

EFFECTIVENESS OF THE ADDITION OF ALKALINE MATERIALS AT SURFACE COAL MINES IN PREVENTING OR ABATING ACID MINE DRAINAGE: PART 2. MINE SITE CASE STUDIES

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Abstract. The effectiveness of preventing or ameliorating acid mine drainage (AMD) through the application of alkaline additives is evaluated for eight surface coal mines in Pennsylvania. Many of the mine sites had overburden characteristics that made prediction of post-mining water quality uncertain. Alkaline materials were applied at rates ranging from 42 to greater than 1,000 tons as calcium carbonate per acre. In addition, two sites that were mined and reclaimed without alkaline additives are included for comparative purposes.

Overburden sulfur concentration and "neutralization potential" (NP) data for multiple strata at each mine site were used to compute the cumulative, mass-weighted "maximum potential acidity" (MPA) and "net neutralization potential" ($NNP = NP - MPA$) by using three different calculation methods. Post-reclamation water-quality data were used to compute the net alkalinity (= alkalinity - acidity). The most conservative determination of NNP, whereby MPA is calculated by multiplying the total sulfur concentration, in weight percent, by 62.5 instead of 31.25, yielded the best agreement with net alkalinity (patching signs on NNP and net alkalinity). The error in prediction using each method was that the reclaimed overburden was computed to be alkaline overall ($NNP > 0$), but the post-reclamation water was acid (net alkalinity < 0).

In general, alkaline addition rates were probably insufficient to neutralize, or too late to prevent, acid production in the mine spoil. At six of the seven mine sites that had overburden with insufficient NP relative to MPA ($NNP < 0$), the addition of alkaline materials failed to create alkaline mine drainage; AMD was formed or persisted. A control site which also had insufficient alkaline material, but did not incorporate alkaline additives, generated severe AMD. Two sites that had substantial, natural alkaline overburden produced alkaline drainage. Although the addition rates appear to be inadequate, other factors, such as unequal distribution and exposure of the acid-forming or neutralizing materials and hydrogeological variability, complicate the evaluation of relative effectiveness of using different alkaline materials and placement of the acid- or alkaline-producing materials.

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Introduction

Acid mine drainage (AMD) from surface coal mines is a severe problem in Pennsylvania as well as other Appalachian coal mining states. Discharges of water from reclaimed mine sites must meet acceptable effluent limits; treatment of the discharges can be a major financial burden to a coal mine operator.

In Pennsylvania, the strata at some mine sites cannot be mined without causing AMD pollution because insufficient quantities of naturally alkaline material are present to neutralize the AMD. At coal mines with abundant naturally alkaline strata, mine drainage is commonly alkaline. Therefore, the importation and addition of alkaline material to alkaline-deficient mine spoil may produce sufficient neutralization potential to prevent or abate AMD. However, the majority of mine sites that have been reclaimed using imported alkaline materials produce AMD. One problem is knowing the quantity of alkaline material that must be added to produce the desired effect. Another problem is knowing the best place to add alkaline material within a mine site.

This paper summarizes the history of alkaline addition as a reclamation technique, and presents the results of a study of overburden and water-quality data at 10 reclaimed surface coal mines in the bituminous coal fields of Pennsylvania (fig. 1). Emphasis is placed on evaluating the recommended alkaline-addition rates as compared to the calcium-carbonate deficiency calculated by acid-base accounting (Sobek et al. 1978; Smith and Brady 1990; Cravotta et al. 1990). Factors such as the mine hydrogeology, operational history, mining method, placement and type of imported alkaline material, and selective handling of strata are evaluated. The study sites include mines where alkaline addition was used in an attempt to abate existing AMD problems, as well as mines where alkaline addition was used in an attempt to prevent AMD in areas not previously mined.

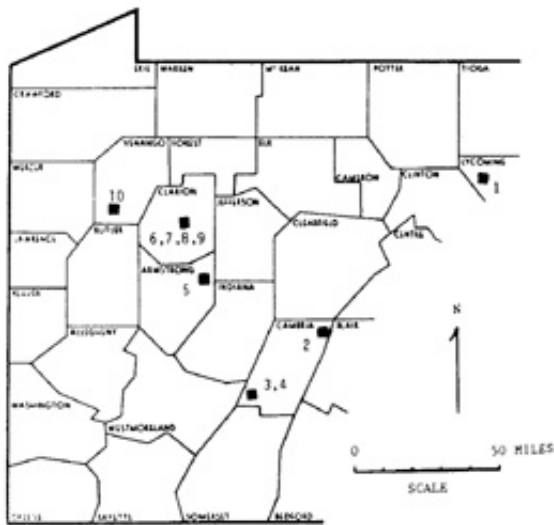


Figure 1. Map showing the locations of mine sites 1 through 10 in western Pennsylvania.

Historical Background on Alkaline Addition in Pennsylvania

The Pennsylvania Department of Environmental Resources (PaDER) is responsible for the review and approval of permits for surface coal mines in Pennsylvania. The PaDER developed procedures for review of plans for alkaline addition on the basis of two reports. The first report is, "Suggested Guidelines for Method of Operation in Surface mining of Areas with Potentially Acid-Producing Materials," by the West Virginia Surface Mine Drainage Task Force (1979). In "Appendix C" entitled "Immediate Lime Requirement" was the suggestion that, "A realistic lime requirement figure is probably a third of the maximum potential acidity from total sulfur." The second report is, "The Application of Limestone and Lime Dust in the Abatement of Acidic Drainage in Centre county, Pennsylvania" by Waddell et al. (1980). Rock, stratigraphically lower than the coal-bearing units, was excavated and redeposited during construction of Interstate 80. Acidic discharges flowed from the toe of this spoil. A mixture of limestone and lime-kiln flue dust was added to part of the spoil at the rate of 267 tons per acre (tons/acre). Although improvements in water quality were observed within the treated and untreated areas, the improvements in the treated areas were thought to be the most significant.

These early suggestions of success in correcting AMD encouraged the PaDER to permit alkaline addition at surface coal mines where the strata, according to acid-base accounting (ABA), showed only a slight deficiency of calcareous material. ABA considers two variables - - neutralization potential (NP), in tons of calcium carbonate per 1,000 tons of overburden (tons CaCO_3 /1,000 tons), and total sulfur, in weight percent (%), which is converted to "maximum potential acidity" (MPA) reported as tons CaCO_3 /1,000 tons. A detailed discussion of the chemical stoichiometric relations that are assumed in ABA is given in Cravotta. et al. (1990). The net neutralization potential (NNP) of mine spoil is computed by subtracting mass-weighted MPA from NP. A negative, or deficient, NNP has been interpreted as the quantity of CaCO_3 that must be added to prevent or abate AMD. Alkaline addition rates were generally calculated at one-third the NNP as suggested by the West Virginia Surface Mine Drainage Task Force (1979), although sometimes the addition rate was increased slightly as a "safety factor."

As this study clearly shows, most reclamation using alkaline addition at surface coal mines in Pennsylvania has failed to prevent or abate AMD.

Previous studies focused on alkaline addition as a means of abating existing AMD problems (Geidel 1982; Lusardi and Erickson 1985; Caruccio and Geidel 1984, 1986; Waddell et al. 1980) and not as part of the ongoing mining operation. In general, two alkaline-treatment schemes were advanced: (1) Waddell et al. (1980) hypothesized that it was unnecessary to neutralize all the potential acidity in pyritic spoil because the addition of alkaline materials to create pH greater than 4.5 would inhibit the bacterial catalysis of pyrite oxidation. (2) Lusardi and Erickson (1985) assumed that most acid is produced near the surface and that it was only necessary to add sufficient limestone to balance the net deficiency in the upper spoil zone. However, these attempts to abate AMD by adding alkaline material to pyritic spoil resulted in limited, if any, success because effluent limits were seldom met or maintained.

The advent of alkaline addition and selective handling, as well as the poor success of literal interpretation of ABA, necessitated the development of guidelines for understanding which strata were potentially alkaline or acid producing. on the basis of PaDER's experience it was concluded that a NP of 30 tons CaCO_3 /1,000 tons (and "fizz", effervescence during reaction with dilute hydrochloric acid) and a total sulfur content of 0.5% were reasonable guidelines to be used in defining strata that were potentially alkaline or acid producing (Brady and Hornberger 1989). Addition rates were generally calculated on the basis of total sulfur values greater than 0.5%; the permittee was given "credit" for strata with NP's greater than 30 tons CaCO_3 /1,000 tons.

Methods

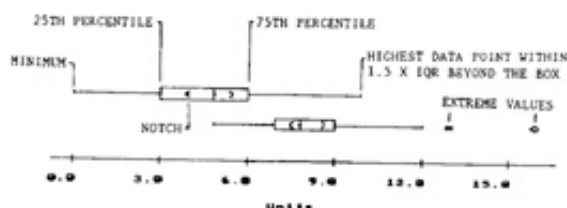
The method of selection of mine sites for this study was one of gathering data and then eliminating sites for which necessary information was lacking. The data required for site selection included ABA overburden data and post-mining discharge or ground-water-quality data (pH and concentrations of alkalinity, acidity, iron, manganese, and sulfate). Overburden samples must have been collected from drill holes no farther than a few hundred feet from the area mined. Furthermore, the mining methods and plans must have been documented and the alkaline addition must have been performed as specified in the permit. All sites that met the selection criteria were included.

Overburden analysis data for total sulfur and NP at sites 1 through 8 and 10 (fig. 1) were obtained from PaDER permit files. Data for mine site 9 were obtained from U.S. Geological Survey (USGS) project files. Cumulative mass-weighted NNP was calculated by using a computer-spreadsheet program (Smith and Brady 1990) that included multiplication factors of 31.25 and 62.5 to compute MPA from the total sulfur data (Cravotta et al. 1990).

Water-quality data were obtained from coal-company files and PaDER permit or USGS project files; PaDER and USGS samples were analyzed by the PaDER laboratory. Water samples were collected from toe-of-spoil seeps, monitor wells, and (or) deep mine discharges that were downflow from the mine site. Net alkalinity [in milligrams per liter as calcium carbonate (mg/L CaCO_3)] was calculated by subtracting acidity (base-neutralizing capacity) from alkalinity (acid-neutralizing capacity) (Stumm and Morgan 1981, p. 163-166). Net alkalinity was used in previous AMD studies (diPretoro 1986¹; diPretoro and Rauch 1988; Erickson and

Hedin 1988) because it reflects the regulatory requirement that alkalinity exceed acidity, and it allows comparison of a single water-quality parameter with overburden NNP.

Water-quality data were evaluated using "notched" boxplots (Velleman and Hoaglin 1981; Helsel 1987) (fig. 2). The box is defined by the interquartile range (IQR = 25th to 75th percentiles). The median (50th percentile) is shown as a "+" within the box. Notches "()" identify the 95-percent confidence interval around the median (Hettmansperger and Sheather 1986) and are useful in testing the difference between median values for data subsets. For example, a pair of boxplots in figure 2 shows that the medians for two subsets of data are significantly different at the 95-percent confidence level. The notches enclosing the median do not overlap - - the right-side notch of the upper box is not greater than the left-side notch of the lower box. However, if the notches for a pair of boxplots overlap, then the medians for the two subsets are not significantly different at the 95-percent confidence level.



The mining history for individual case studies was determined from permit-file inspection reports, discussions with coal-company personnel and PaDER mine inspectors, and field investigations by the authors. The historical information gathered includes the area mined, mining method and equipment used, compliance record, hydrologic conditions during mining, speed of the operation, and size of the active mine.

Case Studies

Eight surface-coal mines where alkaline addition was permitted by the PaDER met the selection criteria for inclusion in this study. Two additional mines, where alkaline materials were not added, are also included: Mine site 3 is a Control for comparison with site 4, and site 10 is an example with abundant naturally alkaline strata. For comparison of similarities and differences of the ten mine sites selected for study, table 1 lists site characteristics, and table 2 lists the NNP of the overburden and net alkalinity of post-mining water samples. Each mine site is unique in terms of mining methods, size of the mine, hydrogeology, stratigraphic interval, overburden quality, pre- and post-mining water quality, monitoring program, and so forth. With the exception of mine sites 3 and 9, the mines were developed after 1980, and modern mining and reclamation practices were used. Overburden NP and total sulfur data were available for all sites except site 2, for which only total sulfur data were available. Pre- and post-mining water-quality information was available for all sites except mine site 10. References to MPA and NNP are based on the revised chemical stoichiometry of Cravotta et al. (1990). The following discussions are provided to address the mine and overburden characteristics, methods and materials used for alkaline additives, and related water-quality data.

Mine Site 1: Lycoming County. Mine site 1 is situated on a relatively flat, isolated hilltop. Approximately 210 acres of the lower Kittanning (Bloss) coal were mined, along with lesser acreages of the overlying middle Kittanning, upper Kittanning, and lower Freeport coals.

Maximum highwall height was about 135 ft. The mining area includes an abandoned deep-mine complex of approximately 70 acres in the lower Kittanning coal. It also includes approximately 34 acres where the lower Freeport coal was previously surface mined; drainage was diverted from the surface mined lower Freeport to the deep mine via an underdrain system. Mining has taken place continuously since the early 1970s and continues to date. Underground mine workings were first encountered in late 1984. Approximately 45 acres have been daylighted using a dragline.

Table 1: Mine Site Characteristics

MINE SITE	COUNTY	AREA (ACRES)	NO. OF OVERBURDEN HOLES	-----Tons as CaCO ₃ per acre-----				QUALITATIVE OVERBURDEN COMPOSITION**	SELECTIVE OVERBURDEN HANDLING
				ALKALINE ADDITION TOTAL	PIT FLOOR	SPOIL	SURFACE		
1	Lycoming	45	3	500	50	350	100	Low NP/Low S	NO
2	Cambria	26	1	42	22	10	10	Low NP/Low S	YES
3	Cambria	47	2	0	0	0	0	Low NP/Med S	NO
*4	Cambria	75	2	648	54	0	594	Low NP/Med S	YES
5	Armstrong	19	1	140	0	0	140	Med NP/Med S	NO
6A	Clarion	54	2	100	20	0	80	Low NP/Low S	NO
7	Clarion	60	2	300	20	0	280	Low NP/Low S	NO
*8	Clarion	29	2	54	0	0	54	Low S/Low NP	YES
*9A	Clarion	2.5	2	1,120	0	0	1,120	Low NP/High S	NO
*9B	Clarion	2.5	2	724	0	0	724	Low NP/High S	NO
*9C	Clarion	2.5	2	6	0	0	6	Low NP/High S	NO
10	Venango	41.5	2	0	0	0	0	High NP/Med S	YES

*Alkaline material includes hydrated lime, Ca(OH)₂, which is reported as equivalent tons CaCO₃ (see Cravotta et al., 1990).

**NP = neutralization potential, in tons CaCO₃/1000 tons; S = total sulfur concentration, in weight percent.

Table 2: Comparison of net neutralization potential of overburden^{1, 2} and post-treatment net alkalinity³ of coal-mine drainage

Mine Site ⁵	NNP Before Alkaline Addition (no thresholds)		NNP After Alkaline Addition MPA = 31.25 x % S		NNP After Alkaline Addition MPA = 62.5 x % S		Post-treatment Median Net Alkalinity of Coal-Mine Drainage
	MPA = 31.25 x % S	MPA = 62.5 x % S	(no threshold)	(thresholds) ⁴	(no threshold)	(thresholds) ⁴	
1	+6.03	+1.51	+6.90	-0.31	+2.31	-1.43	+67
2	-3.92	-7.84	-3.06	-1.73	-6.98	-4.32	-62
3	+2.85	-4.97	+2.85	-3.76	-4.97	-7.71	-468
4	+2.77	-10.81	+4.91	-6.07	-7.97	-13.03	-74
5	+15.69	+3.91	+16.68	+14.65	+4.91	+7.06	+11
6 A	+4.10	-3.82	+4.36	+2.88	-3.56	-1.71	-55
7	-3.88	-11.67	-1.14	-1.03	-9.43	-4.30	-685
8	+5.55	+1.90	+5.76	+3.17	+2.32	+1.88	-184
9 A	-3.40	-7.92	-0.81	+0.61	-2.91	+1.04	-2190
B	-6.16	-13.23	-3.65	-2.20	-9.99	-6.19	-860
C	-9.68	-20.74	-9.66	-6.83	-20.70	-13.65	-3332
10	+170.47	+156.81	+170.47	+168.77	+156.81	+156.6	+118

¹ "Net neutralization potential" (NNP = NP-MPA) reported in tons CaCO₃/1,000 tons (Smith and Brady 1990); "maximum potential acidity" (MPA) computed by multiplying total sulfur (S), in weight percent by 31.25 and 62.5, respectively (Cravotta et al. 1990).

² An appendix with the actual overburden analysis data is available from the authors.

³ Net alkalinity (= alkalinity - acidity) in mg/L as CaCO₃.

⁴ Threshold where total S<0.5%, calculated MPA=0; where NP<30 or no effervesence reaction with dilute HCl, calculated NP=0.

⁵ Mine sites 3 and 10 did not have alkaline additives incorporated with the mine spoil. These sites are included for comparative purposes.

Most ground water from the site discharges from the abandoned underground mine via an air shaft. Water quality was monitored at this discharge Point since 1979, and flow rates were monitored continuously since 1982. Prior to the 1985 water year (October 1, 1984 through September 30, 1985), pH and net alkalinity were relatively constant, while iron and manganese concentrations varied by a factor of 10 (fig. 3).

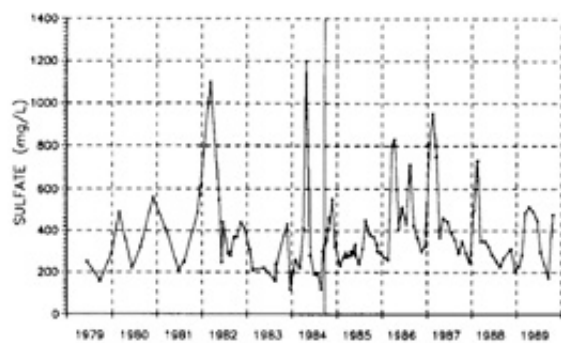
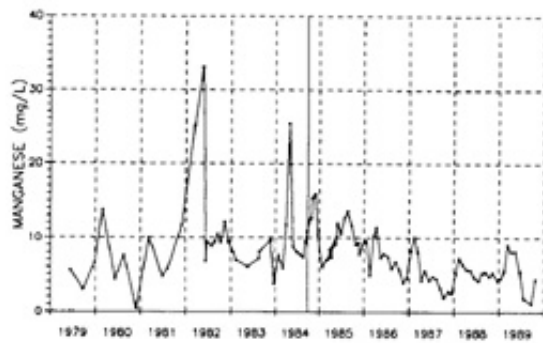
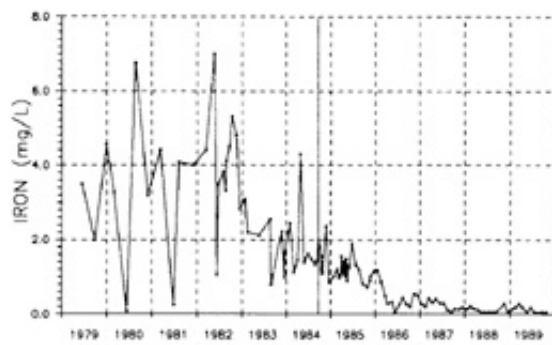
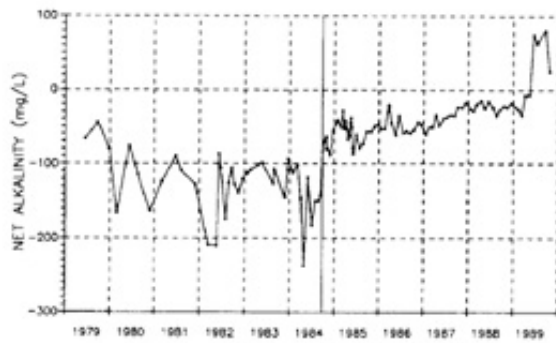
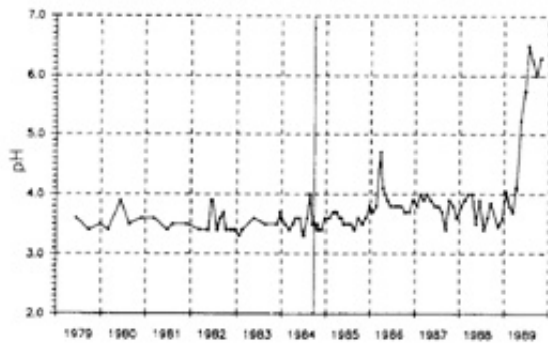


Figure 3. changes in selected water-quality characteristics over time at mine site 1 in Lycoming County. The vertical line in 1984 indicates the time when deep mine daylighting and increased alkaline addition began.

Overburden from the three drill holes sampled is characterized by low total sulfur and low NP contents. However, many samples are composites of strata from large intervals (up to 28 ft thick). The highest total sulfur content measured was 1.29%. only one sample, other than the coals, contained sulfur exceeding 0.5%. The highest NP was 33 tons CaCO_3 /1,000 tons.

Pit cleanings were segregated from the overburden using a loader and were placed high in the backfill. The operator initially applied nearly-pure CaCO_3 (a limestone crusher screening waste product) to the pit floor and upper part of the backfill at a total rate of about 50 tons/acre. In late 1984, roughly at the same time the deep mine complex was encountered, this rate was increased to approximately 500 tons/acre, a rate that exceeded permit requirements. Approximately 50 tons/acre were spread on the pit floor and 100 tons/acre were applied to the upper surface of the rough backfill. The remaining 350 tons/acre were distributed through the backfill using limestone crusher screenings as blast hole stemming. From January 1985 through September 1989, a total of 19,000 tons of calcareous material were applied over 48 acres. Table 2 indicates that the overburden NNP increases, and is positive, after the addition of limestone on the basis of MPA computed by multiplying total sulfur by 31.25 or 62.5; however, NNP is negative if thresholds are used. For site 1 the NNP computed using the thresholds is unreliable because large intervals of strata were sampled and composited causing the possible dilution of high-sulfur or high-NP concentrations.

Figure 3 shows that a dramatic increase in net alkalinity, accompanied by a decrease in iron concentrations, occurred during the 1985 water year and continued through the 1989 water year. Sulfate and manganese concentrations, however, show little change (fig. 3). Manganese has a tendency to remain dissolved in acidic to neutral solutions ($\text{pH} < 8$) whereas iron will readily precipitate at $\text{pH} > 4.5$ (Hem, 1985). This increase in alkalinity is concurrent with the deep-mine daylighting and the application of alkaline material at a rate of 500 tons/acre. The increasing alkalinity of the water in combination with the persistently elevated sulfate concentrations indicates that acid production continues in the spoil but is neutralized. Since 1988, water quality at the deep-mine discharge has attained "conventional mine-drainage effluent standards" (alkalinity > acidity; $6 < \text{pH} < 8$; $\text{Fe} < 6 \text{ mg/L}$; $\text{Mn} < 4 \text{ mg/L}$).

The apparent neutralization of acidity indicates that the addition of alkaline materials played the dominant role in effecting the water-quality improvement. The removal of unmined, pyritic coal pillars by daylighting may have reduced that contribution of sulfate; however, surface mining may have produced additional sulfate which offsets the daylighting reduction. Furthermore, if neutralizers were liberated from the overburden, net alkalinity would have increased prior to the alkaline addition.

Mine Site 2: Cambria County. Site 2 Encompassed 26 acres of Mercer coal removal by Surface mining. No part of the permit area had been Previously mined, although the adjacent Property had been extensively mined, with AMD resulting. A period of 43 months elapsed from initiation of mining on Mine site 2 to final backfilling (0.6 acres/month). Maximum highwall height was 45 ft.

Site 2 occupies the crest of a gently sloping hill and recharge to the site is predominantly

from precipitation. Because AMD occurred at an adjacent mine, the Permit approval for mining at site 2 required Overburden analysis and alkaline addition. The strata were assumed to lack substantial carbonate minerals, so only total sulfur was determined in the overburden samples.

The sulfur concentrations and lithologic descriptions of samples from One overburden hole drilled within the area mined were used in ABA calculations (table 2); however, additional lithologic data from other drill holes were used to define the stratigraphy. The overburden composition and thickness differed across the site, because of removal of strata by erosion and replacement by channel sandstones, and because of bifurcation (splitting) of the coal seam. The number of splits in, and thickness Of the Coal (2 to 5 ft), differed from hole to hole. The majority of the strata consists of sandstone, with "coal spars" at the base. In most drill holes a 0.5- to 3-ft-thick, black, carbonaceous shale was encountered immediately above the coal. The overburden hole encountered 1.5 ft of this black shale, which contains 1.12% total sulfur, and 2 ft of coal, which contains 2.64% total sulfur. Because of the numerous binders in the coal, approximately 30 percent of the coal horizon was spoiled as "pit cleanings." The pit cleanings were segregated and placed in pods a minimum of 10 ft above the pit floor to keep them above the water table after the mine was reclaimed. Because of the large amount of pit cleanings and the thin cover, some of this material was placed within a few ft of the final graded surface.

The alkaline material consisted of baghouse limestone (captured air-borne particulate material), which was applied at a rate of 42 tons/acre- About 22 tons/acre were added to the Pit floor; about 10 tons/acre were added to the tops of the pit-cleaning pods and to the backfilled surface prior to replacement of topsoil.

About 200 ft downslope and downdip from mine site 2, water discharges from a seep on the adjacent, previously mined area. Samples collected over 3.5 years define conditions prior to mining at site 2 (fig. 4). Since mining at site 2, the pH of the seep has decreased, and acidity, sulfate, iron, and manganese concentrations have increased. Following backfilling, the seep water quality has maintained significantly lower pH and net alkalinity and greater iron, manganese, and sulfate concentrations than are present in the premining samples (fig. 4). Water from a monitor well screened through the backfill was similar in quality to that from the seep. Alkaline addition has not prevented acid formation at this mine site. AMD may have been predicted on the basis of the negative NNP (table 2).

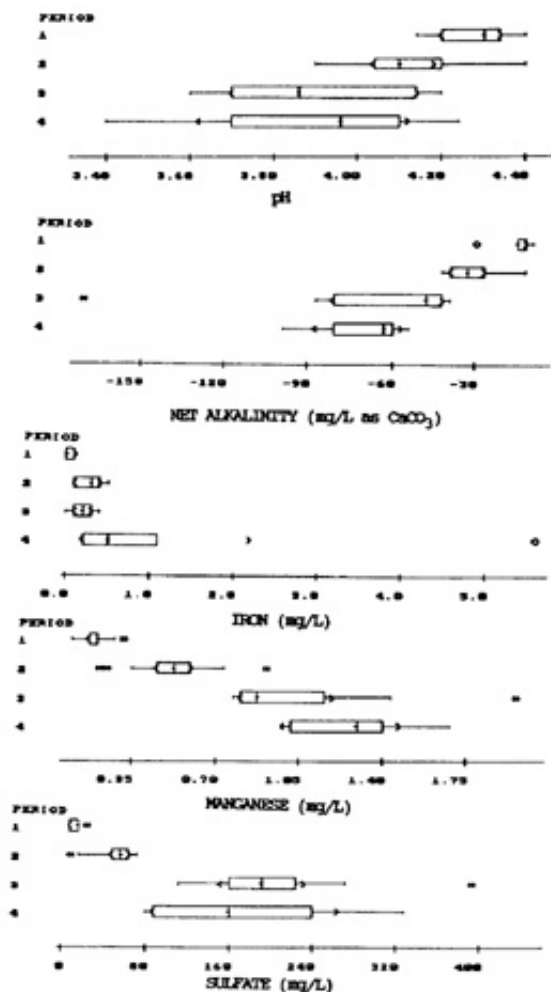


Figure 4. Boxplots showing changes in water quality at mine site 2 in Cambria County. Period 1 represents data collected over a 3-year period prior to activation of mining (N=14). Period 2 is the first 20 months of mining (N=14), and period 3 is the second 20 months of mining (N=11). Period 4 represents post-mining water quality (N=6).

Mine Sites 3 and 4, Cambria County. Site 3 is an unreclaimed mine similar in size and configuration to the adjacent mine site 4. No alkaline addition or special handling was conducted at mine site 3, and the backfilling and reclamation are incomplete. In contrast, mine site 4 is a recently reclaimed mine where alkaline materials have been added to a 75-acre area where the lower Kittanning, lower Kittanning rider, and upper Kittanning coals were mined. The site was active for 60 months (1.25 acres/month). Site 4 can be categorized as a contour block-cut operation with a maximum highwall height of 125 ft. Mining and backfilling were on a continuous basis; the open pit area did not exceed 100 ft by 300 ft.

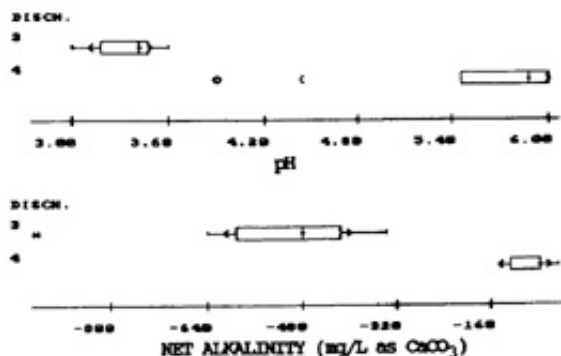
Surface and ground waters affected by nearby deep mining or surface mining of the lower Kittanning are severely degraded, whereas waters from unmined areas have near-neutral pH, low buffering capacity, and low concentrations of metals. Although mine site 4 is adjacent to previously affected areas (including mine site 3), it is neither upflow nor downflow from preexisting AMD.

Overburden-analysis data for mine sites 3 and 4 indicate the presence of some potentially acid-producing strata associated with and overlying the lower Kittanning and lower Kittanning

rider seams and the absence of strata having NP greater than 30 tons CaCO_3 /1,000 tons. Overburden quality is summarized in tables 1 and 2. Selective handling of pyritic materials, removal of pit cleanings, and alkaline addition were performed at mine site 4 to avoid post-mining water-quality problems associated with mine site 3. Hydrated lime was added at a total rate of 240 tons/acre [648 tons CaCO_3 /acre] assuming $\text{Ca}(\text{OH})_2$ has 2.7 times the neutralization capacity of CaCO_3 (Cravotta et al. 1990)] - a rate that exceeded permit requirements. The alkaline material was distributed on the pit floor at a rate of 54 tons CaCO_3 /acre; the remaining 594 tons CaCO_3 /acre were spread over the surface of the rough backfill prior to topsoil replacement (table 1). In accordance with the CaCO_3 deficiency, the above alkaline addition rate represented 44% of the total calculated deficiency. The plans for special handling and alkaline addition were diligently implemented, and most of the pyritic materials associated with the lower Kittanning coal were exported from the mine site.

Figure 5 compares the post-mining water quality for two toe-of-spoil discharges at the downdip boundaries of mines 3 and 4. Both sites have AMD; except for iron, the water quality at the alkaline addition site 4 is significantly better than that at site 3. The traditional method of computing the overburden MPA yields positive NNP (table 2); however, use of thresholds or a multiplication factor of 62.5 in ABA computations yields negative NNP values (table 2), which are consistent with the negative value for post-treatment net alkalinity at both sites. The water-quality difference between sites 3 and 4 is attributable to the addition of alkaline materials and the different mining and reclamation methods employed at the two sites.

Mine Site 5: Armstrong County. Mine site 5 encompasses 19 acres. The lower and middle Kittanning coal were removed by surface mining of cover that was 30 to 80 ft thick. The area had been mined previously to a depth of 30 to 40 ft. Eight months elapsed from initiation of mining to completion of backfilling (2.4 acres/month) Reclamation was concurrent with mining.



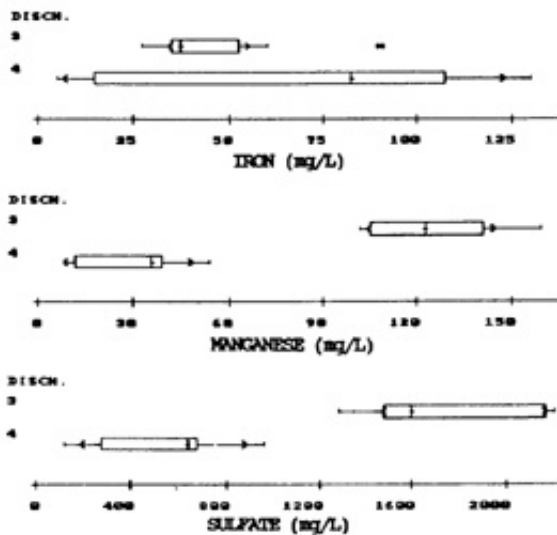


Figure 5. Boxplots showing comparison of water quality data for mine sites 3 (N=8) and 4 (N=5) in Cambria County. Mine site 4 had alkaline addition; mine site 3 did not and served as a control.

Several toe-of-spoil discharges emanated from the previously mined area. The water quality was generally alkaline, and the pH was 5 to 6. Site 5 is located on a hillside with a substantial area upslope from the mine. Ground-water recharge to the site is from direct precipitation and from the drainage of upslope areas.

The overburden hole closest to the area mined was drilled above the highwall through strata that were not mined. The unmined, upper cover was not included in the ABA calculation, and the top part of the hole, to the weathered depth of 20 ft, was assumed to be inert (NP and sulfur are 0). Nine ft of shale above the lower Kittanning coal had total sulfur content ranging from 0.69 to 1.36%, and 28 ft of overlying strata had NP ranging from 30 to 72 tons $\text{CaCO}_3/1,000$ tons. The composite strata from this hole contained an equivalent NP as 3,875 tons $\text{CaCO}_3/\text{acre}$ extrapolated over the area mined. Although the overburden analysis for the area mined shows an overall excess of neutralizers (table 2), overburden holes outside the area mined lacked alkaline strata, and AMD discharges from nearby mines. Therefore, alkaline addition was performed at mine site 5 because of the uncertain effect of mining on water quality and the variable overburden composition. The alkaline material consisted of imported limestone dust that was added at a rate of 140 tons/acre to the backfill surface prior to topsoil replacement.

Boxplots in figure 6 show the quality water from a toe-of-spoil seep below mine site 5. The initial water quality is representative of the effects of the preexisting shallow-cover mining on water quality. The subsequent samples illustrate water quality during and after the thick-cover mining. There is no significant difference between the pre- and post-mining water quality (pH, net alkalinity, iron, manganese, and sulfate) at the 95-percent confidence level. Even the lowest pH and highest concentrations of sulfate and metals measured during the post-mining period meet conventional effluent limits. The positive net alkalinity of the post-treatment drainage is consistent with positive NNP computed by any method (table 2).

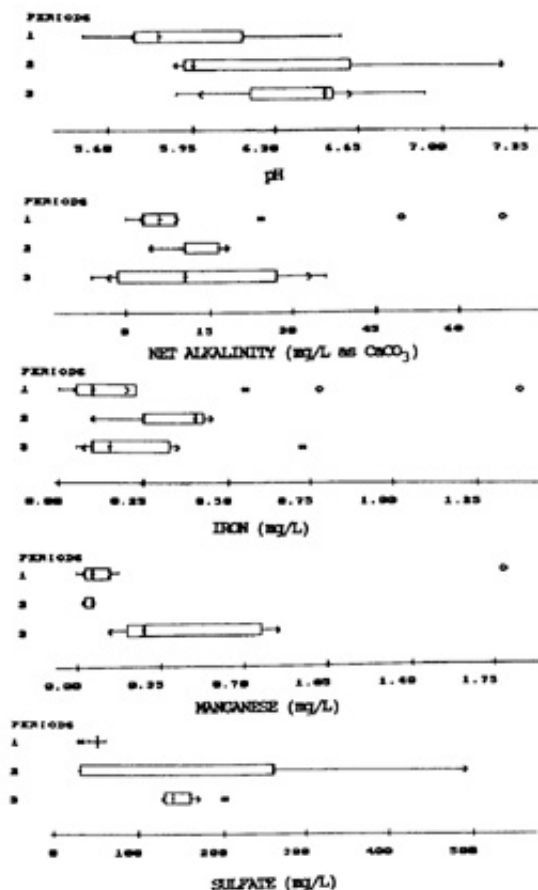


Figure 6. Boxplots showing changes in water quality through time for mine site 5 in Armstrong County. Time 1 represents "premining" data (N=13) over a 2-year period. Time 2 is data collected during mining (N=3), and time 3 is 1 year of post-mining water quality (N=7).

The mining and reclamation at site 5 did not cause degradation of the seep; however, the remedial effects of alkaline addition cannot be isolated from those of naturally occurring calcareous strata. The quantity of naturally alkaline material in the mine spoil was much greater than that of imported alkaline material. Additionally, ground water seepage to the open pit was probably alkaline, and the mining operation Proceeded very quickly, thus limiting the aeration of the spoil.

Mine Site 6: Clarion Mine site 6 consists of two adjacent, similarly-sized mines, 6A and 6B. Approximately 54 acres of upper and lower Clarion coal were mined at site 6A where alkaline materials were applied during mining and reclamation. The same seams of coal were removed at mine site 6B, but alkaline addition was not implemented; mine site 6B serves as a control. Both mines are located on the side of a hill, and both mines receive some recharge from areas above the area mined. Prior to mining at site 6A, water did not discharge from the coal outcrop, but during mining, seepage(?) water was observed in the open pit.

Rock samples from the two overburden holes indicate considerable differences in the stratigraphic positions of the high-sulfur and alkaline strata. The strata with the highest sulfur content were encountered between the lower and upper Clarion coal seams. Other than the coal samples, no strata contain sulfur greater than 1.0%. Drill hole 1 encountered a 12-ft-thick shale between the Clarion coals that had NP of 36 to 43 tons CaCO₃/1,000 tons. Drill

hole 2 encountered strata between the coals that had a maximum NP of 21 tons CaCO_3 /1,000 tons and strata immediately above the upper Clarion coal that had a NP of 32 tons CaCO_3 /1,000 tons. The amount of naturally alkaline material (composite NP for all strata) was equivalent to 1,925 tons CaCO_3 /acre for the mined area. A summation of the overburden quality is given in table 2.

Approximately 21 months elapsed from initiation of mining to completion of backfilling at mine site 6A (2.6 acres/ month). Maximum highwall height was about 85 ft. Pit cleanings were selectively handled, and placed at least 10 ft above the pit floor. Alkaline materials were applied as a "safety factor." Baghouse limestone with a CaCO_3 equivalent of nearly 100 percent was applied to the pit floor at a rate of 20 tons CaCO_3 /acre and near the top of the backfilled spoil, but beneath the topsoil, at a rate of 80 tons CaCO_3 /acre. Application rates on the pit floor on at least one occasion were greater than 20 tons CaCO_3 /acre. Nevertheless, the quantity of alkaline material added to the spoil may not have been adequate to offset the pre-treatment, negative NNP (table 2). If MPA is computed by multiplying total sulfur by 31.25, then NNP is positive after alkaline addition; however, if MPA is computed by multiplying total sulfur by 62.5, then NNP is negative. Addition of limestone increased the overburden NNP from -3.82 to only -3.56 tons CaCO_3 /1,000 tons on the basis of the 62.5 factor (table 2).

Discharges from mine sites 6A and 6B were both alkaline and acidic. Special handling of overburden or addition of alkaline material was not performed at mine site 6B, which serves as a control. Post-treatment water-quality data for several discharges are grouped by mine site and are shown as boxplots in figure 7. There is no significant difference between the post-treatment water quality of sites 6A and 6B at the 95-percent confidence level. The negative values of NNP after alkaline addition, on the basis of MPA computed using the factor of 62.5 (table 2), suggest that acidic discharge from mine site 6A may have been predicted. Thus, the alkaline-addition rate at site 6A may not have been adequate to cause substantial improvement in the water quality.

Mine Site 7: Clarion. Minesite 7 encompassed a mined area of approximately 60 acres of lower Clarion coal and 31 acres of upper Clarion coal. A period of 20 months elapsed from initiation of mining to completion of backfilling (3 acres/month). The maximum highwall height was 60 ft. Although mine site 7 is situated on a hilltop, in a groundwater recharge area, considerable water was encountered during mining. The downflow monitor well consistently had a static water level of 0.5 to 1 ft above the bottom of the coal. A 2- or 3-acre portion of site 7 was previously mined and abandoned. It had developed a mildly acidic discharge, which could possibly be eliminated by additional mining and reclamation. Because the overburden analysis characterized this site as low sulfur and low NP (tables 1 and 2), mining of the additional 60 acres was planned with an alkaline addition rate of 300 tons CaCO_3 /acre (about 19 percent of the calculated NNP, where MPA is computed using a factor of 62.5). A 2-ft-thick sandstone stratum contained total sulfur of 0.78% and NP of 28 tons CaCO_3 /1,000 tons, the highest measured in the overburden, respectively. A 5-ft-thick shale stratum had 0.53% total sulfur. Other than the coal, these are the only strata that contained greater than 0.5% total sulfur.

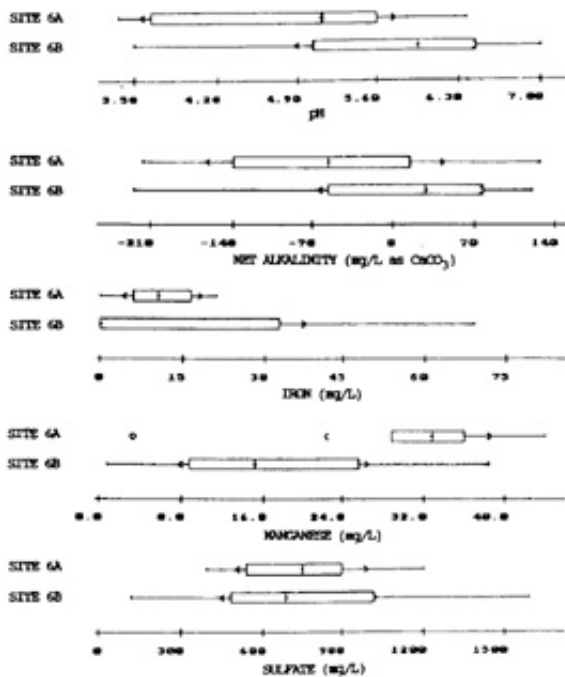


Figure 7. Boxplots comparing water quality of multiple discharges from mine site 6A (N=6) with those from mine site 6B (N=11) in Clarion County. Mine site 6A had alkaline addition; mine site 6B did not and served as a control.

There was no selective handling plan, however the rock between the Clarion coal seams was routinely placed high in the backfilled mine spoil above the mine floor. Baghouse limestone with a CaCO_3 equivalent of nearly 100 percent was applied at a total rate of 300 tons CaCO_3 /acre- Approximately 280 tons CaCO_3 /acre were placed on the backfilled surface, below the topsoil, and an additional 20 tons CaCO_3 /acre were spread on the pit floor.

Figure 8 shows temporal variations in concentrations of acidity and iron in water sampled from a downflow monitor well from 1982 through 1986. Water quality of seepage prior to mining in 1982 can be characterized as mildly acidic with moderate metals and sulfate concentrations, which indicate some effects from previous mining. Figure 8 shows that the concentrations of acidity and iron increased through the period of mining, and then decreased following backfilling. The addition of alkaline materials had no apparent effect on the water quality, which remained considerably worse than that of the pre-mining period. Although the preexisting discharge disappeared, alkaline addition failed to prevent or abate acid ground water. The negative NNP after alkaline addition (table 2) suggests that insufficient quantities of alkaline materials were added and that acidic, post-mining water quality may have been predicted.

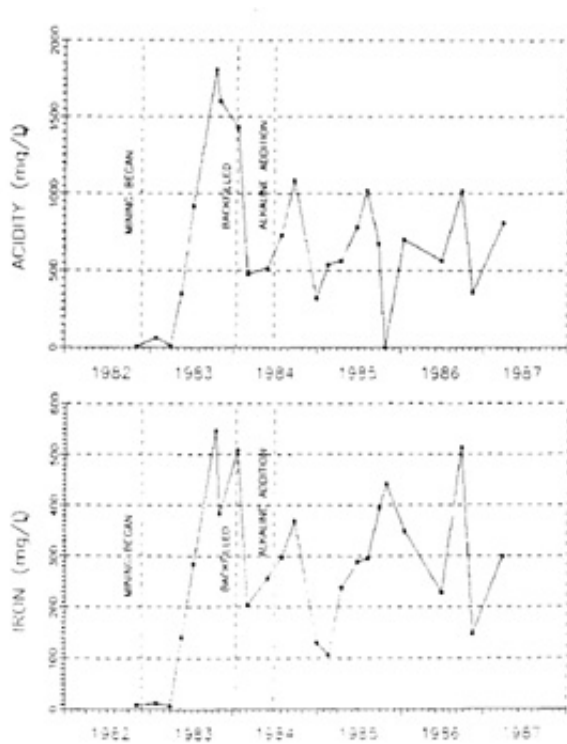


Figure 8. Acidity and iron concentrations over time for a downflow monitor well at mine site 7 in Clarion County.

Mine Site 8. Clarion county. mine site 8 encompassed a 29-acre area mined for the middle Kittanning coal, 2 acres of which were mined for the upper Kittanning coal. The mine site can be characterized as a hilltop removal/block - - cut operation. The maximum overburden thickness was 85 ft. Mining occurred on a continuous basis over a 22 month period (1.3 acres/month), and the open pit area did not exceed 300 by 500 ft. The premining water quality at site 8 can be characterized by near-neutral pH, positive net alkalinity, and low concentrations of iron, manganese, and sulfate (fig. 9).

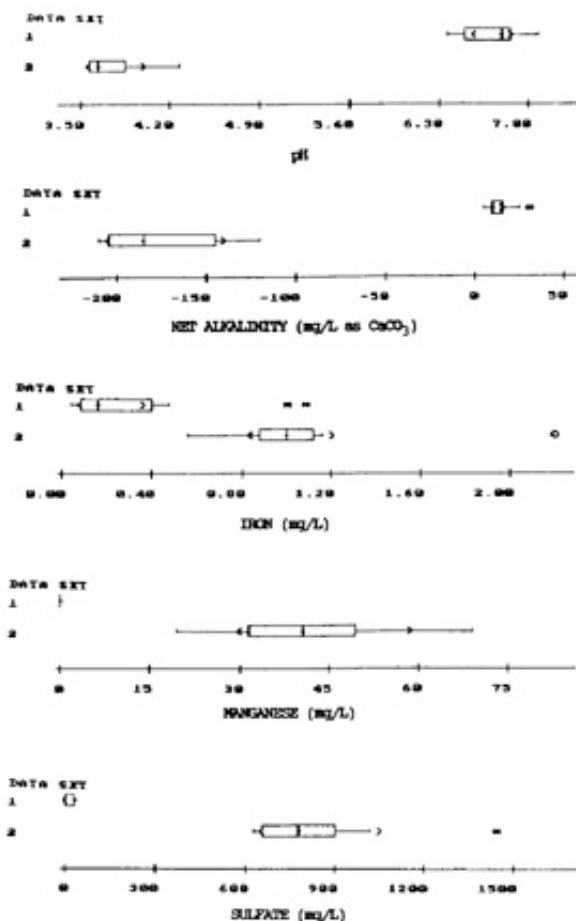


Figure 9. Comparison of pre- (data set 1) and post-mining (data set 2) water quality at mine site 8 in Clarion County. Data set 1 is for a monitor well (subsequently mined through) (N=12). Data set 2 is for a toe of spoil discharge (N=6).

Two holes were drilled in overburden at or near the maximum anticipated final highwall. one of the holes penetrated some strata with NP exceeding 30 tons CaCO_3 /1,000 tons, but overall the strata had only a slight positive NNP; however, the overburden penetrated by the other hole exhibited a negative NNP (alkaline deficiency). Table 2 summarizes the ABA results of the overburden analysis. The overburden is predominantly sandstone, which contains carbonaceous inclusions and which extends down to the middle Kittanning coal. The sandstone interval from the top of the coal to 2.5 ft above the coal had total sulfur contents ranging from 0.56 to 2.63%.

Most mining took place in the alkaline-deficient area; only a small part of the mine uncovered alkaline strata. Table 2 shows a positive NNP, which is probably higher than was actually encountered by mining. The alkaline-deficient strata encountered by one overburden hole are probably representative of the majority of the strata mined. However, overburden data for samples from both holes were used in ABA calculations.

The 2-ft thick sandstone stratum overlying the middle Kittanning coal seam was selectively handled and segregated. For the alkaline-deficient part of the permit area, alkaline materials were applied a rate of 52 tons CaCO_3 /acre over the surface of the backfill prior to topsoil replacement.

Following backfilling and reclamation, acidic water began to discharge from an adjacent area downflow from site 8. Figure 9 compares the pre-mining quality of water from a well within the area mined with that from the post-mining discharge. The pH is lower, and concentrations of net alkalinity, iron, manganese, and sulfate are higher in the post-mining discharge than in premining water at the 95-percent confidence level. No mitigative effects are apparent following the alkaline addition. Furthermore, alkaline, not acidic, discharge would be predicted on the basis of the positive NNP data in table 2; however, the calculated NNP may not be accurate because few alkaline strata were mined.

Mine Site 9. Clarion Approximately 48 acres of upper and (or) lower Clarion coals were mined intermittently from 1961 through 1975 at mine site 9. About half the area was mined for the lower Clarion coal leaving a 70-ft highwall separating an upper and lower bench. At the completion of mining, the mine was backfilled with overburden and coal waste, including tippie refuse from other mines, and was regraded to the original hillside configuration. A toe-of-spoil seep produced severe AMD that required treatment. In 1984, calcareous waste materials were applied to the surface in quantities that were not sufficient to neutralize MPA but sufficient to produce alkaline water in the unsaturated zone ($\text{pH} > 4.5$) that would presumably inhibit bacteria thought to catalyze pyrite oxidation (Waddell et al. 1980).

The mine receives recharge from the reclaimed hillside and undisturbed hilltop. The reclaimed mine spoil has a total thickness ranging from about 10 to 70 ft, in which ground-water saturation varies from less than 5 to nearly 20 ft. The lower Clarion coal crops out along an intermittent stream at the southern boundary of the mine. The coal was not mined near the stream channel in an attempt to restrict the discharge of ground water from the mine; this ground water is acidic ($\text{pH} < 3$) and contains substantial concentrations of dissolved sulfate, iron, and manganese (Williams et al. in press).

The overburden and coal are characterized as having high sulfur and negligible calcareous contents (tables 1 and 2). Eleven samples collected during drilling of a 90-ft-deep drill hole through the highwall represent a relatively complete stratigraphic column; typical concentrations of total sulfur range from 0.05 to 4.77%. The highest sulfur concentrations were from the lower Clarion coal and from strata about 1 ft above and below the coal. None of the sampled strata had a NP greater than 3.5 tons CaCO_3 /1,000 tons. Samples of the tippie refuse had a sulfur content of 1.5 to 2.18%.

In the spring of 1984, limestone fragments (nearly pure CaCO_3) and lime-kiln flue dust [$\text{Ca}(\text{OH})_2$] were applied on the land surface within two 2.5-acre treatment plots and a control plot. ABA computations were performed using overburden analyses of samples from two or more drill holes in each 2.5-acre plot. Treatment plot 9A had a net deficiency of -1,769 tons/acre and received 40 tons/acre limestone plus 400 tons/acre hydrated lime. Treatment plot 9B had a net deficiency of -2,955 tons/acre and received 400 tons/acre limestone plus 120 tons/acre hydrated lime. However, the control plot 9C had a net deficiency of -3,990 tons/acre and received only 2.4 tons/acre hydrated lime (to allow grass planting). Thus, after alkaline addition, assuming hydrated lime has 2.7 times the neutralization capacity as CaCO_3 , the net neutralization potentials for plots 9A, 9B, and 9C, respectively, were about -649, -2,231, and -3,984 tons CaCO_3 /acre.

Ground-water-quality data were collected from two or three monitor wells in each of plots

9A, 9B, and 9C that were screened through the spoil to the mine floor (bedrock). Data for plots 9A and 9B were collected monthly during 1 year before and 3 years after surficial treatment with calcareous materials; however, monthly data for plot 9C were collected only 1 month before but 3 years after treatment. Figure 10 shows that the ground water in the mine spoil, before and after treatment, contained high concentrations of acidity ($\text{pH} < 4.5$; net alkalinity < 0) and of dissolved sulfate, iron, and manganese and that the water-quality generally differed between 9A, 9B, and 9C, reflecting variations in overburden composition and possibly other factors. A comparison of data before and after alkaline addition at plot 9B, shows that none of the parameters (pH , net alkalinity, Fe, Mn, or SO_4) is significantly different at the 95-percent confidence level. Data collected at plots 9A and 9C before and after treatment indicate that pH increased, and Mn concentrations decreased significantly after treatment. However, because the water quality at the control plot 9C may have improved, the improvement in water quality at treatment plot 9A cannot be attributed solely to the addition of alkaline material. Because pyrite and leachable minerals will be depleted as the spoil weathers, a gradual improvement in water quality is expected in both untreated and treated spoil. Nevertheless, if alkaline additives were to prevent or slow the oxidation of pyrite, a difference in the rate of improvement would be expected for the treatment plots 9A and 9B compared with the control plot 9C. However, nonparametric trend tests of the post-treatment data indicate that the rates of concentration changes are not significantly different between treated and untreated plots (Cravotta, U.S. Geological Survey, written commun., 1989).

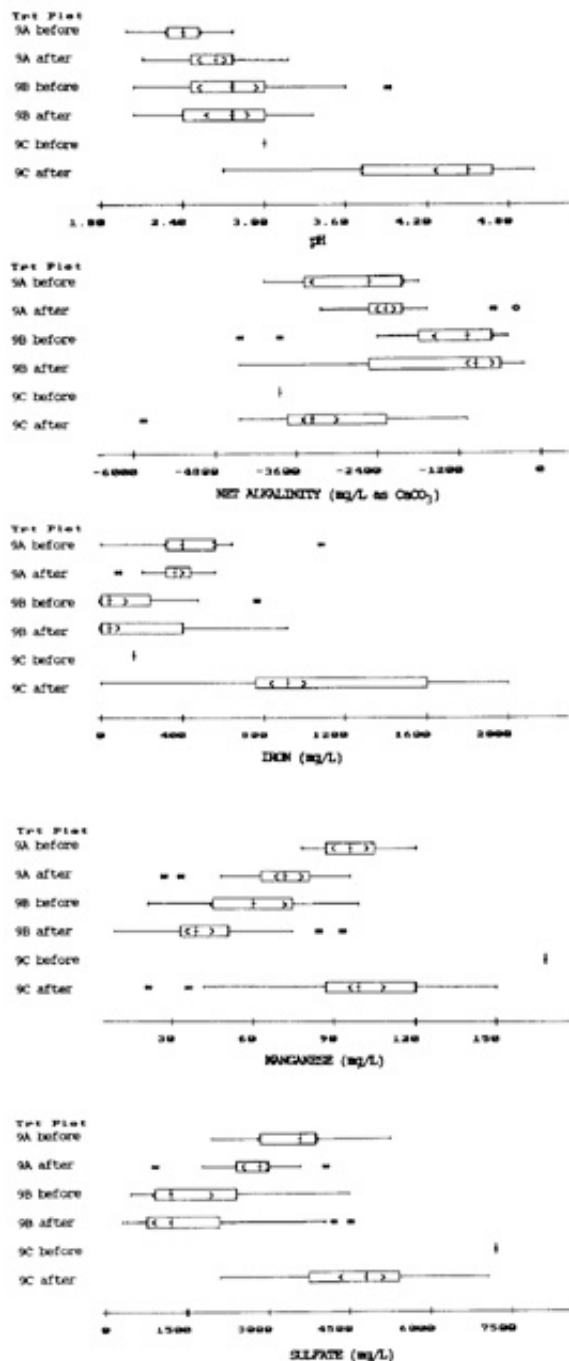


Figure 10. Boxplots of water quality from monitor wells for three 2.5-acre plots at mine site 9 in Clarion County. Plots 9A and 9B had alkaline addition, plot 9C served as a control. The boxplots compare water quality before and after treatment with alkaline additives. Number of samples for each boxplot are as follows: 9A before (N=12), after (N=39); 9B before (N=23), after (N=70); 9C before (N=1), after (N=61).

Acid-mine drainage was not abated nor groundwater quality noticeably improved by the surficial application of alkaline materials at mine site 9. The NNP data in table 2 suggest that acidic ground water at each plot likely could have been predicted considering the MPA computed using the factor of 62.5 following the method of Cravotta et al. (1990). One possible explanation for the persistent acidic ground water in the reclaimed mine spoil is that prior to treatment, pyrite in the stockpiled overburden or mine spoil had been oxidized to

ferric-sulfate minerals, which then provided a source of long-term, leachable acid, sulfate, and iron; the alkaline materials may have been applied too late to inhibit the oxidation of pyrite. Another explanation is that the rate of pyrite oxidation exceeds the rate of dissolution of calcareous materials.

Mine Site 10: Venango County. Mine site 10 was included in the study because limestone and other calcareous rock were present and abundant relative to potentially acid-producing strata. Forty-one acres of Brookville coal were mined, using the box cut method, with trucks and loaders. Maximum highwall height was about 50 ft.

About 8 to 10 ft of marine limestone strata is present about 25 ft above the coal at site 10. The limestone has NP ranging from 536 to 932 tons CaCO_3 /1,000 tons. Another 7 to 13 ft of strata has NP over 100 tons CaCO_3 /1,000 tons. However, a 1-to-1.5-ft-thick stratum immediately above the coal contains 1.09 to 5.5% sulfur, and underclay below the coal contains 1.53 to 2.9% sulfur. No alkaline addition was proposed because the natural strata contained the equivalent of about 18,000 tons CaCO_3 /acre. The sulfur-bearing strata immediately overlying the coal were segregated and placed high above the mine floor in the backfilled mine spoil.

The NNP and net alkalinity data in table 2 indicate that the discharge would be alkaline on average. Post-mining discharge quality, however, has varied from highly alkaline to moderately acid (fig. 11). The most acidic water was collected after heavy rains. The acidity probably result from recharge that dissolves ferric-sulfate minerals that had accumulated in the unsaturated zone during drier periods and from unequal rates of pyrite oxidation and dissolution of limestone. The water samples contain iron and manganese concentrations that exceed conventional effluent limits (6 and 4 mg/L, respectively). These metals and the elevated sulfate indicate that the abundant alkaline material has not prevented the oxidation of pyrite in the backfill, but has neutralized the acidity produced by the oxidation reaction.

Results and Discussion

Every mine site is unique. overburden composition, mining methods employed, volume of rock disturbed, pre- and post-mining ground-water chemistry, hydrogeology, weathering, and many other factors differ among the sites. Each of these factors affects the associated post-mining water quality. Consequently the water quality at each mine site is monitored according to a unique program. Table 1 illustrates some similarities and differences among mine sites in this study. Alkaline-addition rates ranged from zero at sites 3 and 10, which were included for comparative purposes, to greater than 1,000 tons CaCO_3 /acre for a part of site 9.

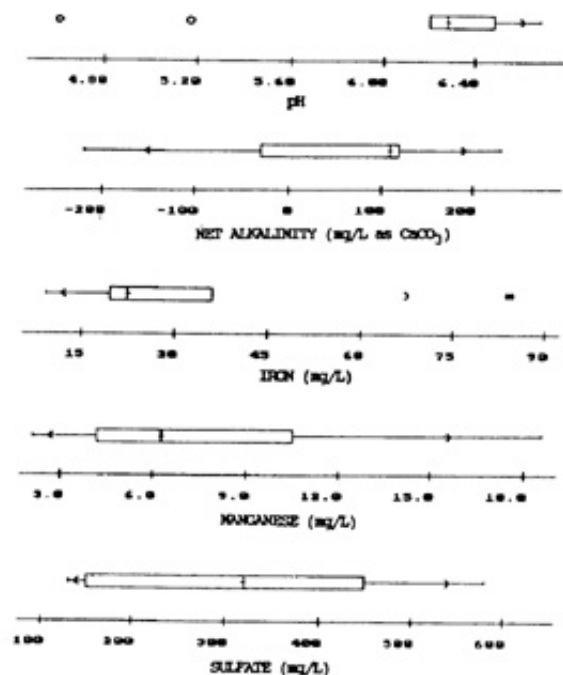


Figure 11. Post-mining water quality of discharge from mine site 10 in Venango County (N=5). This mine had abundant naturally occurring alkaline strata.

The uniqueness of the mines and number of variables to be considered makes a comparison of mine sites difficult; however, some relations between post-treatment, cumulative NNP of overburden and median net alkalinity of mine drainage from the 10 mine sites are apparent (table 2). Six of the eight alkaline-addition plans (mine sites 2, 4, 6, 7, 8, and 9) failed to prevent AND. Of the two sites where post-treatment discharge water was alkaline (sites 1 and 5), site 5 has a substantial thickness of naturally alkaline strata, which were likely to produce alkaline drainage without the supplemental addition of limestone. After alkaline addition, the overburden NNP at mine site 1 was positive (+6.90 tons CaCO₃/1,000 tons) if calculated by the traditional methods of ABA; however, NNP was slightly negative (-0.31 tons CaCO₃/1,000 tons) if calculated using thresholds (table 2). The water quality at site 1 improved after the addition of alkaline material (fig. 3). The formerly acidic discharge from the deep mine that underlies much of the site now meets conventional mine-drainage effluent standards. Although discharges from alkaline-addition site 4 do not meet conventional effluent limits, the water quality is substantially better than that of nearby discharges from mine site 3, an untreated control (fig. 5).

Mine sites 1 and 4, the two sites where water quality improved after the addition of imported alkaline materials, had several things in common: (1) They were treated with the largest total quantities and the second and third largest alkaline-addition rates of the sites studied (table 1). (2) The mining and reclamation techniques used at both sites included selective handling of pyritic materials, timely backfilling, and alkaline-addition rates that exceeded permit requirements. (3) Some potentially acid-forming strata were removed from the mine sites. The coal seam on mine site 1 that was causing acid water to emanate from the deep-mine discharge was removed from the mine site by daylighting. Mine site 4 included removal of most of the pit cleanings.

Two adjacent mine sites were also examined in Clarion County. Mine site 6A received alkaline

additives, and mine site 6B did not. No observable improvement in water quality is apparent from the alkaline additives, which may not have been applied in adequate amounts.

Mine site 9 is the only site in this study where alkaline material was applied solely as a remedial measure 9 years after completion of mining and reclamation. Three 2.5-acre plots were studied, two with alkaline addition and one without. All three continued to produce severe AMD through 1987 (fig. 10). The AMD production results from the limited amount of alkalinity generated from the limestone relative to the amount of acidity produced by pyrite oxidation and by leaching of previously formed ferric-sulfate minerals in the mine spoil.

Alkaline materials were not added at mine site 10, but the site was included in this study to illustrate the potential effect of large amounts of naturally alkaline strata on water quality at a site where there is also some potentially acid-producing strata. The strata at site 10 contained the equivalent of 18,000 tons CaCO_3 /acre. On average, the post-mining water quality was alkaline but the concentrations of metals and sulfate were elevated (fig. 11). Apparently, the presence of large amounts of naturally alkaline material do not always preclude pyrite oxidation and the dissolution of metals and sulfate from the mine spoil.

The variable alkaline and acidic water quality of several discharges from site 6 show that alkaline and acid conditions can be created within the same spoil. Mine site 10, which had an abundance of limestone strata, had a single discharge that varied from alkaline to acid following recharge events. Alkaline-addition sites also have produced alkaline and acidic discharges, but with median net alkaline discharge. Clearly, the process of pyrite oxidation and carbonate neutralization are complicated by the unequal distribution of acid-forming and neutralizing materials. Under some conditions, alkaline waters need to contact the locally pyritic zones of the mine spoil to prevent or neutralize AMD. Hydrogeochemical factors such as the microbial activity; mineral-surface areas; O_2 , CO_2 , nutrient, and moisture contents; temperature; and pH of mine spoil also must be considered.

Table 1 generally indicates mine sites where imported alkaline materials were placed, and if special overburden handling was implemented. Each of the eight alkaline-addition sites, except site 1, had alkaline materials placed entirely, or mostly, at the spoil surface - - the easiest method of application. Alkaline materials were incorporated on the pit floor and within the spoil at five and two of the sites, respectively. Although alkaline-materials were spread on the pit floors at mine sites 1 and 4, where water quality improved after alkaline addition, alkaline materials were also incorporated with the backfill at site 1 and pyritic materials were selectively handled at site 4. Furthermore, sites 2 and 8 also employed selective handling of pyritic material and small amounts of variably placed alkaline additives, but both produced AMD (table 2). Therefore, effects of placement of alkaline materials or selective handling of acidic materials cannot be readily evaluated in this study.

Table 2 shows the overall mass-weighted NNP for each study site before and after alkaline addition. Although total quantities, or rates of application, of alkaline materials appear to be large, they generally are insignificant relative to the NP or NNP of the entire overburden volume before alkaline addition. Table 2 also shows the median post-mining net alkalinity of associated mine drainage or ground water for the 10 mine sites. Mine site 9 was subdivided into three plots 9A, 9B, and 9C, which in combination with mine sites 1-8 and 10, allows comparison of overburden NNP and water-quality net alkalinity for 12 sets of data. By

comparing the sign on NNP and net alkalinity values in table 2, it is apparent that the traditional ABA computation of MPA, by multiplying total sulfur, in weight percent, by 31.25, results in mismatched signs-a wrong prediction of water quality - - for 4 of the 12 sites. The errors in prediction are that the mine spoil is alkaline ($NNP > 0$), whereas the associated water is acidic (net alkalinity < 0). Prediction was not improved by using thresholds, where only values of NP greater than 30 tons $CaCO_3/1,000$ tons (with fizz) and of total sulfur greater than 0.5% are used to compute NNP, although substantially different values of NNP resulted. However, if MPA is calculated by multiplying total sulfur, in weight percent, by 62.5 following the method of Cravotta et al. (1990), then the sign of NNP matched the sign of the overall net alkalinity of waters at 11 of 12 sites (table 2). The acidic discharge from mine site 8 was not predicted by any of the acid-base accounting computation methods, possibly because of an inaccurate estimate of NNP.

The method of ABA calculation that used "thresholds" eliminated some of the problems associated with low-NP overburden, which typically produces AMD even though the sulfur content may be low. For example, mine sites 3 and 4 produced AMD which was correctly predicted by the NNP "with thresholds" (table 2). Using only NP values greater than 30 tons $CaCO_3/1,000$ tons, with a "fizz," eliminated much of the presumed influence of siderite on NP determinations (Morrison et al. 1990). Unless the influence of siderite in NP determinations can be eliminated, thresholds remain a useful concept. However, a disadvantage of assuming strata are inert if total sulfur and NP content do not exceed the threshold values is when large intervals of strata are sampled and composited, causing dilution of high-sulfur or high-NP concentrations. For example, the NNP calculated using thresholds are unreliable for mine sites 1 and 9, for which large thicknesses (up to 28 ft) of composite overburden samples were analyzed.

The results of this study are consistent with previous reports that concluded that NP and "traditional" MPA values, despite being reported in the same units (tons $CaCO_3/1,000$ tons), are not equivalent. In previous practice, it appeared that overburden NP must be at least twice MPA to produce alkaline mine drainage (diPretoro 1986; Skousen et al. 1987; Brady and Hornberger 1989; Ferguson and Erickson 1988). The observed inequality in NP and MPA is partly attributable to the incorrect assumption that CO_2 is completely exsolved during neutralization. Cravotta et al. (1990) argue that some CO_2 will dissolve in the ground water and form $H_2CO_3^*$ a weak acid. Therefore, MPA should be computed by multiplying total sulfur, in weight percent, by a factor of 62.5 instead of the traditional factor of 31.25. Use of the 62.5 factor assumes that the total sulfur is pyritic and that 4 moles of $CaCO_3$ are required to neutralize the acidity from 1 mole of pyrite.

Mining practices such as selective handling of coal pit cleanings, removal of acidic material from the mine site, and concurrent reclamation, appear to have enhanced the success of the alkaline addition.

Summary and Conclusion

In summary, empirical as well as theoretical considerations suggest that alkaline-addition rates are typically inadequate to neutralize AMD. Application rates for alkaline additives are best computed by considering a conservative estimate of MPA, which may be computed by

multiplying total sulfur, in weight percent, by a factor of 62.5 (Cravotta et al. 1990; Smith and Brady 1990). Furthermore, the alkaline material may be most effective if incorporated concurrent with mining and backfilling, when and where the acid-production reactions occur. The alkalinities that can be generated from alkaline additives may be insufficient to abate the acidity of severe AMD and the localized production of acidity from reactive pyrite and ferric-sulfate minerals. Adequate alkaline-addition rates that create positive NNP at mine sites containing acidic strata may neutralize acidity and produce alkaline effluent water, which still contains unacceptable concentrations of sulfate, iron, and other metals.

On the basis of this study of the addition of alkaline materials to selected surface coal mines in western Pennsylvania, the following conclusions were made:

1. Previous methods for determining alkaline-addition rates, especially the concept that only one-third the calculated deficiency was necessary, have failed to prevent or abate AMD. Most alkaline addition rates are negligible relative to calculated deficiencies ($NNP < 0$) and insufficient to prevent or neutralize AMD.
2. The addition of alkaline materials to prevent AMD from surface coal mines may be effective providing that the alkaline-addition rates are sufficient (to offset negative NNP) and the overburden has relatively low-sulfur content. Alkaline materials added to high-sulfur mine spoil, even if sufficient to neutralize acid water, may not reduce concentrations of dissolved iron, manganese, and sulfate.
3. Certain mining practices, such as addition of more alkaline material than required by permit conditions, selective handling of pit cleanings, removal of pyritic material from the mine site, and concurrent reclamation appeared to enhance the effect of alkaline addition on reducing acidity.
4. There is good agreement of signs on post-treatment Overburden NNP and median net alkalinity of associated mine-drainage water when overburden MPA is computed by multiplying total sulfur, in weight percent, by 62.5.
5. Additional studies are needed to determine the most beneficial rates of application and Placement of the alkaline materials. Calculations of deficiencies (NNP) and application rates should be conservative and consider the theoretical arguments given by Cravotta et al. (1990) and the empirical results of this study.

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