

INFLUENCE OF NEUTRALIZATION POTENTIAL ON SURFACE MINE DRAINAGE QUALITY IN PENNSYLVANIA

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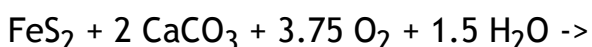
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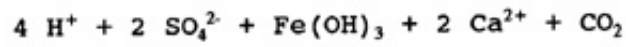
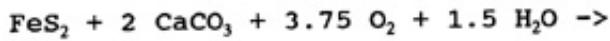
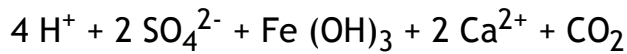
INTRODUCTION

In a previous study (Brady et al, 1994), we evaluated the application of and relation between Acid/Base Accounting (ABA) data and postmining drainage quality on about 40 bituminous surface coal mines in Pennsylvania. We suggested that the presence of carbonate is especially important in preventing acid drainage formation. The dissolution of carbonate minerals not only neutralizes acid drainage, but seems to inhibit its' formation. We examine this theme further in this paper.

ABA has been used in Pennsylvania to predict surface mine drainage quality since the late 1970's. Sampling, analytical and interpretive methods were initially developed and applied to surface mine reclamation by R. M. Smith and coworkers at West Virginia University (Skousen et. al., 1990). ABA was adapted and refined by the Pennsylvania Department of Environmental Resources (PaDER) as one method of several interpretative techniques for mine drainage prediction (Brady and Hornberger, 1990).

ABA consists of measuring total sulfur (S) and neutralization potential (NP), from which maximum potential acidity (MPA) and a Net Neutralization Potential (NNP) are derived. The calculations are based on the following assumed reactions and stoichiometry (Cravotta et. al., 1990):





The presence of carbonate minerals in the above reaction is represented by the measurement of Neutralization Potential (NP) in ABA.

HISTORICAL BACKGROUND

We are not the first to suggest that carbonate dissolution neutralizes and inhibits acid drainage. The importance of carbonates and alkalinity was recognized in field studies over 60 years ago. Lietch et.al., (1932) in a survey of drainage quality from deep mines in the "Thick Upper Freeport" coal in western Pennsylvania found "the absence of acid drainage in the mines described seems due to the bicarbonates in solution which tend to neutralize any acid as soon as it is formed, or inhibit the formation of sulphuric acid... "

Lietch et.al. further noted that "the high alkalinity shown by analyses of water from the mines visited indicates that at some point before its entry into the mines, the water has been in contact with alkaline earths and holds in solution sufficient alkalinity to neutralize the acid forming effects of pyrite in the coal measures. That the persistence of alkalinity is not due solely to the low sulphur content of the coal is shown by unpublished data of the authors which indicate that low sulphur coals frequently produce drainage of a high-acid character. Samples from beds other than the thick Freeport have shown that when coals are low in sulphur as 1.5 percent the drainage water may still be highly acid."

The ability of calcareous rocks to neutralize acid drainage has probably long been recognized. The study by Leitch et. al., is the earliest reference we have found suggesting an inhibitory effect. Lorenz and Tarpley (1963) in laboratory weathering experiments with eleven coals, noticed that three samples containing calcite "had markedly low values of oxygen consumption." They concluded that "calcite increased the pH of the reaction from the 3.5 needed for optimum growth of Ferrobacillus ferrooxidans to a higher value that inhibited the catalytic effect of the bacterium". Other studies have also reported an inhibitory effect on acid generation by carbonate minerals (e.g. Infanger and Hood, 1980; Williams et. al., 1982).

CARBONATE MINERALS AND NP MEASUREMENT

Under mine site conditions, only dissolution of carbonate minerals proceeds rapidly enough to be an important generator of alkalinity. The dominant carbonate minerals present in coal overburden in Pennsylvania are calcite, siderite, ankerite and dolomite. Calcite is important from the standpoint of acid neutralization. Carbonate minerals occur in coal overburden as a solid solution series or mixtures rather than pure end members. Consequently, manganese, iron, strontium and other elements may be present as impurities. Trace inclusion of iron and manganese in calcite, and siderite, have been noted in other coal basins (Kolker and Chou, 1994; Dixon et. al., 1979).

The analytical procedure for NP was adapted from a test for the purity of agricultural limestone (Jackson, 1958), i.e., rocks with simple mineralogical composition dominated by

calcite. Coal overburden rocks, however, contain various silicate, sulfide, oxide and carbonate minerals. In overburden and minespoil, besides dissolving carbonates, the NP procedure may extract some silicate minerals which weather only slowly under field conditions. The net effect can be to overestimate the readily available neutralizing capability (Lappako, 1994). Other studies of NP analyses found that the amount of acid added in sample digestion and the presence of siderite can also overestimate the neutralizing capability (Leavitt, these proceedings, Morrison et. al., 1990; Wiram, 1992).

A simple, qualitative interpretation of NP measurements has been developed by PaDER based on accumulated experience. Samples with a visible "fizz" and NP greater than 30 tons/1000 tons are expected to generate alkalinity (Brady and Hornberger, 1990). Sobek et. al. (1978) report that rocks with a visible fizz have NP of at least 20 tons/1000 tons. These "threshold" criteria of fizz and NP can be used to identify significant alkaline strata and as a check on NP data.

METHODS

ABA and postmining groundwater quality information were analyzed with statistical and graphical methods. Selected waters with major cation and anion analyses were examined for element speciation and mineral saturation using the geochemical model WATEQ4F (Ball and Nordstrom, 1991). Eleven different coal beds are represented from the Allegheny, Conemaugh, Monongahela and Dunkard groups. The distribution of mined seams is shown in Table 1.

TABLE 1
COAL BEDS REPRESENTED IN ACID BASE ACCOUNTING STUDY

FORMATION	COAL BED	NUMBER OF MINES
Dunkard	Waynesburg	6
Monongahela	Pittsburgh	1
Conemaugh	Brush Creek	1
Allegheny	Upper Freeport	4
	Lower Freeport	5
	Upper Kittanning	11
	Luthersburg	1
	Middle Kittanning	12
	Lower Kittanning	8
	Clarion	6
	Brookville	3

ABA data were available for two or more drillholes per mine. These data were mass and volume weighted to produce summary ABA values for each mine (Smith and Brady, 1990). Water quality data ranged from several months to several years of regular monitoring.

Net alkalinity (Total Alkalinity - Total Acidity) was used as the principal post mining water quality indicator, following the approach of diPretoro and Rauch (1988), and Erickson and

Heiden (1988). The parameters of acidity, alkalinity and net alkalinity are measures of the complete acid and alkaline generating capabilities of a water. Ground waters from mined areas are often only partly oxidized, and can have neutral pH with dissolved metals. When aerated, they undergo hydrolysis with acid generation. For these reasons, ground water pH alone may not completely indicate water quality conditions.

PREDICTING MINE DRAINAGE QUALITY

Neutralization potential (NP) and Net Neutralization Potential (NNP) were the most visible factors controlling mine drainage quality. No significant relationships were found between MPA and postmining water quality conditions, except where carbonates were absent.

NEUTRALIZATION POTENTIAL AND NET NEUTRALIZATION POTENTIAL

Sites with neutralization potential (NP) greater than about 21 tons/1000 tons produced net alkaline water (Figure 1). Eight of eleven sites with NP less than 10 ton/1000 tons had negative net alkaline (net acid) water. NP values between 10 and 21 tons/1000 tons included net acid and net alkaline sites (variable water quality). Two low NP sites with net alkaline water were anomalous. The anomalies could result from nonrepresentative overburden sampling, an influx of alkaline ground water from offsite, or alkalinity production from noncarbonate sources.

For Net Neutralization Potential (NNP), all sites greater than about 10 tons/1000 tons produced net alkaline water as shown in Figure 2. Seven of nine sites with NNP less than 0 produced net acid water, and variable results were obtained between NNP 0 and 10 tons/1000 tons.

ABA values were computed where only rocks with NP greater than 30 ton/1000 tons were considered significant alkalinity sources, and rocks with greater than 0.5% sulfur were considered significant acid generators. All rocks not meeting these "thresholds" were assigned values of zero. For these computations, sites with NP greater than about 10 ton/1000 tons produced net alkaline water; mines with NP less than 1 ton/1000 tons were acid. NNP results computed with threshold were: net alkaline waters at greater than 5 ton/1000 ton; and dominantly acid waters at NNP less than -5 ton /1000 ton. The comparative results are shown in table 2.

Figure 1

Neutralization Potential vs. Net Alkalinity

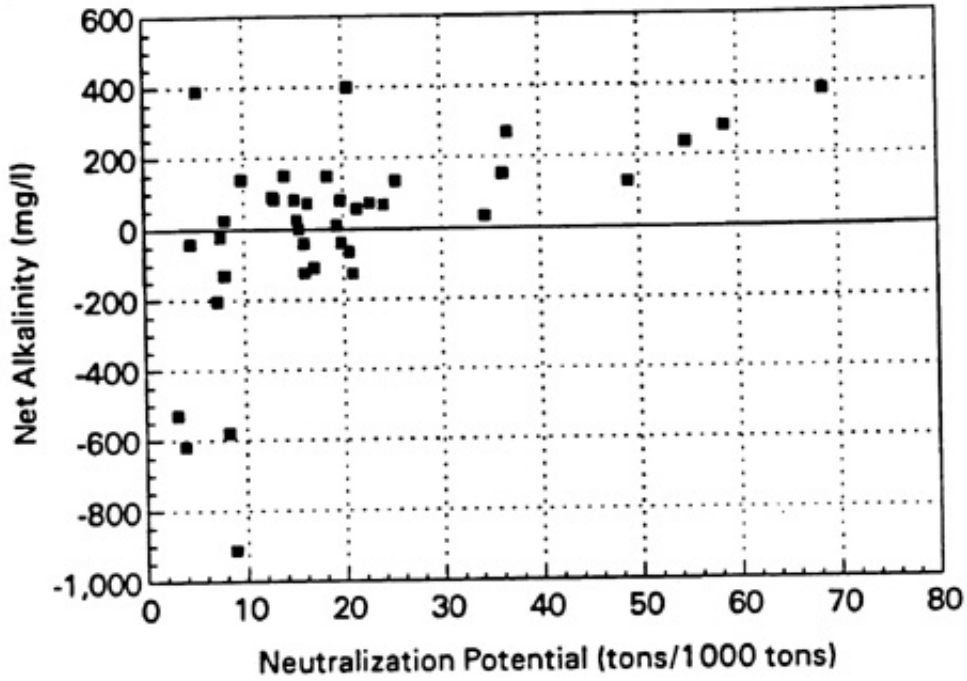


Figure 2

Net Neutralization Potential vs. Net Alkalinity

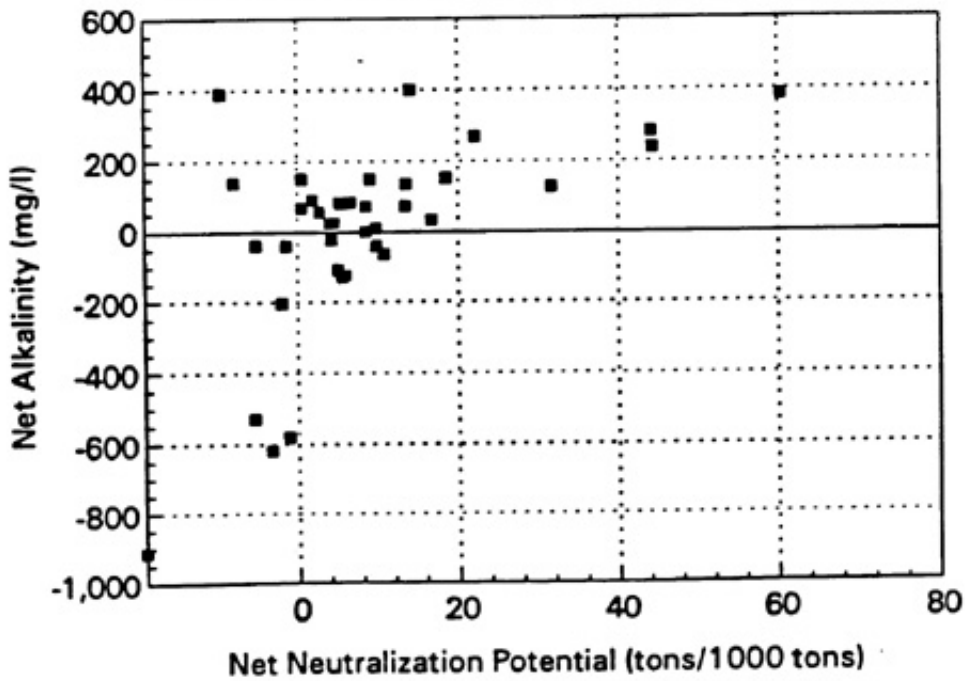


Table 2
 Net Alkalinity vs. Neutralization
 Potential (NP) and Net Neutralization
 Potential (NNP) Computed With and Without Thresholds

Overburden Quality	Water Quality		
	Net Acid	Variable	Net Alkaline
Neutralization Potential (NP)	< 10 ton/1000	10 to 21	>21 ton/1000
Neutralization Potential (NP) with thresholds	< 1 ton/1000	1 to 10	>10 ton/1000
Net Neutralization Potential (NNP)	< 0 ton/1000	0 to 12	>12 ton/1000
Net Neutralization Potential (NNP) with thresholds	< -5 ton/1000	-5 to +5	>5 ton/1000

NEUTRALIZATION POTENTIAL AND ALKALINITY

Neutralization Potential (NP) and alkalinity are related as shown in figure 3. From this plot, a "best fit" regression equation shows post mining alkalinity (mg/1) can be roughly estimated as about 5 times NP.

At NP values of less than about 20 ton/1000 ton, the NP to alkalinity relation shown in figure 3 is much more erratic. A subgroup of twelve mines with measurable NP between 1 and 20 tons/1000 and low alkalinity (less than 20 mg/1) was examined further. These mines characteristically had little or no high NP strata present. NP computed via the threshold method (NP>30 with fizz) for seven mines was zero. The other five mines had their computed NP reduced by 40 to 90 percent when threshold criteria were applied. These sites have carbonate minerals dispersed at low concentrations, or the NP is from siderite or acid extractable silicates. These sites cannot be viewed as dependable producers of alkalinity.

We also determined if active carbonate dissolution is occurring, by examining mineral saturation indices for waters with sufficiently detailed analyses. All waters were undersaturated with respect to calcite; that is calcium carbonate will dissolve. Equilibrium calculations determined from WATEQ4F are expressed as a logarithm of the ratio of ion activity product to equilibrium constant. Values less than zero indicate undersaturation (mineral is expected to dissolve), values of zero indicate saturated conditions (equilibrium), while values greater than zero indicate oversaturation (mineral could precipitate). The highest saturation index obtained on any water was -0.13 or about 73% of saturation. Most waters were one or more orders of magnitude below saturation. Calcite saturation indices are shown in figure 4.

Figure 3
Neutralization Potential vs. Alkalinity

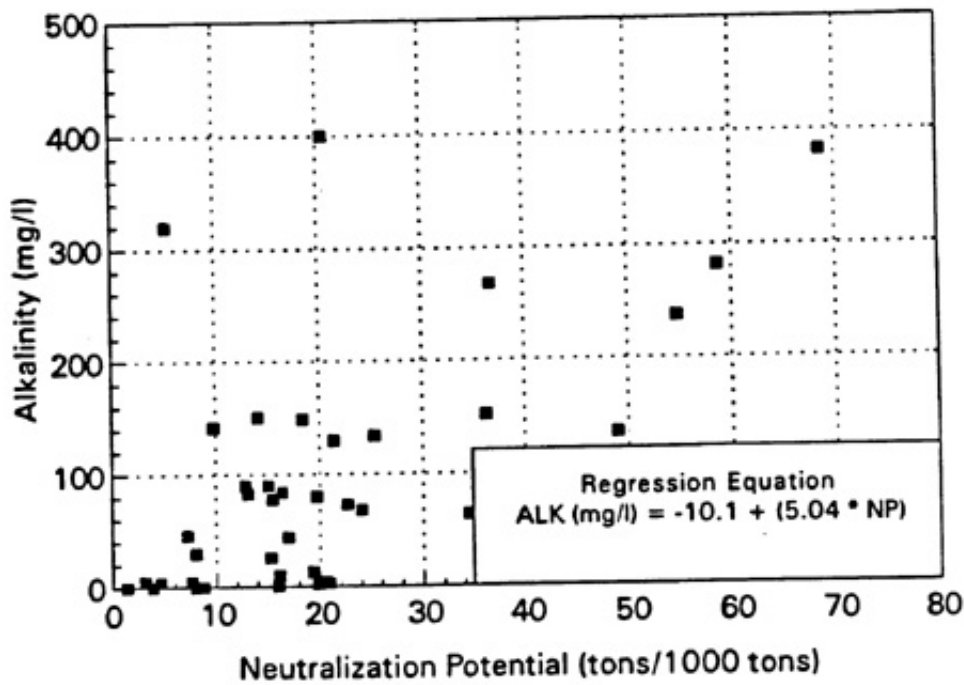
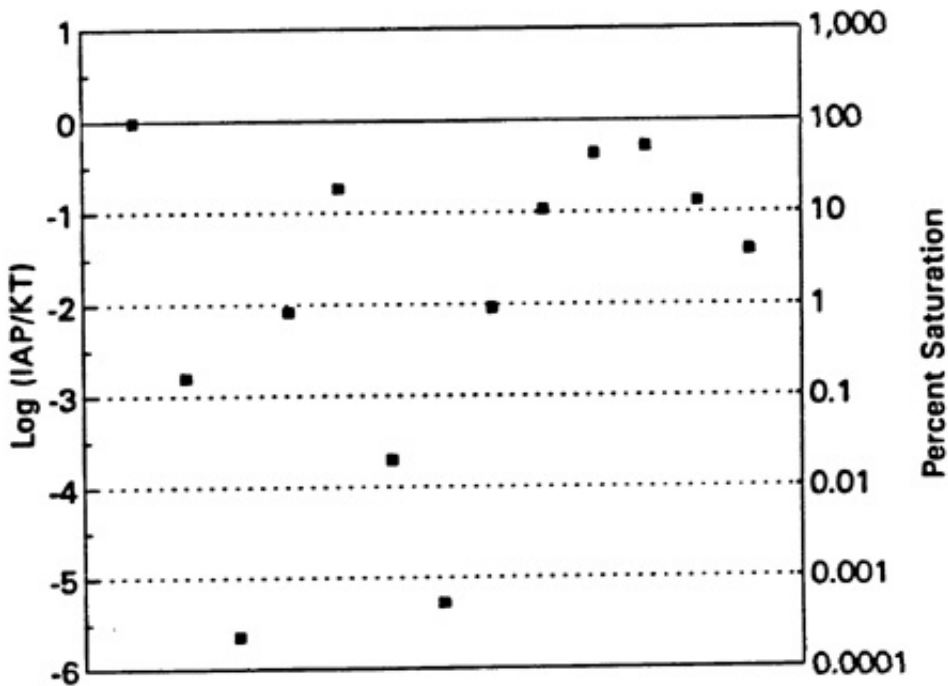


Figure 4
Calcite Saturation Indices



NEUTRALIZATION POTENTIAL AND SULFATE

Postmining sulfate concentrations decrease as NP increases (Figure 5). In this plot, sulfate is normalized per unit mass of pyrite in the overburden. We interpret these data to indicate

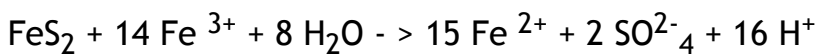
that pyrite oxidation is inhibited by the presence of carbonate minerals in amounts as low as 1 to 3 percent (10 to 30 tons NP).

Carbonates, with the exception of siderite, have at least three different inhibiting effects on pyrite oxidation and acid generation.

1) Carbonates are acid reactive, with their dissolution rate a function of H^+ activity (pH) and the partial pressure of CO_2 (Plummer et. al, 1978). As acidity increases, the rate of carbonate dissolution increases. Conversely, under alkaline conditions, carbonate dissolution slows until equilibrium is reached.

2) Alkaline conditions created by carbonate dissolution are not conducive to bacterial catalysis of ferrous iron oxidation. Singer and Stumm (1970) showed that the activity of Thiobacillus species could increase the rate of ferrous to ferric iron conversion by six orders of magnitude. These bacteria are active in the pH range of about 2 to 4. Ferrous to ferric iron conversion is the "rate determining step" in the overall sequence of acid generation from pyrite (Singer and Stumm, 1970). Thus, inhibiting bacterial activity slows pyrite oxidation.

3) Alkaline conditions greatly limit the activity of dissolved ferric iron. Removal of dissolved ferric iron by alkaline conditions is important since it interrupts the self propagating acid cycle. Dissolved ferric iron is capable of rapidly oxidizing pyrite as follows:



We also evaluated whether sulfate concentration might be limited by the formation of gypsum, or metal sulfate salts such as jarosite and alunite. Gypsum saturation indices calculated by WATEQ4F are shown in Figure 6. The indices are logarithms as described previously. All waters are undersaturated with respect to gypsum, although most waters are within one order of magnitude of saturation. The largest saturation index is -0.196, corresponding to about 64% of saturation. It is possible that gypsum may form in minespoils, but likely would not persist under Pennsylvania's humid climate. We have observed metal sulfate salts such as jarosite (a yellow mineral) as intermediate weathering products in minespoils. Jarosite formation proceeds slowly (Nordstrom, 1982) however.

Figure 5
Sulfate Production (Normalized)
vs. Neutralization Potential

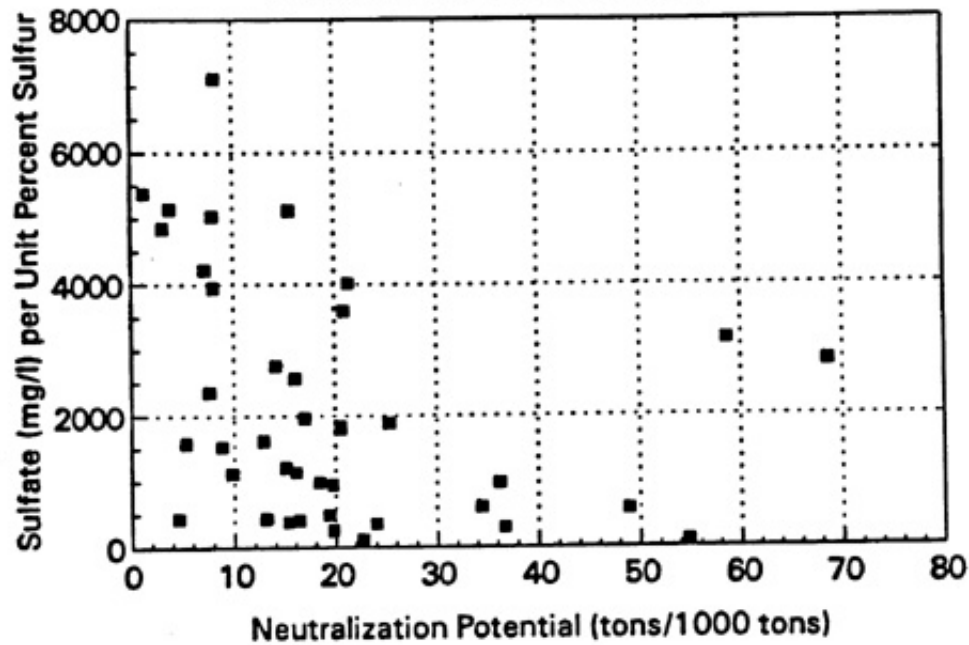
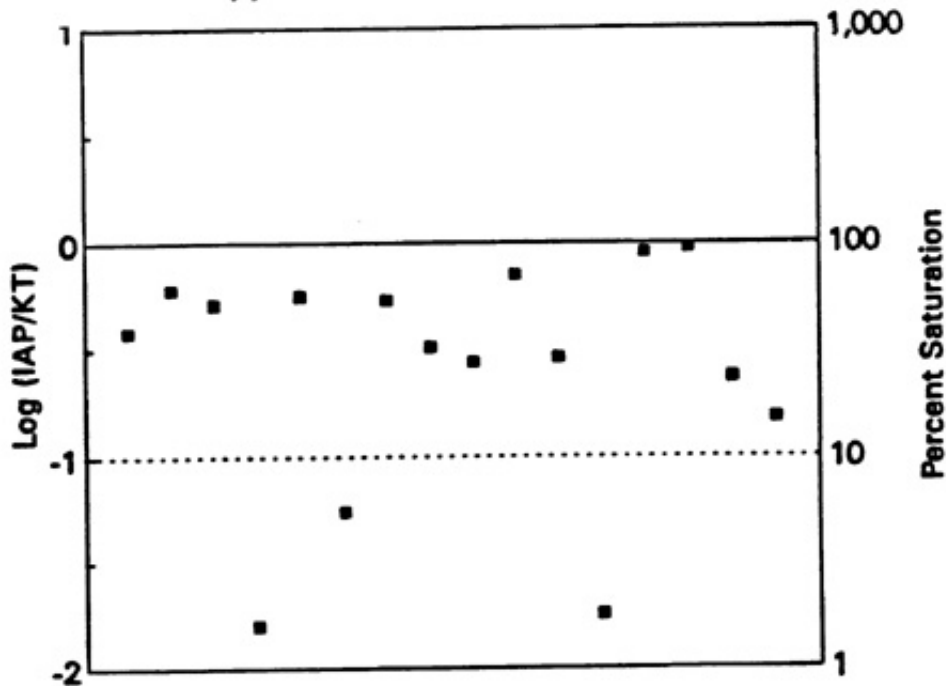


Figure 6
Gypsum Saturation Indices



MAXIMUM POTENTIAL ACIDITY (MPA) AND ACIDITY

There is no obvious relation between MPA and postmining acidity (Figure 7). In fact, we could find no relation with MPA and any parameter in the presence of even small amounts of carbonates. In the absence of carbonates, MPA did show some correlation to acidity on six

sites. The small sample size precludes more rigorous analysis, however.

PREMINING WATER QUALITY AND NP

Carbonate minerals play a significant role in mine drainage quality, and overburden sampling should show the presence and distribution of calcareous rocks within a mine site. Ground water quality, measured prior to mining, can serve to confirm the presence of NP in the overburden and serve as a check on drillhole sampling. Interpretation of premining water quality requires an understanding of the flow systems involved. The following examples are from mines on isolated hilltops where the only recharge is from precipitation.

"Deep" ground waters circulating within the unweathered overburden will dissolve carbonate minerals and produce alkalinity ranging from a few to several hundred mg/l. Figure 8 is a plot of premining ground water alkalinity versus NP for a Lower Kittanning overburden in Clearfield County, Pennsylvania. The ground water sample points and overburden drillholes are located within 500 feet of each other. Clearly, more alkalinity is present where NP is greater. The plot is similar to postmining alkalinity and NP trends in Figure 3.

"Shallow" ground waters circulating through weathered overburden contain little or no alkalinity (typically 0 to 20 mg/l). These rocks are largely leached free of carbonates through long term geologic weathering processes to depths of 20 feet or more. Thus, cropline springs may not reflect water chemistry of the deeper part of the flow system. The cropline springs plotted on Figure 8 have alkalinities of 10 mg/l or less.

Premining water quality shows no relation to pyrite content or MPA. Figure 9 shows MPA plotted against sulfate (a product of pyrite weathering) for the same mine as in Figure 8. The lack of trend reflects the low solubility of pyrite in water, and that in premine overburden under reduced conditions, pyrite is stable. Carbonate minerals, in contrast, are moderately soluble, and can dissolve under reducing or oxidizing conditions.

Figure 10 shows NP and ground water pH versus depth for an Upper Kittanning overburden in Fayette County, Pennsylvania. Carbonate leaching has proceeded to depths of 20 to 30 feet (NP less than 10 ton/1000) and pH is correspondingly low. Significant amounts of NP are available in deeper rocks and this is reflected by increasing pH at depth.

Figure 7
Acidity vs.
Maximum Potential Acidity

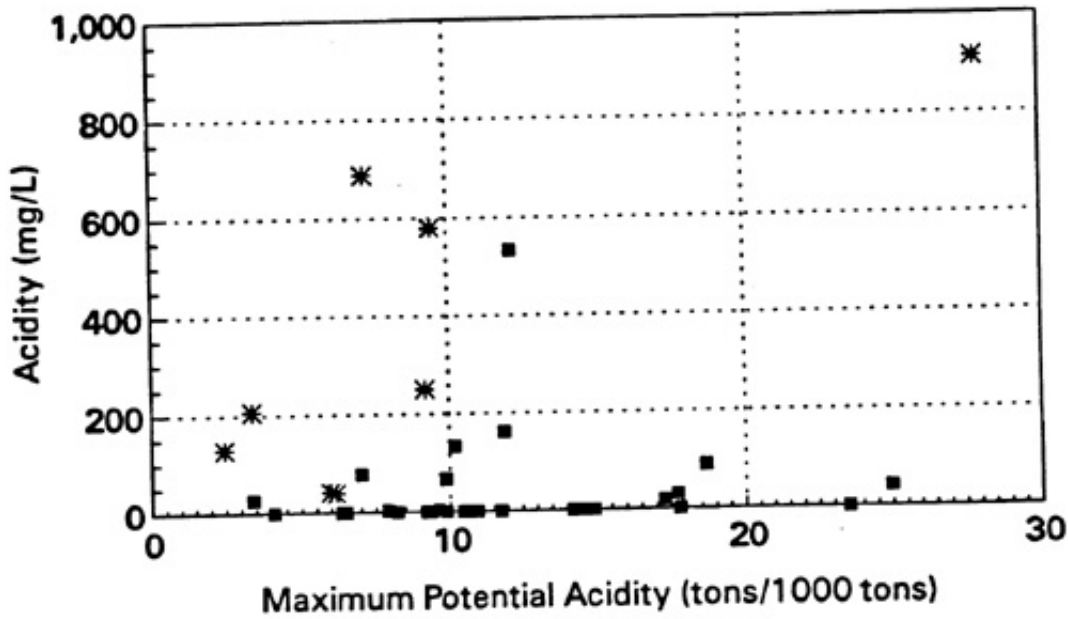


Figure 8
Premining Alkalinity vs. Neutralization Potential

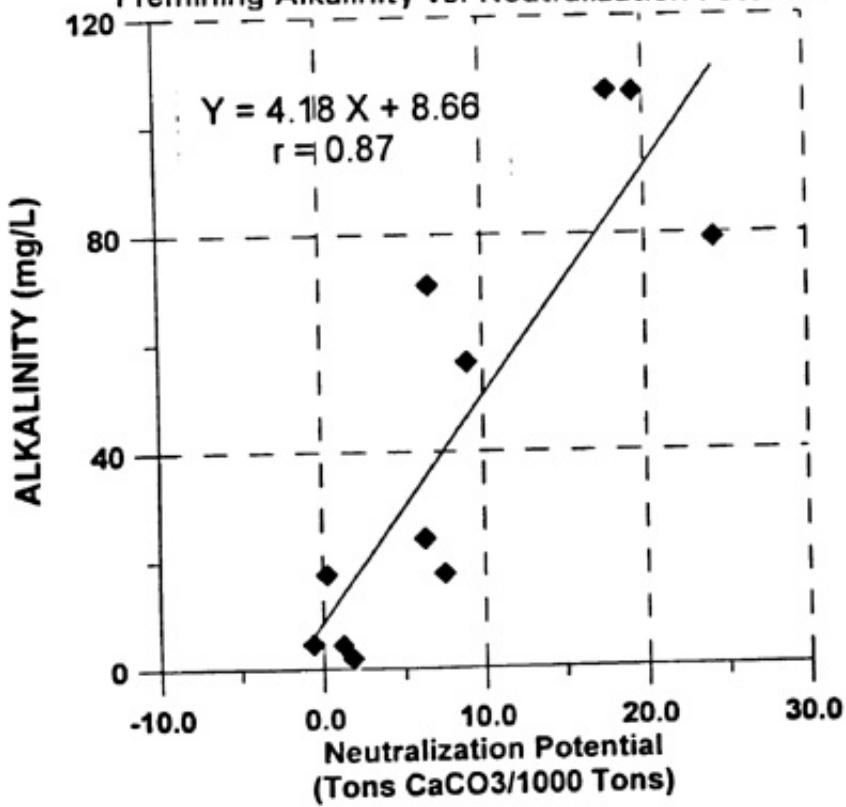


Figure 9

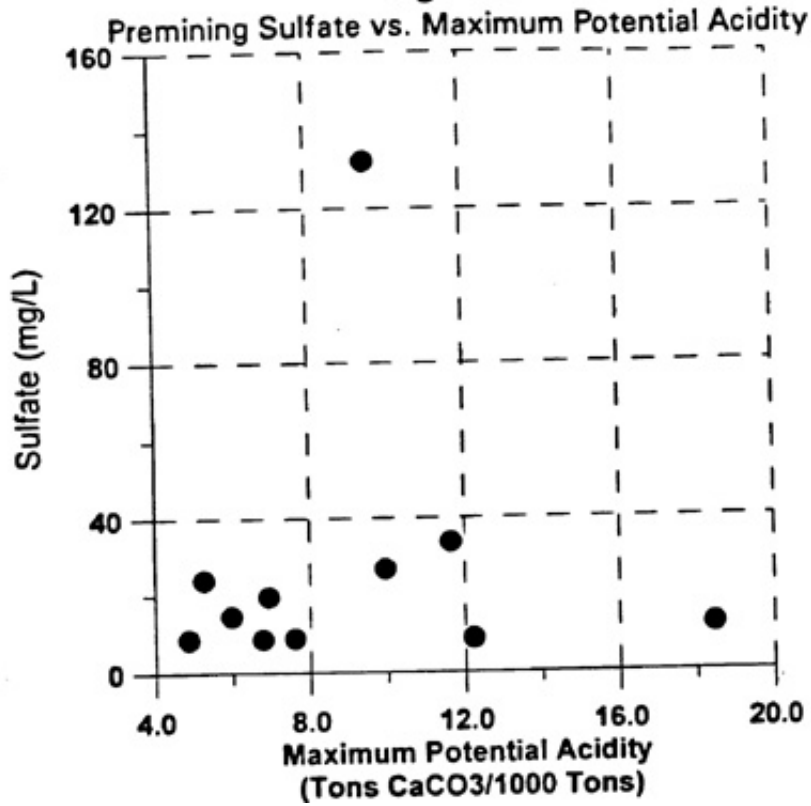
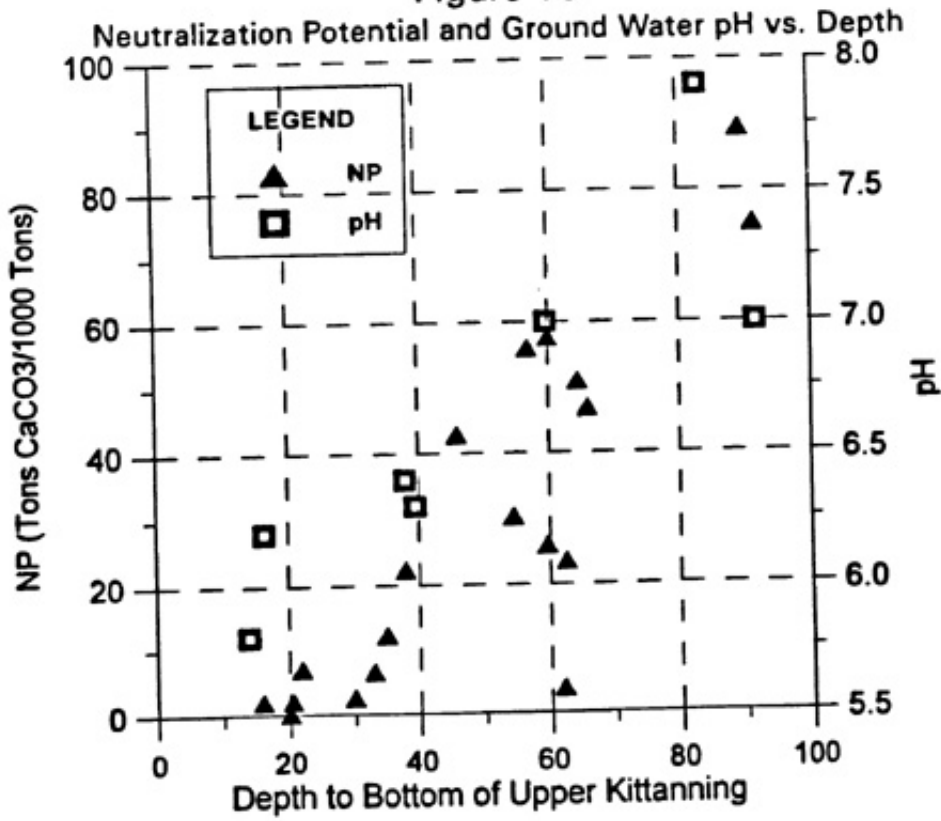


Figure 10



SUMMARY AND CONCLUSIONS

Carbonate mineral content, as represented by NP, is an important factor controlling mine

drainage quality. The significance of alkalinity from carbonate minerals was recognized as long as sixty years ago. NP affects drainage quality at carbonate contents of one to three percent (10 to 30 tons /1000 tons NP). A slight excess of carbonate, or positive NNP, seems necessary to assure alkaline drainage. Pyrite must obviously be present for acid generation to occur. However, MPA is unrelated to water quality parameters except in the absence of carbonate, and by itself, is a poor predictor.

NP in overburden is positively related to aqueous alkalinity in both pre and postmining waters. An empirical relation was found where postmining alkalinity in mg/l is about 5 times NP in tons/1000. A similar relation was apparent for premining water quality. The production of alkalinity at low NP values is less predictable, however. NP and alkalinity also seem related in premining waters. Premining water quality data, coupled with an understanding of ground water flow systems, can be a useful tool for confirming the presence of NP within the overburden.

Carbonate dissolution consumes (neutralizes) acidity and inhibits pyrite oxidation. Alkaline conditions suppress two key components of the acid generating process. Bacterial catalysis of ferrous iron oxidation is inhibited and ferric iron activity is also greatly reduced.

Geochemical modeling showed mine waters were undersaturated with respect to calcite, often by several orders of magnitude and carbonate minerals should dissolve. Modeling also showed the waters to be undersaturated with respect to gypsum, and we concluded gypsum formation was not limiting sulfate concentrations.

This study centered on the use of one analytical tool for mine drainage prediction. Interpretation of complimentary sets of information, such as premining water quality, adjacent mining, depositional settings groundwater flow systems and the proposed mine plan, is useful in understanding mine drainage.

Considerable attention has been focused on the acid generating side of the ledger. Sulfide morphology, pyrite genesis and crystal structure have all been intensively studied with sometimes conflicting or inconclusive results. We suggest that mine drainage prediction and research efforts focus greater attention on the role of carbonate minerals.

The ABA data used in this study were generated using a certain method of data processing. The extent to which these findings apply to other areas of differing geology, geochemistry and climate is not known. Our results do show however, that NP strongly influences mine drainage quality.

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