Chapter 13
ALKALINE ADDITION

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Introduction

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 strata. But many sites contain little or no alkaline materials and, as a consequence, often produce acidic drainage even when sulfur contents are relatively low. One approach to alkaline-deficient sites would be to import alkaline material and amend the spoil in order to obtain alkaline drainage.

This approach, although perfectly logical and reasonable, is deceptively simple. How much material needs to be added and how 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 can be tolerated? 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 conceived before it is put into place. This chapter reviews the theoretical aspects of alkaline addition and empirical studies of alkaline-addition research, and summarizes the current state of the art in the use of alkaline addition to prevent acid mine drainage (AMD).

Theory of Alkaline Addition

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 sulfates (Equation 13.1). Although this process occurs very slowly in undisturbed conditions, it can be greatly accelerated by both surface and underground mining.

$$2\ FeS_2 + 7\ O_2 + 2\ H_2O \rightarrow 2\ Fe^{2+} + 4\ SO_4^{2-} + 4\ H^+ \qquad (13.1)$$

The pyrite oxidation process 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 et al., 1980) (Equation 13.2). Under low pH conditions, ferric iron remains in solution and can directly oxidize pyrite (Equation 13.3). Thus, once AMD formation gets started, decreasing the pH of the mine environment, the AMD reaction is further accelerated by bacteria and the production of ferric iron, resulting in severe acid mine drainage.

$$4\ Fe^{2+} + O_2 + 4\ H^+ \rightarrow 4\ Fe^{3+} + 2\ H_2O \qquad (13.2)$$

$$FeS_2 + 14\ Fe^{3+} + 8\ H_2O \rightarrow 15\ Fe^{2+} + 2\ SO_4^{2-} + 16\ H^+ \qquad (13.3)$$

Acidity produced by acid mine drainage can be neutralized in the presence of sufficient carbonate minerals. This reaction is shown by Equation 13.4, 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% 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 of it dissolves in water and produces acidity. If the reaction product is HCO_3^- (Equation 13.5), twice as much carbonate will be required to neutralize the same amount of material (Cravotta and others, 1990). Both processes occur. Which one is dominant depends on how open or closed the atmospheric system of the mine site is, which is not readily determined.

$$FeS_2 + 2CaCO_3 + 3.75\ O_2 + 1.5\ H_2O \rightarrow Fe(OH)_3 + 2SO_4^{2-} + 2\ Ca^{2+} + 2\ CO_{2(g)} \qquad (13.4)$$

$$FeS_2 + 4CaCO_3 + 3.75\ O_2 + 3.5\ H_2O \rightarrow Fe(OH)_3 + 2SO_4^{2-} + 4Ca^{2+} + 4HCO_3^- \qquad (13.5)$$

Where neutralization is occurring, the pH can remain at a near-neutral value which inhibits bacterial catalysis of iron oxidation and where ferric iron is 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 the availability of calcium carbonate or other neutralizing agents in the coal and overburden.

Brady et al. (1994) and diPretoro and Rauch (1988) found a strong empirical relationship between the neutralization potential (NP) of surface coal mine overburden and whether or not the postmining drainage would be alkaline or neutral. Sites with more than 3% naturally occurring carbonates produced alkaline drainage. Sites with less than 1% carbonate generally produced acidic drainage. Perry and Brady (1995) attribute this effect not only to neutralization but also to the limitation of ferrous iron oxidation by bacterial catalysis and direct oxidation of pyrite by ferric iron. Both of these processes are inhibited in the near-neutral pH environment created by the presence of sufficient carbonate.

The role of carbonate is so important in acid mine drainage formation, that 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 (MPA), calculated from the overburden sulfur content (Brady and Hornberger, 1990, Brady et al., 1994, Perry and Brady 1995). diPretoro (1986) found net neutralization potential and NP to be useable predictors of drainage quality, while MPA was again shown to be an unreliable predictor. Net neutralization potential (NNP) is defined as NP - MPA. 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 would 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 13.1). 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 only 0.03%. At 20% CO_2 content, which has been measured in some backfill environments (Cravotta, et al, 1994), 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 the rock type and the configuration of the backfill. Shallow backfills on steep slopes with blocky overburden and thin soil cover, for example, tend to "breathe", thereby reducing CO_2 partial pressures. Deeply buried backfills or sites with restricted airflow or thick soil covers would tend to have higher CO_2 levels, enhancing calcite dissolution. Calcite solubility also 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 within the backfill.

In theory, almost any acid-prone site could be transformed into an alkaline site if only enough carbonate material were imported. In actual practice, however, it

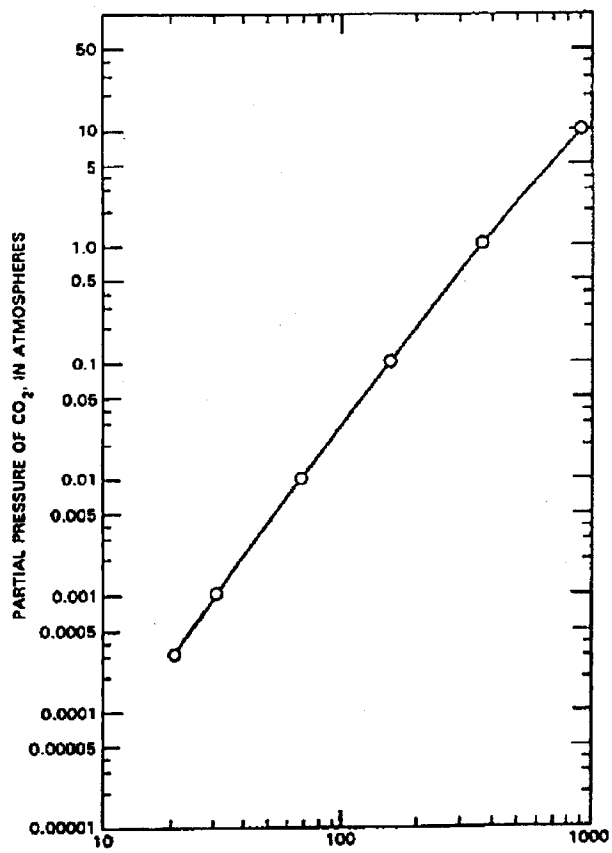

Figure 13.1 Solubility of calcium carbonate (calcite) in water at 25°C as a function of partial pressure of CO_2. From Hem (1985).

becomes necessary to determine: (1) how much alkaline material needs to be applied to ensure a successful result; and (2) how and where within the backfill should the alkaline material be applied. Additionally, ensuring that a site produces alkaline water does not necessarily guarantee that effluent limitations for metals will be met.

Alkaline Addition Studies

The earliest 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 guidelines for surface mining in potentially acid-producing areas (1979). It recommended 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. No specific rationale or empirical evidence was given 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 (1980) used alkaline addition to abate acidic drainage resulting from the construction of Interstate 80 in northcentral Pennsylvania, which disturbed acid-prone overburden. The Waddell study involved a surface application of limestone crusher waste and lime flue dust at the rate of 267 ton/ac (600 t/ha). 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 the pit floor at the rate of 39 tons per acre (87 t/ha). Although the treated site initially produced alkaline drainage, it shortly became acidic. An untreated control site produced acidic drainage throughout the 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 ton/ac (269 t/ha). Although NNP deficiencies at the site ranged from 25 to 590 ton/ac (56 to 1320 t/ha), they assumed that most acid production occurred near the surface and that it may only be necessary to add enough limestone to balance the NP deficiency in the upper two meters of spoil. The limestone was disked into the upper 1.0 ft (0.3 m) of the spoil surface. One year after the 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%) non-calcareous shale produced acidic drainage with no added limestone, mixed neutral / slightly acidic drainage with 1 to 2% admixed limestone, and alkaline drainage with 3% or greater admixed limestone. Later, following longer periods of leaching, the shale with 1 to 2% 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 empirical 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 ton/ac or 1120 to 1450 t/ha) and exceeded permit requirements, (2) pyritic materials were selectively handled, (3) backfilling was timely, 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 where incorporated into the backfill, concurrently with mining and reclamation and when done in conjunction with other best management practices.

Although not directly related to alkaline addition, a subsequent study of the use of acid-base accounting (ABA) for predicting surface coal mine drainage quality (Brady et al., 1994) showed a strong empirical relationship between the presence of neutralizing minerals in the overburden (generally carbonates) and the alkalinity of postmining 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 postmining 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 which simulates a naturally alkaline site should assure alkaline postmining water quality.

Skousen and Larew (1995) studied the economics of an alkaline addition project which imported alkaline shale from a nearby mining operation to an operation which was deficient in neutralizers. Significantly, for this discussion, the alkaline addition project successfully prevented AMD. Although the deficiency calcu-

lated from ABA data was equivalent to a one-foot thick layer of the alkaline shale, 3 to 4 ft of shale was actually imported.

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 data were examined using significance thresholds. Sulfur contents less than 0.5% 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 the threshold concept, overall (representing the entire volume of overburden to be mined) NP and NNP values greater than 10 ppt and 5 ppt $CaCO_3$, respectively, produced consistently alkaline water. NP and NNP values less than 1 ppt and -5 ppt $CaCO_3$, respectively, 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 % (10 to 30 ppt of NP) inhibit pyrite oxidation. Moreover, maintenance of alkaline conditions created by carbonate dissolution are not conducive to bacterial catalysis or ferrous iron oxidation and greatly limits the activity of dissolved ferric iron, interrupting the self-propagating acid cycle (Equation 13.3).

Rose et al. (1995) reported the results from an ongoing alkaline addition demonstration project in Clearfield County, Pennsylvania which indicated positive but preliminary results. More recent data from monitoring wells in the backfill show mixed results. Baghouse lime, a waste product from lime production, was applied at rates ranging from 150 to 1,080 ton/ac (336 to 2420 t/ha), adjusted to 100% $CaCO_3$ content, based on ABA calculations using significance thresholds and making up any 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 (Figures 13.2a through 13.2d). 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 mg/L in all of the monitoring wells indicate that AMD is being produced but neutralized.

Based on the experience from the Rose et al. (1995) study site, it is probably unrealistic to precisely 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 on the Kauffman site. Cells were constructed of material with 2% pyritic sulfur and mixed with different rates of alkaline material. Although alkaline addition reduced the generation of acidity by as much as 96%, even the highest alkaline addition rate, equivalent to 3.4% $CaCO_3$, was insufficient to prevent AMD formation. Two important considerations were suggested by this study. First, the high-sulfur overburden was exposed to weathering for a considerable time period before construction of the cell and application of alkaline material. The 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.

Smith and Dodge (1995) reported on an alkaline addition site in Lycoming County, PA, which was part of the original Brady et al. (1990) study. Alkaline addition rates of 600 ton/ac (1,350 t/ha) and daylighting of an underground mine resulted in dramatic improvements in water quality from the underground mine discharge (Figure 13.3). Pre-mining net acidity values exceeded 100 mg/L. After remining, the discharge was predominately alkaline. Increased sulfate concentrations indicated that the water quality could be attributed to neutralization by imported alkaline material

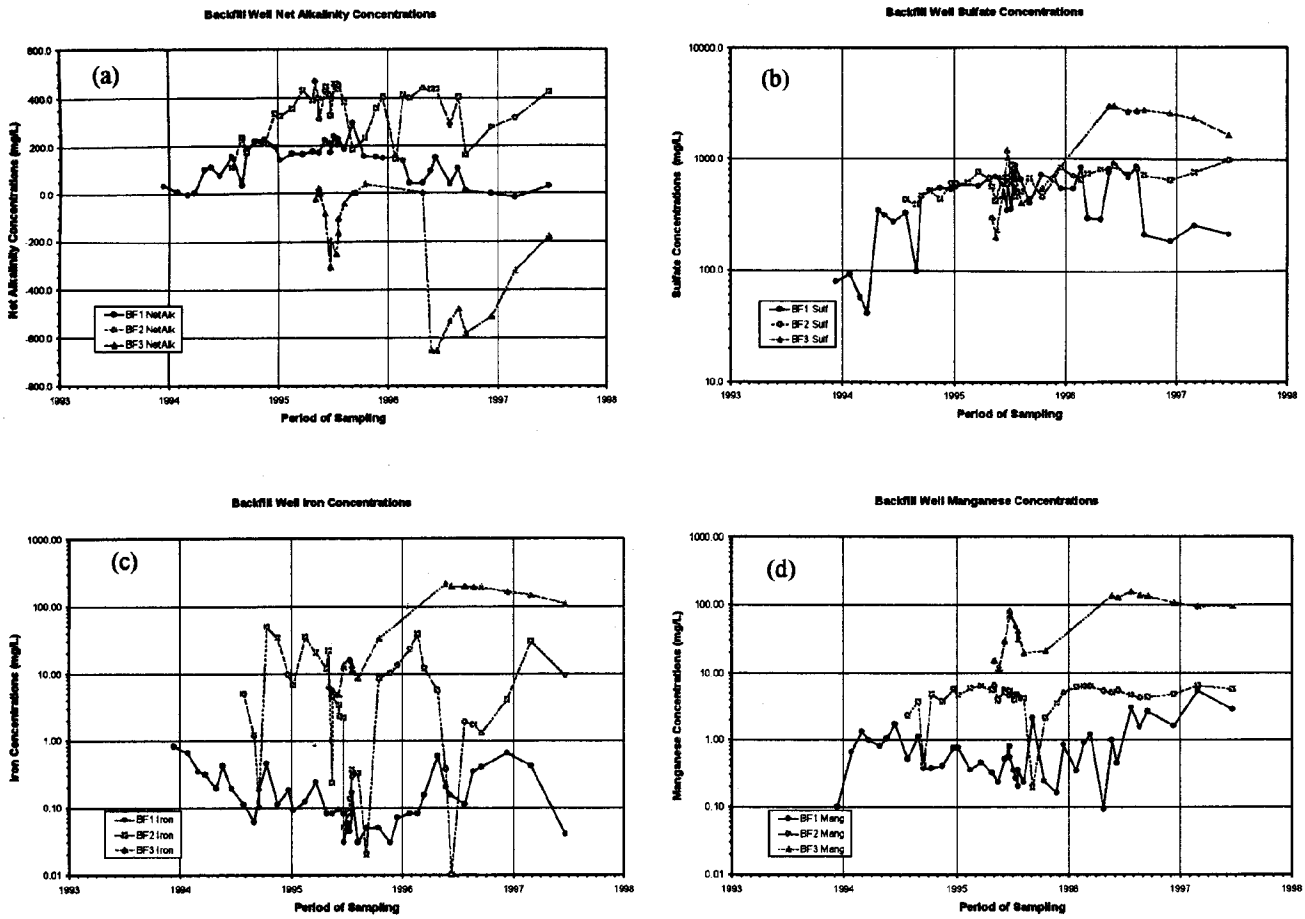

Figure 3.2 Water quality from backfill wells in the Kauffman demonstration surface mine, Clearfield County, PA showing postmining net alkalinity (a), sulfate (b), iron (c), and manganese (d). Well BF1 is located in the area with the highest alkaline addition rate; well BF3 represents the area with the lowest alkaline addition rate; and well BF2 is located near the boundary between the high and low application rate areas.

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.

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. Alkaline addition was employed 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 which 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) and discussed in Chapters 1 and 6 of this report. 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.

The results of the Wiram and Naumann study were favorable. Monitoring wells on the site, which initially produced acidic drainage with excessive iron and manganese, showed marked increases in alkalinity and decreased concentrations of acidity, iron, and manganese.

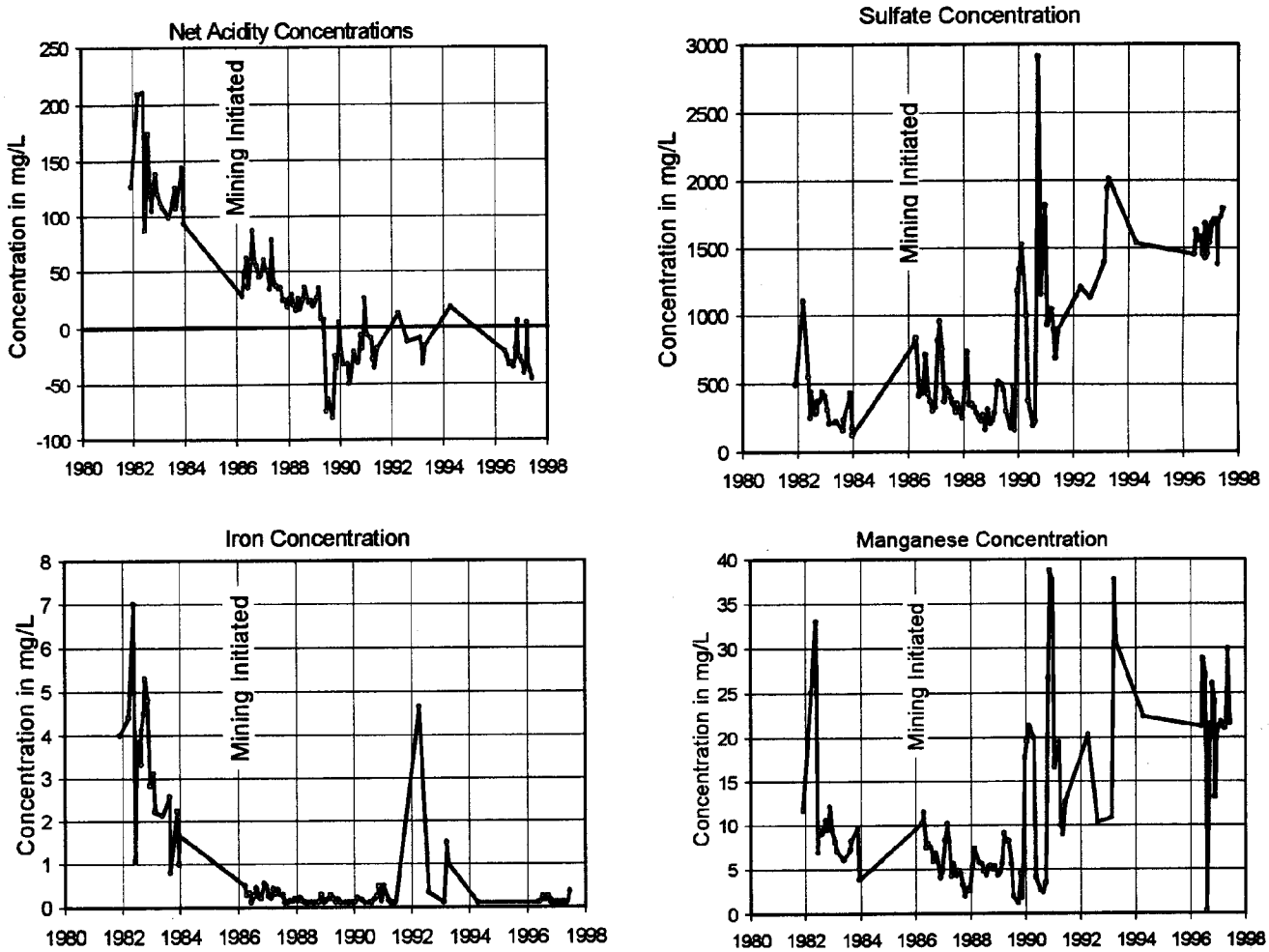

Figure 13.3 Changes in water quality at the Fisher Mining M-1 discharge showing the effects of alkaline addition done in conjunction with daylighting of a deep mine. Updated from Smith and Dodge (1995).

Alkaline Addition Practices

Fifteen years of research into alkaline addition has shown that it 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: (1) How much alkaline material and what type of material should be applied? (2) How should the alkaline material be emplaced in the backfill? and (3) Where is it appropriate to use alkaline addition?

Application Rates

Field studies of alkaline addition appear to be converging on a required application rate sufficient to achieve approximately 1.5 to 3% $CaCO_3$ equivalent in order to effectively prevent acidic drainage from typical surface mines with low to moderate pyrite content. This application rate appears deceptively low. One percent $CaCO_3$ equates to approximately 37 tons of $CaCO_3$ (33,600 kg) for each acre-foot of overburden. A 100-acre (40.5 hectare) surface mine with an average overburden thickness of 50 feet (15.2 m) needing 1% additional $CaCO_3$ would require 183,500 tons (166,500 tonnes) of added alkaline material or 1,835 ton/ac (4110 t/ha). So 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 et al. (1994) and Perry and Brady (1995), Tables 13.1a - 13.1d 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 sampled interval based on an approximation of the areal extent of that interval and unit weights for overburden materials. Coal intervals are multiplied by a pit loss factor of 0.1, assuming approximately 10% 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 ft (0.15 m) 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.

Table 13.1a 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 13.1b 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 13.1c 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 13.1d 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 ABA 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 (Table 13.1). 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% $CaCO_3$. An example calculation is shown below:

Tons of overburden: 1,000,000 (907,200 tonnes)

Acres of mining: 20 (8.1 hectares)

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 (9,072 tonnes)

Tons per acre required: 10,000 tons / 20 acres = 500 ton/ac (1,120 t/ha)

Adjusted for alkaline material with 80% $CaCO_3$ equivalent: 500 tons/acre / 80% = 625 ton/ac (1,200 t/ha)

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, DEP 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, all other factors being equal, is risky at best with only 59% of the study sites in this class producing alkaline drainage. 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 the availability and cost of alkaline additives.

The summary in Table 13,1 is based on a limited number of observations and only separates overburden quality into broad categories. Until more alkaline-addition sites are studied, it may be premature to rigidly apply it to a wide variety of geologic and geographic settings. As more data are compiled, our ability to accurately determine the minimum alkaline addition rate needed to obtain alkaline drainage should improve. Also, based on the limited experience to date with alkaline addition sites, most alkaline addition projects using more than 500 ton/ac (1,120 t/ha) as

$CaCO_3$ have been successful. Except for alkaline addition projects on mines with very low sulfur, projects using less than 500 ton/ac (1,120 t/ha) have consistently failed to produce alkaline drainage. This is based on a very small population of alkaline addition sites and almost no sites having the very worst overburden characteristics. At this point, it would be premature to conclude that alkaline addition of more than 500 ton/ac (1,120 t/ha) will ensure success on all sites or that lower 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 it on the regraded spoil surface and disk it into the upper portion of the spoil. This approach is usually 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 two 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, this report, Figure 1.1). 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. (3) Contact of limestone with acid-producing materials is very limited in the surface environment.

The earliest alkaline addition projects spread all of the alkaline material on the pit floor, prior to backfilling, reasoning 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 was saturated, however, and iron remained ferrous, calcite on the pit floor should function like an anoxic drain neutralizing acidity. Nonetheless, the key appears to be to get the alkaline material mixed throughout the spoil and especially with the more pyritic material. 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 ton/ac (224 t/ha) to the pit floor, although at least 20 ton/ac (4.5 t/ha) should be applied to provide complete coverage.

Alkaline addition is frequently done in conjunction with special handling of high-sulfur zones, where high sulfur material is placed in pods and isolated from percolating ground waters. Alkaline material can be admixed with the high sulfur material to prevent AMD formation within the pod and it 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 and inhibit flow through it (Rose et. al., 1995).

Recommended procedures for the handling of imported alkaline materials have undergone an evolutionary process 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. 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 circumstances which require isolation or neutralization of a high-sulfur pavement, and then no more than is needed to provide sufficient coverage. The use of alkaline addition as part of special materials handling has not yet been fully evaluated although some demonstration projects are underway.

Unless the remaining spoil is clearly alkaline, sufficient alkaline material should also be retained for distribution throughout the backfill.

Alkaline Materials and Verification

Although many different sources of alkaline materials may be available, most alkaline addition projects have used crushed limestone or a limestone-based waste product. Provided that the product grain size is small, the chief factor in determining its required application rate, relative to other alkaline materials, is its neutralization potential, expressed in calcium carbonate equivalence. Twice as much material with 50% $CaCO_3$ equivalent NP would be required, for example, in place of pure $CaCO_3$. Typical alkaline materials which are useful as alkaline additives include kiln dust, crushed limestone, limestone crusher waste, partially burnt lime, off-spec lime products, and fluidized bed combustion ash. Regardless of the alkaline material to be used, the application rate should be adjusted to reflect its neutralization potential as calcium carbonate equivalent. It is also necessary to periodically retest the neutralization potential of the alkaline material being used, with a frequency determined by the variability of the material.

A critical step in a successful alkaline addition project is to insure that the alkaline addition plan is properly carried out - both the amount of material to be applied and its distribution throughout the site. Because of the large quantities of materials involved, this requires careful record-keeping of each shipment of alkaline material and calculation of the quantities of material distributed. Depending on the method of mining, quantities of alkaline material distributed should be tabulated for each individual cut or phase of the operation.

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 their distribution is so uneven that some portions of the backfill will not receive enough neutralizers to prevent or neutralize AMD. Alkaline redistribution then becomes largely an exercise in materials handling. Alkaline stratigraphic units must be clearly identified in the field, segregated, transported to the alkaline-deficient area, and incorporated into the backfill. Depending on the quantity of alkaline material available and its characteristics, 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 exists only in limited areas of the operation and in certain stratigraphic intervals, throughout the site. Through this approach, thorough mixing of alkaline material could be achieved while avoiding the need to field-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, which are currently producing alkaline drainage. The Bridgeview "Morrison" site in Township, Fayette County, PA had abundant calcareous rock over most of the site with NP's as high as 700 ppt $CaCO_3$, but more typically in the 100 to 300 ppt $CaCO_3$ range. There were two areas of about 5 ac (2 ha) each which were of low cover and the calcareous rock was missing due to erosion and weathering. Alkaline material from the high cover area was transported to these low cover areas. Postmining water quality from the lobes is alkaline.

The Amerikohl "Schott" site in Westmoreland County had calcareous rock on only about 8 ac (3 ha) of the 38 ac (15 ha) site. Originally four acid-base accounting holes were drilled. These were supplemented by additional holes that were drilled to determine the lateral distribution of the calcareous rock. The calcareous rock was concurrently mined with other phases of mining 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 ton/ac (44.6 t/ha). Four years of postmining water quality monitoring shows the water to be net alkaline with alkalinity ranging from 10 mg/L to 138 mg/L (Eric Perry, personal communication, 1997). More details are available on this mine in Perry et al. (1997).

Alkaline Addition as a Best Management Practice on Low Cover Overburden

In many cases, relatively low (less than 300 ton/ac (670 t/ha)) alkaline addition rates have been employed on mine sites which indicated a relatively minor potential to produce acid mine drainage but were lacking in any significant calcareous strata. Although these sites commonly have correspondingly 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 (12 m)) overburden have had calcareous minerals and pyrite leached out by weathering (Brady et al., 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, rain water does not meet effluent limits because it has a pH less than 6.0. Thus, postmining water from weathered overburden may also have a pH of 6.0 or less. The addition of alkaline material is needed to ensure alkaline postmining drainage.

Although this scenario seems logical, and general observations over the years suggest this is true, 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. The area had been previously mined on a rider seam 10 ft (3 m) above the main bench of the middle Kittanning (MK) coal. The mined area was not reclaimed. The recent operation mined the MK coal and reclaimed the previously mined area. The total area affected by MK coal removal was 11.5 ac (4.6 hectares) and the maximum highwall height (including old spoil) was about 20 ft (6.1 m). Overburden analysis was performed on five drill holes, but only sulfur was determined. The deepest hole was 18 ft (5.5 m) to the bottom of the coal and shallowest was only 5 ft (1.5 m). The 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 rock encountered, ranging from 0.28 to 0.50%. Sulfur in the rest of the overburden was 0.13% or less. No NP's were determined, but it is near certainty, based on experience with other low cover sites, that calcareous minerals were not present.

Mining began in January, 1988 and was "completed" by the end of March, 1988. It is known that some alkaline material was added during mining, but we have not been able to determine the amount. A permit condition required 10 ton/ac (22 t/ha) of limestone on the pit floor, and there would have been another 5 to 10 ton/ac (11 to 22 t/ha) of limestone added to the reclaimed surface for revegetation purposes. It is suspected that the above amounts are minimums, and the actual amount added was probably several times greater.

A downgradient discharge from an unreclaimed pit, monitoring point K1, was monitored before and after mining. Following mining, the location of the discharge moved down hill to the lower seam that was mined. It is unclear why this point was not monitored during mining although it may have gone dry. Figures 13.4a through 13.4c show water quality through time for pH, net alkalinity, and sulfate. Water quality improved following mining. Because the overburden contained virtually no source of alkalinity other than what was imported, the increase in alkalinity would not have been possible without the importation of limestone. The added material has been adequate to maintain net alkaline conditions from 1990 to when it was last sampled 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 et al., 1996). Iron and manganese data are difficult to interpret because the samples were unfiltered and many samples have elevated suspended solids.

It would have been helpful to know exactly how much alkaline material was added to this site. Comparatively small amounts (perhaps around 40 ton/ac (90 t/ha)) may have been sufficient on this site because of the small amount of overburden present and its highly weathered nature. This site illustrates that a surface mine with weathered overburden, lacking 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.

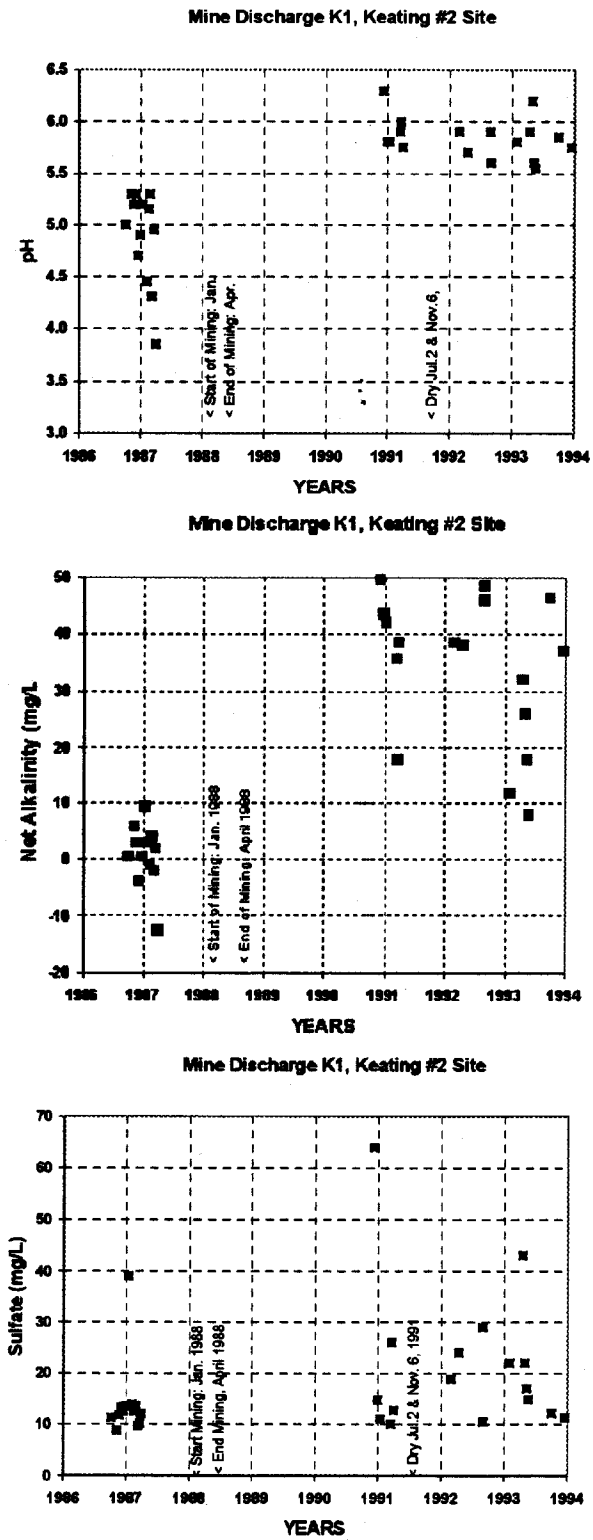

Figure 13.4 Water quality before and after mining at the Keating #2 Site, Clinton County, Pennsylvania where alkaline material was applied to the pit floor at a relatively low rate as a best management practice.

Cost Comparison

The practicality of alkaline addition, as a means of preventing AMD formation, depends largely on economics - how much alkaline material is needed, the cost of the alkaline material, transportation costs, and the added cost of incorporating the alkaline material into the backfill. These costs can vary widely from site to site. In many cases these costs can determine whether or not a site can be mined. But assuming that a site could be permitted for mining with or without alkaline addition, it is also useful to examine the costs which would be avoided if alkaline addition were used in lieu of treatment of a long-term discharge of acid mine drainage. In order to perform this analysis, several assumptions must be made about the expected postmining drainage quantity and quality, with and without alkaline addition. Costs can then be estimated for long-term treatment and for alkaline addition. The following is an example of this type of calculation for a 100-ac (40.5-ha) site which, without alkaline addition, would be expected to produce approximately 50 gpm (3.2 L/sec) of acidic drainage with a net acidity concentration of approximately 100 mg/L and Fe of 20 mg/L. The flow rate is based on expected annual recharge of 10 in (25.4 cm) / year, typical for the northern Appalachians. Acid base accounting data, however, indicate the need for 500 ton/ac (1,120 t/ha) of alkaline material.

Alkaline Addition Costs:
100 ac @ 500 ton/ac = 50,000 tons (45,455 mtons) of alkaline material

Cost of waste lime @ $1/ton:	$ 45,455
Transportation @ $8/ton:	363,640
Materials handling @ $1/ton:	45,455
Total cost of alkaline addition:	$ 454,550

Avoided Treatment Costs:
50-year treatment costs for 50 gpm (3.2 L/sec) discharge, 100 mg/L acidity, 20 mg/L Fe estimated using REMINE computer program (U.S. EPA, 1988) and present value = 27.2 x annual cost: $1,183,445

In this particular example, and assuming that alkaline addition effectively prevents the formation of acid mine drainage which would otherwise be created, it is a far less expensive alternative than long-term (50-year) treatment of a postmining discharge. The treatment cost estimate assumed that caustic soda would be the lowest-cost conventional treatment alternative. This analysis contrasts somewhat with a site-specific analysis performed by Skousen and Larew (1995) which examined the costs of an alkaline redistribution project

and calculated treatment costs over only a 20-year term. Because of the assumptions involved, this cost-analysis should be viewed as a mechanism for comparing the relative costs of treatment versus alkaline addition and not as a reliable cost indicator for a specific mining project.

Summary

The addition of alkaline material, usually a limestone-derived waste product, to surface mine backfills can be an effective method of compensating for overburden that is naturally deficient in neutralizers. In order to successfully prevent the formation of acid mine drainage, a sufficient quantity of alkaline material must be added to the backfill. Most successful alkaline addition sites to date have used substantial application rates, exceeding 500 ton/ac (1,120 t/ha). Lower rates have only proven to be effective for low-cover overburden with very low sulfur content. Alkaline material is best applied by distributing it throughout the backfill although it may be useful to place up to 100 ton/ac (220 t/ha) on the pit floor. Surficial applications of alkaline material are less effective due to low calcite solubility 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.

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