

**EVALUATION OF ACID-BASE ACCOUNTING TO PREDICT
THE QUALITY OF DRAINAGE AT SURFACE COAL MINES IN PENNSYLVANIA, U.S.A.¹**

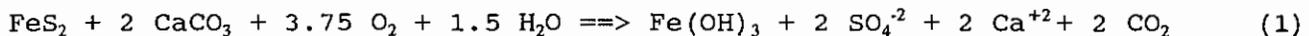
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Abstract: The effectiveness of Acid-Base Accounting (ABA) for predicting surface coal mine drainage quality in Pennsylvania was evaluated. Comparisons between ABA and mine drainage alkalinity, acidity, and sulfate were made for 38 mines in the bituminous coalfield. Neutralization Potential (NP), Maximum Potential Acidity (MPA), and Net Neutralization Potential (NNP) were evaluated with and without "thresholds." Calculations using "thresholds" counted only those values for NP greater than 30 mt CaCO₃/1,000 mt and percent sulfur greater than 0.5%. "Without thresholds" computations included all values. Stoichiometric equivalence factors of 31.25 and 62.5 were used to compute MPA. NP and NNP are the best predictors of postmining drainage quality. Alkaline or acid drainage quality is controlled by as little as 1% to 3% carbonate in the overburden. NNP less than 1% generally results in acidic drainage, and NNP greater than 3% yields alkaline drainage. An empirical relation exists between alkalinity and NP. Postmining alkalinity can be estimated as 4 to 6 times NP (without thresholds). MPA is not a reliable predictor of drainage quality, except in the absence of calcareous strata, where a positive relation exists between acidity and MPA.

Additional Key Words: mine drainage, net alkalinity, neutralization potential, sulfate.

Introduction

Coal mine drainage is the greatest contributor of stream and ground water pollution in Pennsylvania, with more than 3,700 km of stream degraded by mine drainage (Pennsylvania Department of Environmental Resources, 1990). Pennsylvania laws and regulations require a premining evaluation of the probable hydrologic consequences of mining. Pennsylvania has been using acid-base accounting (ABA), since 1978 as one tool for the prediction of postmining water quality. ABA was developed at West Virginia University (Sobek et al. 1978) and is based on the following assumed stoichiometry of FeS₂ and CaCO₃ (Sobek et al. 1978, Williams et al. 1982, Cravotta et al. 1990):



Acidity produced from 1 mol of FeS₂ (64 g of sulfur) is neutralized by 2 mols of CaCO₃ (200 g), or 1 g sulfur to 3.125 g CaCO₃. On this basis, 31.25 mt

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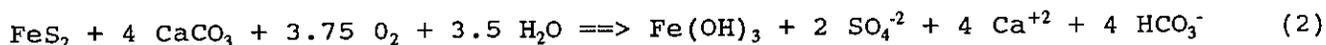
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of CaCO₃ will neutralize 1,000 mt of rock that contains 1.0 wt% pyritic sulfur. Thus, the total percent sulfur is multiplied by 31.25 to obtain a "maximum potential acidity" (MPA), which is in units of mt CaCO₃/1,000 mt of overburden material. This multiplication factor is intended to provide direct comparison with "neutralization potential" (NP) which also has units of mt CaCO₃/1,000 mt.

Cravotta et al. (1990) suggested that the original stoichiometric relationship shown in equation 1 underestimates the maximum potential acidity and proposed the following revised equation:



In this reaction 1 mol of FeS₂ is neutralized by 4 mols of CaCO₃, which results in a mass ratio of 6.25 g of calcite to 1 g pyritic sulfur. MPA is therefore computed as percent sulfur times 62.5. A "net neutralization potential" (NNP = NP - MPA) can be determined for a stratum utilizing the stoichiometry of equation 1 or 2. In theory a positive NNP (surplus) would produce alkaline water and a negative NNP (deficiency) acidic water.

Early ABA interpretations defined "acid-toxic" overburden as any strata with a NNP less than -5 mt/1,000 mt of overburden material (Sobek et al. 1978). This criterion was developed mostly for agronomic purposes, and it was found to be not directly applicable for prediction of mine drainage quality. Some mines evaluated under this guideline produced acid mine drainage and stream pollution. Thus, in Pennsylvania, a more qualitative means of prediction evolved. By the mid-1980's alkaline strata were defined as strata with an NP greater than 30 mt/1,000 mt and a "fizz" (effervescence upon application of dilute HCl). Acidic strata were defined as strata with greater than 0.5% sulfur and an NP less than 30 mt/1,000 mt (Brady and Hornberger 1990).

In Pennsylvania ABA is used in conjunction with other predictive tools. These include consideration of premining water quality, adjacent mining water quality, paleodepositional environments and mine site hydrology.

The objectives of this study were to 1) examine relations among ABA data and postmining water quality parameters, and 2) evaluate the effectiveness of various ways of computing NP, MPA, and NNP for predicting postmining water quality.

Methods

The Pennsylvania Department of Environmental Resources (PaDER) bituminous surface coal mine files were canvassed for potential study sites. Each mine selected for evaluation had postmining ground water data (spoil seeps, monitoring wells, etc.) with multiple samples, and (with one exception) two or more ABA drill holes. Sites approved for refuse or flyash disposal, or having other unconventional conditions like gas well brines or preexisting pollutional discharges, which could complicate water quality interpretations were excluded. Thirty-eight mines in 15 counties were evaluated. Eleven different coal seam horizons are represented with 89% from the Allegheny Group, 7% from the Dunkard group, and the remaining 4% from the Conemaugh and Monongahela Groups.

There is an inherent bias in the sites selected for study. The group consists mostly of mines expected to produce acceptable water quality. A few mines with the worst water quality are older sites that had overburden analysis performed after permit issuance, generally to develop mitigation plans for water quality problems. The PaDER typically does not issue permits with negative NNP results, unless there are compelling reasons to the contrary. In addition to ABA data, the PaDER evaluates all available geologic and hydrologic information. The proposed mine plan and resources that could be affected are also considered in the decision making process. Thus sites at the extreme "bad" end are generally absent from our database. Likewise, where experience has shown that mining a certain seam invariably produces alkaline water (for example, the Redstone coal seam) ABA is rarely requested. Thus the "good" extreme is also missing from our database. This leaves the present study with a preponderance of sites with intermediate ABA properties that are difficult to predict using ABA alone.

Water quality parameters that were evaluated included pH, alkalinity, acidity, and sulfate. Metals data were also compiled but are not reported here. One representative ground water discharge or well was selected for statistical analysis. Selection for sites with multiple sample points was often simplified by one discharge being dominant in flow or all sample points being of similar quality. Water quality data were analyzed with nonparametric statistics because these methods are advantageous for analysis of mine drainage (Helsel 1987). Medians were evaluated as indicating central tendency. Water quality and ABA parameters were summarized and compared using graphical and statistical techniques.

ABA data were processed in an ORACLE database that resides on the PaDER's mainframe computer. This database performed ABA summary calculations using the algorithms and methods described in Smith and Brady (1990) with enhanced capabilities to represent site geometry. Areas of influence were planimetered for each overburden hole. ABA data summary numbers were weighted according to thickness, density, and areal extent of strata based on actual mined area to determine average NP, MPA, and NNP for each hole. MPA was calculated using percent sulfur times 31.25 and 62.5. Data for each hole were combined to obtain average values for the entire mined area.

NP, MPA and NNP were computed with and without "thresholds." Calculations with thresholds "counted" strata that have either a percent sulfur greater than 0.5 wt%, or NP greater than 30mt/1,000 mt with a "fizz." Other strata were considered insignificant in alkaline or acid potential and were assigned a percent sulfur or NP value of "0". Calculations "without thresholds" utilized all reported values for NP and percent sulfur for all strata.

Results and Discussion

Overburden Sampling

Reliable predictions of postmining water quality requires sampling to represent the geochemical and spatial properties of potentially acid-forming and alkaline-forming strata. As density of drill holes increased, the location of calcareous rocks could be determined more easily (fig. 1). Where hole density is less than 4 ha per hole, 93% of the sites had positive NNP and net alkaline drainage. For sites with hole densities greater than 4 ha per hole, only 65%

had positive NNP and only 43% had net alkaline water. This may reflect adjustments to the mine plan to selectively include areas with favorable ABA properties or exclude unfavorable areas on intensively sampled sites. A strong regional and stratigraphic bias exists in our data, as 14 of 15 intensively sampled mines are in one of the four PaDER mining districts.

Calcareous rock can occur as laterally extensive units of fresh or marine limestones and calcareous sediments, discontinuous carbonate strata due to facies changes, and secondary cements and fracture fills. Superposed on these diagenetic and postdiagenetic processes are the effects of more recent weathering of carbonates (Brady and Hornberger 1990). Drilling programs and borehole locations should anticipate these depositional and post depositional processes.

Vertical sampling intervals are also important. Most intervals were less than 1.5 m and usually less than 1 m. Intensive vertical sampling is necessary for computation of reliable ABA summary parameters using "thresholds" for percent sulfur or NP. Large intervals can dilute high sulfur or high NP strata.

Net Neutralization Potential and Neutralization Potential

NNP and NP are reliable indicators of postmining water quality in this study. Figure 2 shows NNP (without thresholds and $MPA = 31.25 \times \%S$) and net alkalinity for the 38 sites evaluated. All sites with NNP greater than 15 mt/1,000 mt produced net alkaline water. Of the nine sites with NNP of 0 mt/1,000 mt or less, seven (78%) were acid producing. The "gray zone" in figure 2, where predictions were uncertain, appears to be between 0 and 15 mt/1,000 mt. Two mines that had positive NNP but negative net alkalinity were anomalies throughout this study. ABA analyses for these two sites may not represent the actual acid/base conditions.

The same postmining water quality trends are evident when NNP is examined with thresholds. All sites with NNP greater than 5 mt/1,000 mt have

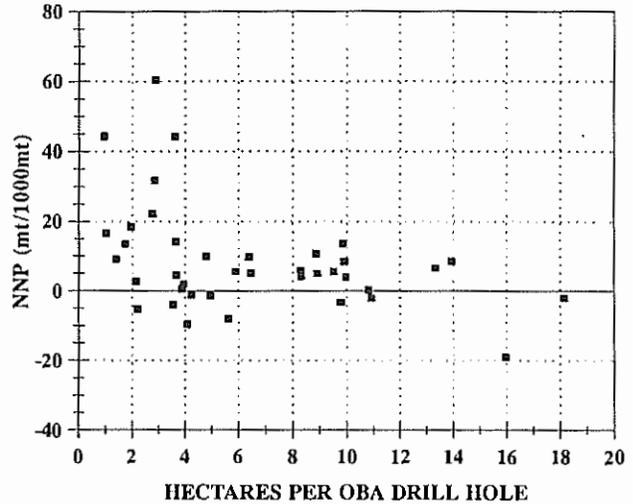


Figure 1. Plot of drilling density vs. net neutralization potential.

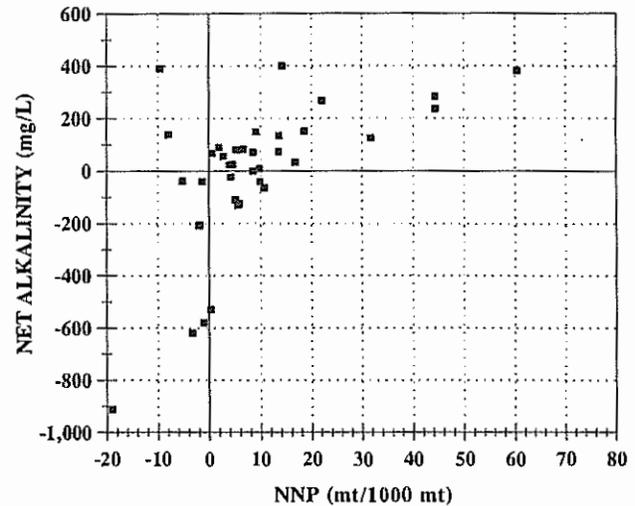


Figure 2. Net neutralization potential (no thresholds) vs. net alkalinity.

positive net alkalinity (fig. 3) and pH greater than 6.0. The "gray zone" of variable water quality extends from -5 to +5 mt/1,000 mt NNP.

Values of NNP above which alkaline water is consistently produced are lower in this study than in previous work. diPretoro and Rauch (1988), Erickson and Hedin (1988) compared net alkalinity and volume weighted NNP. MPA was computed the traditional way, using 31.25 times percent sulfur. Erickson and Hedin (1988) evaluated no sites with NNP between 20 and 80 mt/1,000 mt, however all sites greater than 80 mt/1,000 mt had net alkalinity. Nine of 11 sites (82%) with NNP less than 0 mt/1,000 mt had negative net alkalinity. Between NNP 0 and 20 mt/1,000 mt, 7 of 15 (47%) sites were alkaline.

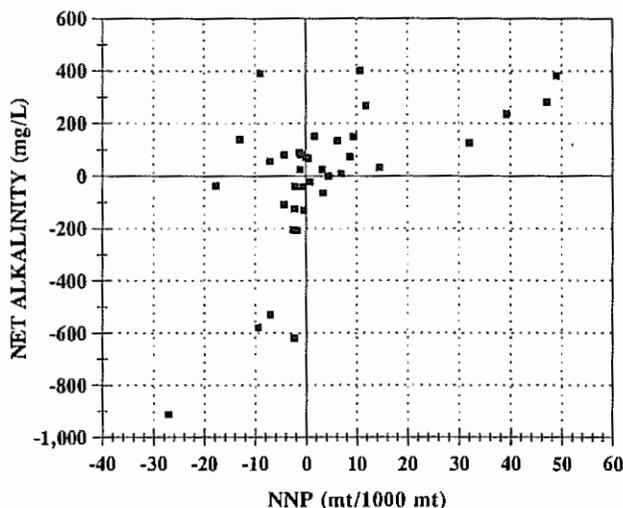


Figure 3. Neutralization potential (with thresholds) vs. net alkalinity.

diPretoro and Rauch found that sites with NNP greater than 30 mt/1,000 mt had net alkaline drainage and that sites with NNP less than 10 mt/1,000 mt had net acidic drainage. Between 10 and 30 mt/1,000 mt was a "gray zone" where 7 of 10 sites were alkaline. diPretoro and Rauch also found that all sites with NP greater than 40 mt/1,000 mt produced net alkaline drainage, while sites with NP less than 20 mt/1,000 mt were acidic (diPretoro and Rauch 1988).

Regardless of the specific values reported, this study and previous work point to the importance of carbonates in determining postmining drainage quality. The presence of as little as 1% to 3% carbonate content may determine whether postmining drainage is alkaline or acid. Different critical values among this and previous studies may reflect different methods of ABA data reduction to produce summary values. Earlier studies used "right triangle" approximations to volume weight their data. This study used a more precise method to produce mass-weighted ABA data (Smith and Brady 1990), and we used multiple ABA holes to define parameters. Different values may also reflect regional or stratigraphic variations in rock properties.

Correct prediction of net acidic or net alkaline water quality was most successful using NNP calculated without thresholds and a 31.25 multiplier, followed closely by NNP with thresholds and a 31.25 multiplier (table 1). A number of sites are clustered near the zero NNP line. The error types are also significant. The highest success rate (NNP, no thresholds, 31.25 multiplier) produced five of seven "errors" where a site was in fact acid when predicted to be alkaline (an undesirable consequence). The "errors" are reversed for NNP with thresholds and 31.25 multiplier. Here, seven of nine "errors" predicted acid sites that in fact were alkaline. This category therefore produced the least number of unanticipated acid sites.

For NP values computed with thresholds, all sites with NP greater than 10 mt/1,000 mt produced drainage with positive net alkalinity. Eight of nine sites

Table 1. Prediction of net alkalinity from net neutralization potential.

NNP calculation	Correctly predicted of 38 Mines	Errors in predicted water quality	
		Predicted acid, but alkaline	Predicted alkaline, but acid
NNP, without threshold, 31.25 multiplier	31 (82%)	2 (5%)	5 (13%)
NNP, with threshold, 31.25 multiplier	29 (76%)	7 (18%)	2 (5%)
NNP, without thresholds, 62.5 multiplier	22 (58%)	11 (29%)	5 (13%)

(89%) having a computed NP less than 1 mt/1,000 mt, exhibited negative net alkalinity (fig. 4). One alkaline site with NP less than 1 is anomalous. NP values between 1 and 10 mt/1,000 mt include sites with both positive and negative net alkalinity, and comprises a "gray" zone, where mine drainage quality is not predictable from NP alone. Sites with NP values greater than 10 mt/1,000 mt also produced drainage of pH greater than 6.0, while "gray zone" sites exhibit variable pH.

Neutralization Potential and Alkalinity

Postmining alkalinity is related to NP (without thresholds) as shown in figure 5. A statistically significant relation at the 95% confidence level was found using simple linear regression. From this empirical relation, it may be

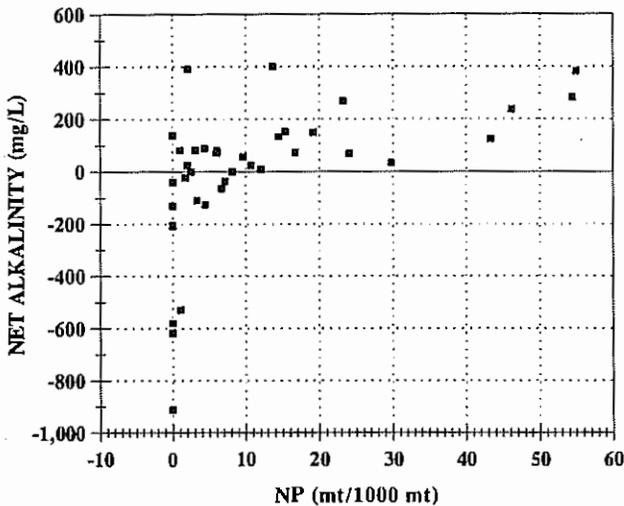


Figure 4. Plot of neutralization potential (with thresholds) vs. net alkalinity.

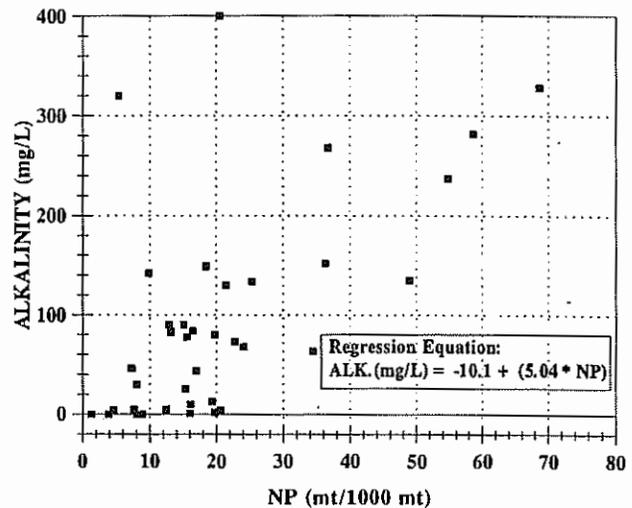


Figure 5. Plot of neutralization potential (no thresholds) vs. alkalinity.

possible to predict postmining alkalinity (in mg/l) as about five times the computed NP value. The predictive relation extends to maximums of about 70 mt/1,000 mt for NP and 400 mg/L alkalinity and has a range in slope of about four to six. The shape and slope of the plot may be explained by active dissolution of carbonate minerals. In addition to availability of carbonate minerals, alkalinity concentration is a function of partial pressure of carbon dioxide in spoil gases, pH, and ionic strength. We do not have mineralogical analyses of carbonate species, but assume that NP reflects mostly calcite with lesser amounts of dolomite, and possibly ankerite and siderite (Cravotta et al. 1994).

Maximum Potential Acidity

MPA, which is a measure of pyrite concentration, was compared against all postmining water quality parameters; no consistent or clear trends were apparent. Our results are similar to those reported by diPreto and Rauch (1988). Figure 6 is a plot of MPA versus net alkalinity. We attribute the lack of trends to the mechanisms involved in acid generation and transport. Pyrite weathering is a multistep oxidation, dissolution and precipitation reaction with at least four reactions involved (Nordstrom, 1982; Kleinmann et al. 1980). Additionally, pyrite oxidation appears to be inhibited by the presence of carbonates, and many of the pyrite oxidation products are not conservative.

A significant positive linear relation between acidity and MPA was apparent for the eight acid sites that had NP's less than 1 (computed using threshold value of 30 mt/1,000 mt). Morrison et al. (1990), in laboratory weathering experiments of strata lacking carbonate minerals, also observed a linear relation. However, in similar experiments Williams et al. (1982) observed an exponential increase in acidity as sulfur increased. Our small sample size does not permit further evaluation.

Sulfate

Sulfate is a direct product of pyrite oxidation. Ambient sulfate levels in unmined areas of the Appalachian basin are usually low in surface and fresh ground waters. In mine drainage, sulfate usually acts conservatively in solution. Figure 7 is a plot of sulfate produced, normalized per unit mass of pyrite (expressed as percent sulfur), as a function of NP. When the data are normalized, a trend of declining sulfate concentration with increasing NP is apparent. Two sites are anomalous, exhibiting high sulfate values at high NP.

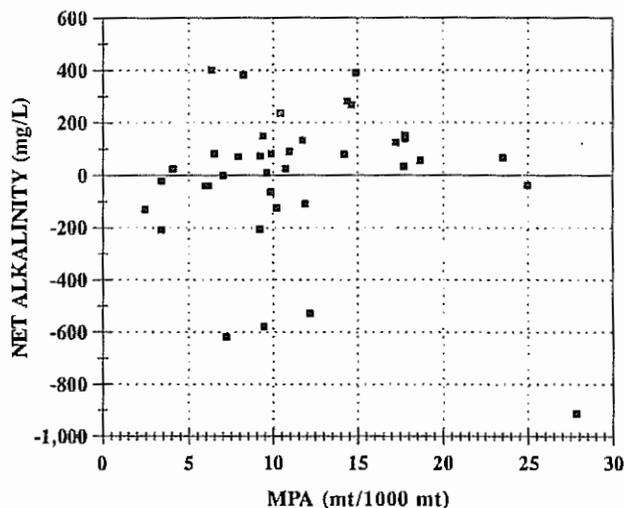


Figure 6. Maximum potential acidity (no threshold) vs. net alkalinity.

We interpret these data to indicate that pyrite oxidation is inhibited by the presence of carbonate minerals in quantities as low as 1% to 3% (10 to 30 mt/1,000 mt). Oxidation may be constrained by suppressing the activity of *Thiobacillus* sp. bacteria which catalyze the oxidation of ferrous to ferric iron (Singer and Stumm, 1970) or the low solubility of ferric iron at circumneutral pH. This is consistent with laboratory weathering studies conducted by Caruccio and Geidel (1982) and Williams et al. (1982), which indicated rocks containing several percent pyrite would produce less acidity and sulfate when carbonate content were only a few percent.

Conclusions

In this study, the quantity of acid neutralizers (presumed mostly carbonates), represented by NP provides the most reliable and clearest demarcation of postmining water quality. At least one to three percent carbonate may be critical for alkaline producing conditions. Although sulfur content and MPA do not readily translate to postmine water quality predictions, they are still necessary to identify whether the risk of acid drainage exists. We do not report on metals concentrations and ABA parameters. Metals behavior is probably best described in terms of mineralogy and solution properties of pH and redox potential.

At the extremes of ABA values of large excesses or deficiencies, rock chemistry may dominate or overwhelm other mechanisms influencing water quality. In the "gray zone," where ABA properties are closely balanced, effects of other factors, such as hydrology, geology, or mining practices can cause variation in water quality among sites that have similar ABA properties. The principal findings and conclusions are:

1. The acid or alkaline character of postmining waters depends mainly on the carbonate or acid neutralizer content of the overburden. NP, a measure of carbonate content, most clearly predicted postmining water quality conditions.
2. The acid or alkaline character of postmining water can be controlled by carbonate content as low as 1 to 3%. Acid generation, as indicated by sulfate concentration, declines as NP values increase, i.e., carbonate minerals in quantities of a few percent can inhibit pyrite oxidation and acid generation. Other water quality impacts, such as increased dissolved solids or metals concentrations may still occur.
3. The use of "threshold" values for NP in processing raw ABA data improves prediction accuracy, especially for acid sites. Of sites where NP was less than 1 mt/1,000 mt, 89% produced net acid water. Sites where NP was greater than 10 mt/1,000 mt all produced net alkaline water.

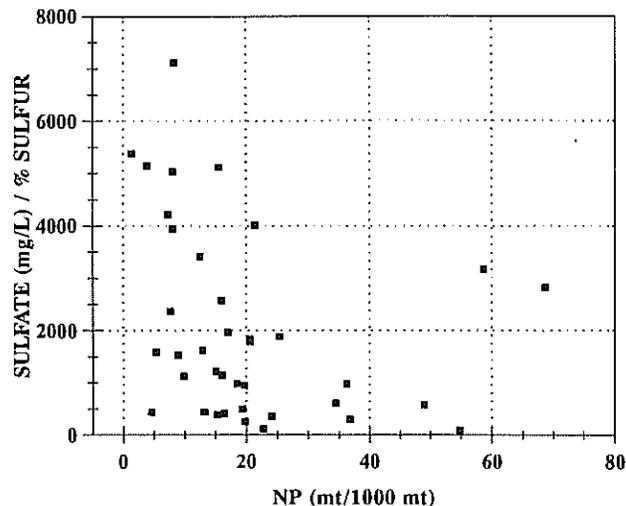


Figure 7. Plot of sulfate production (normalized) vs. neutralization potential.

4. Critical values of NP and NNP (without thresholds) were identified by which postmining waters can be differentiated. Mines with NP values greater than about 15 mt/1,000 mt and NNP greater than about 10mt/1,000 mt have net alkaline drainage.

5. A "gray zone" of ABA values exists where postmining drainage quality is variable. For NP (with threshold), the gray zone extends from about 1 to 10; for NNP (with thresholds) it extends from about -5 to +5 mt/1,000 mt. Within the "gray zone", the prediction of drainage quality cannot be based on ABA alone. If a site falls in the ABA "gray zone" additional information is needed for mine drainage prediction. This information can include results of previous and adjacent mining, paleoenvironmental interpretations, baseline hydrologic data, proposed mining and operational plans, and other analytical procedures.

6. An empirical linear relation exists between median alkalinity and NP. A rough estimate of postmining alkalinity (mg/L) can be derived as five times the computed NP (without thresholds).

7. MPA alone is not a reliable predictor of postmining water quality, except where calcareous strata are absent. For acid sites with average NP less than 1 (with thresholds), acidity and MPA were positively related.

Results and conclusions discussed here are a product of using a certain method of data processing. The extent to which these findings are applicable to other areas with differing climate and geology is not known. However, our results show that the content of acid neutralizers strongly influences mine drainage quality. Future mine drainage prediction research should focus on the role of carbonates and other acid neutralizing minerals rather than sulfide reactivity.

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