ACID BASE ACCOUNTING SUCCESS RATES IN ACID MINE DRAINAGE LABORATORY PREDICTIVE TESTS[1]

by

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Abstract. Acid/base accounting (ABA, evaluates balance of neutralization potential (NP) and maximum potential acidity (MPA)) has been used extensively to classify mine overburdens according to their potential to produce acidic drainages. Unfortunately, ABA interpretation accuracy has been problematic and difficult to quantify. To evaluate the accuracy of ABA interpretation techniques, ABA results for 83 coal mine overburden samples were compared to leachate quality from humidity cell leachings. No ABA interpretation technique resulted in clearly defined acid or alkaline sample clusterings. 100% confidence for alkaline leachate, i.e., 0% occurrence of acid leachate production, was achieved only for a *neutralization ratio*, NR (NP/MPA), of at least 19. Neutralization ratios of 19 resulted in no Type I acid base accounting errors, i.e. those in which an overburden sample is classified as alkaline, but actually produces acid leachate; but resulted in 50 type II errors, i.e. those in which an overburden sample is classified as acidic but actually produces alkaline leachate. The *neutralization potential (NP) threshold* for 100% confidence of alkaline leachate was 73‰. An NP threshold of 73 resulted in no type I errors and in 57 type II errors. Similarly, *net neutralization potentials*, NNP (NP-MPA), were required to be greater than 67‰ to achieve 0 Type I errors. Combined criteria in which the overburden met one of two criteria maintained type I errors at 0, and also slightly reduced type II errors. Acid production rates (APR) were quantitatively correlated with ABA parameters. Poor correlations were exhibited with NP or NR (r=-0.30 and -0.11, respectively), but good correlations (r=0.80) were exhibited with the ratio of maximum potential acidity to neutralization potential, MPA/NP. Linear regression analysis for the relationship between APR and MPA/NP resulted in a linear mathematical equation that suggests a method to calculate acid production rates from weathering cell leach tests.

Additional Key Words: acid mine drainage, acid/base accounting, leaching tests

Introduction

Acid Mine Drainage Prediction

Due to the severity and persistent nature of the environmental effects of acid mine drainages, much effort has been expended developing reliable prediction techniques able to pre-screen mine overburdens for the identification of potentially hazardous overburdens and to make pre-mining determinations of post-mining drainage quality. Overburden analyses, as they are generally termed, have gained much importance in recent years, as state and federal environmental regulations have emplaced increasingly stringent regulatory control on the mining of coal and metals in areas where acidic drainage prone overburdens are disturbed. In many mining states, a mine operator often may obtain a permit only after a successful demonstration that the disturbance of overburdens at the site will not produce uncontrolled acidic drainages.

Originally developed to facilitate the selection of mine overburden material suitable for sustaining plant growth in reclaimed coal mines, acid/base accounting (ABA) (Sobek *et al.*, 1977), is a commonly used overburden analytical technique, and has been adapted as a screening tool to identify overburden rocks that contain large percentages of metallic sulfides, are deficient in acid neutralizing capacity, and are therefore likely to produce acidic drainages. By quantifying 1) the neutralization potential (NP), the total neutralizers in the geochemical system (alkaline carbonates, exchangeable bases, and weathering of silicates), and 2) the maximum potential acidity (MPA), the pyritic sulfur weight percent multiplied by 31.25 (a number derived from the stoichiometric relationship between the amount of acid that can be produced by pyrite oxidation and the amount of calcium carbonate required to neutralize it), ABA examines the balance of acid producing and acid neutralizing overburden materials to assess the final drainage quality. To interpret the acid/base accounting

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data, the result usually is expressed as either a difference;

$$NP\text{-}MPA = \textit{Net Neutralization Potential (NNP)}$$

or as a ratio;

$$NP/MPA = \textit{Neutralization Potential (NR)}$$

In the first equation, NNP's greater than zero (>0), and in the second, NR's greater than one (>1), identify overburdens that possess sufficient quantities of neutralization potential to dissolve and neutralize the acidity produced by the oxidation of all of the pyrite in the overburden material, and therefore, produce non-acid drainages. Conversely, NNP's less than zero (<0), and NR's less than one (<1) identify overburden materials that do not possess neutralization potential in sufficient quantities to neutralize the acidity produced by the oxidation of all of the pyrite in the overburden material. As a result of the ABA analysis, the latter group of samples would be identified as potentially acid producing, and subject to special handling requirements or required to be amended by additions of lime. In some cases, a mine permit may be even be denied if overburdens are found to be highly potentially acid producing.

In practice, although ABA has the advantages of being relatively inexpensive and easy to perform, and is thought to work well in characterizing overburdens that may possess an abundance or paucity of either neutralization potential or potential acidity; the technique often fails to accurately predict drainage quality in marginal cases in which the balance of NP and MPA is not so extreme. Rather than creating a clear delineation between acid and alkaline drainage producing overburdens, the technique results in an "uncertain" zone, in which it is unknown whether an overburden will produce acid or alkaline drainage. For example, overburdens with NNPs greater than 0, or with NRs greater than 1, have been observed to produce acidic drainages, in apparent contradiction to ABA. Similarly, overburdens for which ABA have indicated a risk for producing acidic drainages have instead been observed to produce alkaline drainages. These uncertainties occur, in large part, because ABA does not consider reaction kinetics of pyrite oxidation and alkaline material dissolution, and the manner in which the relative rate at which the two reactions occur affects overall drainage quality. Overburden samples for which ABA produces uncertain results usually must subsequently be tested in kinetic tests (i.e. leaching tests), in which mine overburden is artificially weathered to produce leachates that simulate actual drainage quality. Additional kinetic testing, of course, incurs additional expense, is time consuming, and has been criticized for a lack of standardization in both design and interpretation.

Efforts in recent years to improve the accuracy and reliability of ABA have been directed toward more precise parameter quantification and improved interpretation methods. To obtain more accurate NP quantification, Meek *et al.* added hydrogen peroxide during the NP analysis to negate the effects of siderite, which is thought to elevate the NP in the overburden analysis, but contribute little actual alkalinity under field conditions. Cravotta *et al.* (1990) have suggested that the stoichiometric multiplier for the calculation of MPA of 31.25 doesn't accurately represent carbonate equilibrium in mine spoil environment and should be changed to 62.5. Other researchers have proposed the use of higher NR's such as 2 (Ferguson and Robertson, 1994), 3 (Smith and Barton-Bridges, 1991) or even 4 (Li, 1994) to delineate acid and alkaline drainage generating overburdens. These improvements have achieved varying degrees of success, but still result in errors in overburden screening.

To address some of these concerns, this study was designed to assess commonly utilized acid base accounting interpretation techniques to determine which technique provides the best predictor of potential mine drainage quality. Such analyses typically are evaluated only in a qualitative sense, i.e. making predictions of drainage quality as potentially acid, potentially neutral, or potentially alkaline. Of interest in this study, however, was whether the possibility existed that a variation on currently existing ABA interpretation technique could provide information about potential mine drainage in a quantitative sense, that is, providing an estimation of the magnitude of any potential acid mine drainage problem. To this end, this study was designed to evaluate ABA in both qualitative and quantitative overburden analyses.

Methods and Materials

Acid/base accounting and humidity cell leaching data for eighty-three (83) coal mine overburden samples were examined. The sample suite, collected from mines in western Pennsylvania, West Virginia, Kentucky, and Tennessee, represented a variety of overburden lithologies including sandstones, siltstones, shales, and coal refuses.

Each overburden sample was crushed and mechanically riffled into two representative splits. One overburden subsplit was pulverized and analyzed for neutralization potential and pyritic sulfur. Pyritic sulfur weight percentages ranged from 0.01 to 6.6%, with one sample, a coal refuse at 20%. This latter sample was not included in the quantitative analysis. NP's ranged from 0 to 185 parts per thousand.

The remaining overburden subsplit was crushed to pass 4 mm, and packed into humidity (weathering) cells for leach testing. The humidity cells were small plastic chambers 16 cm in diameter, containing approximately 300 grams of overburden material, connected by Tygon tubing to a source of humid air. The overburden samples were weathered under constant temperature (~ 20°) and constant humidity (~100%) conditions, and leached every seven days with deionized water for approximately 16 weeks. After each leach, leachate was collected and analyzed for pH, specific conductivity, acidity, and alkalinity.

Net acid production rates were calculated using simple linear regression analysis according to the following model:

$$Y_i=\beta_0+\beta_i X_i$$

where:

Y_i is the total acidity produced at time X_i
β_0 is the y intercept and represents the acidity produced on the initial leach
β_i is the slope and represents the acid production rate (APR) in mg acidity (as $CaCO_3$ equivalents)/g sample/day.
X_i is the value of total days
$i= 1,...,n$

Goodness of fit for the linear equation to the actual acid production was verified by calculating correlation coefficients for the linear regression model. Acid production rates for all overburden samples were correlated with total days of leaching with correlation coefficients of 0.9 or higher, indicating that the linear model was appropriate for characterizing quantitative acid production.

Qualitative ABA Analyses

ABA accuracy was evaluated by comparing the ABA result to leachate quality from the overburden leaching (humidity cell) tests. Because ABA results are interpreted almost exclusively in qualitative terms, i.e. indicating potential mine drainage quality in terms of simply acidic, neutral, or alkaline only; the ABA results were initially compared to the sign (i.e. positive or negative) of the acid production rate. The acid/base accounting parameters that were evaluated were those either in common use or suggested in relevant literature as improvements on existing techniques. Net neutralization potential (NNP), for example, was evaluated at quantities of 0 (the theoretical stoichiometric amount), 5 (suggested as a "safety factor" by Sobek), and 10 tons/thousand tons. Similarly, the neutralization ratio (NR) was evaluated at ratios of 1 (the theoretical stoichiometric ratio), 2 (Ferguson and Robertson, 1994), 3 (Smith and Barton-Bridges, 1991), and 4 (Li, 1994). Neutralization potential thresholds (NPT) have also been suggested in the literature, commonly with 20 tons/thousand tons being suggested as an amount above which acid drainages are unlikely to form. NNR's, NR's, and NPT's were also examined to determine appropriate criteria that would result in 0 errors for each technique.

Acid/base accounting errors were quantified as either Type I or Type II errors. Type I errors were defined as *false negative* results, such as those that occur when an acid/base accounting technique predicts an overburden sample to produce alkaline leachate, but actually produces acidic leachate in a leaching test. Type II errors were *false positive* results, occurring when acid-base accounting predicts an overburden sample to produce acidic leachate, but results in alkaline leachate. Type I errors are errors that would be typically of concern to the regulatory agency, in which failure to identify acid producing overburdens may result in adverse environmental impacts. Conversely, while there may be no adverse environmental hazard to a Type II acid-base account error, such errors are of concern to mine operators, because they may result in unnecessary permit litigation, excessive overburden handling expenses, or even failure to secure a permit.

Quantitative ABA Analyses

To evaluate the usefulness of using ABA to estimate mine drainage quality in a quantitative fashion, i.e. to use ABA to assess the magnitude of potential acid or alkalinity generation from mine overburden samples, acid-base accounting parameters were statistically correlated with mine overburden sample acid production rates (APR) from the overburden leaching tests. Acid production rates were correlated to various expressions of acid/base accounting such as % sulfur, % pyrite, maximum potential acidity (MPA), neutralization potential (NP), net neutralization potential (NNP), NP-% pyrite, MPA/NP, NP/MPA, % pyrite/NP, NP/% pyrite, and possible logarithmic transformations.

Results

Qualitative ABA Analyses

Type I and Type II acid base account errors are reported in table 1. As is indicated in Table 1, interpreting ABA data according to current criteria, i.e. NNP=0, NR=1, or NPT=20; resulted in numerous errors of both types. Using an neutralization potential threshold of NP=20 ‰ (parts per thousand) to screen overburden samples, resulted in 7 Type I errors (predicted alkaline, but acidic), and 11 Type II errors (predicted acidic, but alkaline). Raising the NP threshold to 30 ‰ and to 38 ‰ reduced the number of Type I errors, but resulted in increased occurrence of Type II errors. The only NP threshold high enough to allow no overburden samples to be erroneously classified as alkaline producing was NP=73 ‰, an NP high enough to result in no Type I errors, but one at which 56 of 77 (72%) overburden

Table 1: Type I and II Error Rates for Acid-Base Accounting Interpretation Methods

Acid-Base Accounting Interpretation Method		**Predict Acid**	**Predict Alkaline**	**Type I Error**	**Type II Error**
Neutralization Potential Threshold		**#**	**#**	**#**	**#**
Confidence: ~69%	NP>20	25	58	6	11
~84%	NP>30	42	41	3	25
95%	NP>38	59	24	1	39
100%	NP>73.1	77	6	0	56
Neutralization Ratio Criteria					
Confidence: ~67%	NR>1	19	64	8	6
~72%	NR>2	36	47	6	21
80%	NR>3	43	40	4	26
~82%	NR>4	48	35	4	31
95%	NR>9.7	65	18	1	45
100%	NR>19	76	7	0	55
Combined NP Threshold and NR Criteria					
Confidence: 90%	NP>38 or NR>9.7	53	30	2	34
100%	NP>73.1or NR>1	72	11	0	51

Type I errors occur when ABA predicts alkaline results, but samples produce acidity when leached

Type II errors occur when ABA predicts acid results, but samples produce alkalinity when leached

Table 2: Acid Production Rate Correlation

Acid-Base Accounting Parameter	Acid Production Rate (mg/g sample/day)
% Sulfur	0.22
% Pyrite	0.22
MPA	0.29
NP	-0.30
NP-% Pyrite	-0.32
NP-MPA (NNR)	-0.43
MPA/NP	0.80
NP/MPA	-0.11
%P/NP	0.71
NP/%P	-0.13
Log NP	-0.50
Log MPA/NP	0.52
Log NP/MPA	-0.52
Log %P/NP	0.49
Log NP/%P	-0.49

samples were erroneously classified as acid producers (Type II errors).

Similarly, using a net neutralization potential (NNP=NP-MPA) threshold of 0 ‰ to delineate acid and alkaline producing samples resulted in 9 Type I errors and 5 Type II errors. Likewise, NNP's of 5 ‰ resulted in 8 and 6, Type I and II errors, respectively. NNP's of 10 ‰ resulted in 5 and 10, Type I and II errors, respectively. Type I errors could only be controlled at zero by using an NNP criterion of 67 ‰, which resulted in 57 of 78 (73%) of the overburden samples being erroneously classified as acid producers (Type II errors).

Using the neutralization ratio (NR=NP/MPA) as the criterion for delineating acid and alkaline producing overburden samples yielded similar results. When the commonly used criterion of NR=1 was examined, 9 Type I and 5 Type II errors resulted. As can be seen in Table 2, raising the NR criterion to 2, 3, or 4, as has been suggested by other researchers, did have the effect of reducing the numbers of overburden samples that were erroneously classified as alkaline, but only at the expense of an increased occurrence of Type II errors. Only raising the NR criterion to 19 ensured that no overburden samples were erroneously classified as alkaline producers. Doing so, however, resulted in 50 of the 71 (70%) of the samples being erroneously classified as acid producers.

Using combined ABA criteria, i.e. subjecting overburden ABA data to one of two screening statements, had the effect of holding Type I errors to zero, but also reducing the occurrence of Type II errors. For example, combining the criteria of NNP>67 and NR>19, meaning an overburden sample would have to satisfy only one of the two criteria to be classified as alkaline producing, resulted in zero Type I errors, but reduced the Type II error occurrence to 47 (69%). Using a combined criteria of NP>73 or NR>19, yielded the same results, with 0 and 47 Type I and II errors, respectively.

Quantitative ABA Analyses

Acid production rates (APR) from the overburden leaching tests ranged from -0.014 mg/g sample/day (the negative sign indicating that the sample produced alkaline leachate), to 0.06 mg/g sample/day. The highest APR of 0.13 mg/g sample/day was observed in the sample with the highest pyrite weight percent and the lowest NP, sample "LP", a 20% pyritic sulfur, NP<1 coal refuse sample. This sample was not included in the quantitative analysis due to its rather extreme chemistry. As indicated in Figure 1, in a general sense, APR's rose with increasing pyrite percentages and decreasing NP. The sample with lowest APR (most strongly alkaline), however, sample T101, had an NP of 38.3 ‰, only a moderate value within the range of the sample suite, providing indication that measurements of NP did not necessarily assess the reactivity of alkalinity producing overburden materials.

As can be seen in Table 2, APR was not well correlated with MPA (r=0.29), NP (r= -0.30), NR (r= -0.11), or NNP (r= -0.43). Good correlation, however, was observed between APR and the MPA/NP ratio, with a correlation coefficient, r, of 0.80. Not surprisingly, APR's were also reasonably well correlated with % pyrite/NP ratios, at r=0.71, because MPA is calculated by multiplying the % pyritic sulfur by 31.25. Both MPA/NP and % pyrite/NP were slightly correlated with log APR, at r=0.70 and 0.67, respectively. No other acid-base accounting parameter exhibited correlation above r=±0.57 with APR or log APR.

Discussion

When compared with overburden sample leachate quality generated from overburden leaching tests, traditional ABA interpretation techniques performed poorly in delineating potentially acid producing and potentially alkaline producing overburden samples. In a *qualitative* error analysis, ABA interpretation techniques in current usage yielded consistently poor results. For example, as indicated in Table 1, using criteria of neutralization potential thresholds (NPT) >20, net neutralization potentials (NNP) >0, or neutralization ratios (NR) > 1; resulted in as many as 9 Type I (predicted alkaline, but acidic) ABA errors, in which 14% of the overburden samples that were classified as alkaline producers actually produced acidic leachate in overburden leaching tests.

Even when alternate criteria proposed by other researchers were utilized, such as higher NNP's (5,10), NRs (2,3,4), or NPT's (30) the occurrence of Type I errors was reduced, but only at the cost of an increased occurrence of Type II (predicted acid, but alkaline) ABA errors. Only by using ABA criteria much higher than those in current usage, could Type I errors be completely eliminated. For example, as indicated in Figure 2, raising the NR criterion for delineating acid and alkaline producing samples to 19, resulted no overburden samples being erroneously classified as alkaline, when they, in fact, produced acidic leachate in leaching tests. The use of such an extreme criterion, however, resulted in 50 samples being erroneously classified as acid producing, when they, in fact, produced alkaline leachate in overburden leaching tests. Similarly, using a net neutralization potential (NNP) of 67‰, as indicated in Figure 3, eliminated the occurrence of a Type I ABA error, but resulted in 57 Type II ABA errors. A neutralization potential threshold (NPT) of 73‰ (figure 4) was necessary to prevent the occurrence of Type I ABA errors, but resulted in 56 Type II errors.

Figure 1: Acid Production Rates for Overburden Geochemistry Leach Tests

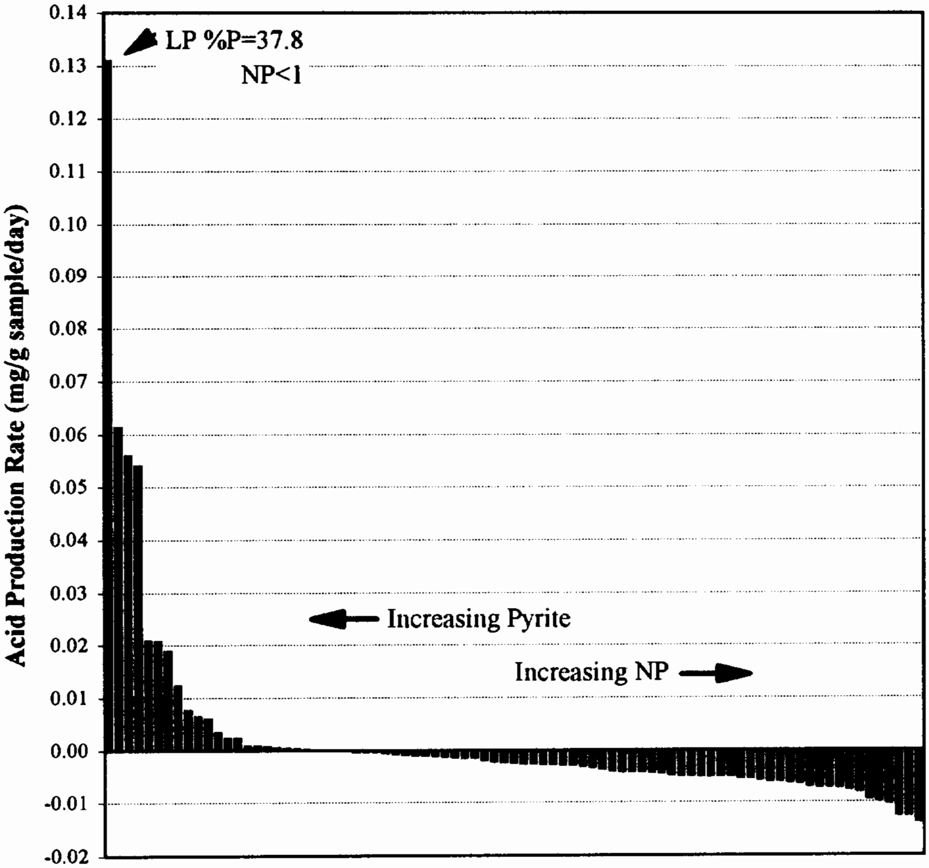


Figure 2: Neutralization Potential (NP) vs. Maximum Potential Acidity (MPA)

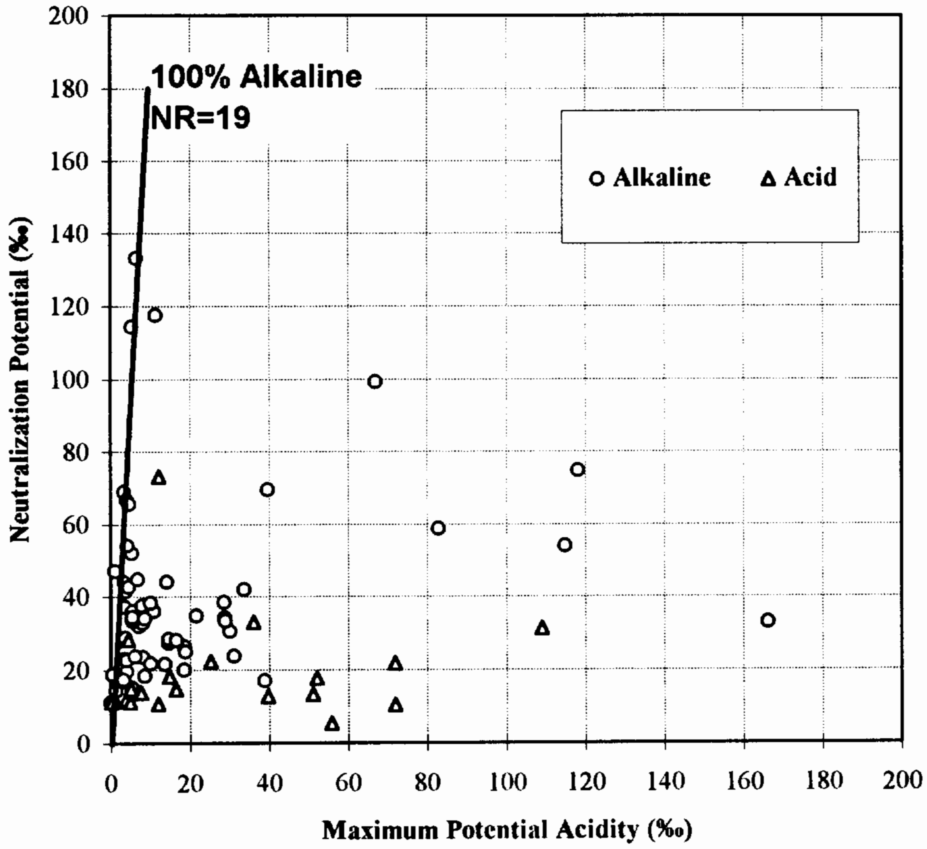


Figure 3: Net Neutralization Potential (NNP)

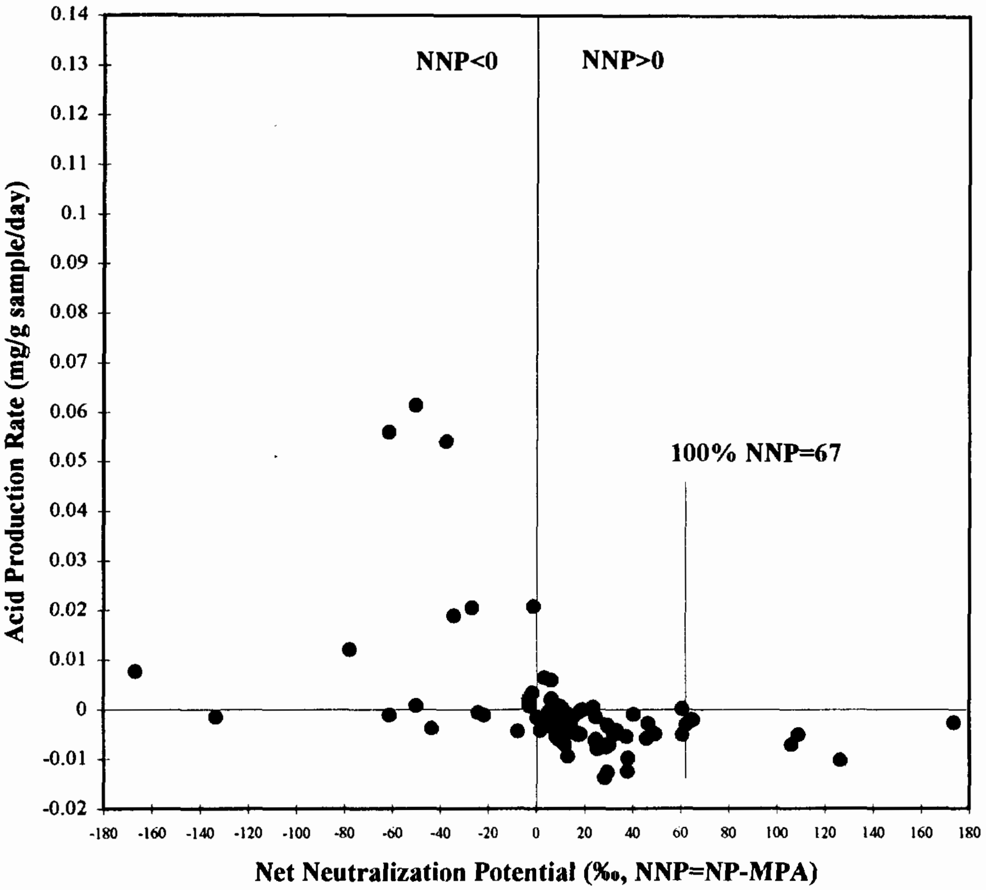
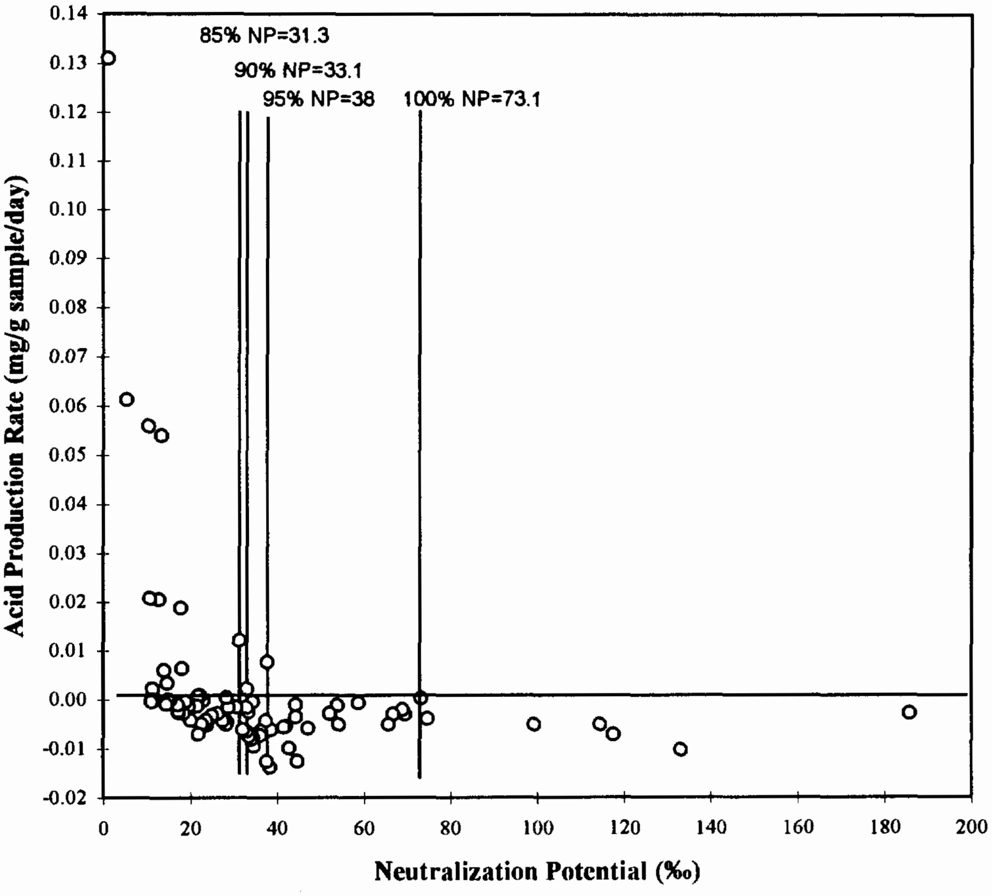


Figure 4: Neutralization Potential Thresholds and Confidence Levels



It is important to note, however, that while overburden samples possessing NR's, NNP's, and NPT's higher than the commonly used criteria did produce acidic leachate in overburden leaching tests; the actual amounts of acidity were actually low. As can be seen in Figure 3, overburden samples with net neutralization potentials higher than 0, and as high as 67‰ produced acidity in overburden leaching tests, but the rates of acid production were below 0.01 mg/g sample/day. Higher rates of acid production occurred only in overburden samples with NNP's less than zero.

Overburden acid production rates behaved in a similar fashion with respect to neutralization potential thresholds. As can be seen in Figure 4, overburden samples with NPT's as high as 73‰ did produce acidity in leaching tests, but unless the NPT dropped below 20, the rate of acid production was low, on the order of 0.01 mg/g sample/day. It was only for overburden samples with NPT's less than 20, were higher APR's generated.

The traditional ABA interpretation methods also fared poorly when evaluated as part of a *quantitative* error analysis. NR and NNP exhibited no correlation with APR, having correlation coefficients of -0.11 and -0.43 respectively. The parameter MPA/NP, however, the ratio of maximum potential acidity to neutralization potential, did exhibit good linear correlation with APR with a coefficient of r=0.80, slope of 0.00602, and Y-intercept of -0.0053.

The regression relationship depicted with 95% hyperbolic confidence bands in figure 5 reveals a quantitative method to estimate APR that would be generated in an overburden leaching test, based on MPA to NP ratios:

$$APR=[MPA/NP \times (6.02\times10^{-3}) + (-5.3\times10^{-3})] \pm [W \times S_{Yi}]$$

where:

$W^2=2F_{(1-\alpha;2,n-2)}$
s_{Yi}=standard deviation at any point Y_i on the regression line

Conclusions

Based on the results above, it is clear that traditional acid/base accounting interpretation criteria such as neutralization ratio (NR), net neutralization potentials (NNP), or neutralization potential thresholds (NPT) do not provide means to clearly delineate mine overburdens into acid or alkaline producing when compared to leachate quality from overburden leaching tests. Much higher values of NR, NNP, and NPT than are currently used were required for absolute assurance that mine overburden samples would not produce acidity. However, it is important to note that while mine overburdens with high NR's (up to 19), NNP's (67‰), and NPT's (73‰), did produce acidity in overburden leaching tests, the actual acid production rates were somewhat low, suggesting that a more quantitative approach to acid base account may be more suitable. Such a quantitative approach may not explicitly delineate acid from alkaline producing samples, but might allow the classification of overburden samples into classifications of low, medium, or high potential acid production. The regression equation resulting from the relationship of acid production rate to MPA/NP, correlated at r=0.80, may provide a rudimentary method of doing so.

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Figure 5: Acid Production Rates vs. MPA/NP