# Mine Water Quality Prediction at Surface Coal Mines in the United States

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**Abstract.** This paper briefly summarizes the contents of a recently completed book on the subject of predicting water quality at surface coal mines. The book was prepared by a segment of the Acid Drainage Technology Initiative, (ADTI) and is available at nominal or no cost. ADTI is a joint venture of the U.S. government and industry dedicated to the development and use of best science applications to the problem of acid mine drainage. Several significant recommendations are made. First, if adjacent surface mines are geologically similar to the site to be mined, the water quality at such sites provide the best indication of the water quality likely to be encountered at the new mine. Little or no additional overburden sampling may be necessary. Second, when sampling is necessary, an absolute minimum of three, and more likely six or seven holes, are needed per 40 hectares (100 acres) if one hopes to capture the geological variability of the site. Site-specific criteria might dictate that sampling density be increased beyond this range. Third, the effect of weathering must be accounted for during sampling; the top 6 or 7 m of a site is likely to be leached of carbonate minerals and/or pyrite. Fourth, the effectiveness of the most widely used overburden analysis method, acid-base accounting, has been improved by modifying the determination of neutralization potential (NP) to eliminate the effects of siderite and the subjectivity of the fizz test. Fifth, the confidence one should have in the results of such an analysis is high if one has a NP less than 10 or greater than 21 tons per 1000 tons, or a net neutralization potential less than 0 and greater than 12 tons per 1000 tons. The lower range will most likely produce acid drainage, while the higher rage will most likely produce alkaline drainage. For strata lying between these values (in what is conventionally referred to as the *gray zone*), kinetic tests (humidity cell or leaching tests) might be useful. These values are based on the previous incarnation of acid-base accounting; it is anticipated that as the modified method becomes more widely used, the gray zone will shrink.

## INTRODUCTION

In the United States, the regulatory authorities and the mining industry have worked hard to improve water quality during and after mining. A key component of this activity is predicting the post-reclamation water quality before mining occurs. The regulatory agencies do this to aid in permitting decisions. Generally, where analysis indicates that poor post-reclamation water quality is anticipated, permits to mine are granted with restrictions (requiring the use of special preventive practices, such as alkaline addition to overcome neutralization deficiencies, or deleting a coal seam or an area from the permit) or are denied altogether. The mining industry is generally required to demonstrate that no pollution will result. Despite these efforts, acid mine drainage (AMD) is common at reclaimed surface mines, in part because the task of predicting post-mining water quality is highly problematic. As a result, the U.S. mining industry spends over a million dollars a day chemically treating contaminated mine water. The industry can only afford the long-term liability of water treatment if it is planned for; unanticipated water treatment that must continue after mining and reclamation can bankrupt a company.

At surface coal mines where the overburden chemistry is dominated by either calcareous or highly pyritic strata, the prediction of post-reclamation water quality is relatively straightforward. However, at sites where neither clearly predominates, predicting post-reclamation water quality can be complex. Fifteen years ago, researchers found that at these more difficult-to-predict sites, overburden analysis procedures generally used to predict post-reclamation water quality at surface coal mines were no more effective than flipping a coin. Since then, a great deal of effort has gone into improving the procedures. One state, Pennsylvania, has compiled statistics indicating that overall, its permitting decisions are now accurate 98% of the time; that is to say, only a small percentage of the mines they anticipate producing neutral or alkaline water produce AMD. (It is not possible to estimate how many mines are not permitted to open in Pennsylvania because of anticipated AMD that, in fact, might have produced acceptable water.) Other states are now beginning to similarly assess their permitting practices. However, even without the statistics from other states, it is clear to all of those working in the field that prediction of post-reclamation water quality has improved.

Currently, although similarities exist, each State's permitting agency has its own mine drainage prediction methodology. The amount and types of data required vary from state to state, including different requirements for documenting pre-mining water quality, overburden lithology and geochemical properties, and the proposed mining and reclamation plans. As a result, the degree of success in preventing AMD on new permits varies. The author hopes that all of the regulatory agency personnel reviewing this document will learn ways in which they can improve their permitting process by incorporating techniques successfully being used elsewhere.

It should be noted that this report presents only the components relevant to predicting water quality at surface mines at which coal is being mined. Although the general approach is similar, issues and interpretation of results can be quite different for hard rock operations and underground coal mining.

## FORMATION OF ACID MINE DRAINAGE

Acidity is formed at coal mines principally due to the oxidation of pyrite, $FeS_2$, which is commonly associated with the coal and surrounding strata. Coal owes its origins to the burial of organic matter in swamps; pyrite also forms in such environments. Several types of pyrite may be present, and the reactivity of the different forms can be significantly different due to the nature of their formation and the effect that grain size has on surface area. Mining disrupts the rock strata and exposes the pyrite to air and water, allowing oxidation to take place. Oxidation of the sulfide component of the pyrite to sulfate produces two moles of acidity for every mole of pyrite. Sulfur may also be present in the rock as sulfate minerals, such as jarosite ($KFe_3(SO_4)_2(OH)_6$), or as organic sulfur. Some of the sulfate minerals can dissolve and form acid solutions, but the organic sulfur is organically bound with the coal and has little or no effect on acid potential. Acidity is also produced by the oxidation of the iron and its subsequent hydrolysis. The acid water that results from all of these reactions leads to the dissolution of other common contaminants, such as aluminum and manganese, and occasionally other metals such as copper, zinc, and nickel.

At the same time, the rock strata typically include components that dissolve and produce alkalinity. In coal-bearing strata, alkalinity is principally represented by $CaCO_3$, either as limestone, calcareous cement or calcite, or as $CaMg(CO_3)_2$, dolomite. $FeCO_3$, siderite, is also commonly present but does not contribute alkalinity.

Although these minerals can oxidize and/or dissolve in the absence of mining, the disruption and displacement of the rock strata accelerates the processes. Accurately predicting post-reclamation water quality involves understanding how the minerals will react in the mine environment and how the acid-forming reactions and the acid-neutralizing or alkalinity-generating reactions will balance at a given site. There are many complicating variables. For example, concentrations of pyrite and carbonate minerals vary both horizontally and vertically, so that accurately determining the amount of each at a site can be very difficult. The kinetics of the reactions change as the water quality changes (for example, as pyrite oxidizes and the pH drops). Reaction rates are also affected by such variables as climate, the activity of iron-oxidizing bacteria, the rate of diffusion of oxygen, water infiltration rates, atmospheric chemistry within the mine spoil, the degree of compaction, the relative locations of the pyritic and calcareous rocks, and the location of the water table. Predictions involve measuring the most important variables, making certain assumptions relative to less-important variables, extrapolating from what has been learned through experience at other sites, and sometimes conducting laboratory simulations to evaluate kinetic aspects. Generally, one attempts to predict whether the site will produce acidic or alkaline drainage, though sites that produce alkaline water may still require chemical treatment or special handling due to the level of metal contaminants present.

## METHODS OF PREDICTION

Most frequently, prediction of post-reclamation water quality involves analysis of overburden samples. These samples can be analyzed using one of several static tests, which involve determining and comparing the amount of potentially acidic and alkaline constituents in the rock. There are also kinetic tests, which are principally leaching methods in which rock samples from the proposed mine site are subjected to simulated weathering conditions and the leachate is analyzed in a laboratory for mine drainage quality parameters. These kinetic tests may be conducted in an apparatus in the laboratory or in the field, and the test results may be evaluated independently of static tests or integrated with static test results on the same rock samples. Other methods of prediction include the use of geophysical and/or geochemical procedures, such as wireline logging.

As an alternative approach, the prediction of drainage quality from the natural background water quality at the site or from the chemistry of water at an adjacent mined site involves scientific inference and common sense. If representative samples of surface and ground water are collected on or near a proposed site, it is reasonable to assume that they should indicate something about the geology of the site and the quality of the mine drainage that will be produced after mining. For example, within areas of the Appalachian Coal basin of the eastern United States where major stratigraphic sections of carbonate rocks are present, surface and ground water will have a relatively high concentration of alkalinity, particularly in the head waters of small tributaries and in springs and ground water seeps. If the springs, seeps and tributary samples on or near a proposed mine site have low buffering capacity, it is less likely that carbonate rock will be present to produce alkaline drainage or to neutralize AMD. However, a major problem in relying solely upon background water quality is that significant sections of potentially acidic strata may be present on site, but not reflected in the pre-mining water quality. This occurs because the high acidity only results after the pyrite or other acid-producing minerals are exposed to increased oxidation and weathering during mining.

The use of mine water quality at nearby sites is a very similar, and generally more useful, technique. Post-mining discharges, highwall seeps, and pit waters at adjacent active, reclaimed, or abandoned sites can provide very good indications of whether future mine drainage is likely to be highly alkaline, highly acidic, or somewhat neutral, if adequate stratigraphic correlations of coal seams and overburden lithologic units can be made. Discharges from active or abandoned underground mines are of some value, but not as useful as surface mine data. Such data can be compiled from permit files of active or completed sites. At least two major problems may impede the accurate prediction of proposed mine site drainage quality from nearby sites. One is that the proposed mine site may have significantly different overburden chemistry due to facies changes, differences in depths of weathering, or other local-scale geologic variations. A second is that the existing water quality may reflect past mining and reclamation practices. For example, the existing reclaimed site may have coal preparation plant refuse or large amounts of alkaline additives, such as flyash, buried in the backfill, both of which will skew the water quality one way or the other.

Static and kinetic tests incorporate chemical analyses performed on rock samples from the actual mine site. A critical point is that these methods are only valid if the rock samples are truly representative of the site where mining is proposed. Geologic variability within a site must be captured through the use of a sufficient number of samples. The effect of weathering on the sampled strata must also be considered; the absence of carbonate minerals or pyrite in the top 20 feet of overburden sampled is likely not representative of the same strata at greater depths (Hawkins et al., 1996; Singh et al., 1982). Studies in Pennsylvania have shown that an absolute minimum of three and more typically six or seven holes are needed per 100 acres in order to capture the geologic variability of a site (Brady et al., 1994). The collective experience of the ADTI underscores Pennsylvania's findings, though of course each site is different and it is hard to generalize. Rock samples may be collected from exploration boreholes or other sources (e.g. exposed highwalls). Both static and kinetic tests produce site-specific geochemical evaluations of potential acidity or alkalinity, and possibly other parameters of predicted water quality. The major difference between static and kinetic tests is that static tests provide measurements of the amount of selected chemical constituents in the rock sample (e.g. total sulfur, neutralization potential), while kinetic tests provide measurements of the amount of selected chemical constituents that come out of the rock samples in leachate (e.g. acidity and iron concentrations) under specified conditions. The total amount of an element or mineral (e.g. sulfur or pyrite) in the rock sample may not be directly proportional to the amount of the associated parameter (e.g. sulfate or iron) in the simulated effluent produced in a leaching test or actual mine drainage in the field. This is due to reaction kinetics, mineral solubility controls, crystallinity and morphology of the minerals, and other physical, chemical, and biological factors. However, both static and kinetic tests have potential value, provided that their limitations are recognized when interpreting the results.

Acid-base accounting (ABA) is the static test that is most commonly used to predict mine drainage quality in the eastern United States. This method involves a comparison of the maximum potential acidity (MPA), typically calculated from the total sulfur in the sample, to the neutralization potential (NP). Other static tests have been developed and employed for use in coal mine drainage prediction, but ABA is the most routinely used method for coal mine drainage prediction.

## Conventional Neutralization Potential Methodology

The natural base content of overburden materials, commonly present as carbonates or exchangeable cations on clays, is important in evaluating the future chemical producing potential of the overburden. The amount of alkaline material in unweathered overburden may be sufficient to counteract or overwhelm the acid produced from S oxidation in the material.

The NP procedure in ABA quantifies the neutralizing compounds in coal and overburden. Alkalinity production potential (APP) is equivalent to the term NP. Of the many types of basic compounds present, carbonates and exchangeable bases are the only alkaline compounds that occur in sufficient quantity in most sedimentary strata to effectively neutralize acid mine drainage. Siderite, a ferrous carbonate ($FeCO_3$), is not a desirable neutralizer because it does not yield an alkaline-producing material upon complete weathering and oxidation of iron.

The NP test involves treating the pulverized overburden sample with a known quantity of HCl, heating it to ensure complete dissolution of bases, and back-titrating with sodium hydroxide (NaOH) (Sobek et al., 1978). The NP test relies on an initial subjective carbonate ranking procedure based on adding a few drops of dilute HCl to the sample and rating the observable fizz. Based on the fizz rating, a quantity of HCl (either 20 or 40 ml of 0.1M or 0.5M) is added to a sub-sample of the overburden and heated for complete reaction with the sample. After the sample has cooled, it is back-titrated with 0.1M or 0.5M NaOH to determine the quantity of HCl that was neutralized by the sample. This value is then used to calculate the NP of the sample and is expressed as $CaCO_3$ equivalents in metric tons per 1000 metric tons of material. The NP procedure is simple, can be done quickly, and is very accurate in determining alkaline content of most overburden materials.

## The Modified Neutralization Potential Technique

Siderite ($FeCO_3$), when present in the overburden, reacts quickly with HCl in the standard NP procedure in ABA and falsely indicates that the rock will behave as a net alkaline contributor after weathering (Cargeid, 1981; Morrison et al., 1990; Wiram, 1992). Continued weathering of $FeCO_3$ actually produces a neutral (Meek, 1981; Shelton et al., 1984) to slightly acid solution (Cravotta, 1991; Doolittle et al., 1992; Frisbee and Hossner, 1989). If insufficient time is allowed for complete iron oxidation and precipitation of ferric hydroxide during back titration, erroneously high NP values can be generated on samples containing $FeCO_3$, yielding misleading NP information. Such an analytical oversight can lead to incorrect post-mining water quality predictions and produce costly, long-term reclamation liabilities (Wiram, 1992).

Meek (1981) and Morrison et al. (1990) suggested adding a small quantity of 30% $H_2O_2$ to the filtrate of an overburden sample to oxidize ferrous iron to ferric iron before back-titration is initiated. Leavitt et al. (1995) proposed a modified NP procedure that includes boiling a 2-gram overburden sample for 5 min after the acid is added, filtering the suspension, and adding 5 ml of 30% $H_2O_2$, then boiling for an additional 5 min. Significant reductions in NP values were found for $FeCO_3$ samples using the modified NP method compared to the standard Sobek et al. (1978)

method (Table 1). Variations in NP determinations among laboratories were also dramatically reduced by using this modified method compared to the standard NP method on $FeCO_3$ samples (Table 2).

**Table 1.** Neutralization potential (NP) values for the standard Sobek and the modified NP ($H_2O_2$) digestion methods on overburden samples. Prominent minerals are given for each sample (Skousen et al., 1997).

| Sample Description | Sobek | $H_2O_2$ |
|---|---|---|
| (Metric tons/1000 metric tons) | | |
| 49% Siderite | 70 a[1] | 16 b |
| 65% Siderite | 62 a | 19 b |
| 65% Siderite | 63 a | 17 b |
| 61% Siderite | 62 a | 15 b |
| 8% Siderite, 55% Clays | 88 a | 26 b |
| 18% Siderite, 48% Clays | 64 | 56 |
| 20% Siderite, 11% Calcite | 367 | 322 |
| 90% Calcite | 926 | 924 |
| 83% Calcite | 835 | 847 |

[1] Values within rows without letters are not significantly different; values within rows with different letters are significantly different at $p < 0.05$.

**Table 2.** Neutralization potential values using the Sobek and modified NP ($H_2O_2$) digestion methods among three laboratories on overburden samples containing $FeCO_3$ and calcite (Skousen et al., 1997).

| Sample Description | Sobek Method | | | $H_2O_2$ Method | | |
|---|---|---|---|---|---|---|
| | Lab 1 | Lab 2 | Lab 3 | Lab 1 | Lab 2 | Lab 3 |
| ---------------(Metric tons/1000 metric tons)------------- | | | | | | |
| 49% Siderite | 70 | 89 | 29 | 16 | 14 | 20 |
| 65% Siderite | 62 | 88 | 25 | 19 | 21 | 28 |
| 65% Siderite | 63 | 87 | 14 | 17 | 16 | 25 |
| 61% Siderite | 62 | 93 | 445 | 15 | 12 | 43 |
| 8% Siderite, 55% Clays | 88 | 95 | 50 | 26 | 11 | 27 |
| 18% Siderite, 48% Clays | 64 | 82 | 26 | 56 | 25 | 77 |
| 20% Siderite, 11% Calcite | 367 | 607 | 363 | 322 | 301 | 277 |
| 90% Calcite | 926 | 928 | 936 | 926 | 926 | 924 |
| 83% Calcite | 835 | 828 | 837 | 847 | 844 | 851 |

Fizz ratings are done to assess the relative amount of carbonate present in a rock sample, which are then used to determine the amount and strength of acid to use in the NP digestion process. Conflicting NP values were found when overburden samples were assigned different fizz ratings and thereby digested in different amounts of acid (Table 3). At higher fizz ratings (more acid added), the NP values increased substantially. Since the subjective fizz rating was not found to be repeatable among laboratories and not reflective of the carbonate content of a rock, a quantitative and repeatable method to determine carbonate content was proposed (Skousen et al., 1997). The method uses the percent insoluble residue after acid digestion to assign a carbonate rating (Table 4), and has been found to accurately determine the amount and strength of acid to add for NP determination.

A 2-g sample of overburden is placed in a beaker. The appropriate amount and strength of HCl (Table 4) is added to the beaker. The suspension in the beaker is then brought to 100 ml volume prior to heating. Boiling chips are added to the suspension, the beaker is covered with a watchglass, and the suspension is boiled gently for 5 minutes. After cooling, the contents of the beaker are gravity filtered using a 0.45um (Whatman #40) filter. The filtered solution is then treated with 5 ml of 30% $H_2O_2$. The solution is then boiled for an additional 5 minutes (using boiling chips and watch glasses), and allowed to cool. The solution can then be hand-titrated using NaOH, to achieve and hold an endpoint pH of 7.0 for 30 seconds. However, since most analytical laboratories have auto-titrators, we recommend that auto-titration be used to determine the volume of NaOH needed to achieve and hold a pH 7.0 endpoint. The titration rate can be varied on most machines, so the middle setting is normally used for titrations.

**Table 3.** Neutralization potential values of overburden when samples were digested according to standard fizz ratings compared to increasing the fizz rating and adding a corresponding higher amount of acid (Skousen et al., 1997).

| Sample Description | Acid Added | Sobek | Acid Added | Sobek |
|---|---|---|---|---|
| 49% Siderite | 40 ml 0.1 M | 70 | 40 ml 0.5 M | 192 |
| 65% Siderite | 40 ml 0.1 M | 62 | 40 ml 0.5 M | 155 |
| 65% Siderite | 40 ml 0.1 M | 63 | 40 ml 0.5 M | 166 |
| 61% Siderite | 40 ml 0.1 M | 62 | 40 ml 0.5 M | 192 |
| 18% Siderite, 48% Clays | 40 ml 0.1 M | 64 | 40 ml 0.5 M | 234 |
| 20% Siderite, 11% Calcite | 40 ml 0.5 M | 367 | 80 ml 0.5 M | 440 |
| 90% Calcite | 80 ml 0.5 M | 926 | 60 ml 1.0 M | 919 |
| 83% Calcite | 80 ml 0.5 M | 835 | 60 ml 1.0 M | 842 |

**Table 4.** Carbonate rating based on percent insoluble residue with corresponding acid volumes and acid strengths.

| **Carbonate Rating** | **Percent Insoluble Residue** | **Amount of Acid** | **Strength of Acid** |
|---|---|---|---|
| | **(%)** | **(ml)** | **(M)** |
| 0 | 95 - 100 | 20 | 0.1 |
| 1 | 90 - 94 | 40 | 0.1 |
| 2 | 75 - 89 | 40 | 0.5 |
| 3 | < 75 | 80 | 0.5 |

Calculations:

1. ml of acid consumed = (ml acid added) - (ml base added);
2. tons $CaCO_3$ equivalent/thousand tons of material = (ml of acid consumed) x (25.0) x (M of acid).

## Interpretation of Overburden Quality by Acid-Base Accounting

ABA assesses the total amount of acidity or alkalinity that is contained in a specific rock unit. The assessment is based on the total S content and the carbonate content of the rock. The aim of ABA is to determine how much material is needed to neutralize all of the acid that could potentially form in coal overburden when pyrite is present. The use of total S provides a margin of neutralization safety against S percentages that may not all be pyritic and for pyritic S that may not all react.

Three basic assumptions should be understood when using ABA for overburden prediction (Perry, 1985). First, the values for MPA and NP represent maximum or ultimate quantities from pulverized, whole rock analysis. Complete reaction of all pyrite and bases probably does not occur in a mine backfill, thereby reducing the total amount of acidity or alkalinity produced in the ABA procedure. Second, S exists in three chemical forms in coal bearing rocks: sulfide, sulfate and organic, with sulfide S (pyrite) being the predominant acid producer. Third, pyrite may oxidize faster or slower than the dissolution of carbonate materials. Conventional ABA does not determine reaction rates of pyrite and carbonates, though the new EGA method can apparently indicate the reactivity of the pyrite.

If the strata are adequately sampled, overburden analysis, and in particular, ABA, works well in most overburden. However, an overburden analysis located between analytical results clearly associated with alkaline discharges and those that are clearly associated with acidic discharges is said to fall within a *gray zone*. The uncertainty is caused by variability in rock strata and the ability to adequately represent those strata with a limited volume of sample material, as well as sources of error in the analytical procedures.

Skousen et al. (1987) suggested that overburden with NNP values less than 5 metric tons per 1000 metric tons produce acid, while values greater than 20 metric tons per 1000 metric tons produce alkaline drainage. However, that was based on soil science and plant growth requirements. Today, the consensus view, based on field validation studies, is summarized in Table 5. As the ABA modifications recommended in this text are applied in the field, it is anticipated that the accuracy of predictions should improve. These values should therefore be re-assessed once the modified test procedures have been adopted. It is anticipated that the elimination of the siderite problem and the elimination of subjectivity in the fizz test should reduce the size of the undecided gray zone, and lower the break points for the generation of an alkaline discharge.

**Table 5**. A generally accepted guideline for defining strata as either acid-generating or alkaline.

| | Acid Tons / 1000 Tons | Undecided Tons / 1000 Tons | Alkaline Tons / 1000 Tons |
|---|---|---|---|
| NP | < 10 | 10 - 21 | >21 |
| NNP | < 0 | 0 - 12 | >12 |

A common error when using ABA as a predictive method occurs when the Max Needed and Excess columns are summed together for the entire overburden above the coal bed (the Max Needed column representing a negative number and the Excess column representing a positive number). Summing the ABA values for an overburden column falsely assumes thorough mixing of all overburden in a backfill, uniform rates of weathering of all materials, and water contact throughout the backfill.

## Acid-Base Accounting by Down-Hole Prompt Gamma Ray Spectroscopy Wireline Logging

The U.S. Geological Survey, in cooperation with the West Virginia Geological and Economic Survey, Schlumberger HydroGeological Technologies and West Virginia University, are attempting to apply oil and gas industry well logging technology to the chemical characterization of coal-bearing strata. The methodology is based on chemical analyses of boreholes using prompt neutron gamma ray spectroscopy wireline logging, hereafter referred to as geochemical logging (GCL). Traditional methods generally involve coring, core sampling, and chemical analysis of selected core samples. In contrast, GCL consists of wireline logging of a drill hole. The logging provides continuous chemical analyses, top to bottom, of a 6.5 inch drill hole, thereby eliminating sampling bias and error as well as other analytical error associated with sample preparation and analyses of a core. The GCL tool also interrogates a formation volume that is much larger than that analyzed by core. The data generated should be directly applicable to the chemical characterization of coal-bearing strata and the ABA of overburden.

In order to compare results from GCL with conventional analytical methods, two study sites were selected in an area known to have a variety of rock types and chemistries and histories of acid mine drainage, near the eastern edge of the bituminous coal field. The total suite of one-foot increment core samples was analyzed for total sulfur using a commercial analyzer. Calcium carbonate as calcite plus dolomite was determined by XRD, while calcium calculated as CaO was determined by XRF. MPA and NP were determined by standard wet chemical methods. The GCL analyses consist of continuous weight percent Si, Ca, Fe, Ti, K, and S determinations, for the entire length of the two test holes.

The preliminary data indicate that GCL can provide a level of accuracy equivalent to chemical analyses of one-foot increment samples of core, and can be used for chemical characterization of coal-bearing strata and ABA of overburden. The logging has the advantage of providing accurate data at the well site in a matter of minutes for an individual drill hole or any number of holes. If further testing demonstrates that wireline logging is as accurate as conventional chemical methods of overburden characterization, then GCL of air rotary holes may eliminate the need for coring. The objectives of accuracy and rapid analysis appear to be met by GCL; now the industry will have to address the issue of cost effectiveness.

## Evolved Gas Analysis

Evolved Gas Analysis (EGA) also deserves mention as it has the potential to fill a gap between static and kinetic tests since it is a static test that provides some information that can be used to factor in reaction kinetics. EGA is a direct, one-step procedure that has been used for quantitatively evaluating the acid-producing and acid-neutralizing minerals in coal overburden samples. Hammack (1987) applied EGA to coal overburden analysis using a quadrapole mass spectrometer to detect carbon dioxide and sulfur dioxide evolution as samples were subjected to increasing temperatures.

A variant of the EGA procedure, a method termed controlled-atmosphere programmed-temperature oxidation (CAPTO) (LaCount et al., 1983), has recently been applied to the analysis of coal overburden samples. The method employs a primary and secondary tube furnace design, slow linear temperature ramp and plug flow of an oxidizing or anoxic atmosphere through a sample diluted with an inert solid. Oxide gases evolved are measured with respect to temperature using a fast fourier transform infrared spectrometer (FTIR). Transition metal carbonates (siderite and rhodochrosite) decompose to yield carbon dioxide under the above conditions at 300 to 600°C, depending on the oxygen concentration applied to the samples. At low oxygen concentrations, transition metal carbonates decompose at lower temperatures than the corresponding carbonates analyzed using higher oxygen concentrations. Alkaline earth metal carbonates (calcite and dolomite) evolve carbon dioxide at higher temperatures (600 to 830°C). The alkaline earth metal carbonates do not show the same oxygen concentration decomposition dependence exhibited by the transition metal carbonates.

Pyrite and marcasite oxidize under these same conditions, to yield sulfur dioxide, at temperatures ranging from 350 to 560°C. Marcasite and more reactive morphologies of pyrite oxidize in the range of 350 to 440°C, while more stable forms oxidize at temperatures from 450 to 550°C.

Using one analysis procedure, it is thus possible to determine the amount of acid-neutralizing carbonate (calcite and dolomite) present, to determine the amount of siderite, and to distinguish acid-producing minerals such as pyrite and marcasite from other sulfur forms that do not generate acidity, for example, calcium sulfate.

Recent work using mine overburden core samples has shown that the decomposition of alkaline earth metal and transition metal carbonates can be resolved to quantify the amount of each of the carbonate forms present. The acid-producing minerals are quantitatively determined from the same analysis. Additionally, this technique can predict the reactivity of pyrite morphologies under weathering conditions, since pyrites that weather more readily tend to oxidize at lower temperatures than pyrites that are more resistant to weathering. Otherwise this information can only be obtained using simulated weathering (kinetic) tests. Further work to compare these results with conventional and kinetic tests is planned.

Examples of two profiles are shown. The first example shows the oxidation of pyrite and the decomposition of sulfate from an overburden sample. The sulfur dioxide evolution at 412°C is produced from the oxidation of pyrite; 800 to 1000°C is the temperature range where various calcium sulfate morphologies decompose. The second profile shows the carbon dioxide evolution for a mine overburden sample. The evolution centered at 529°C is produced from the decomposition of transition metal carbonates and that at 751°C is derived from alkaline earth metal carbonates. With all of the variables analyzed, one can calculate an ABA that is based only on the active constituents.

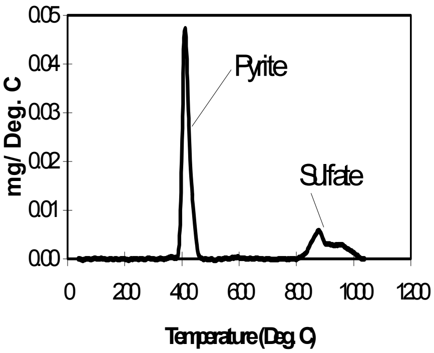
Figure 1: Sulfur Dioxide Evolution Profile for Overburden Sample

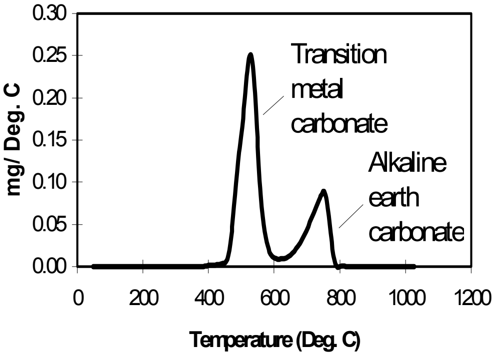
Figure 2: Carbon Dioxide Evolution Profile for Overburden Sample

Currently, the estimated costs to perform an ABA analysis using CAPTO is about twice that of conventional ABA methods so, at this time, the method would be best reserved for problematic sites where conventional ABA methods cannot definitively predict water quality. However, this method is significantly less expensive than the more time-consuming simulated weathering tests and may prove to be an effective alternative to those methods.

## Kinetic Tests

Kinetic tests are most appropriately used when the results of static tests falls between the regions defined (by practice) as acid or alkaline. The most commonly used kinetic tests for mine drainage prediction involve either leaching columns or humidity cells. These tests have been used, evaluated, and compared in many coal mine drainage prediction studies, but are in fact only occasionally used by the mining industry and state regulatory agencies in the Appalachian Coal Basin. Other kinetic test methods, such as the Soxhlet reactor, have also been used in prediction efforts, but even less frequently than humidity cells and leaching columns. Kinetic test methods are more routinely used by the metal mining industry and regulatory agencies in the western U.S. and Canada. Barriers to their use in the eastern United States include their expense and the time (months) needed to obtain results, as well as the fact that they have not had the widespread field validation that ABA has had.

Kinetic tests incorporate dynamic elements of the physical, chemical, and biological processes involved in the weathering of mine rock, and attempt to simulate the kinetics of the chemical reactions that control the production of acidic or alkaline mine drainage. If the critical physical, chemical and biological conditions are proportionally representative of the natural environment, the water quality of the leachate can be used to predict or estimate the water quality from the proposed mine site. Unfortunately, kinetic test procedures are necessarily simplifications of the natural environment, and it is easy to be fooled by laboratory procedures that underestimate or overestimate some component of the real world. In addition, the validity of kinetic tests, like static tests, depends on how well the samples represent the site. It is important to remember these two caveats, and that despite apparently precise laboratory analyses, test results may not accurately predict mine drainage quality.

Few field calibration studies and screening criteria for kinetic tests are published. This stems from the application of kinetic tests on a case by case basis, rather than on a broad scale. The data are presented in a manner similar to the column leaching tests shown in Figure 3, or alternatively, plotted on a daily, rather than a cumulative basis. Figure 3 shows an example of a plot of net cumulative acidity (as mg of acidity/g of sample) in which two of the samples were alkaline and one exhibited low acidity. While Net Acidity is presented in Figure 3, other parameters, such as sulfate and metals, can also be presented in a similar manner. Either daily or cumulative data can be plotted and the interpretation is related to the differing slopes of the lines. With cumulative data, the chemical weathering attributes are usually defined by one of three trends. Figure 3 is an example of relatively straight slopes indicating that the acid and alkaline production potentials vary little with time and that few weathering products had accumulated in the sample prior to leaching. This is common for all alkaline samples.

A second common trend is a steep acid slope for 3 to 6 weeks and then a gently increasing slope for the remainder of the test. This suggests that acidic weathering products had accumulated during the sample collection and processing stage and that the second slope is more indicative of the expected field conditions. In some cases, depending on the nature of the rock, the decreasing slope could indicate a decline in the rate of acid production. However, a very steep slope also indicates that this particular sample will weather quickly when exposed during the mining operation. This may be related to the physical attributes of the sample and suggests that reclamation efforts must deal quickly with this rock type.

The third major trend, which is seen in acid samples, is the inverse of the second trend. The sample may exhibit low acidity or sulfate values initially and after several weeks, begin to produce significant acidity. These samples are normally high acid producers. The slower initiation of acidity could be due to a number of factors such as carbonate suppression and carbonate neutralization. It may also indicate rock types that initially exhibit no problem, but begin to produce acidity if reclamation is delayed for any reason.

Because the data are calculated on a weight per weight per time basis, samples can be compared and evaluated. Furthermore, the slopes of the lines can be statistically evaluated to compare multiple samples and rock types.

## CONCLUSION

The full report will be made available to anyone who is interested; details on how to get a copy will be provided at the conference. It provides information on numerous methods to predict post-reclamation water quality. The various advantages, disadvantages and assumptions of the principal methods are discussed; these must be understood by anyone selecting or interpreting the results from these techniques. This array of prediction methods is analogous to a collection of tools in a toolbox. The choice of which tool to use is ideally a function of site-specific circumstances, but in the past, the decision has often been dictated more by familiarity with the test and the ability of practitioners to extrapolate the test results to mine scale decisions. In the context of compliance and enforcement, when the only tool in your toolbox is a hammer, everything begins to look like a nail. It is the hope of the ADTI participants that, with sufficient information, practitioners will feel comfortable using tools that are more appropriate, rather than

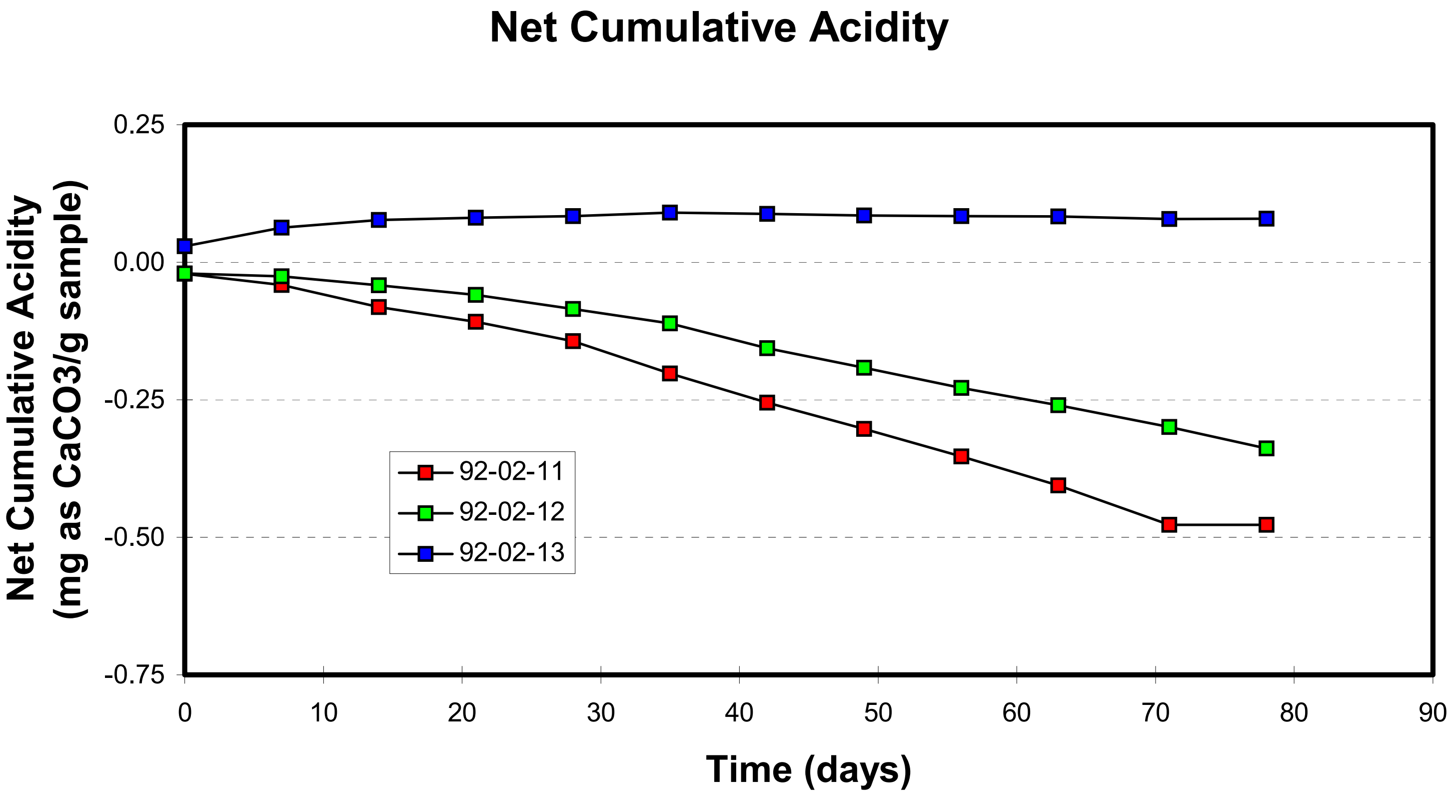

**Figure 3**. Net cumulative acidity data from leaching tests for three overburden samples.

just familiar. Regulatory agencies and the mining industry should both consider and promote the proper use of all mine drainage prediction tools, and become comfortable using them in concert to optimize the odds of accurately predicting the effects of mining a given site in a particular manner.

Finally, it should be emphasized that regardless of whether one is preparing or reviewing a permit, the unique character and condition of each mine site precludes a simple cookbook approach. If site characterization is adequate, it is generally possible to predict post-mining water quality. This evaluation should then be factored into a consideration of whether this predicted water quality is likely to have unacceptable effects on local water quality, and if so, whether anything can be done during mining and reclamation to allow it to proceed without such adverse effects.

## REFERENCES

Brady, K., E. Perry, R. Beam, D Bisko, M. Gardner, and J. Tarantino, 1994. Evaluation of acid-base accounting to predict the quality of drainage at surface coal mines in Pennsylvania, USA. p. 138-147. In: International Land Reclamation and Mine Drainage Conf., Vol 1. USBM SP-06A-94. Pittsburgh, PA.

Cargeid, 1981. An evaluation of the proposed Holly Grove mine to impact the Little Kanawha River with acid water. Unpublished report to U.S. EPA, Columbia, SC.

Cravotta, C.A., 1991. Geochemical evaluation of acidic groundwater at a reclaimed surface coal mine in western Pennsylvania. p. 43-68. In: Proc., Meeting of the American Society of Surface Mining and Reclamation, Vol 1. Durango, CO.

Doolittle, J.J., N. Frisbee, and L.R. Hossner, 1992. Evaluation of acid-base accounting techniques used in surface-mine reclamation. p. 68-76. In: Proc., Meeting of the American Society of Surface Mining and Reclamation. Duluth, MN.

Frisbee, N.M. and L.R. Hossner, 1989. Weathering of siderite from lignite overburden. In: Proc., Meeting of the American Soc. for Surface Mining and Reclamation. Calgary, CN.

Hammack, R.W., 1987. Evolved gas analysis - A new method for determining pyrite, bicarbonate, and alkaline earth carbonates. In: Proc., 8th WV Surface Mine Drainage Task Force Symp., April 7-8, 1987, Morgantown, WV.

Hawkins, J.W., K.B.C. Brady, S. Barnes, and A.W. Rose, 1996. Shallow ground water flow in unmined regions of the northern Appalachian Plateau: Part 1. Physical characteristics. In: Annual Meeting of the American Society for Surface Mining and Reclamation, Knoxville, TN, May 18-23, 1996, p. 42-51.

Kleinmann, R.L.P. (Ed.), 2001. Mine Water Quality Prediction at Surface Coal Mines, WVU, Morgantown, WV.

LaCount, R.B., R.P. Anderson, C.A. Helms, S. Friedman, and W.B.Romine, 1983. Construction and Operation of a Controlled-Atmosphere Programmed-Temperature Reaction Apparatus, DOE/PETC/TR-8315, April, 1983, 115 pages.

Leavitt, B., J. Skousen, and P. Ziemkiewicz, 1995. Effects of siderite on the neutralization potential in the acid-base account. In: Proc., WV Surface Mine Drainage Task Force Symp., Morgantown, WV.

Meek, F.A., 1981. Development of a procedure to accurately account for the presence of siderite during mining overburden analysis. In: Proc., WV Surface Mine Drainage Task Force Symp. Morgantown, WV.

Morrison, J.L., S.D. Atkinson, A. Davis, and B.E. Sheetz, 1990. The use of $CO_2$ coulimetry in differentiating and quantifying the carbonate phases in coal-bearing strata of western Pennsylvania: its applicability in interpreting and modifying neutralization potential (NP) measurements. p. 243-247. In: Proc., Mining and Reclamation Conf., WVU, Morgantown, WV.

Perry, E., 1985. Overburden analysis: an evaluation of methods. p. 365-375. In: Proc., Symp.on Surface Mining, Hydrology, Sedimentology, and Reclamation. U.KY, Lexington, KY.

Shelton, P.A., J.T. Ammons, and J.R. Freeman, 1984. NPs: a closer look. Green Lands 13(4):35-37.

Singh, R.N. W.E. Grube, Jr., R.M. Smith, and R.F. Keefer, 1982. Relation of pyritic sandstone weathering to soil and minesoil properties, In: Acid Sulfate Weathering. Soil Science Society of America, p. 193-208.

Skousen, J.G., J. Renton, H. Brown, P. Evans, B. Leavitt, K. Brady, L. Cohen, and P. Ziemkiewicz, 1997. Neutralization potential of overburden samples containing siderite. J. Environ. Qual. 26(3): 673-681.

Skousen, J.G., J.C. Sencindiver, and R.M. Smith, 1987. A review of procedures for surface mining and reclamation in areas with acid-producing materials. WVU Energy and Water Research Center, Publication No. EWRC 871, Morgantown, WV.

Sobek, A.A., W.A. Schuller, J.R. Freeman, and R.M. Smith, 1978. Field and laboratory methods applicable to overburdens and minesoils. U.S. EPA 600/2-78-054. Washington, DC.

Wiram, V.P., 1992. Siderite masking: a factor to consider in overburden acid-base balancing. In: Proc., WV Surface Mine Drainage Task Force Symp. Morgantown, WV.