RELATIONSHIPS BETWEEN THE INITIAL GEOCHEMISTRY AND LEACHATE CHEMISTRY OF WEATHERING OVERBURDEN SAMPLES

Robert S. Hedin and Patricia M. Erickson[2]

Abstract.--The relationships between geochemical measurements and the chemistry of leachates collected in weathering tests were explored for 139 overburden samples. All samples were analyzed for total sulfur (ST) and neutralization potential (NP) and 95 had sulfur fractionated into pyritic, sulfate, and organic forms. All samples were weathered for 6-8 weeks in a laboratory, and leachates were collected and analyzed weekly for acidity, alkalinity, and sulfate. All data were normalized with logarithmic transformations.

Cumulative sulfate produced in the weathering tests was strongly correlated with total sulfur ($r=+.83$). The relationship with pyritic sulfur was much weaker. NP had a negative influence on sulfate production, but the correlation was weak ($r=-.27$), especially for samples with NP less than 30 tons per 1000 tons. Multiple regression analyses relating weekly sulfate production to neutralization potential and sulfur forms identified sulfate sulfur as the most important independent variable. Pyritic sulfur was not a significant factor in any week's analysis. When only samples that had produced more sulfate than could be accounted for by sulfate sulfur measurements were considered, pyritic sulfur became a significant component in the sixth week, and the dominant component in the eight week.

Cumulative acidity/alkalinity, expressed on a single scale, was significantly correlated with total sulfur ($r=+.37$), NP ($r=-.43$) and the difference of neutralization and acid potential Net NP ($r=.61$). Estimates were made of the cumulative neutralization generated by each weathered sample by comparing sulfate and acidity/alkalinity production. For most samples, less than 10% of the NP had been consumed in the 6-8 week tests. All samples with more than 25% consumption produced acidic leachates.

---

[1] Paper presented at the 1988 Mine Drainage and Surface Mine Reclamation Conference sponsored by the American Society for Surface Mining and Reclamation and the U.S. Department of the Interior (Bureau of Mines and Office of Surface Mining Reclamation and Enforcement), April 17-22, 1988, Pittsburgh, PA.

[2] Robert S. Hedin is an Ecologist, Oak Ridge Associated Universities, under contract to U.S. Bureau of Mines, Pittsburgh Research Center, Pittsburgh, PA, and Patricia M. Erickson is a Supervisory Physical Scientist, U.S. Bureau of Mines, Pittsburgh Research Center, Pittsburgh, PA.

INTRODUCTION

Two procedures commonly used in acid mine drainage prediction efforts are acid-base accounting and weathering tests. Both procedures require that the overburden be adequately sampled. With acid-base accounting, the samples are analyzed for neutralization potential and sulfur content, which is converted into an acid potential. These values are compared to determine whether the sample is likely to develop acidic or alkaline conditions. Samples are often aggregated, by various weighting methods, so that the acidity or alkalinity of the entire overburden can be represented by a single value.

The acid-base method has several important limitations. Sulfur measurements, using current procedures, cannot account for the variability that exists in sulfide reactivity (Caruccio 1969; Hammack 1985; Hammack, elsewhere in these procedings). The method used to determine neutralization potential can give inflated results if the sample contains significant amounts of siderite (Caruccio 1967). More importantly, acidity and alkalinity are generated by quite different processes that are not additive. Caruccio and Parizek (1967) have suggested that a better approach is to artificially weather samples and monitor the chemistry of regularly collected leachates. After an appropriate period, samples are characterized by their actual production of acidity or alkalinity.

The acid-base method is preferred by most mine operators because it has significant cost advantage over weathering tests. When overburdens are dominated by either acidic or basic materials, errors introduced by the acid-base procedure are not important. However, when overburdens are roughly balanced with respect to acidic and basic materials, the errors of the accounting method may be unacceptable and weathering tests may be required. Despite these additional efforts, post-mining water quality is often quite different from its predicted composition.

We evaluated the usefulness of these methods for sites with balanced overburden chemistries by comparing the results of acid/base accounting and weathering tests to measured post-mining water quality. In another paper we describe the relationships between these prediction methods and the drainage chemistry (Erickson and Hedin, elsewhere in these proceedings 1988). In this paper we discuss the relationship between the methods. We try to fit these relationships within the current tenets of spoil acidification, and where they do not mesh, we identify theoretical or methodological problems that cause the failures.

METHODS

The overburdens at 32 active mining sites were described and sampled. At 9 sites preserved overburden cores were inspected and sampled. At 23 sites fresh highwalls were described and channel samples were collected after removing weathered surface materials. Each overburden was described by the thickness and type of individual stratigraphic unit. The entire length of each unit was sampled and, when this resulted in an unmanageable amount of material, a subsample was taken. All samples were stored in sealed plastic bags.

A total of 264 samples were collected, and a determination of total sulfur (ST) (Fisher automated sulfur analyzer) and neutralization potential (NP) was made for each (Sobek et al. 1974). (See (table 1) for acronyms of all variables discussed). For samples with a total sulfur content greater than 0.5% (n=95), sulfur was fractionated into organic (SO) sulfate (SS) and pyritic (SP) forms using leaching procedures described by Sobek et al. (1974). We use the term "pyritic" to refer to the sulfur which can be extracted by HNO_3 but not by HCl. This value is believed to represent all forms of reduced sulfur, that upon oxidation, would produce acid products.

Neutralization potentials were expressed in tons of $CaCO_3$ equivalent per 1000 tons.[3] Sulfur contents were expressed as percent of dry weight. Acid potentials (AP), expressed in the same units as neutralization potential, were estimated by multiplying the total sulfur content by 31.25. Net NP was calculated by subtracting acid potential from neutralization potential.

Student's t-test comparisons of the pyritic sulfur ($t=0.83$, $P>0.05$) and sulfate sulfur ($t=1.30$, $P>0.05$) contents of samples collected from highwalls and from preserved cores revealed no significant differences. Thus, differential weathering of highwall and preserved core samples was not indicated and all samples were subsequently pooled.

Weathering tests were performed on all 152 samples from 16 mines. Sample splits of 300 grams were crushed to pass a 2mm sieve, and placed in plastic boxes which were continuously aerated with humid air for 6-8 weeks. Each sample was initially spiked with 10 ml of acid mine drainage to insure the presence of iron-oxidizing bacteria. At weekly intervals the boxes were filled with 300 ml of distilled water and drained after one hour. The volume of the collected leachate was determined, and the samples were analyzed for pH, sulfate, acidity, alkalinity, and iron.

Weathering test results were expressed as milligrams of sulfate or acidity, which were calculated by multiplying measured concentrations by the volume of leachate collected (table 1). Unless otherwise noted, the results of the first leachate were not included in calculations.

Unit sulfate production, (USP), which related the cumulative milligrams of sulfate leached to the grams of total sulfur present in the sample, was calculated:

$$USP = SO_4 \text{ mg}/(\text{sample grams} * ST)$$

An estimate of the total neutralization generated, (NG), was calculated from the stoichiometry of pyritic oxidation in the absence of secondary neutralization as two moles of H^+ associated with each mole of sulfate:

$$NG = (SO_4 \text{ mg} * 100/96) - \text{acidity}$$

where acidity was expressed as a positive value, and alkalinity was a negative value.

---

[3] The unit derives from agronomic applications, where 1000 tons is equivalent to an acre-plow layer. Parts per thousand (PPT) is the generic term.

Table 1.--Key to Abbreviations and Calculations.

Abb.	Variable	unit	Measurement or Calculation
GEOCHEMICAL MEASUREMENTS			
ST	Total Sulfur	% of dry wght	LECO Sulfur Analyzer[1]
SP	Pyritic Sulfur	% of dry wght	acid leaches and LECO[1]
SS	Sulfate Sulfur	% of dry wght	acid leaches and LECO[1]
SO	Organic Sulfur	% of dry wght	acid leaches and LECO[1]
NP	Neutralization Potential	tons/1000 tons	titration[1]
AP	Acid Potential	tons/1000 tons	ST X 31.25
NETNP	Net NP Potential	tons/1000 tons	NP - AP
NP/AP	Ratio	ratio	NP / AP
LEACHATE MEASUREMENTS			
SO4	Cummulative Sulfate Production	milligrams	sum of (sulfate mg/L X L leached)
ACID	Cummulative Acidity Production	mg $CaCO_3$ equiv	sum of ((acidity-alkalinity) mg/L X L leached)
NG	Neutralization Generated	mg $CaCO_3$ equiv	(SO4 X 100/96) - ACID
NC	Neutralization Consumed	% of NP	NG / NP
USP	Unit Sulfate Production	Sulfate per gram of total sulfur	SO4 / (ST X 300 gm/sample)

[1] methods from Sobek et al. 1974

Data were analyzed using the SPSSX computer package. We used a 0.05 probability level to judge the significance of correlations and regressions. Alkalinity was treated as negative acidity so that both could be expressed on a single scale. None of the data were normally distributed in their raw form. Normal distributions of ST, SP, SS, NP, USP, NG, and sulfate were obtained with logarithmic transformations. Transformations did not normalize organic sulfur determinations, so statistical evaluations of this minor sulfur fraction should be viewed cautiously. Logarithmic transformations of acidity values were made after adding 150 to each to correct for negative (alkaline) values. For a similar reason, Net NP values were increased by 50 before making logarithmic transformations.

Because we were most concerned with roughly balanced overburdens, we eliminated samples with extreme ST or NP values from the analyses. This restriction caused the elimination of one sample with a total sulfur content of 8.2% and 12 samples with NP > 200. The data set analyzed thus contained 139 samples for which weathering results, neutralization potential and total sulfur were known, and a subset of 51 samples for which sulfur fractions were also known.

RESULTS

The average sample had a total sulfur content of 0.64% and an neutralization potential of 13.3 tons $CaCO_3$ per 1000 tons (n=139). The average difference between neutralization potential and acid potential (Net NP) was -7.10. Sulfur was fractionated for 51 samples which averaged 1.47% total sulfur, of which 77% was classified as pyrite, 17% as sulfate, and 6% as organic sulfur.

The average sample produced in the weathering tests a total of 281 mg of sulfate and 98 mg of net acidity (calculated: acidity minus alkalinity). The 51 samples with fractionated sulfur forms, produced on average 624 mg of sulfate and 291 mg of net acidity.

Cumulative Sulfate Production and Acid Potential

The first hypothesis about relationships between leachate chemistry and sample geochemistry considered was that sulfate production was related to a sample's total sulfur content. This expectation was strongly supported (table 2, figure 1). Regression of acid potential on sulfate indicated the following log-log relationship:

$$\log(\text{sulfate}) = 0.675 \log(\text{AP}) + 1.446$$
$$(r^2 = .77,\ n=139)$$

This estimate of acid potential was based on total sulfur values. We expected that acid potential values based on pyritic measurements (APSP) would result in a stronger relationship. Instead, regression analysis revealed a similar equation, but a much weaker relationship.

$$\log(\text{sulfate}) = 0.754 \log(\text{APSP}) + 1.510,$$
$$(r^2 = .35,\ n=51)$$

The strongest correlation between sulfate production and a sulfur fraction was with sulfate sulfur (r=.78). Multiple regression of sulfur fraction percentages (SP, SO, SS) and NP on cumulative sulfate production, produced the

Table 2.--Pearson correlations between sample geochemistry and leachate chemistry.

Geochemical Measurement	Leachate measurement Sulfate	 Acidity	 USP	 NG
AP	$+.83^{***}$	$+.37^{***}$	$-.46^{***}$	$+.84^{***}$
NP	ns	$-.43^{***}$	$-.27^{**}$	$+.33^{***}$
Net NP	$-.55^{***}$	$-.61^{***}$	ns	$-.30^{***}$

** P<0.01; *** P<0.001; ns P>0.05
All variables were log-transformed before calculations.

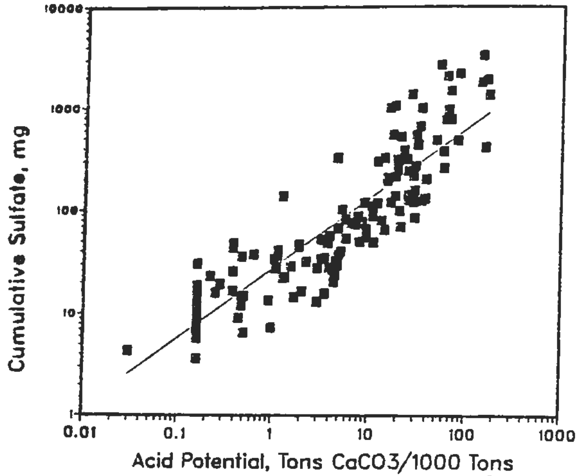

Figure 1.--The relationship between cummulative sulfate production by weathering samples and their intitial acid potential. Coefficients of the regression line are given in the text.

following relationship.

$$\log(\text{sulfate}) = 0.631\ \log(\text{SS}) + 0.189\ \log(\text{SO}) + 3.434,\ (r^2 = .68,\ n=51)$$

Pyritic sulfur and neutralization potential were not significant components of the regression equation.

Cumulative Sulfate Production and Neutralization Potential

Several studies have produced results that suggest that neutralization potential has a negative influence on sulfate production, presumably because it inhibits activity by iron oxidizing bacteria (Caruccio, et al. 1980; Williams et al. 1982, Poissant and Caruccio 1986). We tested this hypothesis by comparing NP to cumulative sulfate production and unit sulfate production.

NP was not significantly correlated with cumulative sulfate production (table 2). This finding was further supported by the observation that several limestone samples (excluded from these analyses) produced very high amounts of sulfate. At the sites where these limestones were collected, the drainage was characterized by alkaline water with extremely high sulfate concentrations. Clearly, high NP does not, by itself, cause radical reductions in sulfate production.

Caruccio and his students have tested for a neutralization effect by comparing unit sulfate production (USP) to alkaline production potentials. Samples with high NP relative to sulfur, generally result in lower production of sulfate per unit of sulfur. Caruccio has only discussed a small number of samples, all with total sulfur contents > 1% (Caruccio, Geidel and Pelletier 1980). We tested a larger number of samples with a wider range of sulfur values. Because very low sulfur values inflate USP values and the variation in very low sulfur values may be instrument or operator related, only materials with ST contents greater than 0.05% were considered in our analysis. A significant, negative correlation was found between NP and USP, but it was weak (table 2, figure 2).

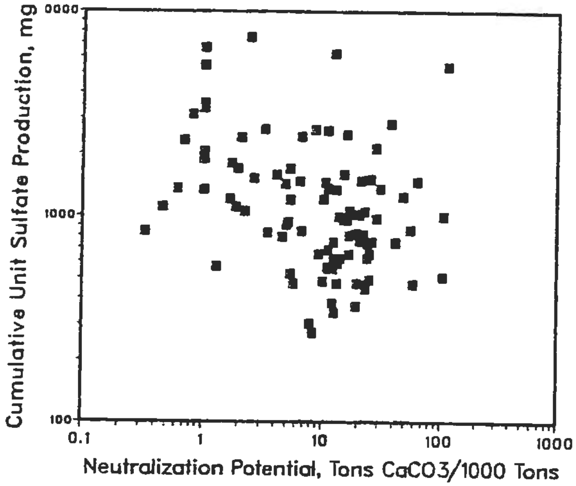

Figure 2.--The relationship between unit sulfate production and nuetralization potential.

Cumulative Sulfate Production, AP and NP

Because both acid potential and neutralization potential influence sulfate production, a multivariate analysis was used to test the complexity of the relationship. Various combinations of AP and NP have been suggested as appropriate for acid mine drainage prediction models. We tested NP, AP, Net NP, and the ratio of NP to APST (NP/AP). The best fit was with AP and the ratio.

$$\log(\text{sulfate}) = 0.484\ \log(\text{AP}) - 0.215\ \log(\text{NP/AP}) + 1.608,\ (r^2 = .80,\ n=139)$$

Note that when NP is less than AP, the ratio is less than one and log(NP/AP) is a negative value. This results in a higher prediction of sulfate production. At ratios greater than 1.0, the sulfate production prediction is decreased. This relationship indicates that NP only inhibits sulfate production when it is present in excess.

Weekly Sulfate Production by Weathering Samples

Thus far, only cumulative production of sulfate during the weathering tests has been discussed. Because leachates were collected and analyzed on a weekly basis, analysis of temporal changes in the relationships was possible. For each week's data, regression equations were calculated which related that week's sulfate production to the original measurements of neutralization potential, pyritic, sulfate and organic sulfur. Of the 51 samples analyzed, all were weathered for at least 6 weeks, and 45 were weathered for 8 weeks.

We predicted that the first week's sulfate production would be strongly related to sulfate sulfur because during this first leach much of the rock's original sulfate content would be dissolved. In subsequent weeks we expected that pyritic sulfur would be the most important component, because of oxidation, and that NP would have a minor negative effect on sulfate production.

Our first prediction was supported by the regression analysis (table 3). Sulfate sulfur was the most important geochemical component and pyritic sulfur was not a significant factor. Unexpectedly, sulfate sulfur remained a significant part of the regression equations for the entire weathering period (8 weeks). Pyritic sulfur never became a significant component. Neutralization potential acted as a negative factor after four weeks. Organic sulfur was a significant factor throughout the experiment, but its low degree of contribution and its non-normal distribution makes specific interpretations difficult.

Table 3.--Relationships between sample geochemistry and weekly sulfate production. The coefficients values were calculated for the equation:

$$SO4 = b_1(SP) + b_2(SS) + b_3(SO) + b_4(NP)$$

Week	r	b_1	b_2	b_3	b_4
1	.69	ns	0.70	0.32	ns
2	.77	ns	0.72	0.27	ns
3	.84	ns	0.71	0.14	ns
4	.82	ns	0.66	0.21	ns
5	.86	ns	0.64	0.24	-0.17
6	.87	ns	0.72	0.18	-0.25
7	.82	ns	0.59	0.24	-0.24
8	.75	ns	0.56	0.22	-0.25

ns $P>0.05$; all other coefficients, $P<0.05$; All variables were log-transformed before regression analysis.

To further explore these unexpected findings, samples were classified each week according to the fraction of sulfate sulfur leached. This fraction was calculated by dividing the cumulative sulfate leached by the amount of sulfate available in the original sample. Samples with a fraction greater than 1.0 had produced more sulfate than could be accounted for by the original sulfate sulfur content. We tested the hypothesis that sulfate production by samples which had been, theoretically, depleted of their original sulfate sulfur content, was more dependent on pyrite than samples for which residual sulfate sulfur still existed.

The highest r-square values for the regression equation relating sulfate production to SP, SS, SO and NO were obtained when a ratio of 0.80, not 1.00, was used as the sorting criteria. We suspect that this may be because some of the sulfate sulfur present was not readily leached by our weathering procedures. The correlations and r-square values obtained were consistently higher than those obtained in the initial analysis.

Table 4.--Relationships between sample geochemistry and weekly sulfate production that are sorted according to the proportion of sulfate leached to that originally available.

a.--Samples with CUMSO4/SSAVAIL > 0.80

$$SO4 = b_1(SP) + b_2(SS) + b_3(SO) + b_4(NP)$$

Week	n	r	b_1	b_2	b_3	b_4
1-3	0					
4	14	.84	ns	0.76	ns	ns
5	22	.90	ns	0.67	0.22	-0.18
6	26	.91	0.52	0.64	ns	-0.36
7	25	.89	0.46	0.44	0.15	-0.33
8	30	.84	0.84	0.36	ns	-0.40

b.--Samples with CUMSO4/SSAVAIL ≤ 0.80

$$SO4 = b_1(SP) + b_2(SS) + b_3(SO) + b_4(NP)$$

Week	n	r	b_1	b_2	b_3	b_4
4	37	.87	ns	0.87	ns	ns
5	29	.91	ns	0.86	0.13	ns
6	25	.94	ns	0.98	ns	-0.16
7	20	.92	ns	0.93	ns	ns
8	15	.79	ns	0.85	ns	ns

ns $P>0.05$; all other coefficients, $P<0.05$
CUMSO4 is the cummulative sulfate produced by samples in the appropriate week; SSAVAIL is an estimate of the total amount of sulfate contained by each sample before weathering;
All variables were log-transformed before regression analysis.

Sulfate production by samples with less than 80% of the original sulfate leached was very strongly related to sulfate sulfur and generally unrelated to neutralization potential, pyritic or organic sulfur (table 4b). The importance of sulfate sulfur did not decrease between the fourth and eighth weeks for these samples.

The equations for samples with more than 80% of the original sulfate accounted for in the leachate, were considerably different (table 4a). Pyritic sulfur was a significant factor after 5 weeks and the most important factor at eight weeks. Sulfate sulfur was a significant component of all equations, but its importance decreased with each additional week. Neutralization potential was a significant negative influence in all but the fourth week.

Two alternative explanations can account for the unexpected importance of sulfate sulfur and the relative unimportance of pyritic sulfur in predicting sulfate production. One explanation is that the sulfate sulfur may not have been completely solubilized during the first leaching. Instead, it could have been gradually released over the 6-8 weeks of testing. We find little theoretical support for this hypothesis because equilibrium and kinetic factors favor complete sulfate dissolution. Common sulfate minerals, such as gypsum and jarosite, have very rapid dissolution kinetics and have high solubilities. All of the leachates, which sat for 60 minutes before being drained off, were undersaturated with respect to these minerals. More importantly, this explanation cannot explain the negative influence of neutralization potential since it is unlikely that calcite or dolomite effect the solubility of sulfate minerals or the kinetics of their dissolution. It is possible that sulfate is contained within particles that are not penetrated by the solvent (distilled water) until they undergo weathering. We find this process also difficult to support.

Our second explanation is that the sulfate sulfur measurement technique is flawed. In our method, determinations were made of total sulfur for a raw sample and for one which was leached with HCl to remove all sulfate sulfur. Sulfate sulfur was calculated as the difference of the two measurements. A crucial assumption of this method is that HCl does not effect reduced forms of sulfur. Although valid for crystallized, stable forms of pyrite, the assumption is not true for unstable mono-sulfides. Soil scientists who work with sulfide-containing sediments commonly use HCl to dissolve and quantify reduced sulfur. When we perform HCl leaches on overburden samples, we commonly observe hydrogen sulfide fumes, an indication of sulfide oxidation (R. Hammack, personal communication). This fraction of reduced sulfur is the most unstable and most easily oxidized. In a weathering experiment, we would expect that these sulfur compounds would be the first to oxidize and, if present in sufficient quantities, significantly effect sulfate production during the first several weeks of weathering. We would also expect that neutralization potential, if present in sufficient quantities, could inhibit this source of sulfate. Thus, the finding that NP has a significant negative role before pyrite has a significant positive one is not unexpected.

Cumulative Net Acidity and AP and NP

Net acidity (acidity minus alkalinity) produced in leaching tests was significantly correlated with both acid potential and neutralization potentials, but was most strongly related to the net NP (table 2). A plot of net NP against net acidity is shown in figure 3. Samples with large excesses of neutralization potential never produced cumulative alkalinities (negative net acidities) greater than 100 mg $CaCO_3$ equivalent, while several samples with large excesses of acid producing potential resulted in more than 1000 mg of cumulative net acidity. This result is primarily an artifact of the weathering experiment and would be expected for all tests with a similar design. Constant aeration of the weathering boxes prevented the accumulation of carbon dioxide and thus limited alkalinities to approximately 100 mg over the 6-8 weeks of weathering. Even limestones, which are not included in Figure 3, never produced more than 200 mg of alkalinity (40-50 mg/L). These conditions do not represent those commonly observed in spoil piles (Lusardi and Erickson, 1985).

All samples, but one, with positive Net NP produced alkaline or only slightly acid leachates (less than 50 mg $CaCO_3$ equivalent of acidity). This relationship held until Net NP reached -8.0 tons/1000 tons. Below this value there was considerable variation in the relationship between Net NP and net leachate acidity. In particular, several samples that were extremely deficient in neutralization potential (negative Net NP) produced alkaline leachates. For two of these samples sulfate levels were high, suggesting that the high alkalinity was due to a high amount of neutralization. For the other samples with unexpectedly high alkalinities, sulfate production was low, suggesting limited acid production despite high acid producing potentials.

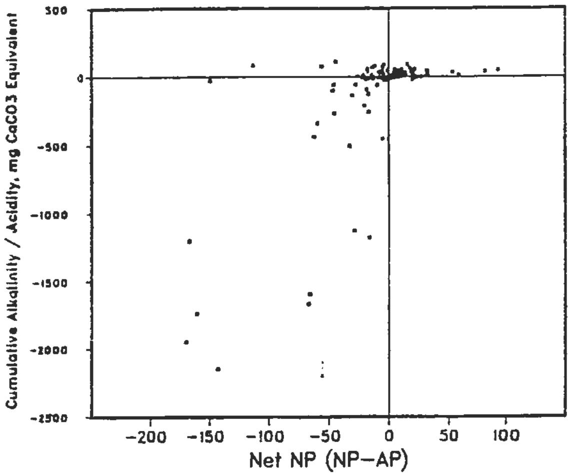

Figure 3.--The relationship between cummulative production of net acidity by weathering samples and their initial Net NP.

The best fit regression relating net acidity to geochemical measurements was:

$$\log(\text{Acidity}) = -0.364 \log(\text{NP/AP}) - 0.257 \log(\text{AP}) - 0.802 \log(\text{Net NP}) + 4.150$$
$$(r^2 = .54, n = 139)$$

As with sulfate production, a logarithmic model best explained production of net acidity, but the explained variation was less. This is partially a result of the difficulty in fitting a single model to data that is influenced by two different processes. Generation of alkalinity is limited by solubility constraints forced by the gas compositions in the weathering vessels. Acidity is only limited by the rate of acid potential and, for our purposes, is unconstrained by any solubility limitations.

In a second analysis, the influence of alkalinity limitations was minimized by only considering samples with Net NP less than -8.0. The relationship improved considerably and the best equation was non-exponential:

$$\log(\text{Acidity}) = 0.004\ \text{AP} - 0.036\ \text{NP} - 0.828\ \text{NP/AP} + 2.550, \quad (r^2 = .77)$$

Again, the ratio of neutralization potential to acid potential, not the difference, is a significant addition to the model.

Cumulative Neutralization Generation

Cumulative generation of neutralization was estimated from cumulative sulfate production and cumulative acidity/alkalinity. The calculation is based on the assumption that two moles of H^+ are associated with each mole of sulfate. When the measured acidity of a leachate sample is less than the acidity estimated from sulfate measurements, then a calculable amount of neutralization has occurred. Generation of neutralization (NG) was significantly related with all measures of acid potential and neutralization potential (table 1). Multiple regression revealed that a logarithmic relationship with APST and NP gave the best relationship.

$$\log(NG) = 0.551 \log(AP) + 0.138 \log(NP) + 1.428$$
$$(r^2 = .72)$$

Because high NG is only possible when a high amount of sulfate production has occurred, acid potential is more important than neutralization potential. Unlike the acidity calculations, separating the data into acidic and alkaline overburden samples did not improve the relationship. This was because NG was less constrained by solubility limitations than raw alkalinity measurements. Many alkaline samples had high sulfate values, which resulted in high NG estimates.

The above equation also suggests that NP was rarely a limiting component of the generation of neutralization. To determine the percentage of neutralization consumed in the weathering experiments, we compared the neutralization generated to the neutralization potential originally measured.

Neutralization Consumed = NG mg / NP mg

Less than 10% of NP had been consumed in 58% of the samples. Four of 136 samples had consumption percentages greater than 100 indicating that the neutralization potential had been theoretically exhausted. These samples produced some of the most acid leachates. All samples with more than 25% consumption produced acidity (figure 4). All of these samples had NP values less than 5.0. Samples with similar NP values, but lower estimates of consumption, generally had alkaline or only slightly acid leachates.

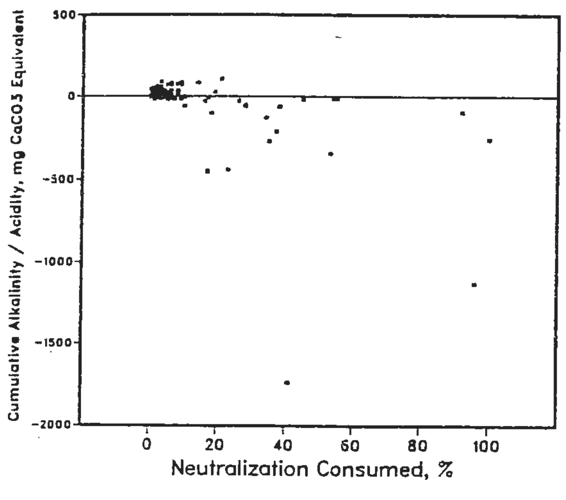

Figure 4.--The relationship between cummulative production of net acidity by weathering samples and the percentage of NP consumed during the weathering tests.

DISCUSSION

These results support the general tenets of the spoil acidification process. Sulfate production by a weathering sample is strongly correlated with its sulfur content. The relationship is best characterized by logarithmic equations. Neutralization potential has an inhibitory influence on sulfate production, but the effect is variable. It cannot be determined from these results whether NP actually inhibits sulfate production, or if it is negatively correlated with sulfur reactivity. The acidity of a sample is strongly related to both its acid producing potential (based on total sulfur) and its neutralization potential. Both models of sulfate and acidity production are improved by the incorporation of the ratio of neutralization to acid potentials.

We also found some unexpected results. Pyritic sulfur was not a better predictor of a leachate's sulfate content or its net acidity than total sulfur. This result may be an artifact of the limited length of our weathering tests (6-8 weeks) since, for some samples, pyrite was increasing in significance in the final weeks of weathering. However, this explanation indicates that the results of weathering tests are strongly dependent on the period over which they are conducted. Because the goal of these tests is to obtain an estimate of the acid potential, it is important that they are conducted until significant pyritic oxidation and acid production has occurred. According to Caruccio et al. (1980), the tests should be conducted until the rate of sulfate production levels off which generally takes 5-10 weeks. Our results, which are based on obtaining a statistically significant relationship between sulfate production and the pyritic content of the sample, suggest even eight weeks is not sufficient. During this study we reviewed an alarming number of overburden analyses, done by coal companies or consulting firms, which reported leachate results after only 3-4 weeks.

The expected relationship between sulfate production and pyritic sulfur only existed for samples which were, theoretically, completely leached of their original sulfate content and had been weathering for at least six weeks. It might thus be appropriate to determine the length of a weathering test by the ratio of sulfate leached to sulfate contained in the original sample. Sulfate production rates would not be estimated until more sulfate had been leached than had been measured in the original sulfate sulfur determinations.

The unexpectedly strong relationship between sulfate production and a sample's sulfate sulfur content suggests that sulfate sulfur measurements are in error. It is likely that unstable sulfides are dissolved in HCl during the sulfate sulfur procedure. Although these compounds may be a small fraction of the total pool of reduced sulfur, they represent the most reactive forms and would oxidize very quickly in weathering tests. If quantifiable, this methodological error might be developed into a useful indicator of the reactivity of pyritic sample. We are currently exploring this possibility by analyzing the relationship between sulfate sulfur estimates and evolved gas analyses.

Finally, we address the problem of predicting drainage chemistry on a mine level. Are the errors calculated and discussed in this paper responsible for predictive failures? We think not. The error of our relationships is about 25%, which is not great enough to account for the large differences between expected and actual drainage chemistry observed in our study (see Erickson and Hedin in these proceedings). Indeed, we appear to have an accurate understanding of the acid and sulfate production process under controlled, laboratory conditions. More likely, the failure of the methods lies in conservative assumptions and design features that are inappropriate. In the acid-base accounting method, the assumption is made that all sulfur will oxidize, and all basic materials will dissolve. Several surveys of the sulfur content of abandoned spoil piles have shown that unweathered portions of the spoils retain significant quantities of pyritic sulfur (Lusardi and Erickson 1985; von Demfange and Warner 1975). In our weathering tests, we produced conditions that maximized pyritic oxidation and minimized alkalinity. Both of these problems can be justified when one wishes to make conservative judgments. However, if accurate predictions are the goal, the assumptions and methodologies must be thoroughly reevaluated.

LITERATURE CITED

Carucci, F. T., and R. R. Parizek. 1967. An evaluation of factors influencing acid mine drainage production from various strata of the Allegheny Group and the ground water interactions in selected areas of western Pennsylvania, Coal Research Section, SR-65, Pennsylvania State University.

Caruccio, F. T. 1969. Characterization of strip mine drainage, in ecology and reclamation of drastically disturbed sites, Gordon and Breach, p. 193-224.

Caruccio, F. T., G. Geidel, and A. Pelletier. 1981. Occurrence and prediction of acid drainages, in proceedings 1981 symposium on surface mining, hydrology, sedimentology and reclamation, University of Kentucky, p. 437-443.

Hammack, R. W. 1985. The relationship between the thermal activity of pyrite and the rate of acid generation, in proceedings 1985 symposium on surface mining, hydrology, sedimentology and reclamation, University of Kentucky, p. 139-144.

Lusardi, P., and P. Erickson. 1985. Assessment and reclamation of an abandoned acid-producing strip mine in northern Clarion County, Pennsylvania, in proceedings 1985 symposium on surface mining, hydrology, sedimentology and reclamation, University of Kentucky, p. 313-323.

Poissant, S., and F. Caruccio. 1986. The occurrence and viability of thiobacillus ferroxidans under varied geochemical conditions in Upshur and Lewis Counties, West Virginia, in Proceedings 1986 symposium on surface mining, hydrology, sedimentology and reclamation, University of Kentucky, p. 141-147.

Sobek, A., W. Schuller, J. Freeman, and R. Smith. 1974. Field and laboratory methods applicable to overburdens and minesoils, EPA-600/2-78-054.

von Demfange, W., and D. Warner. 1975. Vertical distribution of sulfur forms in surface coal mine spoils, in proceedings 1975 symposium on surface mining, hydrology, sedimentology and reclamation, University of Kentucky, p. 135-147.

Williams, G., A. Rose, R. Parizek, and A. Waters. 1982. Factors controlling the generation of acid mine drainage. Final report on grant G5101086, Pennsylvania Mining and Mineral Resources Research Institute, Pennsylvania State University, p. 265.

Information Circular 9183

Mine Drainage and Surface Mine Reclamation

Proceedings of a conference sponsored by The American Society for Surface Mining and Reclamation, The Bureau of Mines, and The Office of Surface Mining Reclamation and Enforcement. The conference was held in Pittsburgh, Pennsylvania on April 19-21, 1988.

Volume I: Mine Water and Mine Waste.

Volume II: Mine Reclamation, Abandoned Mine Lands and Policy Issues, is also available from The Bureau of Mines as Information Circular 9184.

UNITED STATES DEPARTMENT OF THE INTERIOR
Donald Paul Hodel, Secretary

BUREAU OF MINES
David S. Brown, Acting Director