Section 2.0 Geochemical Best Management Practices

Introduction

The previous section discussed how hydrologic best management practices (BMPs) can reduce pollution load from remining sites. This section will discuss BMPs that use geochemical approaches to reduce pollution load. Effective use of geochemical BMPs requires at least a rudimentary understanding of the acid-producing and acid-neutralizing chemical processes.

Acid mine drainage results from the oxidation of pyrite (FeS_2). The following summary equation shows the reactants and products:

$$FeS_2 + 3.75\ O_2 + 3.5\ H_2O \rightarrow Fe(OH)_{3(s)} + 2\ SO_4^{2-} + 4\ H^+ \qquad \text{(Equation 1)}$$

Pyrite in the presence of oxygen and water will oxidize to form "yellowboy" [$Fe(OH)_{3(s)}$], sulfate (SO_4^{2-}) and acidity (H^+). Equation 1 is a summary equation. The following reactions are important intermediate steps:

$$FeS_2 + 3.5\ O_2 + H_2O \rightarrow Fe^{2+} + 2\ SO_4^{2-} + 2\ H^+ \qquad \text{(Equation 2)}$$

$$Fe^{2+} + 0.25\ O_2 + H^+ \rightarrow Fe^{3+} + 0.5\ H_2O \qquad \text{(Equation 3)}$$

A product of Equations 2 and 3 is ferric iron (Fe^{3+}). Ferric iron can oxidize pyrite in the absence of oxygen:

$$FeS_2 + 14\ Fe^{3+} + 8\ H_2O \rightarrow 15\ Fe^{2+} + 2\ SO_4^{2-} + 16\ H^+ \qquad \text{(Equation 4)}$$

The oxidation of pyrite by ferric iron can become cyclical and self-feeding (Stumm and Morgan, 1996). Chemical reactions represented by Equations 1 through 4 occur "naturally," but the rate of reaction can be enhanced by orders of magnitude by the catalytic influence of bacteria, primarily *Thiobacillus ferrooxidans*. The bacteria obtain energy for their metabolism from the above reactions.

Equally important to any of the above acid-producing reactions is the ability of certain minerals to neutralize acid. This is illustrated by the dissolution of calcite:

$$CaCO_3 + H^+ \rightarrow Ca^{2+} + HCO_3^- \qquad \text{(Equation 5)}$$

$$CaCO_3 + 2\ H^+ \rightarrow Ca^{2+} + CO_2 + H_2O \qquad \text{(Equation 6)}$$

In Equation 5, acidity (H^+) is neutralized and alkalinity (HCO_3^-) is produced. In Equation 6 acidity is neutralized, but no alkalinity is generated. Whether Equation 5 or 6 dominates depends on how open or closed the system is to the atmosphere (Guo and Cravotta, 1996). In a more closed system Equation 5 will dominate.

Two overall reactions can be written to describe pyrite oxidation (acid production) and carbonate dissolution (acid neutralization) in a closed (Equation 7) and open (Equation 8) system:

$$FeS_2 + 4\ CaCO_3 + 3.75\ O_2 + 3.5\ H_2O \rightarrow Fe(OH)_3 + 2\ SO_4^{2-} + 4\ Ca^{2+} + 4\ HCO_3^- \qquad \text{(Equation7)}$$

$$FeS_2 + 2\ CaCO_3 + 3.75\ O_2 + 1.5\ H_2O \rightarrow Fe(OH)_3 + 2\ SO_4^{2-} + 2\ Ca^{2+} + 2\ CO_2 \qquad \text{(Equation 8)}$$

Chemical BMPs attempt to counter the acid-generating chemical reactions in one or more ways. Approaches include the following:

- preventing pyrite from being oxidized
- keeping water away from pyrite
- neutralization of acid by dissolution of calcareous materials
- inhibition of the bacterial catalysis.

The chemical BMPs examined in this section are alkaline addition, induced alkaline recharge, special handling of acid-forming materials, and bactericides. Alkaline addition can positively affect mine drainage in several ways. It can neutralize acid generated from pyrite oxidation, it can elevate pH, which can have an inhibitory effect on bacteria, and it can facilitate precipitation of ferric iron (Fe^{3+}), thus reducing its role in pyrite oxidation. Induced alkaline recharge is a hybrid of geochemical and hydrologic controls. The geochemical aspect is largely neutralization of acid. Special handling can be used to keep water or oxygen away from pyrite. Bactericides are used specifically for stopping the influence of bacteria on the acid mine drainage (AMD)-generating process.

2.1 Sampling

Introduction

Proper planning for implementation of geochemical BMPs requires an adequate understanding of overburden characterization and sampling. This discussion on sampling is primarily taken from Tarantino and Shaffer (1998), and supplemented by data from Sames and others (in preparation). Sames and others surveyed all Appalachian coal mining states to determine sampling protocol and interpretative techniques used by the various states.

The results of overburden analyses are generally used in two ways: 1) as a permitting decision-making tool (determining whether the permit is issuable), and 2) as a management tool (using the information to design best management practices for avoidance or remediation of pollution).

This section will concentrate on using overburden sampling for providing insights into the design of best management practices. Representative overburden sampling is used to:

- determine overall acid or alkaline-producing potential of a proposed mine;
- calculate alkaline addition rates;
- determine the distribution of pyritic zones that may require special handling or avoidance;
- identify alkaline zones which can be incorporated into a mining plan to prevent acidic drainage (i.e., alkaline redistribution); and,
- determine the economic feasibility of mining without unacceptable environmental impacts.

Acid-Base Accounting

Overburden analysis (OBA) refers to determination of the acidity or alkalinity producing potential of the rocks that will be disturbed by mining. OBA methods fall into two broad categories: static and kinetic. Static tests are "whole rock analyses" that determine the concentration of elements or minerals. Kinetic tests are simulated weathering procedures that attempt to reproduce weathering. In short, static tests measure what is in the rock and kinetic tests measure what comes out of the rock. By far the most commonly used overburden analysis method in the Appalachian region is static "acid-base accounting" (ABA).

Components of ABA

ABA is based on the premise that the propensity for a site to produce acid mine drainage can be predicted by quantitatively determining the total amount of acidity and alkalinity contained in samples representative of site overburden. The maximum potential acidity (expressed as a negative concentration of $CaCO_3$) and total potential alkalinity (termed neutralization potential and expressed as concentration of $CaCO_3$) are summed. If the result is positive, the site should produce alkaline water. If it is negative, the site should produce acidic water. The maximum potential acidity (MPA) is stoichiometrically calculated from the percent sulfur (S) in the overburden. Sobek and others (1978), noting that 3.125 g of $CaCO_3$ is theoretically capable of neutralizing the acid produced from 1 g of S (in the form of FeS_2), suggested that the amount of potential acidity in 1000 tons of overburden could be calculated by multiplying the percent S times 31.25. This factor is derived from the stoichiometric relationships in Equation 9 and carries the assumption that the CO_2 exsolves as a gas.

$$FeS_2 + 2\ CaCO_3 + 3.75\ O_2 + 1.5\ H_2O \dashrightarrow Fe(OH)_3 + 2\ SO_4^{2-} + 2\ Ca^{2+} + CO_2(g) \qquad \text{(Equation 9)}$$

Cravotta and others, (1990) suggested that, in backfills where CO_2 cannot readily exsolve, the CO_2 dissolves and reacts with water to form carbonic acid and that the maximum potential acidity in 1000 tons of overburden should be derived by multiplying the percent S times 62.50.
In short, however, it can be said that interpretation of ABA data is far more complicated than simply summing the MPA and neutralization potential (NP) values. In addition to the percent sulfur and NP determinations, two other measured parameters in an ABA overburden analysis are paste pH and "fizz."

Paste pH

Paste pH has its origin in soil science, where weathered material (soil) is analyzed. A portion of prepared sample is mixed with deionized water, and then tested with a pH probe after one hour. The paste pH test indicates the number of free hydrogen ions in the prepared sample, However, since pyrite oxidation reactions are time dependent, the paste pH results provide little indication of the propensity of a sample to produce acid mine drainage. In fact, the paste pH of a unweathered, high-sulfur sample is likely to be near that of deionized water, while a weathered sample with relatively low percent sulfur (but which includes a small amount of residual weathering products) may have a significantly depressed paste pH. Thus, paste pH is of limited use when dealing with unweathered rock.

Percent Sulfur

Since acid mine drainage results from weathering of sulfide minerals, the amount of sulfur in a sample, or in an overburden column, is obviously an important component of ABA.

Sulfur determinations for ABA are often performed for total sulfur only, however, determinations for forms of sulfur are sometimes included. Sulfur generally occurs in one of three forms in the rock strata associated with coals in Appalachia: sulfide sulfur, organic sulfur, and sulfate sulfur.

> <u>Sulfide sulfur</u> is that sulfur that reacts with oxygen and water to form acid mine drainage. The sulfide minerals most commonly associated with coal in Appalachia are pyrite and marcasite, both of which have the formula FeS_2.
>
> <u>Organic sulfur</u> is that sulfur which occurs in carbon-based molecules in coal and other rocks with significant carbon content. Since organic sulfur is tied up in compounds that are stable under surface conditions, it is generally not considered a contributor to AMD. Organic sulfur is only a small percentage of total sulfur for most rock types, but can be significant in coal.
>
> <u>Sulfate sulfur</u>, in humid climates, is generally found in relatively small concentrations due to its association with high-solubility minerals. However, when present in Appalachia, sulfate sulfur often occurs in partially weathered samples as a reaction by-product of sulfide-mineral oxidation. When solubilized, these by-products are the source of the contaminants found in acid mine drainage. For that reason, when determinations for forms of sulfur are performed, sulfate sulfur should be considered in the calculation of MPA. Alkaline earth sulfate minerals such as gypsum ($CaSO_4$) can also contribute to the sulfate sulfur fraction, but generally are not abundant in coal-bearing rocks in Appalachia. Where they are present, the alkaline earth-sulfate minerals do not contribute to acidity and should not be counted in the calculation of MPA (Brady, Hornberger, and Fleeger, 1998).

A review of the methods for sulfur determinations described in Noll and others, (1988) reveals that the methods for total sulfur determinations have a relatively high degree of precision with few notable interferences and precautions, while methods for determination of the forms of sulfur had lesser degrees of precision and more numerous potential interferences. Stanton and Renton (1981) examined the nitric acid dissolution procedure, which is the cornerstone of the most frequently used methods for determining pyritic sulfur, including American Society for Testing and Materials (ASTM) D2492. They found the procedure frequently does not succeed in digesting all the pyrite, and thus underestimates the pyritic fraction of the sulfur. Brady and others (1990) compared total sulfur and forms of sulfur determinations performed by various laboratories. Their findings include:

- While the results generated by each laboratory were internally consistent in terms of the ratio of pyritic sulfur to total sulfur, there were significant differences between laboratories in the median percent pyritic sulfur/total sulfur. Where the same samples were analyzed by different laboratories, differences were noted in the pyritic determinations, but total sulfur determinations were comparable.

- There was no significant difference in the percent pyritic sulfur/total sulfur between rock types (excluding coal). This contradicts one of the primary reasons for determining forms of sulfur: that some rock types contain significant percentages of organic sulfur.

- With one exception, all laboratories used high temperature combustion for determining weight percent total sulfur. The high temperature combustion results compared well on duplicate samples, while the pyritic results on the same samples did not.

- Standards are available from the National Institute of Standards and Technology for total sulfur but not for pyritic sulfur.

- A wide range of methods for determining pyritic sulfur were in use and individual laboratories had their own variations of the methods.

- According to ASTM Committee D-5 on Coal and Coke, the most commonly used method of pyritic sulfur determination, ASTM D2492, was developed for use on coal and is probably not appropriate for determinations on rock overburden.

The above findings can be summarized as:

- Total sulfur determinations are typically simple to perform, are reproducible, and can be calibrated and verified using available standards;

- pyritic sulfur is determined using a variety of methods (the most common of which is considered inappropriate for rock samples),

- pyritic sulfur methods produce results which are often not reproducible between laboratories, and cannot be calibrated and verified using available standards.

Given these considerations, and that pyritic sulfur is the most abundant form in coal overburden (but not necessarily in the coal), total sulfur determinations currently provide the best basis for calculating MPA.

Fizz Rating

The fizz test is a subjective test measured visually and rated as to the amount of effervescence when one to two drops of 25 percent HC1 is added to a small amount of finely-ground sample (Sobek and others, 1978). Fizz ratings range from strong effervescence to none. The fizz test serves two functions:

- as a check on the NP determination, since there should be a qualitative correlation between the two. Calcareous rocks with high NP should show a strong fizz, whereas non-calcareous rocks should not; and
- more importantly, the fizz rating determines the volume and the strength of the acid that is used to digest samples for NP determinations.

Neutralization Potential

The first step of the NP test is to conduct a qualitative fizz test on a small amount of the prepared sample as described above. Based on the fizz test results, an appropriate volume and normality of HCl is selected then added to 2.0 grams of prepared sample (Noll and others, 1988; Sobek and others, 1978). The strength of the acid is chosen to assure complete digestion of acid-neutralizing minerals. The neutralization potential is calculated by determining the amount of acid that has been neutralized by the rock.

Carbonate minerals, such as calcite and dolomite, are known to be major contributors to groundwater alkalinity in the coal regions of the Appalachians. The acid-digestion step of the NP test is suspected of dissolving various silicate minerals, which results in a NP determination that overstates the amount of carbonate minerals in a sample. Lapakko (1993) noted that since this dissolution will only take place at low pH values, it is unlikely to help maintain a drainage pH of acceptable quality.

Siderite ($FeCO_3$) is common in Appalachian coal overburdens, and has long been suspected of interfering with the accuracy of NP determinations and of complicating the interpretation of the data (Skousen and others, 1997). If iron from siderite is not completely oxidized when the titration is terminated, the calculated NP value will be overstated. Skousen and others (1997) found that the addition of hydrogen peroxide (H_2O_2) following sample digestion can expedite oxidation and precipitation of iron. Samples exposed to H_2O_2 digestion produced results similar to those of samples containing little pyrite or siderite. The additional H_2O_2 digestion step provided the lowest NP values for samples with significant siderite content and the best reproducibility between laboratories.

Net Neutralization Potential

Neutralization potential and maximum potential acidity are both expressed in units of tons $CaCO_3$ equivalent per 1000 tons of material (e.g., parts per thousand $CaCO_3$). Net neutralization potential (NNP) is neutralization potential minus maximum potential acidity. Thus, if the NNP is positive, there is an excess of neutralizers. If the NNP is negative there is a deficiency of neutralizers.

Studies comparing ABA with post-mining water quality have consistently shown that although NP and MPA have the same units of tons $CaCO_3$ per thousand tons of material, and in theory should be "equal," their relative importance is not equal. It takes an excess of NP to assure that post-mining water will be alkaline (diPretoro, 1986; Erickson and Hedin, 1988; Brady and others, 1994; Perry, 1998). Post-mining water quality predictions should not be based on ABA alone, but should employ an array of prediction techniques. The best decisions involve consideration of as much data as is available (Kania, 1998b).

Information Needed to Conduct an Overburden Analysis

The site-specific data needed to properly plan an overburden analysis (OBA) includes:

- Mining limits: -boundaries of the proposed area to be affected by coal removal;
  -proposed maximum highwall heights;
  -type of mining (e.g., contour/block cut or hill top removal); and
  -accessibility to drilling locations
- Geologic considerations such as coal-seam identification, depth of weathering, and stratigraphic variation.
- Information available in state mining office permit files, such as water quality data from previous permits or applications covering the same or adjacent areas.
- Overburden analyses from the same or adjacent areas.
- Publications of state geologic surveys, the US Geologic Survey (USGS), the former US Bureau of Mines (USBM), US Army Corps of Engineers, and miscellaneous other state specific publications (e.g. the Pennsylvania “Operation Scarlift” reports from the late 1960s and early 1970s). These publications can include information such as:

-coal-bed outcrop maps,
-generalized stratigraphic sections,
-coal seam thickness maps,
-structure contour maps.

Old and current deep mine maps are available from the Office of Surface Mining, Appalachian Region Coordination Center, at 3 Parkway Center, Pittsburgh, PA, 15220, and various state agencies. These agencies have map repositories containing prints, originals, and microfilm, and copies can be readily obtained. These repositories include the Works Progress Administration (WPA) deep mine maps prepared in the 1930s, which cover an area that is 1/9 of a 15 minute quadrangle. In addition to showing mining limits, deep mine maps frequently show structure contours. This information can be very helpful in planning OBA drilling.

Other considerations in developing an OBA drilling plan include:

- Exploration equipment. It is important to understand the limitations that are inherent with different types of drilling equipment. These limitations can have an impact on the ability to obtain unbiased, representative samples. The choice of exploration equipment can influence costs.
- The type of overburden analysis to be performed. This is important in determining how much sample and what size fraction is required for the specific type of testing to be employed.
- Time constraints. Air rotary drilling is normally faster than coring.
- Economic constraints. Air rotary drilling is generally less expensive than coring.

Preparing for Overburden Analysis Sampling

The obvious questions that need to be asked when planning an OBA drilling plan are:

- How many OBA holes are needed ?
- Where should the drill holes be located ?

Once these details have been worked out, preliminary work can start.

The first step in the development of an OBA proposal is to plan for the drilling. While there may appear to be savings associated with performing the drilling for the overburden analysis as part of the initial exploration drilling, it is generally preferable to perform exploratory drilling throughout the entire site before OBA drilling is initiated. This preliminary drilling enables the determination of depth to coal and the lateral extent of strata. This information can then be used to locate overburden holes best suited to represent the lithologic variation and degree of weathering within the site. If research and exploration are done prior to drilling the OBA holes, it is less likely that there will be a need to drill additional OBA holes later during the permitting process.

Areal Sampling-A Survey of State Practices

Sames and others (in preparation) surveyed Appalachian coal states to determine rules-of-thumb for areal sample coverage. According to Sames and others (in preparation) “all the states interviewed, except Virginia, have some minimum spatial distribution requirements for overburden analysis that should be supplemented upon request from the reviewing professional(s).” Table 2.1a shows the minimum drill hole spacing requirements by state.

Table 2.1a: Minimum Overburden Analysis Drill Hole Spacing Requirements by State (Sames and others, in preparation)

State	Minimum Requirement	Comments
AL	Two drill holes on small permit properties (<10 acres). One drill hole per 160 acres, or one per property quarter on larger permits.	-
KY	Eastern KY: Drill holes should be distributed on a staggered, one-quarter mile grid pattern. Western KY: Drill holes should be distributed on a staggered, one-half mile grid pattern.	-
MD	One drill hole per site regardless of size	-
PA	Two drill holes per site regardless of size. However, a rule-of-thumb of 2 drill holes per site plus 1 drill hole per 100 acres is usually requested.	On average, most applications contain 1 overburden analysis hole for every 20 permit acres.
TN	One drill hole per 60 to 100 acres for permits to mine coal beds considered a high risk for AMD, based on past experience. One sample point per one-quarter mile in coal beds considered a low risk for AMD.	-
VA	-	In general, accepts any information submitted by the applicant, considers the quantity, quality, and consistency of the OBA for the permit area, and decides whether a reasonable characterization of the site is possible based on the spatial distribution provided.
WV	One drill hole in low cover and one in high cover. Otherwise, regulatory agency geologists to utilize Best Professional Judgement when determining the number of drill holes required for a permit.	In general, accepts any information submitted by the applicant, considers the quantity, quality, and consistency of the OBA for the permit area, and decides whether a reasonable characterization of the site is possible based on the spatial distribution provided.

Areal Sampling Experience: Pennsylvania

Pennsylvania has grappled with the issue of drill hole distribution since the advent of overburden sampling. A rule of thumb developed in Pennsylvania in the 1980s to determine a suggested minimum number of overburden holes was:

$$\frac{\text{Number of acres to be mined}}{\text{100 Acres}} + 2 = \text{Number of Overburden Holes}$$

If the first part of the equation resulted in a fraction, it was rounded to the closest whole number. For example:

$$\frac{\text{143 acres}}{\text{100 acres}} + 2 = \text{3 Overburden Holes}$$

$$\frac{\text{49.99 acres}}{\text{100 acres}} + 2 = \text{2 Overburden Holes}$$

$$\frac{\text{179 acres}}{\text{100 acres}} + 2 = \text{4 Overburden Holes}$$

This equation assumes that, for mines where OBA was requested, at least two holes are needed to determine whether the drilling was representative. This two-hole minimum is still in use. More recent data show that the actual sampling density for acid base accounting drill holes is greater than the “rule of thumb.” A recent survey of overburden hole coverage for 38 sites in Pennsylvania revealed that on average, there is one OBA hole for every 15.5 acres of coal removal (Table 2.1b).

Table 2.1b: Number of Acres per Overburden Analysis Hole (Brady and others, 1994)

n = 38	Coal Acreage	Acres per OBA Hole
Mean	43.5	15.5
Median	30.3	11.9
Minimum	5.0	2.3
Maximum	172.5	44.9
Std. Deviation	38.0	10.6

A similar survey of 31 Small Operator Assistance Program (SOAP) applications received in Pennsylvania during the 1993 calendar year revealed that on average, there was one hole for each 18.8 acres of coal removal (Table 2.1c).

Table 2.1c: Number of Acres per Overburden Analysis Hole Based on SOAP Applications Received in 1993 (Tarantino and Shaffer, 1998)

n = 31	Coal Acres	Acres per OBA Hole
Average	72.6	18.8
Median	55.0	15.7
Minimum	6.0	3.0
Maximum	220.0	53.5
Std. Deviation	54.6	12.3

The above tables give an idea of the range of overburden analysis sampling intensity used in Pennsylvania. The ranges in the data are due to a multitude of factors including stratigraphic complexity of the site, shape of the site, and availability of other prediction tools. Approximately 30 to 40 percent of applications in Pennsylvania do not require submittal of overburden analysis because of the availability of equivalent prediction data. The data included in these tables apply only to permit applications that included overburden analysis data.

Operational Considerations

The overburden analysis drilling program should accurately represent the overburden that will be encountered during mining operations. Therefore, the overburden holes should be located within the limits of the proposed mining area. Some holes should be located at maximum highwall conditions (maximum overburden cover to be mined), and the holes should represent all of the strata that will be encountered. Additional holes should be located under both low and average cover conditions to provide representative sampling of the overburden where stratigraphic units may be missing or the strata may have been chemically altered due to surface weathering.

Stratigraphic Variation

It is important to provide enough drill holes to adequately represent the site, including any spatial lithologic variation. One of the first references to the minimum overburden hole spacing is contained in the West Virginia Surface Mine Drainage Task Force’s “Suggested Guidelines for Surface Mining in Potentially Acid-Producing Areas” (1978), which recommended that all surface mining in potentially acid-producing areas be within approximately 3300 feet of a sampled overburden analysis hole or highwall.

Donaldson and Renton (1984) and Donaldson and Eble (1991) indicated that although drill cores spaced up to two miles apart in the Pittsburgh coal seam were adequate to reflect major thickness and sulfur trends for the coal seam, this spacing was not adequate for mine operation design. They felt that sampling at intervals on the order of 1200 to 1400 feet for the Pittsburgh coal and sampling at intervals of less than 500 feet for the Waynesburg coal would be necessary to determine small-scale sulfur content trends within the coal seams.

Representative Samples

Each OBA bore hole contains sample intervals representing various unit thicknesses of each lithologic unit encountered. Vertical sample interval thicknesses are typically three feet. The maximum thickness of each lithologic unit to be represented by one vertical sample interval will be discussed under “Compositing and Laboratory Preparation.” It is also discussed on pages 29 to 30 of Part 1 “Collection and Preparation of Sample” in the “Overburden Sampling and Testing Manual” (Noll and others, 1988).

Noll and others (1988) do not, however, discuss the complexity of ensuring that accurate, non-biased, representative samples are collected. They do stress that it is critical that 100 percent of the sample volume of each sample interval be included for compositing purposes, because of possible geochemical variations within the 3-foot interval. The ultimate sample size used in ABA is 1 gram for total percent sulfur and 2 grams for the neutralization potential (NP) test. Assuming no loss or contamination of the zone being sampled, only 1 gram to 2 grams are tested out of a 25,550 gram sample (based upon a 4.5 inch diameter drill bit and using an average rock density of 170 lbs/ft^3). Fortunately, sample preparation procedures have been developed to obtain representative, small sample aliquots. These procedures are discussed below in “Preparation of Samples.”

Extensive literature has been published, and a complete science has been developed to integrate geology and statistics for spatial sampling and the determination of optimal sampling patterns for estimating the mean value of spatially distributed geologic variables. Textbooks on the subject include Journel and Huijbregts (1981), Webster and Burgress (1984), J.C. Davis (1986) and Koch and Link (1970).

Fortunately, the geologic systems responsible for the deposition and alteration of 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. Although there are exceptions, most stratigraphic systems, especially those which produce calcareous material, operate over large areas with some degree of order, and deposit laterally pervasive units (Caruccio and others, 1980). Lateral continuity has also been observed in high-sulfur strata. Abrupt lateral changes in stratigraphy can occur such as where channel sandstones cut out and replace other strata. Surface weathering also causes 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, and adequate exploratory drilling is essential for a representative overburden sampling plan.

Sample collection and handling

Sample Collection

Overburden sampling is accomplished by drilling or direct collection of the sample from an open surface such as a highwall. Sample methods used to obtain overburden samples include air rotary (normal circulation), air rotary (reverse circulation), diamond core, augering, and highwall sampling.

Air rotary (normal circulation) - This type of drill is the method most commonly used for the collection of overburden samples in Pennsylvania. Drilling in this manner uses air to blow rock chips (cuttings) to the surface for collection. The most common disadvantage of normal circulation air rotary drilling is that 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. Rock chips traveling in this 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 allow any upper loose particles to blow out prior to continuing downward.

Contamination of the sample can also occur at the surface from 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 or first sample interval has 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 when sampling wet test holes where the ejected materials consist primarily of mud. Before drilling the overburden hole, the dust collector hood should be cleaned to remove any accumulated materials that may dislodge and contaminate the samples being collected.

<u>Air rotary (reverse circulation)</u> - This type of drill rig is less commonly used for the collection of overburden samples, primarily because of availability. A reverse circulation rig uses a double-walled drill stem. 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, offering a much cleaner and quicker means of obtaining overburden samples, without requiring that the drilling 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 can accumulate on the chips during drilling with air. This allows for much easier rock type identification and logging.

<u>Diamond core</u> - Diamond core barrels can be used on both types of rotary drilling platforms. Coring provides a continuous record of the lithology and provides more information than can be obtained through the collection of rock chips. Cores can provide a better overall view of the lithology by providing information necessary to judge rock color, gross mineralogy, grain size/texture, fossil content, and relative hardness. 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, coring is very time consuming and costly, especially if the entire overburden section is to be sampled. Diamond cores can be used as a secondary means of data collection to target previously identified problem zones, or as a primary sampling tool in the coal area (i.e. the interval 5 feet above and below the coal horizon). The entire sample interval from the core should be collected and processed for analysis to ensure representative sampling, as opposed to only collecting and analyzing a portion of the sample interval.

A problem that can occur with coring is "core loss." The problems of core loss can be reduced by regulating the drilling speed, (i.e., rotational speed of the bit, and down pressure), diameter and type of core bit, and amount of water; by minimizing the overbearing weight in the core barrel through emptying it prior to drilling the coal, and by keeping the equipment in good condition. Knowing what drilling adjustments to make can prevent blocking of the core barrel.

Successful coring is dependent primarily upon the experience of the on-site geologist, project engineer, or driller. Factors that are important include total years of core drilling experience, experience with the drill being used, and previous drilling experience in the same region, including exposure to the same rock formations and weathering characteristics. Having as much geologic data as possible (e.g. approximate depth to the coal, extent of weathering) prior to drilling is also particularly useful. It is especially useful to have air rotary pilot holes to evaluate the site prior to the core drilling. These pilot holes allow particularly troublesome formations to be identified and avoided. Particularly troublesome conditions include highly fractured rocks, joints or intersections of joints or fractures.

Mine voids, solution cavities, unconsolidated soil and rocks, and the transition through weathered rock into competent rock are the zones most subject to core loss. Core recovery on the order of only 50 to 60 percent or less in these situations is not unusual. When drilling is performed in unweathered rock core recovery approaching 100 percent is the norm rather than the exception.

When coring into the coal, it is advisable to use a core barrel long enough to core the entire thickness of the coal. The core barrel should be no more than 20 percent full when the coal is first encountered. It is preferable to have a nearly empty core barrel containing 6 to 12 inches of overburden before drilling into the coal. The small amount of overburden aids in determining if the entire coal section has been sampled (i.e., knowing the starting point of the coal) and helps protect the coal from being crushed by the "ram" when extracting the coal from the core barrel.

In addition to actual core sample loss, drilling data can be lost due to improper handling of the cores. Data loss causes include placing cores in the core boxes in the wrong order or upside down, or damage caused to the core during handling and shipping.

Augering - Auger drilling is not recommended for general overburden sampling. The materials lifted by the auger screw are in constant contact with the overlying stratum, thus providing for intermixing and contamination. Augering is typically used for unconsolidated or highly weathered sections.

Highwall sampling - Direct collection of samples from an open source, such as a highwall, can be used for overburden analysis, provided several caveats are understood. First, samples may be weathered to such a degree that the strata to be mined is not accurately represented. Second, there is limited availability and accessibility of highwalls. Care should be taken to collect only unweathered samples in close proximity to and representative of the proposed mining. It is recommended that open source (e.g. outcrop, highwall, etc.) samples be used primarily to supplement drilled overburden samples.

Sample Description (Log)

For each sample or composite of sample intervals collected, an accurate description of the gross lithology should be determined. This lithologic description should include the rock type (e.g. shale, sandstone, etc.), rock color (as determined by comparison with the Munsell Rock Color Chart), texture/grain size, moisture conditions, and relative degree of weathering. Where applicable, a description of the gross mineralogy should be included with particular emphasis on the presence of any calcite ($CaCO_3$), siderite ($FeCO_3$), or pyrite (FeS_2). In addition, fossils should be noted to provide insights into coal seam correlations and depositional environment interpretations. The sample description should include the relative degree of fizz (effervescence) when doused with a 10 percent solution of hydrochloric acid (HCl). A field fizz based on a scale of " none, slight, moderate, or strong" should be used. A dilute (10 percent) HCl solution is widely used by field geologists to differentiate calcium carbonate ($CaCO_3$) from other carbonate rocks. Fizz determinations are highly subjective and should be made by the same individual for every sample on every hole for a particular site. Extreme care should be exercised to be sure that the displacement of trapped air is not mistaken for CO_2 evolution. It is also important to identify whether the fizz is from the matrix or from the cementing material. It is recommended that logging of test holes, including sample descriptions, be performed by a qualified geologist**.**

Sample Preparation and Compositing

Proper sample preparation techniques are essential for maintaining sample integrity. Preparation is divided into steps that occur in the field and steps that occur in the laboratory. Field preparation of samples is discussed in Tarantino and Shaffer (1998), Noll and others (1988), and Sobek and others (1978). Procedures discussed in these publications include the use of proper containers, labeling, preservation, and field logs. Field sample preparation will not be discussed further in this section.

Sample compositing and laboratory preparation techniques are just as important to the integrity of a sample. The purpose of compositing overburden samples is to reduce the cost of overburden analysis by minimizing the volume and number of samples to be tested, without sacrificing the accuracy and precision needed to predict post-mining water quality. Sobek and others (1978), in the first generally accepted “manual” on overburden sampling, recommend that most rock types should not be combined into composites representing more than 3 feet. They suggest that sandstone can be composited into 5-ft increments. Experience in some regions, such as Pennsylvania, has indicated that it is often prudent to sample sandstone at the same resolution as other rock types (Tarantino and Shaffer, 1998). As with any well-intended cost-saving procedure, if not done properly, the real long-term costs might far outweigh the small cost saving.

Table 2.1d lists vertical sampling practices of Appalachian coal-producing states.

Table 2.1d: Overburden Interval Sampling Requirements (Sames and others, in preparation).

STATE	INTERVAL SAMPLING REQUIREMENTS
AL	One sample every 5 feet or at a significant lithologic change, whichever comes first. Sample compositing is not allowed. Regulatory agency reserves the right to request core drilling in permit areas where there are known acid-forming lithologic units.
KY	Same treatment required for samples from eastern and western region. One sample for suspected acid-producing strata and coal seams less than one foot thick; smaller strata and seams may be grouped with the next lower unit. One sample within the lithologic unit for strata one to five feet thick. Two samples for strata ranging from five to ten feet thick. One sample every 5 feet for strata more than ten feet thick.
MD	For rotary drill cuttings, one sample every 1 foot or at a significant lithologic change; for core samples, 3 foot composite samples or at a significant lithologic change.
PA	One sample per 3 vertical feet or at a lithologic change plus 1 foot above and below the coal bed. Rotary drill samples should be collected in 1-foot increments that then can be composited up to 3 feet. Core sample composites also limited to 3-foot increments regardless of the unit thickness; an equal portion of the entire core length should also be crushed and split for analysis.
TN	One sample every 3 feet or at a significant lithologic change, whichever comes first.
VA	Sobek and others (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 and others (1978) followed as the official guide. Permit geologists also refer to NPDES, DMR discharge data, and other historical data from adjacent operations in the same seam.

Some sandstones, such as portions with significant coal inclusions, may need to be sampled at a greater resolution. Till, when from separate glaciations, should be sampled separately. The reason for the 1-foot sample intervals above and below the coal (Pennsylvania) is that these are frequently the highest sulfur strata present. Mixing of these strata with overlying strata can result in dilution and a falsely low-percent sulfur, or make a thicker zone (e.g., 3 feet) resemble a high sulfur zone. The coal seam may also require greater sample resolution than the suggested 3-feet if a portion of the coal will be left in the pit as pit cleanings or unmarketable coal. The coal that remains behind should be sampled separately.

As can be seen from Table 2.1e, if too many 1 foot intervals are composited or too large a vertical sampling interval is chosen, a high total sulfur, potentially acid-producing zone can be masked by dilution with adjacent low sulfur strata. The net effect is an underestimation of the potential for a site to produce acid mine drainage. Compositing one foot of 2.34 percent sulfur black shale with an overlying four feet of low-sulfur sandstone results in a 0.48 percent total sulfur for the composited five-foot zone. If, for example, 0.5 percent sulfur is the "threshold" above which a unit is considered acid producing and thus targeted for special handling; this dilution effect would underestimate the acid-producing potential of the black shale and result in the strata not being specially handled.

Table 2.1e: Compositing of Too Many 1-foot Intervals Can Underestimate Acid Producing Potential (Tarantino and Schafer, 1998)

Thickness (feet)	Lithology	Total % S	Average % S of Interval			
1	sandstone	0.01				0.48
1	sandstone	0.01			0.59	
1	sandstone	0.01		0.79		
1	sandstone	0.01	1.18			
1	black shale	2.34				

Sobek and others (1978) suggested that for core samples, a 5-inch section of the core could be extracted from the middle of a 1 foot interval to represent the entire one-foot interval. The best way to ensure representativeness of an interval is to sample the entire interval. In order to avoid bias, one of the following two methods is recommended:

1) The entire core interval whether it be a 1, 2, or 3 foot interval, should be entirely crushed and reduced in size via a riffle or rotating sectorial splitter until a suitable amount of sample remains for analysis.

2) 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 entire other half of the core is crushed for the entire sampling interval. After crushing, the sample is divided and reduced in volume via a riffle or rotating sectorial splitter.

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 analyzed to evaluate percent sulfur and NP for acid base accounting.
3) To reduce samples to a small size fraction that maximizes surface area and minimizes the analytical time.

2.2 Alkaline Addition

It is widely recognized that mine sites with an abundance of naturally-occurring limestone or alkaline strata produce alkaline water, even in the presence of high sulfur. However, many sites contain little or no alkaline material and, as a consequence, often produce acidic drainage even when sulfur contents are relatively low. One approach to improving alkaline deficient sites is to import alkaline material to amend the spoil in order to obtain alkaline drainage.

Before implementing an alkaline addition BMP, the following factors should be considered: How much material should be added and how and where should it be applied to the backfill? When is additional alkaline material needed? What are the prospects of obtaining alkaline drainage for a given application rate and how much risk of acidic drainage is acceptable? Ultimately, whether or not alkaline addition is a feasible alternative is driven by the economics of the operation. Therefore, it is important that an alkaline addition project be carefully evaluated and designed before it is implemented. This section reviews theoretical and practical aspects of alkaline addition and summarizes the current state-of-the-art in the use of alkaline addition to prevent acid mine drainage.

Theory

AMD is formed when pyrite and other iron disulfide minerals present in coal and overburden are exposed to oxygen and water by mining. The oxidation of pyrite releases dissolved iron, hydrogen ions (acidity), and sulfate (Equation 1). Although this process occurs very slowly in undisturbed natural conditions, it can be greatly accelerated by both surface and underground mining.

Pyrite oxidation is further accelerated by the iron-oxidizing bacterium *Thiobacillus ferrooxidans,* which thrives in a low-pH environment and oxidizes ferrous iron to ferric iron (Kleinmann and others, 1980). Under low pH conditions, ferric iron remains in solution and can directly oxidize pyrite. Thus, once AMD formation gets started, the reaction is further accelerated by bacteria and the production of ferric iron. The result can be severe acid mine drainage.

Acidity produced by acid mine drainage can be neutralized in the presence of sufficient carbonate minerals. This reaction is shown by Equation 6, for which it is assumed that CO_2 will be produced and will exsolve from solution. Using this equation, it takes 31.25 tons of $CaCO_3$ to neutralize 1000 tons of material with 1 percent sulfur. This is the traditional method used for acid-base accounting calculations. The main shortcoming of this equation is that there is no "alkalinity" (bicarbonate or HCO_3^-) produced. Under normal conditions, not all CO_2 escapes to the atmosphere. Some CO_2 dissolves in water producing acidity. If the reaction product is HCO_3^- alkalinity (Equation 5), twice as much carbonate will be required to neutralize the same amount of material (Cravotta and others, 1990). Whether it is the process in Equation 5 or Equation 6 that is dominant depends on the extent of how open or closed the mine is to the atmosphere.

Where neutralization occurs, the pH can remain near-neutral, inhibiting bacterial catalysis of iron oxidation and keeping ferric iron relatively insoluble. Thus, the quality of drainage produced by a given mine is largely dependent not only on the presence or absence of pyritic sulfur, but also on the availability of calcium carbonate or other neutralizing agents in the coal and overburden.

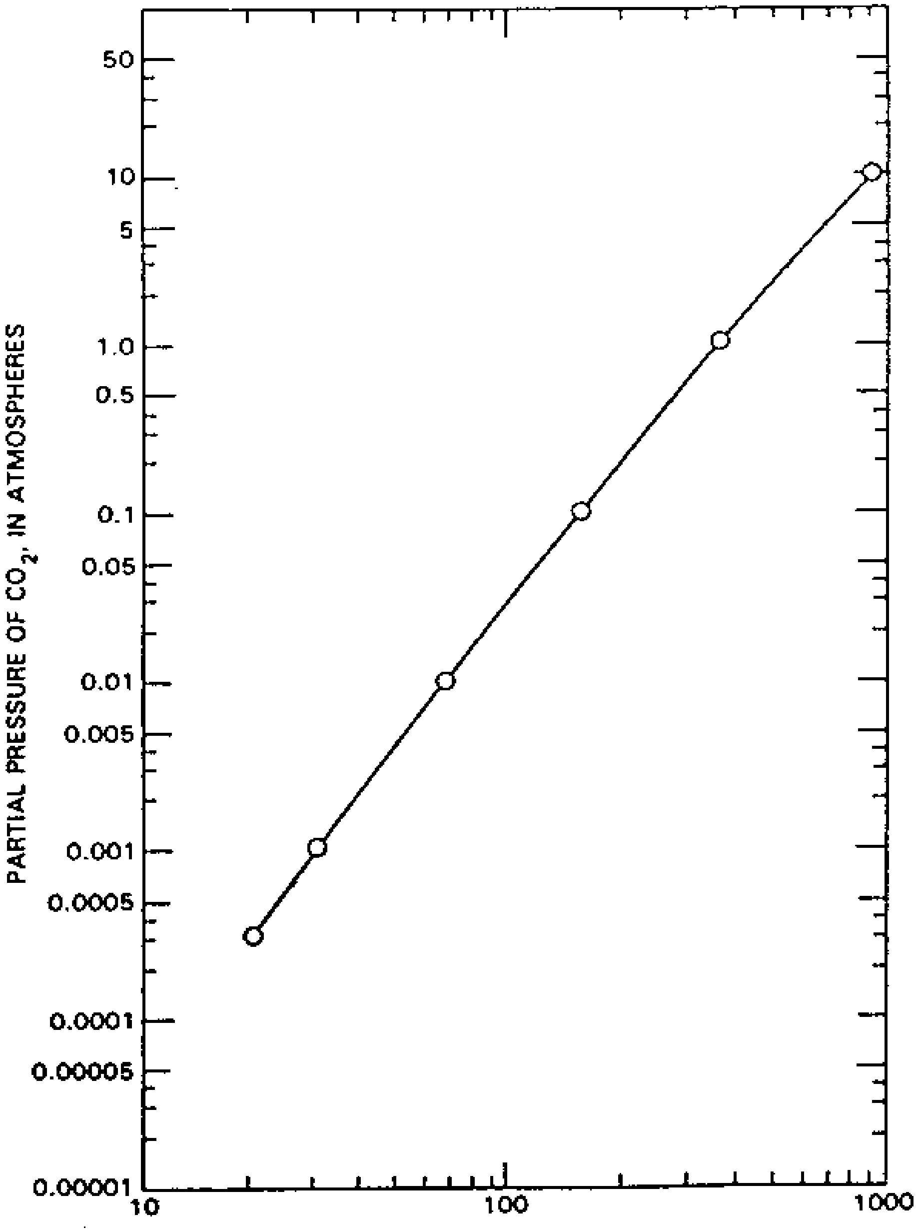
Brady and others (1994) and diPretoro and Rauch (1988) found a strong relationship between the neutralization potential of surface coal mine overburden and the alkalinity or neutrality of post-mining drainage. Sites with more than 3 percent naturally occurring carbonates produced alkaline drainage. Sites with less than 1 percent carbonate generally produced acidic drainage. Perry and Brady (1995) attribute this effect not only to neutralization but also to near-neutral conditions limiting bacterial catalysis of ferrous iron oxidation and oxidation of pyrite by ferric iron.

NP was found to be a much better predictor of whether a mine would produce alkaline or acidic water than was the maximum potential acidity, calculated from the overburden sulfur content, thus demonstrating the importance of carbonates on mine drainage quality (diPretoro, 1986; Brady and Hornberger, 1990; Brady and others, 1994; Perry and Brady 1995). For mines which are naturally deficient in carbonates, and therefore likely producers of acidic drainage, the implication is obvious. If sufficient alkaline material is imported from off-site to make up the deficiency in NP, the site will produce alkaline rather than acidic drainage.

The solubility of calcium carbonate also plays an important role in whether a site can generate sufficient neutralization to prevent acidic drainage. Calcite ($CaCO_3$) solubility is dependent on the partial pressure of CO_2 (Figure 2.2a). At atmospheric conditions, the solubility of calcite is limited to approximately 20 mg/L Ca (50 mg/L as $CaCO_3$ or 61 mg/L as HCO_3^- alkalinity) assuming a CO_2 content of the pore gases of only 0.03 percent. At 20 percent CO_2 content, which has been measured in some backfill environments (Cravotta and others, 1994a), calcite solubility exceeds 200 mg/L Ca (500 mg/L as $CaCO_3$ or 610 mg/L as HCO_3^- alkalinity). Guo and Cravotta (1996) note that CO_2 partial pressures vary from mine site to mine site depending on rock type and backfill configuration. Shallow backfills on steep slopes with blocky overburden and thin soil cover, for example, tend to "breathe," thereby reducing CO_2 partial pressures (Pco_2). Deeply buried backfills or sites with restricted airflow or thick soil covers would tend to have higher CO_2 levels, enhancing calcite dissolution. At these sites, Pco_2 tends to increase with depth. The Pco_2 has implications for the placement of alkaline materials within the backfill. Near-surface placement of alkaline material, where CO_2 partial pressures approach atmospheric conditions, may not be as desirable as distribution deeper within the backfill.

In theory, almost any acid-prone site could be transformed into an alkaline site, if enough carbonate material is imported. For this to be achieved, however, it is necessary to determine: (1) how much alkaline material should be applied to ensure a successful result; and (2) the optimum place within the backfill where the alkaline material should be applied.

Figure 2.2a: **Solubility of Calcium Carbonate (Calcite) in Water at 25°C as a Function of Partial Pressure of CO_2 (Hem, 1985)**



2.2.1 Implementation Guidelines

Fifteen years of research has shown that alkaline addition can improve water quality and prevent AMD production, but that failures are common, especially where alkaline addition rates are too low. Based on these studies, any alkaline addition project should consider:

- how much and what type of alkaline material should be applied,
- how should the alkaline material should be emplaced in the backfill, and
- when is alkaline addition appropriate?

Seventeen of sixty-one mining site data packages submitted by Appalachian coal mining states (Appendix A, EPA Remining Database, 1999) had alkaline addition listed as a BMP. Alkaline addition, like any other BMP, is seldom used alone. Table 2.2.1a lists additional significant BMPs that were used in conjunction with alkaline addition at these sites. In a Pennsylvania study of closed remining sites (Appendix B, PA Remining Site Study), alkaline addition was always used in conjunction with some other BMP. Other BMPs included daylighting of deep mines, special handling of acidic materials, surface regrading, ground-water handling, and surface revegetation.

Table 2.2.1a: Distribution, Type and Amount of Alkaline Materials Used (Appendix A, EPA Remining Database, 1999)

Mine, Type	Placement	Type of Alkaline Material	Other Major BMPs
PA(1) ^{S}	30 tons/acre applied to pit floor	Crushed limestone (>95% $CaCO_3$)	Daylighting
PA(2) ^{R*}	Alternate refuse & coal ash. 1,650,000 tons of reject refuse, 1,350,000 tons ash	Power plant coal ash. 5.8% $CaCO_3$	Removal of Acid-Forming materials, Revegetation
PA(7) ^{S}	10ft thick layer in backfill. Compacted/set as cement. Above post-mining water table	Coal ash	Daylighting, Regrading Revegetation, Special Handling
PA(8) ^{S*}	360 tons/acre applied to pit floor. 240 tons/acre in blast holes; dispersed throughout spoil	Limestone Screenings	Daylighting Special Handling
PA(10) ^{S}	Ripping of calcareous pit floor material	Pit floor rock is 15 to 20% $CaCO_3$	Bactericide, Special Handling Regrading
PA(11) ^{S*}	50 tons/acre applied to pit floor	Agricultural Lime	Regrading, Revegetation
PA(12) ^{S*}	Within spoil. Compacted to 90% maximum dry density	Coal Ash	Daylighting, Regrading, Revegetation
PA(14) ^{A*}	In abandoned strip pit. 5 million yds^3 compacted to min. 90% dry density	Coal Ash	Revegetation
PA(18) ^{A*}		Coal Ash, pH 11	Daylighting, Regrading, Revegetation
PA(19) ^{S*}	100 tons/acre applied to surface and pit floor. Approx. 800 tons/acre in spoil	Lime processing flue dust	Regrading Revegetation
TN(3) ^{S}		Limestone	
TN(4) ^{S*}	“Spoil side” of dragline bench	Limestone	Special Handling, Chimney Drains, Regrading, Backfill Innundation
WV(3) ^{S*}	2 ft lifts through overburden	Coal Ash	
WV(5) ^{S*}	2 ft applied to surface. Mixed through overburden	Coal Ash	Anoxic Limestone Drains
WV(6) ^{S*}	12 to 18 inches applied to pit floor. 2 ft applied to surface	Coal Ash, pH 10.5 to 12	
WV(8) ^{S*}	Min. 1 ft thick, 30 ft wide channel		Regrading
AL(10) ^{S}	20 tons/acre applied to pit floor		Regrading

* Mine is still active ^{S} Surface
^{A} Anthracite ^{R} Refuse Reprocessing

Alkaline Materials

A variety of alkaline materials are available as alkaline additives. Traditionally alkaline addition projects use crushed limestone or limestone-based waste products. Limestone-based waste products include crusher waste, kiln dust, partially burnt lime and "off-spec" lime products. More recently alkaline waste products from other sources have been considered. Chief among these is fluidized-bed combustion fly ash and bottom ash. An examination of Table 2.2.1b shows the range of products being used and the current trend in using coal combustion ash.

Table 2.2.1b: Example Analyses of Coal Ash. (Units are percentages) (Scheetz and others, 1997)

Oxide	**Coal Ash with < 10% CaO** [a]	**Coal Ash with > 20% CaO** [b]	**High BTU Coal** [c]	**Anthracite Culm** [c]	**Bituminous Refuse** [c]
SiO_2	52.5 ± 9.6	36.9 ± 4.7	24	58	34
Al_2O_3	22.8 ± 5.4	17.6 ± 2.7	6.05	20.4	2.15
Fe_2O_3	7.5 ± 4.3	6.2 ± 1.1	2.05	5.74	5.98
CaO	4.9 ± 2.9	25.2 ± 2.8	42	4.11	30
MgO	1.3 ± 0.7	5.1 ± 1.0	0.045	0.62	0.62
Na_2O	1.0 ± 1.0	1.7 ± 1.2	0.07	0.59	0.11
K_2O	1.3 ± 0.8	0.6 ± 0.6	0.51	2.56	1.49
SO_3	0.6 ± 0.5	2.9 ± 1.8	20.8	1.1	13.0
Moisture	0.11± 0.14	0.06 ± 0.06	+ 0.25	+ 0.49	3.70
LOI	2.6 ± 2.4	0.33 ± 0.35	2.03	3.31	10.0

[a] Characteristics of eastern bituminous and anthracite coal

[b] Characteristics of western lignitic and sub-bituminous coals

[c] Ash resulting from burning coal, culm and refuse with limestone

LOI = Loss on ignition

Limestone and Limestone-Based Products

The chemical principles of neutralization by limestone are presented above in the section "Theory of Alkaline Addition" and the neutralization reactions are shown in Equations 5 and 6. Limestone, which is composed mainly of the mineral calcite ($CaCO_3$), occurs naturally on many mine sites. An advantage of limestone is that it dissolves more slowly than quick lime or hydrated lime, thus lasting longer. A disadvantage is that its solubility is limited, such that alkalinity higher than ~400 mg/L as $CaCO_3$ is rarely achieved. At atmospheric pressures of CO_2, calcite will produce an alkalinity of <100 mg/L $CaCO_3$ (Hornberger and Brady, 1998). Another mineral that has neutralizing properties and occurs naturally in coal overburden is dolomite [$CaMg(CO_3)_2$]. Neutralization by dolomite is similar to that shown in Equations 5 and 6, but the reaction rate in slower than limestone.

"Quick lime" (calcium oxide, CaO) and "hydrated lime" [calcium hydroxide, $Ca(OH)_2$] are produced by heating limestone and driving off CO_2. These are more soluble than calcite and can produce a pH as high as 11 or 12. The advantage of quick lime or hydrated lime is its high solubility and ability to generate high pH. The disadvantage is that because of its high solubility it may be consumed quickly. The neutralization processes are represented by Equations 6 and 7 (Cravotta and others, 1990).

$$Ca(OH)_2 + 2\ H^+ \rightarrow Ca^{2+} + 2H_2O \qquad \text{(Equation 9)}$$

$$CaO + 2\ H^+ \rightarrow Ca^{2+} + H_2O \qquad \text{(Equation 10)}$$

The neutralization of acid generated from pyrite oxidation by hydrated lime is represented by Equation 11 (Cravotta and others, 1990):

$$FeS_2 + 2\ Ca(OH)_2 + 3.75\ O_2 \rightarrow Fe(OH)_3 + 2\ SO_4^{2-} + 2\ Ca^{2+} + 0.5\ H_2O \qquad \text{(Equation 11)}$$

The purity of limestone or other alkaline additives is an important factor. Many rocks with the potential to generate alkaline water are not limestones, but calcareous shales or other rock. If a rock that is not nearly pure calcite is used, alkaline addition rates should be adjusted to compensate for the lack of purity. For example, if the material that is proposed for alkaline addition has a NP of 500 tons $CaCO_3$/1000 tons of material (50 percent purity), twice as much material would be required to provide the necessary amount of $CaCO_3$. Regardless of the alkaline material to be used, the application rate should be adjusted to reflect the material's neutralization potential as calcium carbonate equivalent.

Coal Ash

Coal ash has been used in a variety of ways for abatement of mine drainage pollution, including the following:

- injection into underground mines with the intention of abating acid mine drainage by sealing (Aljoe, 1999; Canty and Everett, 1999; and Rafalko and Petzrick, 1999),
- as an additive to help create a suitable soil substitute out of acidic spoil (Stehouwer and others, 1999),
- as an impermeable cap for reduction of infiltration into acidic surface mine spoil (Hellier, 1998). Ash has been mixed with reprocessed coal refuse for AMD abatement (Foster Wheeler Corp., 1998; Panther Creek Energy Facility, n.d.),
- as a grout to isolate acidic material in surface mine spoil (Schueck and others, 1994),
- as fill material for abandoned surface mines and anthracite region "crop falls" (Scheetz and others, 1997), and
- as an alkaline additive to neutralize acidic mine spoil.

The use of coal ash as an alkaline additive will be discussed in this section. The use of ash for low-permeability caps and seals is discussed in Section 1.1 and its use for grout curtains is discussed in Section 1.2.

The popularity of using coal ash as an alkaline additive is demonstrated by the fact that it is being practiced by eight of the 17 mines listed in Table 2.2.1a. The alkalinity generating properties of coal ash vary depending on the type of power plant producing the ash. Most alkaline ashes are generated by fluidized bed combustion (FBC) power plants. These plants burn high-sulfur coal or coal reject material as fuel. Limestone is used to absorb the sulfur. The limestone calcines leaving calcium oxide. According to Skousen and others (1997), about one-half of the CaO reacts with sulfur dioxide to form gypsum and the rest remains unreacted. The ash can be 10 to 20 percent calcium carbonate equivalent. The amount of limestone used can be substantial. For example, the Colver, Pennsylvania, power plant burns 600,000 tons of "gob" (coal refuse) annually, requiring 120,000 tons of limestone to remove the sulfur (Foster Wheeler Corp., 1998). Table 2.2.1b shows the neutralizing properties of various coal ashes. As can be seen, not all coal ash is alkaline. In fact, some ash has to have alkaline material added for proper disposal.

A problem that exists with using coal ash as an alkaline additive is that it can exhibit cementitious behavior. The cementitious behavior is activated by alkali materials. The making of cement from ash (volcanic ash) dates back to the time of the Romans. Many of these structures are still standing today (Scheetz and others, 1993) which is testimony to its durability. Cementitious behavior is an advantage if one is proposing ash as a grout or an impermeable cap. Scheetz and others (1993) list the following "advantages" for the use of coal ash for cementitious material:

- low cost of raw materials
- grouts can be formulated to gain strength rapidly
- grouts have low heats of hydration
- grouts are less soluble than portland cement-based materials
- grouts can be less permeable than portland cement-based materials
- grouts can be activated with alkali chlorides and sulfates.

Many of these same properties that are advantageous for impermeable grouts and caps are a disadvantage for its use as an alkaline additive. For example, low solubility and low permeability are not properties that are desirable for an alkaline additive. Pulverized coal combustion fly ash exhibits a pozzolonic reactivity "that is directly correlated to the calcium content of the ash" (Scheetz and others, 1997). In other words, the lime portion of the ash is an activator that can make the ash into cement.

Coal combustion ash, if it is to be used as an alkaline additive, should be evaluated for its calcium carbonate equivalency and its cementitious properties. It should be spread and mixed with spoil so as to maximize its surface area. If not adequately mixed, the ash may set up as large blocks of cement with minimal surface area for reactivity, thus resulting in an ineffective alkaline additive.

Coal ash, even with pozzolanic properties, has potential as an effective "seal" on acidic pit floors. This application would also provide an alkaline substrate for spoil waters.

Other Alkaline Additives

Information on other alkaline sources is scarce. Skousen and others (1997) briefly discusses the use of steel slags and states that these slags often have NPs from 45 to 90 percent, but warns that slags "are produced by a number of processes so care is needed to ensure candidate slags will not leach metal ions such as Cr, Mn, Ni, or Pb." Phosphate rock has been proposed for use as an alkaline additive, but no full-scale field projects have been commenced and the cost is high (Skousen and others, 1997). Phosphate rock can contain significant quantities of calcium carbonate. Thus it may be difficult to determine the relative effectiveness of the phosphate relative to the carbonate. Other alkaline additives or alkaline-producing additives mentioned by Skousen and others (1997) are AMD sludge and organic wastes. AMD sludge is the waste product from mine drainage treatment. Lime-treated flocs can contain up to 50 percent unreacted lime. Field results are limited. Organic waste is different from the other alkaline generating processes in that it does not directly impart alkalinity. Several species of bacteria can obtain metabolic energy by reacting sulfate with simple organic compounds. In the process sulfate is reduced and bicarbonate is created (i.e., alkalinity). Stalker, Rose and Michaud (1996) performed laboratory studies on a variety of organic materials. The rates of sulfate reduction for cellulose materials (sawdust, pulped newspaper & mushroom compost) were slow, but for milk products (cheese whey and lactate) the rates were more rapid.

Application Rates

Published studies on alkaline addition primarily examine mines in the northern Appalachian. The transferability of this research to the southern Appalachians is not fully known. The overburden in the southern Appalachians is typically lower in sulfur than overburden in the northern Appalachians. Field studies of alkaline addition in the northern Appalachians appear to be converging on required application rates. The amount needed to produce alkaline drainage is approximately 1.5 to 3 percent $CaCO_3$ equivalent for sites with low to moderate pyrite content. This application rate appears deceptively low. One percent $CaCO_3$ equates to approximately 37 tons of $CaCO_3$ for each acre-foot of overburden. A 100-acre surface mine with an average overburden thickness of 50 feet needing 1 percent additional $CaCO_3$ would require 183,500 tons of added alkaline material or 1,835 tons/acre. Thus, the feasibility of an alkaline addition project usually becomes a matter of economics as well as science. The challenge is to determine the minimum alkaline addition rate which will still be effective in preventing acidic drainage.

Using data from Brady and others (1994) and Perry and Brady (1995), Tables 2.2.1c - 2.2.1f show overall NP and NNP requirements in order to produce alkaline drainage using acid-base accounting data. In all cases, NP and NNP calculations are made using the method described by Smith and Brady (1990). Total weights of overburden, NP, and MPA are determined for each drill hole interval, based on an approximation of the areal extent of that interval and unit weights for overburden materials. The total weights of the coal intervals are multiplied by a pit loss factor of 0.1, assuming approximately 10 percent of the coal will be lost in the pit and not removed. A higher or lower pit loss factor can be used if warranted by site-specific conditions. The uppermost 0.5 feet of strata underlying the bottom coal seam is also included in the calculation. These quantities are summed to determine the total tonnage of overburden, NP, MPA and to represent the overall NP, MPA and NNP in parts per thousand as $CaCO_3$ for the site.

Multiple overburden holes are combined by considering an area of influence of each hole using the Theissen polygon method (Smith and Brady, 1990).

Table 2.2.1c: Percentage of Sites Producing Net Alkaline Drainage by Net NP without Thresholds

Net NP (ppt $CaCO_3$)	Number of Sites (n)	% with Net Alkaline Drainage
< -10	1	0.0
-10 to 0	11	18.2
0 to 12	17	58.8
>12	10	100.0

Table 2.2.1d: Percentage of Sites Producing Net Alkaline Drainage by Total NP without Thresholds

Total NP (ppt $CaCO_3$)	Number of Sites (n)	% with Net Alkaline Drainage
<5	3	0.0
5 to 10	9	33.3
10 to 18	10	50.0
18 to 22	7	71.4
>22	10	100.0

Table 2.2.1e: Percentage of Sites Producing Net Alkaline Drainage by Net NP with Thresholds

Net NP (ppt $CaCO_3$)	Number of Sites (n)	% with Net Alkaline Drainage
< -2	14	28.6
-2 to 6	14	57.1
>6	11	100.0

Table 2.2.1f: Percentage of Sites Producing Net Alkaline Drainage by Total NP with Thresholds

Total NP (ppt $CaCO_3$)	Number of Sites (n)	% with Net Alkaline Drainage
<2	12	16.7
2 to 9	12	50.0
>9	15	100.0

When all acid base accounting data are considered (i.e., there are no significance thresholds), an overall NNP greater than 12 ppt $CaCO_3$ or a NP greater than 22 ppt $CaCO_3$ is very likely to assure alkaline drainage. Based on these data, a conservative approach to determining alkaline addition rates would require application of alkaline material at a rate equal to the difference between an overall NNP of 12 ppt $CaCO_3$ or a NP of 22 ppt $CaCO_3$ and the actual premining overall NP or NNP. A site having a NNP of 2 ppt $CaCO_3$, for example, would require the application of an additional 1 percent $CaCO_3$ (10 ppt). An example calculation is shown below:

Tons of overburden: 1,000,000 tons
Acres of mining: 20 acres
Average Net NP: 2 ppt $CaCO_3$
Deficiency: (12 - 2) ppt $CaCO_3$ = 10 ppt $CaCO_3$ = 1%

Tons additional NP required for Net NP of 12: 1% X 1,000,000 tons overburden = 10,000 tons
Tons per acre required: 10,000 tons / 20 acres = 500 ton/acre
Adjusted for alkaline material with 80% $CaCO_3$ equivalent: 500 tons/acre / 80% = 625 ton/acre

Similarly, where significance thresholds are used to analyze ABA data, a "safe" alkaline addition rate would bring the overall NP value above 9 ppt $CaCO_3$ or the NNP above 6 ppt $CaCO_3$.

Traditionally, the Commonwealth of Pennsylvania has required most alkaline addition sites to produce an overall NNP of 0 ppt $CaCO_3$ with thresholds. The success rate for sites with this application rate is risky at best with only 59 percent of sites in this class producing alkaline drainage (Smith and Brady, 1990). To a great extent, the selection of the appropriate alkaline addition rate is determined by the risk of failure that can be tolerated, as well as by the availability and cost of alkaline additives.

As more data are compiled, the ability to accurately determine minimum alkaline addition rates needed to obtain alkaline drainage should improve. Also, based on the limited experience to date, most alkaline addition projects using more than 500 tons/acre as $CaCO_3$ have been successful. Except for sites with very low sulfur, alkaline addition rates less than 500 tons/acre have consistently failed to produce alkaline drainage. This is based on a small population of alkaline addition sites (~5), none of which contained the worst possible overburden. It would be premature to conclude that alkaline addition of more than 500 ton/acre will ensure success on all sites or that lower addition rates guarantee failure.

Materials Handling and Placement

Most successful alkaline addition sites have employed thorough mixing of alkaline material throughout the backfill. This can be done using various methods. One innovative and effective approach is to use the alkaline material as blast hole stemming (Smith and Dodge, 1995). Depending on the material being used and how well it packs, it may also result in more effectively directing the blast energy at breaking overburden. Alternately, alkaline material can be placed on the surface of the overburden where it will be subsequently redistributed following excavation and placement.

Another method of alkaline addition is to place the material on the surface of regraded spoil and disk it into the upper portion of the spoil. This approach usually is used either in combination with mixing in the backfill or as a remedial measure after the site has already been backfilled. Although it was originally thought that this method would take advantage of the added alkalinity in the most active zone of AMD production and create an alkaline environment, inhibiting AMD formation, most projects employing only surface application have not been successful. There are at least three possible explanations: (1) Dissolution of $CaCO_3$ and the production of alkalinity at near surface conditions is limited by the partial pressure of CO_2. Typically, the maximum alkalinity which can be achieved under thin soil cover is approximately 75 to 150 mg/L, (Rose and Cravotta, 1998). This greatly limits the effectiveness of near-surface alkaline material and usually does not produce enough alkalinity to neutralize acidity generated elsewhere in the backfill; (2) Mine spoils do not transmit water as a uniform wetting front (Caruccio and Geidel, 1989). Rather, surface waters tend to preferentially infiltrate the spoils at the most conductive areas, effectively bypassing much of the near-surface alkaline material; and (3) Contact of limestone with acid-producing materials is very limited in the surface environment.

The earliest alkaline addition projects involved spreading all of the alkaline material on the pit floor, prior to backfilling. The assumption was that this portion of backfill was the most likely to be saturated, allowing the alkaline material to neutralize all of the acidity produced. These sites tended to produce alkaline drainage initially, which soon changed to acidic drainage. This is presumably because the pit floor environment was not anoxic and the alkaline material became ineffective due to armoring with ferric hydroxide precipitate. Alkaline addition to the pit floor still has utility, however, when there is a need to neutralize a high-sulfur pit floor. If the pit floor is saturated, and iron remains ferrous, calcite on the pit floor should function as an anoxic drain neutralizing acidity. Putting most of the material on the pit floor fails to take advantage of the inhibitory effect of maintaining a near-neutral pH within the spoil environment. There probably is little utility in application rates of more than 100 tons/acre to the pit floor, although at least 20 tons/acre should be applied to provide complete coverage. Again, the key appears to be getting the alkaline material mixed throughout the spoil, especially throughout the more pyritic material.

Alkaline addition is frequently implemented in conjunction with special handling of high-sulfur zones, where high sulfur material is placed in pods and isolated from percolating ground water. Alkaline material can be mixed with the high-sulfur material to prevent AMD formation within the pod and can be placed in conjunction with a cap to enhance hydraulic isolation and to help maintain an alkaline environment near the pod. Observations at the Kauffman project suggest that lime kiln dust may actually cement the material, inhibiting ground-water flow (Rose and others, 1995).

The use of alkaline addition as part of special materials handling has not yet been fully evaluated although some demonstration projects are underway. Recommended procedures for handling imported alkaline materials have undergone continuous modification as more is learned about AMD prevention and the interaction between acid-forming materials and neutralizing agents. Currently, the recommended procedure is to first ensure that enough alkaline material is thoroughly mixed within the backfill. In addition, smaller amounts of imported alkaline material should be applied to the surface of the regraded backfill. Applications to the pit floor should be limited to conditions requiring isolation or neutralization of a high-sulfur pavement, and to no more than is needed to provide sufficient coverage. Unless the remaining spoil is clearly alkaline, sufficient alkaline material also should be retained for distribution throughout the backfill.

Alkaline Redistribution

A practice similar to alkaline addition is the redistribution of alkaline materials to alkaline-deficient areas from areas of the same or adjacent mine sites which have more than ample alkaline strata. This procedure is practical where sufficient quantities of alkaline material are present, but distribution is so uneven that some portions of the backfill do not contain enough neutralizers to prevent or neutralize AMD. Alkaline redistribution then becomes largely an exercise in materials handling. Alkaline stratigraphic units should be clearly identified, segregated, transported to the alkaline-deficient area, and incorporated into the backfill. Depending on the quantity and characteristics of the alkaline material available, it may also be necessary to crush the material prior to redistribution. The obvious advantage to redistribution, if it can be done, is the ready availability of the material and the low or zero cost of transportation.

Michaud (1995) developed a mining plan for a proposed surface mine where alkaline redistribution was fully integrated into the operation, minimizing the need for stockpiling and rehandling of alkaline overburden. Through the implementation of a complex series of selective sequencing of cuts and multiple benches, the handling plan provided for redistribution of alkaline strata, which existed only in limited areas and stratigraphic intervals throughout the site.

Through this approach, thorough mixing of alkaline material could be achieved while avoiding the need to identify, segregate, and redistribute specific geologic units, usually the most difficult part of a spoil redistribution plan.

Alkaline redistribution has been successfully employed on several surface mining sites that are currently producing alkaline drainage. The Bridgeview "Morrison" site in Township, Fayette County, PA, had abundant calcareous rock over most of the site with NPs as high as 700 ppt $CaCO_3$, but more typically in the 100 to 300 ppt $CaCO_3$ range. The site included two areas of about 5 acres each, containing shallow overburden and lacking calcareous rock due to erosion and weathering. Alkaline material from the high cover area was transported to these low cover areas. The resulting post-mining water quality from the areas was alkaline.

The Amerikohl "Schott" site in Westmoreland County, Pennsylvania, had calcareous rock on only about 8 acres of the 38 acre site. Originally four acid-base accounting holes were drilled. These were supplemented by additional holes drilled to determine the lateral distribution of the calcareous rock. The calcareous rock was removed during mining operations and incorporated into the spoil on all portions of the mine. Waste limestone was also placed on the pit floor at the rate of 100 tons/acre. Four years of post-mining water quality monitoring data shows the water to be net alkaline with alkalinity ranging from 10 ppt to 138 ppt $CaCO_3$.

Alkaline Addition as a Best Management Practice on Shallow Overburden

In many cases, relatively low (less than 300 ton/acre) alkaline addition rates have been employed on mine sites that indicated a relatively minor potential to produce acid mine drainage, but were lacking in significant calcareous strata. Although these sites commonly have low sulfur contents, they frequently produce mildly acidic drainage due the lack of any significant NP. In other cases, alkaline addition was used as an added safety factor to assure alkaline drainage. Alkaline addition has proven to be an effective "best management practice" for these types of sites.

Often, mine sites with shallow (less than 40 feet) overburden have had calcareous minerals and pyrite leached out by weathering (Brady and others, 1988). Since easily weatherable minerals have been removed, water flowing through the overburden material picks up very little dissolved solids and emerges essentially with the characteristics of rain water. In Pennsylvania, precipitation typically has a pH less than 6.0. Thus, post-mining water from weathered overburden may also have a pH of 6.0 or less. The addition of alkaline material is needed to ensure alkaline post-mining drainage. An example of this implementation is described in Case Study 1, Section 2.2.3.

2.2.2 Verification of Success or Failure

A critical step in successful alkaline addition is to ensure that the alkaline addition plan is properly implemented. Both the amount of material to be applied and its distribution throughout the site should be appropriate. Because of the large quantities of materials involved, careful record keeping of each shipment of alkaline material and calculation of the quantities of material distributed is required. Depending on the method of mining, quantities of alkaline material to be applied or distributed should be tabulated for each individual cut or phase of the operation.
It is necessary also to periodically retest the neutralization potential of the alkaline material being used, with a frequency determined by the variability of the material.

Inspections by the regulatory agency of sites with alkaline addition as a BMP should be frequent and detailed enough to document compliance with the mining plan. An inspection checklist identifying key aspects of the plan will be useful in many cases.

Implementation Checklist

Recommended items to be considered during the permit review process include:

- Site-specific overburden data should be available for determination of the amount of alkaline material.

- The site-specific overburden data should be representative of the mine overburden. This will typically require multiple holes and appropriate vertical sampling.
- Plans should be clearly designed with appropriate maps, cross-sections and narrative.
- The plan should be feasible in the field, not just on paper.
- The plan should be enforceable.

Recommended items to consider in an alkaline addition implementation inspection checklist include:

- Does what is being done in the field correspond with the plan that is specified in the permit plans, as shown on maps, cross-sections, and in the narrative?
- Is the appropriate equipment available?
- Is the alkaline material being placed where specified?
- Is the alkaline material being brought to the site the material that was specified in the permit plan?
- Are weigh slips or other records available to verify the amount of materials being imported? Are they up to date? Do these records match what can be observed on the site, in terms of material stored and applied?
- Is water-monitoring data being submitted?

2.2.3 Literature Review and Case Studies

There has been an extensive body of literature published on alkaline addition. This literature is discussed below along with selected case studies. An early published report regarding the use of imported alkaline material as a method of preventing the formation of acidic drainage was in the West Virginia Surface Mine Drainage Task Force's *Suggested Guidelines for Method of Operation in Surface Mining of Areas With Potentially Acid-Producing Materials* (1979). The Guidelines recommend that alkaline material be added to the backfill at the rate of one third of any net deficiency in neutralization potential as determined by acid-base accounting. However, it is uncertain as to why this rate was selected. Many sites with alkaline application rates based on this recommendation have subsequently failed and are producing acidic drainage.

Waddell and others (1986) used alkaline addition to abate acidic drainage resulting from the construction of Interstate 80 in north central Pennsylvania. The Waddell study involved surface application of limestone crusher waste and lime flue dust at the rate of 267 tons/acre. It improved pH values from 3.9 to 4.4. Sulfate concentrations were also reduced, indicating that the alkaline addition not only neutralized AMD, but slowed its production.

Geidel and Caruccio (1984) examined the selective placement of high-sulfur material in combination with the application of limestone to a pit floor at the rate of 39 tons/acre. Although the treated site initially produced alkaline drainage, the drainage soon became acidic. An untreated control site produced acidic drainage throughout the same period.

Attempting to abate acidic drainage from a Clarion County, Pennsylvania mine site, Lusardi and Erickson (1985) applied high-calcium crushed limestone at the rate of 120 tons/acre. Although NNP deficiencies at the site ranged from 25 to 590 tons/acre, they assumed that most acid production occurred near the surface and that it was necessary to add only enough limestone to balance the NP deficiency in the upper two meters of spoil. The limestone was disced into the upper 1.0 feet of the spoil surface. One year after application, no substantial neutralization or inhibition of acid formation was noted.

O'Hagan and Caruccio (1986) used leaching columns to examine the effect of varying rates of limestone application on alkaline and non-alkaline shales. A sulfur-bearing (1.07 percent) noncalcareous shale produced acidic drainage when no limestone was added, mixed neutral/ slightly acidic drainage when 1 to 2 percent limestone was added, and alkaline drainage when 3 percent or greater limestone was added. Following longer periods of leaching, the shale with 1 to 2 percent limestone produced consistently acidic drainage. The alkaline shale produced alkaline drainage regardless of whether or not any limestone was added.

By 1990, there were enough well-documented surface mining operations that had employed alkaline addition to allow an extensive review of the effectiveness of alkaline addition in preventing or ameliorating acid mine drainage. Brady and others (1990) examined 10

Pennsylvania mine sites. Of these 10 sites, 8 employed alkaline addition as a means of preventing postmining AMD. Six of the eight alkaline-addition plans failed to prevent AMD. The sites which were successful in preventing or at least ameliorating AMD had several things in common: (1) alkaline addition rates were among the highest (500 to 648 tons/acre) and exceeded permit requirements, (2) pyritic materials were special handled, (3) backfilling was performed in a timely manner, and (4) some potentially acid-forming materials were removed from the mine site. The study concluded that most unsuccessful attempts at alkaline addition were too conservative in terms of the application rate, particularly the practice of applying one-third the calculated deficiency. Further, alkaline addition is most effective when incorporated into the backfill concurrently with mining and reclamation and when implemented in conjunction with other best management practices.

A study of the use of acid-base accounting for predicting surface coal mine drainage quality (Brady and others, 1994) showed a strong relationship between the presence of neutralizing minerals in the overburden (generally carbonates) and the alkalinity of post-mining discharges. Critical values of NP and NNP were identified. Mines with NP values greater than about 15 ppt and NNP greater than 10 ppt $CaCO_3$ had net alkaline drainage. Sulfur content alone was not a reliable predictor of post-mining water quality, except where calcareous strata were absent. The implication for alkaline addition is clear. If it is assumed that imported alkaline material behaves no differently than native alkaline strata, the application of alkaline material at a rate that simulates a naturally alkaline site should assure alkaline post-mining water quality.

Skousen and Larew (1995) studied an alkaline addition project that imported alkaline shale from a nearby mining operation to an operation that was deficient in neutralizers. Although the deficiency calculated from ABA data was equivalent to a one-foot thick layer of the alkaline shale, 3 to 4 feet of shale were actually imported. Significantly, for this discussion, the alkaline addition project successfully prevented AMD.

Perry and Brady (1995) found that overall NP values in excess of 21 ppt $CaCO_3$ and NNP values greater than 12 ppt $CaCO_3$ would produce net alkaline water. Overall NP and NNP values less than 10 ppt $CaCO_3$ and 0 ppt $CaCO_3$, respectively, produced net acidic water. Variable water quality was found for NP and NNP levels between these limits. The same water quality data were examined using significance thresholds. Sulfur contents less than 0.5 percent and NP values less than 30 ppt $CaCO_3$ for individual strata were considered to be insignificant producers of acidity or alkalinity, hence, values which do not exceed these thresholds are assigned a value of zero for the NP and NNP calculations. Applying significance thresholds, overall (the entire volume of overburden to be mined) NP and NNP values greater than 10 ppt and 5 ppt $CaCO_3$ produced consistently alkaline water. NP and NNP values less than 1 ppt and -5 ppt $CaCO_3$ produced consistently acidic drainage. Noting decreased sulfate concentrations with increasing NP, they concluded that the presence of carbonate minerals in amounts as low as 1 to 3 percent (10 to 30 ppt of NP) inhibit pyrite oxidation. Moreover, maintenance of the alkaline conditions created by carbonate dissolution is not conducive to bacterial catalysis or ferrous iron oxidation and greatly limits the activity of dissolved ferric iron, thus interrupting the self-propagating acid cycle.

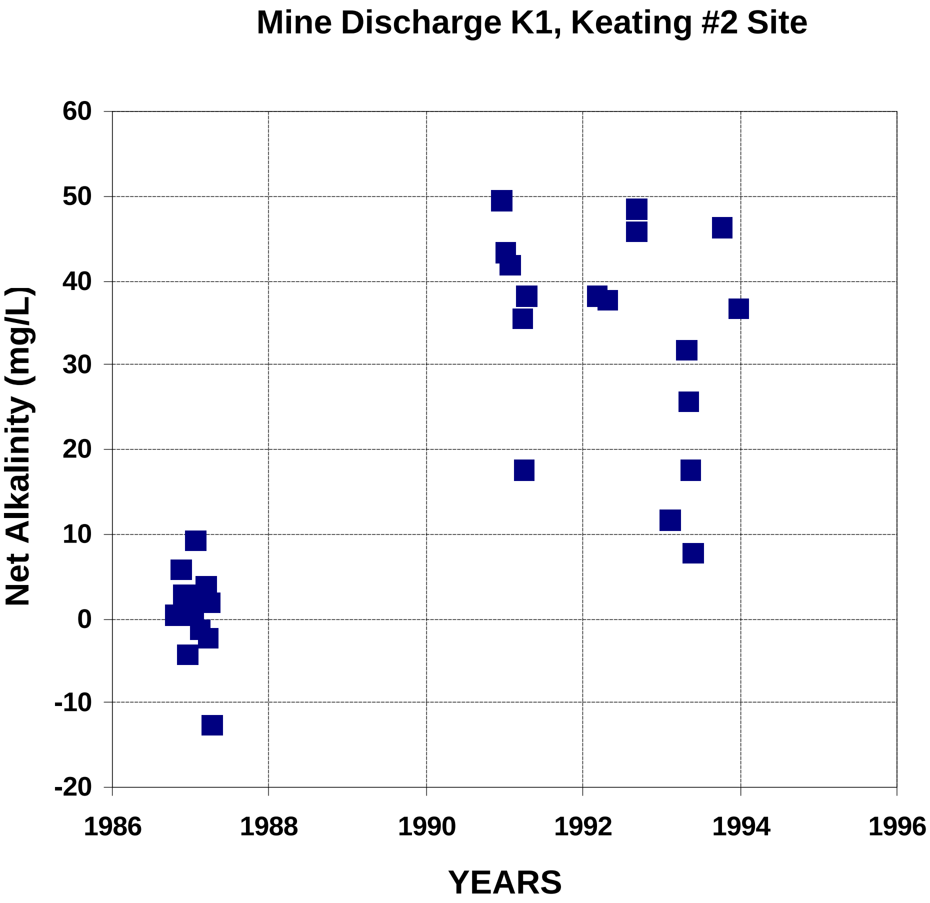
Case Study 1 (West Keating Township, Clinton County, Pennsylvania)

Unfortunately, actual mine sites having adequate acid-base accounting data, water quality monitoring, and records of mining practices (including alkaline addition rates and placement of materials) are difficult to find. One such site, however, is located in West Keating Township, Clinton County, Pennsylvania. The area had been previously mined on a rider seam 10 feet above the main bench of the middle Kittanning (MK) coal, and had not been reclaimed. The recent operation mined the remaining MK coal and reclaimed the previously mined area. The total area affected by MK coal removal was 11.5 acre and the maximum highwall height, including old spoil, was about 20 feet. Overburden analysis was performed on five drill holes, but only sulfur was determined. The deepest hole was 18 feet to the bottom of the coal and seam and the shallowest was 5 feet. Rock between the rider coal and the MK was described as "soft brown shale," indicating weathering. The coal had the highest sulfur of any of the strata encountered, ranging from 0.28 to 0.50 percent. Sulfur in the rest of the overburden was 0.13 percent or less. No NP was determined, however, based on experience with other sites with shallow overburden in the same region, it can be assumed that no significant carbonates were present.

Mining began in January 1988, and the site was backfilled by the end of March 1988. Some alkaline material was added during mining, but the precise amount is not clear. The operation permit required 10 tons/acre of limestone to be added to the pit floor, and there would have been another 5 to 10 tons/acre of limestone added to the reclaimed surface for revegetation purposes. It is suspected that these alkaline addition amounts are minimums, and the actual amount added was probably several times greater.

A downgradient discharge from an unreclaimed pit (K1) was monitored before and after mining. Following mining, the location of the discharge moved down hill to a lower seam that also had been mined. It is unclear why this point was not monitored during mining, although it may have gone dry. Figure 2.2.3a shows water quality over time for net alkalinity and sulfate. Water quality improved following mining. Because the overburden contained virtually no source of alkalinity, the increase in alkalinity would not have been possible without the importation of limestone. The added material was adequate to maintain net alkaline conditions from 1990 through sometime in 1994. The sulfate concentrations, mostly less than 40 mg/L, confirm that there was little pyrite available for oxidation. These concentrations are typical of premining sulfate within the Appalachian Plateau (Brady and others, 1996). Comparatively small amounts (perhaps around 40 tons/acre) of alkaline addition may have been sufficient because of the small amount and highly weathered nature of overburden present at this site.

Figure 2.2.3a: Water Quality Before and After Mining at the Keating #2 Site, Clinton, PA

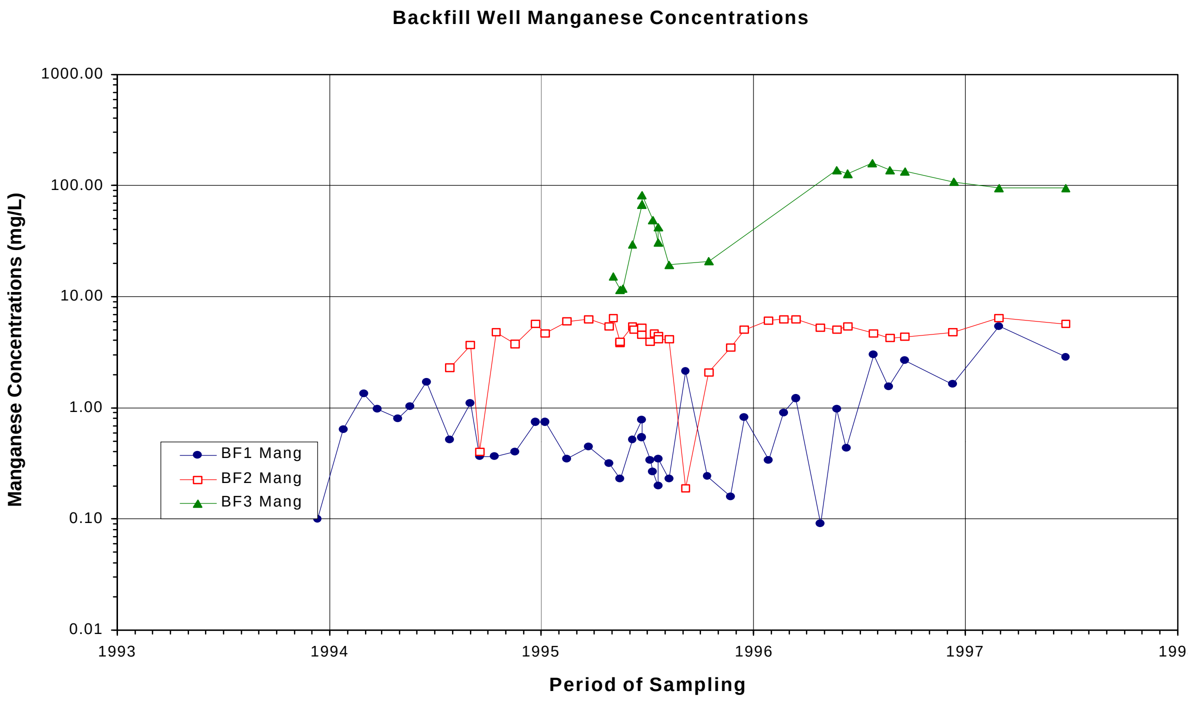


The Case Study 1 site illustrates that a surface mine with weathered overburden that lacks pyrite can produce alkaline drainage with a minimal quantity of alkaline material added as a safety factor. Without the addition of alkaline material, there would have been little or no alkalinity produced.

Case Study 2 (Boggs Township, Clearfield County, PA)

This study site is just to the south of the PA(19) site (Appendix A, EPA Remining Database, 1999). The alkaline addition measures used on PA(19) were partly derived from experience gained from this site. Rose and others (1995) reported results from an ongoing alkaline addition demonstration project in Clearfield County, Pennsylvania that indicated positive but preliminary results. More recent data from monitoring wells in the backfill show mixed results. Baghouse lime, a lime production waste product, was applied at rates ranging from 150 to 1,080 tons/acre, adjusted to 100 percent $CaCO_3$ content, based on ABA calculations using significance thresholds and correcting for deficiencies in NP. Areas with the highest alkaline addition rate (and the most acidic overburden) were successful in producing alkaline drainage with low concentrations of dissolved iron and manganese (Figure 2.2.3b). Backfill wells in areas which received lower alkaline addition rates showed both alkaline and acidic water and relatively high levels of dissolved iron and manganese. Post-reclamation sulfate levels of 300 to 800 ppt in all of the monitoring wells indicate that AMD is being produced but neutralized.

Figure 2.2.3b: Water Quality Before and After Mining at the Case Study 2 Site



Based on the experience from this demonstration project, it is probably unrealistic to adjust alkaline addition rates based on minor overburden quality variations between drill holes. Unless there is a corresponding change in stratigraphy, alkaline addition rates should reflect aggregate (average) overburden quality.

Evans and Rose (1995) also reported the results of alkaline addition to large test cells constructed solely of high-sulfur overburden from this site. Cells were constructed of 2 percent pyritic sulfur mixed with different amounts of alkaline material. Although alkaline addition reduced the generation of acidity by as much as 96 percent, even the highest alkaline addition amount, equivalent to 3.4 percent $CaCO_3$, was insufficient to prevent AMD formation. Two important considerations resulted from this study. First, the high-sulfur overburden was exposed to weathering for a considerable time period before cell construction and application of alkaline material. Test cells remained exposed without a soil cover for an extended time period thereafter. More rapid application of alkaline material and timely covering may have reduced the likelihood of AMD formation. In other words, once AMD generation starts, it is much more difficult to slow its formation than to keep it controlled in the first place. Second, because complete mixing of alkaline material may be difficult or impossible to achieve, microenvironments within the spoil can still allow acid production and bacterial activity. AMD formation in very high-sulfur mine sites or areas of concentrated high-sulfur refuse, represented by the concentration of highly pyritic material in the cells, may be impossible to ameliorate using alkaline addition rates which have otherwise been successful in mines with more typical sulfur values.

Case Study 3 (Appendix A, EPA Remining Database, 1999 (PA (8))

Smith and Dodge (1995) reported on an alkaline addition site in Lycoming County, PA, which was part of the original Brady and others (1990) study. Alkaline addition rates of 600 tons/acre and daylighting of an underground mine resulted in dramatic improvements in water quality from the underground mine discharge (Figure 2.3.3c). Pre-mining net acidity values exceeded 100 mg/L. After remining, the discharge was predominately alkaline. Increased sulfate concentrations indicated that the improvement in water quality could be attributed to neutralization by imported alkaline material rather than daylighting. No naturally occurring alkaline material was present. This operation is one of the oldest successful alkaline addition sites. It has exhibited improved water quality since the onset of large-scale alkaline addition in 1986 and produced predominately alkaline water since 1989, suggesting that the impact of alkaline addition will be long-term or permanent.

Figure 2.2.3c: Water Quality at the Case Study 3 Site

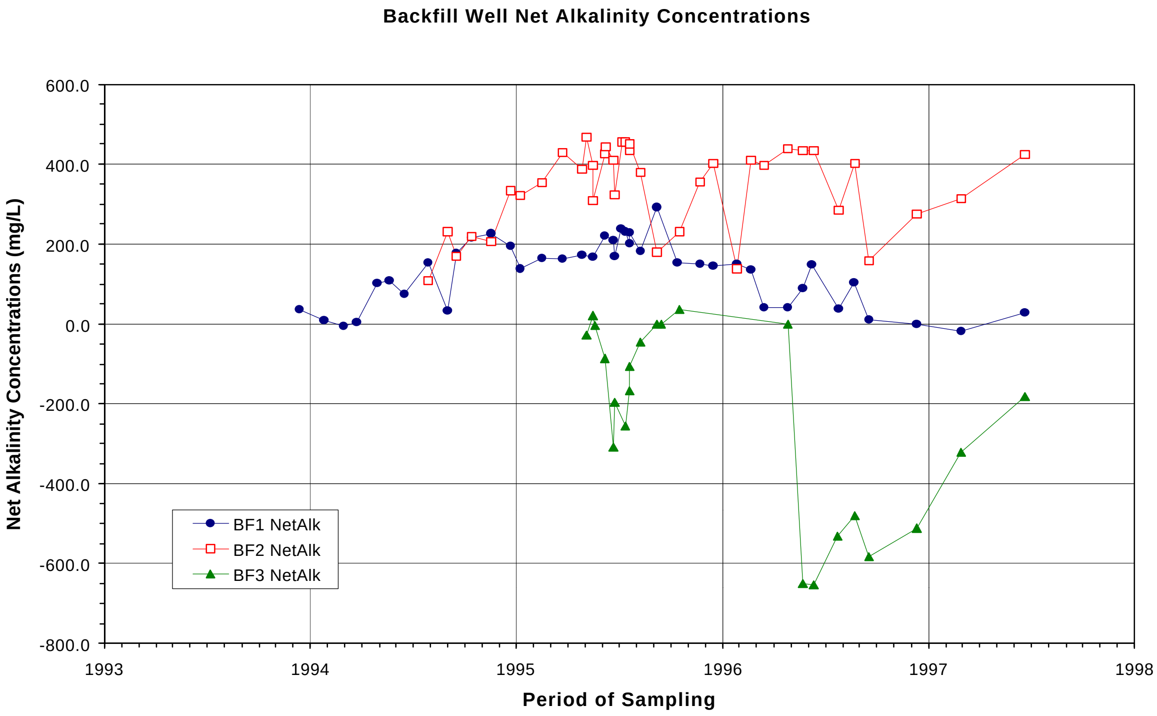
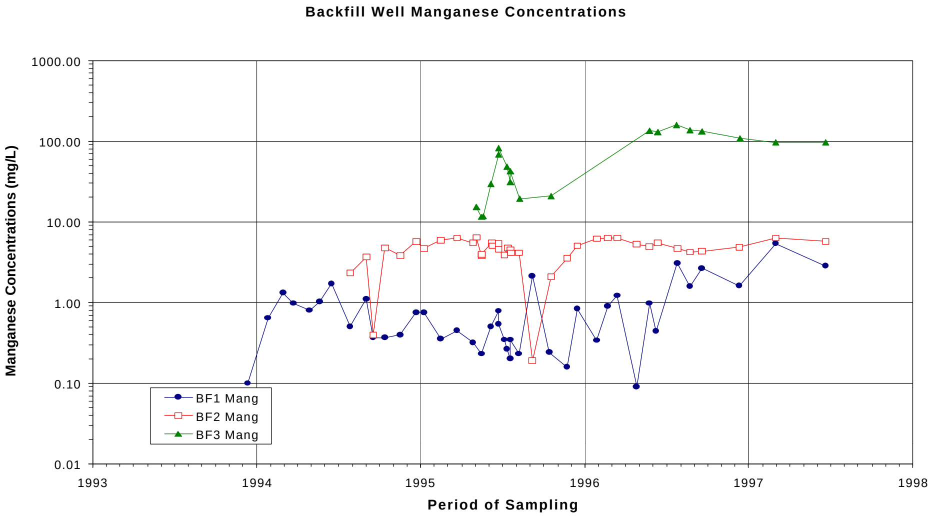


Figure 2.2.3c: Water Quality at the Case Study 3 Site (continued)



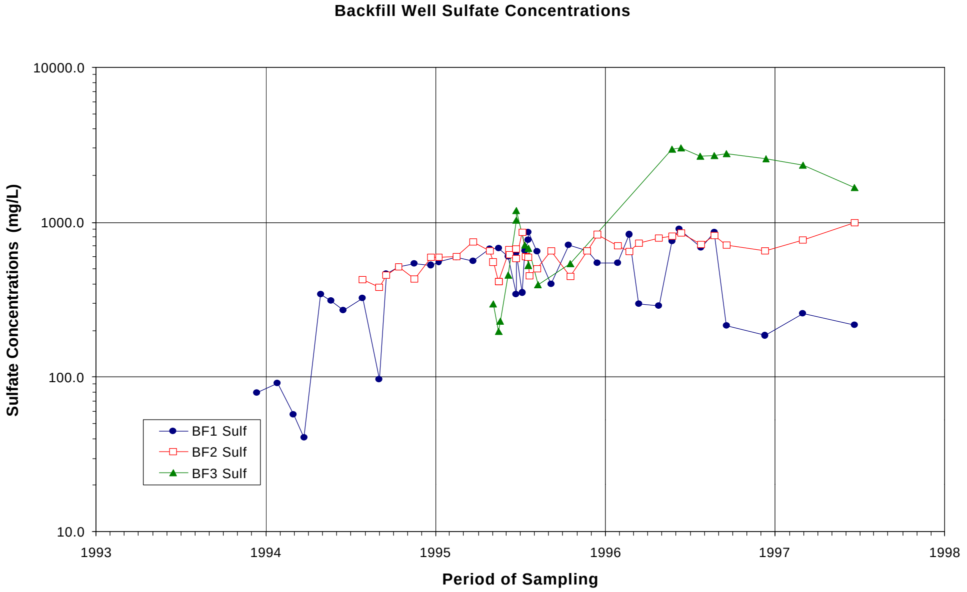
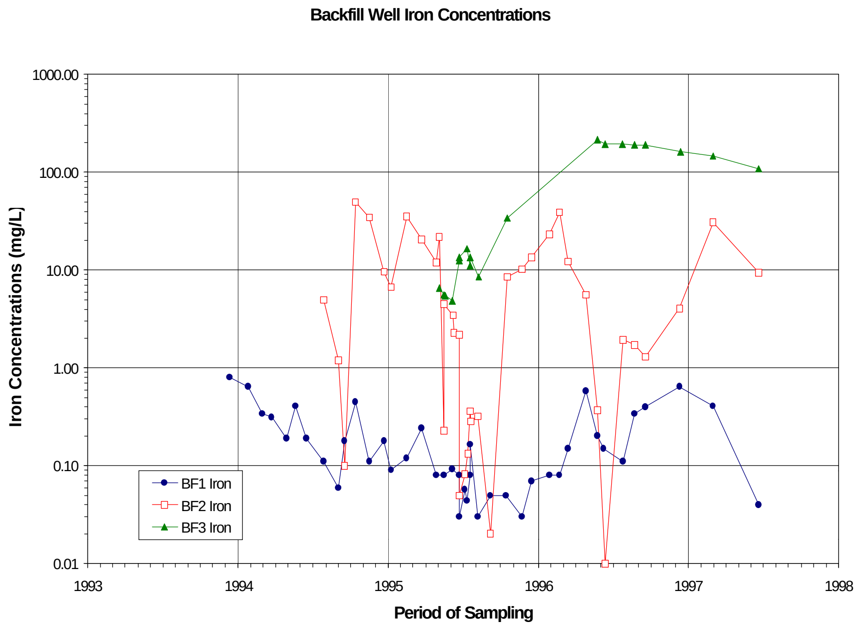


Figure 2.2.3c: Water Quality at the Case Study 3 Site (continued)



<u>Case Study 4</u> (Sequatchie County, Tennessee)

Most of the published research in alkaline addition has taken place in northern Appalachian states. An exception is the work done by Wiram and Naumann (1996) on an AMD-producing surface mine in Sequatchie County, Tennessee. This site is adjacent to the TN(4) site (Appendix A, EPA Remining Database, 1999) and the pollution prevention measures used on TN(4) were first applied at this study site. Alkaline addition was implemented as the principal component of a toxic materials handling plan that also included selective overburden placement and the construction of chimney drains and alkaline recharge basins. Alkaline addition rates were determined for individual stratigraphic intervals having a NNP less than -5, however, a modified NP test was used in order to exclude the apparent NP contribution from siderite ($FeCO_3$).

Previous overburden analysis results erroneously predicted alkaline drainage due to the presence of siderite that falsely indicated the presence of significant alkaline strata. The role that siderite plays in mine drainage and acid-base accounting are explained by Skousen and others (1997). Limestone application rates for each of these intervals were summed to determine the application rate for the area around each bore hole. Net neutral zones were not factored into the alkaline addition calculations.

Results of the Wiram and Naumann study were favorable. Monitoring wells on the site in the backfill spoil area that had alkaline addition have higher alkalinities than wells into areas that did not have alkaline addition.

2.2.4 Discussion

It has long been known that mines with sufficient naturally occurring calcareous strata produce alkaline mine drainage. It is a logical next step that sites without sufficient naturally occurring alkaline strata can be made to produce alkalinity by importing the appropriate amount of alkaline material. The questions are: how much alkaline material should be added, and where should it be placed? Another question that can be of equal importance, especially in sensitive watersheds, is how much risk of failure can be tolerated. The literature and the case studies cited above provide some insights into these questions and identify benefits and limitations of the methods.

Benefits

- Alkaline materials are an effective means of neutralizing and preventing acid mine drainage.
- Alkaline materials are generally readily available, and in some cases available as waste products that would otherwise be landfilled.
- Alkaline addition is probably the best understood "chemical" BMP, and there are natural analogues (i.e., calcareous mines) for comparison.
- The amount of material required to assure alkaline drainage for low to moderate sulfur sites is well understood.

- The chemistry of the alkalinity generating processes of carbonate minerals is well understood.
- Site-specific data can be obtained to determine the amount of alkaline material that needs to be added.

Limitations

- Alkaline addition is not generally effective at fixing a problem once it has been created.
- Alkalinity from carbonate dissolution is limited and may not be adequate for high sulfur mines and coal refuse materials.
- Alkaline materials can armor with iron precipitates and become ineffective. Proper placement of alkaline materials to avoid high iron water is a way to prevent this problem.
- Ensuring that a site produces alkaline water does not guarantee that effluent limitations for metals will be met.
- Siderite can produce overburden analyses that falsely predict alkaline drainage. A modified method for determination of neutralization potential can greatly reduce this risk.

Efficiency

- Alkaline addition has proven to be an effective mine drainage prevention technique for mines with low to moderate sulfur content.
- Studies show that mines with net neutralization potentials greater than 12 produce alkaline drainage.
- For sites with moderate sulfur, alkaline addition rates below 500 tons/acre typically have not produced alkaline drainage.
- Alkaline addition rates at less than 500 tons/acre can be effective for low sulfur sites that would not otherwise produce alkaline water because of a lack of naturally occurring carbonates.
- More work needs to occur in the southern Appalachians to determine appropriate addition rates for those geologic conditions.

2.2.5 Summary

The addition of alkaline material to surface mine backfill can be an effective method of compensating for overburden that is naturally deficient in neutralizers and thus, reduce the potential for acid mine drainage. Two categories of alkaline additives currently are being used on Appalachian mine sites, limestone (and its derivatives) and coal ash. Coal ash addition was proposed for 8 of the 17 alkaline addition sites in the BMP-site data packages.

To successfully prevent the formation of acid mine drainage, a sufficient quantity of alkaline material should be added to the backfill. Most successful alkaline addition sites to date have used substantial application rates, exceeding 500 ton/acre. Lower rates have proven to be effective only for low-cover overburden with very low sulfur content. Alkaline material is best applied by distributing and thoroughly mixing it throughout the backfill. It also may be useful to place up to 100 ton/acre on the pit floor. Surficial applications of alkaline material are less effective due to low solubility of calcite and limited contact with acid-producing materials deeper in the backfill. Most failed alkaline addition sites either had used application rates that were too low or employed ineffective placement of the alkaline material.

2.3 Induced Alkaline Recharge

Constructed recharge infiltration pathways composed of limestone within mine backfill have been used to increase alkalinity in mine spoil and to increase oxygen availability within spoil. These pathways can be near surface features (trenches) or deeper structures that extend from the surface to the base of the spoil (funnels). Surface runoff is directed into these pathways where it contacts the limestone and generates alkalinity. The pathway is positioned such that infiltrating water would not contact potentially acid-generating rock. As originally envisioned, the goal is net alkaline water in the mine spoil. A second goal at some sites is to induce oxygen into the backfill with the purpose of precipitating iron from solution. The principal studies on this subject have been conducted by Caruccio and Geidel (1984, 1985, 1989 and 1996) and Wiram and Naumann (1996).

Theory

Pyrite oxidation can result in significant quantities of soluble, acid-producing oxidation products. In fact, mine drainage acidities in the hundreds or even thousands of milligrams per liter are not uncommon. Calcite dissolution on the other hand is much more limited in terms of alkalinity generation. At surface conditions the maximum alkalinity is less than 100 mg/L. Carbonates are more soluble at elevated partial pressures of carbon dioxide and under high Pco_2 they can produce alkalinity as high as 500 mg/L, a condition that can occur in mine spoil. Alkalinity and acidity are both reported in the same units of calcium carbonate equivalent and, for example, 100 mg/L of alkalinity will neutralize the acid from 100 mg/L of acidity. A good discussion on the chemistry of pyrite oxidation and carbonate dissolution at coal mines is in Rose and Cravotta (1998).

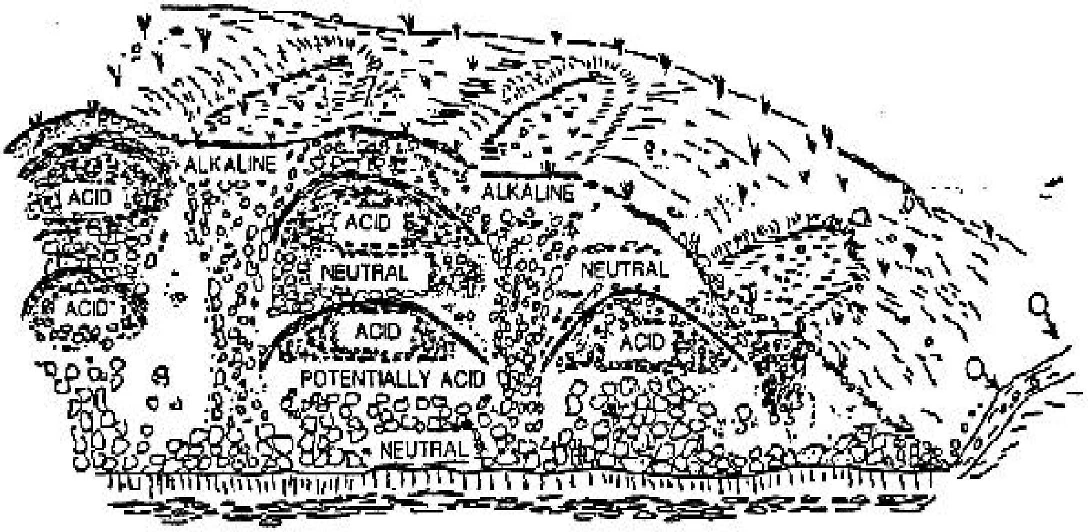
It has been proposed that one way to offset the frequently unequal generation of acidity in comparison to alkalinity was to increase the load of alkalinity. Load is concentration times flow and is reported in units of mass per time period (e.g., pounds per day). The means proposed to do this was to divert surface runoff into trenches and/or funnels filled with limestone. This water would contact and dissolve some of the limestone. Thus the water flowing from these structures into the spoil would be alkalinity enriched. It was hoped that the increase in the volume of water, even with limited alkalinity, would result in a large enough alkalinity load to offset the spoil water's acid load. It has been estimated that it would require 3 to 8 times more water in contact with the calcareous material than the water in contact with the acidic material. This concept was developed by Caruccio and Geidel (1984) based on laboratory work by Geidel (1979).

A second purpose for recharge pathways is to promote the inflow of oxygen into the spoil. Oxygen could enter the spoil in three ways, dissolved in the infiltrating water, entrapped in the infiltrating water, and with air directly entering the recharge structure. This would be used where waters are already alkaline or only slightly acidic and where the water is iron-rich. Reduced iron (Fe^{2+}) precipitation is very slow even at neutral pH, however, oxidized iron (Fe^{3+}) precipitates rapidly under alkaline conditions. The additional oxygen would help to enhance oxidation and precipitation of iron within the backfill.

2.3.1 Implementation Guidelines

Caruccio and Geidel (1984) suggest a refinement to the above concept which would incorporate special handling and capping of acidic material. Acid-producing material is placed in pods and capped with clay. Alkaline recharge channels are located such that infiltrating water enters "neutral" or alkaline spoil located between the pods of acidic material. This concept is depicted in Figure 2.3.1a. The purpose is to minimize the amount of acidic water and maximize the amount of alkaline water that reaches the water table in the spoil.

Figure 2.3.1a: **Alkaline Recharge Channels and Capped Acid-producing Material Pods (Caruccio and Geidel, 1984)**



If recharge trenches are installed for the purpose of inducing oxygen into the backfill the limestone (or other type of rock) should be of sufficient size and sorting to be easily permeable to air.

2.3.2 Verification of Success or Failure

- The BMP should be constructed as designed and the on-site construction plan should be documented. Means of documentation include:
  - Engineer's certification of construction.
  - Photographs of the structure as it is being constructed.
  - Locations of the recharge structures accurately located by survey or global positioning system.
  - Verification of the amount of imported alkaline material by weigh slips or another accounting method. Weigh slips would be submitted to the regulatory authority at specified intervals. A copy should also be available for inspection at the mine site by the mine inspector.

- Increased inspection frequency may be needed to verify that a BMP is being constructed as designed. Inspections can include examination of limestone weigh slips and verification of the size and type of imported material.

- Photographs of the construction process can be taken by the mine inspector, company engineer or other qualified person. Copies would be placed in the state permit file. A narrative, including date and location, should accompany each photograph.

- Water quality monitoring should include both concentration and flow at discharge points. This is especially critical for remining sites where the intent and purpose is to reduce loads of constituents. Because alkaline recharge structures increase flow into the ground- water system, being able to determine load is critical.

Monitoring for concentration and flow, as well as other accurate documentation of construction, will allow for future improvements in design and determination of the efficiency of alkaline recharge structures.

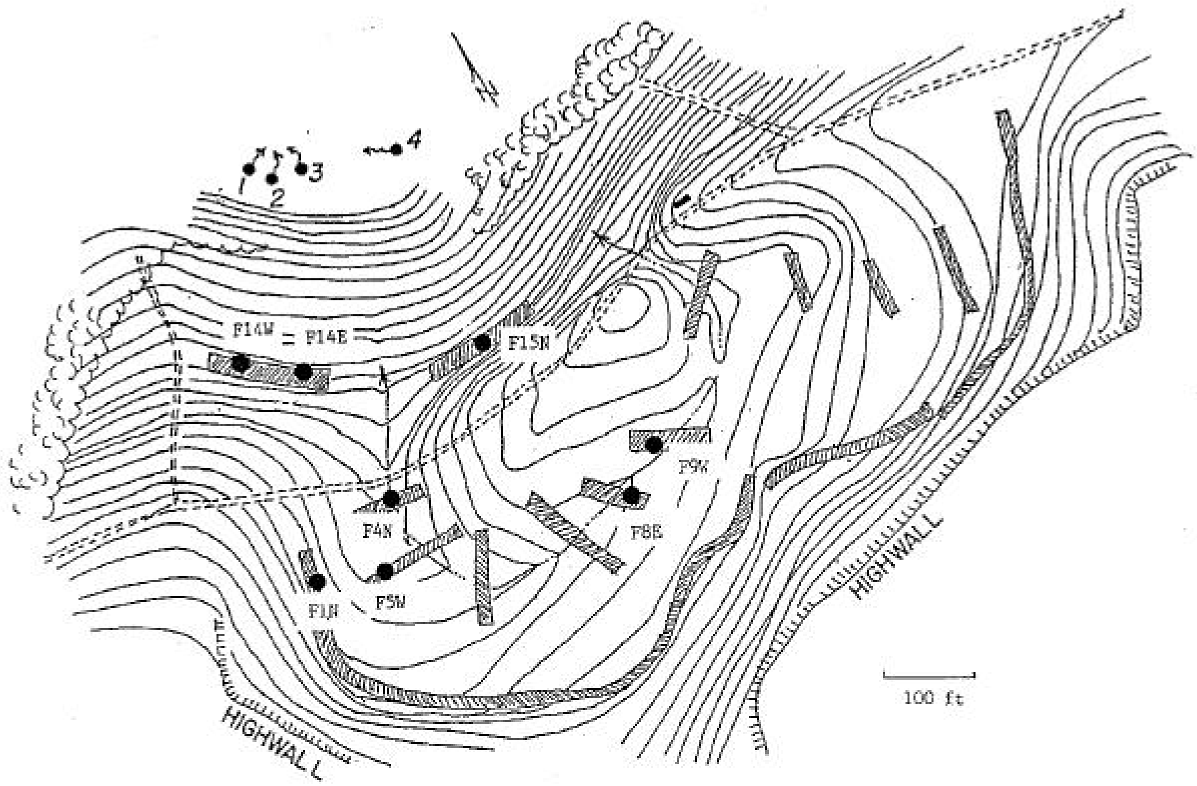
2.3.3 Case Studies

The case studies discussed below are examples of sites where the alkaline recharge concept has been applied.

Case Study 1 (Caruccio and Geidel, 1984, 1985 and 1996)

A site in Upshur County, WV is approximately 20 acres and was mined in the early 1970s. Acidic discharges developed following reclamation. Four post-mining discharges from the toe-of-spoil had acidities between 400 and 600 mg/L. Caruccio and Geidel have attempted, over the course of more than a decade, various means of reducing the acidity, most of which involved alkaline recharge structures. Figure 2.3.3a shows the topography, location of recharge trenches and funnels, and locations of the seeps at the site.

Figure 2.3.3a: **Topography, Location of Recharge Trenches and Funnels, and Locations of Seeps (Case Study 1, Upshur County, WV) (Caruccio and Geidel, 1984).**

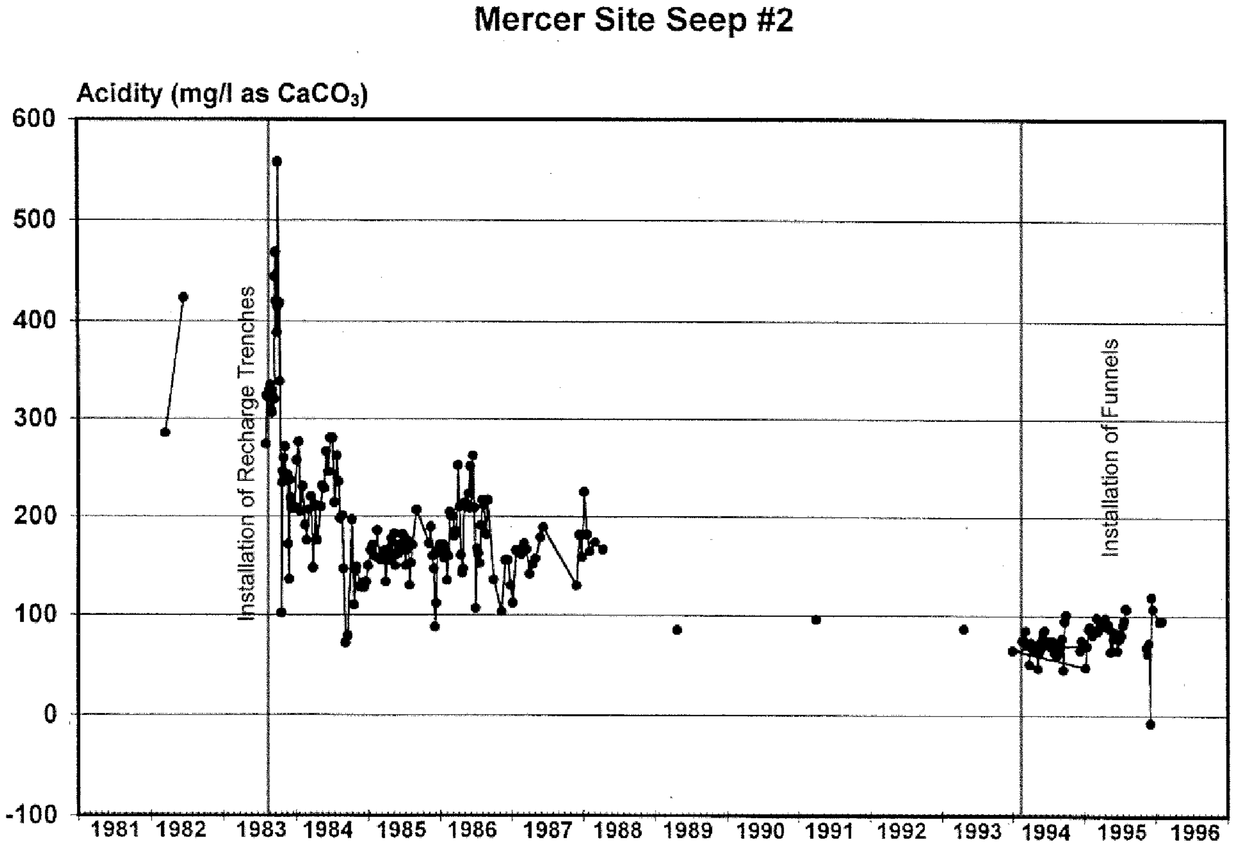


Fifteen alkaline recharge trenches were installed to divert surface water into the ground water system in the summer of 1983. The trenches averaged 10 feet wide, 3 feet deep, and 75 to 725 feet long. Trench floors were capped with sodium carbonate briquettes (0.5 lbs/ft^2) and covered with two feet of limestone reject. Halogen tracers (KI and KBr) were placed at the base of the trenches to serve as tracers for infiltrating water. Eight months after installation, the tracers appeared at the seeps. At this time the acidity decreased to a range of 75 to 125 mg/L. Because the water was still acidic, fine limestone (up to ½ inch) was broadcast over the site at a rate of 100 tons/acre in 1984. The acidity continued to hover at around 100 mg/L.

In February 1994 eight funnels were installed adjacent to or within the trenches. These funnels were excavations of approximately 4 feet x 7 feet x 8 feet, and were filled with a total of 60 to 80 tons of coarse limestone having a $CaCO_3$ equivalent of ~70 percent. The purpose of the funnels was to transmit water directly from the surface to the water table. Following funnel installation acidity was 50 to 100 mg/L.

Figure 2.3.3b shows acidity concentrations for Seep #2 and time lines showing when the alkaline recharge trenches and funnels were installed. The data indicates a decrease in acidity concentration following the installation of each BMP. Flow was not measured, thus load could not be calculated. Without flow information it can not be determined how much of the decrease in acidity was due to dilution from infiltrating precipitation and how much was due to neutralization. Water quality data for the seeps following funnel installation shows alkalinity is occasionally at measurable concentrations, and in a few instances is greater than acidity. This measured alkalinity indicates that, at least occasionally, alkalinity is being generated by the trenches/funnels and sometimes is enough to neutralize all of the acid.

Figure 2.3.3b Plot of Acidity versus Time for Seep #2 at Case Study 1 Mine. (Vertical lines indicate when recharge trenches and funnels were installed.)



There are four possible interpretations of the observed decrease in acidity concentration:

1. Trenches and funnels provided alkalinity to the ground water and thereby neutralized existing acidity.
2. The trenches and funnels increased rain water infiltration into the ground water system, thus diluting the ground water and lowering concentration.
3. Some natural attenuation occurred through time. A control area with similar overburden would have to be monitored to account for the effects of this factor.

4. The decrease in acidity concentration is the result of two or three of the above factors.

If the decreased concentrations are due simply to dilution, increased infiltration could result in an increased acid load and exacerbate the problem. For example if:

<u>Before construction of funnels</u>:
Average flow is 10 gpm and concentration is 250 mg/L.
10 gpm x 250 mg/L x 0.012 = 30 lbs/day acidity

<u>After construction of funnels</u>:
Average flow is 30 gpm and concentration is 150 mg/L.
30 gpm x 150 mg/L x 0.012 = 54 lbs/day acidity

An evaluation of whether this BMP was effective requires a knowledge of both flow and concentration.

<u>Case Study 2</u> (Wiram and Naumann, 1996; Wiram, 1996).

This site is located in Sequatchie County, Tennessee. Mining began in September 1987 and mining used loaders and trucks. Once the initial box cut was in place a dragline was used. Cast-blasting was later employed along with the dragline operation.

In mid-1990 pollutional seepage began to enter a receiving stream. The mine discharge water had pH from 3.4 to 7.5, alkalinity from 0 to 121 mg/L, iron from 4.8 to 48.6 mg/L, manganese from 2.3 to 34 mg/L, and sulfate from 8 to 812 mg/L. The coal company embarked on an extensive investigation to determine the source of the problem and effective methods for resolving the problem. Alkaline recharge structures were just one of several BMPs that were ultimately used. Other BMPs included special handling of overburden and alkaline addition in the backfill. Although special handling and alkaline addition will be touched on in this discussion, the focus is on the alkaline recharge structures.

The alkaline recharge structures were approximately 150 x 50 feet, with a depth of 12 feet, and were often placed over chimney drains which had been constructed in the backfill. The recharge structures were filled with four feet of "crusher-run" limestone (0 to 1.25 inches) overlain by four feet of limestone gravel (2 to 2.25 inches). The remaining four feet was for "free storage." The purpose of these recharge drains was different from that of Case Study 1. In this case, the drains were installed to enhance "the alkaline/oxygen loading" of the backfill ground water. The key objective was to induce metal precipitation within the backfill.

This site can be divided into two areas in terms of BMPs. Most of the site (the southern seven-eighths) was mined conventionally without incorporation of special BMPs to prevent water quality problems. The northern one-fifth was mined using special handling and alkaline addition. Both areas had alkaline recharge structures installed. A map of the site showing the location of alkaline recharge structures, monitoring wells and the area where alkaline addition and special handling were part of the mining plan are shown in Figure 2.3.3c. Monitoring wells OW-2, OW-5, and OW-8 were placed downgradient from recharge trenches. Table 2.3.3a shows the range of water quality in terms of pH, alkalinity, iron and manganese for these wells, as well as water quality for wells OW-7 and OW-10.

Figure 2.3.3c: Map of Case Study 2 Site

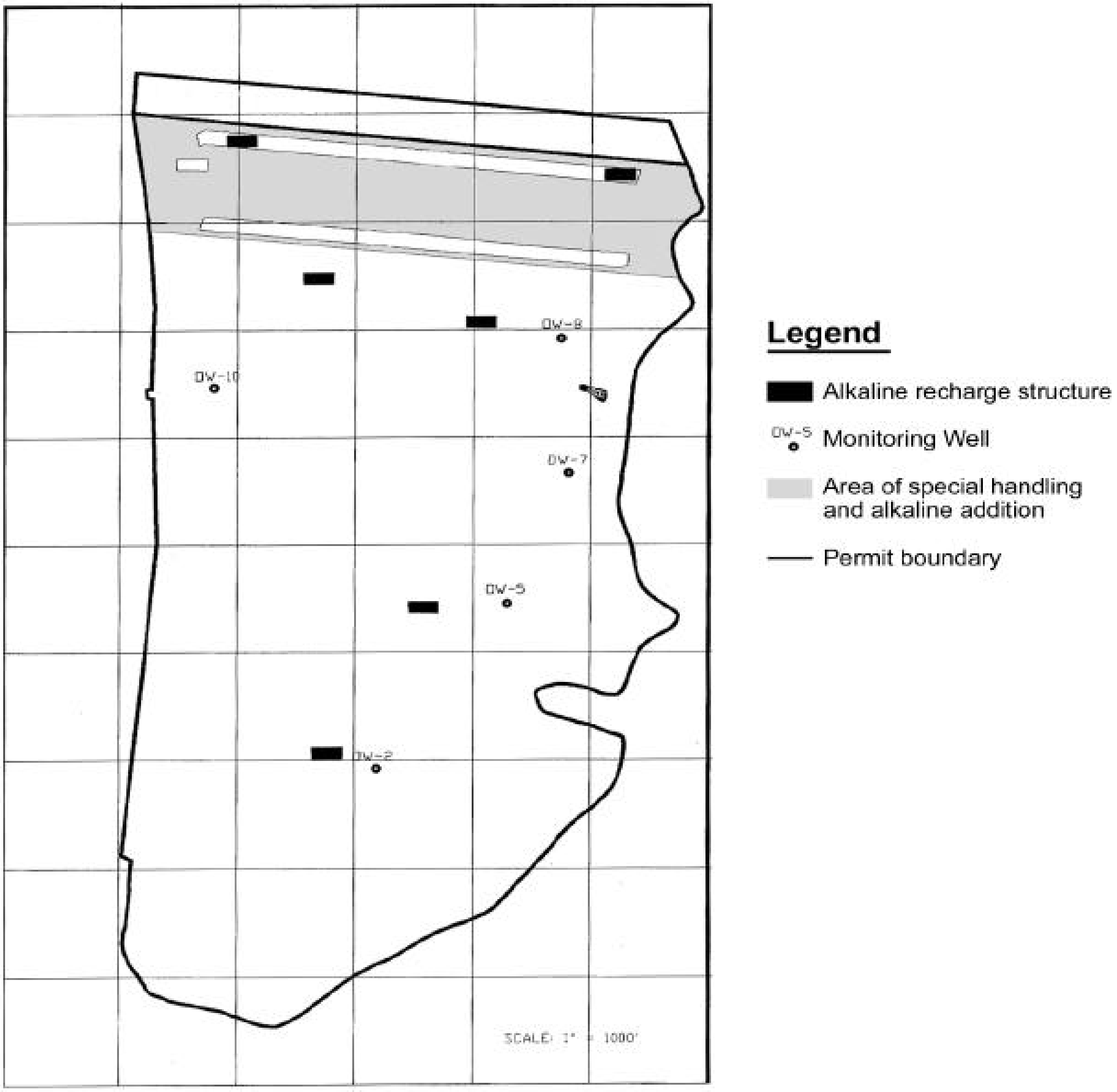


Table 2.3.3a: Water Quality for Wells at the Case Study 2 Site (data interpreted from graphs by Wiram, 1996)

Well	**OW-2**		**OW-5**		**OW-7**		**OW-8**		**OW-10**	
Date	10/90 to 4/93	1995	7/92 to 4/93	1995	7/92 to 4/93	1995	11/92 to 4/93	1995	11/92 to 4/93	1995
pH	6.0	6.0	6.0	6.0	6.5	6.4	6.5	6.3	6.0	6.0
Alk. mg/L	100-175	125-150	~100	150-200	~450	~450	50-500	400-450	150-200	100-200
Fe mg/L	15-30	<1-15	<10	10-20	<1-7	<1-6	<1-5	<1-4	15-30	40-90
Mn mg/L	10-20	8-18	~10	~10	5-8	2-8	2-4	3-8	~10	10-20

Water quality data from the monitoring wells prior to construction of the alkaline recharge structures do not exist. Thus pre- and post-construction data cannot be compared. For purposes of evaluation the data in Table 2.3.3a has been divided into early monitoring data (April 1993 and earlier) and late monitoring data (1995). The differences between early and late monitoring data, overall, are not significant. The biggest differences in water quality is observed when the wells drilled into the area without special handling and alkaline addition are compared with the wells located near the area of alkaline addition and special handling. Wells OW-2 and OW-5 were not influenced by special handling and alkaline addition, whereas there were indications that OW-7 and OW-8 were influenced. The water in OW-7 and OW-8 is more alkaline than in the other wells and in general has lower metal concentrations than wells OW-2, OW-5 and OW-10. Well OW-10 is upgradient from any BMPs and serves as a "control." The water in OW-10 has higher metal concentrations than the other wells. If OW-10 is representative of mine spoil water in the absence of BMPs, then the BMPs do appear to have resulted in water quality improvement.

Case Study 3 (Appendix A, EPA Remining Database, 1999, TN(4))

This site was submitted as one of the 61 state data packages. It is located in Sequatchie County, Tennessee and is immediately to the east of the Case Study 2 site. The same company is mining both sites and experience gained at the Case Study 2 site was incorporated at the Case Study 3 site. This site incorporated numerous BMPs in addition to alkaline recharge structures, including alkaline addition, special handling, compaction of spoil, backfill hydrology routing, backfill water inundation, and stream buffer zone expansions. Only the induced alkaline recharge structures will be discussed here. The surface feature is a depression that is about 150 feet long by 75 feet wide and 12 feet deep. The area filled with limestone is somewhat smaller and the depth of limestone is about 8 feet. As with the Case Study 2 site one of the goals is to promote the flow of oxygen into the spoil for in situ precipitation of metals. The effectiveness of the measures used at this site can not be evaluated because the site is still active.

2.3.4 Discussion

The theory of increasing alkaline load by increasing the amount of water that is in contact with calcareous materials is a valid concept, although it is not without potential problems and is not applicable to all mine sites. The benefits and limitations of implementation of this BMP are highlighted below. Most of the potential problems have not been discussed in previous literature.

Benefits

- Surface water is preferentially directed to calcareous material that can produce alkalinity. The water will flow through the limestone in the recharge structure and avoid contact with acidic material.

- Water flowing into the structures will be surface runoff (i.e., essentially rainwater) that is low in dissolved solids, and more importantly, has low metals concentration. Water containing high concentrations of metals, such as mine drainage, can coat (armor) limestone and other calcareous materials rendering them ineffective.

- Limestone recharge structures are passive and require little, if any, maintenance.

- Recharge structures can introduce oxygen into the backfill to facilitate oxidation and, if the water is sufficiently alkaline, metals will precipitate in the backfill rather than at a surface water discharge point.

Limitations

- Limestone only dissolves when in contact with water, thus only during precipitation events is the limestone in contact with water.

- Permeable trenches can increase the flow of air into and out of spoil. This could increase oxygen availability and decrease carbon dioxide within the spoil. Increases in oxygen can be desirable (as in Case Studies 2 and 3 where the goal was/is to precipitate iron in the backfill), or undesirable (if the spoil is highly pyritic). Retention of carbon dioxide (CO_2) in spoil can be important if calcareous minerals are present because carbonates are more soluble when CO_2 is elevated, a condition that often exists in surface coal mines (for examples of mine sites where elevated CO_2 has been measured see Guo and Cravotta, 1996, Lusardi and Erickson, 1985, and Jaynes and others, 1983). This is the reason that many mine waters have alkalinities greater than 200 mg/L (for examples, see Hornberger and Brady, 1998; and Brady and others, 1998, Table 8.2).

- The increased flow into spoil could potentially increase load of undesirable constituents such as acidity, metals and sulfate, especially if the water entering the spoil flushes oxidation products that have built up between precipitation events.

- To reach saturation with respect to alkalinity, water should be in contact with calcareous minerals for a sufficient length of time. If contact time is not enough, sufficient alkalinity may not be generated.

- Intentional diversion of surface water into the ground water system can result in a fluctuating water table. This could adversely affect water quality if pyrite oxidation products, which can build up between flushing cycles, are flushed during this fluctuation.

The effects of induced alkaline recharge structures have been studied at few sites. Thus there are unanswered questions regarding the effectiveness of this BMP. Although concentrations decreased at the Case Study 1 site, flow data was not evaluated, and BMP effects on acid load can not be assessed. The Case Study 2 site lacked pre-installation ground water monitoring data, but contained a single well in an area that was not affected by the BMPs. This control well has higher metal concentrations than wells below the recharge trenches. The recharge structures may have been effective at in-situ metal removal. Water in all the wells in Case Study 2 was alkaline. An evaluation of the effectiveness of alkaline recharge structures at the Case Study 3 site cannot be made at this time because the site is still active.

Efficiency

Until efficiency can be further demonstrated, it would be prudent to restrict the use of alkaline recharge structures as a BMP to the following scenarios:

- Sites where the overburden contains very little acid-producing material and there is a lack of calcareous rocks. In other words, this BMP should be implemented on "marginal" sites that would not create severe acid mine drainage in the absence of alkaline recharge structures, but likewise would not produce alkaline drainage. In cases where this technology is implemented and where selective handling of acidic materials has occurred, the acid material should be placed above the highest water table anticipated to occur during a recharge event. Otherwise the acidic material may be in a zone of water table fluctuation.

- This BMP has potential use at sites with alkaline or near-alkaline ground water with elevated metals. The purpose at these sites is to enhance the amount of oxygen that will reach the ground water and this in turn will promote in-situ precipitation of metals.

2.3.5 Summary

Although alkaline recharge structures have the potential to induce alkalinity in mine spoil, experience is limited and there are possible drawbacks that have not been evaluated, such as the potential for increasing the load of undesirable chemical constituents. The Case Study 1 site had several acid seeps which had resulted from mining. Following installation of recharge trenches and funnels there were decreases in acidity concentration. Flow data, however, was not available so it can not be determined whether acidity load decreased. The mine spoil monitoring wells at the Case Study 2 site lack pre-installation data. A single control well in an area where BMPs were not applied is of poorer quality than wells in areas with induced alkaline recharge trenches. At this site, the primary problem was the discharge of metals offsite. The recharge trenches were constructed with the intent of causing precipitation of metals in the backfill by increasing alkalinity and oxygen availability. If a comparison between the control well and the other wells is valid, this could indicate that the efforts at the Case Study 2 site did result in better water quality. The Case Study 3 mine incorporated most of the measures adopted at the adjacent Case Study 2 site including using the recharge structures to enhance the flow of oxygen into the backfill. The Case Study 3 mine is still active and it is too early to evaluate effectiveness.

The number of sites where alkaline recharge structures have been constructed as a BMP are few and many questions remain as to their effectiveness. Some implementation considerations can be suggested, the most important being that it should be certain that an increase in surface infiltration will not also result in an increase in acid load. The methodology will probably be most effective on sites with minimal amounts of pyrite and a lack of naturally occurring calcareous rocks. Recharge structures may also be effective where the goal is increased oxygen in the backfill, so as to precipitate metals within the backfill.

Measures should be taken to ensure that plans were carried out as designed, including increased inspection frequency and engineer certification of on-site design. Monitoring of ground water discharges should include flow as well as concentration so that load can be determined.

2.4 Special Handling

Special handling at surface mines encompasses the selection, handling, and controlled placement of acid-producing and/or calcareous rock. The primary purpose of special handling is to place acidic or alkaline strata in such a way as to minimize acid production and transport, and to maximize the alkalinity generation within the mine spoil water.

Special handling is often used in conjunction with other acid mine drainage prevention techniques such as alkaline addition, water management (e.g., pit floor drains), and surface reclamation (e.g., slope grading to promote runoff) to improve the water quality. For example, special handling, in the absence of calcareous material, cannot by itself produce alkaline drainage. Thus, where calcareous strata are absent, offsite calcareous material can be imported to offset these natural deficiencies in acid-neutralizing rocks. Pit floor drains can be used to engineer where the post-mining water table will re-establish within the spoil, thus assuring that special handled material will remain above the water table.

Special handling is a common practice, occurring on at least 35 of the 61 mines included in the EPA Remining Database (Appendix A and Table 2.4a). It affected at least 78 of 231 discharges in Pennsylvania (Appendix B, Pennsylvania Remining Site Study). An examination of both databases shows that special handling is not a “stand-alone” BMP. It is always used in conjunction with other BMPs.

Table 2.4a: EPA Remining Database (Appendix A), Special Handling of Toxic/Acid Forming Materials

ID	Type of Mine	Mine Closure Date	Cover Material	Placement	Blending of Overburden	Other Major BMPs	Comments
AL (2)	Surface	3/90				Regrading Revegetation Terraces	
AL (7)	Surface	5/92	4' Non-toxic			Regrading Revegetation	
AL (10)	Surface Auger	12/95			Yes	Regrading Revegetation Temp. Diversions	
AL (11)	Surface	No mining taking place.	Yes	On pit floor		Old washer fines to be relocated. Alkaline addition	Reclamation will occur through a party other than the mining company
AL (14)	Surface Coal Refuse Disp.	10/89	4' clay over fines 4' over rest			Regrading Revegetation	
KY (1)	Surface Coal Refuse Repr.	Active	4' Non-toxic	On pit floor		Regrading Revegetation	
KY (2)	Surface Auger	Active	4'	Against Highwall		Regrading Revegetation Daylighting	
KY (3)	Surface Auger Refuse Storage	Shut down - 11/98	4' Non-toxic			Regrading Revegetation	Shut down due to low coal demand. Will be reopened.
KY (4)	Surface Auger	Active	4' Non-toxic			Regrading Revegetation Seals	Acid material minimal
PA (1)	Surface	10/98	5' Non-toxic	10' above pit floor; 10' from highwall		Revegetation Daylighting Alk. Addition Clay Seals	Alternating layers of 2 ft "toxic", 2 ft clean spoil

ID	Type of Mine	Mine Closure Date	Cover Material	Placement	Blending of Overburden	Other Major BMPs	Comments
PA (3)	Surface	6/98	4' Non-toxic	10' above pit floor		Regrading Revegetation Daylighting Clay Seals	Alternating layers of 2 ft "toxic", 2 ft clean spoil
PA (5)	Surface	4/98	4' Non-toxic	20' above ground water; 10' from highwall	Yes	Regrading Revegetation	Alternating layers of 2 ft "toxic", 2 ft clean spoil
PA (6)	Surface Auger	8/96				Regrading Revegetation Daylighting	
PA (7)	Surface Auger Coal Refuse	5/96	15' Neutral Spoil; 2' Clay Shield	15' above pit floor; 15' from highwall		Regrading Revegetation Daylighting Alk. Addition	
PA (8)	Surface	Active				Regrading Revegetation Daylighting Alk. Addition	
PA (9)	Surface Rock	Active				Regrading Revegetation Daylighting Alk. Addition Biosolids	
PA (10)	Surface	11/95	Yes	Above ground water		Regrading Revegetation Scarification Bactericide	
PA (11)	Surface Auger	Active	4' Clean Fill	25' above pit floor		Regrading Revegetation Daylighting Alk. Addition	25 T/ac Lime added 24" Toxic 30" Clean
PA (13)	Surface Auger	1996		70' above ground water			
PA (19)	Surface	Active	10'	10'		Regrading Revegetation Alk. Addition	
TN (1)	Surface Auger	Active	Non-acid strata	On pit floor		Backfill Drains	
TN (4)	Surface Auger	Active				Alk. Addition Backfill Inun.	

ID	Type of Mine	Mine Closure Date	Cover Material	Placement	Blending of Overburden	Other Major BMPs	Comments
VA (1)	Surface Auger	10/98			Yes	Regrading Revegetation Daylighting	Excess of NP
VA (2)	Surface Auger	12/93	4' Non-toxic			Regrading Revegetation Topsoil Repl.	
VA (3)	Surface Auger	4/92	4' Non-toxic			Regrading Revegetation	
VA (4)	Surface	88/90	Yes			Regrading Revegetation Bactericide Underdrains	
VA (6)	Surface	Active	4' Non-toxic			Regrading Revegetation Underdrains Diversions Compaction	
VA (7)	Surface	Active	4' Non-toxic	4' above pit floor; 4' from highwall; not in bottom fills		Regrading Revegetation Daylighting Drainage	
WV (1)	Surface Deep	Active	6' Non-toxic			Regrading Revegetation Daylighting Alk. Addition	
WV (4)	Surface	11/95	Calcareous rock	On pit floor Against highwall	Surround w/calcareous rock	Regrading Revegetation Sed. Ditches	
WV (5)	Surface Ash Disposal	Active			Blend w/calcareous rock	Regrading Revegetation ALD Alk. Addition	
WV (6)	Surface	Active	1' non-toxic	On pit floor	Surround w/calcareous rock	Regrading Revegetation Alk. Addition	
WV (7)	Surface	6/87	10'	12-15'		Regrading Revegetation	24" Acid

ID	Type of Mine	Mine Closure Date	Cover Material	Placement	Blending of Overburden	Other Major BMPs	Comments
WV (8)	Surface Deep Ash Disp.	Active	4' Non-toxic	4' above pit floor		Regrading Revegetation Alk. Addition Underdrains	Add Alkaline Mat'l
WV (9)	Surface	1/91	Yes	Yes	Mixed w/ calcareous	Regrading Revegetation	

Theory

There are essentially four methods of special handling:

- Blending: mixing of naturally occurring calcareous and acid producing rocks.
- Dark and deep: placement of acidic materials consistently below the water table
- High and dry: placement of acidic materials consistently above the water table
- Alkaline redistribution: distributing alkaline material from areas with an excess to areas with a deficiency of neutralizing rock.

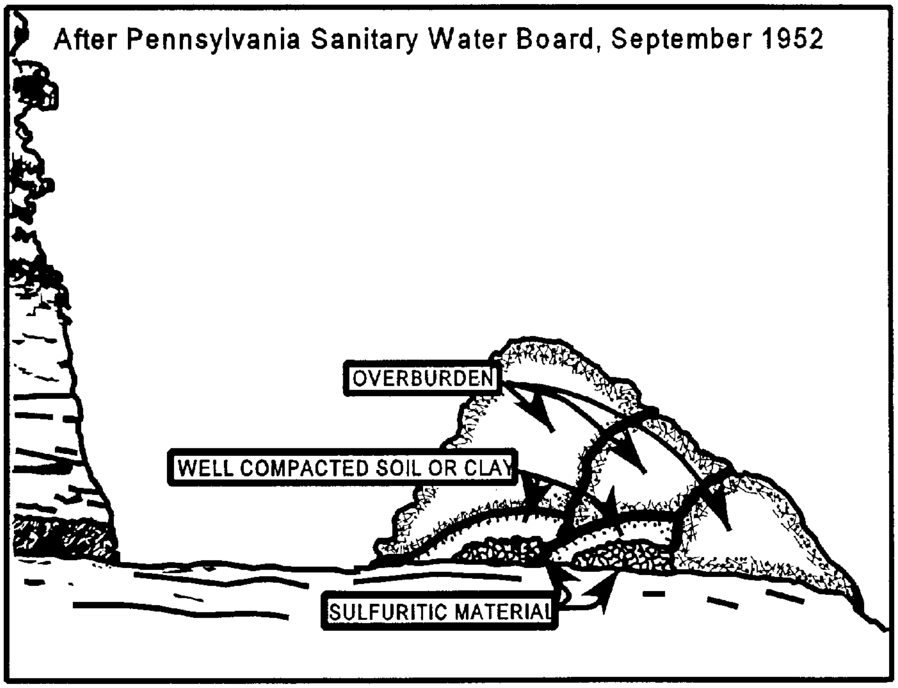
These four processes rely on different methods of avoiding acid production. Blending relies on the presence of a sufficient amount of calcareous rock throughout the overburden to produce enough alkalinity to offset acidity production from pyritic rocks. “Dark and deep,” or submergence, relies on the fact that water can contain only a small amount of dissolved oxygen (at most ~10 mg/L) and that water is therefore an effective barrier to atmospheric oxygen (Watzlaf, 1992). This lack of oxygen reduces the potential for the pyrite to oxidize and produce acid mine drainage. “High and dry” is based on the premise that ground water plays a role in the chemical reaction that takes place to form AMD and also acts as a transport medium. Placement above the water table cannot preclude the contact of water with pyritic material. Even in the unsaturated zone, there is gaseous water in the pore gases and ground water can adhere to particle surfaces hydroscopically. Thus, the primary effect of high and dry is avoidance of the transport of pyrite weathering products. Alkaline redistribution takes advantage of naturally occurring alkaline strata where portions of the mine site lack sufficient neutralizers. This alkaline material is redistributed such that all parts of the site have sufficient alkaline material to prevent or neutralize AMD.

Blending is being used on at least 5 of the special handling sites listed in Table 6.4a. Blending takes advantage of naturally-occurring calcareous strata. In its simplest form, mixing of the strata occurs in the coarse of overburden removal. Blending plans can be more intentional with specific strata targeted to assure adequate mixing.

Typically, in the Appalachians, acidic material is placed above the post-mining water table to minimize water contact. Calcareous materials, on the other hand, are placed such that their dissolution will be maximized, which can mean placement below the ground-water table. Combinations of special handling, alkaline addition, water management, and surface reclamation can allow the mine operator some control over acid- and alkaline-generating processes.

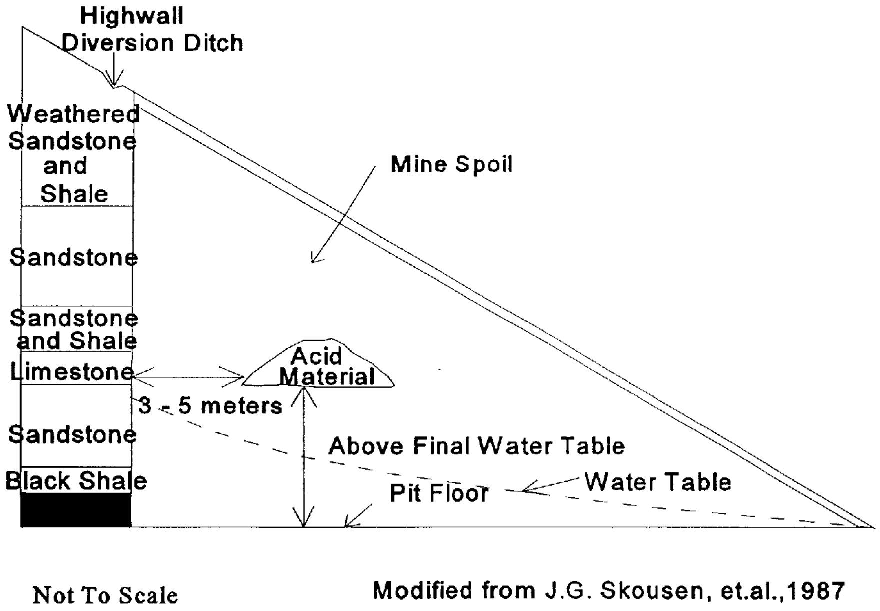
Probably the first special handling concept involved the recognition of black or very dark colored rocks and coal reject (“gob,” “bone coal”) as potential acid formers. Initially, it was proposed that the material be buried on the pit floor. Deep burial was thought to prevent contact with oxygen, and hence shut off acid production. This approach was discussed as early as 1952 by the Pennsylvania Sanitary Water Board and is shown in Figure 2.4a. The Sanitary Water Board also recommended highwall diversion ditches, pit floor drains, contemporaneous backfilling, and grading topography to limit water infiltration.

Figure 2.4a: **Early Recommendation of the Pennsylvania Sanitary Water Board for Handling Sulfuritic Material (suggested placement was on the pit floor under the unreclaimed spoil piles).**



Experience with deep burial of potential acid-forming materials in Pennsylvania showed that water quality problems were not always eliminated and sometimes were more severe. This is because of difficulties maintaining a sufficient water table to keep the material submerged. In most Appalachian states, special handling strategies began to evolve towards isolation of material above the post-mining water table with isolation from preferred ground-water flow paths. This remains the most common special handling technique used in the Appalachians and is illustrated conceptually in Figure 2.4b.

Figure 2.4b: **High and Dry Placement of Acidic Material (commonly used method of special handling in Appalachia).**



Modified from J.G. Skousen, et.al.,1987

Sampling and Site Assessment

Special handling plans are site specific and should include consideration of the following factors:

- **Geologic and Geochemical Conditions**: identifying acidity- and alkalinity-generating rocks in the overburden and determining the distribution, location, and volume of these rocks.

- **Hydrogeologic Conditions**: identifying ground- and surface-water conditions on the site. This would include examination of the geologic structure in relationship to the area to be mined; the occurrence, quantity, and quality of surface and ground water; and estimating the highest post-mining ground-water elevation in the backfill based on projected spoil transmissive properties.

- **Operational Considerations**: determining an appropriate mining method(s), sequence of mining, area to be mined, equipment to be used, and placement and amount of acidic and alkaline materials.

- **Field Identification**: determination of whether the alkalinity- or acidity-producing rocks be identified in the field so that they can be properly handled.

Geologic and Geochemical Considerations

Development of a special handling plan requires knowledge of the stratigraphic position, aerial extent, and total volume of acidity- and alkalinity-generating rocks (See Section 2.1). Horizontal sampling should be sufficient to define the lateral distribution of calcareous or high-sulfur strata. Likewise, vertical sampling should be of adequate resolution to discriminate calcareous and high sulfur strata. Too large a sample interval can result in loss of resolution and an inability to determine acidic or alkaline rocks. Acid-base accounting (ABA) is the overburden analysis procedure most commonly used for these determinations, and is discussed in Section 2.1.

Hydrogeologic Conditions

Hydrologic conditions are an important consideration in the design of a special handling plan. The position of the post-mining water table has bearing on where materials are placed, and is an important consideration in whether materials should be submerged below the water table or placed above the water table. Whichever method is chosen, the goal is typically to keep the material out of the zone of water table fluctuation.

The information needed to predict the post-mining water table includes a determination of the type of ground-water system (regional, perched, unsaturated zone). Considerations include premining ground-water levels, examination of ground-water conditions on nearby mined areas, relationship to adjacent streams, geologic structure, and water management designs in the mine plan and pit design. Overburden lithology and mining methods also play a role in the hydrologic characteristics of mine spoil, which ultimately impacts the post-mining water table.

Table 2.4b is a statistical summary of saturated thickness of ground water in spoil wells. The summary represents data from Kentucky, Ohio, West Virginia and Pennsylvania, with 5, 9, 27, and 83 wells, respectively. Data are from measurements made by Hawkins (1999). The data have been split into two categories, wells that were developed in spoil less than 15 meters thick and wells in spoil greater than 15 meters thick. The median saturated thickness for the deeper wells is twice that for the shallower wells (4 and 2 meters). This difference is significant at the 95 percent confidence limit. The range, however, in both categories is extreme, ranging from a fraction of a meter to 8 and 11 meters, respectively. The significance for special handling is profound. The "dark and deep" method will not work where the saturated thickness is a fraction of a meter. Conversely, "high and dry" will not work where the overburden is less than 15 meters and the saturated thickness is 8 meters. With a water table this high special handled acidic material would be near the surface, thus exposing it to oxygen and placing it near or within the rooting zone. The values in Table 2.4b are a "snapshot" in time. They were a one-time sampling event and do not represent seasonal and climatic variations which would extend the range. These data, however, provide insights into the variability of saturated thickness in mine spoil.

Table 2.4b. Saturated Thickness in Meters for Wells Developed in Appalachian Mine Spoil. (Hawkins, 1999).

	Saturated Thickness (meters)		
Summary Statistics	**All Wells**	**Spoil < 15 m Thick**	**Spoil > 15 m Thick**
Median	2.94	2.08	4.08
Minimum	0.18	0.26	0.18
Maximum	11.03	8.08	11.03
Lower Quartile	1.44	1.30	2.55
Upper Quartile	4.52	3.22	5.49
Number of Wells	124	69	55

It is also important to understand the sources of ground-water recharge. These sources include infiltrating precipitation, ground-water recharge through the final highwall or adjacent mined area, and upward flow through the pit floor. Monitoring wells, piezometers and aquifer tests may be necessary to provide insight into ground-water conditions. However, one should be cognizant that ground-water flow in the coal fields of the Appalachians, is largely fracture controlled and that wells not located in fractures may underestimate the amount of water present and it’s stratigraphic location. Another technique that can be used to estimate the amount of water present is the determination of flows from cropline springs. Insights can also be gained by looking at post-mining water conditions at nearby mines with similar geologic, hydrologic, and mining conditions.

Ground-water conditions are not “static” and vary seasonally and in response to recharge events. Monitoring should be sufficient to account for these variations. If, for example, the chosen placement technique is submergence below the ground-water table, and monitoring occurred only during the period of seasonally-high water, there may be times of the year when the water table would be below the placement position, and the special handled material would not be submerged. Alternatively, if the design is “high and dry” and monitoring only took place when the water table was low, there may be times of the year when the material is within or below the ground-water table.

Operational Considerations

Implementation of a special handling plan is also dependent on operational considerations. These considerations include: the amount of area to be mined, total overburden thickness, amount of material to be special handled, sequence of mining, time needed to complete mining, the need for blasting, the mining method, and equipment. The equipment should be appropriate for the special handling plan and site conditions. For example, truck and loader operations are able to easily remove distinct portions of overburden and to transport the overburden from one area of a mine to another. This type of segregation is not performed as easily with a dragline. Operational considerations will be discussed in more detail under Section 2.4.1.

2.4.1 Implementation Guidelines

Prior to developing a special handling plan the overburden should be sampled and acid- and alkaline-forming strata should be identified. Ground-water conditions should be well understood. The shape of the area to be mined should be considered. Only then can a plan be designed and the appropriate mining methods determined. Special handling plans should be clear, simple, and easily implemented by field personnel. Maps and cross-sections should show the positions of the materials to be special handled, and locations where these materials are to be placed. The materials should be readily identifiable in the field by color, position or rock type. The plan should be logistically feasible and field verifiable.

Geologic and Geochemical Considerations

Stratigraphic position of the material is an important planning consideration. If the material lies immediately above or below the coal seam to be mined, segregation is usually not a problem. Segregating strata located in other positions above a coal seam may be more problematic.

Feasibility will require consideration of equipment and blasting plans, how readily identifiable the strata is in the field, and costs of implementing the plan. “Fizz tests” using dilute hydrochloric acid can be performed in the field to identify alkaline strata. Unfortunately there is no comparable filed test for acid-forming strata.

Hydrogeologic Conditions

In situations where the operator is attempting to special handle acid-forming material by submergence, the length of time required for the post-mining water table to re-establish is important. If the operator wishes to place this material above the post-mining water table timing of water table reestablishment is not important.

The contribution to the post-mining water table from infiltrating precipitation during the first few years following reclamation will be less than that for unmined areas. Jorgensen and Gardner (1987), Guebert and Gardner (1992), and Ritter and Gardner (1993) investigated infiltration and runoff on newly reclaimed surface mines in central Pennsylvania. They found that infiltration rates on newly reclaimed mine soils are an order of magnitude lower than adjacent, undisturbed soil. However, within four years after reclamation, infiltration rates on some mine surfaces approach pre-mined rates (8 cm/hr). During the topsoiling operation, the soil is compacted by the equipment. This compaction promotes runoff. During freeze/thaw and wet/dry cycles, macropores develop in the surface soils which promote infiltration. The reestablishment of soil structure and plants also promotes infiltration.

Re-establishment of a post-mining water table will probably occur most rapidly for those mines where the lowest seam mined lies beneath the regional water table. Once the pumps are shut off, the regional water table will typically re-establish itself in a relatively short period of time. It becomes somewhat more difficult to predict the configuration and rate of rebound of the post-mining water table for mines with aquifers perched above the regional water table.

Where the mine is situated above the regional ground-water table, the hydraulic characteristics of the pit floor will determine whether a post-mining water table will be intermittent or permanent. If the pit floor material is a thick underclay, it will tend to serve as an aquitard inhibiting further downward migration. In other cases, the floor might be massive, fractured sandstone, which will allow the downward percolation of ground water. The post-mining, ground-water table is dependent on the structure of the lowest mined coal seam and the final highwall configuration. Where a down-dip highwall remains after mining and the pit floor retards vertical percolation, ground water may become impounded on the pit floor against the highwall, resulting in a higher post-mining water table than is typically the case with an up-dip highwall. In the case where a downdip highwall remains after mining and conditions are present which promote impounding of the ground water against the highwall, the "rule of thumb" placement 10 to 20 feet above the pit floor may be inadequate. If the intention is to keep the ground-water table low, it may be desirable to change the orientation and/or location of the final highwall to avoid impounding water, or to incorporate underdrains to minimize ground-water buildup in the backfill.

Spoil hydrology plays a role in the configuration of the water table. Low-permeability spoil will tend to maintain a higher water table than high permeability spoil. However, most mine spoil is highly permeable compared to undisturbed strata.

Operational Considerations

The mining plan is often based on the configuration of the land that is to be mined rather than the optimum configuration for overburden and coal removal. The stratigraphic and areal distribution of the acid- and alkaline-forming materials, as they relate to the mining plan, are important in determining how these strata can be special handled and how much is to be segregated. However, several pit orientations are often possible, and some may be more efficient for a particular handling plan.

Typically, when blasting, the total overburden column above the coal is broken up in one shot (lift). However, if the strata to be segregated lies at some distance above the coal, it will probably be necessary to blast in multiple lifts. The first lift removes the overburden above the unit to be special handled, and the unit to be special handled is removed separately. The remaining overburden above the coal is then removed. This process can easily increase blasting costs by more than 50 percent, and may result in poor rock breakage at the top of the lift because of stemming requirements (Getto, 1998). Blast hole "stemming" refers to material that is placed in the shot hole above the explosive. Stemming confines the energy of the explosion to the area around the explosive.

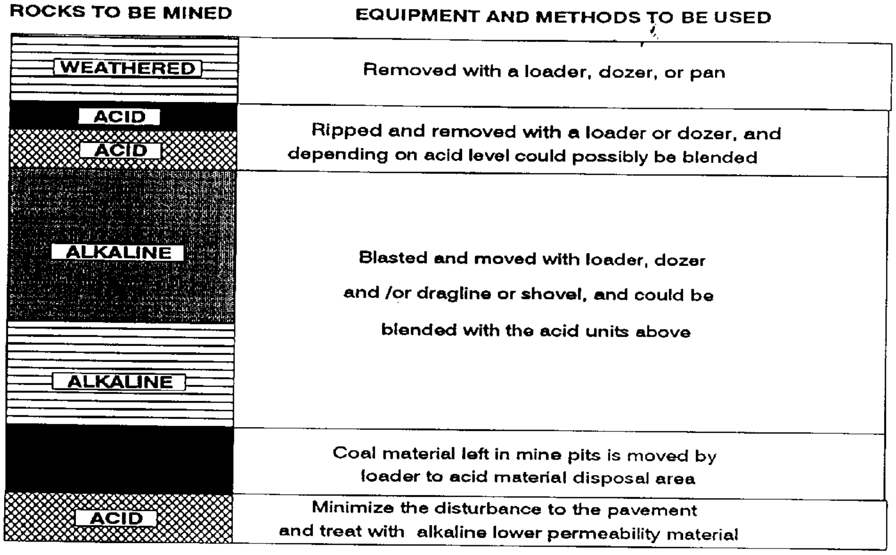
When potentially acid-forming strata are exposed, rapidly covering the strata helps prevent the onset of acid-forming reactions (Skousen and others, 1987). Perry and others (1997) examined seven sites with special handling and found timeliness of reclamation to have some influence on water quality. Extended exposure of unreclaimed spoil to infiltration and circulation of water and to oxygen apparently allows accelerated acid production.

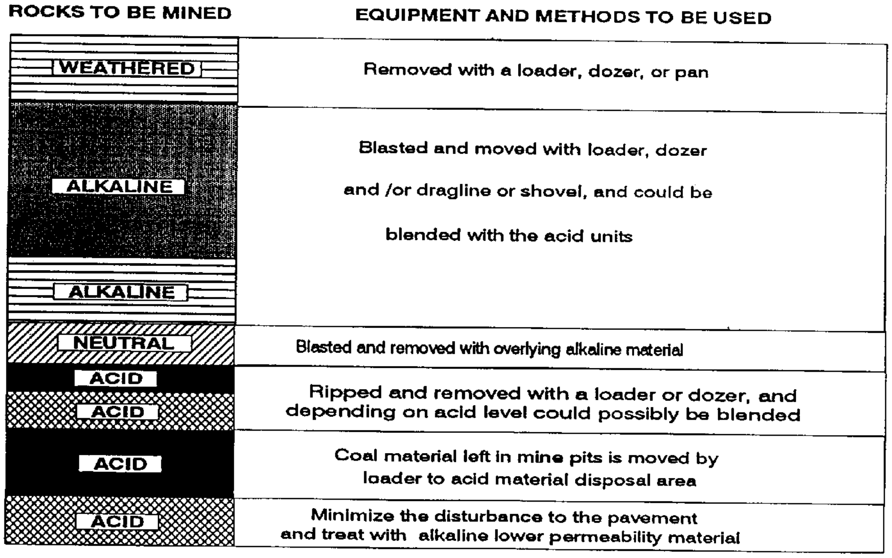
In general, segregation of spoil material is more difficult when using a dragline. In many cases, dragline operators do not have visual contact with the spoil that is being loaded. Also, typically, for a dragline to remove material it has to be "shot" and this often results in random material mixing. Even without mixing, draglines are not good at separating discrete stratigraphic layers.

"Blending" of overburden is often appropriate where the alkaline and acidic overburden occur in proximity. Blending may not require anything out of the ordinary and may occur simply as a consequence of overburden removal and replacement.

Two overburden removal plans are shown in Figures 6.4.1a and 6.4.1b. In Figure 6.4.1a, acidic material is located in the upper part of the rock column and requires separate removal. In Figure 6.1.4b, acid material is located directly above the coal. In the later scenario the entire overlying rock column can be blasted and removed in one lift, resulting in a blending of the alkaline- and acid-forming material.

Figures 2.4.1a and 2.4.1b: **Overburden Handling Procedures Depending on Stratigraphic Position of Acid-producing Materials (figures show the types of equipment that may be appropriate for handling the overburden).**





Another operational constraint occurs when the alkaline material is located beneath the coal being mined. Ripping (disaggregating) the pit floor can be done to incorporate alkaline material into the mine backfill at sites where alkaline strata exist below the lowest coal seam to be mined. This method involves removing the coal and ripping the pit floor to expose the alkaline strata to ground water on the pit floor. It is a suitable practice if the pit floor or underclay is not acid forming. The operator should have equipment capable of ripping the pit floor to the needed depth and sufficiently breaking up the alkaline zone. Typically, an average size dozer can rip to a depth of approximately 3 feet (1 m), while a D-11 dozer is capable of ripping to greater depths. If the alkaline material is at a depth greater than the depth accessible by ripping, the overlying material will need to be removed prior to ripping.

Limestone is generally a durable rock and is resistant to abrasion. When ripped, limestone tends to be of a much larger size than is normally associated with alkaline addition or redistribution, hence, increased surface area is limited. This method is adequate for mines where alkaline deficiencies are small, as it may have a limited effect on ground-water quality when compared to alkaline addition of fine-grained material or alkaline redistribution in the spoil. Section 2.4.4, Case Study 6 discusses a mine where the pit floor was ripped to expose alkaline material. This site is a rare case in which a Pennsylvania remining site resulted in degradation of water quality.

Special handling is an overburden management technique by which acidic and alkaline materials are selectively placed in the backfill. Special handling is rarely used alone and is typically used with other BMPs. Special handling techniques and associated BMPs include:

- Relocation of potentially acid-forming strata above the anticipated post-mining ground-water table,
- Constructing "pods" of acid-forming materials
- Capping the acid-forming material
- Submergence or flooding;
- Blending including alkaline redistribution;
- Operational considerations; and

- Incorporation with other BMPs such as alkaline addition, daylighting and surface- and ground-water management.

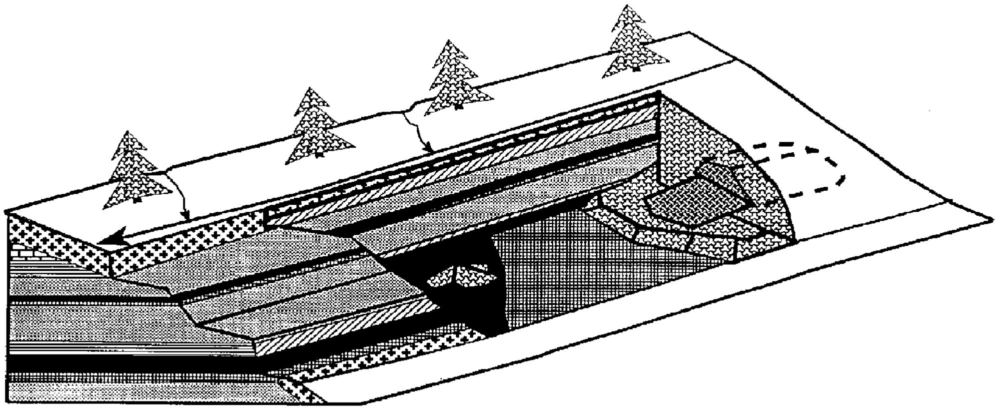
Discussion of Theory

Placement above the water table and encapsulation

Placement of acidic materials above the water table using segregation, isolation, and encapsulation techniques minimizes contact between acid-forming material and ground water. Special placement usually occurs in "pods" or discrete piles that are located above the expected post-mining water table in the backfill; thus it is often referred to as the "high and dry" method.

A few mines have constructed liners and caps that are designed to prevent ground-water contact with the acid-forming materials. This method is encapsulation. Segregation and isolation from the ground-water system does not totally prevent pyrite oxidation. Oxygen, microbes and water are still present in the pods. Segregation and isolation are directed at preventing massive downward leaching, or upward migration of oxidation products. The technique is illustrated and described in Figure 2.4.1c.

Figure 2.4.1c: Three-dimensional Conceptual View of High and Dry Placement of Acid-forming Materials



SEGREGATION AND ISOLATION (HIGH AND DRY) TECHNIQUES

STEPS INVOLVED IN SPECIAL HANDLING ACID MATERIALS

1) Conduct drilling and blasting to expose acid materials,
2) Remove acid materials with a loader or dozer,
3) Construct the disposal site in the backfill where:
   - at least 10-20 feet from the highwall,
   - above the final water table to be developed in the post mining backfill,
   - out of the root zone probably at least 10- feet below the surface
   - away from natural drains that would flow across the post mining backfill
4) Place the acid material either in on the constructed pad in the backfill or in a in a temporary storage for transport offsite or to another part of the permit
5) Add alkaline material to acid material to reduce acid generation, and
6) Complete the reclamation and revegetation as quickly as possibly

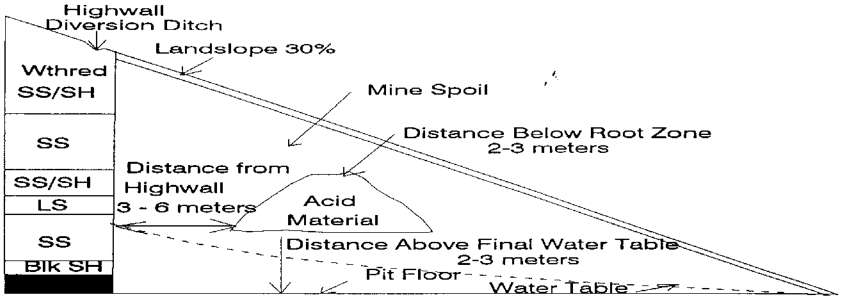
Construction of acid-forming material pods is one of the oldest techniques used to isolate potentially acidic strata. The purpose is to inhibit percolation or recharge of ground water through the potentially acid-forming strata. Pods are constructed in compacted layers, sometimes with potentially acid-forming material alternated with alkaline strata. Pods are placed above the highest anticipated ground-water elevation in the backfill, and usually at least 25 feet away from the final highwalls and lowwalls and 10 feet from the surface. Potentially acid-forming material needs to be rapidly excavated and covered to prevent prolonged exposure of the materials to oxygen and water.

Cravotta and others (1994a and 1994b) compared the abilities of a dragline versus trucks and front-end loaders on two areas of the same mine to special handle acid-forming strata. Both handling methods tended to invert the original rock column. Where loaders were used, pyritic shale was selectively placed in pods near the final surface, and only low sulfur material was near the pit floor. On the area mined with a dragline, the overburden with the highest-sulfur content was placed near the surface, but the sulfur contents for the material at the bottom of the spoil were higher than they were for the area mined with loaders. A special handling study in Montana with dragline mining also reported that the overburden profile was inverted (Dollhopf and others, 1977a, 1977b, 1978, and 1979). Both studies compared chemical and lithologic properties of drillholes in mine spoil to premining conditions.

Improper construction of pods, especially the failure to construct an impervious cap over the top of the pod, can result in conditions favorable to the formation of AMD. High and dry burial places pyritic material closer to the surface where atmospheric oxygen is more abundant. This, in conjunction with percolating precipitation and the high concentrations of pyrite, creates an environment that can allow the bacteria *Thiobacillus ferrooxidans* to thrive. Schueck (1998) found severe AMD formation associated with segregated, but improperly isolated pyritic material. Subsequent drilling and ground-water sampling confirmed that the AMD associated with these improperly constructed pods was more severe than AMD generated elsewhere on the site. In many cases, the operator confirmed that the pods were segregated acid-forming materials, often pit cleanings, but that impervious caps were not constructed on top of the pod.

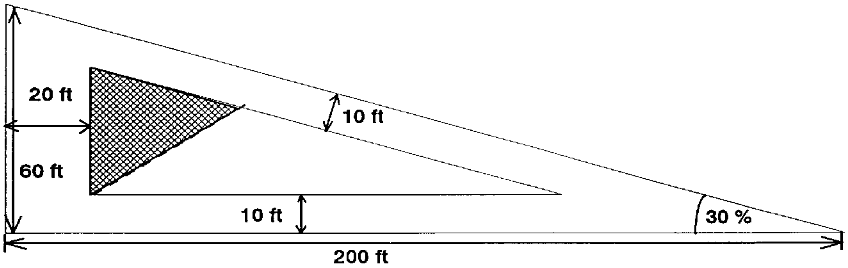
Placement of acidic material into a contour surface mine backfill should fall within a projected target zone (See Figure 2.4.1d). The bounds of this zone are established by the distance from the highwall, height above the pit floor, post-mining water table, the depth below the root zone, the distance from the outcrop, and the distance from reestablished drainageways and various barrier areas. In the example provided in Figure 2.4.1d, a simplistic approach is demonstrated to indicate the <u>maximum</u> amount of acid material that can be placed in the target zone.

Figure 2.4.1d: Projected Target Zone Determination for Placement of Acid Forming Material within the Backfill



Not To Scale

Modified from J.G. Skousen, et.al.,1987



Total Mined Area Triangle = 6000 sq ft

Acid Material Target Area Triangle = 1900 sq ft

32% of the Backfill is Available for Disposal

Reduction of the Target Zone Due to the Angle of Repose (Loader) Limitation:

27% of the Backfill is Available for Disposal

The values used for the Total Mined Area Triangle (TMAT) include:

Maximum Highwall Height	60 feet
Coal Thickness	4 feet
Stripping Ratio	15:1
Landslope	30%
Calculated Maximum Pit Floor Width	200 feet

The values for the Acid Material Target (Area Triangle TMAT) include:

Distance from the highwall	20 feet
Distance above the pit floor	10 feet
Depth below the root zone	10 feet
Distance above the post-mining water table	Variable
Away from re-established surface drains	Variable

The TMAT square footage value is 6000 feet^2 using the maximum pit floor width and highwall height. The maximum height of the TMAT to which the acid material could be placed (and still meet the segregation and isolation disposal conditions) is 34 feet on the side nearest the highwall. The maximum width of the TMAT is 112 feet. At most, only 32 percent (roughly one third) of the total mined area can be used for acid material placement. This value will change depending on highwall height, land slope and placement constraints. As a general rule, as land slope increases, the size of the target area for acidic material will decrease.

Further reductions in the amount of acidic material placement result from the practicalities of handling and construction of the top portion of the TMAT. If the material is dumped at the angle of repose (assumed to be 30) before being compacted, a portion of the TMAT would not be available for use during placement. This zone (cross-hatched area in Figure 2.4.4b) represents about 5 percent of the fill cross section. Under these conditions, no more than approximately 27 percent of the total backfill is available for acidic material placement. This target triangle area for acidic material placement is not continuous around a hill (along the contour) because of the natural drainageways, which occur every few hundred feet in the Appalachian Plateau. Other obstacles such as gas wells, gas lines, power lines, and houses may further reduce available placement area, and further limit the lateral extent of placement. A high water table will often require placement more than 10 feet above the pit floor. Due to these constraints, the acid material should be less than 20 percent of the material to be backfilled.

Meek (1994) monitored acid production on surface mined areas with segregation and several different alkaline amendments. Acid load, on an area with segregation, was reduced about 50 percent compared to a control area with no segregation or alkaline addition.

Phelps and Saperstein (1982) suggested that pods should have a bulk density of 1.1 to 1.5 times the surrounding spoil to minimize infiltration. These investigators also observed that the highest spoil bulk densities occurred at 50 to 80 percent depth of spoil for most mining methods. They suggested that the high density spoil zones should be favorable locations for pods, if hydrologic requirements are satisfied.

Schueck and others (1996) reported on attempts to grout buried refuse with fluidized bed combustion ash as a method of isolating pods after the fact. This was done on a site where the lower Kittanning coal seam was mined and most of the overburden is apparently acid-forming. Grout was injected directly into the buried pods to fill the void spaces and directly coat the refuse. Grout caps were also constructed over several of the pods. Combined grouting affected only 5 percent of the site but resulted in a 50 to 60 percent decrease in acid concentration in downgradient monitoring wells.

Short exposure time before burial and reclamation can reduce weathering and acid generation. As the acid-forming material remains exposed, rocks break down exposing more surface area, and weathering proceeds to produce acid products along with the subsequent buildup of soluble acid salts. In practice, potentially acid-forming materials are often stockpiled until enough material to start pod construction is accumulated. To reduce exposure, some mines in Pennsylvania construct temporary stockpiles covered with soil and vegetation, or cover the material with lime for neutralization.

When acid-forming material is handled from a cut, the construction of pods should be concurrent with mining and backfilling. This ensures that acid-forming material is rapidly buried. Rose and others (1995) reported on experimental test pods where the high-sulfur material was stockpiled for several months before construction of the pods. Some pods unexpectedly produced very acidic drainage even though they had been amended with alkaline materials. Delay in construction of the pods may have allowed significant acid generation to start even before the acid material was placed in pods.

Capping: A cap refers to an overlying low-permeability zone created through placement of compacted, fine-grained soil material (clay), combustion byproducts (fly ash, fluidized bed wastes), kiln dust, or synthetic (plastic or geotextile) fabric. The cap is significantly less permeable (at least two orders of magnitude difference) than the surrounding material. Caps inhibit or prevent the infiltration of water into acidic material from above.

The term liner is normally used in the context of an underlying low-permeability zone created through placement of an earthen or synthetic material which is at least two orders of magnitude less permeable than the surrounding units. However, materials used for liner construction can also be used as a cap over the specially handled pod. Liners restrict or prevent the adjacent and underlying ground water from encountering the acid-forming material. Caps and liners can also restrict diffusion of atmospheric oxygen; a key component of acid generation.

A detailed study of special handling at a Montana surface coal mine included the construction of a 3-feet-thick clay cap over special handled material (Dollhopf et al., 1977a, 1977b, 1978, and 1979). Construction of the cap required several pieces of equipment, including pans and bulldozers. Maintaining clay at optimum moisture content for maximum compaction was difficult; water sometimes had to be added to the clay material. The region in which the mine was located was semi-arid. Cost of special handling with the clay cap was about 1.5 times "normal" operations due in large part to idling the dragline at certain stages of cap construction. An experienced mining engineer was needed on-site to supervise operations and schedule equipment. Special handled material was maintained in a dry state, and the investigators concluded that capping was successful.

Synthetic plastic and geotextile “liners” are a technology borrowed from the waste management industry. Thick, high-strength plastics of 20, 30, 40 or even 80 mil thickness can be used to isolate acid-forming material from infiltrating precipitation and ground-water interflow. The liners are designed to be resistant to a wide range of leachate conditions. They are laid out in sheets with the seams welded by heat or solvent or stapled. Synthetic liners require a smooth, firm base to avoid puncture or stretching. A potential area of weakness is the seams which should be joined properly to avoid leakage or failure. The cost of synthetic liners is high in comparison to other capping methods. Refuse piles may be amenable to capping with liners due to their engineered structure and more controlled particle size distribution. Meek (1994) reported that a plastic cap reduced acid load by about 70 percent compared to no special handling and that a cap was one of the most effective treatment measures evaluated in that study.

Caruccio and Geidel (1983) used a 20-mil liner at a 40-acre site in West Virginia as an infiltration barrier. The acid load from two highly acidic seeps was reduced such that the liner would pay for itself in 6 years. Because of a steep outslope, the liner only covered the flatter, upper portion of the mined area. Recharge along the outslope area probably accounted for most of the remaining flow to the seeps.

Earthen materials can be placed and compacted to form relatively impervious-flow barriers. Cap thickness is frequently an issue, but a rule-of-thumb from the solid waste industry is a 2-foot minimum. Little information, directly applied to mining, is available to determine if 2 feet is adequate. Permeability of a cap is affected by grain size, mineralogy, and moisture content of the earthen material, the degree of compaction, and the thickness of the lifts (lifts of 6 inches are frequently required). Bowders and others (1994) tested mixtures of flyash, sand, and clay as candidate hydraulic barriers in minespoil. They found that a mix of particle sizes and materials provided the highest packing density and lowest permeability, rather than flyash alone. Hydraulic conductivity varied about 2 orders of magnitude from 10^{-5} to 10^{-7} cm/sec over different mixes and moisture contents. Rubber tired equipment or a sheepsfoot roller is required for good compactive efforts. Caps constructed of earthen material can shrink and crack if allowed to dry out. Caps can also be damaged by differential settlement of spoil, which commonly continues for over 10 years after backfilling.

Design geometry of the cap may enhance or reduce the volume of water passing through the cap. A dome shape tends to "shed" water, while flat caps could impound water.

Handling of Acid Materials Using the Submergence or "Dark and Deep" Technique

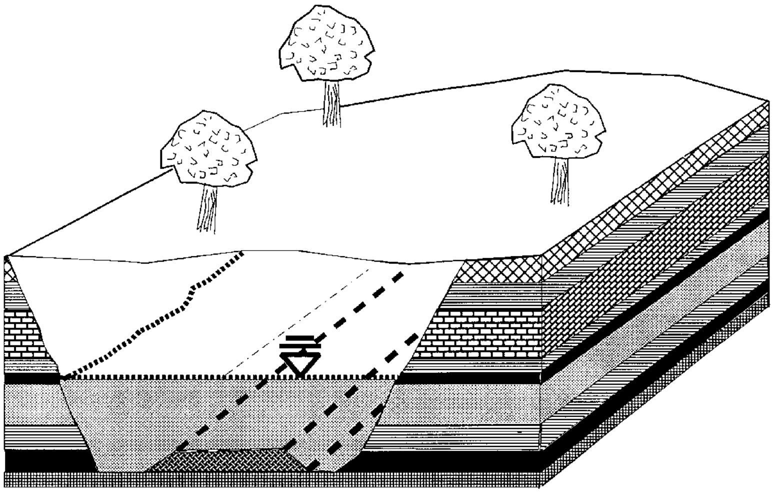
Submergence involves the placement of special handled material below the lowest level of the water table. This method is expected to exclude oxygen from pyrite and is similar in concept to sealing and flooding of underground mines to reduce acid generation. Watzlaff (1992) showed that complete submergence will virtually shut down pyrite oxidation, even with maximum dissolved oxygen. Submergence or "dark and deep" generally requires a relatively flat area with a thick saturated zone. A stationary water table helps to produce a near stagnant condition. The technique is not widely used in Appalachian states because of thin and seasonally variable saturated zones. It is used in Canada and elsewhere for tailings disposal at hard rock mines (Fraser and Robertson, 1994; Robertson and others, 1997) and in the Interior Coal Basin of the United States where thick and stable saturated zones are more conducive to this method.

In Canada, tailings disposal in lakes usually involves water bodies with minimal circulation and anoxic conditions at depth. Tailings may also be buried on the lake floor by naturally accumulating sediment and organic debris, providing a further barrier to oxygen. In the US mid-continent, topographic relief is low, water tables tend to be near ground surface, and flow gradients are small. Surface mining is conducted mainly by area mining methods, and the final cut is often allowed to flood at reclamation, leaving a relatively deep narrow lake incised into the terrain.

Leach and Caruccio (1991) characterized backfill materials as consisting of three broad hydrologic zones. The first zone is the vadose (unsaturated) zone or zone of high oxygen concentration. Next is the zone of water-table fluctuation with alternately higher and lower oxygen concentration. The final zone is saturated, with very low oxygen concentration. Leaching experiments representing the three zones showed acid load under saturated conditions to be about 5 percent of that produced in the unsaturated zone. They recommended that acid-forming material should be in the saturated portion of the backfill to restrict oxidation.

Submergence has not been widely documented as a disposal technique in the Appalachian coal fields. Perry and others (1997) found that submergence of acid material buried on the pit floor produced very poor quality drainage at one Appalachian surface mine. In the Interior Coal Basin of the central United States, flooding of final pits and development of a thick saturated zone occurs on many sites. The water quality of most flooded last cut lakes is alkaline; some also have elevated concentrations of dissolved solids and sulfate (Gibb and Evans, 1978). The alkalinity is due to calcareous bedrock and till. A typical submergence scenario for the Interior Coal Basin is shown in Figure 2.4.1e.

Figure 2.4.1e: Schematic of Special Handling of Acid-forming Materials by the Submergence Technique



SUBMERGENCE (DARK AND DEEP) TECHNIQUES

STEPS INVOLVED IN SPECIAL HANDLING ACID MATERIALS

1) Conduct drilling and blasting to expose acid materials,
2) Remove acid materials with a loader or dozer,
3) Construct the disposal site in the backfill at a location:
   - on the mining pit floor,
   - below the final water table to be developed in the post mining backfill,
   - within a hydrologic "no flow" (very low) zone,
   - out of the root zone probably at least 10- feet below the surface
4) Add alkaline material to acid material to reduce acid generation, and
5) Complete the reclamation and revegetation as quickly as possible.

Submergence in the Appalachians entails some risk. If post-mining hydrology is not correctly anticipated, substantially more acid may be generated. Weathering products are leached or mobilized by flowing ground water. Therefore, it is imperative that the site hydrology be well understood. Information necessary to characterize the ground-water flow system includes:

- Estimates of ground-water recharge to ensure a permanent and sufficiently thick water table.
- Determination of how isolated the site is hydrologically from adjacent ground-water systems.

- Determination of whether the backfill can be constructed to produce a reservoir that will keep the acid-forming material continually submerged.

This type of disposal during the mining operation should involve handling the acid-forming material only one time before permanent placement (such as on the pit floor of a previously excavated pit).

A possible disadvantage of submergence is that pyrite oxidation may have already begun before the material is submerged, forming ferric-sulfate salts. This can occur during storage and while the water table is rebounding. Upon dissolution, these salts release ferric iron that can oxidize pyrite and sustain acid generation in the absence of atmospheric oxygen. If material handling is unsuccessful (i.e., the water table is not stagnant or thick enough), resultant drainage problems can be large scale. This technique might require a relatively long lag time before success/failure can be determined and large areas can be impacted before the results are known.

Handling of Acid and Alkaline Materials Using Blending Techniques and Alkaline Redistribution

Blending is the mixing of rocks on a mine site to promote the generation of alkaline drainage. The term "blending" has been used widely in the past to refer to the mixing that occurs during the routine mining process. This technique has been recognized since at least the mid 1970s. Anecdotal information exists to suggest that it is an effective practice. It can be effective if sufficient carbonates are present and can maximize the contribution of carbonates by mixing them with acid-forming rock. This can inhibit oxidation of pyrite as well as neutralize acidity. In theory, it is possible to blend rocks from virtually any position in the overburden column, but the actual practice is dependent on the mining method and spoil handling equipment.

A spoil mixing experiment with dragline mining was conducted in Montana where saline or “toxic” overburden was present in varying amounts across a mined area (Dollhopf et al., 1977a, 1977b, 1978, and 1979). Premining distribution and properties of the toxic material were determined from overburden analyses. Systematic drilling and sampling of the reclaimed spoil after mining showed:

- When the toxic material constituted about 5 percent or less of the overburden, the material was undetectable in the regraded spoil.
- When the toxic material constituted 5 to 15 percent of the overburden, partial to complete mixing occurred.
- At concentrations greater than 15 percent toxic material, partial mixing occurred.

Special handling and spoil mixing were conducted on this mine primarily to protect the root zone. It should be kept in mind that the potential problem was saline overburden, not pyritic overburden. Dilution is not always a solution when dealing with pyritic materials. Dilution of pyritic materials with inert materials frequently does not prevent the formation of AMD. Broadly disseminating a substantial amount of reactive, acid-forming rock throughout relatively inert material can allow for widespread generation of AMD.

Alkaline redistribution is a special handling strategy that is used when only a portion of a mine site contains and large portions are devoid of calcareous materials. Without redistribution or off-site importation of alkaline materials (alkaline addition), the portions of the site lacking calcareous materials will produce acidic mine drainage. Examples of sites where alkaline redistribution was used are given in Case Studies 2 and 5 in Section 2.4.4.

General considerations for use of alkaline redistribution include:

- Areal distribution of alkaline materials,
- Position of alkaline materials within the overburden section,
- Volume present at the mine site, and
- Calcium carbonate content of the material.

Location and available volume of alkaline material largely determine the feasibility and effectiveness of alkaline redistribution. If the material is present as a discrete identifiable unit, it can be moved as such. However, if the alkaline material is laterally discontinuous, or dispersed through the column, a plan to isolate and move this material will be difficult to implement.

Alkaline redistribution strategies can include:

- Determining the proportions of alkaline material to be placed on the pit floor, mixed into the spoil, and added to the spoil/soil interface,
- Determining the methods for incorporating the alkaline material into the backfill,
- Choosing the best pit orientation to minimize haulage of the alkaline material,
- Designing a multiple pit operation to facilitate redistribution of alkaline material, and
- Ripping the pit floor to expose alkaline material (when present) beneath the coal.

Actual implementation of alkaline redistribution generally requires the use of rock trucks, since the alkaline amendment is not an integral part of coal overburden removal. The amount of alkaline amendment per acre is calculated via overburden analysis and mass balance equations.

Operational Considerations

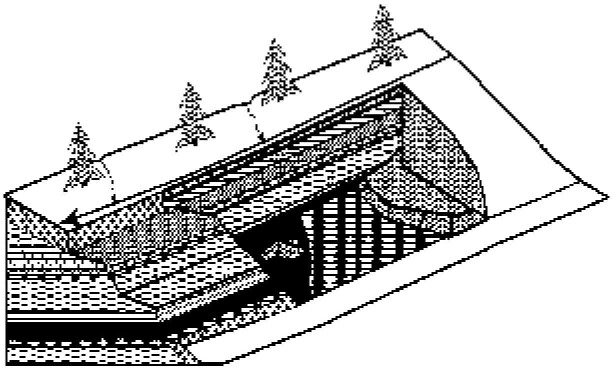
When special handling is part of the mine plan, keeping the pit clean (e.g., removing pit cleanings) and quickly covering acid-forming strata are simple and important activities to reduce the potential for acid production. Removing pit cleanings, will ensure that any ground water that reaches the pit floor will encounter reduced amounts of potentially acid-forming material.

Equipment availability is an important consideration in the development of the special handling plan. If the proposal is to move discrete rock units, a truck-shovel operation may be necessary. In addition, if two pits are open at once, a truck-shovel operation facilitates the movement of overburden from one pit to another. However, if large sections of strata are to be removed, a skilled dragline operator may be required.

If an alkaline stratum lies adjacent to a potentially acid-forming stratum, the strata may become mixed without additional effort during the overburden removal operation, and separation of the potentially acid-forming strata may not be needed.

Generally an excess of neutralizers dispersed throughout the overburden profile is necessary to offset both acid production and imprecise mixing. A simple blending plan is shown in Figure 2.4.1f.

Figure 2.4.1f: Blending and Alkaline Redistribution Do Not Require the Isolation of Acid-forming Materials in Isolated Pods



BLENDING AND ALKALINE REDISTRIBUTION TECHNIQUES

STEPS INVOLVED IN SPECIAL HANDLING ACID AND ALKALINE MATERIALS

1) Conduct drilling and blasting to expose acid and alkaline materials,

2) Remove acid and alkaline materials with a loader or dozer,

3) Blend (mix thoroughly) the acid and alkaline materials, and

4) Complete the reclamation and revegetation as quickly as possible.

2.4.2 Verification of Success or Failure

A critical step in successful special handling is to ensure that the special handling plan is properly implemented. It may be necessary to periodically perform additional testing of the overburden to assure that the proper material is being handled.

Inspections by the regulatory agency, of sites with special handling as a BMP, should be frequent and detailed enough to document compliance with the mining plan. An inspection implementation checklist identifying key aspects of the plan will be useful.

Implementation Checklist

Recommended items to be considered during the permit review process include:

- The overburden data should be sufficient enough to identify which strata will require handling.
- The overburden data should be sufficient enough to provide representative sampling for the mine. This will typically require multiple bore holes and appropriate vertical sampling.
- Plans should be clearly designed with appropriate maps, cross-sections and narrative.
- Plans should be feasible in the field and not just on paper. For example, the strata to be special handled should be easily identifiable in the field.
- The plan should be enforceable.

Recommended items to consider in a special handling implementation inspection checklist include:

- Field implementation should correspond with the plans in the permit application (e.g, agreement with the permit maps, cross-sections and narrative)
- The appropriate equipment should be available.
- The blasting method should be appropriate.

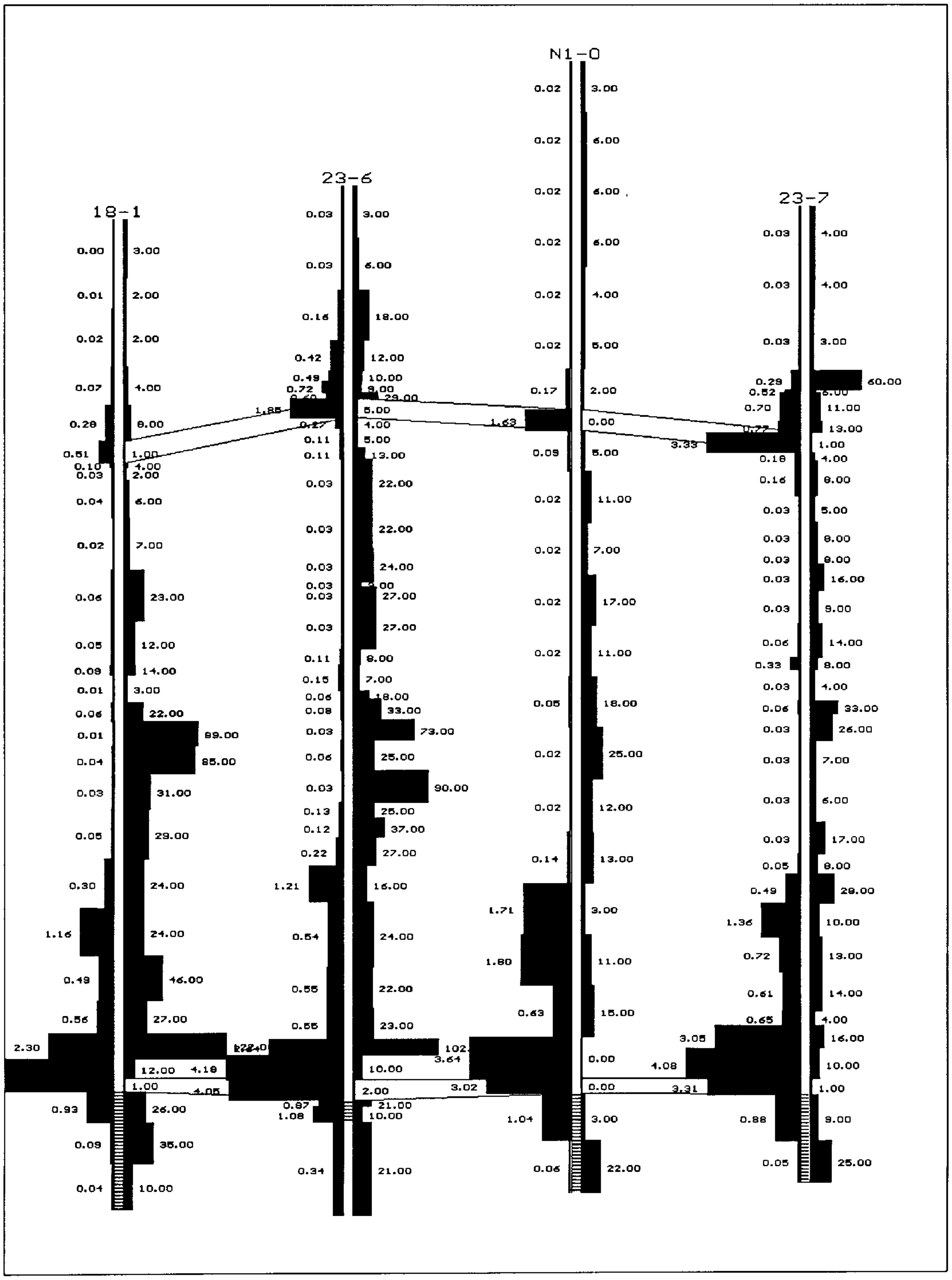
- The material to be special handled should be identifiable in the field by the equipment operators.
- The water monitoring data should be submitted.

2.4.3 Case Studies

Case Study 1

Cravotta and others (1994b) compared the distribution of sulfur and neutralization potential in undisturbed overburden strata (Figure 2.4.4a) with the post-mining redistribution of these parameters in the disaggregated mine spoil (Figures 2.4.4b and 2.4.4c) for two mining methods. The mine site studied was a reclaimed surface mine on two adjoining hilltops in Clarion County, Pennsylvania. The southern area was mined with a 45 yd^3 dragline. The northern area was mined with bulldozers and front-end loaders, which selectively handled the high-sulfur strata near the coal.

Figure 2.4.3a: **Distribution of Sulfur and Neutralization Potential for Bedrock at the Special Handling Site in Clarion County, PA. (Drill logs are to scale. Most sample intervals for N1-0 are five feet.)**



The original plan for the 16-acre northern area called for placing the high-sulfur rock in pods 10 feet above the pit floor, with low-sulfur material placed between the pods and the pit floor. Drill holes N2-0 and N2-2, located 5 feet apart, encountered one of the specially handled pods. The other drill logs show that mining, in general, inverted the high-sulfur (>0.5 percent) material and located it near the spoil surface. Most logs show low-sulfur (<0.15 percent) material near the pit floor. Maximum saturated thickness of spoil in the northern area was 18 feet and in the area of N2-0 the saturated thickness was 10 feet. The spoil sulfur data and spoil water level data suggests that the high-sulfur spoil was successfully placed above the water table within the northern area. The permit specification for placement 10 feet above the pit floor, however, would have been inadequate to keep the high-sulfur material above the spoil water table.

Spoil in the 34-acre southern area was also inverted, with the highest sulfur rock predominantly in the upper part of the spoil. The sulfur in the lower part of the spoil is typically between 0.25 and 0.4 percent, higher than typical on the northern area where the spoil was selectively handled. The highest saturated thickness in the spoil was about 20 feet. Thus the highest sulfur material in the southern area was also placed above the water table.

Spoil handled by bulldozers and loaders can be expected to have a more uniform particle-size distribution, exhibit similar or greater compaction, and exhibit lesser hydraulic conductivity than that handled by the dragline (Hawkins, 1998; Phelps and Saperstein, 1982; and Phelps, 1983). Air circulation commonly was lost in shallow spoil during air rotary drilling in the dragline-mined southern area. However, no air losses occurred in the bulldozer-mined northern area, suggesting greater compaction and more uniform particle size distribution from bulldozers and loaders than from a dragline. Nonetheless, hydraulic conductivities for saturated mine spoil were similar among the two areas. For saturated spoil, median hydraulic conductivities were $10^{-3.8}$ to $10^{-3.6}$ m/s in each area. The similarity in hydraulic conductivities could result from similar lithologies, and piping and settling processes (Hawkins, 1998, and Pionke and Rogowski, 1982) by which fines are transported downward and large voids fill or collapse. Mine spoil in the southern area is several years older than that in the northern area, so a longer time has elapsed for these processes to occur.

Figure 2.4.3b: **Distribution of Sulfur and Neutralization Potential for Spoil in the Northern Hilltop Where Bulldozers and Loaders Were Used (Note the "pod" of selectively handled high sulfur material in N2-0 and N2-2. Sample interals are five feet.)**

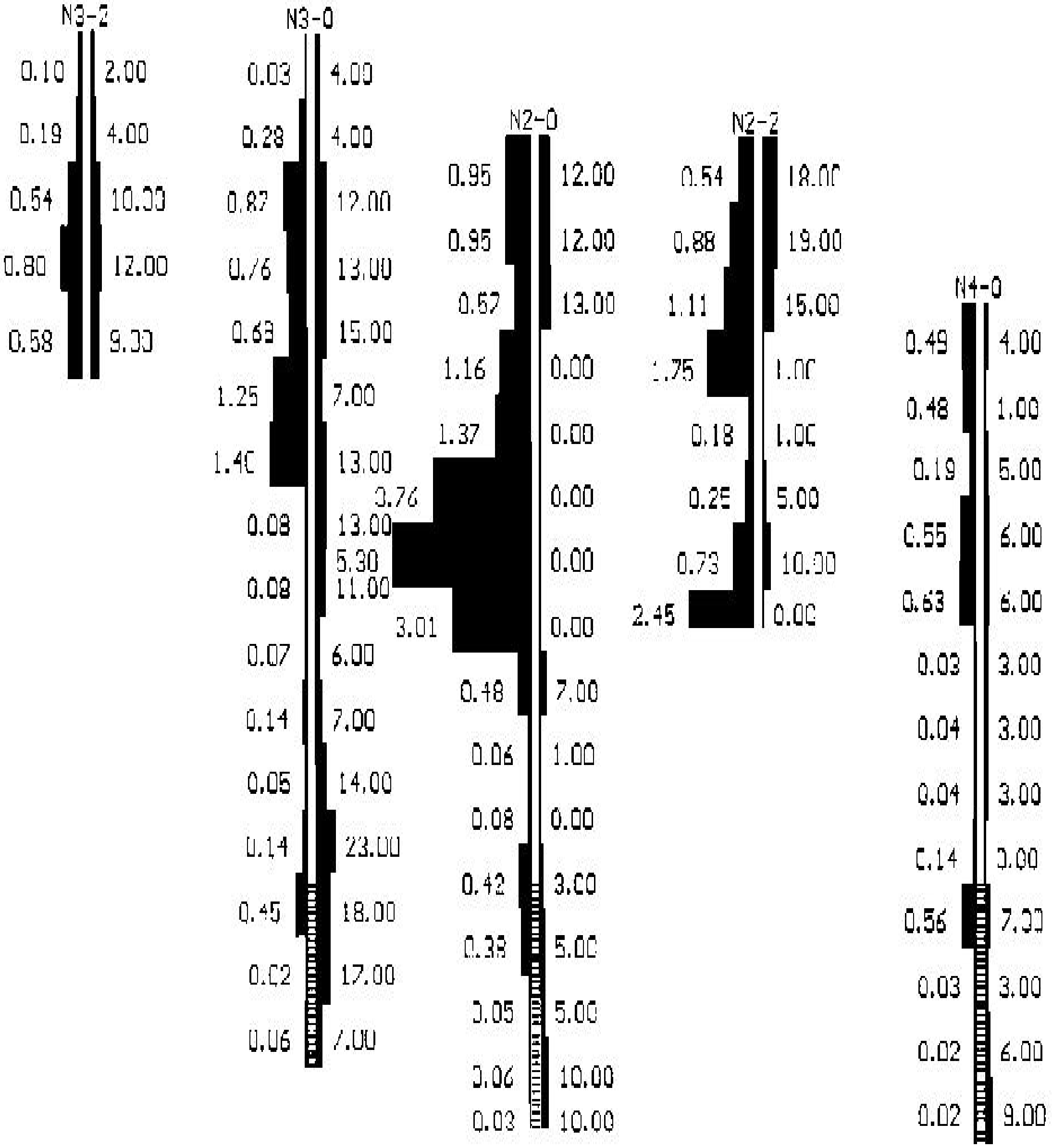
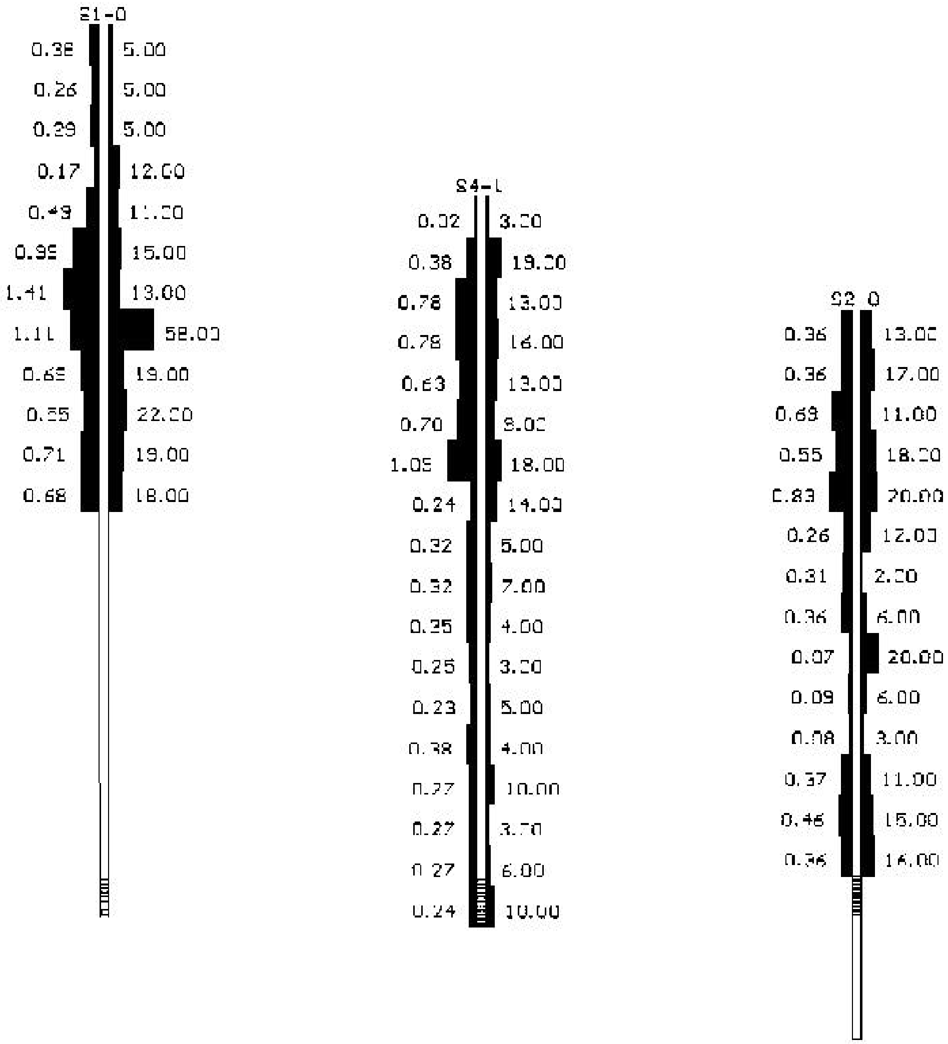


Figure 2.4.3c: Distribution of Sulfur and Neutralization Potential for Spoil in the Southern Hilltop Where a Dragline was Used (Sample intervals are five feet.)



Alkalinity, sulfate, iron, and manganese concentrations in the spoil ground water produced by the selective-handling method was similar to that in spoil produced by the dragline method. Median values for alkalinity of ground water in the saturated zone were between 100 and 400 mg/L. Sulfate ranged from 600 to over 1000 mg/L (Cravotta and others, 1994b).

Case Study 2 (West Virginia)

Skousen and Larew (1994) describe the redistribution of alkaline material from separate but adjacent mine sites. Calcareous rock was hauled from a mine extracting Bakerstown coal to a mine on the upper Freeport coal. Alkaline redistribution consisted of placement of about 3 feet of calcareous shale on the pit floor, partial backfilling, then placement of acidic material about 20 feet high in the spoil, followed by capping with more calcareous shale. A pre-existing, mildly acidic discharge (acidity about 75 mg/L $CaCO_3$) was ameliorated and made alkaline.

Case Study 3 (Clearfield Co., PA)

A cementitious cap constructed of fluidized bed combustion (FBC) ash mixed with waste lime has been placed on a 97 acre reclaimed mine site in Clearfield County, Pennsylvania. Hellier (1998) reports on the successful efforts of the operator. Surface mining on the lower and middle Kittanning coal seams began in the 1940s on this site. Upon completion of the mining in 1991, the operator was required to pump and treat an acidic post-mining discharge. Treatment costs threatened to bankrupt the operator. Most of the mining on the site predated special handling techniques. The operator removed the top 3 feet of material and spread a 3-feet layer of FBC ash mixed with 10 percent waste lime. Water was added to increase the moisture content. The ash/lime mixture hardened to form a low-strength cement. The top material was then replaced and revegetated. The cap served to inhibit infiltration, which was thought to be the primary source of water at this site. The cap would also inhibit oxygen from entering the backfill. At 80 percent completion, the operator no longer has to provide chemical treatment, pumps significantly less water, and the chemistry of the water remaining in the backfill has improved. A passive treatment system, which is in place, is adequate to mitigate the reduced flows of AMD.

<u>Case Study 4</u> (Green Co., PA)

A mine in Greene County, Pennsylvania produced both alkaline and acid water on two segment phases (Perry and others, 1997). The two segments had similar geology and hydrology, and were mined by the same company. Alkaline drainage was produced on the segment where mining was completed without stoppage and where a special-handling plan was followed. Acidic drainage was produced from the Phase 2 segment where mining ceased for an extended period before the site was completely reclaimed. The poor quality drainage on the Phase 2 segment was attributed to weathering of partly reclaimed material during mining cessation and poor adherence to the special handling plan. Median water quality data for the two sites is summarized in Table 2.4.4a.

Table 2.4.3a: Summary Water Quality for Greene County Site Phases 1 and 2

Monitoring Point	pH	Net Alkalinity (mg/L CaCO3 Eq.)	Total Fe (mg/L)	Total Mn (mg/L)	Sulfate (mg/L)
Phase 1, Mining	6.5	176	0.3	6.5	606
Phase 2, Mining	3.6	- 488	71.4	105	2233
Phase 1, Post Mining	7.2	151	1.88	16.35	1197
Phase 2, Post Mining	4.0	- 128	18.7	62.7	1770

<u>Case Study 5</u> (Westmoreland Co., PA)

A mine in Westmoreland County, Pennsylvania used alkaline redistribution to amend a portion of the site that was deficient in carbonate-bearing rocks. Acid-forming materials were laterally continuous and had 0.5 to over 2 percent total sulfur. A zone of calcareous materials, with carbonate content exceeding 20 percent, was present over a small area of the site. Special handling consisted of moving excess calcareous strata from the upper end of the mine and redistributing it in the alkaline deficient areas. Three pits were operated simultaneously. Operations were timed so alkaline material was available and cut and fill balances could be maintained. Material placement and backfilling included crushed limestone on the pit floor, "neutral" spoil backfill, placement of potentially acid material in lifts covered by more "neutral" spoil, and finally topsoil.

Wells and springs have been monitored for four years after reclamation at the alkaline redistribution site (Table 2.4.4b). In Well MW-6 (located downgradient of the site), median sulfate concentration decreased by approximately 70 percent, and net alkalinity rose above zero after reclamation was completed. MP-10 (a spring located downgradient of the mine) is representative of shallow ground-water conditions and contains negligible alkalinity. Overburden rocks in the recharge area for MP-10 and well MW-6 were likely acid forming. Post-mining water quality for MP-10 and MW-6 show a small but significant increase in net alkalinity. Sulfate concentrations indicate a lesser amount of oxidation and leaching is continuing within the spoil.

Table 2.4.3b: Summary of Water Quality Conditions, Alkaline Redistribution Site

Monitoring Point	pH	Net Alkalinity (mg/L CaCO3 Eq.)	Specific Conductance (umhos/cm)	Sulfate (mg/L)	Total Fe (mg/L)
MW-6, Mining	6.1	- 8	855	398	0.15
MW-6, Post Mining	6.1	24	404	115	1.5
MP-10, Mining	6.5	6	N/A	19.5	0.04
MP-10, Post Mining	7.1	20	280	90	0.09

Key factors influencing post-mining water quality are the redistribution of calcareous rock to alkaline-deficient areas, and rapid completion of mining and reclamation. Responses in water chemistry are attributed to placement of acid-forming materials above the water table to minimize leaching, while the calcareous rocks are dissolving and producing alkalinity.

Case Study 6 (EPA Remining Database, PA(10))

The PA(10) is also discussed in Section 1.1.4, Case Study 3. This site included the following BMPs: regrading of abandoned spoil, alkaline addition, hydrologic controls, revegetation and scarification of the calcareous pavement, and application of bactericides. The only calcareous stratum was the underclay beneath the lowest coal seam. There was a significant amount of high sulfur rock above the coal. To counter the lack of calcareous rock above the coal, the coal company proposed scarifying the pit floor (to expose the calcareous underclay) and a negligible alkaline addition rate of 3 tons/acre (applied to the spoil surface). Bactericide was added to prevent oxidation of pyrite through the retardation of the pyrite-oxidizing bacteria. Scarifying of the underclay is the form of special handling implemented at this site.

This site is one of only a handful of remining sites in Pennsylvania that have resulted in poorer post-mining water quality (see Section 1.1.4, Case Study 3). Several factors may have worked together to contribute to poor water quality. Failures have been observed at other, non-remining sites, where the bulk of the alkaline material was located on the pit floor (Smith and Brady, 1998). Scarifying may not have broken the rock sufficiently to allow for exposure of adequate surface area of the calcareous strata. Perhaps this plan would have been more successful if the calcareous material had been mixed through the spoil.

2.4.4 Discussion

Despite years of implementation, few studies of special handling and its effect on post-mining water quality have been performed. Special handling is almost always used in conjunction with other BMPs, thus separation of the effects of special handling alone is often not possible. For sites lacking calcareous strata, special handling alone will not create alkaline water. For this reason, special handling is often combined with alkaline addition. For a site to be a remining site, the area has to have been previously affected by mining. This previous mining and the type of associated remining is of three types: deep mining and subsequent daylighting, strip mining and subsequent regrading and revegetation, and coal refuse removal and subsequent regrading and revegetation. Thus remining sites with special handling do not occur without one of these additional BMPs.

Special handling methods fall into four categories: 1) blending, 2) high and dry, 3) dark and deep, and 4) alkaline redistribution. Blending is generally used where both calcareous and acid-producing rocks occur within the stratigraphic column. Mining is done in such a way as to blend the two materials together such that AMD should be prevented. “High and dry” and “dark and deep” are intended to limit the amount of water and oxygen in contact with the special handled material, respectively. Limitation of water will be most effectively accomplished if the surface of the special handled pod is sloped to achieve ground-water runoff, the pod is capped with a low permeability material, and the material is placed above the post-mining water table (“high and dry”). Limitation of oxygen can probably only realistically be achieved by submergence below the water table (“dark and deep”). Alkaline redistribution is used where calcareous materials occur on only part of a site. Excess alkaline material is redistributed to the portions of the site lacking alkaline materials.

Benefits

- Blending of calcareous material in the spoil has the advantage of being accomplished during the regular course of mining.
- Dark and deep (i.e., submergence below the water table) has the benefit of limiting oxygen available for pyrite oxidation.
- Alkaline redistribution results in calcareous rocks being distributed to parts of the mine where they did not occur naturally, thus providing the benefits inherent in calcareous rocks.
- High and dry, if material is capped and placed above the water table, should reduce the transport of pyrite-weathering products.

Limitations

- Blending is only effective if the calcareous material is can be adequately mixed in the spoil.

- Sites that can satisfy the requirements for “dark and deep” do not always exist in the Appalachians due to thin saturated zones and fluctuating water tables.
- High and dry technology has been inadequately studied and some of the studies are inconclusive. Without capping and proper placement it may be ineffective. The post-mining hydrology should be well understood.

Efficiency

Blending is the most common handling method, but is not strictly “special handling” because it does not require additional selective handling of materials and is accomplished as part of the routine mining process. The many sites in the Appalachians that have compliant post-mining water quality demonstrate its success. The key is to have sufficient calcareous strata present. The success of this method is probably reflected in the fact that mines that had regrading and revegetation as their only BMPs (Section 6.0, Table 6.3g) had 50 percent of discharges improve in acidity load, with the other 50 percent remaining unchanged. As discussed in Section 6, remining operations in the Pennsylvania Remining Site Study (Appendix B) that implemented these minimal BMPs, probably contained better overburden quality than many of the sites that employed multiple BMPs.

The effectiveness of high and dry placement is not as clear. Studies that have been performed are few and some are inconclusive. High and dry is the most commonly used special handling method in Pennsylvania, and it can be assumed that most of the sites listing special handling as a BMP in the Pennsylvania Remining Site Study were using this method. Data from this study were used to predict the effectiveness of special handling for improving water quality during remining operations. Section 6.0, Table 6.3a shows special handling can be predicted to result in slightly lower water quality improvement in regards to acidity loading than can be predicted if no BMPs are implemented. Section 6.0, Table 6.3g provides some different insight into the effectiveness of special handling. Special handling in conjunction with the minimal BMPs of regrading and revegetation, resulted in the same effectiveness rating as did the combination of regrading and revegetation alone. As other BMPs were added (regrading, revegetation, special handling, plus other BMPs), efficiency generally declined, with less discharges showing improvement in acidity load. This is probably due to the presence of greater amounts of acid-producing overburden and/or lesser amounts of calcareous overburden, with the additional BMPs added to offset the effects of the poorer overburden.

When deep mines are daylighted, there is often acidic material that requires special handling. This acidic material is typically unrecoverable coal and roof-rock. Section 6.0, Table 6.3m compares the implementation of daylighting alone to seven other BMP combinations. Four of these seven BMP combinations involve special handling. Three of the four resulted in a higher percentage of discharge water quality improvement than daylighting alone. Two of these three successful BMP combinations included the addition of alkaline materials. The fourth BMP group included a combination of five BMPs that routinely produced the poorest results. It is suspected that this is because additional BMPs were implemented in an attempt to counter poor quality overburden.

The dark and deep method of special handling has been shown to be a good means of AMD prevention. Its usefulness in the Appalachians, however, is often limited because of a thin saturated zone and a fluctuating water table that allows the acidic material to be exposed part of the year. The effectiveness of dark and deep cannot be evaluated using the Pennsylvania data because it is used so seldom.

Alkaline redistribution has had a high degree of success. Evaluation of the Pennsylvania data (Section 6.0 and Appendix B) suggests that alkaline redistribution has been a very successful special handling practice. Section 6.0, Table 6.3a shows that the predicted odds for improvement of acidity load when alkaline redistribution is used is eight times greater than when no BMPs are implemented. The only other BMP that gave a greater odds of improving discharges was mining of alkaline strata (nearly 19 times greater than when no BMPs are implemented).

Special handling by itself may reduce acid production, but it can not produce alkalinity in the absence of calcareous materials. Special handling in conjunction with alkaline addition or other means of incorporating alkaline strata can result in better water quality than using special handling alone.

2.4.5 Summary

- Special handling practices used in the Appalachians include: blending of acid and alkaline materials, the segregation and isolation of acidic materials (high and dry), and alkaline redistribution.

- Special handling is often used in conjunction with other BMPs such as management of ground water and alkaline addition.

- Submergence (dark and deep) is seldom used in much of the Appalachians because the saturated thickness of the water table is generally thin and the water table can undergo large seasonal fluctuations.

- Special handling in the absence of alkaline materials cannot produce alkaline drainage.

- Special handling often involves both acid and alkaline materials and may also include clay materials for capping and lining pods of acidic materials.

- Special handling is most effective in conjunction with other BMPs such as alkaline addition and surface- and ground-water management techniques.

- Alkaline redistribution and mining of high-alkaline strata (which often involves special handling) have been very successful in improving post-remining water quality.

- The volume of the material to be special handled should generally be less than 20 percent of the mine backfill volume because of the need to keep acidic materials away from the surface, water table, highwalls, etc.

- Special handling is not necessary on all mine sites.

- Identification and segregation of acid material is extremely difficult if multiple zones exist in the stratigraphic section, unless these zones are persistent laterally and vertically, of uniform thickness, and distinctive in appearance.

- Special handling requires that the proper earth-moving equipment be used at the mine site.

- Monitoring during and after mining is necessary to evaluate special handling techniques.

2.5 Bactericides

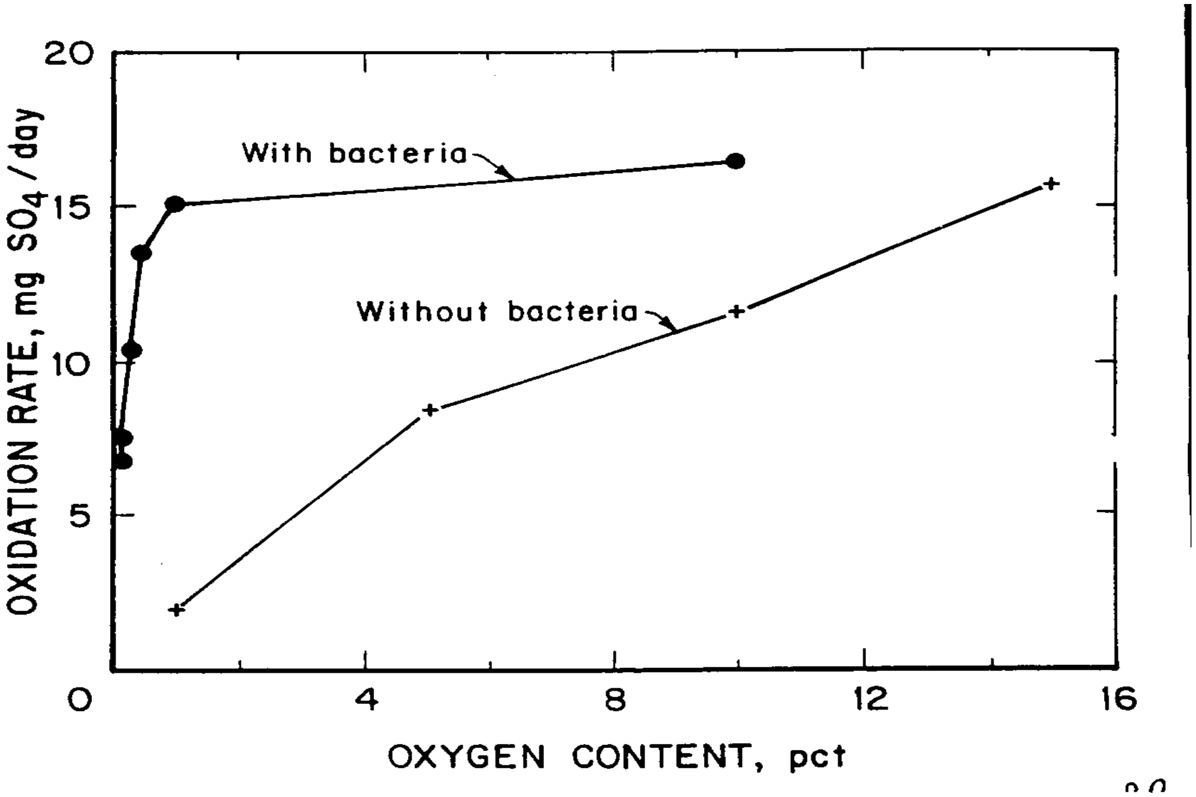
Introduction

Bacteria can play an important role in pyrite oxidation. They can cause pyrite to oxidize at a much faster rate at low oxygen levels than would occur in the absence of bacteria under the same conditions. Bactericides attempt to block the catalytic effects of certain bacteria on the pyrite oxidation process.

Theory

Pyrite-oxidizing bacteria, in particular *Thiobacillus ferrooxidans,* are responsible for the increased oxidation of pyrite over what would occur abiotically (Figure 2.5a), especially at low oxygen concentrations. Although numerous bactericides have been tested against pyrite-oxidizing bacteria, the bactericides of choice for mine sites have been anionic surfactants. These bactericides occur in household cleansers and soap products. At near-neutral pH these surfactants generally are considered to be poor bactericides, but they are markedly more inhibitory at low pH (Kleinmann, 1998). *T. ferrooxidans* has a near-neutral pH internally, but it can exist in low pH conditions (in fact, the conditions that it creates by oxidizing pyrite) because of a coating that protects the cell from the externally low pH environment. Anionic surfactants dissolve the protective coating, thus subjecting the bacteria cell to low pH conditions, conditions under which it can not survive unprotected.

Figure 2.5a: Rates of Pyrite Oxidation with and without Iron-oxidizing Bacteria (In small columns maintained at different oxygen partial pressures) (Hammack and Watzlaf, 1990).



The amount of oxygen present within the pore gas of mine spoil or coal refuse is an important factor when considering the use of bactericides. Figure 2.5a shows pyrite oxidation rates under biotic and abiotic conditions. At oxygen levels of approximately 14 percent, biotic and abiotic rates are about equal. Below oxygen levels of 14 percent, pyrite oxidation rates are considerably slower when bacteria are absent. In the presence of bacteria, pyrite oxidation can be significant even at oxygen concentrations as low as one percent. Thus bactericides are most advantageous where oxygen concentrations are low.

Bactericides have a limited period of effectiveness, and typically are only effective for up to four months. This limitation can be compensated for by repeated application or by application of time-release pellets.

Cations such as calcium and magnesium can cause water "hardness" which can reduce the effectiveness of surfactants in much the same way that hardness reduces the effectiveness of soap. Calcite and dolomite, which contain calcium and magnesium, are common minerals in coal overburden. Kleinmann (1999) felt that this surfactant inhibition would be greatest with highly-soluble neutralizers such as quick lime (CaO) and hydrated lime ($CaOH_2$). Something to keep in mind is that bactericides in-and-of-themselves do not produce alkalinity, and compounds that produce alkalinity frequently contain calcium and magnesium which may inhibit the effectiveness of bactericides. That is, the minerals that result in acid neutralization can retard the effectiveness of bactericides.

Site Assessment

The initial site assessment for bactericides is similar to that for other geochemical BMPs. First, the acidity- and alkalinity-generating potential of the site should be determined by evaluating overburden and water-quality data. If the site has little or no potential to produce acidity, bactericides are not necessary.

Kleinmann (1998) points out that application rates of anionic surfactants are site-specific, and heavily dependent on the adsorptive capacity of the material being treated. He suggests that pilot-scale field tests in plastic 55-gallon drums be used to determine the adsorptive properties of the surfactant. He cautions that small test piles may not accurately simulate larger sites because of higher oxygen concentrations in the small piles (Kleinmann, 1998). Determination of the amount of adsorption is important to assure that there will be adequate bactericide available to combat the bacteria on the surfaces where it is needed.

It is important to estimate the oxygen concentration in the mine spoil or coal refuse. For bactericides to be effective the oxygen concentration should be relatively low (<10 percent). Most experiments with bactericides have been done on compacted coal refuse. This material, because it is compacted (and often contains a high percentage of fine materials) can have low concentrations of oxygen. The use of bactericides at surface coal mines is potentially less effective because of likely higher concentrations of oxygen. If oxygen levels are high (>10 percent) there may be very little benefit from bactericides because abiotic pyrite oxidation is sufficient to create significant amounts of acid.

Spoil pore gas oxygen concentrations can be related to the type of rock that was mined, or disposed of (in the case of coal refuse). Some examples of oxygen levels in pore gas, which can serve as guidelines, are given below in the literature review/case study section.

Site evaluation should include assessment of:
- the acid-producing potential of the site
- the adsorptive capacity of the overburden
- prediction of the percent oxygen in spoil or coal refuse pore gas

2.5.1 Implementation Guidelines

The following guidelines are recommended for application of bactericides:
- Surfactants should be targeted to treat unweathered acid-forming material, such as coal refuse, that can be quickly buried.
- They should be applied at a rate higher than the rate they are adsorbed by the rock.
- They should not be applied to soils if the intention is to treat spoil, because soils will adsorb the surfactant leaving little to act on the underlying spoil.
- They are probably only effective where oxygen content is low (< 10 percent), thus an estimation of pore gas oxygen should be made.
- Surfactant solutions can be applied to acid-producing materials prior to their disposal. Time release pellets can be mixed with the spoiled material. Both methods may be needed for long-term effectiveness. If used in solution form, the surfactant may need to be applied 3 to 4 times per year.
- Carbonate content may also be important. Kleinmann (personal communication, June 28, 1999) says that high calcium water can inhibit the effectiveness of some anionic surfactants. More soluble neutralizers such as hydrated lime and quick limes are most

problematic. Essentially calcium can cause hard water and inhibit the effectiveness of the surfactant.

2.5.2 Verification of Success or Failure

As with all BMPs, bactericide application should be implemented as described in the plans. Means of documentation include:

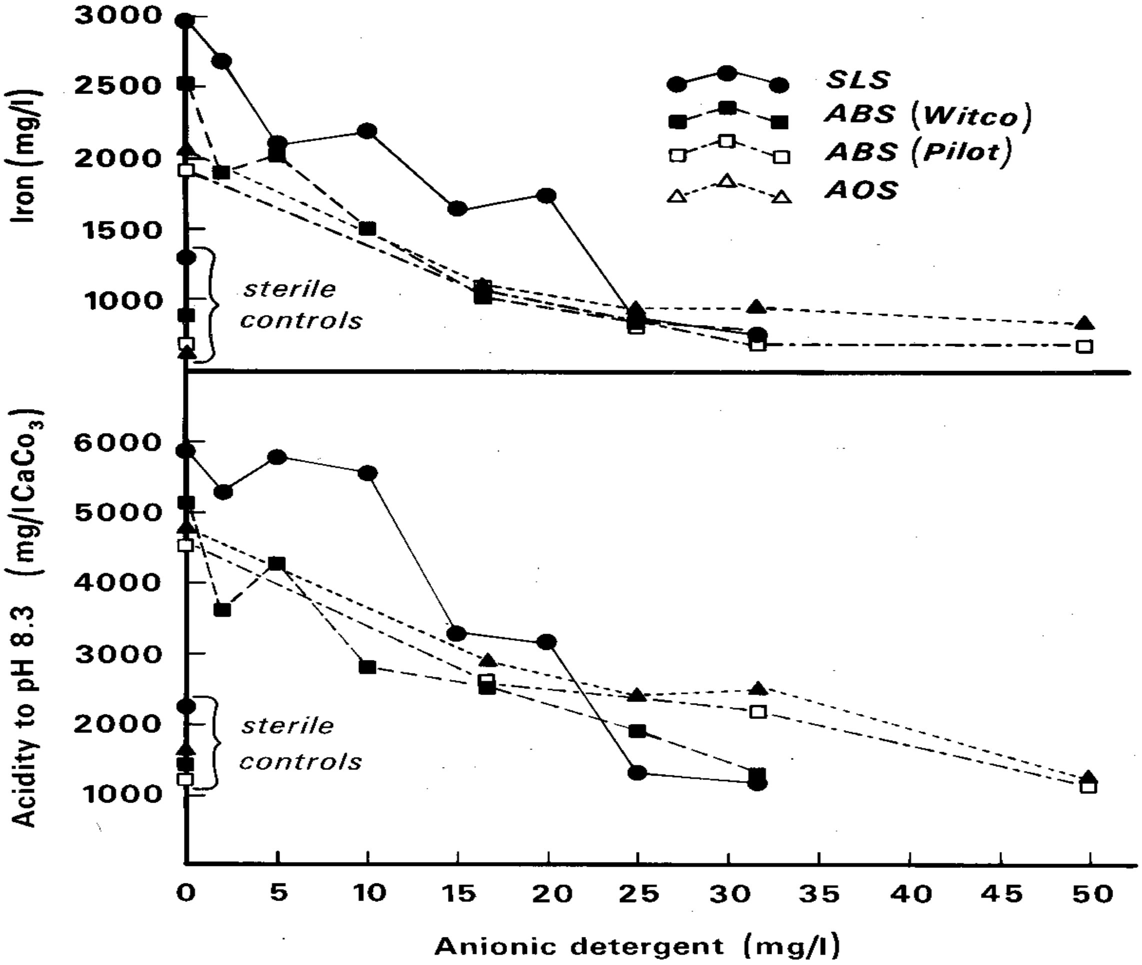
- Engineer's certification and increased inspection frequency to verify that the bactericide was implemented as planned
- Photographs of the bactericide application
- Locations of bactericide applications being accurately recorded through surveying or global positioning systems
- Verification of the amount of bactericide used by submittal of receipts.
- Laboratory analyses of the acid-forming materials to assure proper placement of bactericides
- Water-quality monitoring for flow and concentration of mine drainage parameters and bactericide.

Monitoring of water quality and flow, as well as accurate documentation of implemented plan, will allow for future improvements in design and determination of the efficiency of bactericides.

2.5.3 Literature Review/Case Studies

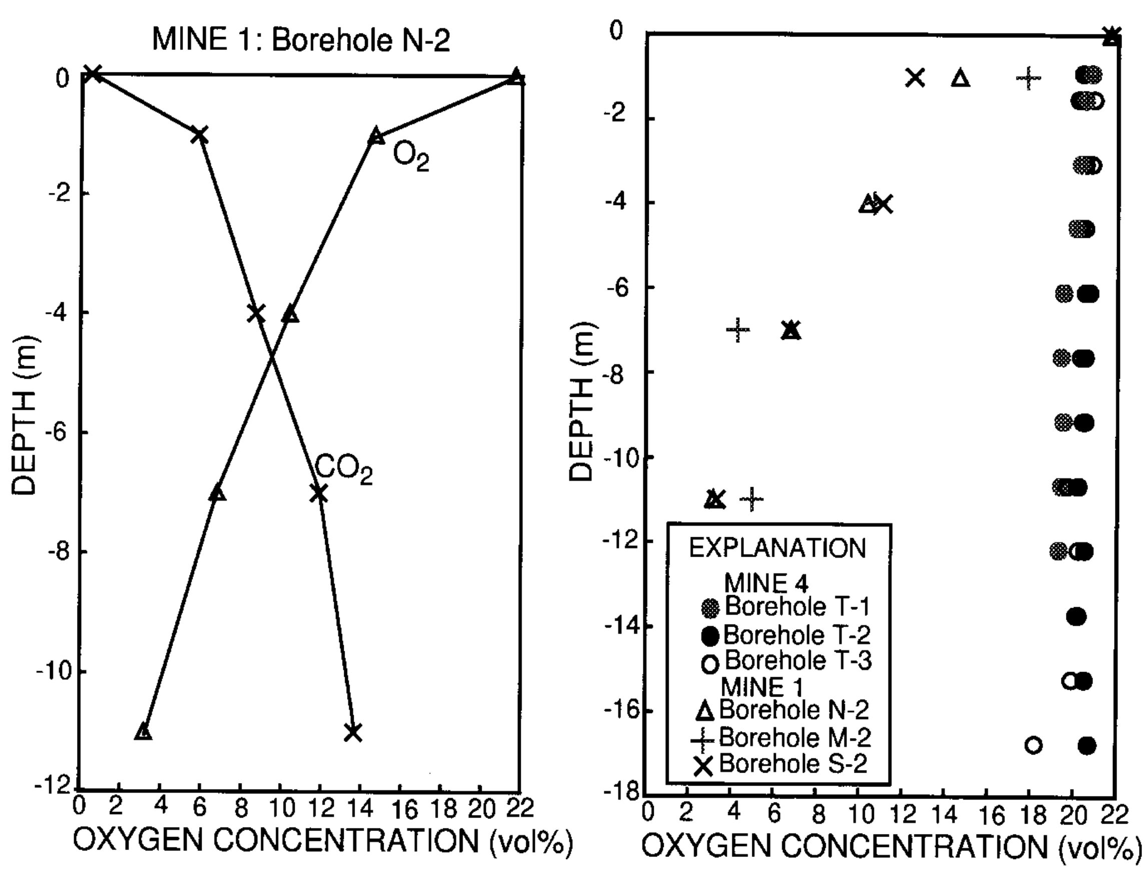
There are a variety of substances that can inhibit pyrite-oxidizing bacteria, but Kleinmann (1998) states that only anionic surfactants proved to be cost effective. Kleinmann tested, in the laboratory, the relative effectiveness of three anionic surfactants in preventing acid formation. He found sodium lauryl sulfate (SLS) to be the most effective (Figure 2.5.3a). Higher concentrations of the other surfactants were required to get the same effect.

Figure 2.5.3a: **Effect of Anionic Detergents on Acid Production from Pyritic Coal. (SLS = sodium lauryl sulfate, ABS = alkyl benzene sulfonate, AOS = alpha olefin sulfonate) (from Kleinmann, 1998).**



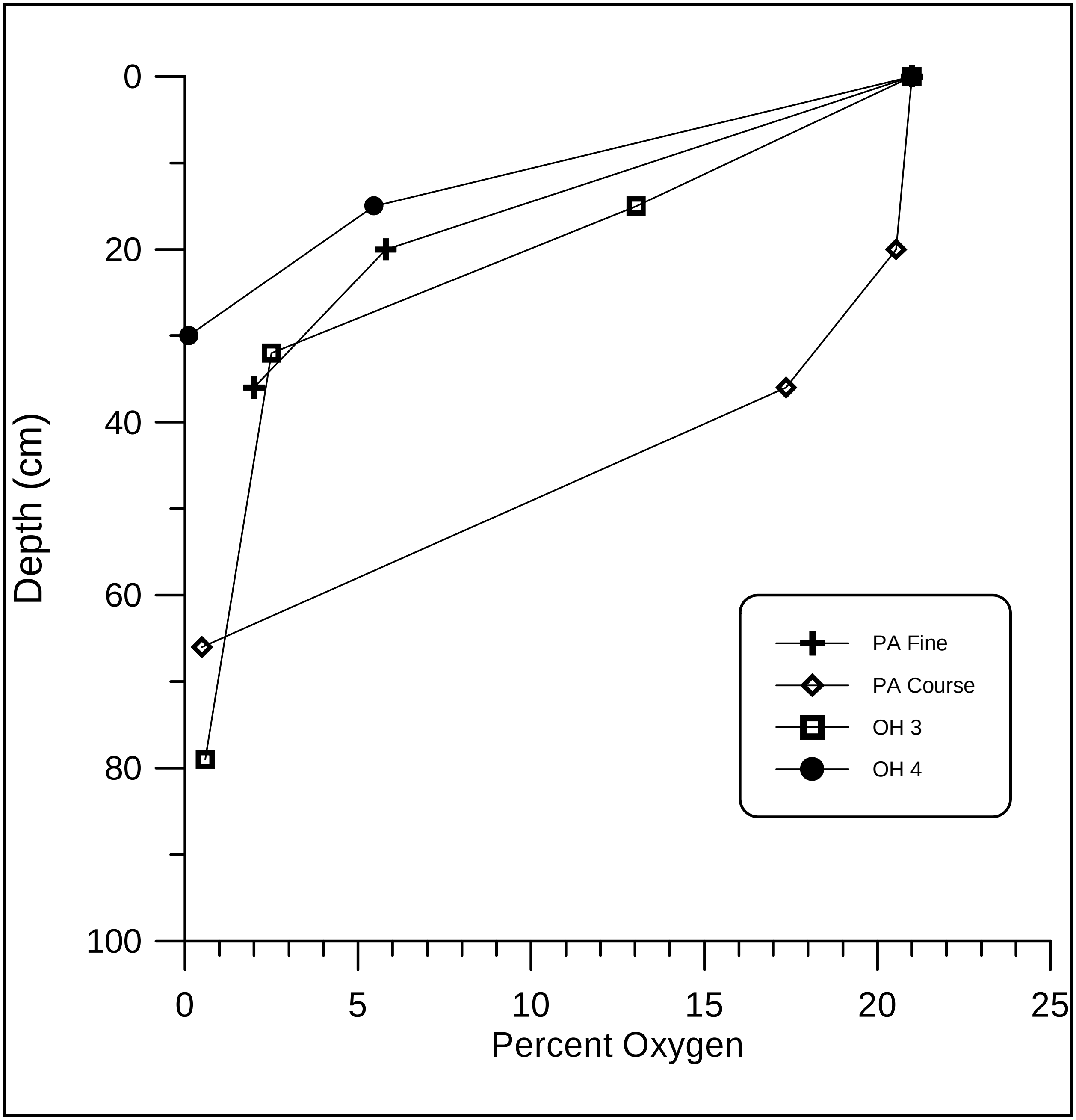
As mentioned earlier, an important consideration as to the effectiveness of bactericides is pore gas concentration of oxygen. Oxygen concentrations in pore gas have been measured for refuse material and for surface mines. Guo and Cravotta (1996) reported oxygen concentrations with depth for two surface mines in Pennsylvania (Figure 2.5.3b). Mine 1 contained predominantly shale/siltstone overburden and Mine 4 contained predominantly sandstone overburden. Mine 1 shows significant decreases in oxygen with depth, with concentrations as low as 2 to 4 percent at 11 meters. By contrast, oxygen was never below 18 percent at Mine 4, even at depths of 17 meters. This is probably due to the blocky nature of the sandstone which allows more atmospheric exchange than the smaller-sized rubble resulting from shale/siltstone.

Figure 2.5.3b: Measured Profiles of Oxygen in Unsaturated Spoil (after Guo and Cravotta, 1996) (At Mine 1 gas transport is by diffusion and at Mine 4 it is by convection. Mine 1 has shale/siltstone overburden and Mine 4 has sandstone overburden.)



Erickson and Campion (1982) report on oxygen concentrations with depth in coal refuse for sites in Pennsylvania and Ohio. The results of their measurements are shown in Figure 2.5.3c. All gas probes were installed at less than one meter deep. Three of the four plots show similar declines in oxygen concentration with depth (PA Fine, OH 3 and OH 4). The "PA Course" refuse had substantially higher oxygen concentrations at a depth of 36 cm than did the other refuse. The courser nature of the refuse apparently allowed for greater exchange with the atmosphere.

Figure 2.5.3c: **Oxygen Concentration with Depth in Coal Refuse in Pennsylvania and Ohio.**



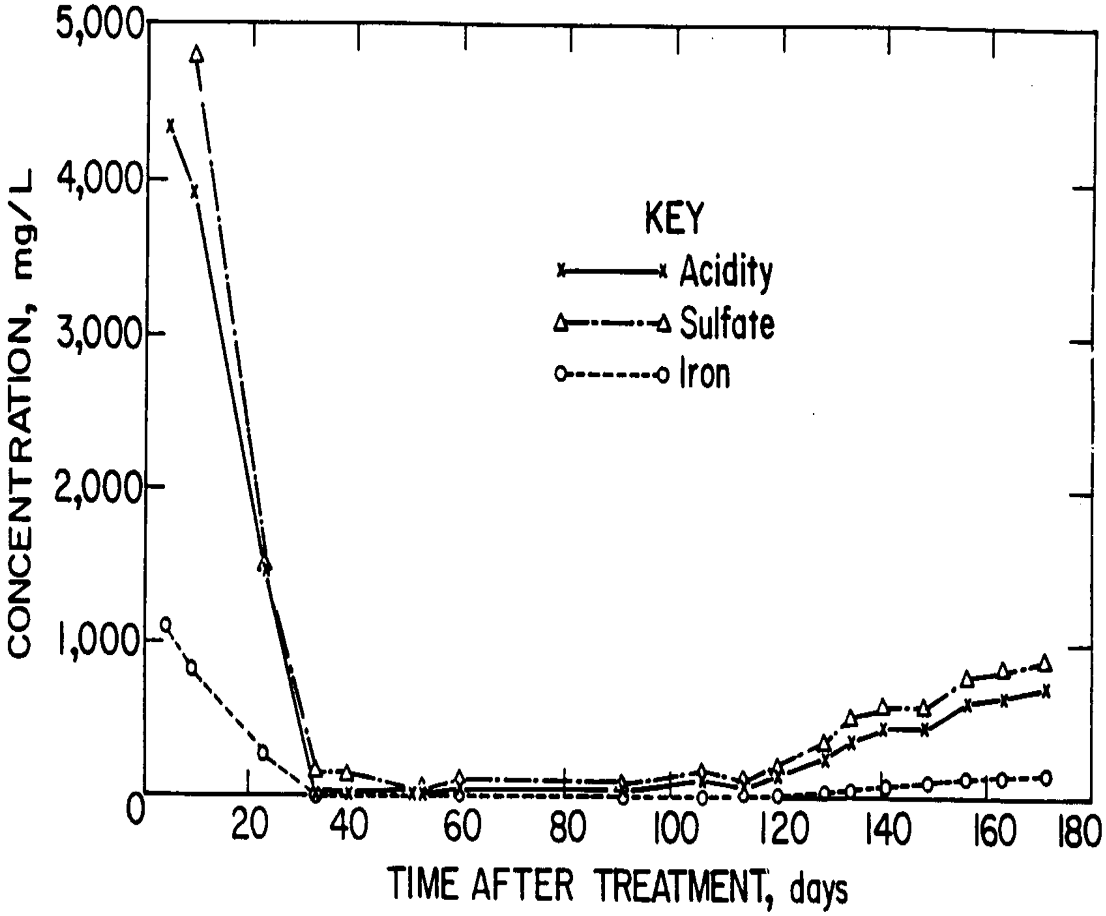
The course refuse had less than 1 percent oxygen at less than 1 meter, whereas oxygen concentrations in surface mines had 12 percent and greater at one meter depth. At 7 meters, the surface mines had at least 4 percent oxygen, even where the overburden was shale (a rock that breaks into small sizes). There are a couple of explanations for these results. First, coal refuse is generally composed of highly pyritic material that will consume and deplete oxygen near the surface. Surface mine spoil, by comparison, is lower in sulfur and oxygen consumption is not as great. Second, coal refuse is typically finer-grained and more compacted than mine spoil. This permits less oxygen exchange between the pore gas and the atmosphere.

Case Study 1 (Preston Co., WV) (Kleinmann and Erickson, 1983)

This site was an 8-acre active coal refuse disposal area. Because the area lacked background water quality data, a pond was constructed to collect runoff for monitoring purposes. Adsorption tests indicated that an application rate of one 55-gallon drum of 30 percent SLS would be needed per acre. The bactericide was diluted with water by a factor of 50:1. A larger dilution factor would have been preferred, but good-quality water was limited.

Water quality improved dramatically within a month of the SLS application. Acidity, sulfate and iron were reduced by 95 percent and remained low for approximately four months following application (Figure 2.5.3d). A complicating factor with this study was that coal refuse not treated with bactericide was added during the study period. It is thus impossible to separate out whether the increases in acidity starting at 120 days was due to this untreated refuse or diminishing effects of SLS.

Figure 2.5.3d: **Effect of Sodium Lauryl Sulfate on Runoff Water Quality at an 8-acre Active Coal Refuse Pile in Northern West Virginia (Application rate: 55 gal/ac of 30 percent solution, diluted 50:1 (Kleinmann and Erickson, 1983))**



Effluent concentrations of surfactant remained extremely low (consistently less than 0.1 mg/L) throughout application with none being detected in the receiving stream.

Case Study 2 Ohio (Kleinmann, 1998)

This site provides a long-term evaluation of bactericide application to a refuse pile. The initial field test was conducted in 1984 by the Ohio Department of Environmental Resources. A 2.5

acre area was treated with SLS and an adjacent 2.2 acre area served as an untreated control. SLS was applied in solution at a rate of 200 lbs/acre and as pellets composed of a rubber matrix at a rate of 500 lbs/acre (containing 16 to 28 percent SLS). Both areas were covered with 6 to 8 inches of topsoil which was fertilized, limed, seeded and mulched.

Five years after reclamation, biomass production on the treated area was 9 times greater than the untreated area. Acidity in the vadose zone in the treated area was 80 percent lower than in the untreated area. After 10 years, 35 to 40 percent of the control area was barren and eroding, whereas the treated area showed no significant erosion and the vegetative cover was dense.

Case Study 3 West Virginia (Skousen and others, 1997)

A 35-acre coal refuse pile was first regraded. Controlled release surfactant pellets were applied to the surface, which was then topsoiled, limed and revegetated. The treated area had a pH of 6.2 compared with a pH of 2.9 in a 1.2-acre untreated control area. Acidity was as low as 1 mg/L compared to 1680 mg/L, and reductions in iron and manganese were equally significant.

Case Study 4 Ohio (Skousen and others, 1997)

Bactericides were applied to an abandoned surface mine that was poorly vegetated. The application was in the form of slow-release pellets that were spread by a hydroseeder. The overburden was predominantly sandstone with abundant pyrite. Seeps with acidity of 1000 to 3000 mg/L have remained acidic, showing little sign of improvement.

Case Study 5 Appendix A, EPA Coal Remining Database (PA (10)), Somerset Co., PA

Details on the specifics of this site are presented under Section 1.1 Case Study 3 in regards to Control of Infiltrating Surface Water. Multiple BMPs were implemented at this site including surface regrading, scarification of calcareous pavement (seat rock), alkaline addition, hydrologic controls, and bactericides. The bactericides were applied in the form of time release pellets on the spoil surface prior to spreading of topsoil.

Two of four seeps have had increases in acid and sulfate post-mining loads compared to baseline loads. The other two seeps show no significant statistical difference in load. In all cases the concentrations of acidity have increased.

Case Study 6 Remining Database VA (4), Wise Co., VA

A blend of polymers and a bacteria inhibiting agent were formulated to retard acid soil formation. The bactericides were used as part of a plan to reduce the thickness of topsoil from four feet to one foot. In addition to bactericide use, the topsoil was limed, seeded, fertilized and hay mulched. Erosion control blankets were applied to reduce erosion and to protect the seed. Tree seedlings were planted on slope areas. Vegetation remains successful after more than a decade.

2.5.4 Discussion

The literature review and case studies suggest that bactericides have been successfully used on fresh (unweathered) coal refuse to inhibit pyrite oxidation (Case Studies 1, 2 and 3) and for revegetation purposes (Case Studies 2 and 6). Case Studies 4 and 5 concern application of bactericides at remining sites, and in both cases the water quality was not improved. This lack of improvement at remining sites containing abandoned surface mines may be due to the high oxygen concentrations present in spoil pore gas, the large volume of material that needs to be treated, and adsorption of much of the bactericide on non-acidic rock. An additional complication with surface mines is that calcareous strata or alkaline amendments may cause water hardness that can decrease the effectiveness of bactericides.

Bactericides are regulated under the Federal Insecticide, Fungicide and Rodenticide Act (FIFRA). Only bactericides registered under FIFRA can be legally used.

Benefits

- Can inhibit pyrite oxidation in low oxygen environments
- Can assist in revegetation efforts by acting as a wetting agent.

Limitations

- Limited to low oxygen environments, such as coal refuse disposal
- The bactericide will be adsorbed onto rock and soil, thus an excess should be applied
- Bactericides have a limited period of effectiveness and should continually be replenished
- Works best on fresh materials
- Limited by the presence of certain cations (Ca, Mg)

Efficiency

Not enough data regarding the application of bactericide is available for statistical analysis. However, review of the case studies cited above allows for some tentative efficiency statements to be made:

- Bactericides appear to have successfully reduced acidity at active refuse piles where it can be applied directly to fresh refuse.
- Very few studies exist for surface coal mines. The two case studies cited above were not successful. This may be due to oxygen availability in surface mine spoil. Another complicating factor is "hard water," due to the high concentration of calcium and magnesium. Much of the bactericide may be adsorbed on non-acid-producing rocks, thus diminishing its availability for acid-producing rocks
- Can be effective for enhancement of revegetation efforts by acting as a wetting agent

2.5.5 Summary

As a remining BMP, the evidence to date does not support the use of bactericides for prevention of acid water on surface coal mines. It appears, however, that bactericides have assisted in enhancement of revegetation efforts and bactericides have successfully reduced acid production from active coal refuse piles.

References

Aljoe, W.W., 1999. Hydrologic and water quality changes resulting from injection of CCP grout into a Maryland underground mine. In: Proceedings 13th International Symposium on Use and Management of Coal Combustion Products (CCPs), Vol. 3, January 11-15, 1999, Orlando, FL. American Coal Ash Assoc and EPRI, Palo Alto, CA, paper 66.

Bowders, J.J., M.A. Gabr, E.M. Boury, and R. C. Baker, 1994. Engineering evaluation of amended flyash for hydraulic barriers. In: Proceedings International Land Reclamation and Mine Drainage Conference and Third International Conference on the Abatement of Acidic Drainage, US Bureau of Mines Special Publication SP 06B-94, pp. 226-233.

Brady, K.B.C., 1998. Ground water chemistry from previously mined areas as a mine drainage quality prediction tool. Chapter 9, Coal Mine Drainage Prediction and Pollution Prevention in Pennsylvania. The Pennsylvania Department of Environmental Protection, pp. 9.1-9.21.

Brady, K.B.C. and R.J. Hornberger, 1990. The prediction of mine drainage quality in Pennsylvania. Water Pollution Control Assoc. PA Magazine, v. 23, no. 5, pp. 8-15.

Brady, K.B.C., M.W. Smith, and J. Schueck, eds, 1998. Coal Mine Drainage Prediction and Pollution Prevention in Pennsylvania. Pennsylvania Department of Environmental Protection.

Brady, K.B.C., R.J. Hornberger and Gary Fleeger, 1998. Influence of geology on post-mining water quality: Northern Appalachian Basin. In: Coal Mine Drainage Prediction and Pollution Prevention in Pennsylvania, Brady, K.B.C., M.W. Smith and J. Schueck, eds., The Pennsylvania Department of Environmental Protection, pp. 8.1-8.92.

Brady, K.B.C., A.W. Rose, J.W. Hawkins, and M.R. DiMatteo, 1996. Shallow ground water flow in unmined regions of the Northern Appalachian Plateau: Part 2 - Geochemical characteristics. In: Proceedings of the 13th Annual Meeting ASSMR, Knoxville, TN, May 18-23, 1996, pp. 52-62.

Brady, K.B.C., E.F. Perry, R. L. Beam, D.C. Bisko, M.D. Gardner, and J. M. Tarantino, 1994. Evaluation of acid-base accounting to predict the quality of drainage at surface coal mines in

Pennsylvania, USA. In: Proceedings of International Land Reclamation and Mine Drainage conference and Third International Conference on the Abatement of Acidic Drainage. U.S. Bureau of Mines Special Publication SP 06A-94, pp. 138-147

Brady, K.B.C., J.R. Shaulis, and V.W. Skema, 1988. A study of mine drainage quality and prediction using overburden analysis and paleoenvironmental reconstructions, Fayette County, Pennsylvania. In: Proceedings of Mine Drainage and Surface Mine Reclamation, Vol. 1. Mine Water and Mine Waste. U.S. Bur. Mines IC 9183, pp. 33-43.

Brady, K.B.C., M.W. Smith, R.L. Beam, and C.A. Cravotta III, 1990. Effectiveness of the addition of alkaline materials at surface coal mines in preventing or abating acid mine drainage: Part 2. Mine site case studies. In: Proceedings of 1990 Mining and Reclamation Conference and Exhibition, Vol. 1, Charleston, WV, April 23-26, 1990, pp. 227-241.

Canty, G.A. and J.W. Everett, 1999. An in situ remediation method for abandoned underground coal mines using coal combustion products. In: Proceedings 13th International Symposium on Use and Management of Coal Combustin Products (CCPs), Vol. 3, January 11-15, 1999, Orlando, FL. American Coal Ash Assoc and EPRI, Palo Alto, CA, paper 67.

Caruccio, F. T., 1982. The geologic distribution of pyrite and calcareous material and its relationship to overburden sampling. US Bureau of Mines Information Circular 8863, pp. 2-12.

Caruccio, F.T. and G. Geidel, 1996. Induced alkaline recharge to remediate acid mine drainage. Final Report Submitted to the U.S. Bureau of Mines, Contract No. 1432-J0230004.

Caruccio, F.T. and G. Geidel, 1989. Water management strategies in abating acid mine drainage - Is water diversion really beneficial? In: Proceedings, International Conference on Mine Planning and Design, Univ. of KY, pp. 167-172.

Caruccio, F.T. and G. Geidel, 1985. Induced alkaline recharge trenches - An innovative method to abate acid mine drainage. In: Proceedings, Surface Mining and Water Quality. 6th Annual West Virginia Surface Mine Drainage Task Force Symposium.

Caruccio, F.T. and G. Geidel, 1984. Induced alkaline recharge zones to mitigate acidic seeps. Symposium on Surface Mining, Hydrology, Sedimentology, and Reclamation, Univ. of KY, pp. 43-47.

Caruccio, F.T. and G. Geidel, 1983. The effect of plastic liner on acid loads: DLM site. Proc. 4th Annual WV Surf. Mine Drainage Task Force Symp., Charleston, WV.
Commonwealth of Pennsylvania Sanitary Water Board, 1952. Control of Acid Drainage from Coal Mines, Harrisburg, PA., 28 p.

Caruccio, F.T. and G. Geidel, 1982. The geologic distribution of pyrite and calcareous material and its relationship to overburden sampling. U.S. Bureau of Mines Information Circular 8863. pp. 2-12.

Cravotta, C.A. III, D. L. Dugas, K.B.C. Brady, and T.E. Kovalchuk, 1994a. Effects of selective handling of pyritic acid forming materials on the chemistry of pore gas and ground water at a reclaimed surface coal mine, Clarion County, PA, USA. In: Proceedings International Land Reclamation and Mine Drainage Conference and Third International Conference on the Abatement of Acidic Drainage, US Bureau of Mines Special Publication SP 06A-94, pp. 365-374.

Cravotta, C.A. III, K.B.C. Brady, L.C. Gustafson-Minnich, and M.R. DiMatteo, 1994b. Geochemical and geohydrological characteristics of bedrock and spoil from two methods of mining at a reclaimed surface coal mine, Clarion County, PA, USA. In: Proceedings International Land Reclamation and Mine Drainage Conference and Third International Conference on the Abatement of Acidic Drainage, US Bureau of Mines Special Publication SP 06B-94, pp. 242-249.

Cravotta, C. A. III, K. B. C. Brady, and R.L. Beam, 1990. Effectiveness of the addition of alkaline materials at surface mines in preventing or abating acid mine drainage: Part 1. Theoretical considerations. In: Proceedings: 1990 Mining and Reclamation Conference and Exhibition, Charleston, WV, pp. 221-225.

Davis, J. C., 1986. Statistics and Data Analysis in Geology. Second Edition. John Wiley & Sons, Toronto. 646 p.

diPretoro, R.S., 1986. Premining prediction of acid drainage potential for surface coal mines in northern West Virginia. M.S. Thesis, West Virginia Univ., 217 p.

diPretoro, R.S. and H.W. Rauch, 1988. Use of acid-base accounts in premining prediction of acid drainage potential: A new approach from northern West Virginia. In: Mine Drainage and Surface Mine Reclamation, vol.1, Mine Water and Mine Waste. U.S. Bur. Mines IC 9183, pp. 1-10.

Dollhopf, D.J., W.D. Hall, W.M. Schafer, E.J. DePuit, and R.L. Hodder, 1977a. Selective Placement of Coal Strip Mine Overburden in Montana: I. Database. Prepared for U.S. Bureau of Mines, Contract No. H0262032, 109 p.

Dollhopf, D.J., W.D. Hall, C.A. Cull, and R.L. Hodder, 1977b. Selective Placement of Coal Strip Mine Overburden in Montana: II. Initial Field Demonstration. Prepared for U.S. Bureau of Mines, Contract No. H0262032, 98 p.

Dollhopf, D.J., J.D. Goering, C.J. Levine, B.J. Bauman, D.W. Hedberg, and R.L. Hodder, 1978. Selective Placement of Coal Strip Mine Overburden in Montana: III. Spoil Mixing Phenomena. Prepared for U.S. Bureau of Mines, Contract No. H0262032, 68 p.

Dollhopf, D.J., J.D. Goering, C.J. Levine, B.J. Bauman, and R.L. Hodder, 1979. Selective Placement of Coal Strip Mine Overburden in Montana: IV. Hydrogeologic Studies. Prepared for U.S. Bureau of Mines, Contract No. H0262032, 55 p.

Donaldson, A. C. and Eble, C., 1991. Pennsylvanian coals of central and eastern United States. The Geology of North America. Vol. P-2, Economic Geology, U.S. Chapter 33, Geological Society of America. pp. 523-546.

Donaldson, A. C. and Renton, J.J., 1984. A Model for the Evaluation of Systematic Variability in Composition and Thickness of High Sulfur-High Ash Coals. U.S. Dept. of Interior, OSM, Report No. OSM MR1 G1105090, FINAL REPORT FOR BOM Grant No. 1115542 and preceding OSM Grants G5105090 & G5195050, 108 p.

Erickson, P.M. and R.S. Hedin, 1988. Evaluation of overburden analytical methods as means to predict post-mining coal mine drainage quality. U.S. Bureau of Mines Information Circular 9183, pp. 11-19.

Erickson, P.M. and P.S.A. Campion, 1982. Reducing oxidation of pyrite through selective reclamation practices. Symposium on Surface Mining Hydrology, Sedimentology and Reclamation, Univ. of KY, Lexington, KY, pp. 97-102.

Evans, D.R. and A.W. Rose, 1995. Experiments on alkaline addition to coal mine spoil. In: Proceedings of the Conference on Mining and the Environment, Vol. 1, Sudbury, Ontario, May 28 - June 1, 1995, pp. 49-58.

Foster Wheeler Corporation, 1998. Energy, economic development and a cleaner environment: The Colver Power Project. Heat Energy, v. 61, no. 4, pp. 2-11.

Fraser, W.W., and J.D. Robertson, 1994. Subaqueous disposal of reactive mine waste: an overview and update of case studies - MEND Canada. In: Proceedings International Land Reclamation and Mine Drainage Conference and Third International Conference On the Abatement of Acidic Drainage, US Bureau of Mines Special Publication SP 06A-94, pp. 250-259.

Geidel, G., 1979. Alkaline and acid production potentials of overburden material: The rate of release. Reclamation Review, v. 2, pp. 101-107.

Geidel, G. and F.T. Caruccio, 1984. A field evaluation of the selective placement of acidic material within the backfill of a reclaimed coal mine. In: Proceedings of the 1984 Symposium on

Surface Mining, Sedimentology and Reclamation, Univ. of Kentucky, Lexington, KY, pp. 127-131.

Getto, Michael, PA Department of Environmental Protection, personal communication with Keith Brady, 1998. Details available from the U.S. Environmental Protection Agency Sample Control Center, operated by DynCorp I&ET, 6101 Stevenson Avenue, Alexandria, VA, 22304.

Gibb J.P. and R.L. Evans, 1978. Preliminary Evaluation of Last Cut Lakes. Illinois Sate Water Survey Circular 130, State of Illinois, Dept. of Education and Registration.

Guebert, M.D., and T.W. Gardner, 1992. Macropore flow effect on infiltration, throughflow, and surface runoff on a reclaimed surface-mined watershed. In: Proceedings International Symposium on Land Reclamation: Advances in Research and Technology, American society of Agricultural Engineers, Nashville, Tenn., 10 p.

Guo, W. and C.A. Cravotta III, 1996. Oxygen transport and pyrite oxidation in unsaturated coal-mine spoil. Proceedings 13th Annual Meeting American Society for Surface Mining and Reclamation, May 18-23, 1996, Knoxville, TN, pp. 1-14.

Hammack, R.W. and G. R. Watzlaf, 1990. The effect of oxygen on pyrite oxidation. In: Proceedings of the 1990 Mining and Reclamation Conference and Exhibition, Vol. 1, pp. 257-264.

Hawkins, J.W., OSMRE, personal communication with Keith Brady, 1999. Details available from the U.S. Environmental Protection Agency Sample Control Center, operated by DynCorp I&ET, 6101 Stevenson Avenue, Alexandria, VA, 22304.

Hawkins, J.W., 1998. Hydrogeologic characteristics of surface-mine spoil. Chapter 3 of Coal Mine Drainage Prediction and Pollution Prevention in Pennsylvania. Pennsylvania Department of Environmental Protection, pp. 3-1 to 3-11.

Hedin, R.S., R.W. Narin, and R.L.P. Kleinmann, 1994. Passive treatment of coal mine drainage. U.S. Bureau of Mines, Information Circular 9389, 35 p.

Hellier, W.W., 1998. Abatement of acid mine drainage by capping a reclaimed surface mine with fluidized bed combustion ash. Mine Water and the Environment, v. 17, no. 1, pp. 28-40.

Hem, J.D., 1985. Study and Interpretation of the chemical characteristics of natural water (3rd ed.). U.S. Geological Survey Water-Supply Paper 2254, pp. 90-93.

Holland L.J. and L.B. Phelps, 1986. Topsoil compaction during reclamation: field studies. In: Proceedings Symposium on Surface Mining, Hydrology, Sedimentology and Reclamation, DH Graves (ed), University of Kentucky OES Special Publications, Lexington, pp. 55-62.

Hornberger, R.J. and K.B.C. Brady, 1998. Kinetic (leaching) test for the prediction of mine drainage quality. In: Coal Mine Drainage Prediction and Pollution Prevention in Pennsylvania, Brady, K.B.C., M.W. Smith and J. Schueck, eds., The Pennsylvania Department of Environmental Protection, pp. 7.1-7.54.

Jaynes, D.B., A.S. Rogowski, H.B. Pionke and E.L. Jacoby, Jr., 1983. Atmospheric and temperature changes within a reclaimed coal strip mine. Soil Science, v. 136, no. 3, pp. 164-177.

Jorgensen, D.W. and T.W. Gardner, 1987. Infiltration capacity of disturbed soils: Temporal change and lithologic control. Water Resources Bulletin, v. 23, no. 6, pp. 1161-1171.

Journel, A. G. and Huijbregts, C. J., 1981. Mining Geostatistics. Academic Press, London. 600 p.

Kleinmann, R.L.P., personal communication with Keith Brady, 1999. Details available from the U.S. Environmental Protection Agency Sample Control Center, operated by DynCorp I&ET, 6101 Stevenson Avenue, Alexandria, VA, 22304.

Kleinmann, R.L.P., 1998. Bactericidal control of acidic drainage. In: Brady, K.B.C., M.W. Smith and J. Schueck, eds., Coal Mine Drainage Prediction and Pollution Prevention in Pennsylvania, PA Dept. of Environmental Protection, pp. 15.1-15.6.

Kleinmann, R.L.P. and P.M. Erickson, 1983. Control of acid drainage from coal refuse using anionic surfactants. US Bureau of Mines Report of Investigations 8847, 16 p.

Kleinmann, R.L.P., D.A. Caerar, and R.R. Pacelli, 1980. Biogeochemistry of acid mine drainage and a method to control acid formation. Mining Engineering, v. 33, pp. 300-306.

Koch, G. S. Jr. and Link, R.F., 1970. Statistical Analysis of Geological Data. Vol. 1, Dover Publications, Inc., New York, NY, 296 p.

Lapakko, K., 1993. Evaluation of Tests for Predicting Mine Waste Drainage pH. Draft Report to the Western Governor's Association, Minnesota Dept. of Natural Resources, St. Paul, MN, 71 p.

Leach, E.G. III and F.T. Caruccio. 1991. The effect of hydrologic zonation upon the acid production potential of pyritic rock. In: Proceedings of the Twelfth Annual West Virginia Surface Mine Drainage Task Force Symposium. Morgantown, WV.

Lusardi, P.J. and P.M. Erickson, 1985. Assessment and reclamation of an abandoned acid-producing strip mine in northern Clarion County, Pennsylvania. In: Proceedings of the 1985 Symposium Surface Mining Hydrology, Sedimentology, and Reclamation, Univ. of Kentucky, Lexington, KY, pp. 313-321.

Meek, A. F., 1994. Assessment of acid prevention techniques used in surface mining. In: Proceedings International Land Reclamation and Mine Drainage Conference and Third International Conference On the Abatement of Acidic Drainage, US Bureau of Mines Special Publication SP 06B-94, pp. 41-48.

Michaud, L.H., 1995. Selective spoil placement for the prevention of acid mine drainage formation. Mining Engineering, March 1995, pp. 272-275.

Noll, D. A., Bergstresser, T.W. and Woodcock, J., 1988. Overburden Sampling and Testing Manual. Small Operators' Assistance Program, Commonwealth of PA, Dept. of Environmental Resources, Bureau of Mining and Reclamation, 78 p.

O'Hagan, M. and F.T. Caruccio, 1986. The effect of admixed limestone on rates of pyrite oxidation in low, medium, and high sulfur rocks. [abstract] In: Proceedings of 1986 National Symposium on Mining Hydrology, Sedimentology and Reclamation, University of Kentucky, Lexington, KY, p. 155.

Panther Creek Energy Partners, n.d. Panther Creek Energy Facility, Nesquehoning, PA. 4 p. brochure.

Perry, E.F., 1998. Interpretation of acid-base accounting. Chapter 11 of Coal Mine Drainage Prediction and Pollution Prevention in Pennsylvania, PADEP, Harrisburg, pp. 11.1-11.18.

Perry, E.F. and K.C. Brady, 1995. Influence of neutralization potential on surface mine drainage quality in Pennsylvania. In: Proceedings of the Sixteenth Annual West Virginia Surface Mine Drainage Task Force Symposium, Morgantown, WV, April 4-5, 1995, pp. 159-171.

Perry E.F., M.D. Gardner, and R.S. Evans, 1997. Effects of acid material handling and disposal on coal mine drainage quality. In: Proceedings Fourth International Conference on Acid Rock Drainage, Vol. III, pp. 1007-1026.

Peters, W.C., 1978. Exploration and Mining Geology. John Wiley & Sons, New York, NY pp. 461-475.

Phelps, L.B., 1983. Characterization of mine spoil properties as a tool for premining planning. In: Symposium on Surface Mining, Hydrology, Sedimentology and Reclamation, Univ. of KY, pp. 47-51.

Phelps, L.B., and L.W. Saperstein, 1982. Spoil modification to minimize the mobilization of formed toxic fluids. In: Proceedings 1982 Symposium on Surface Mining, Hydrology, Sedimentology and Reclamation, University of Kentucky, Lexington, KY, pp. 593-599.

Pionke, H.B. and A.S. Rogowski, 1982. Placement of acid spoil materials. Reclamation and Revegetation Research, v. 1, pp. 3-11.

Rafalko, L.G. and P. Petzrick, 1999. The Western Maryland Coal Combustion By-Products / Acid Mine Drainage Initiative: The Winding Ridge Demonstration Project. In: Proceedings 13th International Symposium on Use and Management of Coal Combustin Products (CCPs), Vol. 3, January 11-15, 1999, Orlando, FL. American Coal Ash Assoc and EPRI, Palo Alto, CA, paper 70.

Ritter, J.B., and T.W. Gardner, 1993. Hydrologic evolution of drainage basins disturbed by surface mining, central Pennsylvania. Geological Society of America Bulletin, v. 105, pp. 101-115.

Robertson, J.D., G.A. Tremblay, and W.W. Fraser, 1997. Subaqueous tailings disposal a sound solution for reactive tailing. In: Proceedings Fourth International Conference on Acid Rock Drainage, Vol. III, pp. 1027-1046.

Rose, A.W. and C.A. Cravotta III, 1998. Geochemistry of coal mine drainage. In: Coal Mine Drainage Prediction and Pollution Prevention in Pennsylvania, Brady, K.B.C., M.W. Smith and J. Schueck, eds., The Pennsylvania Department of Environmental Protection, pp. 1.1-1.22.

Rose, A.W., L.B. Phelps, R.R. Parizek, and D.R. Evans, 1995. Effectiveness of lime kiln flue dust in preventing acid mine drainage at the Kauffman surface coal mine, Clearfield County, Pennsylvania. In: Proceedings of the 1995 National Meeting of the American Society for Surface Mining and Reclamation, Gillette, WY, June 5-8, 1995, pp. 159-171.

Rose, A. A., Williams, E.G. and Parizek, R. B., 1983. Predicting potential for acid drainage from coal mines. Earth and Mineral Sciences, Pennsylvania State University, University Park PA, v.52, no.4.

Rymer, T. and Stiller, A., 1989. Sampling for sulfur - how much is enough? Minelands, v.1, no.1, pp. 3-4.

Sames, G. W.P. Chisholm and F. Block, in preparation. A review of mine drainage prediction methods in Appalachian coal producing states. Unpublished US Bureau of Mines report.

Scheetz, B.E., M.R. Silsbee, C. Fontana, X. Zhao, and J. Schueck, 1993. Properties and potential application of large volume use of fly ash-based grouts for acid mine drainage abatement. In: 15th Annual Meeting of the Assoc. of Abandoned Mine Land Programs, Jackson, WY, pp. 44-63.

Scheetz, B.E., M.J. Menghini, R.J. Hornberger, T.D. Owen and J. Schueck, 1997. Beneficial use of coal ash in anthracite and bituminous mine reclamation and mine drainage pollution abatement in Pennsylvania. In: Air & Waste Management Associations's 90th Annual Meeting & Exhibit in, Toronto, Ontario, Canada, pp. 1-24.

Schueck, J., personal communication with Keith Brady, 1998. Details available from the U.S. Environmental Protection Agency Sample Control Center, operated by DynCorp I&ET, 6101 Stevenson Avenue, Alexandria, VA, 22304.

Schueck, J., M. DiMatteo, B. Sheetz, and M. Silsbee, 1996. Water quality improvements resulting from FBC ash grouting of buried piles of pyritic materials on a surface coal mine. In: Proceedings Seventeenth Annual West Virginia Surface Mine Drainage Task Force Symposium, Morgantown, WV.

Schueck, J., T. Ackman and B. Scheetz, 1994. Acid mine drainage abatement using fluidized bed combustion ash grout after geophysical site characterization. In: U.S. Bureau of Mines Special Publication SP 06D-94, pp. 218-227.

Skousen, J. And G. Larew, 1994. Alkaline overburden addition to acid producing materials to prevent acid mine drainage. U.S. Bureau of Mines Special Publication SP 06B-94, pp. 375-381.

Skousen, J. and G. Larew, 1995. Alkaline overburden addition to acid-producing materials to prevent acid mine drainage. In: Acid Mine Drainage Control and Treatment, West Virginia University and the National Mine Land Reclamation Center, Morgantown, WV, pp. 79-85.

Skousen, J.G. and G. Larew, 1994. Alkaline overburden addition to acid producing materials to prevent acid mine drainage. In: Proceedings International Land Reclamation and Mine Drainage Conference and Third International Conference on the Abatement of Acidic Drainage, US Bureau of Mines Special Publication SP 06A-94, pp. 375-381.

Skousen, J., J. Renton, H. Brown, and others, 1997, Neutralization potential of overburden samples containing siderite. Journal of Environmental Quality, Vol. 26, no. 3, 1997, pp. 673-681.

Skousen, J., A. Rose, G. Geidel, J. Foreman, R. Evans, W. Hellier, and members of the Avoidance and Remediation Working Group of ADTI, 1997. Handbook of Technologies for Avoidance and Remediation of Acid Mine Drainage. Acid Drainage Technology Initiative (ADTI), Published by The National Mine Land Reclamation Center, West Virginia Univ., 111 p.

Skousen, J.G., J.C. Sencindiver, and R.M. Smith, 1987. A Review of Procedures For Surface Mining And Reclamation In Areas With Acid-Producing Materials. In cooperation with The West Virginia Surface Mine drainage Task Force, The West Virginia University Energy and Water Research Center and the West Virginia Mining and Reclamation Association. West Virginia University, Energy and Water Research Center, 39 p.

Smith, M.W. and K.B.C. Brady. 1990. Evaluation of acid base accounting data using computer spreadsheets. In: Proceedings of the 1990 Mining and Reclamation Conference and Exhibition, Vol. 1, Charleston WV, April 23-26, 1990, pp. 213-219.

Sobek, A. A., Schuller, W. A., Freeman, J. R. and Smith, R. M., 1978. Field and Laboratory Methods Applicable to Overburden and Minesoils. EPA-600/2-78-054, US EPA, Cincinnati, OH, 203 p.

Smith, M.W. and C.H. Dodge, 1995. Coal geology and remining, Little Pine Creek Coal Field, northwestern Lycoming County. In: Proceedings 60th Annual Field Conference of Pennsylvania Geologists Guidebook, Applied Geology in the Lock Haven and Williamsport Region, Clinton and Lycoming Counties, Northcentral Pennsylvania, Field Conference of Pa Geologists, Harrisburg, PA, pp. 13-26.

Stalker, J., A.W. Rose, and L.H. Michaud, 1994. Remediation of acid mine drainage within strip mine spoil by sulfate reduction using waste organic matter. In: Proceedings American Society for Surface Mining and Reclamation, Knoxville, TN, pp. 321-335.

Stanton, R.W. and J.J. Renton, 1981. Organic and Pyritic Sulfur in Coal: Potential Errors in Determination. WV Geological and Economic Survey Circular No. C-22, Morgantown, WV, 13 p.

Stehouwer, R.C., D.A. Kost, J. P. Vimmerstedt, J.H. Beeghly, 1999. Reclamation of acidic coal minespoils using flue gas desulfurization by-product and sewage sludge. In: Proceedings 13th International Symposium on Use and Management of Coal Combustin Products (CCPs), Vol. 3, January 11-15, 1999, Orlando, FL American Coal Ash Assoc and EPRI, Palo Alto, CA, paper 76.

Tarantino, J.M. and D.J. Shaffer, 1998. Planning the overburden analysis. Chapter 5 of Coal Mine Drainage Prediction and Pollution Prevention in Pennsylvania, PADEP, Harrisburg, pp. 5.1-5.8.

Waddell, R.K., R.R. Parizek, and D.R. Buss, 1986. Acidic Drainage Abatement Through Surficial Application of Limestone Quarry Waste and Limeplant Flue Dust, Jonathan Run, Centre County, PA. Proceedings 7th Annual West Virginia Surface Mine Drainage Task Force Symposium, 45 p.

Webster, R. and Burgess, T. M., 1984. Sampling and bulking strategies for estimating soil properties in small regions. Journal of Soil Science, v.35, pp. 127-140.

West Virginia Surface Mine Drainage Task Force, 1979. Suggested Guidelines for Method of Operation in Surface Mining of Areas With Potentially Acid-Producing Materials, 20 p.

West Virginia Surface Mine Drainage Task Force, 1978. Suggested Guidelines for Method of Operation in Surface Mining of Areas with Potentially Acid-Producing Materials. WV Dept. of Natural Resources, Elkins, WV, 20 p.

Wiram, V.P., 1996. Unpublished notes distributed during a field trip for the American Society for Surface Mining and Reclamation to the Skyline Glady Fork Mine, May 23, 1996.

Wiram, V.P. and H.E. Naumann, 1996. Improving ground water quality in the backfill with alkaline additions. In: Successes and Failures: Applying Research Results to Insure Reclamation Success. Proceedings 13th Annual Meeting American Society for Surface Mining and Reclamation, pp. 336-354.