intensified fracturing and bedding-plane separations, and subsequently, weathering. This physical weathering, coupled with chemical weathering, has resulted in higher permeabilities within the weathered zone (Hawkins et al., 1996).

Physiography and Surface Drainage

The mineable coal seams are located primarily in the Appalachian Plateau physiographic province. The Appalachian Plateau province is a high upland dissected by many incised, dendritic streams. The topography can be generalized as a series of loping, uplifted, dissected plateaus that are topped by resistant layers (Fenneman, 1938). The eastern edge of the Appalachian Plateau province is an escarpment that rises abruptly 1,000-3,000 feet above a valley that bounds it on the east. This eastern ridge is the highest section of the Appalachian Plateau, with elevations ranging up to 4,800 feet in parts of West Virginia. Relief in the western part of the province, in central and southwest Pennsylvania, West Virginia, eastern Kentucky, and northern Tennessee is 500-1,500 feet. This area is carved into small steep-sided hills. Slopes of 45° are common and steep slopes, some vertical, prevail along the major rivers (Davies, 1968).

The surface drainage network generally follows a dendritic pattern indicating minimal underlying structural control. The underlying geology does however exert some control on the degree of valley downcutting and thus on the gradient of individual streams and sections of streams. In the north, the more easily eroded, subhorizontal rocks of the Plateau section have allowed streams and rivers to reduce the land to gentle slopes resulting in mild stream gradients along the valleys of the Ohio, Allegheny, and Monongahela Rivers. Runoff rates for this region are among the highest in the country. Average annual runoff ranges from 10 – 30 inches, generally increasing from north to south (Schneider, 1965). The numerous sub-basins of the Plateau Section are characterized by rounded hills and steep-sided valleys. These tributary streams generally have steeper gradients and more V-shaped valleys than the master streams. To the east, along the anticlines of the Allegheny Mountain Section, the more resistant folded bedrock results in drainage patterns that parallel the ridges, with major rivers cutting through in only a few locations. The gaps where streams cut the ridges are often localized by geologic structure. Stream gradients in this section are therefore significantly steeper than on the adjacent plateau. Unconsolidated deposits (alluvium) overlie the bedrock in some locations, particularly along major stream valleys within the Plateau Section. Stoner et al. (1987) describe typical seasonal streamflow variation in their report on the water resources of southwestern Pennsylvania:

> "…The hydrographs show a typical low flow in October and early November; an increase in flow in late November and December as evapotranspiration decreased and winter rains and snowfall increased; a decrease in flow in late December and January when ice formed on the streams; an increase in flow in February due to thawing and an increase in rainfall; a slight decrease in flow in March due to a decrease in precipitation; an increase in flow in April resulting from increased rainfall and snow melt; a decrease in flow in May as rainfall decreased and evapotranspiration increased; and unusually high flow in June due to large amounts of rainfall; and generally low flow

in July, August, and September, interrupted by high flows in late July and early September caused by thunderstorms."

Climate

In the Appalachian Basin, the average annual temperature in the north is about 50° F (~10° C) ranging up above 60° F (>15° C) in the south. Precipitation also increases from north to south, with rainfall averaging 35 inches (90 cm) in northern Pennsylvania to more than 55 inches (140 cm) in Alabama (Schneider, 1965; Weeks et al., 1968). Precipitation averages about 47 inches annually, much above the national average for regions of comparable size. Most is derived form eastward-moving air masses that lose moisture as they are forced upward over the mountainous areas. High precipitation thus tends to occur along the western sides of mountain ranges, and distinct rain shadows are found east of them. The annual infiltration rate of water is generally sufficient to consistently flush groundwater through the shallow rock strata from recharge to discharge points. This flow tends to leach out the soluble products of the more weatherable minerals.

In general, less than 15 inches (38 cm) of the average precipitation infiltrates the groundwater system, with evaporation and transpiration accounting for roughly 20 inches (51 cm) annually (Becher, 1978). The remaining precipitation directly runs off to surface waterways. These numbers are estimates; actual amounts vary depending on geology, soils, vegetation, and topography.

GROUNDWATER

Regions such as the Appalachian coal measures with their small basins, marked relief, and humid climate generally develop a groundwater system that can be readily broken into distinct parts: local (shallow), intermediate, and regional (deep) (Poth, 1963). The contrast in permeability between the various lithologic units creates a series of alternating aquifers and aquitards. This results in a predominance of lateral groundwater movement within the coal measures. However, well-developed joints systems commonly serve to augment vertical communication.

Flow Systems

The effects of topography, geologic structure, and stratigraphy control the groundwater flow patterns. Williams (1982) describes general groundwater flow on the Northern Appalachian Basin:

"Three general flow systems are recognized within the high-to-intermediate-relief model. Shallow flow systems convey groundwater over short distances, tens to hundreds of meters, and respond rapidly to chemical and physical changes within the environment. Groundwater within intermediate flow systems travels distances of hundreds to thousands of meters and has response times ranging from months to decades. Deep flow systems transport groundwater distances of thousands to tens of thousands of meters from points of recharge to discharge, with travel times measured in years to hundreds of years."
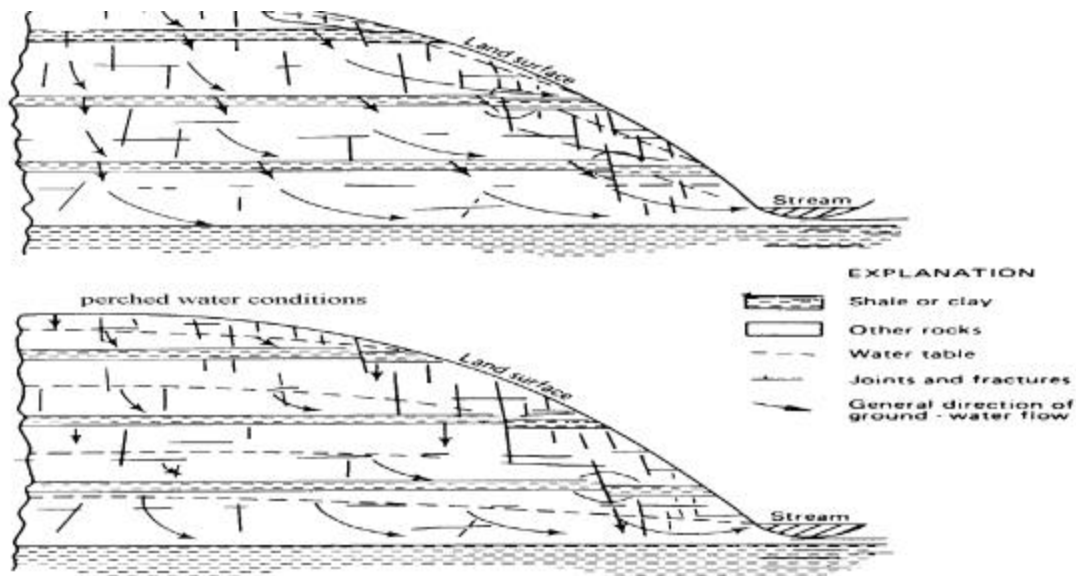
Figure 3.2. Idealized perched and semi-perched groundwater conditions (modified from Ward and Wilmoth, 1986)

The shallow flow system underlies hills, discharges to local streams, and, to some extent, leaks downward into the deeper, intermediate system. Contrasts in the permeability of successive strata can result in marked deflection of flow lines and in greater horizontal flow components than in homogeneous aquifers. In some areas, shallow systems include water that is "perched" above beds of lower permeability (Figure 3.2). This groundwater may then move laterally due to permeability contrasts, and discharge as springs above stream level.

Poth (1963) describes the shallow groundwater as circulating in a series of "hydrologic islands". The water table located within the ridges between surface drainageways tends to become depressed to the level of the surface streams. However, semi-perched zones occur routinely within the ridges due to the numerous low permeability units. The dissected nature of the bedrock surface has resulted in hills, largely surrounded by valleys containing perennial streams. These hills constitute the hydrologic islands (Figure 3.3). A discrete groundwater flow system operates within each hydrologic island and is hydrologically segregated from the local groundwater flow systems in adjacent islands. The base of the local flow system (particularly for islands adjacent to first and second order streams) is a distance below the level of the stream valleys bordering the island. It is defined by the maximum depth at which groundwater originating within the hydrologic island will flow upward to discharge in the adjacent stream valley. Recharge to the local system is completely from within the hydrologic island. Discharge from the local system is into the adjacent stream valleys and via leakage into deeper intermediate and regional groundwater flow systems. In areas adjacent to larger streams and rivers, local groundwater that leaks downward may co-mingle with intermediate or even regional flow, which is rising to discharge within the valley. This shallow flow system is the most active groundwater circulation area, and contributes water to the vast majority of domestic wells.

A prominent subsystem within the region's shallow groundwater flow system is a weathered regolith of approximately 10–20 meters in depth. It is a highly transmissive zone consisting of soil, unconsolidated sediment, and weathered, highly fractured rock. Weathering has removed most soluble minerals, and groundwater flowing through this material picks up little mineral matter. Because of the open nature of the
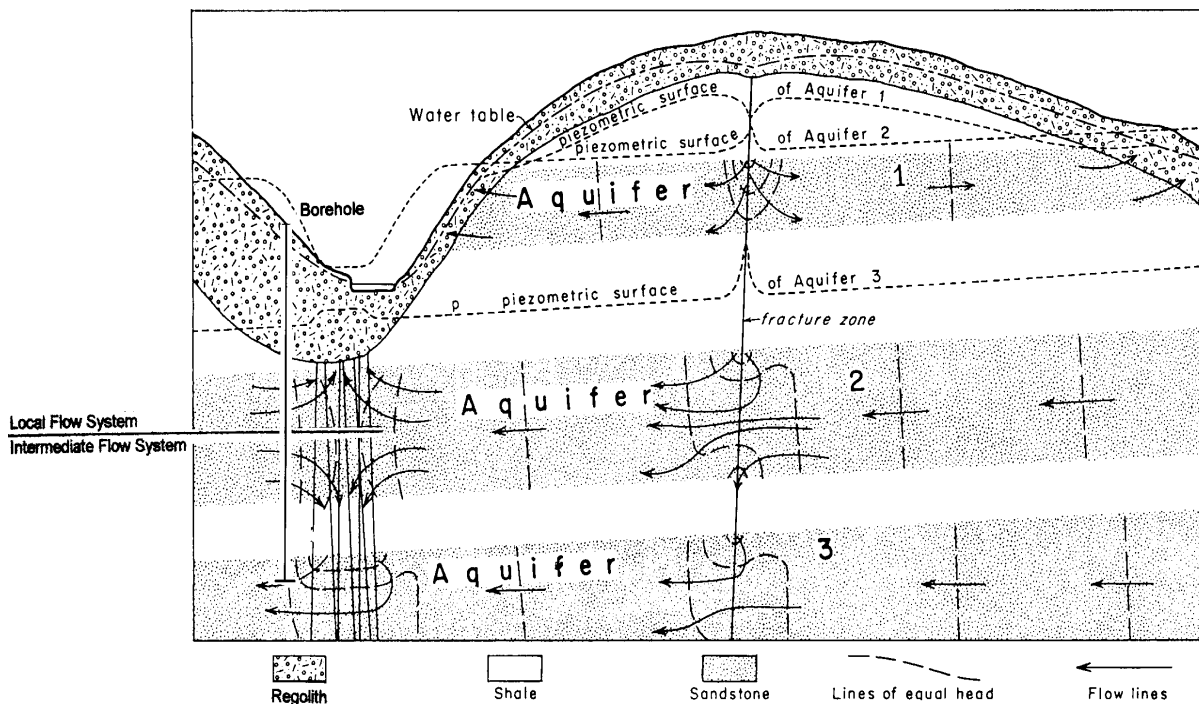
Figure 3.3. Groundwater flow in and beneath a "hydrologic island" (modified from Poth)

fractures within this zone, the groundwater "flow-through" time is short and this subsystem allows a significant portion of recharge to short-cut to local discharge points. Various hydrologic tests have shown hydraulic conductivities within this zone to be one to two orders of magnitude greater than in zones that are only marginally deeper (Schubert, 1980).

Water chemistry within the weathered regolith subsystem should not be used to characterize groundwater under deeper cover, which flows through unweathered rock. For example, rock units closer to the ridge center may contain groundwater with significant alkalinity due to circulation through unweathered calcareous strata. In comparison, an outcrop spring at the same stratigraphic interval shows little or no alkalinity because it is largely fed by groundwater that traveled an abbreviated path through leached and weathered rock along the "rind" of the hill.

Recharge to the weathered regolith subsystem is through ridge-top and valley-wall fractures. Groundwater flows through the interconnected bedding-plane partings and fractures to springs flanking the hillsides (frequently at coal outcrops) and into stream channels. Much of the water that enters this shallow subsystem never penetrates to the nearby ridge-cores, nor to deeper flow systems. Residence time is as short as days to a week (Hawkins et al., 1996).

Lithology and regional joint sets control flow within the ridge-cores. The ridge-core subsystem receives recharge through the weathered regolith subsystem and through the stress-relief fracture system. Groundwater flow is through tectonic fractures, bedding-plane partings, and to a much lesser degree, intergranular porosity. Low permeability units (such as claystones and shales) exert more control within the ridge cores due to the lack of stress-relief joints and weathering, which control groundwater movement along the margins of the hills. Because the integrity of these low permeability layers has not been

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compromised fully in the ridge cores, as may be the case along the hillsides, groundwater can mound on these layers. It then either flows laterally to mix with groundwater within the stress-relief/weathered regolith subsystem and discharges to the local stream valley; or leaks downward to an intermediate or regional flow system.

Residence times and response times to precipitation events within the ridge cores are intermediate between those for the weathered regolith subsystem and deeper systems. The ridge-core subsystem is part of the local flow system because it is part of the hydrologic island that discharges into the valley adjacent to the local recharge area.

The intermediate groundwater flow system is recharged via multiple shallower (local and intermediate) systems and at the drainage basin divide of the defining recharge area. Flow passes beneath two or more hydrologic islands and discharges in valleys above the lowest level of the drainage basin. Flow rates and residence times are generally between those of local and regional groundwater flow systems, probably varying from years to decades, depending on the level of the intermediate system and the length of the flow path. A deep, regional groundwater flow system, which lies beneath the level of the hydrologic islands and intermediate flow system, operates independently of the shallower systems. Highly mineralized water occurs naturally at depths of less than 500 feet over large sections of the basin. The base of the regional system is the fresh water/saline water contact. Recharge to the regional system is from major drainage basin divides and leakage from multiple shallower (local and intermediate) systems.

Fractures

Superimposed on these flow systems (particularly on the shallow system) are additional distinct flow zones (subsystems) defined by the density, interconectedness, and aperture of rock fractures. Fractures and bedding-plane partings are commonly the main groundwater flow paths. The characteristics of the fractures (width, spacing, and frequency) differ between, but may be consistent within, various stratigraphic units. Therefore, it is appropriate to consider the stratigraphic units as the aquifers. Joint permeability is particularly significant, if not dominant, in shallow rock strata (15-50 meters) and may increase permeability values by ten to a thousand times when compared to intergranular permeability values taken alone (Parizek, 1971). Sames and Moebs (1989), working in the eastern Kentucky coal field identified vertical weathered joints ("hillseams") as important groundwater avenues. Fracture zones (areas where numerous fractures dissect the rock mass) are common and can have a profound impact on groundwater flow. Fracture zones are typically 7-12 meters in width (Gold, 1980) and depths can range into the hundreds of meters.

Hydraulic conductivities associated with fracture zones are often several orders of magnitude higher than unfractured rock. These features commonly counteract the layered heterogeneity of the coal measures by augmenting vertical conductivities allowing for significant vertical communication within the system, particular on local scales. Additionally, rock types with relatively low primary permeabilities can become significant water producers due to interconnected fractures. Because of the importance of secondary permeability features to groundwater flow in this setting, the classic use of terms such as aquifer, aquitard, and confining layer can be confusing. A single lithologic unit, such as a shale, can be characterized as either an aquifer or an aquitard over a relatively short lateral distance depending on conditions such as proximity to the shallow

weathered zone, proximity to stream valleys, and magnitude of open joints (generally decreasing with depth).

Valley-related stress-relief fracturing is another important secondary permeability feature. Stress-relief fractures are a fracture network unrelated in age and orientation to tectonic stresses. They are often the most transmissive part of an aquifer. The fracture network has been attributed to "de-stressing" of rocks during downcutting of streams and the formation of the steep and narrow valleys characteristic of the Plateau region (Wyrick and Borchers, 1981). Wyrick and Borchers studied two valley-related stress-relief systems on the Appalachian Plateau in West Virginia and determined that the fractured rock parallels topography. Hydrologic studies in the area have shown that the stress-relief zone is more transmissive than other surficial or bedrock units. Wyrick and Borchers state:

"… ground water occurs mainly in horizontal bedding-plane fractures under the valley floor and in nearly vertical and horizontal slump fractures along the valley wall. The aquifer is under confined conditions under the valley floor and unconfined conditions along the valley wall. The fractures pinch out under the valley walls, which form impermeable barriers. Tests of wells near the valley center indicated a change in storage coefficient as the cone of depression caused by pumping reached the confined-unconfined boundaries; the test also indicated barrier-image effects when the cone reached the impermeable boundaries."

Water levels in wells in the stress-relief zone respond quickly to precipitation events (Hawkins et al., 1996). Wyrick and Borchers (1981) determined that stress-relief fractures significantly affect the surface water hydrology in Appalachian Plateau valleys. Their study in the Black Fork valley in West Virginia showed that stream flow per square mile of drainage area increased 6-11 times downstream from the outcrop of stress-relief and bedding-plane fractures in the stream bed.

Permeability

Groundwater within the area occurs under both water table (unconfined) and artesian (confined) conditions. The vast majority of groundwater circulates in the fractured near-surface bedrock, along stress-relief fracture networks, open joints, and within the weathered regolith zone. Water-bearing zones commonly consist of horizontal fracture openings that occur preferentially at lithologic contacts. Studies indicate that hydraulic conductivity decreases with increasing depth at the rate of an order of magnitude for every 30 meters (Stoner et al., 1987). Water availability and well yield are a function of the number, openness, and interconnectedness of fractures, which in turn is related to proximity to the surface. The yields of bedrock wells generally increase in conjunction with the number and size of water-conveying fractures intercepted. Medium- and coarse-grained sandstone can show significant pore space permeability depending on the degree of cementation between grains and the presence of shale lenses. Many of the lithologies are laterally discontinuous and permeability changes considerably over short distances.

Brown and Parizek (1971) conducted laboratory tests on rock cores using a permeameter to determine vertical and horizontal primary permeability of various rocks within the coal measures of Clearfield County, Pennsylvania. The reported horizontal and vertical permeabilities of shales, claystones, and siltstones were 0.0004 gpd/ft^2 and 0.0001 gpd/ft^2, respectively. Rock cores near Elkins, West Virginia had somewhat

higher conductivities, ranging from 0.0004 to 1.0 gpd/ft^2, as reported by the U.S. EPA (1977). Brown and Parizek followed up their laboratory work by conducting field pumping tests on the same horizons in order to better account for secondary permeability. The pumping tests yielded coefficients of permeability ranging from 0.12 to 680 gpd/ft^2, averaging about 61 gpd/ft^2. Coefficients determined by Schubert (1978) via pumping tests on the Plateau of western Pennsylvania were lower and ranged from 0.023 to 2.20 gpd/ft^2.

Hobba (1991), working in Preston County, West Virginia, conducted aquifer tests on shallow middle and upper Pennsylvania rocks, including the Upper Freeport coal. Hobba describes his hilltop study site as follows:

> "Two aquifers occur within 65 feet of land surface at the test site. The overburden aquifer is the water-table aquifer and it consists of about 50 feet of mainly shale and sandstone beds. The leaky confined coal aquifer lies immediately below the overburden, and it consists of 4.5 feet of coal. Water occurs in both joints and intergranular openings in the overburden aquifer. Sandstones that contain both intergranular and joint openings are commonly filled with secondary minerals and the vertical joints and horizontal bedding plane joints are poorly developed; thus, the sandstones yield little water to wells. In general, shales do not yield large quantities of water, except in area where the rocks are intensely fractured."

Constant-head permeability tests were run at 10-foot intervals throughout the overburden above the coal. The most permeable rock was within 33 feet of the land surface. Testing conducted on the 4.5-foot coal seam indicated that it is almost as transmissive as the 50-foot overburden aquifer. Hobba concluded that major and minor fracture sets create anisotropic hydraulic characteristics that favor groundwater movement parallel to the major fractures in both the coal and the overburden. He also found that the orientation of maximum transmissivity in the coal approximately parallels the direction of face cleats in the coal.

Groundwater Availability

Over most of the area, sufficient water for domestic purposes can be obtained from bedrock wells drilled to the 75-250 feet range. These bedrock wells are naturally low yielding. Well yields can range up to 100 gallons per minute (gpm) or more but are typically below 10 gpm with a large percentage below 3 gpm. Yields large enough for industrial or municipal purposes can be difficult to obtain. Large capacity wells have been successfully developed near or at the intersection of fracture traces to increase the likelihood of fracture-enhanced groundwater flow to the well bore. Bedrock wells often exceed recommended drinking water concentrations for iron. Wells in valleys, where the water table is closer to the land surface, have more available drawdown than wells of the same depth of hills and hillsides, and tend to be less vulnerable to negative impacts caused by groundwater level fluctuations.

Working in the Stillwater Basin on the Appalachian Plateau of east central Ohio, Walker (1962) found considerable variability in yield of bedrock wells. Certain sandstone aquifers supplied up to 25 gpm. However, most bedrock aquifers were found to supply only enough water for domestic uses, generally less than 3 gpm. Jones (1988), also working in eastern Ohio, reported bedrock well yields ranging from 2 to 10 gpm, compared to glacial outwash and alluvial zones along stream valleys, which yielded up to 200 gpm

but typically averaged 20 gpm. Wahl et al. (1971), in their report on Winston County, Alabama, describe the groundwater resources in the Cumberland Plateau's Pennsylvanian coal-bearing rocks as follows:

> "The Pottsville Formation consists of about 1200 feet of sandstone, shale, and coal. Groundwater in the Pottsville occurs in openings along fractures and bedding planes and in permeable sandstone. The quantity of water available from an individual well in the Pottsville depends on the number, size, and extent of water-bearing openings or the permeability and thickness of saturated sandstone penetrated by the well. …The number and size of water-bearing openings decrease with depth and in general only small amounts of additional water are obtained by drilling below a depth of about 350 feet. "

Wahl reports that even those wells that were developed in highly productive sandstone zones rarely yield over 50 gpm and commonly produce 5 to 10 gpm. Causey (1961), working in Etowah County, Alabama, reported low well yields of generally less than 5 gpm for Pottsville Formation units. Moore (1990) also reports generally low yields (10 gpm) for the Pennsylvanian rocks of the Cumberland Plateau of northern Alabama, with a few relatively high-yield wells developed in fracture zones.

In general terms, wells along major anticlines and in valleys tend to be higher producers due to relatively extensive fracturing. Stoner et al. (1987) outlines the following generalities regarding topographic position versus well yield for the coal measures of southwestern Pennsylvania:

> "Hilltop wells – wells are commonly drilled only to the depth of sufficient yield. Increasing the well depth for added yield or storage commonly results in water-level decline and sometimes complete loss of well yield. Also, an uncased deep well can often reduce the yield of a nearby shallow well.

> Hillside wells – In addition to procedures for the hilltop setting, wells need to be sited at some distance from potential contamination points such as septic tanks, trash dumps, or stock pens located upgradient. At many hillside locations, springs are a suitable alternative to wells as a potable water supply….

> Valley wells – Highly mineralized groundwater is shallowest beneath valleys. This condition commonly limits the depth of valley wells to be used for domestic supply. High-yielding shallow wells are possible in the alluvium of major valleys, but groundwater is susceptible to contamination by surface activities. Tightly cased deep wells in large valleys may be free flowing…. Of all the topographic positions, wells in valleys have the greatest probable success of producing high well yields. These high yields are commonly due to fracturing beneath the valley bottom. This fracturing is expected to diminish beneath adjacent hills, thereby limiting the effective areal extent and yield of such aquifers…"

Over the entire study area, alluvium, particularly along major rivers, is generally highly permeable and can yield large quantities of water to wells. However, permeability may change significantly over short distances because of changes in the degree of sorting. Wells penetrating the coarse basal layers of alluvium generally obtain the largest yields (Poth, 1973). Well yields in the 500-gpm range are not uncommon. For example, the narrow flood plain adjacent to the Ohio River may yield 500 to 1000 gpm to properly developed wells

(Schmidt, 1959) and yields of up to 800 gpm are obtained from wells tapping thick alluvial deposits in Ohio County, West Virginia (Robison, 1964). In contrast, thin or fine-grained alluvial deposits, such as those along most small to moderate size streams, have relatively low water-yielding capacities. In Harrison County, West Virginia, alluvial deposits are minor sources of groundwater owing to their thinness, and yields of only 2-3 gpm can be obtained (Nace and Bieber, 1958). In general, water obtained from alluvium is hard, has high iron, manganese, and dissolved-solids content.

Because sandstone typically contains both intergranular and joint openings, it generally yields the most water to wells. However, where the pores are filled with secondary minerals and jointing is relatively undeveloped, sandstone will transmit little water. Williams et al. (1993) ranked hydraulic conductivity from highest to lowest among bedrock water-bearing units: (1) coal, (2) sandstone, (3) siltstone and shale, and (4) limestone.

WATER CHEMISTRY

Groundwater

Because of differences in rock mineralogy, residence time, and influence of the brine underlying the composite flow system, the chemistry of groundwater in different flow systems and subsystems varies. For example, groundwater that has come in contact with sandstone and shale containing pyrite remains soft, but is more acidic and higher in concentrations of iron and hydrogen sulfide than in non-pyritic rocks. Water in limestone or calcareous aquifers is usually a calcium magnesium bicarbonate type. Sodium chloride and other brines occur below a depth of several hundred meters in all hydrostratigraphic units, and waters above this saline water are usually hard (Back, 1988).

Poth (1963) and Rose and Dresel (1990) identify three stages of "flushing" that roughly correspond with the three levels of the previously outlined flow systems. The deepest zone, directly affected by concentrated brines, which exist at depth throughout all areas west of the Allegheny Front, is a NaCl-rich diluted brine zone. This zone is diluted with surface water that has leaked from shallower flow systems, but retains appreciable amounts of both Na and Cl. This chemical signature is indicative of the more regional flow systems described previously.

A shallower system (intermediate zone) exists in which Cl has been removed by flushing with surface waters, but considerable Na remains adsorbed to clays and similar materials, leading to the $Na-HCO_3$ waters that are commonly found at intermediate depths. The elevated Na is a result of cation exchange, with Na released from the exchange sites in response to replacement by Ca, Mg, and possibly Fe (especially with mine waters) (Winters et al., 1999). Piper (1933) outlined this process:

"…Many of the water-bearing beds - whether they are sandstone, shale, or limestone - contain soft sodium bicarbonate water where they lie at intermediate depths. This soft water is believed by the writer to represent calcium bicarbonate water that has exchanged its calcium and magnesium for sodium by reaction with base-exchange silicates in the rock as it has percolated downward along the dip of the water-bearing bed. The hardness due to the bicarbonate of calcium and magnesium is

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removed in proportion to the completeness of the exchange reaction, and the water finally passes into the sodium bicarbonate type…"

In the uppermost zone, Na is completely flushed leaving a Ca-HCO$_3$ water typical of shallow groundwater. The shallow flow system is further divided (Brady et al., 1996) into a low dissolved-solids zone associated with the stress-relief/weathered regolith subsystem, and a zone with higher dissolved solids associated with unweathered rock (ridge cores).

Because stream valleys function as sumps for the discharge of groundwater, the contact between the fresh and saline groundwater probably "cones up" beneath the streams, and lies at successively greater depths away from the streams. Mining activity and practices for controlling water quality or quantity may alter the depth to saline water and the amount of discharge of saline water to the streams (Hobba, 1987).

Wunsch (1993) developed a conceptual hydrochemical-facies model for an unmined ridge based on site-specific data from eastern Kentucky. According to Wunsch (1993, p. 72):

…"The model shows four zones where the major cations and anions comprising the water type for a particular water sample could be predicted with a high degree of probability. The model shows a depressed salt-water interface below the ridge due to downward movement and accumulation of fresh water. The hydrostatic pressure imparted on the salt water is transmitted in the salt-water zone, causing it to rise at locations where fractures breech confining layers (valley bottoms)…"

Data collected at numerous mining sites in southwestern Pennsylvania support Wunsch's hydrochemical model for shallow groundwater flow on the dissected Appalachian Plateau of Pennsylvania (Callaghan et al., 1998). Callaghan et al. provide ranges for water quality for a shallow "rind of hill" system, ridge cores, and intermediate flow systems at a site in southwestern Pennsylvania (Table 3.1).

Surface Water

Generally, the streams draining the Appalachian Plateau contain three types of water, based on major cation and anion concentrations. A calcium-magnesium-bicarbonate type typically dominates in streams draining the limestone and dolomite areas of the Plateau in Tennessee and northern Alabama. Streams containing calcium-sulfate waters with bicarbonate and chloride (dissolved solids less than 150 ppm) drain large portions of West Virginia and eastern Kentucky. Streams containing calcium-sulfate type water that is hard to very hard, with dissolved-solids concentrations from 100 to 2000 ppm, drain the heavily mined areas of southwestern Pennsylvania, northern West Virginia, eastern Kentucky, eastern Ohio, and north-central Tennessee (Schneider, 1965).

Table 3.1. Typical groundwater chemistry ranges for various flow systems (mg/l).

Flow system	# of samples	Alkalinity	Sulfate	Ca	Mg	Na	Spec. Conductivity (umhos/cm)
Rind of hill	22	2 – 38	14 - 45	5 - 38	1 – 7	2 - 13	50 – 136
Ridge core	11	80 – 199	39 - 75	40 - 70	9 – 12	2 - 17	300 – 470
Intermediate	26	8 – 861	108 - 2850	2 – 246	---------	191 - 945	1220 - 4500

CONCEPTUAL GROUNDWATER MODELS

Kipp and Dinger (1987) presented a conceptual model of groundwater flow in the Wolfpen Branch basin in Kentucky:

 "Groundwater flow in the basin is complex. Within the interiors of the hills, water is stored and transmitted in intergranular pore spaces of the predominantly sandstone bedrock. These rocks are saturated, but wells produce little water. Lithologic cores indicate that saturated sandstone zones are separated by relatively impermeable claystone units associated with major coal seams, which limit the vertical movement of water. These confining layers cause lateral flow to the hillsides where ground water may discharge as springs or seeps or move vertically downward through the confining zones via secondary porosity consisting of fractures and bedding-plane openings. Continuous water-level records indicate that bedrock wells monitoring the valley walls and bottom respond quickly to rainfall events, evapotranspiration, and mining activity. This suggests high hydraulic conductivity and direct connection to infiltration from the surface. Lithologic cores indicate that secondary fracture permeability, possibly created by stress-relief fracturing, is responsible for the increased hydraulic conductivity along hillsides and valley bottoms, and controls much of the shallow groundwater flow in the basin. This shallow ground water represents the principal portion of the active groundwater flow system."

Harlow and LeCain (1993), working in coal-bearing Late Mississippian and Pennsylvanian rocks of southwestern Virginia, confirm many of the same hydrologic conditions. They developed a conceptual groundwater flow model using borehole geophysical logging, water quality sampling, and pneumatic straddle-packer assemblies. The following summary highlights some of their findings:

"…Coal seams had a median transmissivity of 0.15 ft^2/d, whereas other rock types and lithologic contacts had median transmissivities less than or equal to 0.001 ft^2/d. All rock types tested usually were permeable to a depth of approximately 100 feet; however, at depths greater than 200 ft only coal seams consistently had measurable permeability (transmissivity greater than 0.001 ft^2/d). Injection testing of intervals immediately adjacent to coal seams usually indicated lower transmissivity than that obtained when the coal seams were isolated within the test interval, indicating that most lateral groundwater flow is associated with the coal seams. Potentiometric-head measurements for these coal seams coupled with the presence of low-transmissivity intervals between the seams indicate that some of the coal seams could be partly saturated, confined, or semi-confined, and, in some instances, water could be perched above these coal seams.

The mean depth to standing water below land surface was 221 feet in core holes located on hilltops, 109 feet in core holes located on hillslopes, and 39 feet in core holes located in valleys. Potentiometric-head measurements indicate downward flow on hilltops, lateral and downward flow on hillslopes, and upward, lateral, and downward flow in valleys. Because of the high topographic relief (600 – 1000 feet) in the area, groundwater flow systems are of small areal extent. Head relations indicate that high topographic areas function as recharge areas: water infiltrates through the surface, percolates into the regolith, and moves downward and laterally through the fractures in the shallow bedrock. Permeability decreases with increasing depth, and most water may move laterally

along fractures or bedding planes, or through coal seams until encountering more permeable rock through which to move downward. If more permeable rocks are not encountered, water continues to move laterally, discharging as a spring or seep on the hillside. Where vertical permeability is appreciable, water follows a stair-step path through the regolith, fractures and bedding planes, and coal seams, discharging to streams and (or) recharging permeable coal seams at depth. …"

Harlow and LeCain's study supports the finding of Williams et al. (1993) that coal seams, sandstones, and lithologic contacts were the most transmissive zones with siltstones and shales having the lowest transmissivities. They confirmed that transmissivities of all rock types generally decreases with depth as fracture aperture and number decrease. Their aquifer test data indicated that the horizontal conductivity of coal is a function of depth and probably decreases under ridges due to increased overburden pressure. Regarding topographic setting, they found that hilltops had sharp downward gradients, hillslopes had downward gradients, commonly with shallow zones exhibiting intervals of equal head, and valley wells typically exhibited shallow intervals of equal head below which head measurements indicated downward gradient. Although valleys serve as discharge zones for shallow and intermediate groundwater in this setting, many wells did not show distinct upward gradients. The few wells tested that showed upward gradients were adjacent to streams, possibly indicating this signature is detected only in very close proximity to the stream. This confirms the observations of Callaghan et al. (1998) regarding the locating of piezometers in discharge zones on the Appalachian Plateau of southwestern Pennsylvania. Callagahan reports that upward gradients associated with stream valleys will be detected routinely only where the piezometers are in proximity to the stream, i.e. the discharge area is very small compared to the recharge and lateral flow zones.

Studies conducted in the eastern Kentucky coal field confirm the complex nature of groundwater flow in this setting and the importance of shallow fracture-controlled flow on the Plateaus. Minns (1993), working in a first-order watershed in eastern Kentucky, concluded:

" …the majority of bedrock groundwater is obtained from fracture zones that are generally within 200 feet of the surface where relatively direct connection to infiltrating groundwater exists. Fractures, coal beds, and bedded strata alter flow paths largely by differences in fracture density that may be lithologically dependent. This creates contrasting conductivities among layers. …A conceptual model for local and regional groundwater flow suggests that local flow systems develop in response to topography: however, the local flow system is contained within the shallow-fracture zone. Flow that does not discharge via the shallow-fracture zone enters the regional flow system. Regional groundwater flow is primarily downward beneath upland areas toward the fresh-saline-water interface. The interface is generally located at its deepest point beneath upland regions and slopes upward toward third-order or larger streams. Regional groundwater flow roughly parallels the interface; consequently, third-order or larger streams are discharge zones for regional flow."

Similarly, work conducted by Wunsch (1993) reinforces the dominant role secondary permeability features play in shallow groundwater movement. Based on data from water-injection packer tests and downhole camera investigations at an unmined ridge in the eastern Kentucky coal field, Wunsch found that only coal seams, vertical fractures, joints, and bedding-plane splits and partings possessed sufficient hydraulic conductivities to transmit significant amounts of water.

HYDROLOGIC EFFECTS OF MINING

It is estimated that millions of cubic meters of groundwater are diverted from natural flow systems every day via drainage from abandoned mines and pumpage from active mines (Sgambat et al., 1980). Mines below the water table in regional groundwater recharge areas can qualitatively and quantitatively impact both shallow and deep aquifers. Mines above the water table in regional recharge areas generally pose more of a water quality problem than quantity problem and may, in some cases, increase groundwater recharge rates over those occurring prior to mining. In discharge areas, mines that intersect the water table can pollute shallow aquifers exposed in highwalls. They can draw down water levels in both shallow and deep aquifers that underlie the mine or that are exposed in highwalls. (Parizek, 1978).
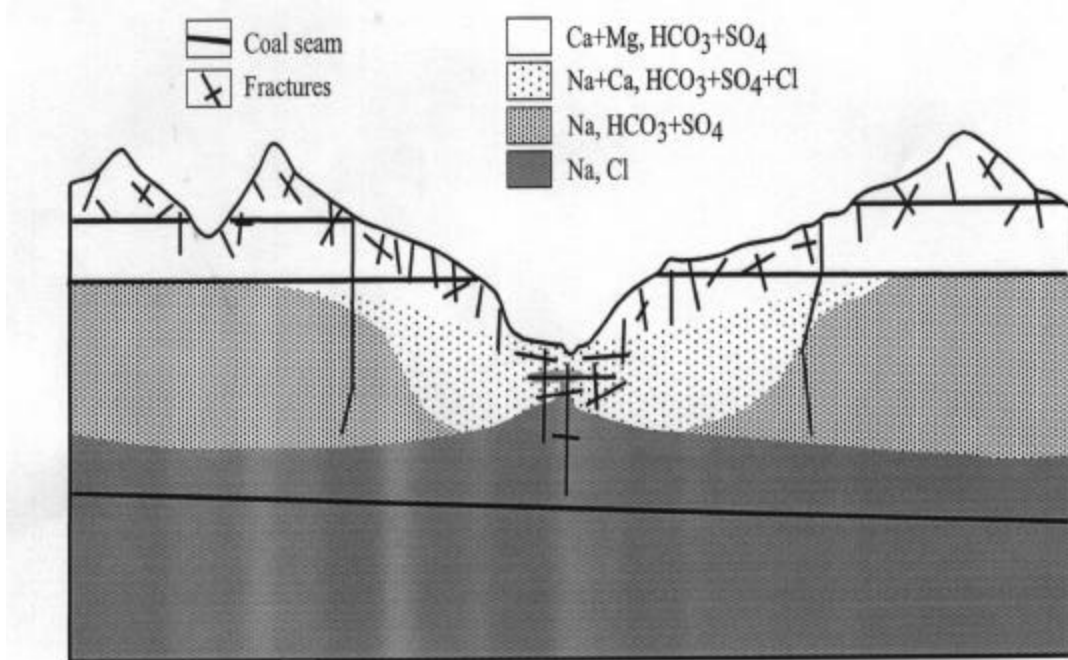
Figure 3.4. Conceptual model of hydrochemical facies (Wunsch, 1993).

The significance of changes in flow systems following mining will vary with the size of the flow system, the position of the mine within the flow system and relative to the initial water table, and the mining-induced fracturing pattern and its interaction with natural fracture sets.

Underground Mining

The hydrologic effects of underground mining are briefly discussed here because they include watershed-wide and even regional scale impacts on groundwater flow systems. Expansive interconnected underground workings act as man-made aquifers with high hydraulic conductivities, and therefore must be accounted for when characterizing groundwater flow systems.

Underground mines can intercept and convey surface water and groundwater. When excavated below the water table, mine voids serve as low-pressure sinks, inducing groundwater to move to the openings from

the surrounding saturated rock. This dewaters nearby rock units via drainage of fractures and water-bearing strata in contact with the mine workings. More remote water-bearing units and surface water bodies can also be affected, depending on the degree of hydrologic communication. Mines located above stream levels serve as free drains and highly permeable aquifers. They promote perched water table formation in poorly permeable overburden deposits, facilitate dewatering of roof rock, and often produce giant man-made springs at mine openings (Parizek, 1978). The extent and severity of the impact on the local surface water and groundwater systems depends on the depth of the mine, the topographic and hydrogeologic setting, and the hydrologic characteristics of the adjacent strata.

In the flat-lying sedimentary rocks of the eastern bituminous coal measures, underground mining is routinely accompanied by overburden movement, rock fracturing, dilation of joints, and separation along bedding planes. Rock movements occur vertically above the mine workings and at an angle projected away from the mine's edge. Mining-induced fracturing within this angle can result in hydrologic impacts beyond the margins of the mine workings. The zone along the perimeter of the mine that experiences hydrologic impacts is said to lie within the "angle of dewatering" or "angle of influence" of the mine. Angle of influence values of 27 to 42 degrees have been reported for the coal fields of northern West Virginia and southwestern Pennsylvania (Carver and Rauch, 1994; Tieman and Rauch, 1991).

Dixon and Rauch (1988) observed stream depletion associated with longwall mining at three mine sites in West Virginia. Dewatering was less severe at mines with greater overburden thickness. Recovery times for stream flow ranged from eight months to five years. Tieman and Rauch (1987) found that streams located above regional base level and undermined by longwall panels less than two and one-half years old were partly to completely dewatered during base-flow conditions. They found that streams located above regional base level and also above panels at least three years old had normal flow. Water lost from streams often did not penetrate to the mine, but instead migrated downward through probable subsidence fractures to near regional base level, where it migrated laterally through a sandstone unit to discharge at a master stream over the mine. Carver and Rauch (1994) drew the following conclusions regarding impacts to streamflow, based on their study of a longwall mine in West Virginia.

> "…Subsidence from longwall mining typically reduced stream discharge for 2-3 years. Panels positioned beneath upland catchment areas and not under streams caused no apparent stream dewatering…. Monitored stream reaches within the angle of draw zone of an adjacent panel did not normally become dewatered for panels older than 2.3 years. However, stream reaches in basins less than 200 acres in size often experienced dewatering for up to 3.1 years after undermining…. After 2-3 years since subsidence, recovered streams display lower high base flow and higher low base-flow discharge, or more uniform base-flow discharge, compared to unsubsided streams….Water diverted from affected streams and supplies remained in the shallow groundwater flow system and probably did not penetrate deeper than local base level, as shown by the reported low groundwater inflow rate to the mine and by the fact that most impacted streams had returned to "normal" down-gradient flows. The lost waters probably moved downgradient as underflow through shallow aquifers and then returned to streamflow in unsubsided or recovered areas."

One important aspect of overburden movement, relative to the potential of high-extraction mining to impact surface waters, is the formation of surface extension zone fractures. An extension zone forms at panel edges and at the traveling panel face and is most pronounced near the surface. Surface extension zone fractures are typically 50 to 100 feet deep. This near-surface zone of increased permeability and storativity can result in shallow aquifer and surface water impacts even where overburden to seam ratios are considerable and there is no direct avenue for drainage to the mine.

Surface Mining

The impacts of surface mining are typically more local than those of underground mining. However, the cumulative impacts from numerous operations can have profound impacts on basin-wide runoff and infiltration, and can even shift the location of surface water and groundwater divides. Such minor shifts in surface water divides can cause significant changes in surface runoff characteristics in small watersheds. This can either increase or decrease total runoff and/or baseflow compared to pre-mining conditions. Shifts in surface water divides tend to be less significant in higher relief areas, such as the Appalachian Plateau, where existing topographic features dominate post-mining topography.

According to Parizek (1978), the effect on groundwater divides is less clear. Highly permeable mine spoil will augment groundwater drainage in a certain direction depending on other controlling factors, such as the dip and lithology of the mine floor. This will cause a shift in the groundwater divide, resulting in a reduction in baseflow or spring flow on the opposing side of the ridge.

Wyrick and Borchers (1981) gave the following reasons for fully assessing stress-relief systems during surface mine design on the Appalachian Plateaus.

> "Strip-mine benches in the Appalachian Plateau are cut through the slump-fracture zone along valley walls, which can affect hydrology significantly. First, aquifer recharge may be increased in several ways during mining by uncovering slump fractures, so that they intercept more surface runoff. The strip mine bench may be so sloped that it retains more runoff water, facilitating aquifer recharge. Second, reclamation regulations require backfilling benches. Such backfilling can seal slump fractures and reduce aquifer recharge if impermeable fill material is used. Third, exposing rocks to weathering and solution on the strip-mine bench can change the chemical quality of aquifer recharge markedly."

PRE-MINING WATER QUALITY AS A PREDICTION TOOL

Natural water quality in shallow groundwater flow systems of the Appalachian Basin results from the influences of three factors: the chemistry/mineralogy of the rock the water contacts, the flow path and the residence time. Shallow flow systems are the key to understanding pre-mining water quality. The recharge area for most springs is the weathered/leached regolith or highly fractured and weathered bedrock (Figure 3.4). The weathered zone is typically 20 to 40 ft (6 to 12 m) thick, but can extend deeper along fractures and is colored red, yellow, or brown due to iron oxidation. The weathered regolith and bedrock has been depleted of the most readily leachable (e.g., carbonate) and oxidizable (e.g., pyrite) minerals. Since this

weathered zone is near the surface, has limited thickness, and has higher permeability (induced by physical (fracturing) and chemical (leaching and oxidation) weathering), groundwater moves through this zone relatively rapidly. Hawkins et al. (1996) estimated the residence time as days to weeks. The lack of readily weatherable minerals and the short residence times result in spring water that is typically dilute.

Below the weathered regolith is a zone of largely unweathered bedrock (Figure 3.5). Weathering is restricted to some fractures and bedding-plane separations. Unweathered rock can contain readily soluble minerals, in particular carbonates, if they are part of the rock composition. The water flowing through the rock has a longer residence time because of lower permeabilities, and the slower flow rate allows longer contact with soluble minerals. The permeability is orders of magnitude less than that for the weathered zone and the residence time is measured in years (Hawkins et al., 1996). Groundwater that has passed through unweathered rock will typically have higher dissolved solids than water emanating from the weathered-rock/regolith zone.

The quality of groundwater from both weathered rock/regolith systems and unweathered rock systems can help to identify the presence or absence of carbonates within the area to be mined. Water chemistry can also shed light on the groundwater flow system. To evaluate the relationship between rock chemistry and water chemistry, Brady (1998a) studied several isolated hilltops where the only recharge was from precipitation, one of which will be reviewed here.
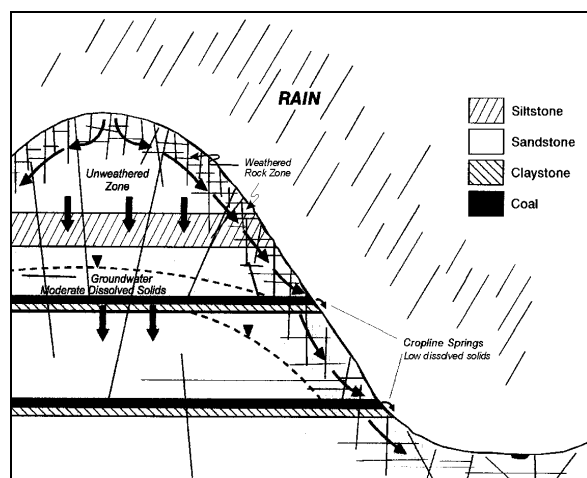
Figure 3.5. Schematic cross section showing conceptual shallow groundwater flow model, which includes the near-surface weathered-rock zone and the deeper unweathered-rock zone (modified from Hawkins et al., 1996).

Field pH and specific conductance were measured prior to mining in several uncased drill holes that were completed down to the upper Kittanning (UK) coal seam. Additionally, numerous UK cropline springs were sampled. Crop springs had alkalinities ranging between 1 and 9 mg/L. Unfortunately, alkalinity was not sampled in the drill holes, but it is a near certainty that the alkalinities were higher, judging from elevated pH and conductance. This hilltop has been mined and the mine is producing drainage with an average alkalinity of 380 mg/L.

The specific conductivity of the crop springs and shallow (near crop) wells had lower values (38 to 62 μS/cm) than the drill holes located toward the middle of the hill where depth to coal was greatest (158 to 221 μS/cm). The pH of the springs was also lower than the pH of the wells. NP is negligible in areas with less than 9 to 12 m of cover, evidently because of weathering. The higher pH and conductance increase are both coincident with an increase in NP. The water in deeper drill holes exhibited higher dissolved solids (reflected as specific conductance) than in cropline springs and holes with shallow cover, due to the increasing abundance of calcareous minerals with increasing overburden. The high NP strata are freshwater limestones and calcareous shales. The geology, stratigraphy, and overburden quality of this area is addressed in Brady et al. (1988), where the mine site is referred to as area "C."

Powell and Larson (1985) investigated water quality in an unmined watershed in a coal-producing region of the Appalachian Plateau of southwestern Virginia. The most common carbonate present was siderite, following by calcite and dolomite. Minor amounts of pyrite were generally associated with coal and adjacent rocks. They observed that water from springs typically had lower concentrations of alkalinity and dissolved solids than water from dug wells, which had lower alkalinity than drilled wells. With one exception, sulfate was less than 40 mg/L for springs, dug wells, and drilled wells. A few of the springs, and many of the deeper wells had high alkalinity (>100 mg/L). Springs with high alkalinity were unusual, indicating that most of the springs were from shallow groundwater sources.

A common misconception has been that water quality from cropline springs in unmined areas is typical of water associated with the coal seam. As already discussed, water associated with coal-cropline springs is typically much more dilute than water from the same coal seam under deeper overburden cover. The cropline springs and shallow wells represent water flowing through the near-surface weathered-rock zone. Calcareous rocks are typically absent or negligible within this weathered zone. Wells penetrating deeper overburden are completed in unweathered or less weathered rock with lower permeability. The combination of calcareous minerals and longer residence time for the groundwater results in significant dissolution of calcareous minerals forming bicarbonate alkalinity. Downward flow and substantially lower hydraulic conductivities probably result in little of this water reaching the cropline springs.

Pre-mining alkalinity in deeper drill holes provides a second confirmatory tool, along with acid-base accounting NP, to determine the relative presence or absence of calcareous rock and its distribution within the proposed mine area. As discussed by Brady (1998a), there appears to be a direct relationship between the amount of calcareous material preserved in the overburden and the alkalinity, conductivity, and pH of the pre-mine groundwater. In contrast, no relationship exists between MPA (i.e., % sulfur) and sulfate concentrations in the pre-mine groundwater. This is probably because of the very limited oxidation of pyrite under saturated conditions. Calcareous minerals are rather soluble in groundwater, while pyrite is not. Beneath the weathered zone, pyrite in unmined areas remains largely unoxidized. If elevated sulfate concentrations are found, it may indicate contamination from an adjoining mine or from an oil or gas well.

To summarize, water quality is directly related to the flow path, the dissolution of minerals contacted by the groundwater, and the contact time of the water with the rock. Cropline springs and shallow wells (6-9 m deep) that have little or no alkalinity indicate shallow leached/weathered overburden. No significant calcareous strata (measured as NP) are likely to occur within this zone. Where calcareous rocks are

present, such as some deeper cover situations, the calcareous minerals will dissolve in the water and can be measured as alkalinity. Low alkalinity in well or spring water indicates the absence of calcareous strata within the groundwater flow path for that well or spring. It might be expected that sulfate would reflect the amount of pyrite that is present, but there is no relationship between the amount of pyrite and sulfate concentrations, indicating that pyrite oxidation prior to mining is typically negligible.

These findings have several important implications:
1. Coal cropline springs typically reflect very shallow flow through the regolith and do not necessarily reflect water quality under deep groundwater conditions.
2. Wells are needed to ascertain water quality in the deeper unweathered-rock zone.
3. There is a relationship between overburden NP and groundwater alkalinity. If alkalinity in wells is relatively high (> 50 mg/L), calcareous minerals are present in the flow system and probably near the water sampling point. Where alkalinity is low (< 15 mg/L), the rocks within the recharge area lack appreciable calcareous minerals.
4. Groundwater alkalinity can be used to help determine whether overburden sampling has been representative. If overburden analysis does not indicate significant calcareous rocks to be present, but water wells into the same units are alkaline, the sampling may not be representative of site conditions and additional drilling would be warranted. The combination of groundwater alkalinity and overburden NP can be used together to better define the extent of calcareous overburden.
5. Overburden sampling and water sampling must represent both shallow and deep overburden cover to adequately represent the entire mine site hydrology and overburden chemistry. Holes drilled at greater than the maximum cover to be mined may overestimate NP in the overburden that will be disturbed by mining.
6. There is no observed relationship between MPA in the overburden and sulfate or any other parameter in the groundwater. Sulfate in groundwater from unmined watersheds is typically less than 40 mg/L, regardless of location within the flow system (Brady, 1998a).
7. The above conclusions are probably applicable to a large portion of the Appalachian Plateau. However, its applicability to other areas is unknown.

State Practices

Of the states interviewed, only Pennsylvania and West Virginia actively use pre-mining water quality to help predict post-mining water quality. All do pre-mining water quality assessments, but they generally do so to establish a baseline that will allow them to detect changes in ground and surface water quality and quantity. Table 3.2 summarizes the text that follows.

Alabama requires at least 6 months of 1 sample per month, to include seasonal variation, for all surface streams and seeps and at least 1 ground water monitoring well. Water sample analyses must include iron, manganese, aluminum, sulfate, alkalinity, acidity, and temperature. Pre-mining ground water quality information must also be provided for the strata below the coal bed.

Indiana requires at least 6 months of 1 sample per month, to include seasonal variation, for all surface streams and seeps. Stream sampling must include data from both upstream and downstream of the permit

Table 3.2. State Requirements for Pre-mining Water Quality

STATE	PRE-MINING WATER SAMPLING REQUIREMENTS		COMMENTS
	SURFACE WATER	**GROUNDWATER**	
AL	A minimum of 6 months of 1 sample per month for streams and seeps. Water analysis: Fe, SO$_4$, Mn, Al, acidity, alkalinity, and temperature.	A minimum of 6 months of 1 sample per month from at least 1 monitoring well. Water analysis same as for surface water, but includes strata below the coalbed.	Performs pre-mining WQ assessments to establish a baseline for detecting any impacts on water quality and quantity.
IN	A minimum of 6 months of 1 sample per month for streams and seeps. Water analysis: flow, TDS or specific cond. TSS, pH, Fe, Mn, acidity, and alkalinity.	A minimum of 6 months of 1 sample per month from all wells. Water analysis same as for surface water.	Same as AL
KY	Surface waters should be sampled at each affected watershed.	6 samples over 6 months prior to mining; quarterly during mining. Must characterize each affected aquifer and hydrologic regime.	Same as AL
MD	At least 6 months of 1 sample per month or quarterly samples for 1 year. Should include: Fe, Mn, Al, SO$_4$, alkalinity, and acidity for surface streams.	Not required	Same as AL
OH	At least 6 months of 1 sample per month or one high flow and one low flow. Must include: flow, TDS or specific conductivity, TSS, pH, Fe, Mn, SO$_4$, hardness, acidity, and alkalinity.	All identified aquifers must be sampled under seasonal conditions on at least 10 (all if less than 10) wells. Analysis must include at least same parameters as surface water; more may be required.	Same as AL. Sampling requirements are being changed to insure that seasonal effects are fully assessed.
PA	2 samples of any surface flow or seep, with monitoring points chosen from background sampling points, which must be sampled monthly for 6 months, including at least 1 month of low flow. Must include: alkalinity, acidity, pH, Fe, Mn, SO$_4$, specific conductance, suspended solids, and Al for high quality streams.	Data can be from on-site or nearby residential wells and must be sampled during mining as a permit requirement. Analyses must include: pH, alkalinity, acidity, Fe, Mn, SO$_4$, specific conductance, and suspended solids. Results are compared with NP values for consistency.	Actively uses pre-mining water quality to help predict post-mining water quality. Performs pre-mining WQ assessments to establish a baseline for detecting impacts on water quality and quantity.
TN	A minimum of 6 months of monthly sampling for surface water, and may request 1 year of baseline data.	Well samples that are representative of undisturbed groundwater quality.	Same as AL
VA	At least 6 month baseline of sampling for surface water. Sampling must include upstream and downstream data.	At least a 6 month baseline of monthly sampling for groundwater quality	Same as AL
WV	A baseline of water quality and flow for all existing surface water for at least 6 months with 1 sample per month. Sampling and analysis according to OSMRE methods. Data are used with models to predict the probable hydrologic consequences.	Well level determinations (if landowners allow access). Sampling and analysis according to OSMRE methods. Data are used, with models, to predict the probable hydrologic consequences.	Actively uses pre-mining water quality to help predict post-mining water quality. Performs pre-mining WQ assessments to establish baseline to detecting any impacts on water quality and quantity.

area. Water samples must include flow, and be analyzed for: total dissolved solids (TDS) or specific conductance, total suspended solids (TSS), pH, total iron, total manganese, acidity, and alkalinity. Additional parameters may be required to adequately characterize the site. For groundwater, a minimum

of 6 months of 1 sample per month is required for operator installed wells and for residential/domestic wells in or within 1000 feet of the permit area. In addition to water level, samples must be analyzed for the same parameters as required for surface water samples.

Kentucky requires six ground water samples over a period of six months prior to mining, and quarterly during mining operations. The data should be adequate to characterize each affected aquifer and hydrogeologic regime. Surface waters should be sampled at each affected watershed.

Maryland requires at least 6 months of 1 sample per month or quarterly samples for one year that include iron, manganese, aluminum, sulfate, alkalinity, and acidity for surface streams.

Premining water quality assessments are performed in Ohio in order to establish a baseline for detecting any mining or reclamation impacts on ground and surface water quality and quantity and to assess the cumulative hydrologic impacts of the proposed operation. Ohio currently requires at least one sample per month for six consecutive months or two samples, one during a high flow period and one during a low flow period to determine seasonal variations, with the periods substantiated with supporting data. Only one sample is generally required from existing water impoundments (especially those from unreclaimed mining operations). The applicant must sample for pH, total acidity, total alkalinity, specific conductivity or total dissolved solids, total manganese, total sulfates, total iron, total suspended solids, total hardness, and flow. Other parameters may be required. Sites reviewed are generally within 1000 feet of the proposed operation, although the review area can be extended on a site-specific basis.

However, changes will likely be implemented in near future. Under the draft, one high flow window, one low flow window, and two intermediate flow windows have been defined, based on historic flow patterns. Each required surface water and ground water site (other than existing impoundments from previous unreclaimed mining) must be sampled in the high flow, the low flow, and one intermediate flow window.

All identified aquifers must be sampled under seasonal conditions. The applicant must sample for pH, total acidity, total alkalinity, specific conductivity or total dissolved solids, total manganese, total sulfates, total iron, total suspended solids, total hardness, flow (for springs and deep mine discharges)and static water level (for wells). Other parameters may be required. Sampling must be conducted on at least ten (all if less than ten), or 25% of the groundwater sites, whichever number is greater. Sites reviewed are generally within 1000 feet of the proposed operation, although the review area can be extended on a site-specific basis.

Pennsylvania requires both ground water and surface water quality data. Groundwater data can be from either onsite or nearby residential wells (within 1000 feet) that, in addition, must be sampled during mining as a permit requirement. Groundwater analyses must include pH, alkalinity, acidity, iron, manganese, sulfate, specific conductance, and suspended solids. Results of the analyses are compared with NP values for consistency. Surface water quality requirements include a background sampling program of 2 samples of any surface flows or seeps. Monitoring points are then chosen from among these background sampling points to be sampled monthly for 6 months, including at least 1 month of low flow in July, August, or September. Analysis is the same as for ground water, with the addition of aluminum for high quality streams.

Tennessee requires a minimum of 6 months of monthly sampling for surface water, and may request 1 year of baseline data for areas that are considered at risk for AMD production. They also request well samples that are representative of undisturbed ground water quality.

Virginia requires at least 6 months of monthly sampling for both surface and groundwater quality. Stream sampling must also include data from both upstream and downstream of the permit area.

West Virginia requires the applicant to establish a seasonal baseline of water quality and flow for all existing surface water of at least 6 months with 1 sample per month. West Virginia also requires well level determinations (if landowners will allow access), and sampling and analysis of ground and surface waters according to OSMRE methods. Together with mathematical models, these data will predict the probable hydrologic consequences of the proposed operation.

GROUNDWATER CHEMISTRY FROM ADJACENT PREVIOUSLY MINED AREAS AS A PREDICTION TOOL

Water quality from prior mining has been used as a prediction tool since at least the early part of the twentieth century. More recently, Brady and Hornberger (1990) and Brady (1998b) discussed the use of post-mining water quality from adjacent sites as a prediction tool for surface mines. The assumption is that if the same coal and overburden are being mined and the mining conditions are similar, hydrogeologic conditions will be sufficiently alike so that the groundwater quality from the proposed mine will approximate that of the previously mined area. Frequently, this is the case. Groundwater chemistry from previous mining, when available and used properly, can be the best prediction tool in the tool kit. In fact, as subsequently discussed, there are times when the requirement for acid-base accounting (ABA) is waived in some states because water quality from previous mining has demonstrated that mining can occur without pollution.

The major advantage of looking at the quality of pre-existing mine drainage is that it is the result of a full-scale weathering (leaching) test, which has incorporated into it climatic, mining and other variables. Climatic variables include site-specific precipitation and field temperatures, including any seasonal variations. Field conditions also include infiltration and runoff factors. The mining variables include the strata (lithologies) encountered by mining, including its variability within the site, and the redistribution of these rocks in the spoil. Other variables include spoil pore gas chemistry, including vertical variations, and real world scale (i.e., rock particle size, ratios of rock volume to water volume). These are factors that are only approximately simulated, if at all, in laboratory leaching tests. Studies of previous mining also provide information on actual concentrations of mine drainage constituents, including pH, alkalinity, acidity, Fe, Mn, Al, and sulfate. Interpretation, however, requires an understanding of the limitations of this method.

The most confident predictions of post-mining water quality will always be those made using a variety of prediction tools, especially if each tool points toward the same conclusion. Adjacent mining is often given precedence when prediction tools are conflicting. Much more often than not (although there are exceptions), if post-mining water quality at adjacent mines is good, the ABA will likewise show calcareous overburden and pre-mining water quality will be alkaline.

However, certain factors must be considered when interpreting water quality from previously mined areas: whether the proposed mining is on different coals and overburden, whether mining is on the same seam(s) but with significant differences in stratigraphy or in amount of area disturbed, and whether potential hydrologic complications or differences in mining practices exist. Each of these, if not properly taken into account, can lead to improper predictions of water quality for the proposed surface mine.

Proper Correlation of Sedimentary Units

Predictions of water quality based on what has occurred at nearby mines can only be valid if the same coal seam(s) and strata are being considered. Accurate geologic maps that show coal croplines and structure are an extremely helpful aid in assuring correct correlations of coal seams. Numerous excellent studies by the state geological surveys have helped resolve stratigraphic correlation problems. Local geologic reports also show stratigraphic correlations, locations of coal outcrops, and structure. However, site specific and nearby permit drilling information should always be used to confirm correlations.

Some examples will illustrate the importance of knowing which coal seams were mined. The first example involves the Clarion and lower Kittanning (LK) coals in Redbank Township, Clarion County, Pennsylvania. Water quality associated with the LK seam is typically acidic, and is consistent with results of ABA, which shows up to 30 ft (10 m) of strata with % S frequently being 0.5 to 7.5%.

The marine Vanport limestone occurs stratigraphically between the Clarion and the LK coals. Although no ABA was performed on the Vanport in this vicinity, it typically has greater than 80% calcium carbonate. The limestone is about 6 ft (2 m) thick in the area of the mine site. Where the spoil is predominately Clarion coal overburden, the drainage is net-alkaline. Mine discharges predominantly associated with the LK coal are net-acidic. Discharges that are a mixture of Clarion and LK spoil range from net-alkaline to net-acidic. The mixed spoil, even when acidic, is less acidic than water from areas where just the LK coal was mined. Thus, the overburden from the two coals produces different water qualities.

The importance of knowing which coals were mined in an area is also illustrated by a study near Luthersburg in Clearfield County, PA (David Bisko, DEP hydrogeologist, personal communication, 1991). The lower through upper Kittanning (UK) coals were mined. The lower and middle Kittanning (MK) coals, if surface mined by themselves, produce acidic drainage. If these coals are mined in conjunction with sufficient calcareous strata associated with the UK coal, the water quality is usually alkaline. Most mines in the area did multiple seam mining, although the combination of seams mined varied from site to site. Overburden above the LK and MK coals is high in sulfur (up to 2.7%), but low in NP. The highest NP's are associated with the Johnstown limestone, which occurs below the UK coal.

The point of the above examples is that mines having similar geology can be meaningfully compared but that mines involving different sections of strata should not be compared. Overburden chemistry above one seam should never be relied upon to represent a different seam. Water quality prediction requires knowing the stratigraphic relationships of the coal seams that were mined, and seam specific data is required.

It is also necessary to accurately correlate drill holes within a mine site. If drill logs are not accurately correlated, the interpretation is erroneous.

Effects of Variations in Stratigraphy, Weathering and Disturbed Area

Mining may be proposed on the same seam, but if there are significant stratigraphic changes between the previously mined area and the proposed area, comparisons may be inappropriate. The two most common factors related to stratigraphic changes are geologic facies differences from one mine to the next, and the mining of differing amounts of cover. Higher cover will encounter additional strata. An additional factor is the role that differing amounts of disturbed area can have on water chemistry.

Paleoenvironmental maps can help predict the distribution of facies; however, studies of this type are rare. Even if good paleoenvironmental maps exist, facies changes can be abrupt, and detailed drilling is typically necessary in areas of facies transition. Paleoenvironmental maps probably are best used as a tool for designing an overburden sampling plan.

An example of the role of facies changes can be illustrated by six mines studied in the Stony Fork watershed in Fayette County, Pennsylvania (Brady et al., 1988). All mined the UK coal seam. The mines developed in the area interpreted as a high-energy depositional environment have sandstone and siltstone overburden. The sandstone and siltstone units are not calcareous, whereas the low-energy deposits contain calcareous shale and freshwater limestones. Mines in the area containing the calcareous strata produce alkaline drainage. Mines with predominately sandstone overburden produce acidic drainage.

One mine is within both the high- and low-energy depositional environments. Inspection of the active highwall revealed an area where the limestone was eroded and replaced by a channel deposit. All the overburden drill holes were located within the low-energy portion of the mine, thus over-estimating the calcareous nature of this site. This permit was issued prior to an understanding of the lateral distribution of depositional facies. If the true nature of the site had been known, the permit would have been denied or the mining plan would have been modified to compensate for the acid potential of the sandstone overburden.

Different amounts of cover mined on the same coal seam can also result in different water quality. Because of equipment limitations, old pre-act mining from the 1940s and 1950s seldom exceeded 40 ft (12 m) of cover. Improvements in mining technology have allowed many of these sites to be remined to greater cover heights. Mining of additional cover can have both positive and negative influences. Figure 2.7 illustrates a situation where low cover mining ~40 ft (12 m) or less would encounter high sulfur strata, but no appreciable calcareous strata. A mine would not encounter calcareous strata until a highwall height of 40 ft (12 m) or more was reached, due to the stratigraphic position of the calcareous strata and the dissolution of carbonates by surface weathering. Shallow mining <40 ft (12 m) would probably result in acidic drainage, whereas mining to a cover height of 85 ft (26 m) should encounter enough calcareous rock to result in alkaline drainage.

An example of where mining more overburden resulted in a deterioration of water quality is illustrated in Brady (1998b). The original shallow-cover <30 ft (10 m) mining occurred in the 1950s, and only a few tens

of acres were affected. This site had some acid-producing strata located near the coal, and essentially no calcareous strata. The water quality in 1978 through 1981 had low concentrations of sulfate, acidity, manganese, and aluminum, and little variation in their concentrations. Specific conductance was also low (~100 μS/cm). Mining that occurred from Nov., 1980 - Sept., 1985 took a maximum of 80 ft (24 m) of overburden and affected approximately 175 acres (71 hectares). Acidity, manganese, sulfate, aluminum and specific conductivity all increased.

Hydrogeologic Complications

There are several hydrologic complications that can affect the use of water quality from adjacent mines as a prediction tool. The most obvious of these is the situation where there is no water discharging from the previously mined area. This can be falsely assumed to mean success, because there are no contaminated discharges. The absence of discharges does not mean that there is no associated water flowing from the mined area. In the humid climate of the northern Appalachian Basin, groundwater recharges the mine spoil and is undoubtedly flowing somewhere. It may not discharge as seeps or springs, but may be entering a deeper groundwater flow system and ultimately discharging as base flow to a stream or contributing to a discharge from a lower stratigraphic interval.

Adjacent mining as a prediction tool only works where there is representative groundwater (from springs or wells) that can be sampled and analyzed. If groundwater sampling points are inadequate, monitoring wells or piezometers can often be installed into previously mined spoil or into an underlying aquifer to ascertain the post-mining water quality. Groundwater chemistry is rarely uniform through time or through space.

When using water quality data as a prediction tool, it must be kept in mind that water quality, even at the same sample point, is not normally a constant, but will vary for a variety of climatic reasons such as seasonal influences and precipitation/infiltration events. In some instances, not only water quality, but also water quantity must be considered. Flow can affect concentration of water quality parameters.

Not all mines respond similarly. Smith (1988) and Hornberger et al. (1990), in discussing flow, concentration, and load, point to three types of discharges. Brady (1998b) describes a fourth type of discharge that is also discussed below. The four types of discharges are:
>   1. High flow - low concentration / low flow - high concentration response, where the flow rate varies inversely with concentration and variability is generally very great;
>   2. Steady or damped response discharges that exhibit relatively minor or delayed response in flow rate with minor changes in chemical characteristics;
>   3. "Slugger" response, where dramatic increases in discharge are accompanied by little change in concentrations, resulting in large increases in loading; and
>   4. "Slammer" response, where dramatic increases in discharge are accompanied by increases in concentration, resulting in extremely large increases in loading.

Since mine drainage discharges vary in response to climatic events, to accurately characterize mine discharge chemistry, it is necessary to have multiple samples that truly represent seasonal variation and

climatic events such as rainfall and snowmelt. The "slugs" and "slams" of sulfate and acidity following rain events at some sites are apparently due to soluble sulfate salts that build up during dry periods as a result of pyrite weathering in the unsaturated mine spoil. These salts are essentially stored mine drainage. Infiltrating waters from rainfall or snowmelt dissolve these salts, and flush them into the saturated groundwater zone (Brady, 1998b). If one fails to sample the site during such events, an important component of the site water chemistry may have been missed.

Another complication in interpreting mine site water quality is that water chemistry can vary within a mine, to the extent that some mines produce both alkaline and acidic water (Brady, 1998b). In addition, even at sites that produce either alkaline or acidic water, water quality trends may change over time. The point to be made here is that a single sample may not reflect the true character of water being produced by a mine.

Another thing that must be kept in mind about groundwater is that its chemistry can change along its flow path. Dissolution or precipitation of minerals can alter the original chemistry of the mine drainage. When conditions allow for oxidation of iron, spoil water within the subsurface may be high in iron, and have a higher pH, than a surface discharge from the "toe" of the spoil. As an acidic plume travels through calcareous rocks, some attenuation of the mine drainage quality should occur. Also, groundwater samples may be a mixture of water from mined and unmined (or mined on a different seam) sources.

Interference from other sources of contamination can also complicate interpretation. Mine drainage from coal mines, however, is typically distinct enough in chemistry that other sources can be readily identified. For example, mine drainage is notorious for containing elevated sulfate, but surface mines normally have low chloride concentrations. Gas and oil well brine waters, on the other hand, have low sulfate in comparison to the high chloride concentrations. The differences are so distinct that they should not be confused. However, sometimes water from the two can commingle, producing a mixed chemistry.

The bottom line is that caution must be exercised when interpreting groundwater chemistry from previously mined areas. Multiple samples from the same location and multiple sample locations, plus an understanding of the groundwater hydrology, are invaluable and will contribute to accurate interpretations of the data.

Surface water is more difficult to use as a prediction tool than groundwater. This is due to dilution of mine drainage by runoff, mixing of waters from tributaries that are not impacted by mining, groundwater baseflow from areas unaffected by mining, flow of ground or surface waters affected by mining on a different seam of coal, and alteration of water quality by oxidation and precipitation of metals (Brady, 1998b). Stream water quality can be useful, however, in presenting a "broad-brush" view of mining-related problems over a large area. It is most useful for relatively conservative parameters such as sulfate and manganese. Surface water quality studies such as Wetzel and Hoffman (1983, 1989) can show broad regional trends in water quality. However, unless more detailed information is available, such as what seams were mined, how much of the watershed was mined and what mining and reclamation practices were used, this information is not generally useful for predicting water quality for a proposed mine site.

Differences in Mining Practices

Differences in mining practices must be considered when water quality from previous mining is being used to make predictions. Recent advances in surface mining practices have the potential to favorably affect water quality, as compared to old pre-act surface mines. Examples are concurrent reclamation, alkaline addition, special handling, and engineering water movement through or around the backfill. A site that includes these pollution prevention measures may produce different quality water than sites that did not.

Mine sites that clearly employed adverse practices may be producing water of poorer quality than what a proposed mine site would produce employing favorable mining practices. Mining practices that could have adversely affected surface mine water quality include disposal of refuse from a coal processing plant, auger mining, improper handling of acidic strata, and non-concurrent reclamation. Other mining practices that may influence post-mining water quality are the type of mining equipment used (dragline vs. trucks and loaders vs. bulldozers), and the length of time a pit remains open and exposed to weathering.

Regulatory agency experience has shown that long-term interruptions in mining and reclamation on surface mine sites with low NP overburden can result in poor post-mining water quality. During the cessation, the acidic spoil is left exposed to the elements to weather and form acid products. When comparing mines on the same coal seam that were mined concurrently with mines that had long-term interruptions, the areas that were mined intermittently frequently had poorer water quality.

Water quality from underground mines may differ significantly from surface mine water quality on the same coal seam. As a general rule of thumb, if an underground mine on a particular coal seam is making alkaline drainage, a surface mine on that same seam will also produce alkaline drainage. The inverse, however, is not necessarily true. If an underground mine is discharging poor quality water, it should not be assumed that a surface mine on the same seam will also produce poor quality water. The reason for poorer water quality from underground mines relative to surface mines is that in underground operations, the strata with the maximum disturbance and exposure to weathering is the coal, roof rock and floor rock. This rock frequently has the greatest amount of pyrite in the overburden. Post-mining caving and collapse of the mine roof and crushing of coal pillars increases the surface area of these pyritic rocks. Water and air flowing through the mine will cause pyrite in the rock to oxidize. In contrast, at surface mines, almost all of the coal is extracted and removed, and stratigraphically higher overburden rock is disturbed. If this overburden rock is calcareous, alkalinity generation can neutralize acid and inhibit pyrite oxidation.

"Daylighting" (remining an underground mine by stripping) can thus dramatically improve water quality (Brady, 1998b; Skousen et al., 1997). For example, at a site mined in Allegheny County, Pennsylvania during the early 1900's, water samples collected in 1974 had a pH below 3 (Pennsylvania DER, 1976). Aloe Coal Company began daylighting the underground mine in the mid-1970's. They daylighted approximately 60 percent of the mine (John Davidson, mine inspector, personal communication in Brady, 1998b). Aloe mined up to 250 ft (87 m) of cover, which is not normally economical; however, this was a "cost-plus" operation (the coal buyer paid costs, plus a profit). There are several freshwater limestone units that were encountered by Aloe, the thickest being the Benwood, which is frequently 50 ft (15 m) thick.

After daylighting, the water had a pH above 7 (1995). Most daylighting will not encounter as much calcareous strata as in the above example and the water quality improvements may not be as spectacular; however, when calcareous materials are encountered during daylighting operations, water quality does generally improve.

State Practices

State practices for the evaluation of data from adjacent mining activities are outlined in Table 3.3.

Alabama permits reviewers look at adjacent permits and make those files available to the applicant. The applicant is required to prepare a 1:2000 scale site map with their hydrologic reclamation plan that includes surrounding mines, the new permit area, monitored streams, and ABA sampling locations. The applicant is also required to collect baseline water quality data on adjacent mines, including all discharges, seeps, and surface streams. The permit reviewer looks at adjacent mining ABA analysis and coal sulfur to compare for consistency with the submitted ABA results for the new permit. Special handling, alkaline addition, or mining practices that may have affected post-mining drainage quality on adjacent sites are also identified.

Illinois and Indiana do not require adjacent mine data, though an operator can include applicable information from adjacent operations. However, information is required for baseline data for wells and streams within 1000 feet (and sometimes more) of the permit area. Available information from adjacent sites is used during permit review. The states may use their own resources to determine the cause of any AMD on adjacent sites and may request the applicant to address the suspected cause. The permit reviewer will compare ABA and water quality analysis from the applicant with data from adjoining sites for consistency. Special attention is given to known acid-producing units to ensure that they are identified and accounted for.

Kentucky may require data from adjacent sites, if problems were previously identified there. Data required may include drainage water quality, overburden quality, and details of the mining history and any spoil handling practices.

Maryland requires 1 to 2 water quality samples from the applicant for every expression of surface water on adjacent mines. The reviewer compares the ABA analysis from the applicant with the ABA data from adjacent sites for consistency, and identifies any special handling, alkaline addition, or mining practices that may have affected post-mining drainage quality.

Ohio requires the applicant to analyze any existing water quality data from nearby permits and to present the data in the form of tables, graphs, or spreadsheets. The permit reviewers also examine geologic and hydrologic data from adjacent mines.

Pennsylvania considers data from adjacent, reclaimed mining to be the most important tool in pre-mining AMD prediction. As a result, only about 50% of new permit applicants are required to provide overburden analysis based on the post-mining discharge quality at adjacent sites. Applicants are required to do an exhaustive background sampling of all accessible discharges within 1000 feet of the new permit or any discharges that are considered hydrologically connected to the new permit. Pennsylvania also reviews all the available adjacent permit applications to check overburden analysis and geologic correlation for

Table 3.3. State requirements for data from adjacent mining activities.

State	Requirements	Comments
AL	A hydrologic reclamation plan with a 1:2000 scale site map. Baseline data on adjacent mines should include seeps, discharges, and streams.	Files from adjacent permits are available. Reviewers compare adjacent mining ABA analysis for consistency with the ABA submitted with the new application. Special practices on adjacent sites are also identified.
IL, IN	Not required.	Data from adjacent sites, if available, is used internally. Agency may use own resources to determine cause of any AMD, and then require the applicant to address the issue. Reviewers compare adjacent mining ABA analysis and water quality analysis for consistency with the ABA submitted with the new application.
KY		May require data from adjacent sites if problems were previously identified there, including drainage water quality, overburden quality, and details of the mining and spoil handling practices.
MD	1 to 2 water quality samples for every expression of surface water on adjacent mining.	Reviewer compares ABA analysis from the applicant with ABA data from adjacent sites, and identifies any special practices that may have affected post-mining drainage quality.
OH	Must present any existing water quality data from nearby sites.	Reviewers also look at geologic and hydrologic data from adjacent mines.
PA	Exhaustive background sampling of accessible discharges within 1000 feet of the new permit or any discharges considered to be hydrologically connected to the new permit.	Data from adjacent, reclaimed mines considered the most important tool in pre-mining AMD prediction. Only about 50% of new applicants are required to provide overburden analysis, based on adjacent site post-mining discharge. All adjacent permit applications are reviewed for consistency, and to identify any special practices that may have affected water quality.
TN	Site surveys on adjacent mines for surface discharges, seeps, and streams. At least 1 water sample for any identified surface water sources.	Reviewers compare ABA analyses from the applicant with ABA from adjacent sites for consistency, and identifies any special practices that may have affected post-mining drainage quality.
VA	No mandatory requirement to submit adjacent mining data.	Data from adjacent mining is used internally. If an adjacent mine has AMD, VA may determine the cause and request the applicant to address it in the application. Reviewers compare ABA analyses for consistency. Special attention is given to known acid-producing units.
WV	No mandatory requirement to submit adjacent mining data.	Data from adjacent mines is used internally. ABA analyses are compared for consistency, and to identify any special practices that may have affected post-mining drainage quality. Emphasis placed on field inspectors' knowledge, their experience with AMD production on nearby permits, and the willingness and ability of operators to follow special handling and mining requirements.

consistency, and to identify any special handling, alkaline addition, or coal or coal preparation waste disposal provisions that may have affected final discharge water quality. Reviewers pay particular attention to inspection reports on adjacent sites for problems or violations, for example, citations for not abiding by

special handling provisions, unauthorized addition of alkaline or acidic material, and violating concurrent reclamation requirements.

Tennessee requires site surveys on adjacent mines for surface discharges, seeps, and streams. At least 1 water quality sample must be submitted from the applicant for any identified surface water sources. The permit reviewer compares the ABA analysis from the applicant with the ABA from adjacent sites for consistency, and identifies any special handling, alkaline addition, or mining practices that may have affected post-mining drainage quality.

Virginia uses data from adjacent mines internally during the permit review process, but does not have any mandatory requirement that permit applicants submit such data. If an adjacent site has any AMD discharges, the reviewing agency may use its own resources to determine the cause and then request the applicant to address the suspected cause in the permit application. The reviewer also compares the ABA analysis from the applicant with any ABA data that is available from adjacent sites for consistency. Special attention is given to known acid-producing units in the permit area to ensure that they are identified and accounted for by the applicant.

West Virginia also uses data from adjacent mines internally during the permit review process without any mandatory data requirement of the permit applicants. The reviewer compares the ABA analysis from the applicant with the ABA from adjacent sites for consistency, and identifies any special handling, alkaline addition, or mining practices that may have affected post-mining drainage quality. Permit reviewers place special emphasis on the knowledge of field inspectors, discussing with them their experiences with AMD production on any nearby permits, and the willingness and ability of those operators to follow any special handling and mining requirements that may have been in place.

HYDROLOGIC CONTROLS

The installation of hydrologic controls, such as highwall drains, floor drains, and surface diversions, can impact post-mining water quality by influencing what materials are encountered by the ground water and the final discharge rate. Hydrologic controls can either enhance drainage, deter it to cause permanent inundation, or be used in conjunction with special handling in an attempt to prevent acid formation. State practices for hydrologic controls are outlined in Table 3.4.

Illinois and Indiana do not require surface infiltration controls except for special situations, such as coal processing waste disposal areas. Ohio requires that all surface drainage be directed to a properly designed sediment control structure, but will grant exemptions for small areas if suitable alternative measures are implemented. The applicant must also describe how the pre-mining recharge capacity will be restored. All of the other states except Kentucky identified the active use of surface infiltration controls, mostly in the form of diversion ditches or french-type drains, to limit the amount and exposure of water to potentially acid materials in the backfill. Maryland, Pennsylvania, Tennessee, Virginia, and West Virginia also note the use of spoil sub-drains and highwall drains in conjunction with selective spoil handling to control post-mining water levels and maintain a *high and dry* isolation environment for acid-producing material. West Virginia also allows encapsulation.

Table 3.4. State practices for hydrologic controls

State	Hydrologic Control Practices
AL	Surface infiltration controls actively used, mostly in the form of diversion ditches or french-type drains, to limit the amount and exposure of water to potentially acid materials in the backfill.
IL, IN	Not actively required except for special situations, such as for coal refuse.
KY	Did not identify any surface infiltration controls.
OH	All surface drainage must be directed to a properly designed sediment control structure. Exemptions may be granted for small areas if suitable alternative measures are implemented. Applicant must also describe how the pre-mining recharge capacity will be restored.
MD, PA, TN, VA	Surface infiltration controls actively used to limit the amount and exposure of water to potentially acid materials in the backfill. Spoil sub-drains and highwall drains are also used, in conjunction with selective spoil handling to control post-mining water levels and maintain a *high and dry* isolation environment for acid-producing material.
WV	Surface infiltration controls actively used to limit the amount and exposure of water to potentially acid materials in the backfill. Spoil sub-drains and highwall drains are also used, in conjunction with selective spoil handling to control post-mining water levels and maintain a *high and dry* isolation environment for acid-producing material. Also allows encapsulation.

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CHAPTER 4: STATIC TESTS FOR COAL MINING ACID MINE DRAINAGE PREDICTION IN THE EASTERN U.S.

by

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INTRODUCTION

Accurate prediction of post-reclamation water quality requires an understanding of many factors, including overburden geochemistry, the method and precision of overburden handling and its placement in the backfill, and site hydrology. Most of the work in prediction has focused on methods to quantify overburden geochemistry. Overburden analysis and characterization provide important information about which strata are acid-producing, potentially acid-producing, neutral, or alkaline. Identification of potential problem overburden aids in developing overburden handling and placement plans. It is then critical for each operator to carefully follow the overburden handling and placement prescription based on the site's overburden characterization.

Overburden analysis to predict overburden quality is not a new concept. Overburden characterization probably developed in Germany during the 1950's (Knabe, 1964), and researchers in the U.S. recognized the importance of overburden characterization for acid mine drainage prediction as early as 1960 (Cornwell, 1966; May and Berg, 1966). This chapter summarizes the laboratory procedures that are available to analyze overburden, as well as current overburden characterization practices in seven eastern mining states, and then provides some recommendations.

STATIC TESTS AVAILABLE FOR PREDICTING ACID MINE DRAINAGE

Acid-Base Accounting

Acid-base accounting (ABA) is an overburden analytical technique that evaluates the most important properties of a rock unit relative to its potential for immediate and future pollution. Early reclamationists realized that the reclamation potential of surface mined areas (relative to plant establishment and growth) was directly connected to the quality of the overburden material placed at the surface. Many early surface mine operators turned the overburden upside down, relative to its original position, as the overburden was removed to reach the coal. Such an operation left unweathered gray or black material associated with the coal bed on the surface. In many situations, the associated sulfur-bearing minerals produced acidic conditions in the minesoil and may have also caused an AMD problem (Greene and Raney, 1974).

Some of the earliest documented work on reclamation of surface mined areas was directed at revegetation efforts (Smith and Tyner, 1945; Tyner et al., 1948). These reports from West Virginia acknowledged the effects of minesoil quality on plant growth and identified three types of overburden material based on rock composition and degree of acidity. A minesoil classification system proved useful to reclamationists in determining lime and fertilizer rates and selecting plant species adapted to these specific minesoil conditions. Because minesoil classification systems proved useful for revegetation, similar systems were subsequently

developed for other coal mining areas including the mid-eastern coal region (Limstrom, 1948), Pennsylvania (Davis, 1965), and eastern Kentucky (Soil Conservation Service, 1973). Nevertheless, these systems were not initially used to predict drainage quality from disturbed sites.

Knabe (1964b) provided one of the earliest examples of characterizing alkaline versus acid materials. He refined overburden classification by placing a positive or negative number as a subscript. A positive subscript detailed the percent of $CaCO_3$ in the minesoil, while a negative number expressed the percent of potential unneutralized SO_4 (the sulfides or pyrite was expressed as SO_4). For example, A_{15} was a minesoil suitable for agriculture (A meaning alkaline, and 15 being the percent calcium carbonate in the material). A minesoil with the designation of T_{-10} was toxic with as much as 10 percent of the material being potentially unneutralized SO_4. Later, Knabe reported that he used a method called a "base-acid balance," which balanced the sum of all bases against all acids. The acids included acid-producing minerals (sulfides) and exchangeable acids like aluminum and iron (Knabe, 1973). His system accounted for the ultimate quantity of acidity or alkalinity that could be produced in the material upon weathering.

The early minesoil classification systems were useful but a premining method or technique was needed that could distinguish between materials that could be placed on the surface for revegetation and materials that should be buried beneath the rooting zone. Soon after Knabe reported on his work, researchers at West Virginia University (WVU) began developing a system for balancing the acid- and alkaline-producing potential of overburdens prior to disturbance. These WVU researchers first studied overburdens in Preston County, West Virginia and defined the acid-producing potential of rocks associated with the Freeport and Kittanning coal beds. Dr. Richard M. Smith recommended that sulfur (S) profiles and neutralization capacities should be determined for all stratigraphic sections from the surface down to and immediately underlying the coal bed before mining (West Virginia University, 1971). The West Virginia University researchers quantified acid-neutralizing materials in overburdens and developed the term neutralization potential (NP) (Smith et al., 1974).

The method of ABA was first described in 1973 (Grube et al., 1973). Logging of overburden cores and/or observations of a fresh highwall are used to distinguish geologic layers. Each of the layers are identified by: 1) color; 2) rock type; and 3) rock thickness. The chemical characteristics of each overburden layer (whether acid-producing, potentially acid-producing, or alkaline-producing) is determined by three measurements: 1) paste pH; 2) total or pyritic S; and 3) neutralization potential (NP). The most important part of the method balances maximum potential acidity (MPA) (from sulfuric acid produced during S oxidation) against total neutralizers (from alkaline carbonates, exchangeable bases, weatherable silicates, and phosphates) (Fig. 3.1). These dominant rock properties produce the most predictable response upon weathering. The MPA of a rock sample is calculated from the total S content. For each %S contained in the material, 31.25 metric tons of calcium carbonate are required for neutralizing the sulfuric acid produced from 1000 metric tons of the material. The NP is determined by reacting a pulverized, 2-gram sample of the rock with a known quantity and strength of acid. The solution is then back-titrated with a known strength of base to a predetermined end point to determine the sample's neutralizing component. Both NP and MPA are determined in parts per 1000 parts of overburden (metric tons per 1000 metric tons).

Further research in other areas in the Appalachian and Eastern Interior Coal Regions confirmed the usefulness and application of ABA (Smith et al., 1976), and final field and laboratory procedures for ABA were published in 1978 (Sobek et al., 1978). Problems with the approach have shown up over time, and various modifications have been suggested. The best are summarized later in this chapter.

Many states began passing laws in the early 1970's requiring prediction of the acid or alkaline nature of overburdens that were to be disturbed. For example, the 1971 West Virginia surface mining and reclamation law required the operator to show in the permit "the presence of any acid-producing materials which, when present in the overburden, may cause minesoils with a pH below 3.5 and prevent effective revegetation." Regulations promulgated to implement the law in succeeding years used acid-base accounting to determine the presence or absence of acid-producing materials in the overburden. Prior to the Surface Mining Control and Reclamation Act (SMCRA), "topsoiling" was seldom practiced. Therefore, ABA was particularly useful in selecting overburden layers that could be placed on the surface as topsoil. It was also used to select materials for special uses (e.g., hard sandstones for rock cores in valley fills, clayey materials for impermeable barriers, etc). ABA was the first technology available to assess the chemical quality of overburdens prior to disturbance. As a result, the concepts of pre-mine planning for reclamation and special handling procedures were formulated. ABA in its original and modified forms has been widely adopted in both the coal and mineral mining industries in the U.S., Canada, Australia and southeast Asia (British Columbia Acid Mine Drainage Task Force, 1989; Miller et al., 1991).

The components of ABA measurements are sometimes referred to by other terms since they have been adapted for use in metal mining and other applications (Miller and Murry, 1988). The term Acid Production Potential (APP) is equivalent to MPA, Acid Neutralizing Capacity (ANC) is equivalent to NP; and Net Acid-Producing Potential (NAPP) is the same as Net Neutralization Potential (NNP) and denoted with a positive or negative prefix.

The quality of drainage from a rock stratum is predicted by subtracting MPA from NP in the sample. If the number for MPA is higher (a deficiency of NP), the rock strata is predicted to produce acidic drainage upon weathering and leaching. If the number for NP is higher (an excess of NP), the rock is predicted to produce alkaline drainage. This 1:1 comparison of acid to base works well when dealing with individual rock units (Skousen et al., 1987). Assessing the quality of drainage that will come from a reclaimed mine site is much more difficult because MPA, NP, and volume in each rock unit in the overburden across the site must be taken into account. There are also many other factors and complex interactions that have an influence on the chemical production potential of rocks including microorganisms, trace elements, depositional environments, forms of pyrite, rare catalytic agents, uncommon compounds, and lithologic peculiarities. Nevertheless, ABA is the most common basis for post-mining water quality prediction (Perry, 1985).

The choice of which stoichiometry of pyrite oxidation most closely describes a mine spoil system directly affects the ABA calculation, alkaline addition rates, and prediction of expected post-mining water quality. Cravotta et al. (1990) noted that the stoichiometry is based on the exsolution of carbon dioxide gas out of the spoil system. They suggested that in a closed spoil system, carbon dioxide is not exsolved, and additional acidity from carbonic acid is generated. Cravotta et al. (1990) proposed that up to four moles

of calcite (or about twice as much) might be needed for acid neutralization. On a mass basis, for each 1% S present, 62.5 metric tons of calcite would then be needed to neutralize the acid in 1000 metric tons of the material. Brady and Cravotta (1992), in analyzing ABA and water quality data from 74 mine sites, showed that correct prediction of post-mining net alkalinity in drainage was improved from 52% to 57% using a stoichiometric equivalence of 62.5. However, a later study (Brady et al., 1994) showed that the 31.25 equivalence factor was more accurate, correctly predicting post-mining net alkalinity in drainage on 31 of 38 mines (82%), while the 62.5 factor correctly predicted 22 of 38 (58%).

Overburden analysis came into widespread use with the passage of SMCRA in 1977. The law requires that an operator must identify in the permit any potentially acid-producing materials in the overburden and determine the probable hydrologic consequences of such materials after disturbance and reclamation. Because little research had been conducted on water quality prediction from disturbed areas, the coal industry and regulatory authorities applied current overburden analytical methods and adapted the available methods to these purposes. ABA, already extensively used in the U.S. and several other countries by this time as an overburden selection tool, was adopted to predict post-mining drainage quality. Its popularity largely stems from its simplicity. However, there has been much controversy concerning the accuracy of such predictions (Erickson and Hedin, 1988; Miller et al., 1991).

One criticism is that the method does not account for the different reaction rates of acid- and alkaline-production in rocks. Other methods to evaluate reaction kinetics or rates include humidity cells or columns (Bradham and Caruccio, 1991; Caruccio et al., 1980; Ferguson and Morin, 1991), hydrogen peroxide (H_2O_2) digestion (Ammons and Shelton, 1988; O'Shay et al., 1990), or soxhlet reactors (Renton et al., 1988). Other options are mineralogical tests (Kwong, 1991), evolved gas analysis (EGA) (Hammack, 1987) and computer modeling (Ferguson and Robertson, 1994; Morin and Hutt, 1988; Rymer et al., 1991). Modifications in the way the acid potential is calculated have been recommended (Cravotta et al., 1990; Smith and Brady, 1990).

diPretoro and Rauch (1988) found that sites which had greater than 3% NP in overburden (or 30 metric tons $CaCO_3$ per 1000 metric tons of material) produced alkaline drainages, while acid drainage resulted at 1% or less NP. Brady et al. (1994) showed that 3% NNP in an overburden caused alkaline drainage while less than 1% NNP produced acidic drainage from 38 mines in PA. Perry and Brady (1995) stated that all sites with ≥2.1% NP (21 metric tons/1000 metric tons) produced net alkaline water, while 72% of sites with ≤1% NP produced net acid drainage. These values are summarized in Table 4.1.

Table 4.1. A generally accepted guideline for defining strata as either acid-generating or alkaline.

	Acid Tons / 1000 Tons	Undecided Tons / 1000 Tons	Alkaline Tons / 1000 Tons
NP	< 10	10 - 21	>21
NNP	< 0	0 - 12	>12

Brady and Hornberger (1990) suggest that NP from ABA shows the strongest relationship with actual post-mining water quality. This relationship is only qualitative (e.g. acid vs. non-acid), and NP must significantly

exceed MPA in order to produce alkaline water. If NP and MPA are similar, acid mine drainage will most likely result.

British Columbia Research Initial Test

The British Columbia Initial Test includes an assessment of the acid-generating potential of a sample compared to its neutralizing capability (Steffen Robertson Kirsten, 1989). In concept and technique, it is similar to ABA, but is sometimes followed by kinetic testing to confirm the initial interpretation. The acid-producing potential is estimated from either a total or sulfide S value. NP is measured by reacting the sample with sulfuric acid (rather than HCl) until a stable endpoint of pH 3.5 is reached. A pH endpoint of 3.5 is used because the bacteria, *Thiobacillus ferrooxidans*, which catalyzes the iron oxidation reaction, is considered to be less significant at pH values above this. The quantity of sulfuric acid consumed is interpreted to represent the neutralizing capability of the sample.

Potential acidity and NP, both expressed in $CaCO_3$ equivalent, are compared to estimate drainage quality. If NP exceeds potential acidity, the sample is considered non-acid or alkaline forming. When potential acidity is greater than NP, or the acid-base balance is nearly equal, the sample may be analyzed further with kinetic tests, such as the British Columbia Research Confirmation Test, or other weathering procedures.

ASTM Carbon/Sulfur Methods

These methods measure the total carbon and total S content by combusting coal, soil or rock materials. The overburden or rock sample is combusted under oxygen flow and converts any carbon or carbonaceous material to CO_2 and any S compounds (organic, sulfate, or sulfide) to SO_2. ASTM D 3177 describes the standard Eschka method for measuring total S in coal materials. ASTM D 4239 uses high temperature combustion methods to determine total S. SO_2 released during combustion is captured and measured in several ways. Method A in ASTM D 4239 uses an acid-base titration to determine the amount of SO_2 released. Method B in ASTM D 4239 uses a solution containing iodine to collect the combustion products and the solution is titrated to determine the amount of SO_2 released. Method C in ASTM D 4239 uses an infrared (IR) absorption detector with microcomputer capabilities to determine SO_2 released. ASTM D 5016 also describes measuring total S in ash and coal materials through combustion and IR absorption.

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ACID POTENTIAL

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Sulfur Forms

Sulfur in coal and associated strata can occur as organic S, sulfate S, and sulfide S. Organic S is complexed within the coal plant material and is organically bound within the coal. This form is only found in appreciable quantities in coal beds and in other carbonaceous rocks. Generally, the organic S component is not chemically reactive and has little or no effect on acid-producing potential. The organic S content of coal and other organic soils can be as high as 0.5% (w:w basis).

Sulfate S is usually only found in minor quantities in rocks of humid areas, but can be present in substantial amounts in more arid areas where leaching is limited. Sulfate is a reaction product of S oxidation. If gypsum ($CaSO_4$) is formed, no more acid is generated because gypsum is a neutral salt. If jarosite ($KFe_3(OH)_6(SO_4)_2$) is formed, then additional acid may be produced by the oxidation of this transient mineral. Acid generation from the oxidation of jarosite would not be large because of jarosite's low solubility ($K_{sp} = 10^{-98.6}$, Vlek et al., 1974). Carson et al. (1982) obtained jarosite (87% pure) from a soil and found that its titratable acidity was 18.7 cmol/kg compared to its theoretical acidity value of 522 cmol/kg.

Sulfide S is the predominant S species in the majority of overburdens and is the S form of greatest concern. Of all the sulfide minerals that may be present, the predominant sulfides are minerals containing iron such as pyrite or marcasite (FeS_2). In some areas, copper (chalcopyrite), lead (galena), and zinc (sphalerite) sulfides can also be found. These minerals are generally far less reactive than iron sulfides due to the greater stability of their crystal structures and the formation of low solubility products that encapsulate them, preventing further weathering (Knapp, 1987).

Iron disulfides are the major acid-producers, and variations in total S and MPA of overburden samples correlates closely with the pyritic S content (Caruccio and Geidel, 1978). Caruccio et al. (1988) provided an extensive review of the different forms and morphologies of pyritic materials.

The formation of acid from the oxidation of pyrites and other sulfide compounds is well known (Grim and Hill, 1974; Nordstrom, 1982). The equation of pyrite oxidation shows that 1000 metric tons of material containing 0.1% S, all as pyrite, would yield upon complete reaction 3.125 metric tons of acidity. 3.125 metric tons of $CaCO_3$ would have to be added to neutralize the acidity. The total S content of the rock accurately quantifies the acid-producing potential (APP) when S in the overburden rock is exclusively pyrite. However, in most cases, not all pyrite oxidizes, and when organic and/or sulfate S are present in significant amounts, total S measurements clearly overestimate the amount of acid that will be formed upon oxidation. However, the use of total S values to determine APP is generally accepted since intentional overestimation of the APP of rocks gives a margin of safety. Overestimation of the APP also helps deal with uncertainties such as rates of reaction (pyrite often reacts faster than carbonates in the system), poor mixing of overburden materials during backfilling, and inconsistent and random contact with water in the backfill. Therefore, maximum potential acidity (MPA) of a rock unit is calculated when the total S value is used. Removal of sulfates and organic S may be necessary to increase accuracy in predicting the APP of partially weathered materials containing mixed S species.

The rate of pyrite oxidation depends on numerous variables such as reactive surface area of pyrite (Singer and Stumm, 1968), ferric iron concentrations and other catalytic agents (Singer and Stumm, 1970), oxygen concentrations and solution pH (Smith and Shumate, 1970), forms of pyritic S (Caruccio et al., 1988), and presence of *Thiobacillus* bacteria (Leathen et al., 1953). The possibility of identifying and quantifying the effects of these and other controlling factors with all the various rock types in a field setting is unlikely. However, precise knowledge regarding the oxidation rates is generally not needed for most field situations.

Methods to Determine Acid Potential

Procedures to determine acid potential generally fall into one of two categories:
1) determination of total S content and use of a stoichiometric equation for pyrite oxidation to calculate MPA;
2) titration of acidity after oxidation of the sample by a strong chemical oxidant (hydrogen peroxide) or after a rigorous simulated weathering procedure (see Kinetic Test section).

Furnace Combustion—The most popular and easiest methods are those that determine total S content. The analysis is usually accomplished using high-temperature furnace combustion. The sample is heated to approximately 1350^0C while a stream of oxygen is passed over the sample (ASTM D 4239). Sulfur dioxide released through combustion can be measured in several ways. Using a LECO Induction Furnace with Automatic Sulfur Titrator, the SO_2 is collected in a 0.2M hydrochloric acid (HCl) solution containing potassium iodide, starch, and a small amount of potassium iodate. The solution is then titrated with a standard potassium iodate solution to determine S content. Using infrared absorption, the resultant SO_2 gas is detected by infrared absorption and compared to a standard calibration.

Eschka Method—The Eschka method (ASTM D 3177 Method A) is a gravimetric procedure using wet chemistry and barium chloride precipitation. A portion of the overburden sample is heated with an Eschka mixture to convert all S to sulfate. The sulfate is then leached with hot water and precipitated as barium sulfate ($BaSO_4$). The total S content is calculated from the weight of $BaSO_4$. The Eschka method agrees closely with the LECO S Furnace for determining total S in coal but the mixed mineralogy of overburden complicates the technique and introduces error (Scholz and Rathleff, 1982). For routine S analysis of coals and overburden materials, the S furnace is recommended.

Bomb Washing—The Bomb Washing method determines total S by combusting an overburden sample in an oxygen bomb; the contents of the bomb are washed into a beaker, neutralized and filtered (Noll et al., 1988; ASTM D 3177 Method B). The S in the filtrate is precipitated as $BaSO_4$, filtered, and ashed. The ashed $BaSO_4$ residue is then weighed to determine the total S in the sample. Most samples will not sustain combustion so a combustion aid is required to quantitatively determine the S content.

X-Ray Diffraction—X-ray diffraction is the scattering of x-rays by mineral crystals, with accompanying variation in intensity due to interference effects. X-ray diffraction analysis evaluates the crystal structure of materials by passing x-rays through them and recording the diffraction (scattering) image of the rays. For inorganic, crystalline minerals, x-ray diffraction has been established as probably the most important, convenient and unambiguous technique applied to the study of soil and overburden mineralogical composition (Bish, 1994). Pyrite and other sulfide minerals, as well as calcite and dolomite can be determined by x-ray diffraction, but the analytical error associated with x-ray diffraction is relatively high, between 5 to 20% of the sample value.

X-Ray Fluorescence—X-ray fluorescence spectrometry, also called x-ray spectroscopy, x-ray emission spectrography and x-ray spectrochemical analysis, is a widely used analytical technique in laboratories

concerned with elemental analysis of soils and overburdens (ASTM D 4326). X-ray emission spectrography depends on the fact that when a beam of x-rays is directed onto the surface of a specimen, secondary (or fluorescent) radiation is emitted that contains wavelengths characteristic of each element present. The emitted radiation is collimated and directed to a detector in such a way that the spectral lines may be measured individually (Jones, 1982). X-ray spectrometers are capable of detecting more than 80 elements with atomic number >8, so S can be detected to determine potential acidity (the use of iron from analysis of the same sample may be used to calculate pyrite content and potential acidity). Calcium and magnesium may be used to estimate the carbonate content. However, the analytical error associated with x-ray fluorescence is between 2 to 10% of the sample value. Both x-ray diffraction and x-ray fluorescence are primarily used for confirmation of the presence and magnitude of minerals and elements in the sample, and are generally not used for determining exact values of minerals or elements (see Skousen et al., 1997).

Fractionation of S—Fractionation of S into its respective forms may be accomplished in three ways: 1) the ASTM Method D 2492, 2) a modified Environmental Protection Agency (EPA) method, and 3) a technique combining the use of both methods. In the ASTM D 2492 Method, a sample is mixed with 4.8M (40%) HCl and heated, then leached with barium chloride to remove sulfate S. The sulfate S content is calculated from the weight of $BaSO_4$ that is precipitated. Pyritic and organic S remain in the sample since neither are soluble in HCl. The sample, after HCl acid extraction, is then leached with 2M (12.5%) nitric acid to dissolve the iron sulfides. The iron in this nitric acid extract is quantified by titration or by atomic absorption spectrophotometry, and this value is used to calculate the amount of pyritic S in the sample. Organic S is calculated from the difference between the total S content measured by combustion and the sum of the sulfate and pyritic S contents.

The modified EPA method uses three portions of the overburden sample. One portion is combusted in a LECO Furnace and analyzed without any pretreatment to determine the total S content. A second portion is leached with 4.8M HCl (thereby removing the sulfate S) and then combusted giving pyritic and organic S. A third portion is leached with 4.8M HCl and 2M nitric acid (thereby removing sulfate and pyritic S) and then combusted giving organic S. The concentrations of each S form are then calculated.

The ASTM/EPA combination method tries to minimize the errors that are possible with the two other procedures. The sulfate S is determined as outlined in the ASTM method. The sample is treated with 40% HCl then leached with barium chloride to precipitate $BaSO_4$. Organic S is determined on a subsample that has been leached with 40% HCl (removing sulfate S) and 2M nitric acid (removing pyritic S), then combusted. The sulfide S content is calculated from the difference of the total S and the sum of the sulfate and organic S contents.

Fractionation of S into its respective forms is helpful in determining actual acid-producing potential. Removing sulfate and organic fractions (which are not typically acid producers) from total S and relying on pyritic S for MPA calculation gives more accurate estimates of acidity concentrations in drainage. However, as mentioned previously, total S values provide maximum potential acidity from a rock sample and intentionally overestimate the acid potential of the rock. Experience has shown that for unweathered material, it is generally preferable to be conservative and use total S values to predict acidity in drainage,

rather than pyritic S values. Table 4.2 compares the MPA values for several overburden samples calculated on total S vs pyritic S.

Table 4.2. Maximum potential acidity (MPA) from overburdens based on total S vs pyritic S (Frost, 1981; Johnson and Skousen, 1995; Tettenburn, 1980).

Overburden Type	Total S	Pyritic S	MPA Total S	MPA Pyritic S
	(%)	(%)	(Metric tons/1000 metric tons)	
Middle Kittanning Overburden	1.55	0.88	48.44	27.50
Middle Kittanning Overburden	0.79	0.62	24.69	19.38
Lower Kittanning Pavement	1.20	0.78	37.50	24.38
Lower Kittanning Overburden	0.34	0.33	10.63	10.31
Upper Freeport Overburden	1.01	0.88	31.56	27.50
Pittsburgh Overburden	0.58	0.32	18.13	10.00
Pittsburgh Overburden	0.97	0.04	30.31	1.25

Simulated Weathering Tests

Another way of measuring acid potential is by leaching the rock with a strong oxidant or with water for long time periods. H_2O_2 has been used as an oxidant to speed the reaction process, with mixed results. A modification of this approach by O'Shay et al. (1990) produced accurate and reproducible results in east Texas overburdens. More conventional simulated weathering tests produce good results, but almost all the techniques require long time periods in order to get sufficient data to develop acid potential determinations (see Chapter 5). There is also no standard leaching technique; the various methods have different flushing cycles, use different amounts of water per flushing cycle, use different particle size of the overburden material, etc.

A relatively short-term, standardized, accurate technique is needed to resolve questions concerning acid potential in situations where acid-base accounting fails to provide an adequate answer. The EGA method, which is discussed in more detail later in this chapter, may one day serve that purpose.

NEUTRALIZATION POTENTIAL METHODS

The natural base content of overburden materials, commonly present as carbonates or exchangeable cations on clays, is important in evaluating the future chemical producing potential of the overburden. The amount of alkaline material in unweathered overburden may be sufficient to counteract or overwhelm the acid produced from S oxidation in the material.

Neutralization Potential (NP) Procedure in Acid-Base Accounting

The NP procedure in ABA quantifies the neutralizing compounds in coal and overburden. Alkalinity production potential (APP) is equivalent to the term NP. Of the many types of basic compounds present,

carbonates and exchangeable bases are the only alkaline compounds that occur in sufficient quantity to effectively neutralize acid mine drainage. Siderite, a ferrous carbonate ($FeCO_3$), is not a desirable neutralizer because it does not yield an alkaline-producing material upon complete weathering and oxidation of iron.

The NP test involves treating the pulverized overburden sample with a known quantity of HCl, heating to ensure complete dissolution of bases, and back-titrating with sodium hydroxide (NaOH) (Sobek et al., 1978). The NP test relies on an initial subjective carbonate ranking procedure based on adding a few drops of dilute HCl to the sample and rating the observable fizz (Table 4.3). Based on the fizz rating, a quantity of HCl (either 20 or 40 ml of 0.1M or 0.5M) is added to a subsample of the overburden and heated for complete reaction with the sample. After the sample has cooled, it is back-titrated with 0.1M or 0.5M NaOH to determine the quantity of HCl that was neutralized by the sample. This value is then used to calculate the NP of the sample and is expressed as $CaCO_3$ equivalents in metric tons per 1000 metric tons of material. The NP procedure is simple, can be done quickly, and is very accurate in determining alkaline content of most overburden materials.

In overburden containing alkaline and pyritic material, the soluble bases may be sufficient to neutralize the acid at a rate equal to or exceeding the rate of acid production. Higher alkalinities also help control bacteria and restrict ferric iron activity, which can both accelerate acid generation (Leathen et al., 1953; U.S. EPA, 1971). Determining the MPA and NP of a sample will indicate the ultimate acidity or alkalinity that may be released from the material upon complete weathering.

Table 4.3. Description of fizz rating and amounts and strengths of HCl added to an overburden sample based on a fizz rating (Noll et al., 1988; Sobek et al., 1978).

Fizz Rating	Description	Amount of Acid	Strength of Acid
0 - None	No reaction.	20 ml	0.1 M
1 - Slight	Minimal reaction; a few bubbles per second to many fine bubbles.	40 ml	0.1 M
2 - Moderate	Active bubbling with only a small amount of splashing.	40 ml	0.5 M
3 - Strong	Very active bubbling that includes substantial splashing.	80 ml	0.5 M

The Modified Neutralization Potential Technique

Siderite ($FeCO_3$), when present in the overburden, reacts quickly with HCl in the standard NP procedure in ABA and falsely indicates that the rock will behave as a net alkaline contributor after weathering (Cargeid, 1981; Morrison et al., 1990; Wiram, 1992). Continued weathering of $FeCO_3$ actually produces a neutral (Meek, 1981; Shelton et al., 1984) to slightly acid solution (Cravotta, 1991; Doolittle et al., 1992; Frisbee and Hossner, 1989). If insufficient time is allowed for complete iron oxidation and precipitation of ferric hydroxide during back titration, erroneously high NP values can be generated on samples containing $FeCO_3$, yielding misleading NP information. Such an analytical oversight can lead to incorrect post-mining water quality predictions and produce costly, long-term reclamation liabilities (Wiram, 1992).

Meek (1981) and Morrison et al. (1990) suggested adding a small quantity of 30% H_2O_2 to the filtrate of an overburden sample to oxidize ferrous iron to ferric iron before back-titration is initiated. Leavitt et al. (1995) proposed a modified NP procedure that includes boiling a 2-gram overburden sample for 5 min after the acid is added, filtering the suspension, and adding 5 ml of 30% H_2O_2, then boiling for an additional 5 min. Significant reductions in NP values were found for $FeCO_3$ samples using the modified NP method compared to the standard Sobek et al. (1978) method (Table 4.4, Skousen et al., 1997). Variations in NP determinations among laboratories were also dramatically reduced by using this modified method compared to the standard NP method on $FeCO_3$ samples (Table 4.5).

Table 4.4. Neutralization potential (NP) values for the standard Sobek and the modified NP (H_2O_2) digestion methods on overburden samples. Prominent minerals are given for each sample (Skousen et al., 1997).

Sample Description	Sobek	H_2O_2
(Metric tons/1000 metric tons)		
49% Siderite	70 a[1]	16 b
65% Siderite	62 a	19 b
65% Siderite	63 a	17 b
61% Siderite	62 a	15 b
8% Siderite, 55% Clays	88 a	26 b
18% Siderite, 48% Clays	64	56
20% Siderite, 11% Calcite	367	322
90% Calcite	926	924
83% Calcite	835	847

[1]Values within rows without letters are not significantly different; values within rows with different letters are significantly different at $p < 0.05$.

Table 4.5. Neutralization potential values using the Sobek and modified NP (H_2O_2) digestion methods among three laboratories on overburden samples containing $FeCO_3$ and calcite (Skousen et al., 1997).

Sample Description	Sobek Method			H_2O_2 Method		
	Lab 1	Lab 2	Lab 3	Lab 1	Lab 2	Lab 3
---------------(Metric tons/1000 metric tons)-------------						
49% Siderite	70	89	29	16	14	20
65% Siderite	62	88	25	19	21	28
65% Siderite	63	87	14	17	16	25
61% Siderite	62	93	445	15	12	43
8% Siderite, 55% Clays	88	95	50	26	11	27
18% Siderite, 48% Clays	64	82	26	56	25	77
20% Siderite, 11% Calcite	367	607	363	322	301	277
90% Calcite	926	928	936	926	926	924
83% Calcite	835	828	837	847	844	851

Fizz ratings are done to assess the relative amount of carbonate present in a rock sample, which are then used to determine the amount and strength of acid to use in the NP digestion process. Conflicting NP values were found when overburden samples were assigned different fizz ratings and thereby digested in different amounts of acid (Table 4.6). At higher fizz ratings (more acid added), the NP values increased substantially. Since the subjective fizz rating was not found to be repeatable among laboratories and not reflective of the carbonate content of a rock, a quantitative and repeatable method to determine carbonate content was proposed (Skousen et al., 1997). The method uses the percent insoluble residue after acid digestion to assign a carbonate rating (Table 4.7), and has been found to accurately determine the amount and strength of acid to add for NP determination.

A 2-g sample of overburden is placed in a beaker. The appropriate amount and strength of HCl (Table 4.7) is added to the beaker. The suspension in the beaker is then brought to 100 ml volume prior to heating. Boiling chips are added to the suspension, the beaker is covered with a watchglass, and the suspension is boiled gently for 5 minutes. After cooling, the contents of the beaker are gravity filtered using a 0.45um (Whatman #40) filter. The filtered solution is then treated with 5 ml of 30% H_2O_2. The solution is then boiled for an additional 5 minutes (using boiling chips and watch glasses), and allowed to cool. The solution can then be hand-titrated using NaOH, to achieve and hold an endpoint pH of 7.0 for 30 seconds. However, since most analytical laboratories have auto-titrators, we recommend that auto-titration be used to determine the volume of NaOH needed to achieve and hold a pH 7.0 endpoint. The titration rate can be varied on most machines, so the middle setting is normally used for titrations.

CO_2 Coulometry

CO_2 Coulometry is an analytical technique that is routinely used to determine carbon (both total carbon and carbonate carbon). It is a two-step process in which total carbon is first determined by measuring the amount of CO_2 evolved when the sample is heated to $1000^{\circ}C$. Then, carbonate carbon is determined by digesting the sample in hot perchloric acid and measuring the amount of CO_2 evolved during the digestion. Organic carbon is then determined by difference (Morrison et al., 1990). Because calcite, dolomite, and siderite exhibit different rates of dissolution in acids (Evangelou et al., 1985), CO_2 coulometry can differentiate these carbonate sources with respect to time of CO_2 evolution. Morrison et al. (1990)

Table 4.6. Neutralization potential values of overburden when samples were digested according to standard fizz ratings compared to increasing the fizz rating and adding a corresponding higher amount of acid (Skousen et al., 1997).

Sample Description	Acid Added	Sobek	Acid Added	Sobek
49% Siderite	40 ml 0.1 M	70	40 ml 0.5 M	192
65% Siderite	40 ml 0.1 M	62	40 ml 0.5 M	155
65% Siderite	40 ml 0.1 M	63	40 ml 0.5 M	166
61% Siderite	40 ml 0.1 M	62	40 ml 0.5 M	192
18% Siderite, 48% Clays	40 ml 0.1 M	64	40 ml 0.5 M	234
20% Siderite, 11% Calcite	40 ml 0.5 M	367	80 ml 0.5 M	440
90% Calcite	80 ml 0.5 M	926	60 ml 1.0 M	919
83% Calcite	80 ml 0.5 M	835	60 ml 1.0 M	842

Table 4.7. Carbonate rating based on percent insoluble residue with corresponding acid volumes and acid strengths.

Carbonate Rating	Percent Insoluble Residue	Amount of Acid	Strength of Acid
	(%)	(ml)	(M)
0	95 - 100	20	0.1
1	90 - 94	40	0.1
2	75 - 89	40	0.5
3	< 75	80	0.5

concluded that CO_2 coulometry can be used to very accurately determine the carbonate carbon contents of overburdens containing calcite, dolomite, and siderite, and samples containing all three phases.

Calculations:

1. ml of acid consumed = (ml acid added) - (ml base added);
2. tons $CaCO_3$ equivalent/thousand tons of material = (ml of acid consumed) x (25.0) x (M of acid)

EVOLVED GAS ANALYSIS (EGA)

Evolved gas analysis (EGA) is a direct, one-step procedure that has been used for quantitatively evaluating the acid-producing and acid-neutralizing minerals in coal overburden samples. Hammack (1987) applied EGA to coal overburden analysis using a quadrapole mass spectrometer to detect carbon dioxide and sulfur dioxide evolution as samples were subjected to increasing temperatures.

This early work showed the potential of EGA for determining the amount and reactivity of pyrite as well as the amount of carbonate minerals in coal overburden samples. However, this EGA application was not quantitative because of problems associated with the quadrapole mass spectrometer.

A variant of the EGA procedure, a method termed controlled-atmosphere programmed-temperature oxidation (CAPTO) (LaCount et al., 1983), has recently been applied to the analysis of coal overburden samples. The method employs a primary and secondary tube furnace design, slow linear temperature ramp and plug flow of an oxidizing or anoxic atmosphere through a sample diluted with an inert solid. Oxide gases evolved are measured with respect to temperature using a fast fourier transform infrared spectrometer (FTIR).

Transition metal carbonates (siderite and rhodochrosite) decompose to yield carbon dioxide under the above conditions at 300 to 600°C, depending on the oxygen concentration applied to the samples. At low oxygen concentrations, transition metal carbonates decompose at lower temperatures than the corresponding carbonates analyzed using higher oxygen concentrations. Alkaline earth metal carbonates (calcite and dolomite) evolve carbon dioxide at higher temperatures (600 to 830°C). The alkaline earth metal carbonates do not show the same oxygen concentration decomposition dependence exhibited by the transition metal carbonates.

Pyrite and marcasite oxidize under these same conditions, to yield sulfur dioxide, at temperatures ranging from 350 to 560°C. Marcasite and more reactive morphologies of pyrite oxidize in the range of 350 to 440°C, while more stable forms oxidize at temperatures from 450 to 550°C.

Using one analysis procedure, it is possible to determine the amount of acid-neutralizing carbonate (calcite and dolomite) present, to determine the amount of siderite, and to distinguish acid-producing minerals such as pyrite and marcasite from other sulfur forms that do not generate acidity, for example, calcium sulfate.

Recent work using mine overburden core samples has shown that the decomposition of alkaline earth metal and transition metal carbonates can be resolved to quantify the amount of each of the carbonate forms present. The acid-producing minerals are quantitatively determined from the same analysis. Additionally, this technique can predict the reactivity of pyrite morphologies under weathering conditions, since pyrites that weather more readily tend to oxidize at lower temperatures than pyrites that are more resistant to weathering. Otherwise this information can only be obtained using simulated weathering (kinetic) tests. Further work to compare these results with conventional and kinetic tests is planned.

Examples of two profiles are shown. The first example shows the oxidation of pyrite and the decomposition of sulfate from an overburden sample. The sulfur dioxide evolution at 412°C is produced from the oxidation of pyrite; 800 to 1000°C is the temperature range where various calcium sulfate morphologies decompose. The second profile shows the carbon dioxide evolution for a mine overburden sample. The evolution centered at 529°C is produced from the decomposition of transition metal carbonates and that at 751°C is derived from alkaline earth metal carbonates. With all of the variables analyzed, one can calculate an ABA that is based only on the active constituents.

ViRoLac Industries is currently evaluating the ability of this new ABA technique to identify sulfur forms and to distinguish transition metal carbonates from alkaline earth metal carbonates present in a wide range of mine overburden core samples. Currently, the estimated costs to perform an ABA analysis using CAPTO is about twice that of conventional ABA methods so, at this time, the method would be best reserved for problematic sites where conventional ABA methods cannot definitively predict water quality. However, this method is significantly less expensive than the more time-consuming simulated weathering tests and may prove to be an effective alternative to those methods.

ACID-BASE ACCOUNTING BY DOWN-HOLE PROMPT GAMMA RAY SPECTROSCOPY WIRELINE LOGGING

The U.S. Geological Survey, in cooperation with the West Virginia Geological and Economic Survey (WVGES), Schlumberger HydroGeological Technologies (HGT) and West Virginia University (WVU), are applying oil and gas industry well logging technology to the chemical characterization of coal-bearing strata. The methodology is based on chemical analyses of boreholes using prompt neutron gamma ray spectroscopy wireline logging, hereafter referred to as geochemical logging (GCL). Traditional methods generally involve coring, core sampling, and chemical analysis of selected core samples. In contrast, GCL consists of wireline logging of a drill hole. The logging provides continuous chemical analyses, top to bottom, of a 6.5 inch drill hole, thereby eliminating sampling bias and error as well as other analytical error

associated with sample preparation and analyses of a core. The GCL tool also interrogates a formation volume that is much larger than that analyzed by core. The data generated should be directly applicable to the chemical characterization of coal-bearing strata and the ABA of overburden.

Figure 1: Sulfur Dioxide Evolution Profile for Overburden Sample
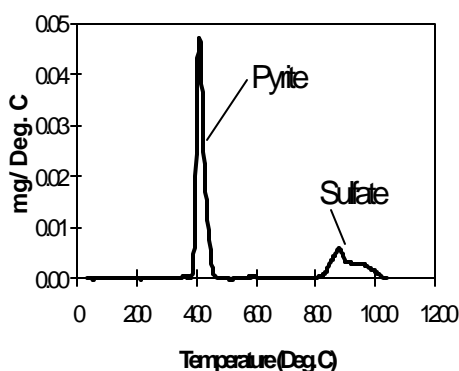
Figure 2: Carbon Dioxide Evolution Profile for Overburden Sample
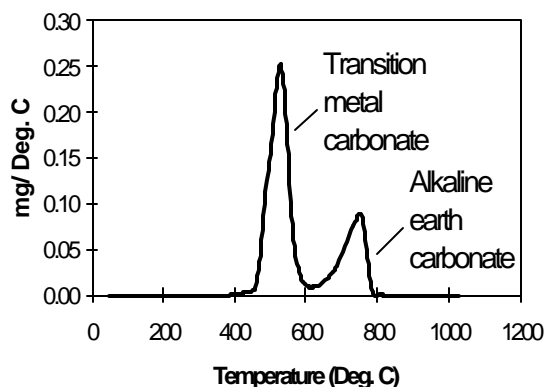
In order to compare results from GCL with conventional analytical methods, two study sites were selected in an area known to have a variety of rock types and chemistries and histories of acid mine drainage, near the eastern edge of the bituminous coal field. The first site, in Tucker County, WV, was approximately 10 miles northeast of Davis, WV. The second site, in Mineral County, WV, was 5 miles west of Keyser, WV.

The core, minus core from coal beds, was boxed and transported to WVGES facilities. One complete set of quartered samples from each of the two cores was submitted to WVU analytical laboratories, where each sample was ground to -200 mesh and prepared for mineralogical and chemical analyses. Mineralogical analyses was conducted by X-ray diffraction (XRD); chemical analyses included major and minor element analyses by X-ray fluorescence (XRF), and ABA was conducted using standard wet chemical procedures. Sampling and analyses of the core in one-foot increments provided data for 650 samples from the first hole and 953 samples from the second.

The total suite of one-foot increment core samples was analyzed for total sulfur using a commercial analyzer. Calcium carbonate as calcite plus dolomite was determined by XRD, while calcium calculated as CaO was determined by XRF. MPA and NP were determined by standard wet chemical methods. The GCL analyses consist of continuous weight percent Si, Ca, Fe, Ti, K, and S determinations, for the entire length of the two test holes.

The chemical data from each of the two holes were compared in two ways. In the first case, data from only the Allegheny Formation were compared. Allegheny Formation samples were compared separately because these strata are known to consistently present problems in acid production when disturbed by surface mining. In the second case, data from the entire stratigraphic section penetrated by coring, which includes the Conemaugh and Allegheny Formations (minus the coal beds), were compared. The second case provided a wide range in lithologies and ABA variables. A comparison of the mean and standard deviation

for the geochemical wireline log data and chemical analyses of one-foot increment core data from Allegheny Formation strata is shown in Table 4.8.

Table 4.8. Comparison of borehole GCL data with chemical data of one-foot incremental samples of core from two bore holes for the Allegheny Formation. The means (m) and standard deviation (sd) values for GCL are based on a running average of direct borehole analyses in six inch increments by the neutron activation tool. The net neutralization potentials (NNP) were calculated for a number (n) of samples from calcium and sulfur values, using standard conversion procedures.

	USGS/WVGES - 1, Allegheny Formation at the 95% confidence level					
	Calcite		**Sulfur**		**NNP**	
	GCL	CORE	GCL	CORE	GCL	CORE
m	0.64	1.28	0.16	0.17	1.5	7.7
sd	2.41	3.92	0.46	0.34	29	42
n	453	229	453	230	453	229
	unequal means		***equal means***		***unequal means***	
	USGS/WVGES-3, Allegheny Formation at the 95% confidence level					
m	1.62	1.22	0.18	0.17	11	7.0
sd	4.03	3.06	0.26	0.24	39	36
N	425	212	425	212	425	212
	equal means		***equal means***		***equal means***	
	USGS/WVGES-1 Conemaugh and Allegheny Formations total core analyses					
	Calcite		**Sulfur**		**NNP**	
	GCL	CORE	GCL	CORE	GCL	CORE
m	1.13	1.93	0.11	0.16	36	43
sd	3.14	4.91	0.35	0.33	34	51
n	1185	575	1185	575	1185	575
	unequal means		***unequal means***		***unequal means***	
	USGS/WVGES-3 Conemaugh and Allegheny Formations total core analyses					
m	4.36	5.06	0.23	0.25	36	43
sd	8.81	10.2	0.46	0.80	86	105
n	1909	945	1909	945	1909	945
	equal means		***equal means***		***equal means***	

The numerical comparison of the results from GCL and core analyses indicates that there are some differences between the GCL data and the chemical data, particularly at the first site, where there was a twenty foot off-set between the core hole and the 6.5 inch air rotary hole. Although the mean values for sulfur were equal for the Allegheny Formation between the two methods, the mean values for calcite and NNP were not equal for either the entire core or the Allegheny Formation. A large part of the differences in data sets can be ascribed to differences in the amount of calcite within each of the two holes, as indicated

by differences in resistivity and density logs. These differences were sufficient to cause a noticeable difference in NNP values between the two holes.

There were fewer differences between the GCL and core data sets in the second site. At this site, the core hole was reamed to a 6.5-inch diameter. When the data were acquired from what was essentially the same hole, the means were equal for sulfur, calcite, and NNP for both the Allegheny Formation and the Conemaugh plus the Allegheny Formations.

The preliminary data indicate that GCL can provide a level of accuracy equivalent to chemical analyses of one-foot increment samples of core, and can be used for chemical characterization of coal-bearing strata and ABA of overburden. The logging has the advantage of providing accurate data at the well site in a matter of minutes for an individual drill hole or any number of holes. If further testing demonstrates that ECS logging is as accurate as conventional chemical methods of overburden characterization, then GCL of air rotary holes may eliminate the need for coring. The objectives of accuracy and rapid analysis appear to be met by GCL; now the industry will have to address the issue of cost effectiveness.

INTERPRETATION OF OVERBURDEN QUALITY BY ACID-BASE ACCOUNTING

ABA assesses the total amount of acidity or alkalinity that is contained in a specific rock unit. The assessment is based on the total S content and the carbonate content of the rock. The aim of ABA is to determine how much material is needed to neutralize all of the acid that could potentially form in coal overburden when pyrite is present. The use of total S provides a margin of neutralization safety against S percentages that may not all be pyritic and for pyritic S that may not all react.

Three basic assumptions should be understood when using ABA for overburden prediction (Perry, 1985). First, the values for MPA and NP represent maximum or ultimate quantities from pulverized, whole rock analysis. Complete reaction of all pyrite and bases probably does not occur in a mine backfill, thereby reducing the total amount of acidity or alkalinity produced in the ABA procedure. Second, S exists in three chemical forms in coal bearing rocks: sulfide, sulfate and organic, with sulfide S (pyrite) being the predominant acid producer. Third, pyrite may oxidize faster or slower than the dissolution of carbonate materials. Conventional ABA does not determine reaction rates of pyrite and carbonates, though the new EGA method can apparently indicate the reactivity of the pyrite.

Skousen et al. (1987) suggested that overburden with NNP values less than 5 metric tons per 1000 metric tons produce acid, while values greater than 20 metric tons per 1000 metric tons produce alkaline drainage. However, that was based on soil science and plant growth requirements. Today, the consensus view, based on field validation studies, is summarized in Table 4.1.

A common error when using ABA as a predictive method occurs when the Max Needed and Excess columns are summed together for the entire overburden above the coal bed (the Max Needed column representing a negative number and the Excess column representing a positive number). Summing the ABA values for an overburden column falsely assumes thorough mixing of all overburden in a backfill, uniform rates of weathering of all materials, and water contact throughout the backfill.

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STATE PRACTICES

All the states interviewed practice overburden analysis using ABA; all use NP and all but Indiana use MPA based on total sulfur to arrive at an NNP value for all permits. Illinois will accept MPA values based on pyritic sulfur or total sulfur. Indiana uses MPA based on pyritic sulfur, though it also requires total sulfur analysis and fizz tests, and reserves the option of requiring additional tests, if warranted. Virginia gives applicants the option to do an organic/mineral sulfur speciation to alter MPA results. Tennessee adjusts total sulfur content of the overburden, and therefore MPA, by adding 10% to 15%, and Pennsylvania by adding 5% to 20%, of the coal mined as waste scatter into the spoil. West Virginia and Tennessee require NP to be adjusted for siderite when its presence is suspected.

Acid/base accounting (ABA), neutralization potential, and potential acidity (based on total or pyritic sulfur) are used to arrive at a net neutralization potential (referred to as *Calcium Carbonate Deficiency*) for each stratum in the overburden. Calcium Carbonate Deficiency is computed by subtracting neutralization potential (NP) from potential acidity (PA); therefore, negative numbers are desirable, since an NP larger than a PA would produce a negative number. A Calcium Carbonate Deficiency of five tons or more per one thousand tons of material is defined as *toxic forming*. Mass-weighted ABA for the entire overburden column is required if marginal values are observed for the individual strata. Additional information can be required if warranted. The applicant may request a waiver for overburden analysis prior to application submittal; the waiver must document that equivalent information is available.

Pennsylvania has a more rigorous requirement for siderite that they implement themselves: on properties with marginal NNP that contain units of high NP with low fizz, Pennsylvania will repeat the NP test with and without a modified H_2O_2 carbonate digestion method (Skousen et al, 1997). If there is a significant difference in the NP value based on the standard and modified H_2O_2 test methods, they will then determine the carbonate mineralogy in the sample by X-ray diffraction to differentiate the siderite and limestone/dolomite portions. ABA analysis is not a blanket requirement for Pennsylvania: ABA information is required for approximately 50% of new permit applications. No ABA analysis is requested if, in the reviewers' opinion, there is sufficient evidence from adjacent mining that any discharges will be alkaline and contain no problematic metal contaminants.

Only West Virginia and Alabama request kinetic tests if the previous history of predicting post-mining discharge quality in the permit area is not completely successful based solely on ABA. Alabama rarely requests leaching column tests, while West Virginia can opt for one or a combination of humidity cell, leaching column, and Soxhlet extraction tests. Kentucky, Maryland, Pennsylvania, and Tennessee do not request, but will accept and consider kinetic tests provided as supplemental information to permit applications. All of this information has been summarized in Table 4.7.

RECOMMENDATIONS AND FUTURE USE OF ACID-BASE ACCOUNTING

ABA has been applied to overburden characterization and water quality prediction on mined lands in many parts of the world for about 30 years. An extensive institutional knowledge base and "rules of thumb" have developed on interpreting ABA data, supplemented by a few published studies. ABA

Table 4.7. State Practices for Overburden Analysis

STATE	REQUIREMENTS	OPTIONS
AL	ABA, NP and MPA (based on total S) to arrive at an NNP value. Kinetic tests required if previous history of predicting post-mining discharge quality using ABA alone is not completely successful. Leaching tests rarely requested.	
IL	ABA, NP and MPA (based on total S) to arrive at an NNP value. Total S analysis may be substituted for MPA. Additional information or testing can be required.	
IN	ABA, NP and MPA (based on pyritic S) to arrive at an NNP value. Total S and fizz tests are required as supplemental information. Additional information or testing can be required.	
KY	ABA, NP and MPA (based on total S) to arrive at an NNP value.	Considers kinetic tests as supplemental information.
MD	ABA, NP and MPA (based on total S) to arrive at an NNP	Considers kinetic tests as supplemental information.
OH	ABA, NP and PA or MPA to determine a calcium carbonate deficiency (CCD). If CCD $\geq$ 5 tons per thousand tons, strata is defined as toxic forming. Mass weighted ABA required for entire overburden column if any marginal values are observed.	Applicants may request a waiver from overburden analysis if equivalent information is available.
PA	ABA, NP and MPA (based on total S) to arrive at an NNP value. ABA not needed if adjacent mines indicate that discharges will be acceptable. When ABA is required, PA tests for $FeCO_3$. At sites with marginal NNP that contain units of high NP with low fizz, PA will repeat NP test with and without modified H_2O_2 carbonate digestion method. If NP values based on H_2O_2 test methods differ, X-ray diffraction is used.	Adjusts total S content of overburden by adding 5-20% of coal mined as waste scatter in spoil. Considers kinetic tests as supplemental information.
TN	ABA, NP and MPA (based on total S) to arrive at an NNP value. Adjust NP for $FeCO_3$ when its presence is suspected.	Adjusts total S content of overburden by adding 10-15% of coal as waste in spoil. Considers kinetic tests as supplemental information.
VA	ABA, NP and MPA (based on total S) to arrive at an NNP value.	Organic/mineral S speciation to alter MPA.
WV	ABA, NP and MPA (based on total S) to arrive at an NNP value. Adjusts NP for $FeCO_3$ when its presence is suspected. Kinetic tests required if history of predicting discharge quality in the permit area using ABA alone is not completely successful.	

is a valuable assessment and prediction tool, and is the fastest and easiest way to begin evaluation of overburden materials for water quality prediction. Its application is most effective when used as part of a group of interpretive techniques for analyzing the interaction of geologic and hydrologic conditions, and mining and reclamation practices.

We recommend the use of ABA as the first test for overburden quality and characterization. The combustion technique has been used extensively to determine total S and it has been shown to be an accurate and repeatable measurement. We also recommend the use of total S (rather than pyritic S) to represent MPA. This intentionally overestimates the acid potential to provide a margin of safety.

Since siderite is a common constituent in coal overburdens of the eastern U.S. and does not actually neutralize acidity, a change in the NP procedure has been recommended (Leavitt et al., 1995; Meek, 1981; Morrison et al., 1990; Skousen et al., 1997). We recommend the modified procedure described earlier in this chapter, which eliminates the subjectivity of the fizz test and accounts for siderite. By using this modified method, the ABA values (incorporating the modified NP values) of overburden samples were much closer to the actual water acidity or alkalinity values from intensive weathering tests. Widespread use of the modified NP procedure will likely improve the accuracy of water quality prediction. Alternatively, if it proves cost effective, then the wireline logging approach may one day supplant in-lab analysis.

In spite of increasingly accurate overburden characterization, further refinements are needed to predict the degree to which discharges will be acid or alkaline from a site. The new EGA techniques, selectively used, may help, once the methodology is field validated. However, there will still be many uncertainties in predicting the quality of water from surface and deep mines, and continued field validation of pre-mining overburden analyses to post-mining water quality is important in refining water quality prediction. The likely effect of mining and reclamation practices and hydrology of the reclaimed area is starting to be factored into predictions of post-mining water quality. Another good sign is that computers are being used to better model the volumes of overburden material in various categories on a site.

In summary, ABA balances maximum potential acidity against total neutralizers in each overburden sample. ABA satisfies the requirement to identify overburden layers that will or will not produce acid, and pinpoints those layers that should be analyzed further by other analytical methods. Borderline samples that give NNP values of 0 to +12 tons/1000 tons should be subjected to other tests to determine the acid-producing potential. Once the total overburden column has been assessed and proper interpretations have been made, practical mining and reclamation plans can be designed and implemented. Despite many criticisms, ABA has been and will continue to be the preferred first measure of overburden chemistry for both the industry and regulatory agencies as long as it remains the fastest and easiest way to evaluate overburden materials. It should be used within its limits, in conjunction with other methods of overburden analysis when necessary, and with good common sense.

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

by

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KINETIC TESTS USED IN COAL MINING PREDICTION

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

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

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

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

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

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

Humidity Cells

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

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

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

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

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

Leaching Columns

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

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

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

1. 15cm (6") by 91cm (3') plastic columns, each with a perforated plastic barrier mounted on a large diameter funnel with the water being added at the top (or modified to introduce water from the bottom) and allowed to drain (Bradham and Caruccio, 1995, 1997);

2. small (3.5cm) diameter leaching columns using glass tubes 122 cm long into which distilled water was introduced into the columns from the bottom upward (Hood, 1984; Hood and Oertel, 1984);

3. large (3.08 m) diameter columns that were actually stainless steel tanks 40 ft (12.19 m) high and 10 ft (3.08 m) in diameter (Cathles et al., 1977).

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

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

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

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

Soxhlet Reactors

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

Shake Flasks

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

Applicability of Other Kinetic Tests

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

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

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

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

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

Field Tests

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

FACTORS TO CONSIDER IN KINETIC TEST DESIGN

Particle Size

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

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

(2) effects of heavy equipment used to remove overburden and conduct backfilling and grading operations;

(3) fundamental properties of the rock units (i.e. mineralogy, grain size, hardness, degree of cementation, porosity, linear sedimentary features (e.g. bedding planes); and

(4) linear structural features (e.g. joints and fractures) within the overburden (Hornberger, 1998).

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

Antecedent Storage Conditions

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

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

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

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

Interleach Storage Conditions

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

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

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

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

Degree of Saturation

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

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

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

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

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

Size, Shape and Structure of Apparatus

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

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

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

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

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

Volume and Placement of Overburden Samples in a Kinetic Test Apparatus

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

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

Leaching Interval

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

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

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

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

Influent Composition

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

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

Rock to Water Ratio

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

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

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

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

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

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

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

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

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

Pore Gas Composition

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

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

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

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

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

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

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

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

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

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

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

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

Bacterial Effects

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

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

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

Pyrite Morphology and Texture

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

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

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

Carbonate

While prediction of AMD rather than water quality has been the focus of many of the kinetic tests of the decades, it has been shown repeatedly that calcium or magnesium carbonates play a significant and perhaps overriding role in the process. Brady et al. (1998), Caruccio and Geidel (1978) and Caruccio and Parizek (1968) have shown that a stratum's potential to produce acidity is determined to a large extent by the amount of calcareous material (Ca-MgCO$_3$) and not the amount of pyrite. Geologic systems enriched in calcareous material produce alkalinity, and highly buffered and potentially neutralizing drainages. In these areas, the calcareous material raises the pH of the ground water regime above 7, which effectively suppresses iron bacteria microbial activity and reduces the oxidation of ferrous iron. Several studies have shown that the calcareous material also serves to inhibit the oxidation of pyrite and stabilize the sulfide (Caruccio et al., 1981; Hornberger et al., 1981; Williams et al., 1982; Perry and Brady, 1995). Bradham and Caruccio (1995) showed that when NP exceeds 38g/kg, the sample would produce alkaline leachate at the 95% confidence level. At an NP of 73 g/kg, a confidence threshold of 100% for alkaline leachates

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

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

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

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

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

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

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

CRITERIA FOR DETERMINING WHETHER TO CONDUCT KINETIC TESTING

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

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

RECOMMENDATIONS/GUIDELINES FOR SELECTION OF KINETIC TEST

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

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

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

RECOMMENDATIONS/GUIDELINES FOR SAMPLE PREPARATION

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

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

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

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

Figure 5.4: Neutralization Potential (NP) vs. Maximum Potential Acidity (MPA)
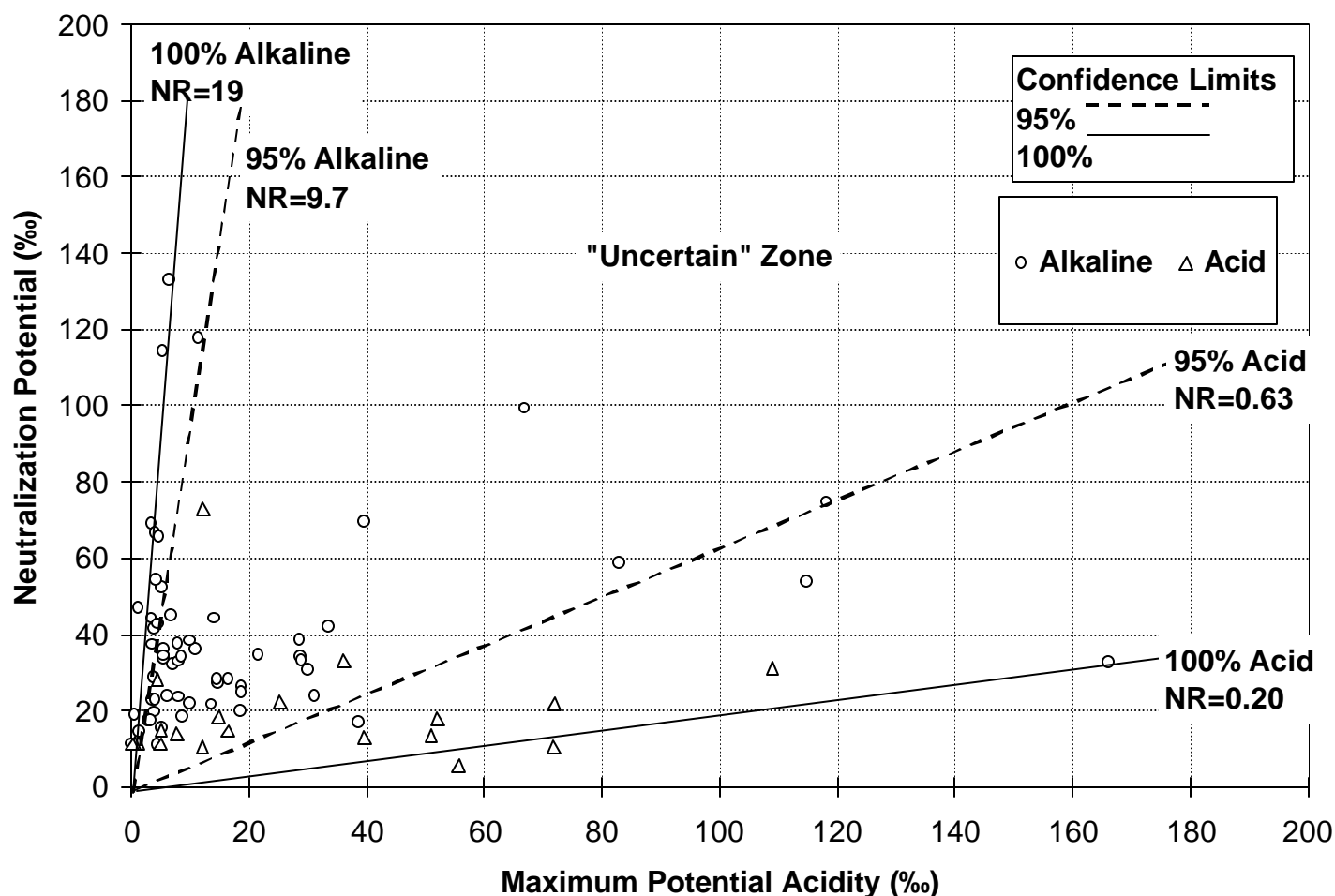
RECOMMENDATIONS FOR STANDARDIZATION OF LEACHING COLUMN TESTS

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

Particle Size

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

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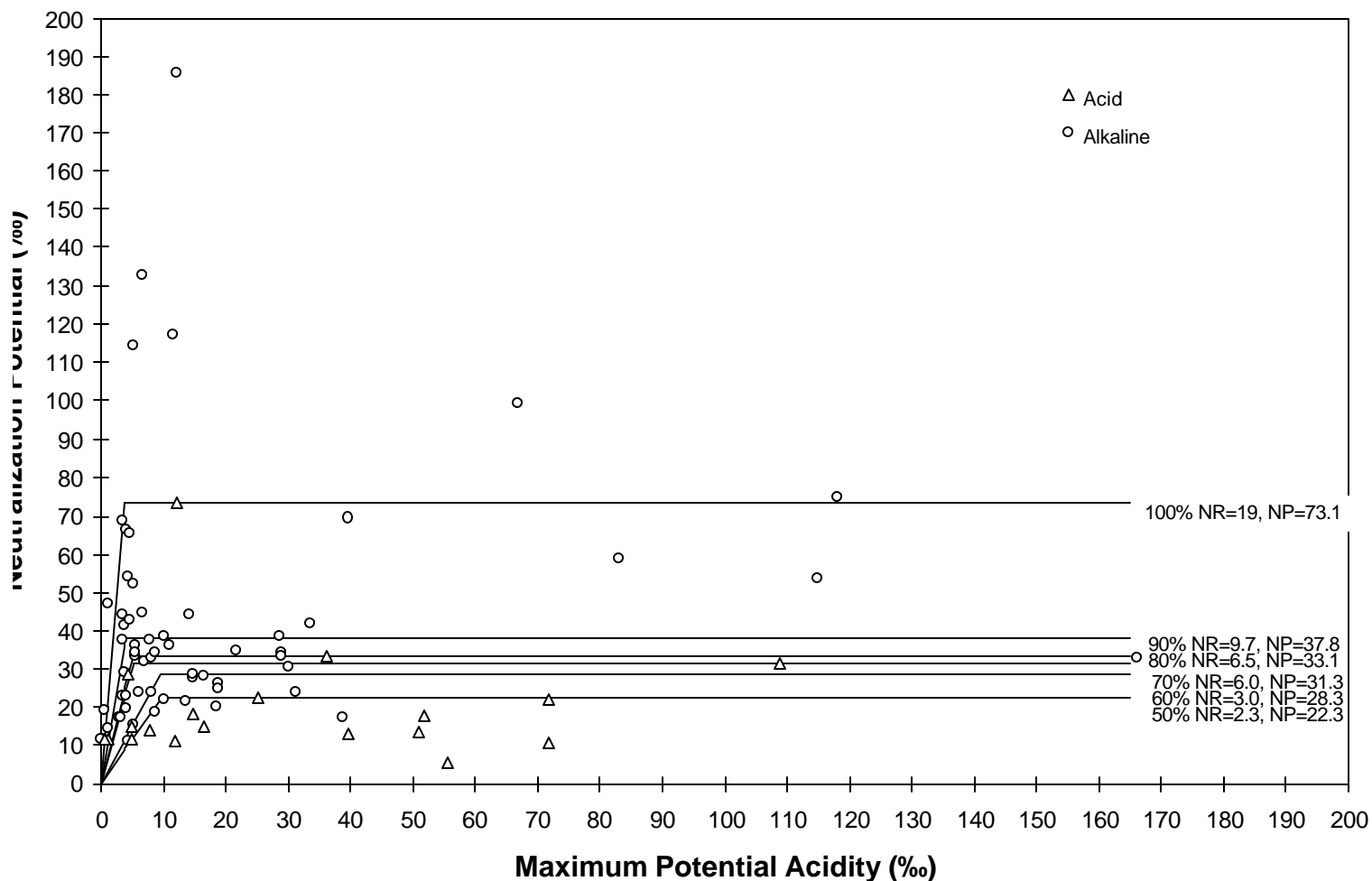
Antecedent Storage Conditions

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

Interleach Storage Conditions

Temperature and humidity

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

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

Degree of saturation

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

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

Size, Shape, and Structure of Apparatus

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

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

Volume of Sample and Placement within a Column

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

Leaching Interval

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

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

Influent Composition and Addition

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

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

Rock to Water Ratio

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

Pore Gas Composition

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

Bacterial Effects

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

Pyrite Morphology and Texture

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

Carbonate

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

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

Data Presentation

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

RECOMMENDATIONS FOR STANDARDIZATION OF HUMIDITY OR WEATHERING CELL TESTS

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

Particle Size

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

Antecedent Storage Conditions

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

Interleach Storage Condition

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

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

Size, Shape and Structure of Apparatus

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

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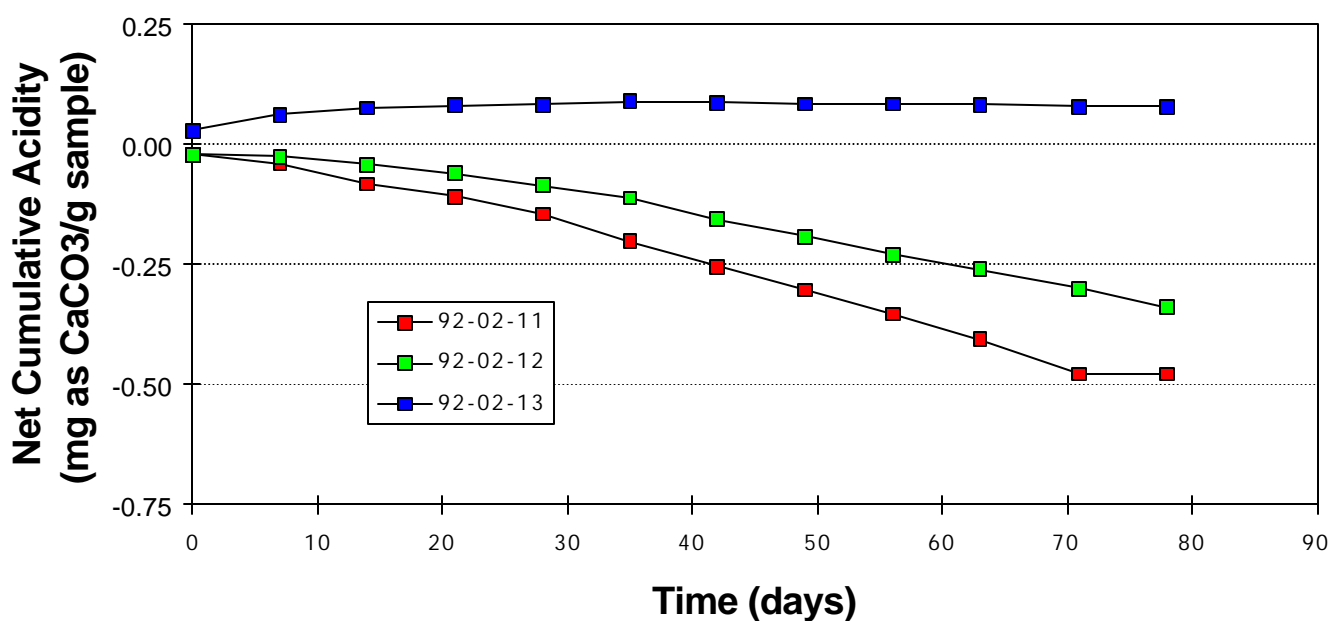
Figure 5.6. Net cumulative acidity data from leaching tests for three overburden samples.

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

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

Volume or Weight of Rock

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

Leaching Interval, Influent Composition and Rock to Water Ratio

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

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

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

Pore Gas Composition

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

Other Effects

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

Data Presentation

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

Data Interpretation

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

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

Figure 5.7 - Net Daily Acidity vs. Time Da
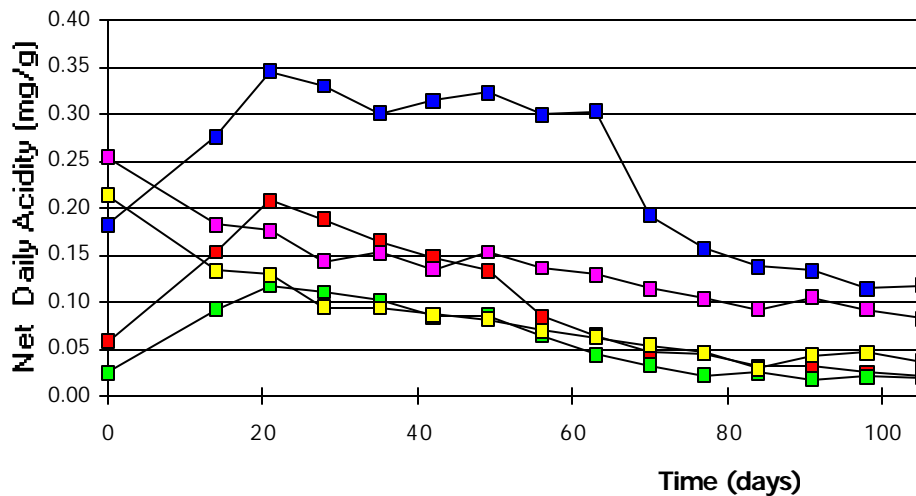
Figure 5.7. Net daily acidity vs. time for five samples, plotted on a daily basis.

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

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

RECOMMENDATIONS FOR STANDARDIZATION OF FIELD SCALE TESTS

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

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

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

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

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

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CHAPTER 6: OVERBURDEN SAMPLING CONSIDERATIONS

by

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INTRODUCTION

This chapter provides guidelines and strategies to adequately assess the vertical and horizontal distribution of rock properties on a mine site as well as the variability in the overburden geochemistry with respect to the potential for acid mine drainage (AMD) formation. The accuracy of overburden analysis, upon which predictions of post-reclamation mine water quality commonly rely, is critically dependant on the sampling procedure used (Donovan and Renton, 1998). The failure of predictions of post-reclamation mine water quality is probably due at least as much to inadequate sampling strategy as it is to inappropriate analytical techniques.

A basic question for anyone attempting to predict AMD prior to mining is whether the sampling strategy representatively (with a predetermined degree of confidence) samples the overburden. Precise analyses performed on an unrepresentative sampling plan will, at best, accurately characterize that unrepresentative population. Another important question is how will that overburden material ultimately affect the chemistry of the mine discharges. The answers to these questions have obvious economic consequences due to the costs of drilling, sampling, and overburden analysis.

Overburden sampling strategies have spatial, vertical, horizontal (sampling density for given geologic units) and temporal (before mine permitting or over the entire life of the mining and reclamation operation) dimensions. The basis of developing a sampling plan varies considerably among sites, among regulatory agencies, and even among permit reviewers. Techniques for sampling overburden range from informal methods based on geological knowledge and rules of thumb to a number of more quantitative methods based on statistics. Among the latter are geostatistical techniques designed to analyze spatially distributed geologic variables, which are used in mineral exploration and reserve calculations. These sampling techniques will be described below and in more detail in Appendix B, where actual mine overburden analysis case studies can be found.

SAMPLING GEOLOGICAL POPULATIONS

The goal of sampling is to collect information about a population. In geological sampling, a sound understanding and knowledge of the geology of the area are key in understanding the nature of the spatial variation of the data being sought and in designing a sampling strategy. This initial discussion introduces broadly applicable principles that are the basis for more specific sampling procedures discussed later in this chapter and is largely based on the fundamental work of Griffiths (1967) and Griffiths and Ondrick (1968).

In the context of evaluating the potential for AMD, the population to be sampled can be defined as the total volume of overburden above the coal seam(s) to be mined. The objective of the sampling is to provide

statistically valid estimates of sulfur and carbonate content of the overburden population. The sulfur and carbonate contents represent measured variables. A variable is a quantity that can assume any of a set of values. Accordingly, we are interested in learning about the quantity, distribution and magnitude of the variability in the data collected for these or any other variables of interest within the population under study. The greater the degree of variability, the greater the number of samples that are generally needed to adequately characterize a site.

We are usually concerned with the total volume of overburden overlying the coal seam(s) to be mined; this is referred to as the *existent population*. However, usually only part of the existent population is actually available for sampling. The available population is that collection of elements that is readily accessible and usually sampled. If the available population represents the existent population and is sampled under the fairly stringent requirements that will provide random samples, we will expect to get results that will adequately describe the existent population. One must invest enough time and money into the sampling program to ensure that the data obtained are reliable and that the interpretations and conclusions based on the sampled available population will apply to the existent population. Obviously, any sampling plan that relies on a single random (drill hole) sample of coal overburden will yield only one mean value for each variable measured, which is unlikely to be representative of the entire overburden population. However, compromises in sampling are often made, resulting in data that are of limited value.

As noted above, a sampling procedure that yields random samples should be followed. Random sampling means that each item in the population has an equal chance of being selected. Random sampling is easy to define, but is usually difficult to achieve in practice. A continuous variable, such as the amount of pyrite or carbonate in overburden, which is randomly distributed, will have a frequency distribution that follows a normal probability distribution model. Random samples from such a population will provide best estimators of the properties being measured. Because of the possible existence of bias in sampling, testing is needed to see if random samples from a known distribution have been achieved. There are a variety of statistical parameters used to test whether the samples collected fit the expected model; these can typically be found in general books on statistical analysis (e.g. Griffiths, 1967).

For stratified geological populations, there are two basic sampling designs. One is to take individual samples across all layers, as in a channel sample. Sampling of an entire section of overburden via a drill hole is equivalent to a channel sample of the entire overburden. Two important parameters of any measured variable are (1) the mean or average and (2) the variance or deviation of the sample values around the mean. One can enhance the degree of precision of the mean and variance of AMD-related variables by simply increasing the number of samples, i.e. drill holes.

The other sampling design for stratified populations is stratified sampling, in which the mean and variance are obtained for each identified layer and the *within-layer* and the *between-layer* statistical estimators can be determined and compared. With appropriate weighting to allow for the thickness of the different layers, an adequate estimate can be obtained for the entire layered population. There are other kinds of variation that could be encountered, including a uniform or massive population and a *patchy* population. A patchy

arrangement can be considered as a special case of a layered arrangement by considering each patch or zone as a layer.

All the above supposes that the arrangement can be discerned at the outset. Sampling sedimentary rocks without knowing the arrangement beforehand has led to the development of a sampling model based on the relative degree of variation between and within samples. If you have a homogeneous or massive population, the relative degree of variation between samples will be small, but the variation within samples will be large. If you have a poorly developed stratified population, the variation between samples will be moderate, and the variation within samples will also be moderate. If you have a well-stratified population, the variation between samples will be large, but the variation within samples will be small.

RATIONAL STEPS IN SAMPLING DESIGN

Sampling in a geological context can be achieved through a number of generic sampling plans or sampling designs. These include multi-stage or hierarchical sampling, in which a large sample unit such as an outcrop or drill core is further subdivided into smaller sample specimens, and these in turn are reduced to the final sample for laboratory or other analysis. Others include: composite sampling, in which a number of individual samples are combined to yield an average value; channel samples (including drill core samples), in which an entire section of overburden is sampled at one time and then further subdivided into subsamples; and stratified [stratified random] samples, in which [random] samples are taken within and between stratigraphic units. There is also cluster sampling, in which sampling is restricted to one or a few particular areas of interest (Griffiths, 1967).

It is generally preferable to do the exploratory drilling first. This preliminary drilling enables the determination of the number of mineable coal seams, maximum and minimum overburden thicknesses (cover heights) and the lateral extent of the various lithologies. This information can then be used to better locate the number and depth of overburden holes to be used for overburden sampling and geochemical analysis. This should yield a valid representation of the lithologic and geochemical variation and the degree of weathering within the site. If this research and exploration is done prior to drilling, it is less likely that additional holes will have to be drilled later in the permitting process. Such a preliminary or reconnaissance sampling program helps to determine the final sampling scheme, both in terms of the number of samples and drill holes, and how they are to be collected. This two-stage process helps to ensure a reasonable degree of confidence that the final sampling will be representative of the geological population under study (Griffiths, 1967). It is as equally important to know and to document the quality of the data collected (see Appendix A).

Site-specific factors should be used to determine the spatial density of an overburden drilling program. The overburden holes must be located within the limits of the proposed mining area. Mine size and layout are also important. A long narrow site may require more drill holes for an accurate characterization than a more rounded site of similar acreage. Mining method and depth of cover will also impact the drilling density. If only shallow cover is to be affected, drill holes in high cover will not accurately reflect the overburden quality. Depth of the weathered zone, topography, stratigraphic variations, and geochemistry will also affect the number of drilling locations, as discussed in Chapter 2 and in Brady et al. (1988). Some holes must be

located at maximum highwall conditions, and the holes must represent all of the strata to be encountered by mining. Other holes should be located under low and average cover conditions to provide representative sampling of the overburden where zones may be missing or may have been altered due to surface weathering (Tarantino and Shaffer, 1998). Exploratory drill holes also may indicate significant facies changes across a site, which would need to be delineated by the overburden analysis holes.

SAMPLING METHODS

Sampling of overburden material was outlined in great detail by Noll et al. (1988). Overburden material is generally sampled by drilling (mainly air rotary or core drilling) or channel sampling. Channel sampling (manual collection of rock samples without a drill rig) is conducted at fresh exposures of the overlying strata, generally along a highwall. The advantages and disadvantages of various sampling techniques along with remedies for problems associated with each sampling type are summarized in Table 6.1.

Air Rotary Rig: Normal Circulation

Air rotary drilling is probably the most common method of sampling overburden. Drilling in this manner breaks the rock into small fragments and uses air to blow the rock chips to the surface where they are collected. The rock chips are bagged and the depth interval sampled is determined. The most common pitfall with normal circulation air rotary drilling is that the individual samples of stratum can be contaminated by an overlying sample zone as the rock chips are blown up the annular space of the drill hole. There is a lag time between drilling a unit and when it is sampled at the surface, caused by the travel time of the rock chips. This becomes especially troublesome as the depth increases and/or when a relatively thin potentially acidic unit is encountered. However, periodically halting drilling and purging the rock chips from the hole can minimize such problems.

The rock chips traveling in the annular drill hole space can dislodge loose particles from an overlying source. Care should be taken to stop the downward progression of the drill stem after each interval has been sampled and to allow any loose particles to blow out prior to continuing downward. Contamination of the sample can also occur at the surface due to the pile of ejected material that forms near the drill hole. These piled materials, if not removed during drilling, can slough back into the open hole and the chip stream. This can be avoided by shoveling the materials away from the hole during the period when drilling is stopped to blow out the hole. Another option is to add a short length of casing to the top of the hole after the upper few feet have been collected. Samples are collected by placing a shovel under the chip stream. Care should be taken to clean the shovel of any accumulated materials from previous usage or sampling. This is particularly important in sampling of wet test holes where the ejecta consist primarily of mud. Before drilling the overburden hole, the driller should be instructed to also clean the dust collector hood to remove any accumulated materials that may dislodge and contaminate the samples being collected.

Air Rotary Rig: Reverse Circulation

This type of drill rig is less commonly used as a drilling platform for the collection of overburden samples than normal circulation rigs, primarily because of availability. A reverse circulation rig uses

Table 6.1. Comparison of Overburden Sampling Techniques

Sampling Type	Advantages	Disadvantages	Remedy
Air Rotary (Normal Circulation)	Very common; drill rigs readily available; fast and inexpensive; less sample processing (crushing) than core drilling.	Potential for cross contamination problems from intermixing; difficult drilling spoil, till or refuse; lack of data regarding fracture systems; and difficulty in determining exact elevation of specific lithologic units and perched water zones.	Halt drilling and purge rock chips from hole; use reverse circulation air rotary for drilling spoil, till or refuse.
Air Rotary (Reverse Circulation)	No cross contamination problems; cleaner and faster than normal circulation air rotary, does not need to be stopped to blow out hole; excellent for unconsolidated materials; less sample processing than core drilling.	Less common than normal circulation air rotary; drill rigs may not be available.	
Diamond Core	Provides a continuous record of the lithology not readily available from rock chips; little chance of cross-strata contamination of lithologic materials.	More expensive due to drilling time and sample recovery and preparation (crushing); problems with core loss.	Use as a secondary means of data collection to isolate previously identified problem zones, or as a primary sampling tool in the area of the coal, i.e. the interval 5 feet above and below the coal horizon.
Auger		Limited depth and great potential for cross contamination and intermixing.	Use for unconsolidated homogeneous strata only; i.e. glacial till or uniform spoil or refuse.
Channel Sampling (Highwall)		Limited to active or abandoned sites with exposures; not always representative; (lithology different from proposed mine area); getting fresh unweathered samples and a vertically continuous sample of the entire strata may require backhoe or excavator; dangers associated with highwalls; sampling and weighting problems due to breaking resistance.	Limit to supplement air rotary or diamond core data; get fresh samples only.

a double-walled drill stem through which water or air is forced down the outer section of the drill stem and the cuttings/chips are forced up the inner section of the drill stem. The cuttings and water or air are brought into a separator and dropped near the rig where the samples can be collected. The samples are isolated from contact with overlying strata, so this type of drilling offers a much cleaner and quicker means of obtaining overburden samples. The drilling does not need to be stopped to blow out the hole. If water is employed in the drilling process, the materials are also washed free of the fine dust coating that accumulates

on the chips during drilling with air. This allows for much easier identification and logging of rock type than is the case for Normal Circulation rotary rigs.

Diamond Core

Core drilling is also a common exploration technique and is an excellent method of sampling the overburden, provided that core recovery is essentially complete. As a rule, core drilling improves the validity and quality of rock samples compared to air rotary. Diamond core barrels can be used on both types of rotary drilling platforms. Coring provides a continuous record of the lithology present with little chance of cross-strata contamination of lithologic materials and can provide the geologist with more information than can be obtained by the collection of rock chips (cuttings). Cores provide a better overall view of the lithology underlying a proposed site by providing the geologist with the ability to judge rock color, gross mineralogy, grain size/texture, fossil content and relative hardness. Fracture zones and any associated mineralization can be evaluated in considerable detail. This type of information is not always readily available from rock chips. Although a core provides an uncontaminated and better source of reliable lithologic data than air rotary drilling does, coring is very time consuming and costly, especially if the entire overburden section is to be sampled by this means. Diamond cores can be used as a secondary means of data collection to isolate previously identified problem zones, or as a primary sampling tool in the area of the coal, i.e. the interval 5 feet above and below the coal horizon. The entire core section must be collected and processed for analysis to ensure representative sampling. Successful coring is mostly dependent upon the experience of the on-site geologist, project engineer, or driller.

A problem that can occur with coring is core loss. This normally occurs when encountering mine voids or solution channels, but is also a common problem in the first 10 feet (3 m) or so of unconsolidated soil and rocks and in the transition through weathered rock into competent rock. Core recovery on the order of only 50 to 60% or less is not unusual for such material. When drilling is done in the unweathered zone (sometimes indicated by an absence of iron staining), core recovery approaching 100% is the norm rather than the exception.

When coring the coal, it is advisable to use a core barrel long enough to core the entire thickness of the coal. It is preferable to have a nearly empty core barrel containing only 6 to 12 inches (15 to 30 cm) of overburden, and at most one that is not more than 20% full when first encountering the coal. The small amount of overburden aids in determining if the entire coal section has been sampled; i.e., knowing the starting and ending points of the coal. It also helps protect the coal from being crushed by the ram when extracting the coal from the core barrel (Personal Communication, Clifford Dodge, Richard Beam, William Marks).

Besides actual core loss encountered while drilling, drilling data can also be lost due to the improper handling of the cores. Common problems include placing cores in the core boxes in the wrong order or upside down, and damage caused to the core during handling and shipping.

Augering

Auger drilling is not recommended for general overburden sampling. It is typically used for unconsolidated or highly weathered materials. The auger lifts the materials on the auger screw. The potential for contamination is high in that the material being lifted is in constant contact with the overlying stratum, thus providing for intermixing. However, augering can be successfully used in homogeneous materials such as glacial till and/or old mine spoil.

Channel Sampling (Highwall)

Samples can be collected directly from an open source, such as a highwall within or near a proposed permit area, for overburden analysis provided several caveats are understood. First, samples might be weathered to such a degree that they do not represent the strata to be mined. Second, the availability and accessibility of highwalls limit highwall sampling. Therefore, care should be taken to collect only unweathered samples from the highwalls in close proximity to and representative of the proposed mining. It is recommended that open source (outcrop, highwall, etc.) samples be used primarily as a supplement to drilled samples.

Overburden Sampling Practices

The ADTI Prediction Work Group surveyed various states to determine how overburden sampling is practiced in the eastern coal producing states. The results are given below. These practices have, in large measure, governed overburden sampling frequency. All of the states surveyed, except Virginia, have some minimum spatial distribution requirements for overburden analysis that must be supplemented upon request from the reviewing professional(s). Even though the states have stated minimum spatial requirements, few new permits are considered with data supplied by the applicant that only meets the minimum requirements. Table 6.2 gives minimum overburden sampling requirements by State.

In addition, all of the states have minimum requirements for vertical sampling intervals. The most commonly submitted sampling data is collected from rotary drill cuttings and core splits; however, all the states will accept fresh highwall samples to extend existing permits. Table 6.3 gives minimum overburden interval sampling requirements by State.

SAMPLING DESIGN CONSIDERATIONS AND GUIDELINES

Relevance to Acid Base Accounting

A critical factor in the use of Acid Base Accounting (ABA) methods (see Chapter 4) is the suitability of the overburden sampling scheme for extrapolation to mine scale. While generalized rules of thumb are being used, no consistent scheme based on either theory or empirical evidence exists for determining the number or spatial distribution of samples required to characterize a given site for ABA. Horizontal drillhole spacings that will provide reasonably accurate ABA estimates are still being debated. In current practice, estimates of NP/MPA are obtained from relatively sparse drillhole sample densities, with one sample representing every 2-5 vertical feet (Tarantino and Shaffer, 1998). Core and rotary samples are normally employed. For example, West Virginia requires that NP and MPA data be derived from core drilling samples, but does not

specify the minimum number of cores. Pennsylvania has found that the 6 to 7 holes it typically requires per 100 acres is generally sufficient to accurately predict whether a site will produce acidic or alkaline water (Brady et al., 1994).

As mentioned in Chapter 1, the collective experience of the ADTI Coal Sector is that Pennsylvania's experience can be generalized though site-specific criteria may require more intense or less intense sampling. Also, ABA should not be used alone for predictions; it is but one of several tools in the mine drainage prediction toolbox. For example, Pennsylvania recognizes that if sufficient information exists from adjoining sites, no overburden analysis at all may be necessary. Further discussion on this subject can be found later in this chapter in the section on Stratigraphic Considerations-Lateral Variation and Number and Distribution of Boreholes.

Table 6.2. Minimum Overburden Sampling Requirements

STATE	MINIMUM REQUIREMENT
AL	Two sample point locations on small permit properties (<10 acres). One sample point location per 160 acres, or one per property quarter on larger permits.
IL, IN	A minimum of one sample point required. Adjacent mine sampling points can be submitted to supplement site specific data. In general, accepts any information submitted by the applicant, considers the quantity, quality, and consistency of the overburden analysis for the permit area, and then makes a decision on whether a reasonable characterization of the site is possible based on the spatial distribution provided.
KY	Eastern KY—sample points should be distributed on a staggered, ¼ mile grid pattern. Western KY—sample points should be distributed on a staggered, ½ mile grid pattern.
MD	One sample point location per site regardless of size.
OH	One geologic test hole for each 25 acres, or fraction thereof, of coal stripped. At least one hole must be located at the point of highest elevation. Holes must be located as far apart as the size and shape of the area to be mined will allow and must be drilled to the bottom of the material underlying the lowest coal seam to be mined. Additional test holes may be required in order to verify the submitted data. Core drilling may be required if it is determined that site conditions warrant more precise information. The applicant may request a waiver for the number of test holes prior to application submittal if equivalent information is available.
PA	Two sample point locations per site regardless of size. However, a rule-of-thumb of 2 holes per site plus 1 hole per 100 acres is usually requested. On average, most applications contain 6-7 overburden analysis hole for every 100 permit acres. These requirements may be waived if it can be demonstrated that equivalent information is available to characterize the AMD potential of the site.
TN	One sample point location per 60-100 acres for permits to mine coal considered a high risk for AMD, based on past experience. One sample point location per mile in coal considered a low risk for AMD.
VA	In general, accepts any information submitted by the applicant, considers the quantity, quality, and consistency of the overburden analysis for the permit area, and then makes a decision on whether a reasonable characterization of the site is possible based on the spatial distribution provided.
WV	At least one hole in low cover and one in high cover. Otherwise, WV permits geologists to use their best professional judgement when determining the number of ABA boreholes required for a permit. In general, accepts any information submitted by the applicant, considers the quantity, quality, and consistency of the overburden analysis for the permit area, and then makes a decision on whether a reasonable characterization of the site is possible based on the spatial distribution provided.

Table 6.3. Minimum Overburden Interval Sampling Requirements

STATE	INTERVAL SAMPLING REQUIREMENTS
AL	One sample every 5 feet or at a significant lithologic change, whichever comes first. Sample compositing is not allowed. AL reserves the right to request core drilling in permit areas where there are known acid-forming lithologic units.
IL	One sample required for each lithologic unit. A composite sample is acceptable for thin, adjacent units. A composite or multiple samples are acceptable for units that exceed 5 feet.
IN	One sample required for lithologic units 0.5-5 feet thick, two samples recommended for strata 5-10 feet thick, and, for strata more than 10 feet thick, one sample every 5 feet or at a significant color or lithologic change, whichever comes first.
KY	One sample for suspected acid-producing strata and coal seams less than 1 foot thick; smaller strata and seams may be grouped with next lower unit. One sample within the lithologic unit for strata 1-5 feet thick. Two samples for strata ranging from 5-10 feet thick. One sample every 5 feet for strata more than 10 feet thick.
MD	For rotary drill cuttings, one sample every foot or at a significant lithologic change. For core samples, 3 foot composite samples or at a significant lithologic change.
OH	Each stratum and coal seam must be analyzed. In practice, sampling intervals greater than 20 feet are discouraged. Requests for waivers from overburden analysis must be submitted prior to application and must document that equivalent information is available.
PA	One sample per 3 vertical feet or at a lithologic change plus 1 foot above and below the coal bed. Rotary drill samples must be collected in 1 foot increments that then can be composited up to 3 feet. Core sample composites limited to 3 foot increments regardless of unit thickness; an equal portion of the entire core length must also be crushed and split for analysis.
TN	One sample every 3 feet or at a significant lithologic change, whichever comes first.
VA	Sobek, et. al. (1978) protocol: one sample every 5 feet for sandstone units; one sample every 3 feet for other lithologies.
WV	One sample every 5 feet or at a significant lithologic change, whichever comes first. Sample compositing is not allowed. Sobek et. al. (1978) followed as the official guide (one sample every 5 feet for sandstone units; one sample every 3 feet for other lithologies). Permit geologists also refer to NPDES, DMR discharge data, and other historical data from adjacent operations in the same seam.

Inherent spatial variation in NP and MPA can be caused by stratigraphy, lithology and/or the effects of weathering. The critical issue is, therefore, the sampling strategy and sampling density required to provide adequate ABA assessments. Also, within a mine setting, compositional variations exist not only between rock facies but also within individual facies, where spatial variations exist both in vertical sequence and in lateral extent (Renton et al., 1989).

As a result of spatial variations in geologic facies, the geochemistry of coal and coal overburden materials display some degree of order over large distances, and overburden samples from different drilling locations need not be treated as being statistically independent (Caruccio and Geidel, 1982; Tarantino and Shaffer, 1998). The development of acid production may be caused by either the distribution of high concentrations of pyrite or by the paucity of carbonate minerals capable of neutralization. The possibility that pyrite may display a *nugget effect* requiring very small sample densities has been raised based on the commonly asymmetric univariate sampling distribution of rock sulfur concentrations (Rymer and Stiller, 1989). Some

site-specific information on the spatial covariance of sulfur and carbonate is included in Appendix B (New Allegheny Mine, West Virginia Case Study); see also Donovan and Renton (1998).

Geologic Considerations Involved in Sampling Design

Numerous geologic factors affecting mine drainage prediction were discussed in Chapter 2 of this volume. Several of these geologic factors affect sampling design, including surface weathering and facies variations. In addition, proper correlation of stratigraphic units is an essential consideration in sampling, because there are a number of legitimate geologic reasons why there can be significant variations in sulfur content, NP, or other parameters in samples of the same stratigraphic interval from different drill holes. Without proper correlation, one cannot be certain of the lateral distribution of rock types, cannot design special handling plans, cannot accurately design a mining plan, and cannot accurately determine alkaline addition rates. Miscorrelation of coal seams or other stratigraphic units introduces an unnecessary source of variation and increases confusion and complexity in making accurate predictions of mine drainage quality.

The geologic considerations in sampling design affect both lateral variations (i.e. how many drill holes at what spacing) and vertical variations (i.e. how deep must the drill holes be; sampling interval within lithologic units) in obtaining representative samples of the overburden strata at a mine site. A description of these geologic considerations in sampling design, with examples from drill holes, is presented below. Additional information is contained in Chapter 2.

Surface Weathering Effects

Weathering results in the near-surface removal of carbonates and sulfide minerals; carbonates by dissolution and sulfides by oxidation. This zone is usually recognizable by the yellow-red hues (indicative of oxidized iron) of the rocks. Generally, in the unglaciated portions of the Appalachian Plateau, the intensely weathered zone extends to 20-60 feet (6-20 m) below the surface. Chemical weathering of bedrock is enhanced by physical factors such as stress-relief fracturing on hill slopes and bedding-plane separations due to unloading. Clark and Ciolkosz (1988) have suggested that periglacial conditions during the Pleistocene contributed to the shattering of near-surface rock. Shattering of rock increases surface area and thus accelerates weathering. These processes acting together also increase the permeability of the weathered zone. The ground water associated with the weathered zone is dilute, in terms of dissolved solids, because readily soluble products have been removed by chemical weathering (Brady, 1998).

Chemical weathering is also influenced by lithology. Coarser, more permeable lithologies may allow oxidation to extend to a greater depth. Kirkaldie (1991) measured the depth of the highly weathered zone. He noted that the maximum thickness of highly weathered rock was 28.9 feet (8.8 m) in sandstone, and only 11 feet (3.3 m) in shale. His observations were based on the physical appearances during drilling and may not directly correlate with chemical weathering.

This weathered-rock zone exists throughout the Appalachian Plateau. It is difficult to determine precise rules of thumb for the depth of leaching of carbonates and oxidation of pyrite because these minerals can only occur where they were originally present (before weathering). If no pyrite was ever present within a

stratigraphic horizon, its absence is not due to weathering, but to the fact that it was never there in the first place. The same is true for calcareous strata. Smith et al. (1974) investigated the effects of weathering on the Mahoning sandstone in northern West Virginia, and noted a "pyrite-free weathered zone approximating 20 feet (6 m) of depth below the land surface." Singh et al. (1982), in addition to noting the pyrite-free zone, also noted a loss of alkaline earth elements within 20 feet (6 m). Brady et al. (1988; 1998) in a study of the upper Kittanning and lower Freeport overburden in Fayette County, PA noted a similar loss of calcareous rocks in the near-surface weathered zone to about 6 m (20 feet) depth. Hawkins et al. (1996) noted weathering to depths of 30-60 feet (10-20 m). Brady et al. (1998) concluded that rarely do NPs greater than 30 tons of $CaCO_3$ per thousand tons or sulfur greater than 0.5% occur within 20 feet (6 m) of the surface in Pennsylvania. This conclusion can probably be generalized for the entire region, based on the fact that shallow groundwater chemistry, which represents water associated with the shallow weathered zone, had low concentrations of ions regardless of geographic location (Brady, 1998).

An accurate knowledge of the extent (depth) of the weathered zone is important from an overburden sampling standpoint. Overburden sampling must adequately represent both the weathered zone and unweathered bedrock. This will entail drilling overburden test holes at maximum cover to be mined and at lesser cover. Drilling only maximum cover or only lower cover overburden holes will probably not adequately define the overburden chemistry of the entire mine.

An understanding of the effects of weathering on the distribution of pyrite and carbonates is important in: (1) accurately defining their stratigraphic distribution within unmined overburden, (2) designing mine plans to prevent post-mining problems, and (3) accurately predicting post-mining water quality. An understanding of the weathering profile is just as important as understanding the lateral and vertical distribution of strata and their pyrite (sulfur) and carbonate content. Adequate characterization of the site is necessary to predict post-mining water quality. It is also necessary for designing pollution prevention measures such as calculating alkaline addition rates and designing special handling plans.

Facies Changes and Other Paleodepositional / Paleoenvironmental Considerations

Rather abrupt changes in overburden lithology can occur due to facies changes, where lateral variations in depositional environments result in contemporaneous deposition of an array of different sediments. For example, in modern coastal zone, barrier-island settings, a transition from beach and dune sands to back-bay brackish black muds to alluvial channel sands may be seen in a lateral distance of a mile to several miles inland from the ocean. A similar array of lithologic units occurs in Pennsylvanian Age coal-measure sedimentary rocks where the overburden above a coal seam may vary from sandstone to shale within a similar lateral distance. This becomes a significant sampling design problem. Generally, a sufficient number of initial exploration and overburden analysis holes must be drilled in order to delineate the facies changes and obtain representative samples of the different lithologic units.

Paleodepositional factors may also affect the vertical distribution of sulfur within a lithologic unit, and consequently have an effect on representative sampling within a drill hole. Numerous studies on the vertical distribution of sulfur and coal have been done for coals around the world, encompassing various geologic periods and ranges of coal rank. Increased sulfur at the top and bottom of coal seams appears to be the

rule rather than the exception, according to Brady et al. (1998) who cite numerous references for coals of the Appalachian Basin. Reidenour (1966) has shown that distribution of sulfur in the Lower Kittanning coal of western Pennsylvania may be significantly affected by local paleotopographic variations, hypothetically attributable to preferential deposition of pyrite in channels whose location in the paleotopograhic lows was controlled by differential deposition and compaction of peat. How to address such vertical variations in sulfur in sampling design is addressed later in this chapter.

Large-scale paleoenvironmental factors influence the distribution of pyrite and carbonate minerals within overburden strata and consequent mine drainage quality, as described in Chapter 2. The array of marine, brackish, and freshwater paleoenvironments of overburden strata for specific coal seams is typically mapped at the regional scale from fossil assemblages (e.g. Williams, 1960), and thus may not be particularly relevant to sampling designs for a single coal mine site. However, information about lateral variations in sulfur content gained from studies concerning these paleoenvironments may be useful in determining how many drill holes are necessary to obtain representative samples and characterize variations in overburden geochemistry at a mine site. For example, Williams and Keith (1963) found regional variations in total sulfur content of the Lower Kittanning Coal in western Pennsylvania, where areas with marine overburden were higher in sulfur than freshwater paleoenvironments. Hornberger (1985) conducted a preliminary sampling study of channel samples of the Lower Kittanning coal and overlying shale in western Pennsylvania in order to test the hypothesis that variations in coal mine drainage production could be attributed to systematic variations in pyritic sulfur content and the abundance of the framboidal form of pyrite between paleoenvironments. Three widely spaced channel samples were collected from the active highwall in each of four surface mines, two from a marine paleoenvironment and two from a freshwater paleoenvironment. While the mean total sulfur and pyritic sulfur content of the freshwater mines was somewhat less than that of the marine mines, an Analysis of Variance (ANOVA) showed that the largest percent of the variance in pyritic sulfur was due to the high variability between channel samples within the mines. (Additional data from that ANOVA study is included in a case study in Appendix B). Another example of high within-mine variability was found by Rooney (1997, personal communication), who used the Pennsylvania Department of Environmental Protection (PA DEP) overburden analysis database to compare NP/MPA ratios for three drill holes from each of three mines in freshwater, brackish, and marine paleoenvironment (nine mines total). The brackish mines generally had lower NP/MPA ratios than the freshwater and marine mines, indicating a greater potential for AMD production, but the variability between drill holes within the same mine is very large for some of these mines. These examples indicate that it may take much more than three drill holes or channel samples per mine in order to characterize patterns of sulfur content variations.

Stratigraphic Considerations-Lateral Variation and Number and Distribution of Boreholes

It is important to adequately represent any spatial lithologic variation by drilling enough boreholes. On an areal basis, a four and one-half inch diameter core is only sampling approximately one four hundred thousandth of an acre. The WV Surface Mine Drainage Task Force's Suggested Guidelines for Surface Mining in Potentially Acid-Producing Areas (1979) recommends that all surface mining in potentially acid-producing areas be within 1 km (approximately 3300 feet) of a sampled overburden analysis hole or highwall. Donaldson and Renton (1984) and Donaldson and Eble (1991) indicated that although cores

spaced up to 2 miles (3 km) apart in the Pittsburgh coal were adequate to reflect major thickness and sulfur trends, this spacing was not adequate for mine design. They felt that lateral Pittsburgh sampling at intervals on the order of 1200 to 1400 feet (365 to 427 m), or less than 500 feet (152 m) for the Waynesburg coal, along with geostatistics, are necessary to determine small-scale sulfur content trends.

Predictions based on overburden analysis require that the drill holes analyzed be representative of the strata present at a site. The more variability that exists in the overburden strata, the more likely it is that, for a fixed drilling density, the samples will not accurately represent the entire mine site. Increasing sampling density is one option to compensate for such variability, but this also increases drilling and analytical costs. While overburden sampling density is a critical component of the prediction process, there are no generally accepted methods currently in use for determining the number or spatial distribution of drill holes required to representatively characterize mine sites.

The geologic systems responsible for the deposition and alteration of the sediments and their chemical quality do not operate in a completely random fashion at the cubic centimeter level and, thus, do not produce overburden samples that are statistically independent (Tarantino and Shaffer, 1998). Although there are exceptions, most of the geologic systems, especially those that produce calcareous material, operate over large areas with some degree of order, and deposit laterally pervasive units (Caruccio and Geidel, 1982). Lateral continuity has also been observed in high sulfur strata. Facies changes can provide variations in lithology and the degree of surface weathering can cause changes to the percent total sulfur and NP over short distances. Therefore, it is imperative to know the areal extent of any alkaline or acidic material, high energy paleodepositional environments (for example, channel sandstones), and the degree or depth of weathering. Adequate exploratory drilling is essential to the development of a representative overburden sampling plan.

A recent study suggested that sulfur is not uniformly distributed in a homogeneous fashion, but is distributed in clusters of hot spots similar to large chips of chocolate in a cake. If this is true, accurately determining the mean percent total sulfur of a particular stratum would be difficult, which could in turn lead to under-predicting the potential to produce AMD (Rymer and Stiller, 1989). However, concern over the clustering effect neglects certain factors, one of which is that the concentration of total sulfur at a mine site may not be the critical factor of whether or not AMD will be produced. Acidity produced in laboratory experiments appears only to be strongly related to percent total sulfur for sulfur values above 1.0 part per thousand with acidity production being negligible for sulfur of lesser value unless there is a paucity of NP (Rose et al., 1983). However, experience has shown that in the field, sulfur as low as 0.5% (and possibly somewhat less) can be a problem. As discussed elsewhere in this volume, the presence of significant NP appears to be the more critical factor.

Another factor to consider is that the tendency for the mean percent total sulfur at a site to be skewed to the right is probably just a natural distribution of data involving the plotting of a quantity where the left boundary or minimum abscissa is zero, and there is essentially no right boundary. For example, most sulfur values in coal overburden are less than 0.5%; a rare few are as high as 10 to 20%. Pure pyrite has a

percent sulfur of 53.4% (the maximum right-hand value). Thus, a few high values will skew data to the right. This is a commonly observed distribution in geologic data (Koch and Link, 1980).

Current West Virginia Division of Environmental Protection (WV DEP) regulations require that a company submit NP and MPA data collected from samples acquired from core drilling; however, no regulations exist as to the minimum number of cores. In some cases, pre-mining environmental assessments have been made based on data from a single core.

Pennsylvania has grappled with overburden drill hole distribution since the advent of overburden sampling. The PA DEP bases its requirements on the mine-site specifics, if it is deemed necessary that the overburden be drilled. A minimum of 2 to as many as 15 holes per 100 acres might be required per mine site (Brady et al., 1994; Tarantino and Shaffer, 1998). The average number of holes for a typical site is 6 to 7 holes per 100 acres, with a high of 43 holes per 100 acres and a low of 2 holes per 100 acres.

A rule of thumb developed in Pennsylvania in the 1980s to determine a suggested minimum number of overburden holes was:

Number of Overburden Holes = (Number of acres to be mined/100) + 2

If this calculation resulted in a fraction, it was rounded to the closest whole number. For example, 3 holes were required for 143 acres, 2 holes per 49.9 acres, and 4 holes per 179 acres. The division factor for hectares (ha) is 40.47 rather than 100. This method assumed that for mines where overburden analysis was requested, at least 2 holes were needed to determine whether the drilling was representative. More recent data from Pennsylvania show that the actual sampling density for ABA drill holes is greater than the rule of thumb. A recent survey revealed that on average, there was one hole for each 15.5 acres (6.3 ha) of coal removal for 38 sites (Table 6.4). A similar survey of 31 Small Operator Assistance Program applications received in the 1993 calendar year revealed that on average there was one hole for each 18.8 acres (7.6 ha) of coal removed, as shown in Table 6.5.

Table 6.4 Number of acres per overburden analysis (OBA) hole (Brady et al., 1994).

Number of Applications =38	Coal Area acres (ha)	Area per OBA hole acres (ha)	Number of holes per 100 acres (40.47 ha) (rounded to next whole number)
Mean	43.5 (17.6)	15.5 (6.3)	7
Median	30.3 (12.3)	11.9 (4.8)	
Minimum	5.0 (2.0)	2.3 (0.9)	
Maximum	172.5 (69.8)	44.9 (18.2)	
Standard Deviation	38.0 (15.4)	10.6 (4.3)	

Table 6.5 Number of acres per overburden analysis (OBA) hole based on SOAP applications received in 1993 (Tarantino and Shaffer, 1998).

Number of Applications: 31	Coal Area acres (ha)	Area per OBA hole acres (ha)	Number of holes per 100 acres (40.47 ha) (rounded to next whole number)
Mean	72.6 (29.4)	18.8 (7.6)	6
Median	55.0 (22.3)	15.7 (6.4)	
Minimum	6.0 (2.4)	3.0 (1.2)	
Maximum	220 (89.0)	53.5 (21.7)	
		153	

Standard Deviation	54.6 (22.1)	12.3 (5.0)	

The ranges in the data are due to a multitude of factors, such as stratigraphic complexity and shape of the site and availability of other prediction tools. The data apply only to permit applications that had overburden analysis data. Approximately 30 to 40% of Pennsylvania's applications do not require submittal of overburden analysis because of the availability of equivalent prediction data, including data from adjacent mine sites. A variety of geological/geochemical clues can provide insight into the presence of acidity- or alkalinity-producing materials. Such clues might include:

- Exploratory drill hole data, to determine the lateral and vertical extent of rock types.

- Premining water chemistry in springs, drill holes and monitoring or water supply wells completed in or hydrologically related to the coal seams being mined. Both shallow and deep aquifers should be examined, but water from zones much deeper than the coal will probably not be useful. As a rule of thumb, if alkaline water is present, alkaline rocks are probably present.

- Water quality from adjacent mining sites within the same coal seam

- Maps and studies of paleodepositional environments

- The extent of glaciation and the carbonate content of glacial drift or till, where present

- The presence of burned out vegetation areas on adjacent mining areas

- Soil surveys can provide information on the variability of the host rock the soil was derived from. They also provide some information on depth of weathering and carbonate content.

These clues can help define the extent and degree of variability of the overburden and in some cases may preclude the need for overburden analysis. Alternatively, where overburden analysis is indicated, these same data also provide information necessary to locate overburden holes to adequately represent the entire site (Tarantino and Shaffer, 1998).

Vertical Sampling Intervals

All distinct discrete lithologic units should be sampled separately. In the northern Appalachian basin, the common lithologic units include: sandstone, limestone, shale (including siltstone and claystone) and coal. The composition of these units can range widely. For example, sandstones can have a calcareous cement and shales can be calcareous or carbonaceous. Noll et al. (1988) use a somewhat different terminology for these rock units. They divided overburden rock units into sandstone, mudrock, limestone, coal, carbolith, intercalate, glacial till, and glacial outwash. The difference in the glacial units is that glacial outwash is stratified and glacial till is not. Sandstone must have over 50% sand-sized (less than 2 mm diameter) quartz particles. The term mudrock is broad and includes mudstone, siltstone, claystone, and shale. Limestones are composed of at least 50% calcium carbonate and should fizz aggressively with 10% HCl. Carbolith is any black or dark colored unit that contains 25-50% by weight carbonaceous matter (coal contains greater than 50% carbonaceous matter by weight). This term includes bone and waste coal, as well as carbonaceous mudrock. Intercalate is a unit which is composed of two or more rock types that are finely interbedded. Because of the high degree of interbedding, individual units cannot be sampled separately. In

other parts of the Appalachian Basin, this definition of lithologic units may have to be modified to allow for different units or conditions peculiar to a given geology.

The sampling interval for indurated strata should not exceed 3 feet within lithologically consistent units, according to Noll et al. (1988). Sobek et al. (1978) suggested that a sampling interval of 5 feet for sandstones and 3 feet for other rock types was adequate, although larger intervals may be considered adequate in various jurisdictions. Determining breaks in the sampling interval within monolithic units can be somewhat subjective, depending on the experience of the geological professional. However, within monolithic units, sampling breaks should occur where significant color, mineralogical, or grain size changes occur. Skousen et al. (1987) suggest sampling intervals as thin as 12 cm, especially if they exhibit a darker color (dark gray or black), which may be indicative of a high carbonaceous content. Sampling breaks should also occur at changes in sedimentary structure (e.g., a change from a cross-bedded to a massive sandstone) and at zones of significant fracturing or jointing. Location within the stratigraphic column can also determine the thickness of the sampling interval (e.g., intensive sampling of the strata directly overlying and underlying the coal). Some units commonly exhibit significant differences in terms of sulfur values compared to adjacent lithologically similar strata. For example, when a sandstone unit rests directly on top of a coal bed, the bottom few feet of that unit commonly exhibit much higher sulfur concentrations than the rest of the unit (diPretoro and Rauch, 1988; Donaldson et al., 1979). Mineralogical changes, inclusions (e.g., coal spars, clay or siderite nodules, clay veins, etc.), secondary mineral deposits (e.g., fracture filling by calcite ($CaCO_3$), and weathered zones should all influence the sampling interval.

There are several criteria for determining the sampling intervals of overburden. The required sampling interval for unconsolidated material (i.e., mine spoil, coal refuse, glacial deposits, and alluvium) should not exceed 5 feet in some jurisdictions, while it can in others (such as up to 10 feet in Texas). Additional sampling breaks within these units are subject to the variability of the material and the experience of the geologic professional. However, at the very least, unaltered portions should be separated from weathered or leached portions. It should be noted that it is neither pragmatic nor economically feasible to break samples out at each minor change. The sampling and compositing of the overburden should be conducted so as to minimize the number of samples to be tested, without significantly decreasing the quality of the overburden characterization. As an example, the mixing of thin high sulfur content strata with adjacent strata can lead to a conclusion that a much larger volume of material must be specially handled than if the sampling intervals were fine enough to resolve the smaller volumes of problematic strata.

The opposite effect can be observed in Table 6.6. In that example, if one assumes (for the sake of argument) that 0.5% sulfur is the threshold above which a unit is considered acid producing, a stratum with greater than 0.5% sulfur would be diluted to less than this value if it was combined with an adjacent low sulfur stratum. Dilution would cause one to under-predict the acid producing potential. For example, if the bottom-most unit on Table 6.6, a 1 foot thick black shale with a 2.34% sulfur content, was combined with the overlying rock, a sandstone with 0.01% sulfur content, a composite sample with a misleading average of 0.48% would be produced. This fine balance lies at the center of controversy between regulatory agencies and mining companies. While there are a number of statistically-based schemes of sampling, in the

final analysis, the development of representative sampling is dependent on the professional skill of the geologist who obtains the samples in the field.

Therefore, sampling intervals should not be increased to the point that there is no clear visual resolution of the individual stratigraphic units. A worst case scenario would be to simply collect one composite sample for an entire drill hole. In most cases, the percentage of sulfur and NP would be very low, but this would not mean that there were no strata within the drill log that have significant amounts of sulfur and NP.

Table 6.6. Compositing of too many 1-foot (0.3 m) intervals can under-predict acid producing potential (Tarantino and Shaffer, 1998).

Thickness (ft.)	Total %S	Lithology	Avg. %S of Interval			
1	0.01	sandstone				0.48
1	0.01	sandstone			0.59	
1	0.01	sandstone		0.79		
1	0.01	sandstone	1.18			
1	2.34	black shale				

Representative Interval Samples

Noll et al. (1988) do not discuss the subtle complexity of ensuring accurate, non-biased, representative samples. They do stress that it is critical that 100% of the sample volume be included for a sample interval for compositing purposes, because of possible geochemical variations within the three-foot (0.9 m) interval. The ultimate sample size used in ABA assessments is 1 g for total percent sulfur and 2 g for the NP test. Therefore, assuming no loss or contamination of the zone being sampled, only 1 to 2 g are tested out of a 25,550 g sample (based upon a 4.5 inch (11.4 cm) diameter drill bit and using an average rock density of 170 lbs/ft^3 (2,723 kg/m^3)). This means that only one out of every 10 billion g contained in a 3-foot interval over an acre is being tested for percent sulfur. Fortunately, sample preparation procedures have been developed to obtain representative small sample aliquots.

Sobek et al. (1978) suggested that a 5 inch (12.7cm) section out of the middle of a 1 foot interval of core can be assumed to be representative of that interval. The best way to ensure representativeness is to sample the entire interval. To avoid bias, one of the following two methods is recommended:

• The entire core interval having the same log description as described above, whether it be a 1, 2, or 3 foot (0.3, 0.6, or 0.9 m) interval, must be entirely crushed and reduced in size via a riffle or rotating splitter until a suitable size fraction remains for analysis.

• The entire core length should be bisected longitudinally using a core-splitter or saw. One-half of the core is retained for historical records and possible additional testing. The other half of the core is crushed for

the entire sampling interval. After crushing, the entire sample is divided and reduced in size via a riffle or rotating splitter until a suitable size fraction remains for chemical analysis.

There are three reasons for splitting and crushing samples:

1. To reduce the bulk (amount) of a geological sample.
2. To provide an unbiased statistically representative sample of small quantity, which can be used in a laboratory for ABA or leaching tests
3. To reduce samples to a small size fraction that maximizes surface area and minimizes the analytical time.

Guidelines for Drilling and Sampling Overburden and Coal at Surface Mine Sites

The following are general guidelines for incorporating geologic considerations in sampling design to account for lateral and vertical variations in geochemical parameters in an attempt to collect representative samples of the strata. The first four guidelines for determining the number and spacing of overburden analysis drill holes on a mine site are largely based upon the common sense application of geologic principles. The last spatial consideration is more difficult to describe or quantify because it attempts to answer the question of how variable is the mineralogy of samples from the same strata within the mine site or from the same stratigraphic interval and resultant mine drainage quality at nearby mine sites. Usually, this question cannot be answered until some overburden analysis holes have been drilled and the sample results have been evaluated, and that evaluation may require the use of geostatistical tools.

- A sufficient number of exploratory drill holes should be drilled throughout a proposed mine site, prior to determining the number, locations and depth of overburden analysis drill holes. These exploration drill holes are routinely used on most mine sites to determine the number and thickness of mineable coal on site (i.e. coal reserves), and the maximum overburden thickness that is economically practical (i.e. stripping ratio). It is very important to perform a geologic evaluation of these exploratory drill holes (i.e. drill cores and/or rock chips) to correlate coal seams and other stratigraphic units throughout the site, and to determine if there are significant variations in lithologic characteristics or thickness of stratigraphic units within the site.

- The first consideration is determining the number and spacing of overburden analysis drill holes on a proposed mine site is related to mining engineering and geology. Most surface mining sites are designed, operated and reclaimed in a series of mining phases. At least one overburden analysis drill holes should be located within the initial mining phase. The placement of the other holes should consider the spatial configuration of the mine site and significant variations in stratigraphy and lithology that will be encountered in the progression of mining phases.

- At least one of the overburden analysis drill holes should be located at the maximum highwall height (maximum cover) and at least one of the overburden analysis drill holes should be located at much lesser cover, in order to evaluate surface weathering effects. (This is not intended to imply that two drill holes will be sufficient to characterize geochemical variability of any mine site.) In the areas of the mine site with low cover, the weathered-rock zone may be more than half of the overburden. For example, a thick shale within this weathered zone may have the top 25 feet fortuitously leached of most of the pyritic sulfur content, but also be leached of most of the carbonate minerals.

- If facies changes occur within the mine site, a sufficient number of exploratory or overburden analysis drill holes are needed to delineate the pattern of facies changes (i.e. paleoenvironmental map) throughout the site. Within each of the major stratigraphic sequences relating to the facies changes (eg. freshwater calcareous shale replaced by thick channel sandstone overburden), a sufficient number of overburden analysis drill holes should be located to obtain representative samples of the lithologic differences.

- A single overburden analysis drill hole is almost never sufficient to characterize the overburden quality of even the smallest of proposed mine sites, because it tells nothing about variability within the mine site and whether that single sample is representative.

The case studies of geostatistical techniques that follow provide examples of how variability of geochemical parameters can be quantified within and between mine sites. In areas of high lateral variability of total sulfur contents or other parameters of interest, it may be necessary to drill many more holes than implied from the preceding four guidelines, in order to adequately characterize these patterns of variation and obtain representative samples.

GEOSTATISTICAL APPROACHES

A large variety of statistical and quantitative techniques are available to evaluate data obtained from overburden sampling and to extrapolate the resulting information to the population represented by the samples. Basic statistical measures include the average or mean value of a measured variable or variables and the variance or the degree of variation around the mean. Statistical procedures in use in geological studies include frequency distribution analysis and analysis of variance procedures. More sophisticated techniques specifically designed to evaluate spatially distributed variables, such as variography, kriging, and three-dimensional modeling, are also being used. The following discussion is provided to illustrate the usefulness of these techniques in overburden sampling for AMD prediction. Some case studies giving more detail on the particular methods are provided in Appendix B. Readers are referred to the many basic works on statistical evaluations in geological studies, such as Koch and Link (1980), Griffiths (1967), and Krumbein and Graybill (1965). Recent works on geostatistics include ASTM Technical Publication 1238, Geostatistics for Environmental and Geotechnical Appications (ASTM, 1996), Practical Geostatistics 2000 (Clark and Harper, 2000), and Introduction to Geostatistics, Applications in Hydrogeology (Kitanidis, 1997). See also the many references noted in the discussion below and in the accompanying case studies.

Analysis of Variance

The analysis of variance (ANOVA) statistical method is commonly used in geological studies. Numerous examples of one-way and two-way classifications and more complex ANOVA models are described in early works by Griffiths (1967), Krumbein and Graybill (1965), Miller and Kahn (1962), Chayes and Fairbain (1951) in petrology, Griffiths et al. (1953) in petrography, Krumbein and Tukey (1956), and many more recent studies.

ANOVA techniques depend on the important property that the variance of a sum of random variables is equal to the sum of the variances of these random variables, provided that these variables are uncorrelated.

If, under these conditions, two or more uncorrelated factors introduce variability into a set of data, the total variability can be divided into individual portions that add up to the total. Each source of variation can then be evaluated to assess its relative contributions to the total variability in the observations (Krumbein and Graybill, 1965).

In the context of sampling geological populations, ANOVA techniques have at least two important uses. The first is to evaluate the results of reconnaissance sampling studies in order to determine if the number of samples collected per site is adequate to solve the geological problem, and if other aspects of the sampling plan are sufficient to implement a full scale sampling of the population. The second is to provide statistical tools to make meaningful interpretations and inferences about the variability of properties or portions of the geological populations under study.

A case study illustrating the use of analysis of variance techniques is provided in Appendix B. This example is based on a sampling study by Hornberger (1985), who examined variations in sulfur content, framboidal pyrite occurrence, and leachate chemistry of the Lower Kittanning coal and overlying shale at surface mines in western Pennsylvania. This case study shows how analysis of variance can provide meaningful information about the variability in sampling data and the sampling design.

Variography and Kriging

In addition to traditional univariate statistics, extensive geostatistical literature exists on determining optimal sampling patterns for estimating mean values of spatially distributed variables (Tarantino and Shaffer, 1998). Nearly all geological properties exhibit heterogeneity, either of a random type or displaying some degree of scale-dependent spatial covariation. Covariance is the tendency for samples close to each other to be similar in some property (e.g., sulfur concentration averaged for two nearby vertical boreholes). The identification of spatial covariance structure is called *variography*, and is performed by sampling at a very detailed scale and calculating covariance empirically at a variety of separation intervals, i.e. groupings of sample pairs (Armstrong, 1984; Journel and Huijbregts, 1978). The results of such an analysis (termed variograms, semivariograms, or correlograms, depending on the variance scaling employed) contain useful information on the covariance of spatially-distributed (or regionalized) variables (Isaaks and Srivastava, 1988). This information on the spatial covariance structure may be applied to estimate sampling needs or to interpolate values between points where information is available, i.e. to contour the data. Successful interpolation schemes obey the covariance structure indicated by the measured data, and minimize or eliminate error between observed data and interpolated values, called *residuals*.

One technique commonly applied to interpolation is *kriging*. Linear kriging, the most commonly applied, produces the best linear unbiased estimate of a variable within a given area based on values at known locations and weighting factors, estimated from variography to minimize residuals (Journel and Huijbregts, 1978). Application of linear kriging assumes that the sampled property is at least weakly *stationary* (spatially uniform with respect to mean and variance), i.e. there is no large-scale spatial trend within the area of study. Kriging across a field with a pronounced trend may require de-trending of the data set prior to analysis. However, kriged estimates employing a trend or *drift* (also known as *universal kriging*) may also be performed, by incorporating the drift into the weighting functions.

Both kriging and variography imply that both local scale variance (*noise*) and large-scale variance (*trend*) are present in observed datasets and, in principle, may be distinguished from, and perhaps separated from, each other. In practice, distinction of noise from trend may be subject to considerable error in estimation, and frequently requires large samples. The application to mine-overburden sampling is to allow estimation of sample number and frequency to distinguish trends in the presence of noise.

Case studies on the application of variography to overburden sampling and characterization are provided in Appendix B. The first one is a study on the application of variography to NP, MPA, NNP, and mineralogy in coal measures at working mines in West Virginia, based on work done by Donovan and Renton (1998). The second describes the use of variography to evaluate the AMD potential of overburden associated with mining operations in South Central Tennessee, based on work done by the Office of Surface Mining's Knoxville Tennessee Field Office (Office of Surface Mining, 1997, 1998). These studies show how variography can be used to detect primary spatial trends in overburden data and to estimate optimal sample spacing.

Visualization and Three-Dimensional Modeling

Visualization and three-dimensional modeling software can be used to portray the three-dimensional characteristics of subsurface overburden units and to produce three-dimensional models. The three-dimensional models can be used to accurately estimate the volumes of overburden materials that are potentially acid-forming. *earthVision,* by Dynamic Graphics, Inc. of Alameda, CA, is one of a number of such software packages that have been applied to AMD assessments of mining operations. *earthVision* software is included in the set of engineering and scientific software tools known as the Technical Information Processing System (TIPS) of the Office of Surface Mining. The TIPS system is available to permit reviewers and reclamation specialists on UNIX workstations in Federal, State and Tribal regulatory agency offices in all coal producing states to assist in the regulation and reclamation of coal mines. In 2000, TIPS plans to distribute a windows NT version of *earthVision* that will enable permit reviewers to utilize the software from their desktops.

Such software can be used to interpret, analyze, interpolate, and present spatially-distributed two-dimensional or three-dimensional data. Data may be analyzed statistically by exploratory data analysis (EDA) techniques including B clustering, three-dimensional viewing, histograms, probability and distribution analysis, regression, and declustering. The spatial covariance may be analyzed by conventional variography, using spherical, exponential, gaussian, or power-law models. Kriging may be accomplished using linear, ordinary, universal, or co-kriging algorithms. The kriged spatial distributions may be integrated to yield volumetric statistics, such as estimation of average or total property values. Volumetric analysis is enhanced using sub-cell sampling, allowing relatively high precision in the volumetric estimates. For overburden analysis, it may be used to estimate ABA from vertical samples over three-dimensional volumes or two-dimensional areas of interest.

A case study illustrating the application of *earthVision* to coal overburden data is provided in Appendix B. This case study, which evaluated overburden characteristics of a large surface mine in Eastern Texas, is based on work done by Behum and Joseph (1997). Three-dimensional models of overburden

characteristics and volumetric calculations of selected overburden zones were produced. This study shows how visualization and three-dimensional modeling software can be useful in AMD prediction and mine planning.

FINDINGS AND RECOMMENDATIONS

The following are our general findings and recommendations on overburden sampling based on the material presented in this chapter:

- Proper overburden sampling and analysis can result in accurate predictions of the potential for AMD prior to mining. However, there is no single way to sample overburden that fits all cases. Instead, there are a variety of tools that can be used to sample overburden. Methods need to be chosen based on site-specific conditions to fulfill the goal of collecting representative overburden samples.

- Accurate water quality predictions and design of pollution prevention techniques can only occur if the sampling strategy and density adequately represents the site variability. The greater the variability in the overburden, the greater the number of samples that are generally needed to adequately characterize a site.

- Predictions based on overburden analysis require that the drill hole or other samples analyzed be representative of the strata present at a site. Increasing sampling density is one option to compensate for such variability, but this also increases drilling and analytical costs. Any sampling plan that relies on a single random (drill hole) sample of coal overburden will yield only one mean value for each variable measured, which may not be representative of the entire overburden population.

- It is necessary to invest the time and money necessary to conduct appropriate sampling to ensure that the data obtained are reliable. Precise analyses performed on an unrepresentative sampling plan will, at best, accurately characterize that unrepresentative portion of the population.

- Sampling should be a two-step process, a preliminary reconnaissance sampling followed by a final sampling plan. While there are a number of statistically based schemes of sampling, in the final analysis, the development of representative sampling is dependent on the professional skills of the geologist who obtains the samples in the field.

- A sound understanding and knowledge of the geology of the area to be sampled are essential in designing a representative sampling strategy. Overburden sampling strategies need to consider both *spatial* and *temporal* factors; i.e., lateral and vertical sampling density of the geological units being sampled and whether sampling should continue over the entire life of the mining and reclamation operation.

- The geologic systems responsible for the deposition and alteration of the sediments and their chemical quality do not operate in a completely random fashion at the cubic centimeter level and, thus, do not produce overburden samples that are statistically independent.

- Near-surface weathering can alter overburden chemistry by decreasing pyrite and carbonate concentrations (by oxidation and dissolution respectively). The effects of weathering can influence the distribution of overburden mineralogy just as dramatically as other geologic processes, such as paleoenvironmental factors. For a site with variable overburden thickness, a sufficient number of high

and low cover overburden holes must be drilled to assure adequate and representative sampling.

- Local overburden sections can include a variety of facies and paleoenvironments. These, in turn, result in compositional variations between rock facies and within individual facies. Spatial variations exist vertically and laterally. Paleodepositional environments influence relative abundances of pyrite and carbonate. If facies changes occur within the mine site, a sufficient number of exploratory or overburden analysis drill holes are needed to delineate the pattern of facies changes (i.e. paleoenvironmental map) throughout the site. Within each of the major stratigraphic sequences relating to the facies changes (e.g. freshwater calcareous shale replaced by thick channel sandstone overburden), a sufficient number of overburden analysis drill holes should be located to obtain representative samples of the different lithologies.

- In order to identify areas of the proposed mine site that may differ from the general stratigraphic conditions, it is helpful to look at, among other things, exploratory drilling logs and groundwater quality. These can provide insight into the presence of acidity- or alkalinity-producing materials and can help define the extent and degree of variability of the overburden so that overburden holes can be located to adequately represent the entire site.

- Conventional air rotary drilling is probably the most common method of sampling overburden; however, air rotary-reverse circulation drilling, although less commonly used, offers a much cleaner and quicker means of obtaining overburden samples. Although core drilling provides a better overall source of reliable lithologic data than air rotary drilling, it is very time consuming and costly. At a minimum, diamond cores should be used as a secondary means of data collection to isolate and zoom in on previously identified problem zones.

- Most surface mining sites are designed, operated and reclaimed in a series of mining phases. One of the overburden analysis drill holes should be located within the initial mining phase; the location of other overburden analysis drill holes should consider the spatial configuration of the mine site and significant variations in stratigraphy and lithology that will be encountered in the progression of mining phases.

- At least one of the overburden analysis drill holes should be located at the maximum highwall height (maximum cover) and at least one of the overburden analysis drill holes should be located at much lesser cover, in order to evaluate surface weathering effects.

- Experience has shown that a minimum of three and more typically six or seven holes per 100 acres are necessary to capture the geologic variability of a site. However, the number of holes needed may vary up or down depending on local site conditions.

- Overburden analysis may not be necessary, if equivalent information is available from adjacent mining, pre-mining water quality, and other site characterization data.

- Analysis of Variance (ANOVA) techniques have at least two important uses: (1) to evaluate the results of reconnaissance sampling studies in order to determine if the number of samples collected per site is adequate to represent the area of study, and (2) to serve as a statistical tool to interpret and infer the degree of variability of the geological populations under study.

- The geostatistical methods of variography and kriging are valuable for determining optimal sampling patterns for estimating mean values of spatially distributed variables and to interpolate values between

points where information is available, i.e. to contour the data.

- Software is available that can perform interpretation, analysis, interpolation, and presentation of spatially-distributed distributed two-dimensional or three-dimensional data. The software may be used to estimate, among other things, ABA from overburden analysis data over three-dimensional volumes or two-dimensional areas of interest. Data may be analyzed using ordinary statistics and by variography and kriging. Kriged distributions may be integrated with a volumetric analysis to yield relatively high precision volumetric statistics of overburden property values. It should be noted that if mine permit data is submitted electronically, time-consuming data entry can be eliminated. Also, coal seams that are to be mined should be modeled separately to ensure these zones can be eliminated in the volumetrics.

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CHAPTER 7: MINE DRAINAGE PREDICTION, A SUMMARY OF CONCEPTS AND PROCESSES

by
Eric Perry

INTRODUCTION

This chapter presents a summary of the key concepts and principles inherent in mine drainage prediction, and outlines a generalized approach to the assessment of coal mine drainage quality. Some issues that currently limit our ability to predict mine water quality and desired improvements are also discussed. The chapter is targeted mainly at water quality prediction from surface coal mines in humid climates. However, certain principles and practices can be applied to the analysis of underground coal mine water quality.

Mine drainage prediction is the integration of chemical, geologic, hydrologic, and biologic processes to arrive at an overall estimate of water quality after mining and reclamation are completed. Currently, the technology allows us to determine whether the water will be net alkaline or net acidic, where:

$$\text{Net Alkalinity} = \text{Total alkalinity} - \text{Total acidity}$$

The practical significance of selecting net alkalinity, rather than pH or metal concentration, lies in its fundamental control or influence on most other chemical properties of mine water. A net-alkaline water is capable of self-neutralizing inherent acid generating capacity, and buffering pH to circumneutral conditions, thereby limiting the activity of iron-oxidizing bacteria. In well aerated or oxidizing environments, the solubility of most metals is at a minimum at circumneutral pH. Treatment options are also controlled by the net alkalinity or net acidity of water. Extremely acidic waters may only be amenable to chemical treatment, while marginally acidic to alkaline water may be suited to various passive treatment technologies (Skousen et al., 1998). At the moment, prediction is qualitative, but as the science continues to advance, predictive capability should become progressively more refined and more quantitative.

Predicting the quality of mine drainage is not easy due to the amount and type of factors involved as well as the way the factors interact. In the simplest case, all components yield the same interpretation and the prediction can be made with a high degree of confidence. In marginal or complex sites, all components may not provide the same signals and the evaluator has to weigh certain factors more or less heavily to arrive at an assessment.

The evaluation process for mine drainage prediction includes analytical data and experiential information. Prediction of water quality is best achieved using a variety of tools. The classes of data and information evaluated directly or implicitly include:
- Qualitative and quantitative hydrologic data for surface and groundwater from mined and unmined areas;
- Geologic information, lithology, structure, and geochemistry;
- Results of past or equivalent mining; and
- Resource sensitivity.

Implicit in water quality and geochemical sampling is a requirement that the samples represent the system of interest. These data, collected at *representative* locations and times, are extrapolated to reach some final conclusion.

The remainder of this chapter is presented in three parts. First is a summary discussion of basic concepts that underlie the procedure of mine drainage prediction, taken in part, from other chapters of this report. Second is a generalized outline of the process of data analysis and interpretation to predict or estimate mine water quality. The chapter concludes with recommendations for improving our understanding and managing mine water impacts.

GEOLOGIC PRINCIPLES

Mineralogy

Mine drainage quality is influenced by the type, amount, and distribution of reactive minerals in contact with water. Two groups of minerals, sulfides and carbonates, largely control mine drainage quality even though they usually constitute only a few percent of the rock mass. Overburden analysis methods, discussed in previous chapters, are designed to quantify the amount of sulfide and carbonate present.

In coal mines, acid potential arises mostly from the sulfide mineral pyrite. In weathered rocks and soils, exchangeable acidity and metal sulfate minerals may also contribute to total acid production. Alkalinity is provided mostly by carbonate minerals. Of these, calcite and dolomite are the most important acid neutralizers. The mineral siderite is problematic for testing and interpretation. It initially provides neutralization, but subsequent iron hydrolysis produces acidity. The net neutralization from siderite is zero. Silicate minerals also provide some acid neutralization, but their rate of reaction is much slower than that of carbonates. Similarly, ion exchange reactions of acidic water with clays can also contribute alkalinity, but this only occurs when the strata are saturated. Small amounts of other elements are often contained in carbonates and can be released when the mineral dissolves. For example, a small percentage of manganese can substitute for iron in siderite.

Paleoenvironment

The vertical and horizontal distribution of sulfides and carbonates in mine site overburden is a function of the paleoenvironment, or conditions under which the sediments were deposited and any alterations that occurred afterward. The sediments that formed these rocks were deposited in a variety of freshwater, brackish and marine environments, such as stream channels, bays, and shallow marine waters. In general, rocks formed in brackish water conditions contain higher levels of sulfides than marine or freshwater deposits. Paleoenvironment can result in large changes in rock type and chemistry over small horizontal distances. Brady et al. (1988) found both acid and alkaline water generated in five surface mines operating on the same seam in Fayette County, Pennsylvania. The mines were in close proximity to each other in the same watershed, but differed markedly in the amount of carbonate minerals and stratigraphy at each mine. The abrupt lateral changes were attributed to depositional history. The acid sites generally lacked calcareous

shales and contained a high percentage of sandstone overburden. Some concepts of paleoenvironment relevant to mine drainage prediction are reviewed in Chapter 2.

Geologic Weathering

The Appalachian Plateau has been subjected to long term chemical and physical weathering. Chemical weathering in a humid climate removes the more soluble and reactive minerals, like carbonates and pyrite, from near-surface rocks and soils (Figure 2.7). The weathered zone, for mine drainage prediction purposes, is inert and has little capacity to either generate or neutralize acidity. Weathered materials are often weakly cemented or partially decomposed, and are often colored brown, yellow, or red. Weathering depth varies, but is often on the order of 20 feet in the Appalachians (Smith et al., 1974; 1976). Groundwater that circulates through the weathered zone contains low amounts of dissolved solids and alkalinity, reflecting the relative lack of soluble minerals in this zone.

Below the weathered zone, the rocks retain most of their original mineral assemblage, and may contain appreciable amounts of sulfides, carbonates or both. Groundwater circulating in this zone generally contains more dissolved solids. Example analyses of two ground waters from the weathered zone and deeper strata are shown in Table 7.1. The samples were taken from the Monongahela Group in northern West Virginia.

Table 7.1. Groundwater Quality from Overburden in the Weathered Zone and Deeper Strata [1]

Sample Location	pH	Spec.Cond.	Alkalinity	Fe	Ca	Mg	Na	SO$_4$	Cl
Weathered zone (15 feet deep)	6.1	61	14.7	0.06	8.0	4.0	2.5	9.8	6.5
Deep Strata (66 feet deep)	7.1	431	124	0.08	55	27	7.8	78	10

(1) pH in standard units, specific conductance in umhos/cm, alkalinity in mg/L as CaCO3, all others in mg/L.

In this example, ground water from the weathered zone has low specific conductance, which indicates low dissolved solids content, and little alkalinity. Groundwater from deeper strata has much higher alkalinity and dissolved solids. The deeper water could add significant buffering to acidic water in surface mine backfills or as recharge to flooding underground mines. The weathered zone groundwater would have little impact on mine water chemistry.

<div align="center">

GEOCHEMICAL PRINCIPLES

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The generation of acidity and alkalinity proceed at different rates and by different geochemical reactions. Pyrite oxidation involves the oxidation of both iron and sulfur and proceeds in four steps. The process is self-propagating, as shown in Figure 7.1, and as summarized in Rose and Cravotta (1998). It is catalyzed by iron-oxidizing bacteria and can proceed very rapidly.

Alkalinity production from carbonates is a dissolution reaction that depends on pH and the partial pressure of carbon dioxide (pCO_2). In general, lower pH and higher pCO_2 promote dissolution of carbonates and alkalinity production. Carbonate solubility is limited, however. Consequently, alkalinity concentrations

seldom exceed about 350 mg/L in surface mine waters, or more than about 600 mg/L in underground mine pool waters.

Simplified model of pyrite oxidation (Modified from Stumm and Morgan, 1981)

Pyrite   Oxygen   Sulfate   Acidity

$$FeS2 + O2 \xrightarrow{\text{Water}} + SO4\ 2\text{-} + H+$$

Ferrous Iron
$$Fe2+$$

SLOW $+ O2$ Oxygen   More Pyrite
(Bacteria accelerate) $+ FeS2$ FAST

                                          "Yellowboy"   Acidity
$$Fe3+ \text{Water}$$ $Fe(OH)3 \quad + H+$
Ferric Iron

Figure 7.1. The fundamental mechanisms of pyrite oxidation.

Field validation studies of mine drainage and ABA have shown that an excess of neutralization potential compared to potential acidity is necessary to obtain alkaline drainage from surface mines (Chapters 2 and 4 of this book; Perry, 1998). How much pyrite or carbonate is needed to have significant capacity to generate acidity or alkalinity? In Pennsylvania, significant strata were defined by *threshold* values (Brady and Hornberger, 1990) for sulfur content and NP as: total sulfur content greater than 0.5%, and NP greater than 30 tons /1000 tons (3% $CaCO_3$ equivalent), with a fizz when treated with 10% hydrochloric acid. A later study of ABA and mine water quality in Pennsylvania (Brady et al., 1994; Perry and Brady, 1995) suggested that an average carbonate content of 1-3% (NP of 10-30 tons/1000 tons) can be sufficient to produce alkaline drainage. These criteria were developed based on experience with rocks in northern Appalachia in middle and Upper Pennsylvanian strata of the Allegheny, Conemaugh, Monongahela and Dunkard groups. These rocks generally contain higher levels of sulfides and carbonates than lower Pennsylvanian rocks. The lower Pennsylvanian rocks in central and southern Appalachians typically have low pyrite contents but also low carbonate contents. In the lower Pennsylvanian rocks, carbonate contents as little as 1% can be important sources of alkalinity and neutralization. The ADTI, after surveying the recent

literature and compiling our own field experience, recommend that one should assume that an NP of less than 10 tons/1000 tons will generate acid conditions and that an NP of greater than 21 tons/1000 tons will produce alkaline conditions. The modified ABA procedures recommended in Chapter 4 should, in the future, reduce that gray zone of 10-21 tons/1000 tons.

HYDROLOGIC PRINCIPLES

Net Recharge

The Appalachian and Midwestern coalfields lie in a humid continental climate with annual precipitation ranging from about 30 to 60 inches. Most of these coal-producing areas have at least 40 inches or more of precipitation. As a consequence, mine sites experience net recharge. The magnitude of recharge varies by location and topography; however, average or long-term recharge values have been developed. In the Appalachian region, recharge generally constitutes 20-30 % of annual precipitation. For example, Hobba (1984) estimates the average recharge within the Monongahela River basin of northern West Virginia is about 7 inches per year. This is equivalent to about 0.36 gallons per acre per minute (gpm/A) of infiltration. Callaghan et al. (1998) report somewhat higher recharge estimates for mining areas in Pennsylvania, ranging from 0.62 to 0.77 gpm/A.

Recharge rates for underground mines are controlled largely by overburden thickness with rates ranging from as much as 0.8gpm/A for mines under shallow cover (less than about 250 feet), to as low as 0.05 gpm/A or less under thick cover (Crichton, 1927; Stoner et al., 1987). In surface mine backfills, the infiltrating recharge is available to leach and mobilize soluble constituents. In underground mines, recharge eventually results in partial to complete flooding after closure.

Groundwater Fracture Flow System

Appalachian surface mines are located within a groundwater flow system largely controlled by fractures and topography. In addition to tectonic fractures, fractures are naturally induced by geologic weathering and stress relief or unloading of overburden. An idealized section of ground water fracture flow in a hill that contains perched water bearing zones in dissected topography is shown in Figure 3.5. Most flow circulates within a few tens or hundreds of feet of the land surface. Overall, hilltops and slopes act as recharge areas, while foot slopes and valley floors are groundwater discharge areas. Surface mines intersect the fracture flow system. During mining, a mine usually acts as a groundwater sink, and groundwater flows into the mine from surrounding strata.

Larger regional aquifers underlie surface mines. These aquifers are slowly recharged by small amounts of deep infiltration. Ground water flow velocity is low and water usually has a very long residence time. A more detailed discussion of ground water flow and mining influences in the Appalachian Plateau is given by Callaghan et al. (1998) and chapter 3 of this report.

Minespoil Aquifers

Mining and reclamation alters the hydrologic properties of rock strata. Mine spoil aquifers are usually 10 to 100 times more permeable than the intact bedrock from which they were derived (Hawkins, 1998a) and exhibit both porous media and conduit type flow. The dip of the pit floor or pavement often controls the direction of flow and buildup of a water table. In the Appalachian region, a thin perched aquifer typically develops in the spoil within about two years after backfilling is completed (Hawkins, 1998b; Razem, 1984). Water table thickness is usually less than ten feet and frequently discharges as *toe of spoil* seeps along the coal cropline. Most of the spoil mass is unsaturated. Nonetheless, ground water storage in spoil aquifers can be substantial. For example, one acre of mined land with a six foot thick saturated zone and a specific yield of 15% stores about 293,000 gallons of ground water.

Spoil recharge occurs from precipitation falling directly on the mined area and by lateral inflow from ground water in adjacent unmined rocks (Hawkins,1998a). Periodic infiltration leaches soluble materials into the aquifer. The spoil/highwall interface has been identified as an area where significant infiltration takes place. Consequently, special handling guidelines recommend placement of acid-forming material away from this interface. High infiltration zones can be used to add alkalinity to mine backfills (Carruccio and Geidel, 1984).

Pre-mining Water Quality

Pre-mining ground water alkalinity concentrations are useful for confirming the presence of carbonates in mine site overburden. Chemical composition of groundwaters reflect the mineralogy of rocks and soils with which the water has been in contact. Brady (1998) suggests that alkalinity concentrations should exceed 50 mg/L from wells drilled in deeper strata if there are significant amounts of neutralizers present. On the other hand, alkalinity less than about 15 mg/l indicates a lack of neutralizers, or that the water sample represents flow through the weathered zone.

However, the presence or absence of significant amounts of pyrite cannot be determined from pre-mining water quality. Elevated sulfate concentrations should signify the presence of pyrite, since sulfate is a direct product of pyrite oxidation. In unmined ground water environments, pyrite is relatively stable and oxidizes only slowly. Data presented by Brady (1998) shows that sulfate concentrations are unrelated to the amount of pyrite in the overburden.

Water Quality from Adjacent Mine Sites

Water quality from adjacent mines can be an excellent indicator of expected mine drainage with certain provisos, which include:
- Mining must be on the same seam with similar stratigraphy, topography, hydrology and mining methods;
- Material that could significantly change water chemistry has not been placed on the adjacent mine, unless the same treatment is proposed for the current mine; and
- The age of the adjacent mine site must be considered. Pollutant concentrations in surface mine discharges often peak within 5-10 years after mining and gradually decline thereafter, though at other

mines, the decline is much more gradual. Examination of an old mine site may not represent water quality that will be generated within the first few years of reclamation.

Resource Sensitivity

Mining can impact water and biota both on and off a mine site. Mine drainage prediction therefore includes an assessment of the resources that could be impacted and an evaluation of a margin of uncertainty in the prediction.

Sensitive resources include lightly buffered streams, waters that serve as sources for drinking water supply, waters with in-stream standards to protect sensitive biota, etc. Table 7.2 includes analyses from a lightly buffered stream sampled upstream and downstream of mine drainage entering the waterway. The upstream water has alkalinity of only 3 mg/L, showing virtually no capacity to neutralize any introduced acidity. Downstream of the mine water discharge, water quality is degraded and generally unsuited for most biota, recreational use or consumption due to acidity and metals concentrations. Even though the mine discharge was only a few percent of the total stream flow, it was sufficient to pollute a sensitive water resource. For such resources, the degree of uncertainty has to be small to prevent degradation.

At the other extreme are resources that are already degraded by past mining or other activities. Re-mining of old abandoned sites with current reclamation technology usually results in pollution abatement and water quality improvements (Hawkins, 1998b). In these instances, the risk to resources is low.

Table 7.2.[1] Water Quality of a Lightly Buffered Stream Upstream and Downstream of an Acidic Discharge

Location	pH	Specific Conductance	Alkalinity	Total Acidity	Fe	Mn	Al	Sulfate
Upstream	5.5	73	3	1.5	0.05	0.06	0.2	18
Downstream	3.7	449	0	97	9.4	2.8	9.4	151

(1)pH in standard units, specific conductance in umhos/cm@250C, alkalinity and acidity in mg/L $CaCO_3$ Eq, all others in mg/L.

SAMPLING OVERBURDEN, SOILS, AND MINE SPOILS

The objectives of an overburden sampling program are to identify acid-and alkaline-forming materials present within the proposed mine area, show the vertical and horizontal distribution of these materials, and identify materials for special handling, alkaline addition, or topsoil substitutes. Exploratory drilling, by continuous core or cuttings from air rotary holes, is most commonly used to obtain samples. Sobek et al. (1978) provided an initial set of guidelines for sampling and characterizing overburden, spoils and minesoils. Most states have since refined their guidelines to reflect a minimum number of drillholes and sampling intervals. Different states follow different guidelines, though often there is a minimum of two drillholes recommended per site, with additional holes added as mine acreage increases. The state-by-state guidelines, based on experience with local geology, are reviewed in more detail in chapter 6. In most states,

a common approach is to add drillholes at a sampling density of about one per 40 acres. For areas known or suspected to exhibit variation in stratigraphy or geochemistry, tighter sampling patterns are necessary. However, Pennsylvania often doesn't require drillholes at all, relying more on information from adjacent mines. However, if no such information is available, or if for some reason it is not valid to use that information, they typically require 6 to 7 drillholes per 100 acres, which they find enables them to be quite accurate. ADTI participants agree with Pennsylvania that this is about the right number of drillholes when relevant adjacent site information is not available.

Drillholes for overburden sampling should intercept all the strata expected to be disturbed during surface mining. In hilly topography, this means placing some holes near the projected maximum highwall development. However, drillholes should also be spaced to provide distributed lateral coverage. Figure 7.2 is a plan of a 70 acre mine site which contained three overburden holes. Based on most guidelines, the number of drillholes was considered adequate for the mine size. All were located near maximum highwall height in one small area of the mine. Overburden analyses (ABA) of all three holes showed an abundance of calcareous shales with a weighted Net Neutralization Potential (NNP) of about 50 tons/1000 tons. On this basis, mine water was expected to be alkaline. Unfortunately, a major facies change occurred in the middle of the site, where the calcareous shales were replaced by sandstone containing some pyrite. The resulting mine water was acidic and is now routed to a passive treatment system. The lesson: it's not only how many sampling holes, but also where they are placed, which determines if one can use the data to accurately determine overburden properties.

Vertical sampling intervals are typically specified at three to five foot intervals in most state sampling recommendations (Chapter 6). Smaller intervals are useful for materials suspected of acid generating potential, such as rocks immediately above and below the coal, and "partings" within the seam. Thin rock units, with very high acid potential, can have a marked influence on mine water chemistry, especially if they are not recognized and are placed at random in the mine backfill. Inappropriate compositing can mask the potential effects of such units. See Table 6.6 and the accompanying discussion.

Another approach to overburden sampling uses the techniques of geostatistics. Geostatistics was originally developed to predict metal concentrations in ore bodies by examining the variation in analyses among spaced drillholes. The technique is not generally used by the coal mining industry, but could be useful for sites exhibiting complex lateral changes in geochemistry. From two such case studies, described in chapter 6, the reader can see that sampling programs need to be tailored to site geology and expected mining plans, and not driven by arbitrary fixed standards. Sites with complex geology, marginal or poor quality overburden quality or sensitive resources require close scrutiny. Conversely, sites with readily predictable geology and geochemistry and favorable overburden need not be sampled as intensively.

OVERBURDEN TESTING AND INTRERPRETATION

Acid generation and neutralization of overburden samples are tested by one of two general methods: static or whole rock analysis, usually ABA, and kinetic or simulated weathering tests, including leaching tests in various column and chamber arrangements. These test methods, and some new techniques currently under development and evaluation, are described in detail in chapters 4 and 5 of this report.

Acid/base Accounting

Conventional ABA reports maximum values of potential acid generation and acid neutralization. These values probably represent the rock's behavior over a long period of chemical weathering. However, the test was not designed for, and gives no information about short term (a few years) chemical weathering rates. From extensive use of ABA on coal mines and base and precious metal mines over the last 20+ years, it has become apparent that an excess of neutralizers relative to acid potential is required to produce alkaline drainage. A summary of suggested criteria for interpreting ABA data for water quality prediction is shown in Table 7.3.

These criteria were developed over a variety of rock types and climates. It is not surprising that the criteria do not identify identical ranges or cutoff points for classifying samples. The reported values consistently show, however, that an excess of neutralizers over acid potential is needed to obtain alkaline drainage.

For the sake of completeness, Table 7.3 contains several criteria that were originally developed for soils and revegetation considerations, not water quality per se. These include pH less than 4.0 to define "acid-toxic" and NNP of less than -5.0 tons/1000 tons for "potentially toxic". The criteria are based on the lower limits of plant growth tolerance to acid conditions and liming requirements for native soils in the Appalachians. Experience with ABA has shown that the same criteria cannot be applied to assess both soils and water quality.

Perhaps the principal caveat to the principle *excess neutralization potential* are those mines where the rocks contain so little sulfur that they are incapable of generating significant acidity, regardless of their carbonate content. As already discussed, weathered strata is typically low in both pyrite and carbonates. Smith et al. (1974, 1976) noted that these conditions also exist for some strata in the central and southern Appalachians.

ABA has also been criticized for not predicting metals concentrations. Without additional detailed information on rock type and mineralogy, ABA cannot be used to predict specific metals concentrations. However, the suite of kinetic tests discussed in Chapter 5 can potentially be used to estimate the relative mobility of metals in acid-forming rocks.

ABA has also tended to overestimate the NP in rocks containing siderite. A modification to the lab test involving hydrogen peroxide addition, described in Chapter 4, should largely eliminate this problem. We recommend the use of this modified NP procedure because it more accurately reflects the NP of overburden materials, reduces analytical variability, and provides a better framework for predicting mine water quality. A new technique, also described in Chapter 4, definitely distinguishes siderite from the alkalinity-producing carbonate rocks, and may become an additional important tool.

Figure 7.2. A plan view of a 70 acre mine site showing the 3 boreholes drilled.
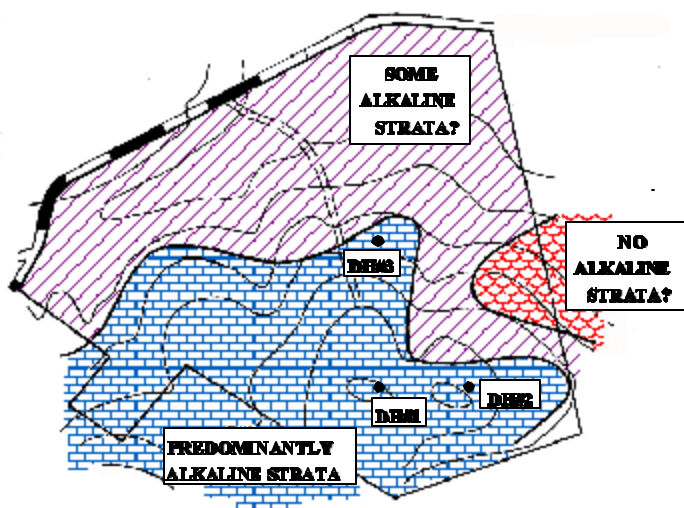
ABA remains the preferred static test for coal mine overburden because it is an established and recognized procedure, is relatively rapid and inexpensive, and has been field calibrated. Table 7.4 summarizes the findings of three studies comparing ABA data with post-mining water quality for surface coal mines in northern Appalachia and the midwest. In all cases, an excess of neutralizers over MPA was needed to obtain net alkaline water. In each of the three studies, there is a mixed zone of ABA values where water may be marginally net alkaline to net acid (range about +100 to -100 net alkalinity). For mines with these types of marginal overburden quality, evaluation of other data, such as adjacent mining, is very important.

An example of a detailed lithologic and ABA log is shown in Table 7.5. The log is from northern Appalachia for a sequence of rocks including the Middle and Upper Kittanning coals. For ABA interpretation, the overburden can be characterized as consisting of five main units:
- The upper 20 feet, which is oxidized and has little potential to generate significant acidity or to neutralize acid.
- The next 18 feet, which lacks appreciable neutralizers, and has some acid potential.
- A fractured but hard high-grade limestone unit, which is present from about 38-50 feet, with NP values as high as 800 tons/1000 tons (80% $CaCO_3$).
- The next 28 feet, which is essentially neutral.
- The interburden from about 78 feet to the top of the Middle Kittanning coal, which has moderate to high sulfur content and lacks significant neutralizers. These rocks are capable of producing moderate to strong acid drainage.

Table 7.3. Summary of Suggested Criteria for Interpreting Acid-Base Accounting [1]

CRITERIA	APPLICATION	REFERENCE
Rocks with NNP less than -5 parts/1000 considered potentially toxic	Coal overburden rocks in northern Appalachian basin for root zone media in reclamation; mine drainage quality	Smith et. al., 1974, 1976; Surface Mine Drainage Task Force, 1979; Skousen et.al., 1987
Rocks with paste pH less than 4.0 considered acid toxic	Coal overburden rocks in northern Appalachian basin for root zone media, mine drainage quality. Base and precious metal mine waste rock in Australia and southeast Asia	Smith et. al., 1974, 1976; Surface Mine Drainage Task Force, 1979 Miller and Murray, 1988
Rocks with greater than 0.5% sulfur may generate significant acidity	Coal overburden rocks in northern Appalachian basin, mine drainage quality. Base and precious metal mine waste rock in Australia and southeast Asia	Brady and Hornberger, 1990 Miller and Murray, 1988
Rocks with NP greater than 30 parts/1000 and "fizz" are significant sources of alkalinity.	Coal overburden rocks in northern Appalachian basin, mine drainage quality	Brady and Hornberger, 1990
Rocks with NNP greater than 20 parts/1000 produce alkaline drainage	Coal overburden rocks in northern Appalachian basin. Base and precious metal mine waste rock and tailings in Canada.	Skousen et.al., 1987; British Columbia Acid Mine Drainage Task Force, 1989; Ferguson and Morin, 1991
Rocks with NNP less than -20 parts/1000 produce AMD	Base and precious metal mine waste rock and tailings in Canada.	British Columbia Acid Mine Drainage Task Force, 1989; Ferguson and Morin, 1991
Rocks with NNP greater than 0 do not produce acid. Tailings with NNP less than 0 produce AMD.	Base and precious metal mine waste rock and tailings in Canada.	Patterson and Ferguson, 1994; Ferguson and Morin, 1991
NP/MPA ratio less than 1 likely results in AMD.	Base and precious metal mine waste rock and tailings in Canada.	Patterson and Ferguson, 1994; Ferguson and Morin, 1991
NP/MPA ratio classified as less than 1(likely AMD), between 1 and 2(possible AMD), and greater than 2(low probability of AMD).	Base and precious metal mine waste rock and tailings in Canada.	Ferguson and Robertson , 1994 Price et al, 1997
Theoretical NP/MPA ratio of 2 needed for complete acid neutralization.	Coal overburden rocks in northern Appalachian basin, mine drainage quality.	Cravotta et.al., 1990
NP/MPA ratio used with NP threshold to determine confidence levels for acid producing samples. 80% confidence of no acid production if NP/MPA ratio of 6.5 and NP threshold of 3.3%.	Coal overburden samples from 4 states: PA, WV, TN, and KY.	Bradham and Caruccio, 1995.
Use actual NP and MPA values as well as ratios to account for buffering capacity of the system.	Base metal mine waste rock, United States	Filipek et.al., 1991

(1) Criteria in this table were developed for classification of <u>individual</u> rock samples

Absent other information, what water quality will result from surface mining of both coals? The overburden data from Table 7.5 were put in a spreadsheet and volume-adjusted ABA parameters were calculated for each individual sample, as well as a summary numbers for the entire section. The basic procedures for performing these calculations have been described by Smith and Brady (1990) and are used in Pennsylvania and other states. The drillhole is located in hilly terrain. The mining area represented by this drillhole covers

about 10 acres at the top of the rock column and about 25.5 acres at the base of the middle Kittanning coal. The area of each sample interval between the top and bottom is interpolated.

Comparing these data to the criteria given in Table 7.4, the large excess of neutralizers should generate alkaline drainage. However, the most significant source of neutralization is the 11 foot thick limestone, located roughly in the middle of the overburden column. To work effectively, the limestone has to be broken or crushed during blasting and grading to relatively small pieces to dissolve and supply alkalinity. Large blocks of limestone will not be chemically active in the spoil pile. The limestone should also be mixed with in the spoil for maximum effect. Studies of alkaline addition have generally shown best results from incorporation of alkaline material and less effect if placement is all at the surface or the bottom of the spoil pile (Smith and Brady, 1998). Thus, mining and reclamation practices will have some influence on the final water quality.

By way of contrast, it is interesting to look at the expected water quality if the Middle Kittanning (lowest coal in the drill log) is extracted by underground mining. Lets assume that the mine is located above local drainage and is developed as a room-and-pillar down-dip mine with retreat mining. The mine would be expected to flood to the portal elevation after closure. The rocks immediately associated with the coal (i.e. roof, floor, and partings) will have the most obvious controls on water chemistry. The roof rock has a strong acid potential, and no significant NP is available at mine level. The mine pool will probably be strongly acidic. Unless the overburden is severely fractured and subsided to at least 40 feet above the mine, the limestone is unlikely to significantly affect mine pool chemistry. Prolonged flooding (decades) may ultimately improve water quality.

Table 7.4. Summary of water quality prediction from three studies of mine drainage and ABA.

Overburden Quality	Water Quality			Study Source
	Net Acid	Variable	Net Alkaline	
Neutralization Potential (NP)	< 10 parts/1000	10 to 21	>21 parts/1000	PA (Brady et al., 1994; Perry &Brady, 1995)
NP with thresholds	< 1 parts/1000	1 to 10	>10 parts/1000	PA (Brady et al., 1994; Perry &Brady, 1995)
Net Neutralization Potential (NNP)	< 20 parts/1000	20 to 40	>40 parts/1000	WV (diPretoro & Rauch, 1988)
NNP	< 0 parts/1000	0 to 12	>12 parts/1000	PA (Brady et al., 1994; Perry &Brady, 1995)
NNP with thresholds	< -5 ton/1000	-5 to +5	>5 ton/1000	PA (Brady et al., 1994; Perry &Brady, 1995)
NNP	< 10 parts/1000	10 to 30	>30 parts/1000	WV (diPretoro & Rauch, 1988)
NNP	< 10 parts/1000	10 to 20	?	USBM (Erickson & Hedin, 1988)

(1) Overburden criteria in this table are developed from volume weighted summaries of overburden data.

Table 7.5. Example—ABA log of Middle and Upper Kittanning coals

Sample Interval (ft)	Lithologic Description	%S	MPA tons/1000tons	Fizz Rating	NP tons/1000tons	NNP tons/1000tons
0-2	Soil					
2-5	Lt brown to lt gray sandy Siltstone	0.15	4.69	0	3.72	-0.97
5-8	" "	0.15	4.69	0	3.72	-0.97
8-10	" "	0.15	4.69	0	4.49	-0.20
10-12.3	" "	0.15	4.69	0	6.01	1.32
12.3-14	" "	0.15	4.69	0	10.99	6.30
14-17	" "	0.15	4.69	0	12.68	7.99
17-19.6	" "	0.15	4.69	0	9.52	4.83
19.6-22	Black Shale, slightly weathered	0.37	11.56	0	11.64	0.08
22-25	" "	0.65	20.31	0	6.93	-13.38
25-25.7	" "	0.93	29.06	0	5.29	-23.77
25.7-26.2	Coal (Upper Kittanning) claystone binder @26.1-26.2	0.17	5.31	0	5.01	-0.30
25.7-27.8	Coal (Upper Kittanning)	0.89	27.81	0	3.92	-23.89
27.8-29.0	Lt gray silty Claystone, soft	0.15	4.69	0	4.89	0.20
29-31.7	" "	0.27	8.44	0	7.75	-0.69
31.7-34	Lt gray sandy Siltstone w\ fine gr Sandstone @ 37.2-37.8,medium	0.17	5.31	0	7.01	1.70
34-37	" "	0.15	4.69	0	6.66	1.97
37-38.2	" "	0.28	8.75	0	18.94	10.19
38.2-40	Lt brown to Lt gray Limestone, Fractured, hard	0.15	4.69	3	679.00	674.31
40-41	" "	0.15	4.69	3	654.00	649.31
41-42	" "	0.15	4.69	3	519.00	514.31
42-43	" "	0.15	4.69	3	773.00	768.31
43-44	" "	0.15	4.69	3	736.00	731.31
44-45	" "	0.15	4.69	3	777.00	772.31
45-46	" "	0.15	4.69	3	814.00	809.31
46-47	" "	0.15	4.69	3	821.00	816.31
47-48	" "	0.15	4.69	3	765.00	760.31
48-49.9	" "	0.15	4.69	3	701.00	696.31
49.9-52.4	Lt gray silty Claystone, vert fractures	0.15	4.69	0	13.18	8.49
52.4-55	Lt gray to brown Siltstone, Fe stains on fractures, medium	0.15	4.69	0	10.94	6.25
55-58	" "	0.15	4.69	0	9.02	4.33
58-61	" "	0.15	4.69	0	10.57	5.88
61-63.7	" "	0.15	4.69	0	8.05	3.36
63.7-66.5	Med to dark gray Shale, Fe stains on fractures, medium	0.15	4.69	0	9.62	4.93
66.5-69	" "	0.51	15.94	0	10.17	-5.77
69-72	Dark gray to black shale, Fe stains	0.56	17.50	0	14.08	-3.42
72-75	" "	0.16	5.00	0	11.34	6.34
75-78	" "	0.52	16.25	0	18.41	2.16
78-81	" "	0.81	25.31	0	11.05	-14.26

81-84	" "	0.94	29.38	0	15.22	-14.16
84-85.5	" "	1.64	51.25	0	13.60	-37.65
85.5-87	Dark gray fine grained Sandstone w\black shale Intbeds, medium	3.26	101.88	0	5.62	-96.26
87-87.9	" "	4.20	131.25	0	2.62	-128.63
87.9-89.5	Coal (Middle Kittanning)		0.00			0.00
89.5-90	Coal (Middle Kittanning) claystone binder @89.5-90.0, soft	4.12	128.75	0	3.60	-125.15
90-92.2	Coal (Middle Kittanning)		0.00			0.00

Apparent water quality in underground mines is also a function of where it is measured. Mine pools tend to stratify chemically, with the best water quality usually found at the top of the water column. The worst or most mineralized water is usually at the bottom of the pool or appears as outcrop barrier seepage. Two samples collected from different elevations in the same well illustrate this phenomenon in Table 7.6. The 100 foot sample is taken at mine level, and contains substantially higher concentrations of all parameters. Significantly, iron, for which this water will require treatment, is over 35 time greater in the pool than in the stratified sample.

Kinetic Tests

Kinetic or simulated weathering tests are not used routinely for coal mine drainage prediction, only when additional information or specific characterizations are needed. However, they should probably be used much more frequently than is now the case, and should be considered whenever the ratio of the NP to S (or MPA) is near 1. They are widely used in the hard rock mining industry. The fundamental concept is to simulate the cyclic wetting, drying and flushing of spoil material. The chief advantages of kinetic tests are simulation of relative rates of acid generation and alkaline production, simulation of relative concentrations of net acidity, metals and sulfate, and simulation of amendments such as alkaline addition.

Unfortunately, no single kinetic test method has emerged as the best or standard technique, although weathering tests have been shown to be more accurate than other kinetic tests in predicting mine water quality (Bradham and Caruccio, 1990). However, since a variety of tests are in use, results must be interpreted on the basis of the specific test protocol used. Net acidity, metals, cations, or sulfate data can be plotted as daily production rates (mg of ion per g of sample per time interval) or as cumulative production rates with time. Although the data are sometimes plotted as concentrations, this defeats the purpose of the kinetic test evaluation and does not allow samples to be readily compared due to variations in rock weight and effluent volume. From the plots of production rates, samples are classified as alkaline or low, medium, or high acid producers or similar descriptive terms. The key aspect of kinetic tests are changes in the rates of production that develop over time, as carbonate minerals are consumed and sulfide minerals oxidize. However, at certain threshold levels of NP, the carbonate minerals inhibit oxidation of sulfide minerals, enhancing stability.

Few field calibration studies and screening criteria for kinetic tests are published. This stems from the application of kinetic tests on a case by case basis, rather than on a broad scale. Figure 5.6 shows an example of a plot of net cumulative acidity (as mg of acidity/gm of sample) in which two of the samples were

alkaline and one exhibited low acidity. Either daily or cumulative data can be plotted and the interpretation related to the differing slopes of the lines. With cumulative data, the chemical weathering attributes are usually defined by one of three trends. Figure 5.6 is an example of relatively straight slopes indicating that the acid and alkaline production potentials vary little with time and that few weathering products accumulated in the sample prior to leaching. This is common for all alkaline samples. A second common trend is a steep acid slope initially, followed by a much flatter slope for the remainder of the test, which suggests that accumulated acid weathering products are initially being flushed. A steep slope also indicates that the sample may weather quickly upon exposure. The third major trend in acid samples is that the sample may exhibit low acidity or sulfate values initially and after several weeks begin to produce significant acidity. These samples are normally high acid producers, as discussed in Chapter 5. Plots similar to those presented in Figures 5.6 and 5.7 can be constructed for metals or other parameters of interest. The interpretation has to be keyed to the specific test method, however. This stems from the use of kinetic tests on a case by case basis, and the variety of test protocols in use.

Figure 7.4a shows an example plot of sulfate and total acidity generated from a 12 week leaching test for two samples. A standard quantity of water was added to columns containing the crushed samples. Sample B produces much higher concentrations of both acidity and sulfate than sample A. Sulfate and acidity concentrations reach a peak after about 5 weeks and decline only slightly thereafter. This is interpreted to mean that sample could still generate additional acidity and sulfate beyond the 12 week test period. Sample A on the other hand, never produces much acidity or sulfate throughout the test, and both parameters are decreasing in the later weeks of the test. Sample A is not expected to be an acid source. Sample B could generate significant acidity.

Figure 7.4b is a cumulative plot of acidity and sulfate generation for two samples from a 70 day (10 week) weathering test. The cumulative production of acid and sulfate is expressed in mg/g of sample. This allows direct comparison of samples on a mass basis. Sample D produces a total of about 3.5 mg acidity/g sample for the test period compared to about 0.32 mg/g for sample C, a difference of about 10 fold. Thus D is expected to be a significant acid source relative to C. The slope of the cumulative acidity plots for both samples continue to increase at a constant rate at the end of the test period. This indicates that both rocks are likely to continue to produce acidity. A decrease in slope or flattening of the line would signify that the rate of acid production was declining.

Table 7.6. Stratification of water quality in an underground mine pool--pH in standard units, specific conductance in umhos/cm@25, alkalinity in mg/L $CaCO_3$ equivalent, all others in mg/L.

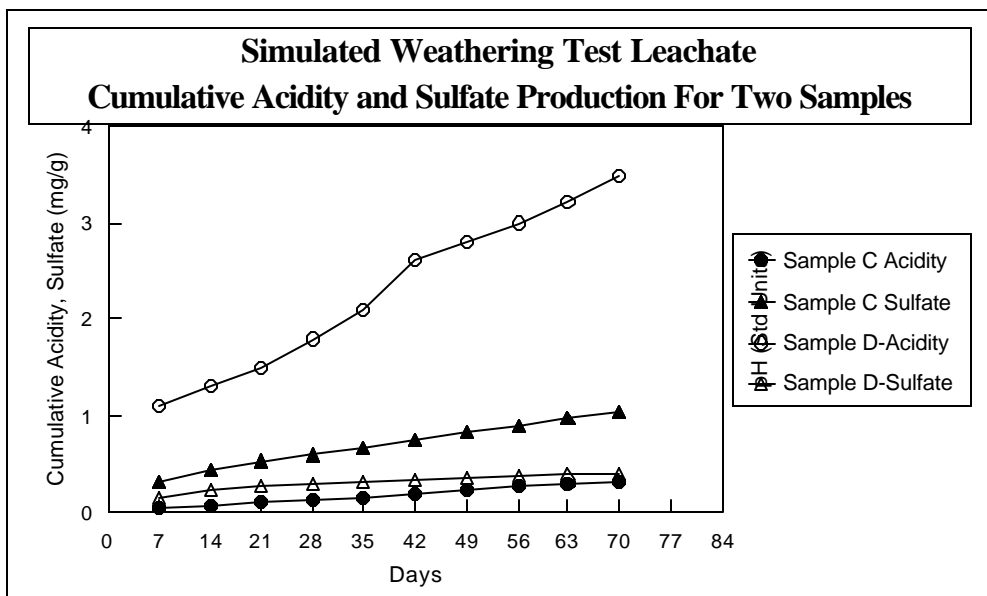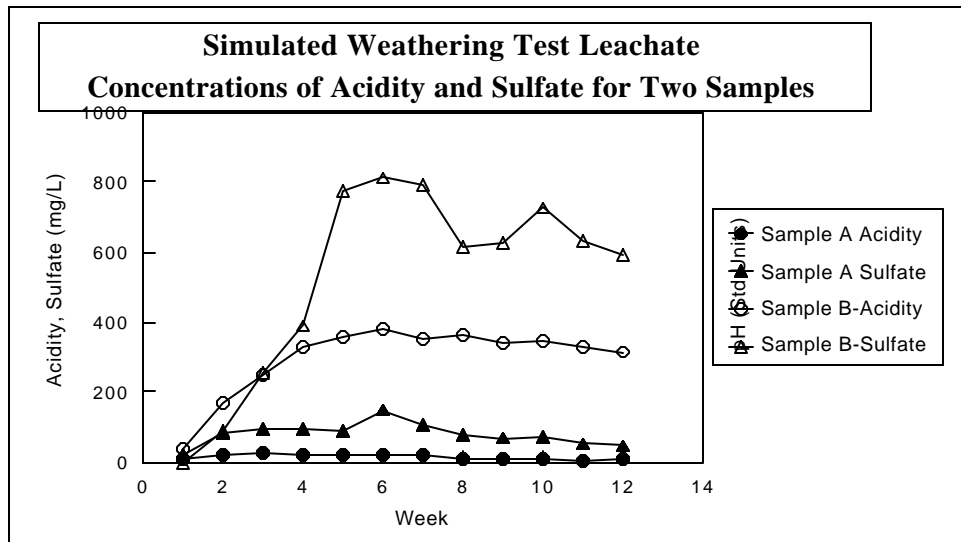| Sample Depth	pH	Alkalinity	Specific Conductance	Fe	Mn	Sulfate
100 feet (bottom)	7.15	565	7000	202	2.8	3654
60 feet	7.60	257	4240	5.6	0.38	1936

Figure 7.4. Two examples of cumulative acidity and sulfate production graphs.

A GENERALIZED APPROACH TO THE ANALYSIS OF SITE DATA AND PREDICTION OF MINE DRAINAGE QUALITY

Mine drainage quality is largely controlled by three major variables: geologic conditions, hydrologic conditions, and the mining and reclamation plans. While these three factors control mine water chemistry, resource sensitivity determines what risk is assumed if the site is mined. Resource sensitivity is therefore part of the evaluation. Finally, adjacent mining, if suitable examples exist, show post-mining results that may be analogous to the site under development. Pennsylvania has demonstrated that properly used, such data can be extremely useful.

The unique character and condition of each mine site precludes a standardized cookbook approach to the evaluation process. Instead, the process can be seen as a series of questions to determine:

- Is site characterization adequate?
- What are site conditions?
- What effect will mining and reclamation have, i.e. what is the expected post-mining water quality?
- Does post-mining water quality produce unacceptable effects?

Whether one is preparing or reviewing a permit, one has to achieve some level of satisfaction that each of these issues has been adequately addressed. The process is conceptually illustrated in Figure 7.5. The proposed mining operation is analyzed for geologic, hydrologic and mining conditions to predict expected mine drainage characteristics. Projected water quality is then evaluated against on- and off-site resources to determine probable impacts. The risk of these impacts must then be classed as acceptable or not, based on legal or regulatory standards, technology limits, or other criteria.

Following is a generalized set of questions, arranged by topics to form a typical evaluation for a surface coal mine. An analogous process can be described for underground mines, with some common elements between the two as, well as features unique to each. The list is not intended to be an inflexible set of rules, but rather a guide that must be adjusted based on site specific issues.
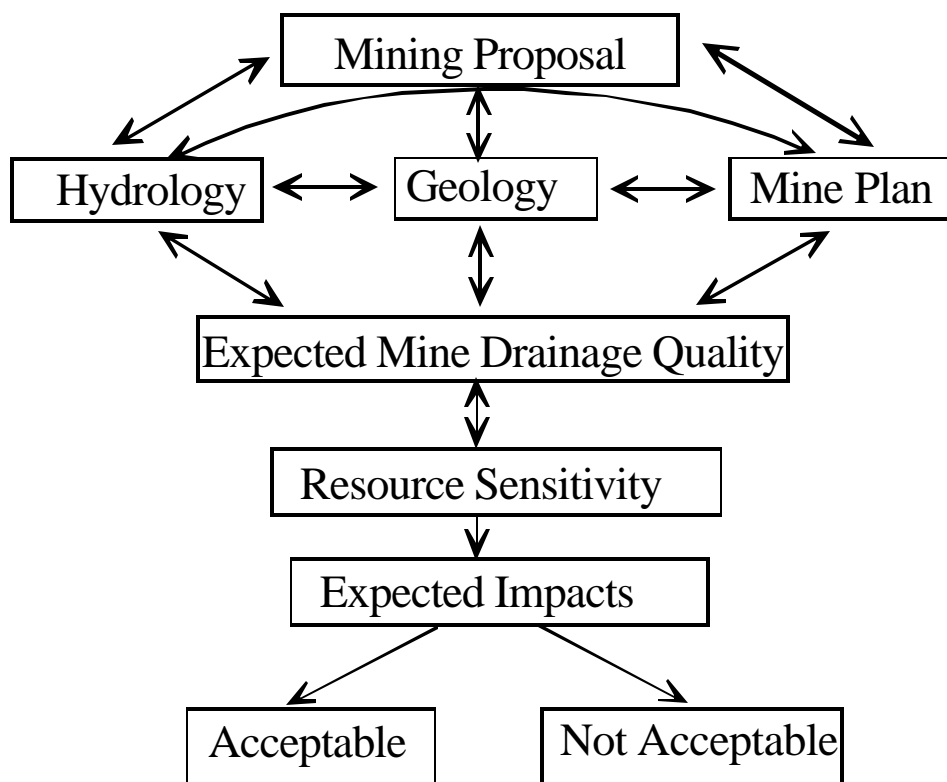
Figure 7.5. Diagram illustrating the major elements of mine drainage prediction and evaluation

General stratigraphy, lithology and structure

Is the reported site geology consistent with published geologic reports that describe the general geology? Large differences between general and site-specific geology indicate that local geology exhibits rapid changes over small distances, or that site characterization is inadequate or inaccurate.

Are the rock types and vertical sequences of rocks laterally consistent across the area? Variation in stratigraphy may signal changes in geochemistry of the rocks as well.

Are there structural features (anticlines or synclines) present? These may control or influence ground water flow direction after reclamation.

What is the degree and direction of dip of the coal beds to be mined? Ground water usually flows in the direction of dip in surface mine spoil aquifers. In underground mines, flooding typically begins at the downdip end of the mine.

Are limestones or limey shales or mudstones present? Limestones contain high percentages of acid neutralizers, but must be broken into small size fragments to be chemically active. Limey shales and mudstones may undergo rapid physical weathering and release alkalinity quickly.

Is the coal bed laterally consistent in thickness and composition? Coal beds can thicken, thin or pinch out entirely. Channel sandstones that replace coal in the latter case sometimes contain pyrite, and usually lack carbonates. Partings within a coal bed frequently form acid.

How much sandstone is present in the overburden? Some of the most severe acid drainage comes from sites with large percentages of sandstone and little carbonates. Hard sandstone that resists physical weathering creates large voids and helps circulate oxygen into the spoil pile. In underground mines, competent sandstones may resist breaking and subsiding.

Hydrogeologic Setting

What is the topographic setting of the mine? Surface mines located on hilltops and upper slopes are likely to be in ground-water recharge areas. Surface mines located on footslopes or valley floors are usually in ground-water discharge zones. These mines will receive flow from upgradient. The possibility of generating acid drainage is higher for mines in discharge zones compared to otherwise similar mines in a recharge area, unless the pyritic material will be permanently inundated after reclamation.

Underground mines located above drainage may flood only partially after closure and discharge by outcrop barrier leakage or at other points. Below drainage mines will usually flood completely after closure.

Where are aquifers located? Mines usually will intercept some ground water from the fracture flow system on hillsides. Mine drainage can move through the fracture flow system to discharge from or recharge aquifers at lower elevations. Underground mines may intercept larger regional aquifers.

Are springs and seeps present on the mine? Springs and seeps indicate local ground water discharge zones and infer that the underlying rock is of lower permeability.

What are static water levels in drillholes and wells? Static water levels indicate in a general manner, the amount of ground water that may be encountered during mining. Water table elevation in surface mine spoil is usually lower than pre-mining water levels.

Where is the coal cropline? The cropline, along with dip largely determines the location of post-mining discharges. For underground mines, the cropline indicates a potential seepage after flooding.

Drillhole Information

Are exploratory holes distributed across the mine site? Distributed drillholes are needed to determine whether stratigraphy is consistent or variable.

Are drill logs and cross-sections plotted in the correct locations with all units described and identified? Accurate locations are necessary to determine structure and to correlate strata.

Are there directional trends in the stratigraphy? Thickening or thinning beds or facies changes within the mine site can affect the distribution of acid forming and acid neutralizing minerals.

Are all of the strata to be disturbed during mining represented in the drillhole data? It is necessary to identify all rocks that may contribute to mine drainage quality.

Do the number and distribution of drillholes provide a clear interpretation of site stratigraphy? If stratigraphic units cannot be correlated or facies changes identified, additional exploratory drilling may be needed.

Geochemical Data

Have the samples been collected, stored and analyzed following generally accepted and documented procedures? Analytical results can vary widely if a quality assurance/quality control plan is not followed, making interpretation difficult or impossible.

Do the geochemical data represent the rocks both vertically and horizontally? Samples must represent the different rock types identified. Subsamples within individual stratigraphic units are needed to identify changes in geochemistry that are not obvious based on visual inspection. Typical subsample units are 3 to5 feet, maybe less when significant acid forming potential is suspected.

For ABA data, reports should include calculated MPA, NP and NNP. Color and fizz rating are useful supplemental information to identify the weathered zone and the presence of carbonates.

For simulated weathering tests, the data report should include tabular summaries and/or plots and graphs of the leachate quality data, and a description of the specific test method used.

Where are the significant acid forming and acid neutralizing materials? Each drillhole is examined by individual sample analyses to identify which rocks are contributing to acid generation or neutralization. Some numeric criteria for characterizing rocks from ABA analysis as significant sources of acidity or alkalinity are shown in Table 8.4.

Are there directional trends in geochemistry? Compare chemical data among drillholes to determine lateral consistency. Both sulfur and carbonate content can increase or decrease across a mine, and the unit may thicken, thin, or pinch out.

Is a weathered zone of low sulfur and low neutralizer content present? These materials will not generate much acidity or alkalinity.

Is old minespoil or coal refuse present? These materials have undergone chemical weathering and can contain metal sulfate minerals such as copiapite, halotrichite and others. The metal sulfate minerals are a source of stored acidity and metals. For these kinds of materials, include sulfate sulfur in the calculation of potential acidity. Weathered samples show spoil quality that could develop on the new mine.

Are there individual samples or strata with high acid generating potential? These rocks may require preventive measures including but not limited to alkaline addition, special handling and water management.

Are there individual samples or strata with high neutralizing potential? These rocks are principal source of alkalinity in the spoil. They should be mixed with acid forming material or otherwise redistributed to offset acid generation.

Are ABA data combined or plotted by a method that simulates the geometry of the mine site? Several criteria for interpreting ABA data from NP, NNP and as ratio of NP to MPA were discussed earlier in this chapter. The criteria were developed from ABA data that were combined into a summary value for the entire mine site.

Does weighted ABA data and interpretive criteria suggest drainage is likely to be alkaline, acidic or marginal quality? In general, an excess of neutralizers are needed to preclude acid drainage. Sites lacking neutralizers are probable acid formers, unless the rocks are also essentially without pyrite. The strength or severity of acid drainage depends on sulfur content, amount of neutralizers present and rock types. Conclusions drawn from ABA data should be compared with other tools like adjacent mining and baseline water quality to strengthen conclusions.

Hydrology

Were water quality samples collected, preserved stored and analyzed using generally accepted and documented methods? Analytical results can vary widely if a quality assurance/quality control plan is not followed, making interpretation difficult or impossible.

How much alkalinity is present in "deep" ground-water (below the weathered zone)? These waters should have appreciable alkalinity (>50 mg/L) if significant NP is present in the rocks.

How much alkalinity and dissolved solids are in springs and seeps? These waters usually circulate in the weathered zone and are generally low in dissolved solids (less than a few hundred mg/L) and alkalinity (often less than 20 mg/L).

Are multiple samples available to characterize seasonal variation in quality? In the Appalachian region, samples collected in late winter to early spring and late summer to fall will display the range in water quality likely to encountered.

Do samples reflect the different aquifer systems that will be encountered or affected by mining? Mixing mine drainage with aquifers of different chemistry will have impacts that differ in type and severity.

Does ground water quality show influence of past mining? Ground waters within a few hundred feet of land surface in Appalachia usually have less than 100mg/L of sulfate as background. Elevated sulfate concentrations can indicate that mine drainage has migrated on site from other surface or underground mines. Mine waters that have been neutralized by carbonate reactions in surface mine spoil often produce water with the cation fraction dominated by calcium and magnesium.

Are there samples from previous or adjacent mining in the same coal bed? Adjacent mining can show the general character of expected water quality from the proposed mine if the sites have similar geology, hydrology and mining techniques.

Are there others sources of ground-water recharge to the site and if so, what is its quality? Drainage from mines on other seams etc. can influence water quality

Are stream sampling sites perennial, intermittent or ephemeral? Water quality is some composite of ground discharge and surface runoff. Concentrations of some parameters like sulfate and alkalinity are sensitive to flow conditions and the contributions of different sources.

Are multiple samples provided to estimate the range in seasonal variation of water quality? In the Appalachian region, samples collected in late winter to early spring and late summer to fall will display the range in water quality likely to encountered. Mine drainage impacts to streams are often most pronounced during low flow conditions, when mine water is a larger percentage of stream flow.

Are measured flow data reported with water quality? These data are needed to perform loading, mass balance, or mixing calculations for projecting the impacts of mine drainage on a receiving stream.

Are streams lightly buffered? Lightly buffered waters have little capacity to neutralize an influx of acid drainage.

Does flow increase or decrease downstream? In most Appalachian drainage basins, flow increases downstream (gaining streams). If flow decreases downstream, the loss could be infiltrating underground mines or karst.

Does surface water quality show influence of mine drainage from past or current mining? Many surface waters in the Appalachian region have background concentrations of less than 50 mg/L of sulfate. Elevated sulfate concentrations often indicate mine drainage effects. Mine waters that have been neutralized by carbonate reactions in surface mine spoil often produce water with the cation fraction dominated by calcium and magnesium.

Mining and Reclamation Plan

What surface mining method and spoil handling/spreading equipment will be used? The mining method and equipment determines pit size, exposure time before reclamation, and the ability to segregate or special handle acid-forming material. In general, area mining by dragline provides the longest exposure time before reclamation, and the least flexibility in handling acid material or installing other preventive measures. Contour haulback or block cut with trucks and loaders usually have the most flexibility to incorporate special handling, water management and alkaline addition.

What materials, if any, are proposed for special handling? In the Appalachian region, special handling involves placement of acid forming material above the expected post-mining water table. Ten to twenty feet above the pit floor is a common target zone for placement. In the mid-continent and rarely in Appalachia, flooding or placing acid forming material below the water table is used.

Are materials to be specially handled easily recognized in the field? They can usually be distinguished by color or rock type

Is alkaline addition proposed? If yes, what quantity and where will it be placed in the backfill? Alkaline addition can be beneficial on marginal sites and as a "best management practice." The common practice is to add alkaline material based on the deficiency expressed by negative NNP for a single strata or an entire overburden section. Adding more alkaline material to raise the NNP above zero seems to increase the chances for success. Placing all the alkaline material at the top or bottom of the backfill is less effective than mixing or incorporating the alkaline material into the spoil pile.

Adjacent Mining

Were mining and reclamation methods including special handling, alkaline addition and water management methods similar on the existing and proposed mine? No mines are identical but the overall mining and reclamation techniques should be similar for a valid comparison.

Do the sites have similar overburden stratigraphy and geochemistry? Even adjacent sites can be geologically dissimilar, due to facies changes, topography, etc. If the sites are not stratigraphically and geochemically similar, using data from the adjacent site will be misleading.

What is the post-mining water quality and quantity from the adjacent site? Assuming the comparison is valid, this information is extremely useful in predicting future water quality at the unmined site.

<u>Resource Sensitivity</u>

Are there lightly buffered surface or ground waters that could be affected? Are there public or private water supplies (intakes, reservoirs, and wells) that could be impacted? Are there sensitive biota that could be affected? Quality could be damaged by small amounts of acid drainage.

Is water quality already degraded by past mining or other activities? This might mean that the watershed cannot withstand any additional degradation or, alternatively, may indicate that the watershed is less vulnerable.

The questions posed in the preceding sections are not all-encompassing. They do, however, flag the major data needs for an analysis and prediction of mine drainage quality and can serve as a starting point for specific case reviews.

DEVELOPING MINE DRAINAGE SCIENCE: ISSUES, OPPORTUNITIES AND NEEDS

An enormous body of scientific research and practical experience in mine drainage has developed over the last century. Nonetheless, our ability to correctly anticipate, prevent, or manage mine drainage and its effects is still limited. Additional effort is needed to:

1. Enhance quantitative prediction of mine drainage chemistry. Currently, assessments are often confined to a determination of net acid or net alkaline. Establishing expected ranges of alkalinity, acidity or other key parameters would reduce levels of uncertainty on marginal or sensitive sites.

2. Establish a consensus on kinetic test methodology. Currently a large number of test protocols are available, and each may produce different results. The lack of consensus has made wide spread application and interpretation of kinetic tests quite difficult.

3. Conduct field calibration studies of mine water quality and analytical/predictive methods. The most comprehensive field calibration studies that exist are for ABA in northern Appalachia and a few mid-continent sites. Analogous studies are needed in central and southern Appalachia and the mid-continent. Few published studies relate kinetic tests and field performance.

4. Develop improved predictive technology for underground mine water quality. Prediction work on underground mines has received less attention compared to surface mines. However, most of the existing mine drainage pollution in Appalachia comes from abandoned underground mines.

5. Pursue the development and testing of new and revised analytical techniques, such as downhole wireline logging, evolved gas analysis, and other methods.

6. Learn from past mistakes and accumulated data. Baseline and monitoring data are available from completed and ongoing mining from companies, consultants and government agencies. Careful examination of quality would help refine predictive techniques.

7. Examine the application of mineralogical data and geochemical modeling techniques to mine drainage prediction. These methods are being applied in the hard rock mining industry to mine drainage prediction.

8. Pursue the use of analytical tools, such as three dimensional modeling software packages that can perform overburden volumetric analysis and statistical analysis procedures, including, where appropriate for detailed sampling and analysis, variography and kriging.

The science of mine drainage prediction has benefited from new and improved testing methods, many field studies and experiments, and practical experience. The need for and possibility of continued improvements and refinements still remains a major challenge.

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APPENDIX A. CONSIDERATIONS FOR CHEMICAL MONITORING AT COAL MINES

by
Charles A. Cravotta III and Gary M. Hilgar

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 ($2Na^+ = Ca\text{-}EX$) 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).
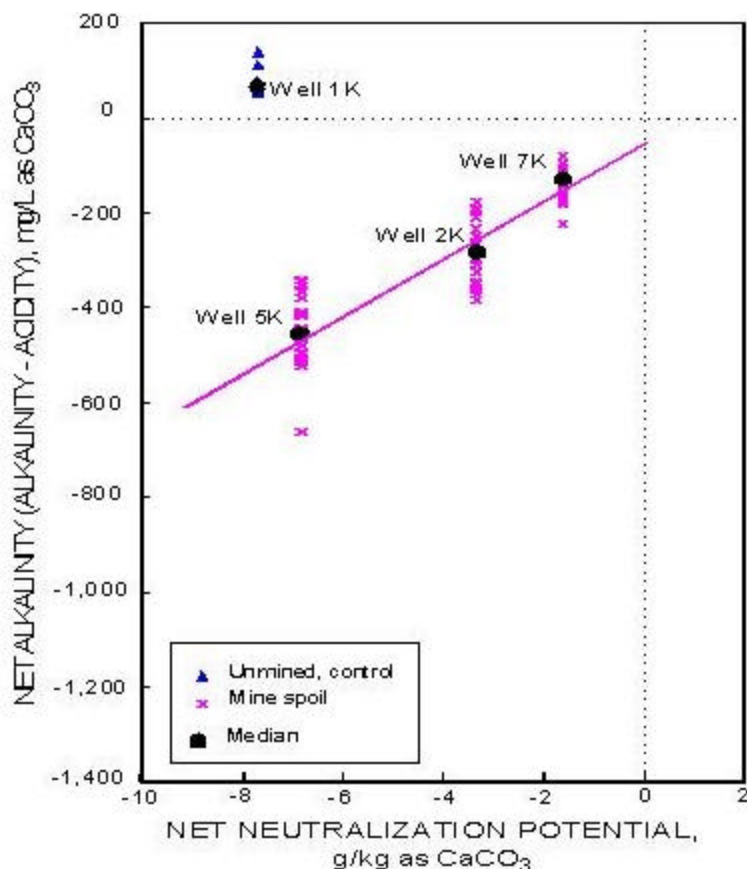
Figure 1. Acid-base accounting and water chemistry data for boreholes installed through the same coal bearing horizon at a coal mine after reclamation (adapted from Cravotta, 1998). NNP is the weighted average of the difference between NP and MPA for rock cuttings from the borehole. Negative values indicate 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:

$$HCO_3^- = CO_2 \text{ (gas)} + OH^-$$
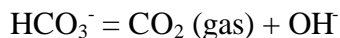
where the reactant HCO_3^- and product OH^- are stoichiometrically balanced and have identical acid-neutralizing capacity. In contrast, the in-bottle precipitation or accidental introduction of hydroxide or carbonate minerals can affect the acid neutralizing capacity of a sample. For example, $CaCO_3$ 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.
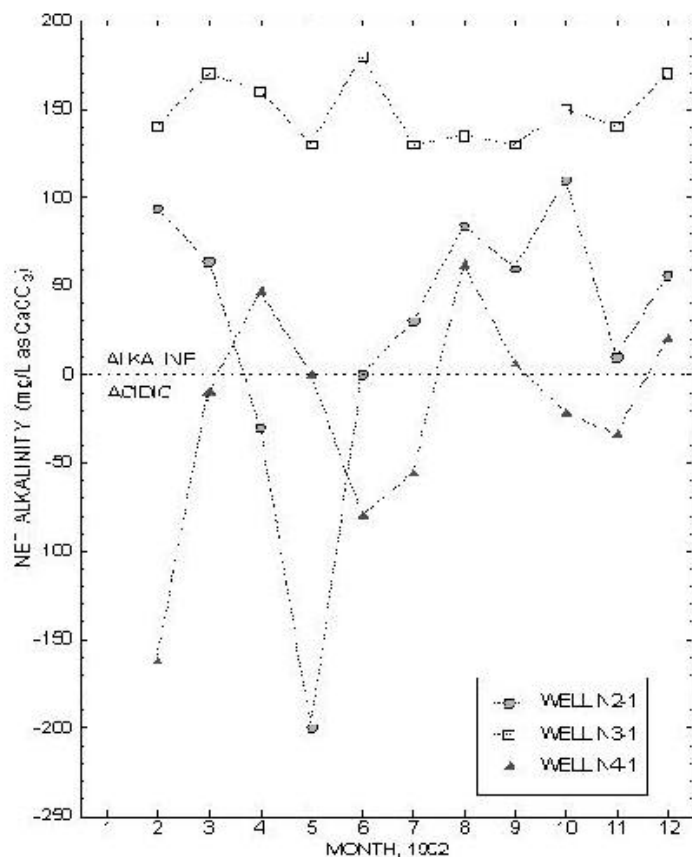
Figure 2. Temporal variations in net alkalinity data for ground water samples from monitoring wells screened through reclaimed spoil at a surface coal mine in Pennsylvania (adapted from Rose and Cravotta, 1998).

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.
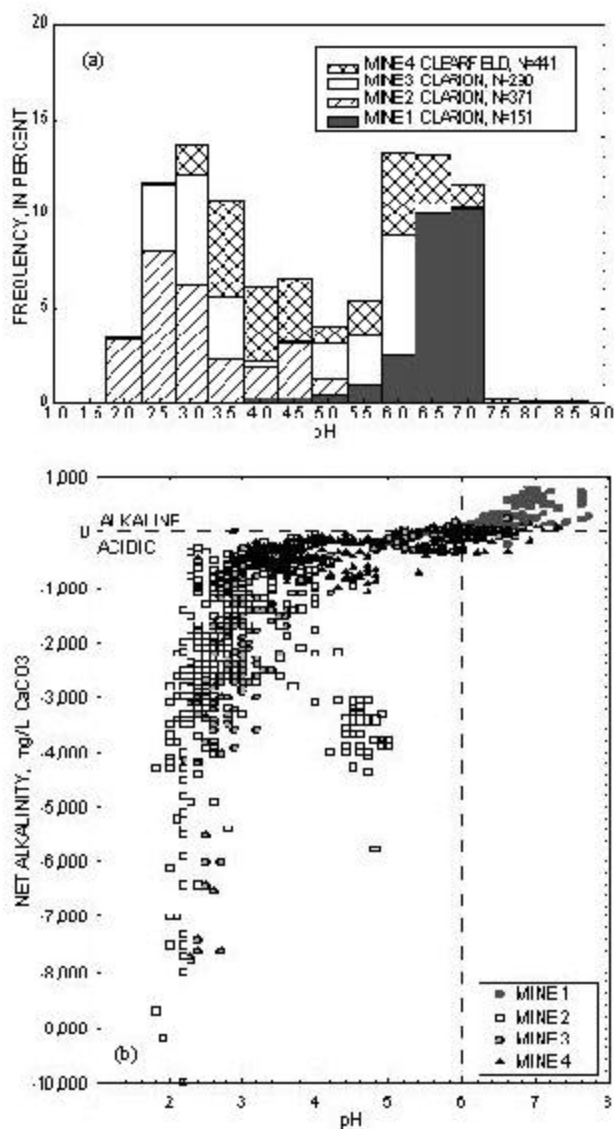
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Figure 3. Acidity, alkalinity, and pH data for water samples from four mines in Pennsylvania (adapted from Rose and Cravotta, 1998): a). frequency data for pH showing bimodal distribution; b). net alkalinity relative to pH. Alkalinity and acidity are 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.
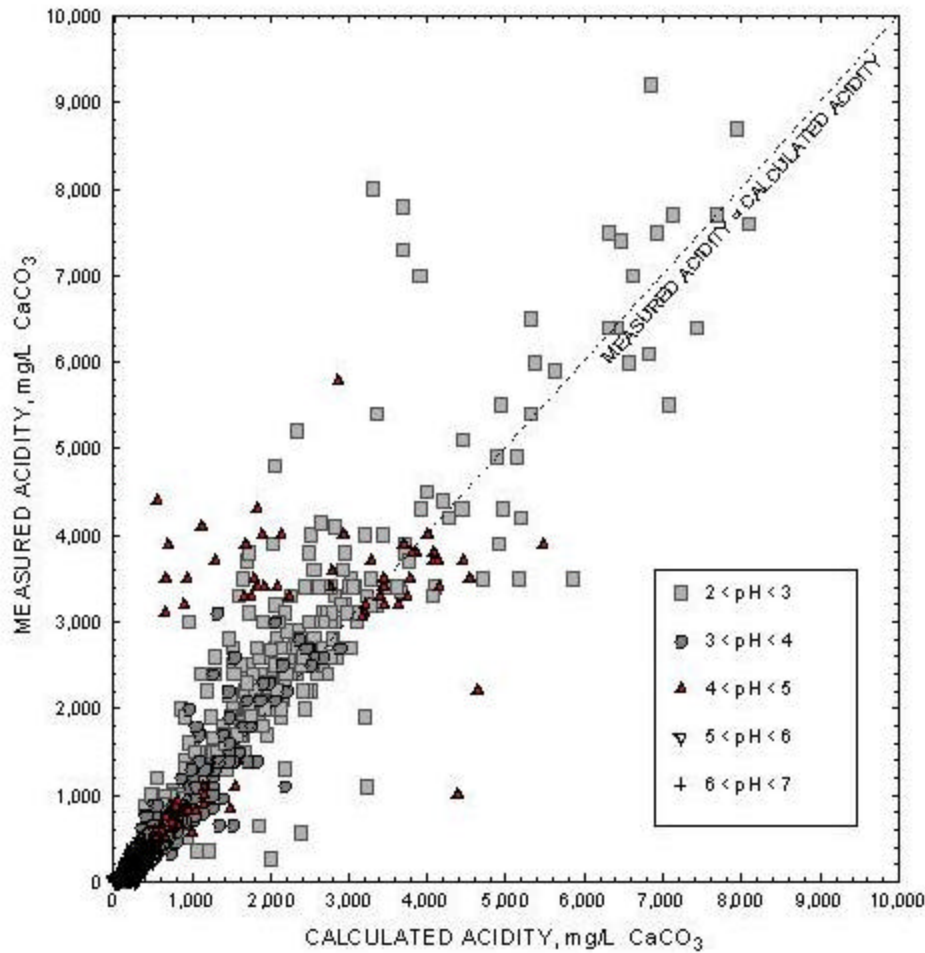
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Figure 4. Comparison of measured and calculated acidity (adapted from Rose and Cravotta, 1998).

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:

$$Acidity(mg/L\ CaCO_3) = 50*\{10^{(3-pH)}+[(3C_{Fe3+}+2C_{Fe2+})/56]+[(3C_{Al3+})/27]+[(2C_{Mn2+})/55]\}$$

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.
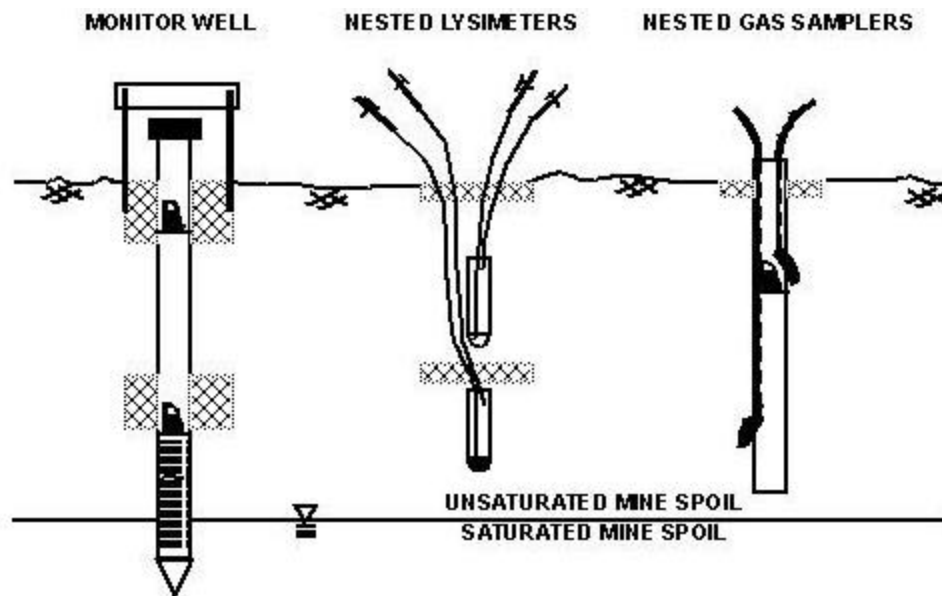

Figure 5. Schematic diagram showing nested monitoring design for evaluation of subsurface chemistry in mine spoil (adapted from Cravotta et al., 1994).

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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Appendix B—CHAPTER 6 CASE STUDIES

ANALYSIS OF VARIANCE (ANOVA)

Lower Kittanning Coal, Pennsylvania

The ANOVA example described below is from a reconnaissance sampling study of Lower Kittanning Coal samples from marine and freshwater paleoenvironments in Pennsylvania (Hornberger, 1985)* . This preliminary sampling study was conducted to determine if three channel samples of coal and/or overlying shale per surface mine would be sufficient to characterize any significant differences in sulfur content, pyrite morphology, and leachate quality between paleoenvironments. Three channel samples of the exposed Lower Kittanning coal and the first three feet of the immediately overlying shale were collected in four strip mines in Armstrong, Jefferson, Lawrence, and Somerset Counties. The Lawrence and Somerset County mines were characterized by a shale of freshwater paleoenvironment. The mines in Armstrong and Jefferson Counties were characterized by a marine shale overlying the Lower Kittanning coal.

The channel samples were collected at widely spaced intervals within the mine sites, and were obtained in accordance with the sample collection procedures outlined by Schopf (1960). The samples were subsequently crushed with a jaw crusher to a nominal quarter inch (6.35mm) size. After crushing, the samples were riffled and split to obtain representative samples for sulfur analyses, leaching studies, and the preparation of polished pellets for reflected light microscopy.

Variations in sulfur content data, framboidal pyrite count data, and leachate chemistry data were statistically examined with ANOVA techniques to determine the magnitude of and significance attributable to variations: between paleoenvironments, between mines of the same paleoenvironment, and within mines (i.e., between channel sample replicates plus error). The total sulfur contents of the Lower Kittanning coal samples are shown in Figure 6.1. The pyritic sulfur, sulfate sulfur, and organic sulfur fractions are also shown to illustrate variations within and among mines and paleoenvironments.

In the ANOVA procedure, the sum of squares (i.e. squared deviations for each source of variation) and mean squares, which are variance estimates computed by dividing the sum of squares by the appropriate degrees of freedom (generally, the number of variables minus 1), are calculated. Tables 6.7a-c show estimated percentages of the total variance attributable to each of the component sources of variation by the total sum of squares. The results for the sulfur forms data are shown in Table 6.7a, along with a one-way ANOVA for each of the sulfur variables. Considering the organic sulfur content, for example, approximately 58% of the variation in the data occurs at the paleoenvironmental level (i.e., between marine and freshwater settings), while approximately 29% occurs between mines, and approximately 14% of the variation remains within mines (i.e., between channel sample replicates plus error).

While division with the sums of squares provides a quick survey of the percentage of the variance

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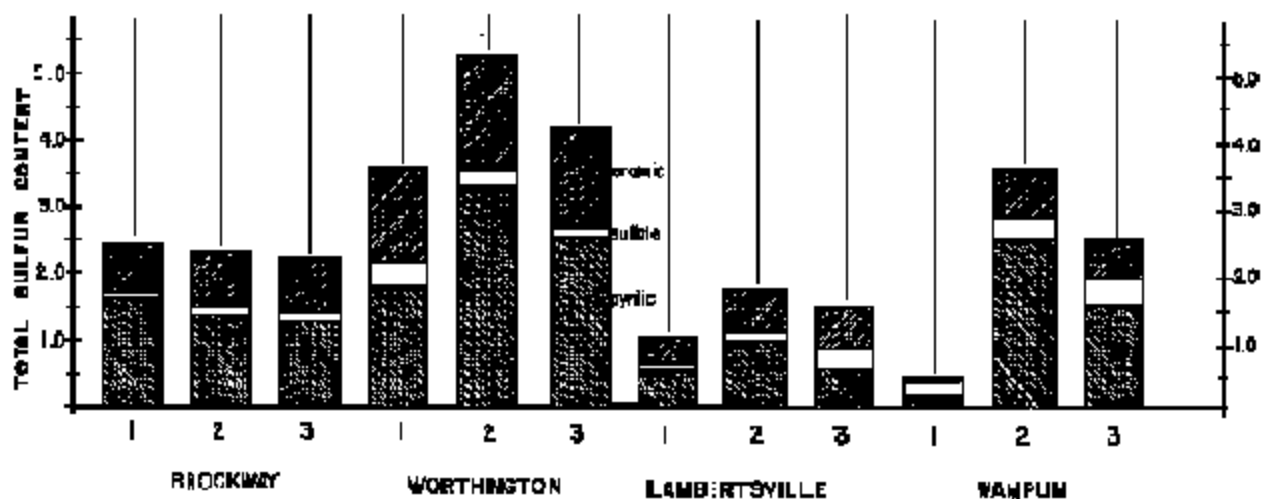* References for Appendix B can be found at the end of Chapter 6, starting on page 165.

Figure 6.1. Sulfur content of Lower Kittanning Coal samples from marine and freshwater paleoenvironments.

explained at each level of the hierarchical experimental design, the F-test or variance ratio test is a formal test of significance. For example, it can be used to determine if the variance attributed to paleoenvironment is significantly different than the error. The value of the component with the greater expected mean square (i.e., paleoenvironment) is divided by the error mean square, and the quotient may be compared to values in a reference table such as in Arkin and Colton (1963).

The F-test and significance levels are shown for the sulfur data in Table 6.7a, where the F value of 33.351 for the organic sulfur data is sufficiently large that there is less than one chance in 10,000 that a value of that magnitude would occur purely by chance. As a result of ANOVA of total sulfur contents and the contents of pyritic, sulfate, and organic forms of sulfur, it was found that variations in organic sulfur content of the coal samples were highly significant between paleoenvironments while pyritic sulfur variations were not. The mean pyritic sulfur content of samples from a marine paleoenvironment is higher than that of the freshwater paleoenvironment, as was true for the organic sulfur content. However, in this study, the major portion of the variance in the pyritic sulfur data remains at the within-mine level of channel sample replicates plus error.

Previous studies have examined the association of the framboidal form of pyrite and other pyrite morphologies with various depositional environments (e.g., Reyes-Navarro and Davis, 1976), and the significance of framboidal pyrite in acid mine drainage production (e.g., Carruccio and Parizek, 1968; Carruccio et al., 1977). Polished pellets made from representative splits of the Lower Kittanning coal samples were examined by reflected light microscopy in order to test the significance of variations in framboidal pyrite occurrences in the array of coal samples. The pellet mounts of the samples were constructed and polished as described in Reyes-Navarro and Davis (1976, p. 52-54). The microscope was equipped with a point-count stage and had a 10-point grid inserted in the ocular. All pyrite occurrences within the field of view were examined during a continuous scan of a 10mm traverse; the pellet was then moved 1mm perpendicular to the completed traverse, and this procedure was repeated until ten traverses

of 10 mm had been scanned. Four classes were established for counting purposes. Two were for discrete classical framboids (less than or greater than 10 microns in diameter). The other two were for clusters of euhedral microcrysts and intergrowths of framboids in which individual framboids could not readily be discerned or counted (having a long dimension less than or greater than 10 microns (Carruccio et al., 1977; Love and Amstutz, 1966; Rickard, 1970).

TABLE 6.7a. Analysis of variance summary table of sulfur content data
Percent of Variance Estimated (from Sums of Squares) F-Test Mean

	P	M	R&E	P/E	Significance Level	Marine Mines	Freshwater Mines
Pyritic Sulfur	26.0	27.8	46.2	4.493	0.0669	2.027	1.133
Sulfate Sulfur	6.7	62.2	31.0	1.736	0.2242	0.162	0.218
Organic Sulfur	57.5	28.8	13.8	33.351	0.0000	1.160	0.505
Total Sulfur	33.2	33.3	33.4	7.960	0.0224	3.348	1.857

Table 6.7b. Analysis of Variance Summary Table of Framboidal Pyrite Occurrence
Percent of Variance (Estimated from Sums of Squares) F-Test Mean

	P	M	R&E	P/E	Significance Level	Marine Mines	Freshwater Mines
Raw Count Data							
Discrete, less than 10 microns	77.3	0.1	22.6	27.331	0.0000	50.833	0.833
Discrete, greater than 10 microns	23.8	12.1	64.1	2.970	0.1231	2.50	0.167
Clusters, greater than 10 microns	76.4	7.7	15.9	38.404	0.0000	16.50	0.667
Clusters, less than 10 microns	94.4	2.4	3.2	234.472	0.0000	113.33	7.000
Total Framboids	91.2	1.1	7.7	95.306	0.0000	183.17	8.667
Square Root Transformed Data							
Discrete, less than 10 microns	89.5	1.1	9.4	76.318	0.0000	6.996	0.50
Discrete, greater than 10 microns	53.2	6.8	40.0	10.629	0.0115	1.402	0.167
Clusters, greater than 10 microns	86.7	5.3	8.0	86.795	0.0000	4.000	0.455
Clusters, less than 10 microns	94.5	0.9	4.6	163.621	0.0000	10.616	2.381
Total Framboids	94.4	0.4	5.2	145.932	0.0000	13.466	2.653

Table 6.7c. Analysis of Variance Summary Table for Leachate Data
Percent of Variance Estimated (from Sums of Squares) F-Test Mean

	P	M	R&E	P/E	Significance Level	Marine Mines	Freshwater Mines
pH	26.9	0.9	72.2	2.611	0.1502	2.559	3.003
Net Acidity	11.7	14.8	73.5	1.114	0.3262	3.216	2.894
Conductivity	5.0	30.8	64.2	0.549	0.4827	3.623	3.544
Sulfate	23.0	4.3	72.7	2.216	0.1802	3.417	2.043

P = Paleoenvironments; M = Mines (within paleoenvironments); R & E = Replicates plus Error

This data is shown in Table 6.8. The results of the ANOVA of the untransformed (raw) and transformed data of the framboidal pyrite point counts are shown in Table 6.7b. Count data are on a discontinuous scale (i.e., as compared to measurement data on a continuous scale) and as such, are typically related to a binomial, a Poisson, or another discrete frequency distribution. A square root transformation of such data is often appropriate (Griffiths, 1967; Krumbein and Graybill, 1965; Tukey, 1977).

A one-way ANOVA was computed on the untransformed and square-root transformed counts of framboidal pyrite in the Lower Kittanning coal samples according to the hierarchical sampling plan of marine and freshwater paleoenvironments, mines within paleoenvironments, and channel sample replicates within the mines. The results of these analyses are shown in Table 6.7b in the same format as the sulfur analyses. As most of the variance explained occurs at the paleoenvironment level, it is obvious that significant differences exist in the abundance of framboidal pyrite in the sampled marine and freshwater paleoenvironmental settings. On the basis of the assembled data on Lower Kittanning coal samples shown in Tables 6.7b and 6.8, there is little doubt that framboidal pyrite is preferentially deposited in marine paleoenvironments and somewhat rare in freshwater paleoenvironmental settings.

The leachate chemistry data used in the ANOVA in Table 6.7c were obtained from simple leaching columns that were used and described in a series of studies (Hornberger, 1985; Hornberger et al., 1981; Morrison, 1988; Rose et al., 1985; Waters, 1981; Williams et al., 1982, 1985). These test procedures include elements of leaching column tests and humidity cell tests that are discussed in detail in Chapter 4 of this volume. The leachate chemistry data in Hornberger et al. (1981, 1985) were expressed as either fast drained (i.e. one-hour contact) or one-week-contact values. This was based on how long the influent water was in contact with the coal sample before the effluent was removed for chemical analyses during each of several weeks of testing.

Using the same procedures as described for analysis of the sulfur data, an analysis of variance was performed on the pH, net acidity, conductivity and sulfate data. These analyses of the leachate data are summarized in Table 6.7c, wherein it is evident that a large portion of the variation (e.g., 64 to 74%) in the leachate data (i.e., pH, net acidity, conductivity, and sulfates) was attributable to variations within mines (i.e., replicates plus error). Differences in leachate quality between paleoenvironments were not significant.

The portion of the total variance of the channel sample replicates plus error level was much greater than the portions of the variance at the mines and paleoenvironments levels for pyritic sulfur and the leachate chemistry variables. This preliminary or reconnaissance sampling study demonstrated that the sampling design must be modified in order to obtain more stable estimates of the means and variances for these variables. Stated another way, there is so much variation between the three channel samples per mine for the variables that these samples cannot be used to detect meaningful differences between marine and freshwater paleoenvironments, even if significant differences actually exist within these populations.

Table 6.8. Abundance of Framboidal Pyrite in Lower Kittanning Coal Samples

Location	Framboids Less than 10 microns	Framboids Greater than 10 microns	Framboidal Clusters Greater than 10 microns	Framboidal Clusters Less than 10 microns	Total Framboids
Brockway No. 1	69	9	12	106	196
Brockway No. 2	50	1	10	101	162
Brockway No. 3	36	1	17	97	151
Worthington No. 1	23	1	14	101	139
Worthington No. 2	80	2	29	139	250
Worthington No. 3	47	1	17	136	201
Lambertsville No. 1	1	0	1	1	3
Lambertsville No. 2	0	0	0	4	4
Lambertsville No. 3	4	1	3	16	24
Wampum No. 1	0	0	0	2	2
Wampum No. 2	0	0	0	4	4
Wampum No. 3	0	0	0	15	15

There are several options to consider in revising the sampling design to address this type of large within-mine variance. For example, one could collect a much larger number of channel samples within each mine (e.g., three closely spaced channel sample replicates at each of three widely spaced sample sites within each mine = nine samples per mine). Alternatively, one could use the means of the three channel sample replicates in the example above rather than the individual measurements. One could also make composite samples by combining representative splits of the three channel sample replicates in the example above to reduce the laboratory analytical costs from nine samples to three samples per mine. In discussing how to determine the number of samples (n) to be collected, Griffiths (1967) depicts the relationship between the standard error of the mean, $\sigma \bar{x}$ (where σ is the sample standard deviation and $\bar{x}$ is the sample mean), and sample size (n) in simple random sampling, and states:

It may be demonstrated under very general conditions that with a small number of specimens each composed of a few measurements, the means of the samples show less variability than the individual measurements (p. 21). Now let us suppose we have a good estimate of σ; we can then reduce $\sigma_{\bar{x}}$ by increasing n.... Increasing n from one to four reduces $\sigma_{\bar{x}}$ to half its value, and increasing n to 16 reduces the value of $\sigma_{\bar{x}}$ to a quarter of its original value. This becomes an expensive way of increasing precision in many experiments because of the rapid increase in n.... The larger the number of measurements, the greater the precision; or, written in another way, the numbers of samples chosen should be proportional to the magnitude of the variability. If one material varies twice as much as another in some property under investigation, then, for equal precision in mean values, there should be four times the number of measurements in the more variable material than in the less variable.

The results of this ANOVA case study have also been applied to evaluating overburden analysis data in the Pennsylvania DEP data base using data on the Lower Kittanning overburden geochemistry described in Brady et al. (1998). A preliminary study with an experimental design similar to the above case study was completed by DEP personnel (Rooney, 1998, personal communication), wherein three mines in each of three paleoenvironments (i.e. marine, brackish, and freshwater) were selected, and the available overburden drill holes were the sample replicates. This preliminary study indicated that some differences in the total sulfur content and neutralization potential values of the Lower Kittanning overburden strata existed between paleoenvironments, but that more samples were needed (i.e., more mines and drill holes) to determine if these inferred differences were actually statistically significant. A much more extensive study is planned to commence when ongoing upgrades to the DEP overburden data base have been completed. That proposed study will include all relevant drill holes from a much larger number of mines within these paleoenvironments.

VARIOGRAPHY AND KRIGING

New Allegheny Mine, West Virginia

The variography example described below is from a study done by Donovan and Renton (1998). To demonstrate the application of geostatistical methods to NP, MPA, NNP, and mineralogy in coal measures, an experiment was performed estimating overburden characteristics from a large number of drill holes placed at close distances in a working mine site. The samples were collected from cuttings of air-rotary holes drilled for setting explosives to break up overburden in advance of mining. The data generated in this study employed detailed sampling substantially exceeding that commonly employed in practice. The drill holes were spaced a minimum of 10 feet apart over a section of highwall 300 feet long.

The New Allegheny Mine (NAM) is located approximately 5 km east of Mt. Storm in Grant County, West Virginia, just south of the Maryland-West Virginia border. Samples were collected using air-rotary drilling, then analyzed for carbonate and sulfur as well as mineralogy. Analytical methods selected excluded alkalinity from siderite or potential acidity from non-pyritic sulfur. Patterns of spatial co-variation were then analyzed using conventional geostatistical techniques, fitting variance models to the spatial distribution of each variable. Specific goals of this analysis were to analyze the relative importance of small-scale variation (i.e.,

variations in properties at distances <30m) in ABA determination, and to estimate the drill hole separation at which variance in properties must be sampled to give sound predictive ABA estimates.

All variables (NP, MPA, and NNP (NP minus MPA); mineral percentages for calcite, dolomite, siderite, pyrite, total clays, and total carbonates) were vertically averaged for each drillhole location, weighting each sample linearly based on the sampling interval thickness. The dataset was thus treated as a two-dimensional array. Variography was performed on the vertically-averaged results for each hole using geostatistical routines included in the VARIOWIN package (Pannatier, 1995). Pair-comparison files (separation distance and variable values for each pair of locations) were prepared for each variable. Both semivariograms (covariance versus sample separation) and correlograms (correlation versus sample separation) were prepared using groupings of sample pairs classed by separation distance in 10 foot increments. The number of pairs in each interval group was 50 or higher, except for the interval group containing the most widely spaced pairs (the variogram tails), which are commonly statistically weak (Isaacs and Srivastava, 1989). Variogram models of exponential form were fit to the field data.

Parameters for each curve-fit included the sill (the variance approached asymptotically at large separation; essentially the maximum variance) and range (the distance at which the variogram value of the variance is 95% of the sill). The fitting was weighted towards the near-field (<100 feet) pairs, with variance at greater separations attributed to large-scale non-stationary spatial trends. No removal of spatial trends or reduction in non-stationarity was performed prior to variogram analysis, because the principal objective was to determine the spatial interval over which local-scale interpolation might be feasible.

Samples were collected from three sub-areas within the mine. Block 1 (12 drill holes, each 42 feet deep, sample interval 3 feet) was located stratigraphically above the Upper Kitanning coal. Block 2 (19 drill holes, each 21 feet deep, sample interval 3 feet) sampled the interval above the lower Freeport coal. Block 3 (15 drill holes, each 21 feet deep, sample interval 3 feet) sampled the stratigraphic interval above the Upper Freeport coal bed. Blocks 1 and 3 were immediately adjacent to each other, while Block 2 was approximately 150 feet north of Block 1 along the same highwall.

The sub-areas were separated by distances within which no samples were collected. As a result, the variograms are gapped in some separation intervals. Again, the large separation intervals contain information primarily on non-stationary differences (i.e., trends) between sub-areas or stratigraphic intervals. These differences may be significant at the scale of an entire mine but were not of principal interest in this investigation. Variograms show systematic increases in covariance with separation for variables that have strong large-scale spatial trends and uniform covariance with respect to separation for more stationary variables.

Table 6.9 shows the results of core 246-023 for ABA using continuous sample splits taken at 1-foot intervals. The NP data contain no siderite. This entire sequence is the target of mining at NAM. The overburden sequence is only weakly acidic (net NNP=-1.3). Vertical averaging sample results yields the following results:

Table 6.9. ABA results for core hole 246-023 at NAM (Donovan and Renton, 1998).

	NP	MPA	NNP
Mean	5.0	6.3	-1.3
Standard Deviation	5.6	12.0	14.7

Thus, as an entire sequence, the overburden for the NAM Pennsylvanian rocks are very slightly acidic, with localized zones of both high sulfur and carbonate content.

Figure 6.2 shows the distribution (from top to bottom) of NP, MPA, and NNP for all NAM samples (n = 53). NP (mean = 2.9) is approximately normally distributed with the exception of a pronounced mode at very low (near detection) values. The distribution for MPA is very similar in appearance, with a mean of 6.7 and a pronounced mode of near-undetectable values. In both cases, the low-concentration modes are comprised wholly of Block 3 (Upper Freeport), which exhibits low values of both sulfur and carbonate and was lithologically much siltier than the other two overburden sequences. The NNP is net acidic (mean NNP = -3.8) and is approximately log-normal in form with left (acidic) skew. One cluster of samples of Upper Freeport overburden has a near-neutral NNP; all other samples are net acidic, ranging from ~4 to ~20.

Frequency histograms for mineralogy show strongly bimodal distributions for total carbonates clays, and pyrite, all consistent with the NP/MPA results (Figure 6.3). The high modes (Blocks 2 and 3) in all three minerals are approximately normal. Histograms for carbonate minerals are shown in Figure 6.4. Calcite was not detected in any sample. Both dolomite (mean 0.2%) and siderite (mean 0.6%) are similarly bimodal, with greater separation between low and high modes for siderite (Figure6.8). As for other parameters, the modes are stratigraphically-related; Block 3 (Upper Freeport) samples are low in dolomite and had no detectable siderite. Siderite, but not dolomite, was removed in the NP determination process so the major source of NP and NNP for these samples is thought to be dolomite; its low concentration contributes to the very low NP values.

There is strong correlation between clay-mineral composition and both dolomite (R^2=0.86) and siderite (R^2=0.85) (Figure 6.5). A similar, but more scattered, relationship exists between pyrite and total clays. While highly significant, all three correlations and their trends are influenced by the strongly bimodal distributions shown in Figures 6.3 and 6.4. It may be inferred that the concentrations of all three minerals are present in higher concentrations in shales and in lower concentrations in sandstone/siltstone.

Figures 6.6-6.8 show sample variograms for the New Allegheny hole means, plotted as class separation versus variance. The total variance in the dataset (all points) is shown as a dotted horizontal line. The fitted exponential-model variance is the solid curve in Figures 6.6-6.8. The observed (sample) semi-variance is calculated so that each pair of points is counted only once; for this reason, such plots are often referred to as *semi-variograms.* As can be seen, the solid curve may stop increasing at a certain distance and become stable, i.e. it reaches a plateau. This plateau represents the upper limit, or sill, of the variance. The drill hole distance corresponding to the point at which the curve flattens out represents the distance beyond which the variance does not increase. This distance is called the range of the variable. The range is often used in a practical sense to
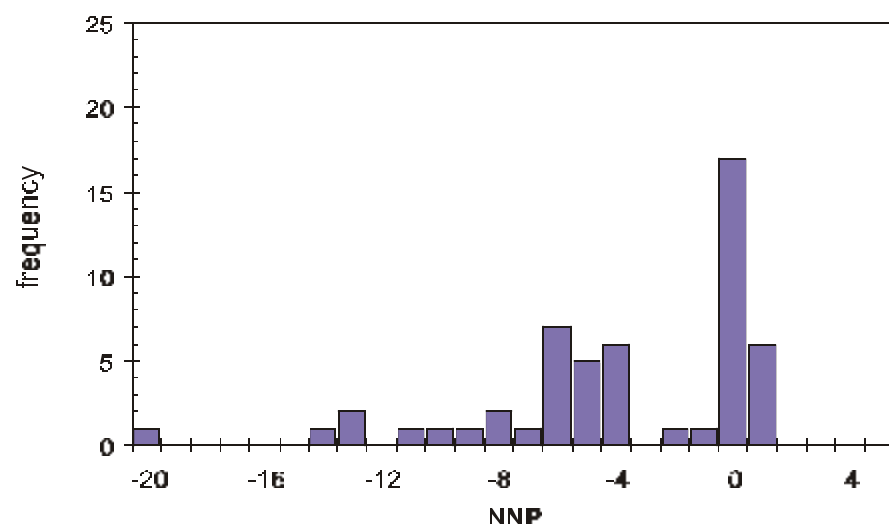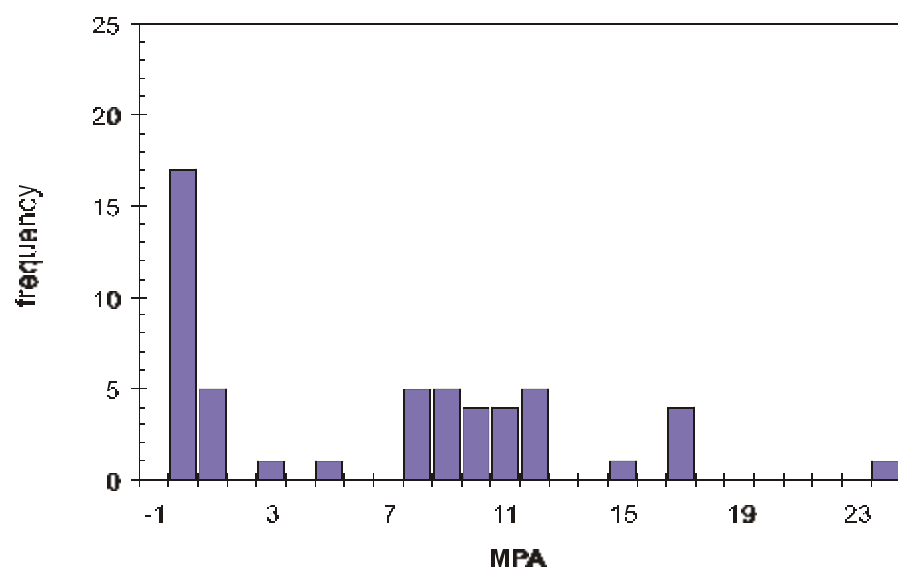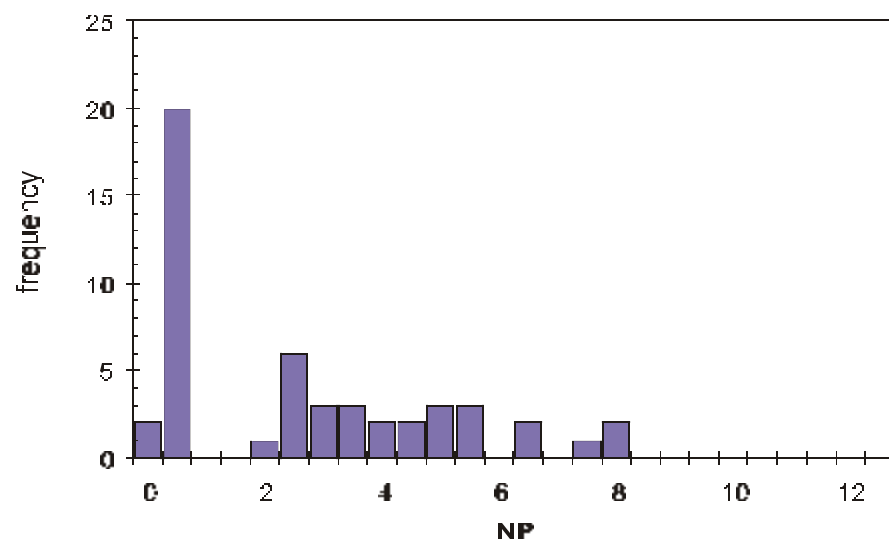
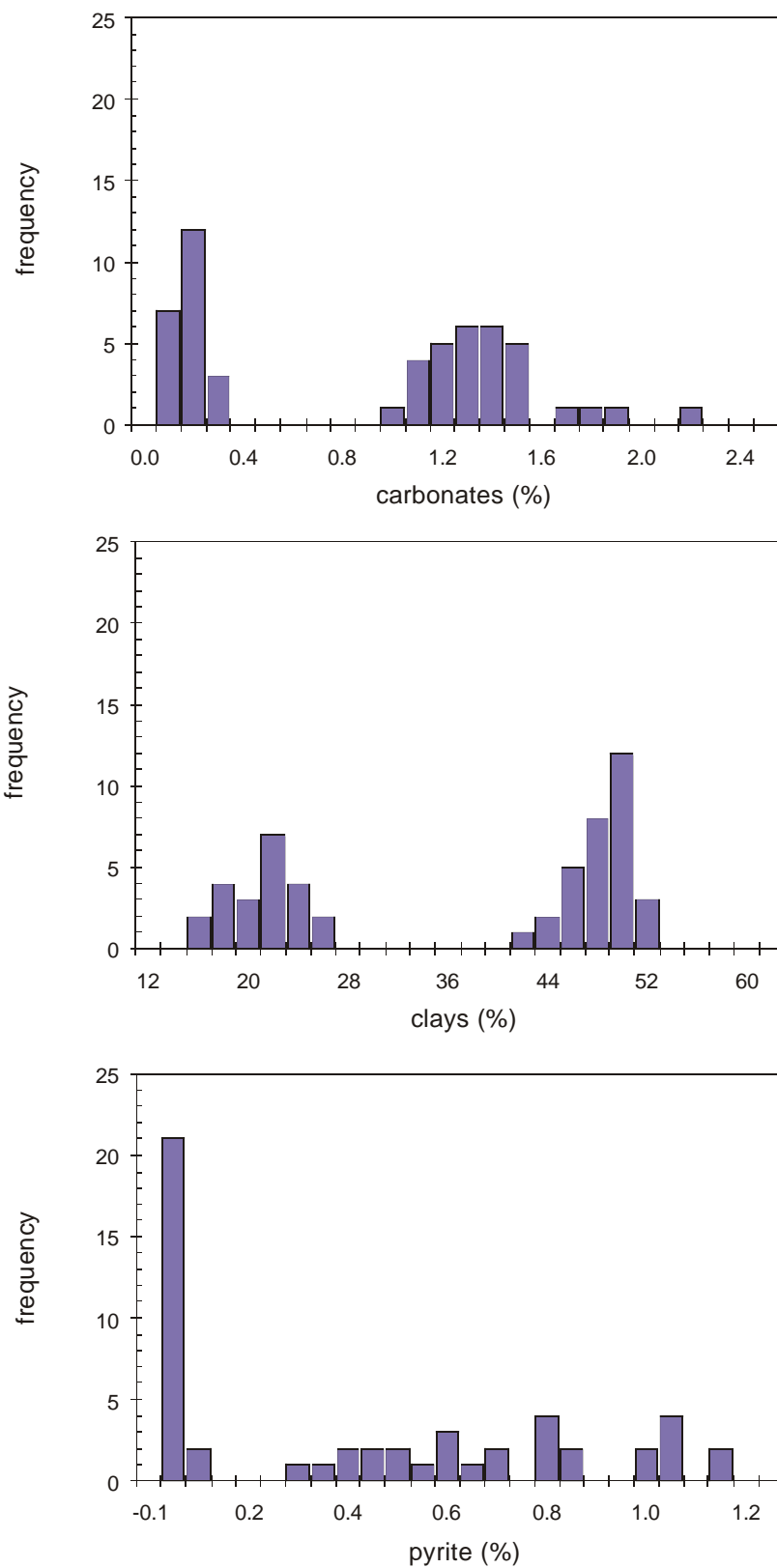**Figure 6.2.** Frequency histograms for NP, MPA, and NNP for New Allegheny samples.

Figure 6.3. Frequency histograms for total carbonates, total clays, and pyrite for New Allegheny samples, determined by XRD.
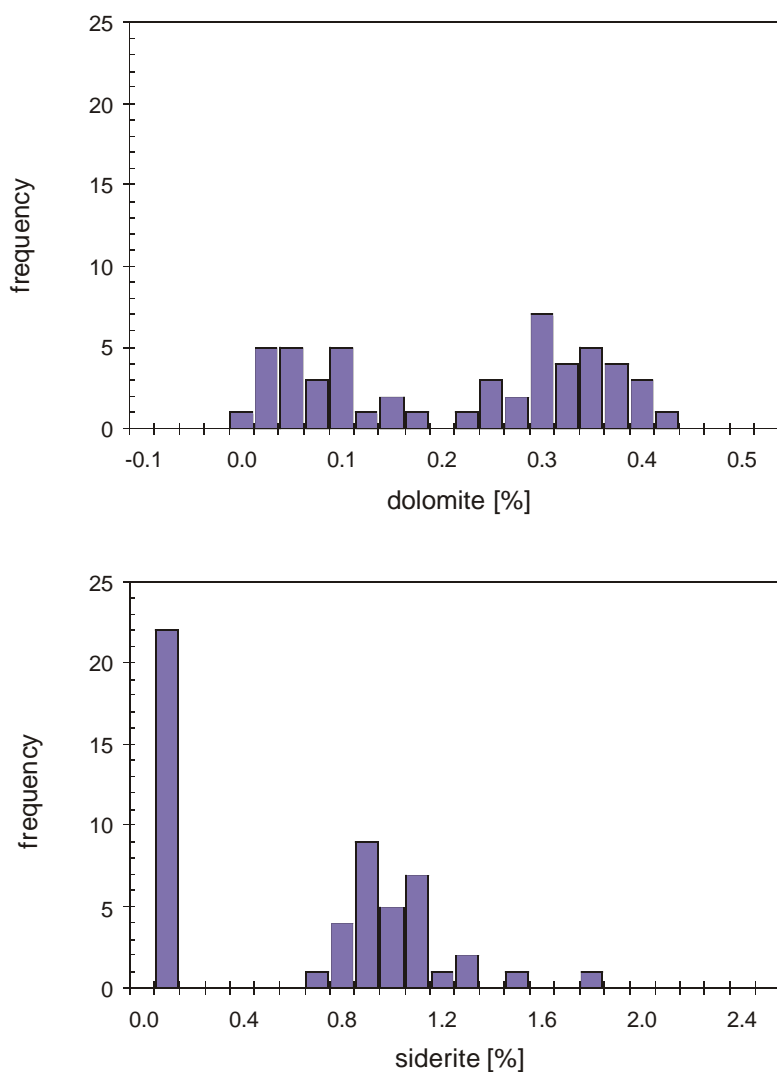
Figure 6.4. Frequency histograms for dolomite and siderite for New Allegheny samples, determined by XRD.

estimate the minimum sample spacing. Drilling closer than this distance generates more data than is needed; drilling beyond this spacing risks missing variation in the geochemistry.

Each variogram may be considered as a comparison of variance at different drill hole separations, relative to the variance for the entire dataset (the dotted horizontal line). Drill hole spacings with lower variance than that of the entire sample are relatively less dispersed (and more correlated with each other) than the dataset as a whole. If a dataset has considerable spatial correlation and has a mean that is spatially stationary (e.g., has second-order stationarity), it is expected that variance will be lower at close separations and, at greater separations, will increase to that of the dataset itself. For the exponential model, it is typical that the sill will approximate the sample variance and the range will represent the *decorrelation length*, beyond which correlation between points is low.
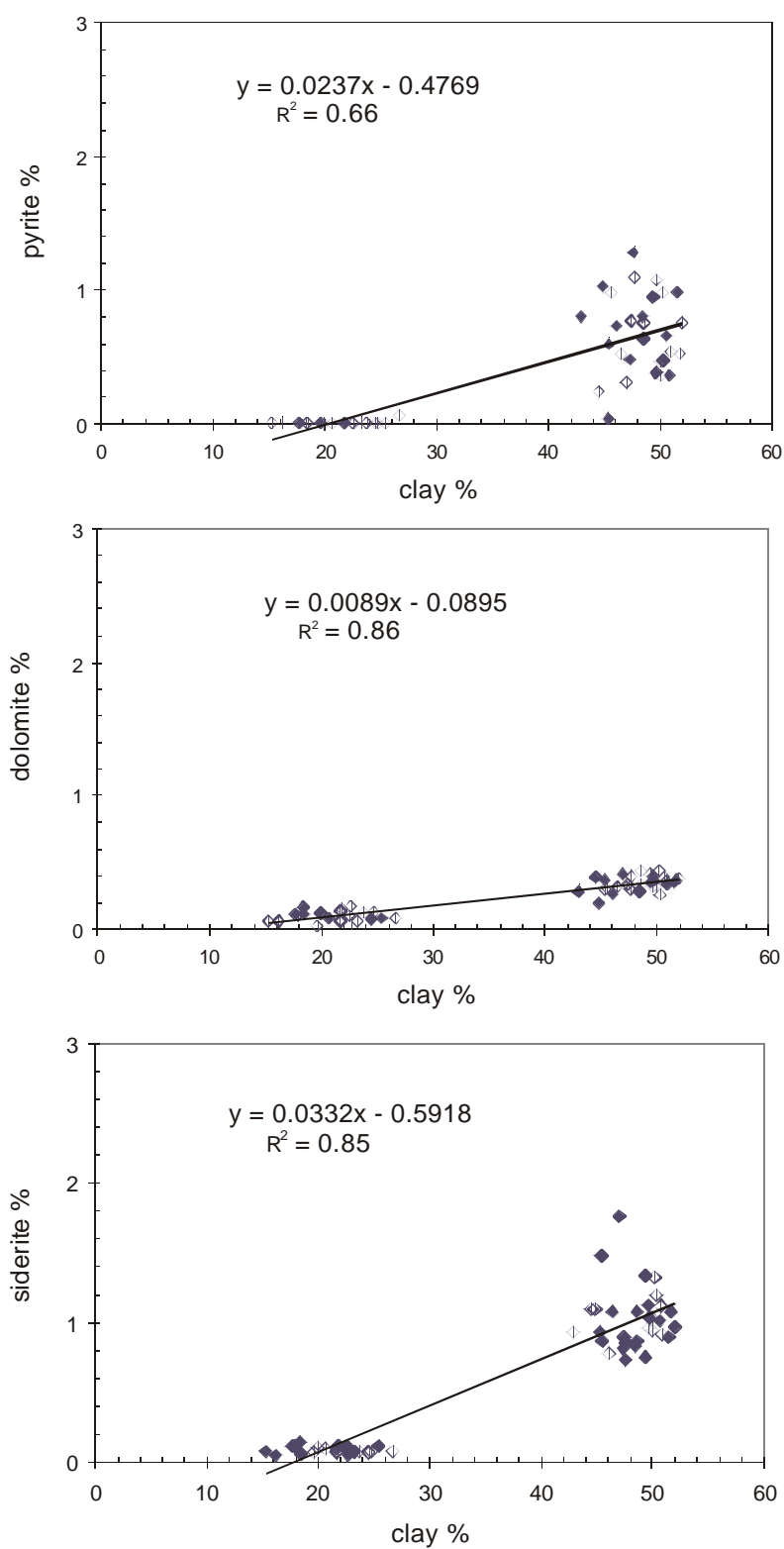
Figure 6.5. Percentage (wt/wt) clay minerals vs. pyrite (top), dolomite (middle), and siderite (bottom) for New Allegheny samples, determined by XRD.
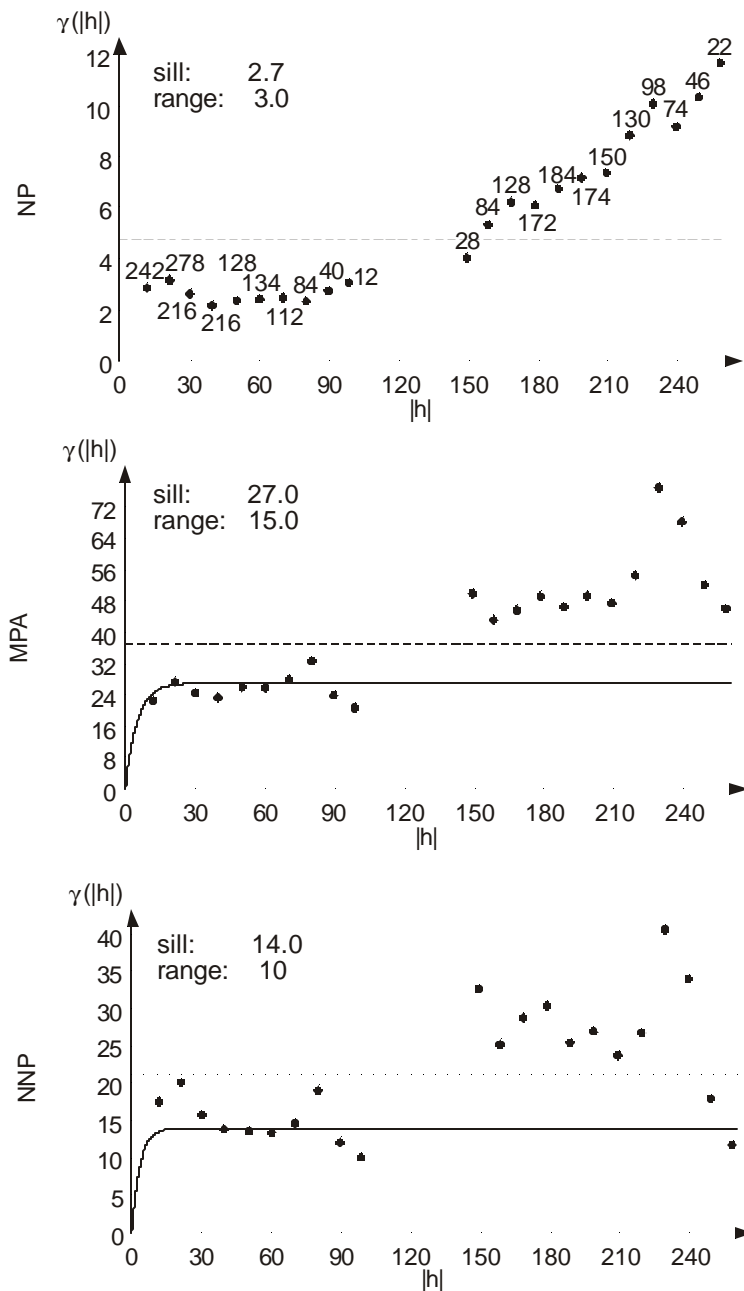
Figure 6.6. Variograms for NP, MPA, and NNP for New Allegheny samples. Dotted line is simple variance; solid line is exponential model. Number of pairs per class is shown on top variogram.

Figure 6.6 shows variograms for NP, MPA, and NNP from the NAM samples. The values of the number of holes per separation interval are posted on the first (NP) variogram; these show that interval size exceeds 70 holes for all but the outermost 2 intervals and the intervals bracketing the sampling gap from 100-140 ft. All three variograms are fitted by a pronounced sill at 60-80% of the sample variance, extending from very close range (3-15 ft) to <u>at least</u> 100 ft. The top two variograms show that there is a stable sill for both
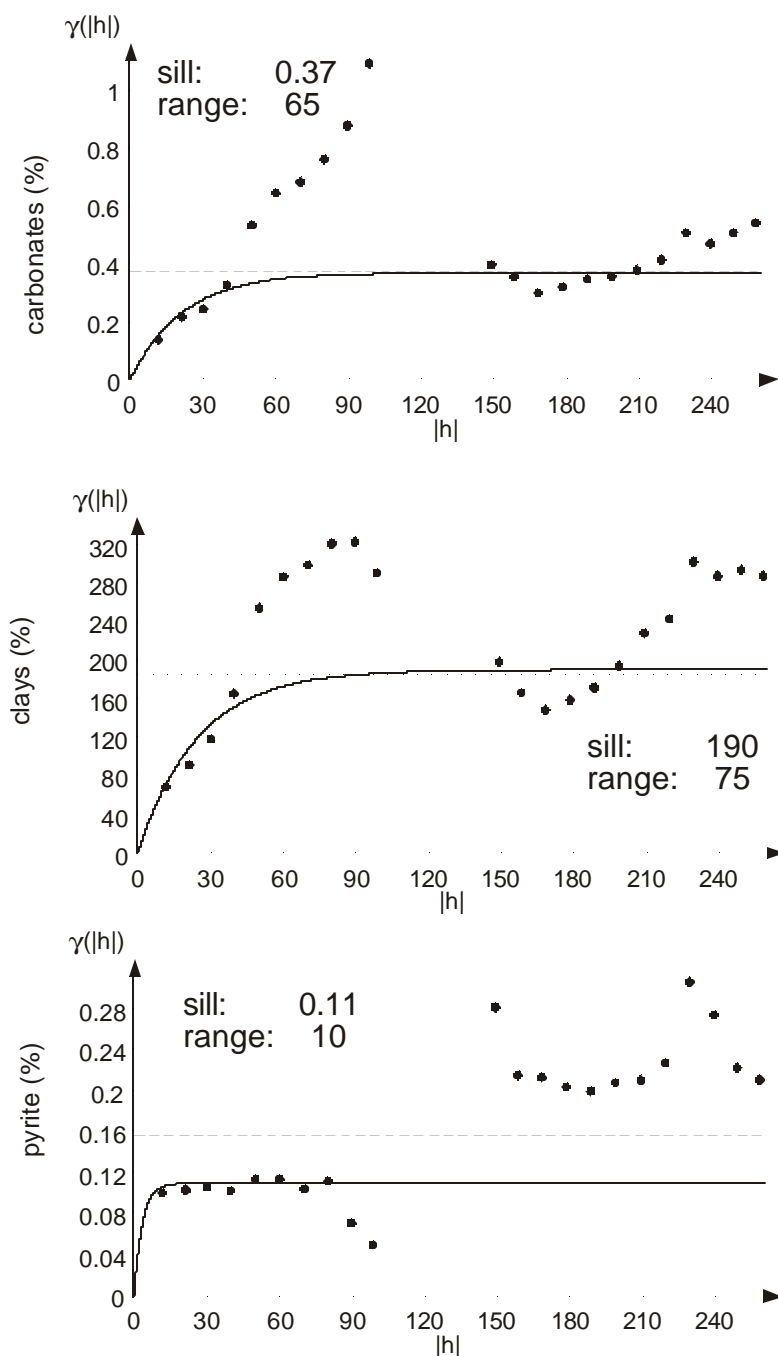
Figure 6.7. Variograms for carbonates, clays, and pyrite for New Allegheny samples, all determined by XRD. Dotted line is sample variance; solid line is exponential model.

NP and MPA that extends from close separation of at least 100 feet, and that it may extend further within each stratigraphic interval.

Figure 6.7 shows mineralogic variograms for total carbonates (siderite + dolomite, as no calcite was detected), total clays, and pyrite, all by XRD. Similar variograms are seen for dolomite and siderite (Figure 6.8). All except pyrite show exponential ranges of about 60 feet; for pyrite it is much closer (10 feet),
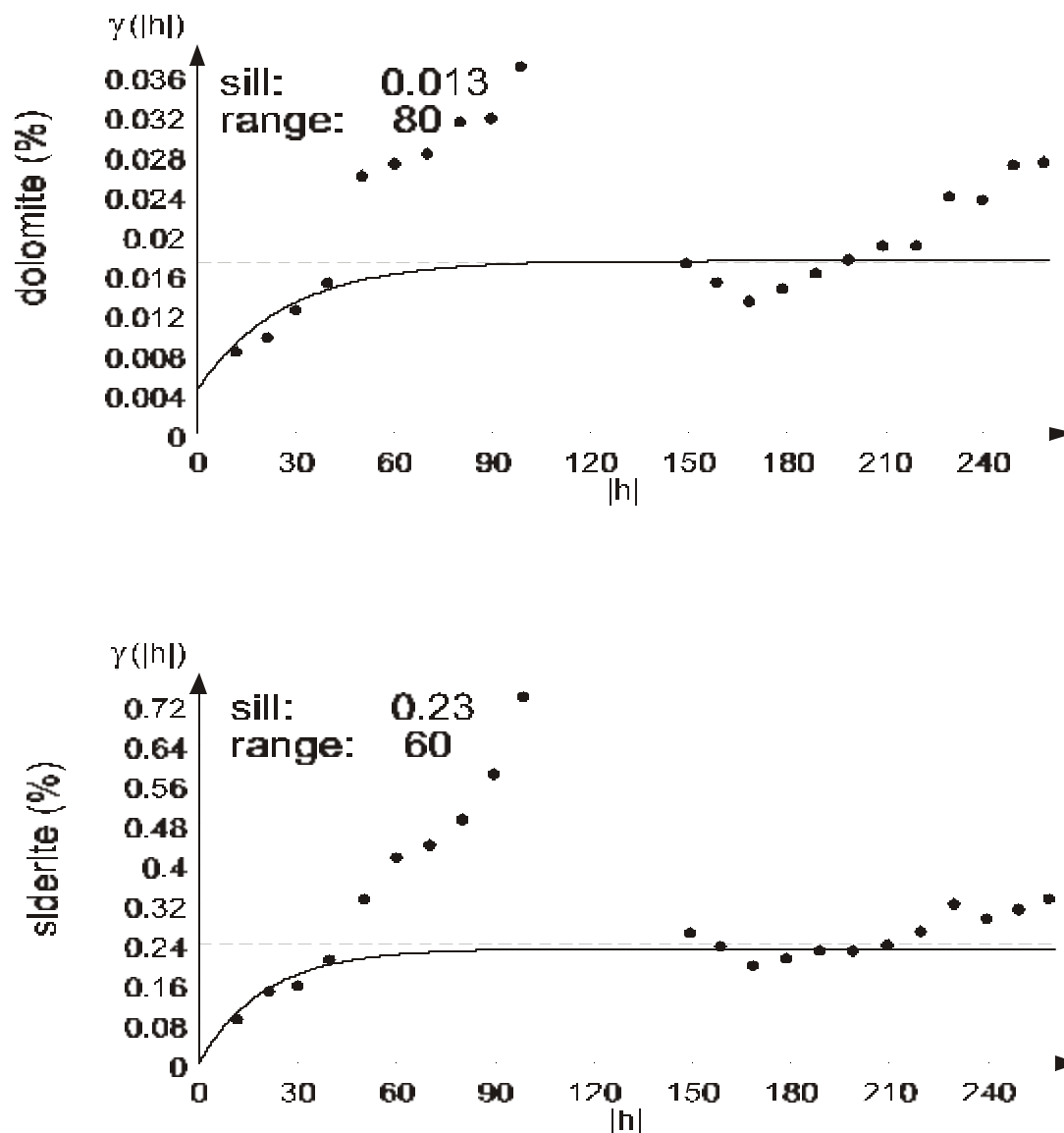
Figure 6.8. Variograms for dolomite and siderite for New Allegheny samples, both determined by XRD. Dotted line is sample variance; solid line is exponential model.

essentially a pure nugget effect. The sill for clays and carbonates, however, has a spatial interval of quite high variance from 60-100 feet. This type of variogram is frequently caused by non-stationarity and local anomalies (Isaaks and Srivastava, 1989). This may be caused by the distinctly bimodal distribution of clays, dolomite, and siderite, all of which are abruptly non-stationary across adjacent Blocks 1 and 3. This artifact of the variography, while spatial, is essentially stratigraphic; Upper Kitanning overburden (Block 1) is much higher in both carbonates, clays, and pyrite than the much sandier Upper Freeport overburden (Block 3). The non-stationarity is less pronounced for pyrite and may be exaggerated for the XRD carbonates because their abundance in Block 3 is close to detection limits and shows compressed variance (see the low modes of Figures 6.3 and 6.4).

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Except for dolomite, siderite, and clay minerals, all variables demonstrated a broad, stable sill to at least 100 feet separation, attributed to a low degree of spatial variability within overburden sections at these spacings. Beyond 150 feet, increases in variance occurs in both NP and MPA, ascribed to a large-scale spatial and/or stratigraphic trend. This large-scale variation would need to be understood in order to estimate spatialy-varying moments of these variables in a reasonably accurate fashion.

Significance of Results

The NAM site was net acidic (average NNP = -3.8) with low carbonate concentrations and moderate acidity (mean MPA=6.7). Variables tend to be bimodally distributed within the mine, but normally distributed within specific overburden intervals. There was a strong tendency for pyrite, dolomite, and siderite to covary with clay mineral percentage, suggesting that these reactive minerals are concentrated in shales. The trend was strongest for siderite.

Four types of spatial covariance may be observed within an individual site, and were observed for the NAM case study:
$ covariance between overburden intervals (stratigraphic covariance),
$ covariance from one hole to another nearby location (nugget covariance),
$ covariance over distances of 100's of feet (primary spatial trend), and
$ covariance of localized pods of alkalinity in contrast with the surrounding primary spatial trend (anomalous covariance).

Stratigraphic covariance must be analyzed for each specific interval. This may be done using high-resolution (1 to 5 feet) vertical sampling intervals, then averaging over larger intervals (the overburden between 2 major coals, for example). For NP, MPA, and MPA, the variance in this closest interval was very close to that of the sill extending out to about 100 ft. This suggests that there is little primary trend in the 100 ft separation range and that there was, for this mine, little to be gained by small-scale (<80 ft) sampling.

A primary covariance trend was observed as a prominent sill extending out to about 100 feet, with an increase in covariance beyond 150 ft. This suggests that separations more distant than about 150 ft may be too widely spaced to provide accurate estimation of the spatial trend.

Anomalous covariance regions for this particular site appear to be restricted to carbonate minerals and NP, not pyrite and MPA. The scale of these regions will generally be site specific and cannot be known a priori; thus a goal of any sampling scheme must be to identify any such anomalies and to determine at what spacing they might be observed. If anomalous alkaline regions are large and of sufficiently high NP, their omission in a sampling scheme might induce considerable error (underestimation of NP) in the ABA process. Similarly, their inclusion by random chance in a small sample as an outlier would tend to overestimate NP. The size and frequency of the anomaly is thought to be the key factor in their location.

The primary spatial trend is the principal objective in sampling to estimate ABA. Based on this study, the trend would be estimated by samples from 100-200 feet in separation. The trend is gradual and continuous for MPA and noisier for NP; also, NP was observed to show local anomalies of <100 feet dimension,

which could influence ABA estimation in some cases. At a separation of 200 feet per hole, a sampling density of one hole per acre would result. However, the number of holes would also be dependent on the configuration of the mine; for example, a long narrow mine of one acre size would require more holes than a mine that was square shaped.

Planning to deal with anomalous covariance in carbonate values is very problematic. For anomalies in which the contrast with the primary trend mean is not great, additional nested sampling may not be required. However, additional, more detailed sampling should be considered for localized areas of mines with large deviations from the mean (>2 standard deviations), at a scale much smaller than that of the primary trend and similar (or smaller) than that of the anomalies themselves. The purpose of this sampling should be to determine whether or not carbonate anomalies are present. If any prominent carbonate-rich anomalies are indicated, these regions may be explored in greater detail to determine their size as well as average concentration. This suggests that a stratified sampling program is required where localized high carbonate zones are anticipated to be present and available for neutralization.

This case study reaffirmed the benefit of mineralogical analysis of carbonate phases. In the absence of such information, care must be taken to exclude siderite from NP estimates. The implications of this study with respect to mine planning in general is that evaluation of data obtained from overburden shot holes drilled in advance of mining, by the methods used in this study or otherwise, can be useful. It permits one to evaluate overburden characteristics on a local scale prior to mining, which should be helpful in identifying the need for selective handling or alkaline addition as mining progresses.

Skyline Mine, Tennessee

This case study is based on work done by the Office of Surface Mining's Knoxville Tennessee Field Office in evaluating the AMD potential of overburden associated with mining operations in South Central Tennessee (Office of Surface Mining, 1997; 1998). The Skyline Coal Company Mining Complex (Skyline Mine) provides a good example of an active mining area where AMD discharges were known to exist from past mining, and where high density sampling helped delineate areas where future AMD problems would likely occur if appropriate actions were not taken to avoid or prevent them.

The Skyline Mine Complex consists of four operations, the Glady Fork, Pine Ridge, Brush Creek #1 and Big Brush Creek #2 mines. The Sewanee Coal seam is mined at all four sites. Draglines, bulldozers, and front-end loaders were utilized for the mining and reclamation operations. The stratigraphic sequence of the mining area includes the Sewanee Conglomerate, Whitwell Shale, Sewanee Coal, and Newton Sandstone. To evaluate the AMD potential at the Skyline Coal Co. Big Brush Creek #2 mine, the applicant drilled 23 drill holes. This is equivalent to one drill hole per 40 acres. Drill hole data from the existing Big Brush #l Mine was also evaluated since it was drilled on 500 foot centers (5.7 acres) (Office of Surface Mining, 1997). Previous sampling used a drill hole spacing on one-half mile centers (Office of Surface Mining, 1998). NNNP values were determined for each drill hole and the results were plotted on mine maps. The resulting data were grouped into three categories, NNP> 10; < 10 NNP > 0; and NNP <0.

The drill hole data for Big Brush Mines #1 and #2 (Office of Surface Mining, 1997) were analyzed by univariate frequency analysis, variogram analysis, and kriging. Three-dimensional modeling software was also used, but this discussion is limited to the statistical analysis. Universal kriging software was used to interpolate the data at the Big Brush #1 mine and extrapolate into the adjacent (at that time proposed) Big Brush Creek #2 mine. The Kriging program calculated a predicted NNP value for empty cells based on cells that contained drill hole data. Ninety-nine drill holes were used in the simulation.

Almost every drill hole showed some acid/toxic forming material, primarily in the Whitwell Shale. Acid/toxic material was also associated with the Lantana coal seam in the western portion of the proposed permit area. A weighted NNP value was calculated for each hole in the Whitwell Shale zone, which contains most of the pyritic material(Office of Surface Mining, 1997). The NNP values for the drill cores appear to be normally distributed with a mean NNP for all drill cores of 7, with a variance of 10 (Figure 6.9).

The statistical technique of semivariogram analysis was used to evaluate proper drill spacing. As described in the introductory material to this section and the previous case study (New Allegheny Mine), variogram analysis calculates the semivariance between each pair of drill holes located so many feet apart. The difference is squared and summed, then divided by the number of pairs squared. This produces a semivariance for a distance h. Then another set of drill holes located a slightly larger distance apart is analyzed. The result is a plot of semivariance verses drill hole distance. The line is fitted to one of several distributions for a proper fit. If the plot results in a plateau, or sill, the distance at which the semivariance flattens out is deemed to be the optimum drill hole spacing. Drilling closer than this distance generates more data than is needed; drilling beyond this spacing risks missing variation in the geochemistry.

In this case study:
• The variogram analysis provided an impartial evaluation of drill hole spacing and appeared to confirm an optimum drill hole spacing of about 650 feet or 200 m (Figure 6.10).
• The variogram and kriging exercises showed that there are areas with good and bad weighted ABA values, and that high and low values are clustered.
• Most of the acid-forming materials are confined to the southern 1/3 of the permit area.

Through intense geologic sampling and overburden analyses, this study identified a potential for acid or toxic drainage in the backfilled material if not addressed during mining and reclamation operations. Skyline had to design a detailed, site specific, and complex Toxic Material Handling Plan. Four acid-producing zones that would be disturbed were identified: 1) the shale immediately under the Sewanee coal seam, 2) coal fines remaining in the pit after mining, 3) lenticular sandy shale zones within the Whitwell Shale, and 4) the Lantana coal seam, which will not be recovered but will be incorporated into the backfilled spoil material.
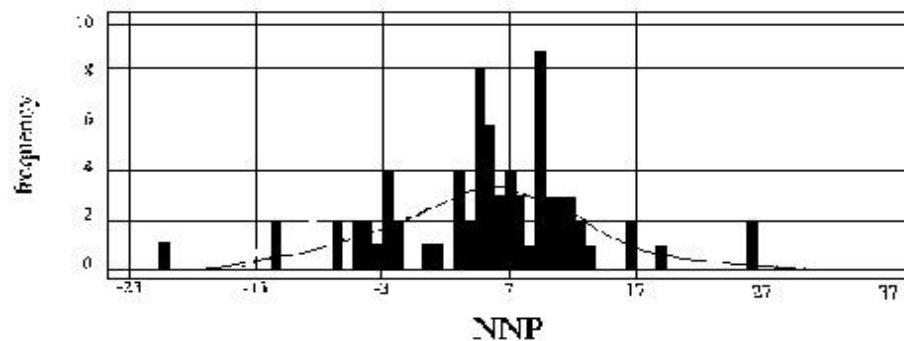
FIGURE 6.9. Histogram of NNP values at the Skyline Mine.

VISUALIZATION AND THREE-DIMENSIONAL MODELING

Jewett Mine, Texas

This case study, from Behum and Joseph (1997), applied three-dimensional modeling software to evaluate overburden characteristics at the Jewett Mine. *earthVision* can produce, among other things, three-dimensional models of overburden characteristics (e.g., pH, sulfur content, etc.) and volumetric calculations of selected overburden zones. This software is available to permit reviewers and reclamation specialists in Federal, State, and Tribal regulatory agency offices in all coal-producing states through the Technical Information Processing System (TIPS) of the Office of Surface Mining. The purpose of this study was to demonstrate the capabilities of *earthVision* in AMD prediction and mine planning, although the results were not actually used to identify acid-forming zones or develop material handling plans during mining.

The Jewett Mine is a large surface operation in Eastern Texas. This study focused on the area to be mined between 1994 and 1999 within Area D, the study area, with emphasis on overburden handling in 1994. The topography of the area is characterized by low hills capped by iron-cemented Carrizo Formation sands. The L6 seam was the principle lignite seam mined in Area D; three other overlying seams were also mined wherever possible. A large dragline and a bucket wheel excavator were used to remove most of the poorly consolidated overburden. The Carrizo Formation sand was selectively handled by a pre-stripping operation, which stockpiled part of the material, followed by placement of the sandy sediments directly above the mine
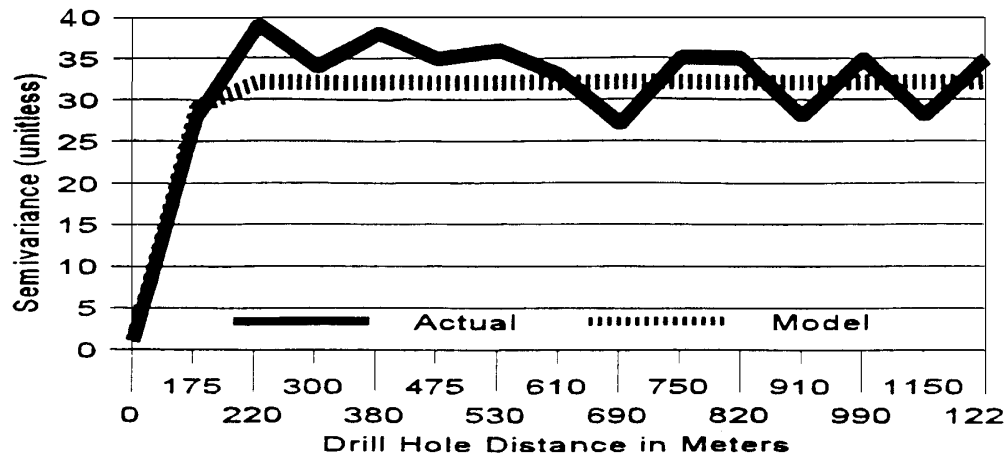
Figure 6.10. Semivariogram of NNP vs. sample distance for Skyline Mine samples.

by the dragline. Figure 6.11 is a three dimensional model of the site.

The acidity of the overburden in this part of Texas is the principle impediment to environmental protection. The State environmental regulatory authority, the Texas Railroad Commission, requires that the cover material have a pH of more than 5 to provide a cover material suitable for plant growth. In his study of an area immediately west of the 1994-1999 permit area studied by Behum and Joseph (1997), Hasan (1995) found that the overburden characteristics were quite variable due to primarily lateral facies changes. In contrast, the overlying Carrizo Formation sands have a more persistent geochemistry, typically a neutral pH, and it is easily identified in the field by color.

earthVision was used to calculate volumes of materials within the selected area. Overburden characteristics were clipped to the 1994 extraction area by a polygon. Volumetric analysis indicated that the Carrizo Sand in the 1994 area is thin and most of it is inadequate for use as cover material without the addition of more suitable material. It also showed that the L6 overburden extracted in 1994 had an overabundance of material in excess of -5 tons $CaCO_3$/1000 tons of material, but that there was limited neutralization potential (<20 tons $CaCO_3$/1000 tons of material).

The overburden sample spacing for this mine should have been smaller than that actually used. Based on the *earthVision* modeling, the lateral stratigraphic variation in this area indicates that the optimum spacing should approach the 200 by 200-foot borehole spacing recommended by Hasan (1995). At other sites, the necessary sample spacing will depend on the consistency of rock unit thickness and chemistry, but if the grid cell spacing is coarse, *earthVision* may not be able to calculate three-dimensional property volumes. The impact of the oxidized zone should also be evaluated. This can be done by contouring the
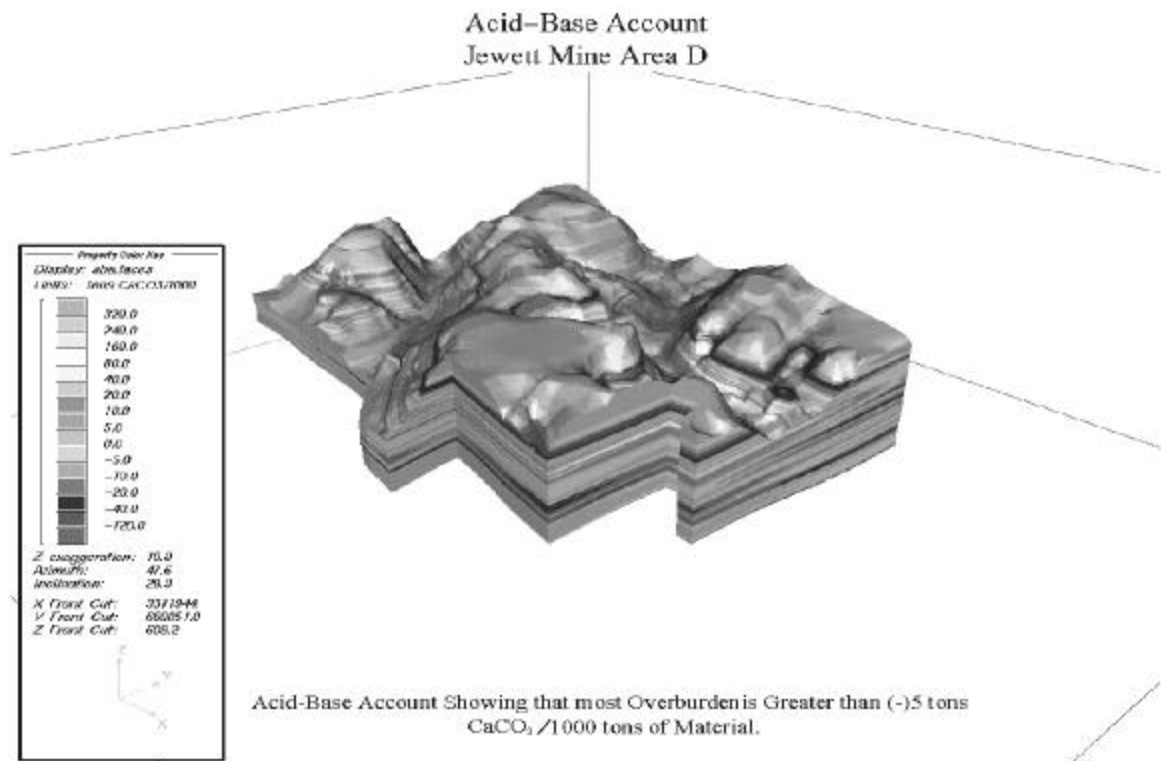
Figure 6.11. Three-dimensional acid-base account diagram for the Jewett Mine, Area D.

elevation of the base of this zone by a two-dimensional grid and by modeling the strata above and below this grid surface separately, in the property gridding.