

IMPROVING THE ACID-BASE ACCOUNT BY USE OF PROGRAMMED-TEMPERATURE OXIDATION AND EVOLVED GAS ANALYSIS

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Abstract – The acid-base account is the most commonly used method for assessing post-mining water quality. Yet, the acid-base account has recognized analytical deficiencies including: (1) the use of total sulfur to calculate potential acidity when only pyritic sulfur is a significant contributor, (2) when pyritic sulfur is used for calculating potential acidity, an ASTM method is specified that does not recover all pyritic sulfur, (3) the determination of neutralization potential depends on results from a subjective fizz test, and (4) the presence of siderite gives an erroneously high neutralization potential. This paper describes a new method for coal overburden analysis that corrects the analytical deficiencies of the acid-base account.

Thermal methodology has been developed that will selectively decompose alkaline earth and transition metal carbonates to provide well-resolved carbon dioxide evolutions for each species. Sulfur forms present in the sample mixture are selectively oxidized to sulfur dioxide and determined from the same analysis. The thermal conditions were developed using a controlled-atmosphere, programmed-temperature oxidation (CAPTO) system where temperature ramp, gas flow, gas composition, and pressure are all under computer control and evolved gases are analyzed using Fourier Transform Infrared (FTIR). The carbon/sulfur dioxide evolution temperatures have been related to the carbon/sulfur forms in the sample producing the evolved gases.

Thermal treatment conditions that produce well-resolved carbon dioxide/sulfur dioxide evolutions were established for a series of individual alkaline earth and transition metal carbonates, synthetic mixtures of these carbonates with pyrite, and finally numerous overburden samples. This thermal procedure provides an alternative method that may be of use in determining NP in mine overburden samples which contain both alkaline earth and transition metal carbonates.

Key Words – evolved gas analysis, acid-base account, coal overburden analysis, acid mine drainage, acid potential, neutralization potential.

INTRODUCTION

Acid-Base Accounting (ABA)¹ was originally developed to estimate the total amount of acidity/alkalinity produced from the weathering of mine overburden as a basis for planning revegetation. ABA test results of mine overburden, now used to predict post-mining water quality, are reviewed along with other factors before surface mining permits are issued. If the ABA acid potential (AP) is based on total sulfur content of the overburden, the method may overestimate the AP since all sulfur forms present in the overburden may not contribute to acidity. The neutralization potential (NP) is used to determine the carbonate contribution to alkalinity. If carbonates present in a mine environment are less soluble than under test conditions, the NP may be over estimated. Alkaline earth carbonates such as calcite/dolomite contribute to the NP. Transition metal carbonates such as siderite/rhodochrosite, if present, provide an apparent contribution to the NP of the overburden. However, these minerals are a potential source of error in determining NP since Fe^{2+} is oxidized to Fe^{3+} , and Fe^{3+} hydrolysis consumes alkalinity, which eliminates any overall siderite contribution to NP. Incomplete oxidation of Fe^{2+} during some of the test procedures used to determine alkalinity results in over estimation of NP. Several modifications of the original NP test method have appeared in the literature and these methods were recently compared by Skousen et. al.². They concluded that the NP values of siderite containing overburden samples varied significantly with the digestion method and, that the H_2O_2 method more accurately reflected NP content compared to the Sobek method. They suggested that use of the H_2O_2 method might reduce the erroneously high NP values observed for siderite containing overburden samples.

As an alternative approach to potentially improve conventional methods of predicting acid mine drainage potential, Hammack³ applied an evolved gas analysis technique to pyrite and reagent grade sodium bicarbonate, manganous carbonate, and calcium carbonate. He established that pyritic sulfur could be readily distinguished from other sulfur forms that do not contribute to potential acidity. However, overlapping carbon dioxide evolutions from manganous carbonate and calcium carbonate prevented use of a direct quantitative measurement to distinguish between the NP of alkaline earth and transition metal carbonates.

MATERIALS AND METHODS

Carbonate Samples

Mineralogical samples of siderite, calcite, and dolomite were obtained from USDOE National Energy Technology Laboratory - Pittsburgh, or purchased from Ward's (Ward's Natural Science Establishment Inc., Rochester NY). The carbonate samples were manually reduced to an intermediate size and then pulverized using a Spex 8000 Mixer/Mill (Spex Industries, Metuchen, NJ) with a hardened steel vial and steel balls. Each sample was pulverized to pass a 150- μm (100 mesh) screen.

Mine Overburden Samples

Mine overburden samples were analyzed as received. Each sample had been pulverized to -60 mesh prior to delivery. No additional sample preparation was required.

CAPTO Analysis - Carbonate Samples

Samples were analyzed using a multiple-sample, CAPTO thermal system (ViRoLac Industries, Waynesburg, PA). Carbonate samples were homogenized with a Spex 8000 Mixer/Mill for 10

minutes (utilizing a figure 8 mixing motion), and a 25-mg representative sample was removed for analysis. The sample was mixed with 6g of sand (washed with 0.1N HCl, 3 washes with distilled H₂O, and heat treated to 1000 °C for 1 hour), and positioned in a quartz combustion tube. The packing of the sample was accomplished by immobilizing the sample with quartz wool plugs (Leco Corp. St. Joseph, MI). Solid quartz rods were used to fill voids in the quartz tube.

The quartz tube was then installed into the CAPTO furnace and a slow linear temperature ramp applied (3-6 °C min⁻¹) from room temperature through 1050 °C while a plug flow of an oxidizing or anoxic atmosphere (100 cm³ min⁻¹) was passed through the sample. Evolving gases were swept from the furnace/combustion zone into Fourier Transform Infrared (FTIR) gas cells. Each of the four different sample streams used a separate gas analysis cell, with an FTIR cell positioning system⁴. The FTIR was used to analyze for CO₂, SO₂, H₂O and other IR-active gases. The resultant gas evolution profiles were collected and total carbon, sulfur and hydrogen were determined from the respective profiles.

Profiles from the FTIR data show a plot of mg carbon/ °C vs. Temperature (°C). Integration of the total profile provides total mg of carbon. The areas under the evolution peaks are integrated to yield the mg of carbon for each type of carbonate.

CAPTO Analysis - Overburden Samples

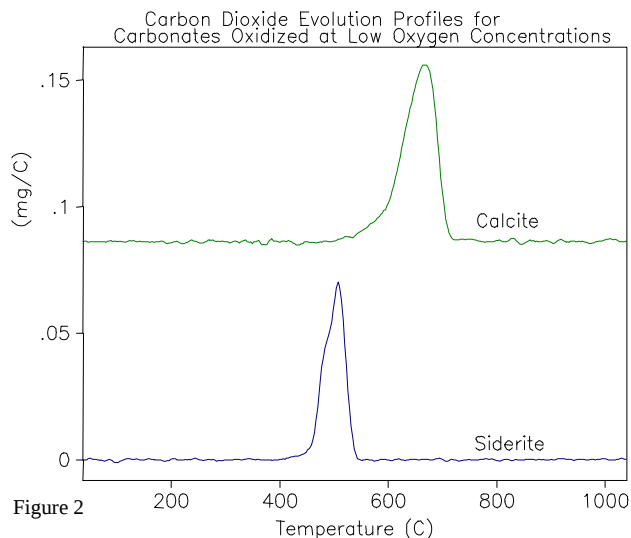
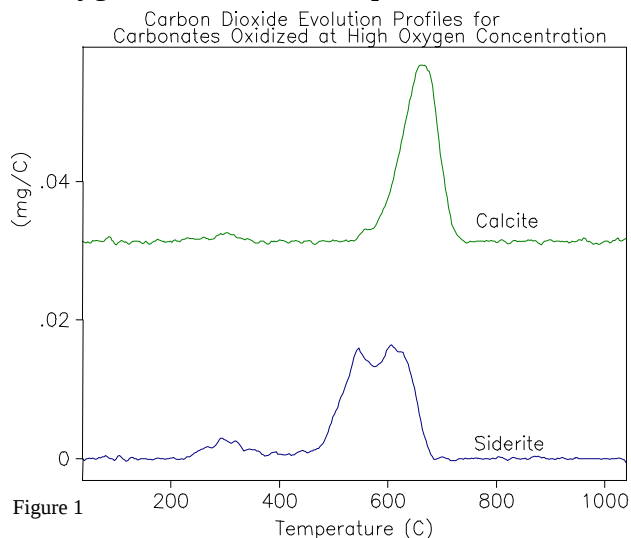
The same analysis method was used for both overburden and carbonate samples, except that much larger overburden samples (500mg) were used.

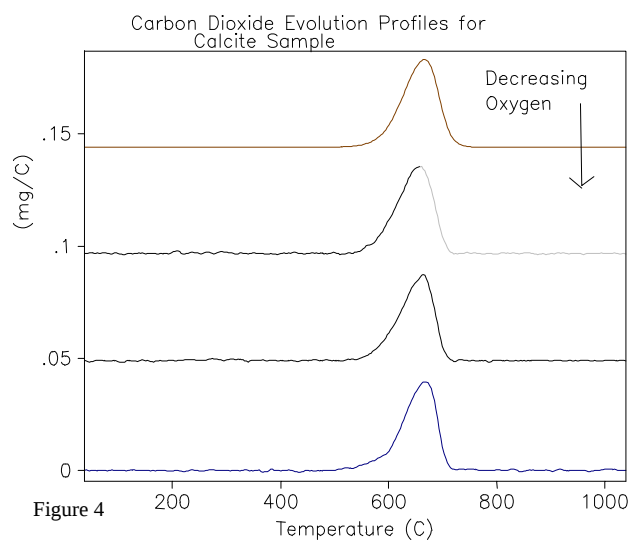
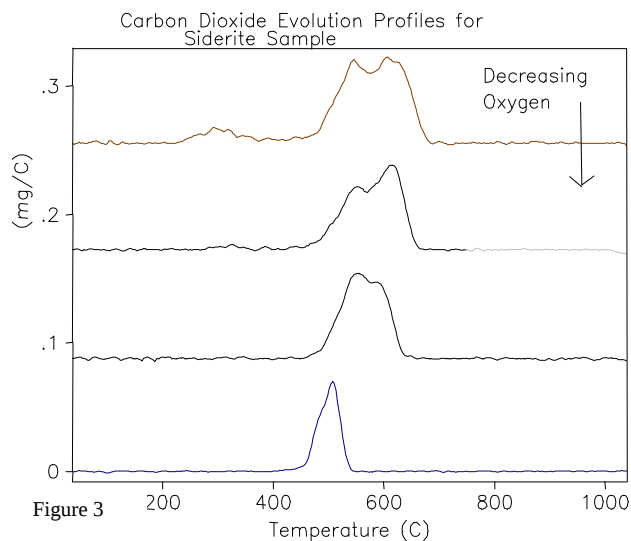
RESULTS AND DISCUSSION

Carbonate Samples - Siderite

Selective analysis of calcite and siderite requires non-overlapping carbon dioxide evolutions for each carbonate. In figure 1, profiles of calcite and siderite (analyzed using high O₂ concentration) are shown. The high temperature siderite peak (temperature maximum at 610 °C) has considerable overlap with the calcite evolution.

At lower oxygen concentration, carbon dioxide evolution from siderite decomposition occurs at a lower temperature. The greater temperature separation between the evolution maxima at lower oxygen concentration simplifies identification and permits a direct measurement of each carbonate

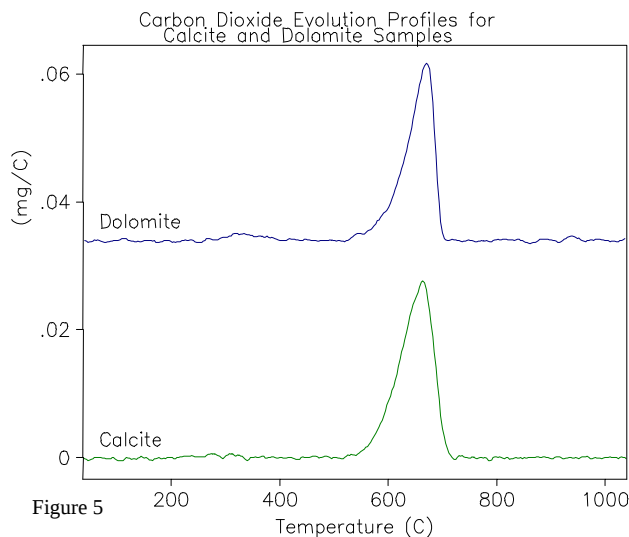




type. The peak-to-peak separation in figure 2 is 159°C (508°C for siderite and 667°C for calcite).

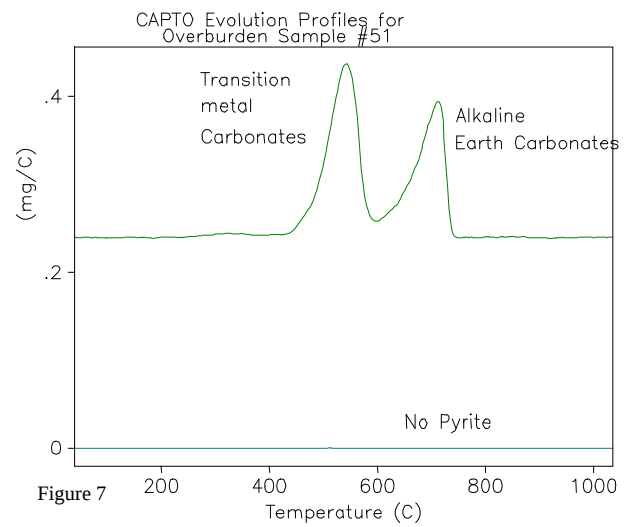
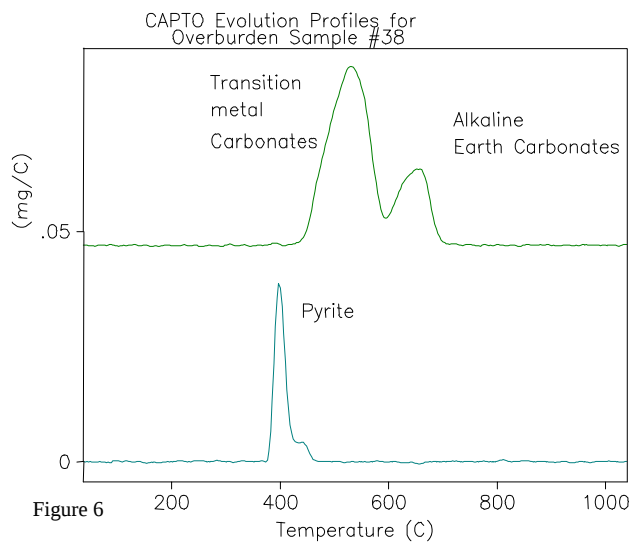
A comparison of the siderite and calcite evolution profiles shows that the decrease in oxygen concentration caused siderite to react at lower temperatures, while the calcite profiles were independent of oxygen concentration. Figure 3 shows the change in the siderite profile with change in oxygen concentration. Figure 4 illustrates the corresponding calcite profiles.

Note that at high oxygen concentrations, siderite has three distinct evolution peaks. By decreasing the oxygen concentration, the individual peaks begin to evolve CO₂ over a more narrow temperature region. More specifically, the high temperature peak appears to evolve at a lower temperature while the center peak appears to remain in the same temperature region.



Carbonate Samples - Dolomite and Calcite

CAPTO analysis of calcite and dolomite show that these two carbonates evolve carbon dioxide in the same region, and are simply reported as alkaline earth carbonates. Figure 5 shows a



comparison of dolomite and calcite. The carbon dioxide evolution peak maximum from dolomite is at 673 °C, and that from calcite is at 667 °C.

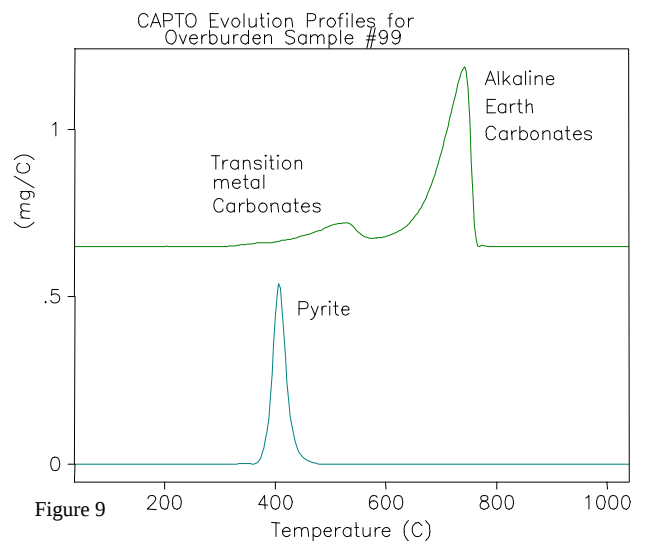
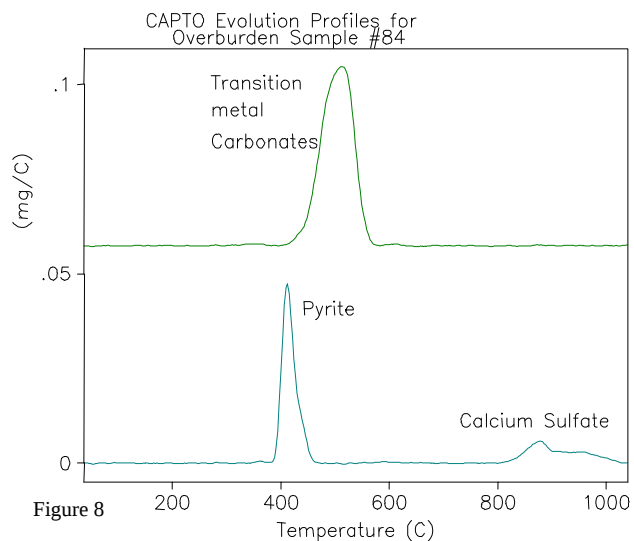
Overburden Samples

Mine overburden samples were supplied by USDOE - NETL and analyzed for total carbon, %C from siderite (transition metal carbonates), %C from dolomite/calcite (alkaline earth carbonates), total sulfur, %S from pyrite and %S from sulfates.

Four representative samples were selected to illustrate the overburden samples analyzed. The %C and %S for the four samples are shown in Table 1. Sample #38 (figure 6) shows the presence of pyrite and both alkaline earth and transition metal carbonates.

Table 1: %C and %S for Selected Overburden Samples

Sample	Alkaline Earth Carbonate (%C)	Transition Metal Carbonate (%C)	Pyritic Sulfur (%S)	Sulfate Sulfur (%S)
#38	0.57	1.73	0.21	0.0
#51	2.08	2.85	0.0	0.0
#84	0.0	2.98	0.29	0.11
#99	6.24	1.46	3.27	0.0



The two carbonate CO₂ evolution peaks in figure 6 are separated by 123 °C. An SO₂ evolution from pyrite is seen in #38 at a temperature maximum of 406 °C, which is a typical oxidation temperature for pyrite present in coal overburden samples.

Contrast sample #51 shown in figure 7 to sample #38. A greater separation of the CO₂ evolution peaks from carbonates (219 °C difference) is seen in sample #51 and no pyrite is detected. The CO₂ evolution from alkaline earth carbonate in #51 shows some of the same evolution characteristics as that from the calcite samples discussed above.

Sample #8 (figure 8) illustrates an example where the acid potential would be over-estimated from a total sulfur analysis. Nearly 1/3 of the total sulfur in the sample is calcium sulfate (SO₂ evolution peak centered at 920 °C), a sulfur form that will not contribute to the acid potential.

In addition, the amount of alkaline earth carbonates in this sample was below the detection limits of CAPTO. None of the carbonate minerals present in this sample will contribute to the actual neutralization potential. However, a conventional acid-base account for this material would erroneously indicate some neutralization potential.

The example illustrated in figure 9, overburden #99, shows a sample with little transition metal carbonate. Most of the carbonate minerals in this sample are alkaline earth carbonates that do contribute to the neutralization potential.

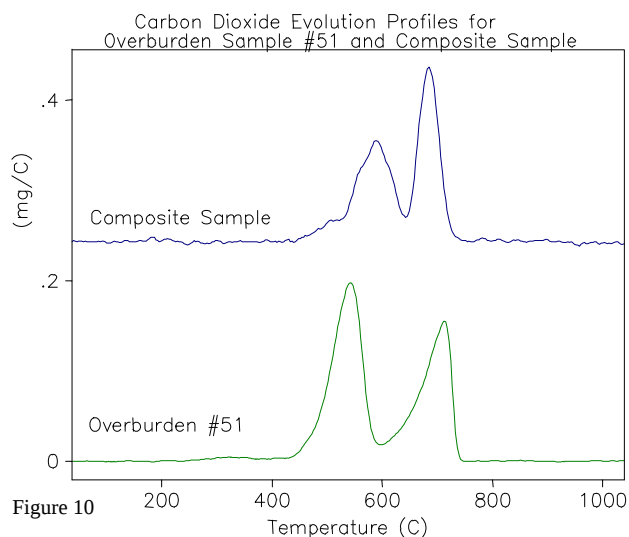
Overburden and Carbonate Samples

If overburden samples and mineralogical carbonate samples are analyzed under the same conditions, the overburden samples, in general, show greater separation between the CO₂ evolution maxima of alkaline earth and transition metal carbonates. To illustrate this point, a synthetic composite sample consisting of equal parts of siderite and calcite, with pyrite and iron sulfate, quartz, illite and kaolinite added was prepared and analyzed. The composite profile is compared in figure 10 with overburden sample #51.

The synthetic composite sample exhibits a separation of 96°C between the high-temperature siderite CO₂ evolution peak (589°C) and that from calcite (685°C) while the separation between the two peaks in overburden sample #51 is 168°C. The overburden samples, in general, show similar or greater separation of the alkaline earth and transition metal carbonate CO₂ evolutions. A

matrix effect in the overburden samples serves to improve the analysis profiles. The overburden samples contain additional components, including quartz, kaolinite, illite, and other materials. The interaction of the carbonates with this native matrix may cause the transition metal carbonates to react at lower temperatures under CAPTO conditions.

CONCLUSIONS



Utilization of very low oxygen concentrations permits a good separation of alkaline earth and transition metal carbonate evolution patterns. The separation of siderite CO_2 evolutions from those of calcite/dolomite evolutions enables a simple and direct determination of the two general types of carbonates present. The siderite (or transition metal carbonate) reacts at a lower temperature, while the calcite/dolomite (alkaline earth carbonates) reacts at the higher temperature range.

A comparison of mineralogical carbonates with the overburden samples shows a greater peak separation of the CO_2 evolutions for the overburden samples than the corresponding mineralogical carbonates. This is due to a matrix effect found in the overburden samples that is lacking in the mineralogical carbonate samples.

Analysis of overburden samples using CAPTO will result in: total carbon, %C from non-neutralizing carbonates (transitional metal carbonates) %C from neutralizing carbonates (alkaline earth carbonates) total S, %S from acid-generating pyrite %S from ferrous sulfates that can hydrolyze to produce acid and %S from calcium sulfate, which does not generate acidity.

RECOMMENDATIONS

Overburden analysis using evolved gas analysis is expected to cost about \$100 per sample, or about twice the per sample cost of the acid-base account. Continued refinements of the technique will probably decrease analysis cost somewhat, but not enough to compete with the acid-base account for most samples. However, the niche for evolved gas analysis is the analysis of problematic samples that will benefit from the increased and more accurate information that this technique offers. Also, from the standpoint of quality assurance, a duplicate from one of every ten samples analyzed by acid-base account should also be submitted for evolved gas analysis. This practice will ensure that the acid-base account is accurately reflecting the actual acid-generating potential of coal overburden.

ACKNOWLEDGEMENTS

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