PREDICTION OF ACID DRAINAGE POTENTIAL IN ADVANCE OF MINING

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INTRODUCTION

Surface coal mine operators are required by law to identify the potential for acidic drainage prior to opening a new mine (9).[4] In many cases, particularly in the Appalachian region, the permit application must contain the results of overburden analyses intended to quantify the acidic or alkaline weathering products of the affected strata. These data serve two purposes: to provide the regulatory agency with a means to estimate the hydrologic consequences of the proposed mine, and to allow the proposed operator to plan the mine with regard for probable water treatment requirements. Until the Bureau's current project, there has been no systematic field evaluation of these analytical techniques.

The acid-base account is the most commonly used overburden analysis technique (6). The method is based on measuring the total sulfur content of each lithologic unit and converting that value to an acid potential based on the stoichiometry of complete pyrite oxidation. Similarly, the neutralization potential is determined for each lithology by its ability to neutralize strong acid. The two values, acid and alkaline potential, respectively, are represented as calcium carbonate equivalents for calculation of a net excess or deficiency of neutralizers. A deficiency greater than 5 tons $CaCO_3$ per 1,000 tons of rock is generally considered a potential source of acid mine drainage (11).

The acid-base account uses rapid and simple analytical techniques; it is, therefore, inexpensive. The results, however, indicate only the total acid and alkaline loads that could be produced if all the pyrite and carbonates reacted. The major flaw in interpreting these data for water quality is that reaction kinetics are ignored. Complete oxidation of pyrite may take decades. even if all the pyrite is reactive; acidity in solution is determined by the rate of oxidation and flushing.

In contrast, calcium carbonate dissolves rapidly to an equilibrium value of approximately 60 mg/L alkalinity at atmospheric CO_2 partial pressure (5). More carbonate mineral dissolves to achieve the same equilibrium concentration if acidity is present; higher concentrations can be dissolved at high carbon dioxide partial pressures (7). Because solution acidity and alkalinity are controlled largely by the kinetics and thermodynamics of many reactions, use of total mass balance data to predict water quality is suspect. The developers of the acid-base account technique did not intend it to predict drainage quality, but rather to identify strata that may produce acid.

Other overburden analytical mathods can be classified as simulated weathering techniques. These have in common that the strata, either individually or as a thickness-weighted composite, are subjected to oxidizing conditions to accelerate chemical weathering of the materials. Chemical composition of drainage obtained from periodically leaching the sample is classified as acidic or alkaline and is presumed to qualitatively predict the nature of postmining drainage at the proposed mine.

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[4]Underlined numbers in parentheses refer to items in the list of references at the end of this paper.

Oxidative processes can be accelerated by heat, addition of chemical oxidants, reduced particle size of the solid phase, inoculation with bacteria, and other means; innumerable protocols could be devised for weathering tests. Two methods that have been used for overburden analysis utilize crushed core samples subjected to humidified air streams; the techniques differ in that one utilizes individual weathering tests for each lithology (2) and the other utilizes a composite sample assembled according to the backfilling plan (8).

Weathering tests may provide a realistic estimate of postmining drainage quality if they duplicate the kinetics of relevant reactions under field conditions. These tests require longer periods of time, from several weeks to months, and are more expensive to use than the acid-base account technique. The accuracy of any simulated weathering technique must be verified to determine its predictive capability.

Prediction of acid drainage potential from overburden analyses and other premining data relies on interpretation by mine operators, consultants, and regulatory personnel. The data merely indicate the maximum acid and alkaline loads (acid-base account) or drainage quality under a given set of conditions (weathering tests). Effects of mining-related factors such as mining method, use of selective handling, and ameliorant applications are not considered in overburden analysis. There is no consensus on a method to combine the lithologic data, mining plans, and reclamation plans into a predictive scheme.

The Bureau is currently conducting contract and in-house research to improve acid drainage prediction. The contract research consists of two phases: (1) field evaluation of three overburden analytical techniques at 30 mine sites and (2) design of an empirical predictive scheme that encompasses overburden data and site-specific factors that could influence actual drainage quality. The in-house research is oriented toward developing an alternative overburden analysis method that takes into account pyrite reactivity. Both projects are discussed in following sections.

CONTRACT RESEARCH PROGRAM--PREMINING PREDICTION OF ACID DRAINAGE POTENTIAL

The Bureau awarded a research contract to Engineers International, Inc., in 1982 to improve the state of premining prediction. Phase 1, nearly complete now, addresses the validity of using available overburden analysis techniques to predict postmining drainage quality. Phase 2 will focus on the development of an empirical predictive scheme encompassing mining-related variables.

FIELD EVALUATION OF OVERBURDEN ANALYSIS

The objective of this phase of the research is to determine the utility of three overburden analysis techniques for predicting drainage quality after mining. To accomplish this goal within a reasonable time, the program plan called for the collection of actual postmining data and the equivalent of premining overburden data from 30 reclaimed mines. The validity of this phase depends mainly on obtaining overburden samples that represent the overburden in the reclaimed section. At nine sites, cores sampled less than 1 yr ago were available for analysis. At the remaining sites, channel samples from an active highwall adjacent to each reclaimed mine section (used as the postmining water data source) were collected for overburden analysis. This method was chosen for two reasons: (1) The cost was much lower than the cost of drilling cores on adjacent unmined land, and (2) visual observation could be checked against company records to verify continuity of the overburden lithology. Fresh material was exposed on the highwall before sampling.

Site-selection criteria were designed to ensure that the predictive capabilities of the overburden analysis methods would be evaluated. Historical records, provided by State regulatory agencies and the coal companies, were used to eliminate mine sites having significant net acid or alkaline potential. It was felt that any overburden analysis technique can adequately predict an acid or alkaline discharge when the carbonate or pyrite is totally absent, respectively; the target sites were those that are presently difficult to assess.

In some cases, disagreement between overburden analysis results at the time of permitting and actual drainage quality was used to select a site; in other cases, professional judgment had to be used. Sites at which nonstandard practices might be the significant determinant in postmining drainage quality were avoided. These included backfills containing acid drainage treatment sludge, fly ash or preparation plant refuse, and sites treated with ameliorative chemicals other than agricultural limestone and fertilizer.

Samples were subjected to laboratory analyses. Acid-base accounting was used on the samples from all 30 sites; weathering tests published by Caruccio (2) and Sturey (8) were performed on samples from 16 and 5 sites, respectively. Cold alkalinity determinations were also made on Caruccio weathering test samples. Table 1 illustrates other types of information obtained from adjacent areas and available records added to the premining data set.

The most critical postmining data involved the quality of water issuing from the reclaimed mine section. To characterize the drainage, a field monitoring program was instituted at each site to measure the volume and quality of discharges at least eight times during a 1-yr period. Analyses are indicated in table 2. Where possible, data collected by the mine operator were also used.

TABLE 1. - Premining equivalent data collected to supplement overburden sampling and analysis

Information	Sources
Local geology, hydrology, and mining history.	Permit applications, State and Federal agencies.
Surface and ground water quality and quantity.	Current project, historical records.
Climatic data.	Government records, mining company records.

TABLE 2. - Analyses performed on premining and postmining water samples

Field measurements	Laboratory analyses
SUITE 1	
pH.................	Iron
Acidity, alkalinity.	Sulfate
Dissolved oxygen....	
Specific conductance	
Temperature.........	
SUITE 2	
pH.................	Iron
Acidity, alkalinity.	Sulfate
Dissolved oxygen....	Calcium
Specific conductance	Magnesium
Temperature.........	Manganese
SUITE 3	
pH.................	Iron
Acidity, alkalinity.	Sulfate
Dissolved oxygen....	Calcium
Specific conductance	Magnesium
Temperature.........	Manganese
	Aluminum

Table 3 summarizes ancillary postmining data, collected primarily for use in phase 2.

Phase 1 data collection is now complete, and statistical analysis is in progress. Table 4 summarizes the ranges of values for acid-base account parameters observed in samples from 30 sites. The most acidic thickness-weighted value for a single overburden column was a

TABLE 3. – Supplementary postmining data

Mining..... Maps.
Drilling logs.
Mining method and equipment.
Materials handling.

Reclamation Backfilling plans and maps.
Materials handling.
Equipment.
Chronological records.
Topsoil storage.
Soil amendments.
Vegetation.

TABLE 4. – Ranges of values of acid-base account parameters for individual lithologies

Parameter	Range
pH, paste..................	3.0 – 7.9
Sulfur, pct:	
Total..................	<.05– 8.3
Pyritic................	<.05– 7.2
Sulfate................	<.05– .73
Organic................	<.05– .31
Neutralization potential per 1,000 tons $CaCO_3$......	-2.7 -940

deficiency of 1,300 tons as calcium carbonate. At the other extreme was a West Virginia site having an excess alkalinity of 1,200 tons as calcium carbonate. Interestingly, one of several toe-of-spoil seeps at the latter site is acidic.

The Caruccio weathering test was performed on overburden samples from 16 sites, having acid-base account results indicating overall neutrality (6 sites), acidity (5 sites), or alkalinity (5 sites). Ranges of cumulative leachate quality for individual lithologies are shown in table 5.

The quality of surface runoff and spoil seepage are the dependent variables for statistical analysis in phase 1. Three sets of primary independent variables were derived from the three overburden analysis methods used in the study. Ancillary data (tables 1 and 3) will be used in this analysis only as needed to

TABLE 5. – Average leachate quality range for Caruccio weathering tests on individual lithologies

Parameter	Concentration range, mg/L
Acidity, as $CaCO_3$:	
Hot total...............	<1-53,000
Mineral.................	0-13,000
Alkalinity..............	<1- 380
Sulfate.................	<1-33,000

classify sites in the case of bimodal distributions. For example, sites may be classified by degree of vegetative cover, time since mining, or other factors. Significant correlations between dependent and independent variables will be identified by simple linear regression analysis, factor analysis, and multivariate regression analysis. The phase 1 research product will be a set of equations that relate observed drainage quality to overburden analysis data.

EMPIRICAL PREDICTIVE METHOD

Phase 2 of the contract research will focus on the design and testing of a method to predict postmining drainage quality. This phase of the research will make extensive use of the data developed during phase 1. Our working hypothesis is that the mining-related factors play a critical role in the observed drainage quality. Therefore, we expect that the phase 1 results will indicate moderate correlation coefficients between overburden analysis data and postmining drainage quality. The objective of phase 2, then, is to improve the prediction by including the nonnumerical (categorical) factors shown in tables 1 and 3.

The output of the research may come in different forms. For example, there may be a nonlinear equation in which nonnumeric factors have been assigned numerical rankings. Alternatively, the predictive method may be based on an n-dimensional decision surface, as in pattern recognition.

IN-HOUSE RESEARCH: PYRITE REACTIVITY ANALYSIS

BACKGROUND

Acid-base accounting methods depend upon sulfur analysis to accurately quantify the potential acidity of overburden materials. Potential acidity is generally considered to be a function of the total sulfur content, although only pyritic sulfur contributes significantly to acid production. Pyritic sulfur must be distinguished from non-acid-producing sulfur forms, in cases where (1) the material is weathered and much of the original pyritic sulfur has been oxidized to sulfate sulfur or (2) the material is carbonaceous and a significant proportion of the total sulfur is bonded to organic molecules.

Pyrite occurs as different forms or morphologies in coal and overburden materials. Many authors have provided petrographic descriptions of various pyrite morphologies; descriptions given by King (3) have been adopted for this study because they are usable and encompass all pyrite morphologies. According to King, pyrite occurs in five basic morphologies: (1) spherical aggregates of euhedral pyrite crystals (framboids), (2) isolated euhedral pyrite crystals, (3) nonspherical aggregates of euhedral pyrite crystals, (4) irregularly shaped massive pyrite, and (5) fracture-filling massive pyrite.

Differences in pyrite reactivity correlative to different pyrite morphologies were first noted by Caruccio (1). Caruccio indicated that framboidal pyrite was the most reactive pyrite form and related the percentage of framboidal pyrite to the acid-producing potential of selected samples. Most researchers agree that, in general, the smaller the grain of pyrite, the more reactive the pyrite and the greater the potential acidity.

The importance of reactive pyrite forms in the generation of acid mine drainage was generally dismissed when it was realized that these forms could not account for all of the acidity observed. However, the oxidation of reactive forms under ambient conditions may establish a chemical environment that favors bacterial catalysis and permits the less reactive pyrite to react. Research into this possible triggering mechanism may identify parameters that are inherently more accurate in predicting potential acidity than total sulfur or pyritic sulfur content alone. Quantification of reactive pyrite forms would not be able to predict total acidity but would allow for more accurate assessment of pyrite oxidation rates, and thus possibly distinguish "go" or "no go" acid generation situations. Initial Bureau research into pyrite reactivity was based on the hypothesis that different pyrite morphologies and grain sizes would thermally decompose and oxidize at different temperatures corresponding to the relative stability of each form; more reactive forms would be expected to react at lower temperatures because of lower activation energies.

Previous studies have used thermogravimetric (TG) and differential thermal analysis techniques (DTA) to investigate the thermal behavior of museum-grade pyrite and marcasite. Warne (10) used DTA thermograms to identify pyrite and marcasite in coal, carbonate, and clay matrices. He found that minimum pyrite concentrations of 0.5 to 1.0 pct could be detected in a coal matrix by DTA despite kaolinite and ankerite interferences. However, DTA thermograms of pyrite and marcasite were so similar that they could not be differentiated. Luganov (4) observed the thermal behavior of pyrite under inert atmospheres. They found that DTA's of pyrite displayed an exothermic effect at 380° C followed by endothermic effects at 480° to 500° C, 550° to 570° C. The exothermic effect at 380° C was attributed to partial oxidation of pyrite by oxygen adsorbed on the surface. Subsequent endothermic effects at 480° to 500° C and 550° to 570° C were thought to represent the reaction of exothermic products with pyrite. DTA's of pyrite

treated with acid and ethanol to dissolve ferric oxides and remove adsorbed oxygen displayed only an endothermic effect at 680° C.

EXPERIMENTAL WORK

A modified evolved-gas analysis technique was used to examine the thermal behavior of sulfur species. This technique employs a resistance furnace for the programmed heating of coal and overburden samples in an oxygen atmosphere. The evolution of sulfur dioxide and sulfur trioxide gases was measured by an infrared detector and recorded simultaneously with the sample temperature on a two-channel recorder. A Leco SC-32 Sulfur Analyzer[5] was used to ignite samples and monitor the evolution of sulfur oxides.

Initial tests of the evolved-gas analysis technique were made to determine if pyritic and sulfate sulfur could be thermally distinguished. Figure 1 is a thermogram of a sample containing 0.480 g $Fe_2(SO_4)_3 \cdot H_2O$ and 0.020 g FeS_2 (pyrite). Results of this test indicate that pyritic sulfur and sulfate sulfur can be temporally differentiated or time-resolved at an isothermal furnace temperature of 767° C. Hydrated sulfate salts of calcium, magnesium, manganese, and ferrous iron were also tested; the sulfate interference in all cases constituted less than 1 pct of the total pyrite response.

Standards of museum-grade pyrite were prepared in a silica gel matrix and tested at a furnace temperature of 767° C. Time-resolved, evolved-gas thermograms of pyrite standards are shown in figure 2. A plot of peak area for characteristic pyrite peaks versus the concentration of pyrite standards (fig. 3) yields a linear relationship. This indicates that the Leco SC-32 Sulfur Analyzer may be useful for quantification of pyritic and sulfate sulfur species in samples of low carbon content. The effect of carbonaceous material on pyrite thermograms is shown in figure 4. The large exothermic effect resulting from the combustion of carbonaceous materials effectively masks all pyrite peaks. Interaction of pyrite with the organic matrix and pyrolysis products may result in the shifting of characteristic pyrite peaks.

The relative reactivity of framboidal and isolated euhedral pyrite morphologies was compared by preparing a 3-pct-S

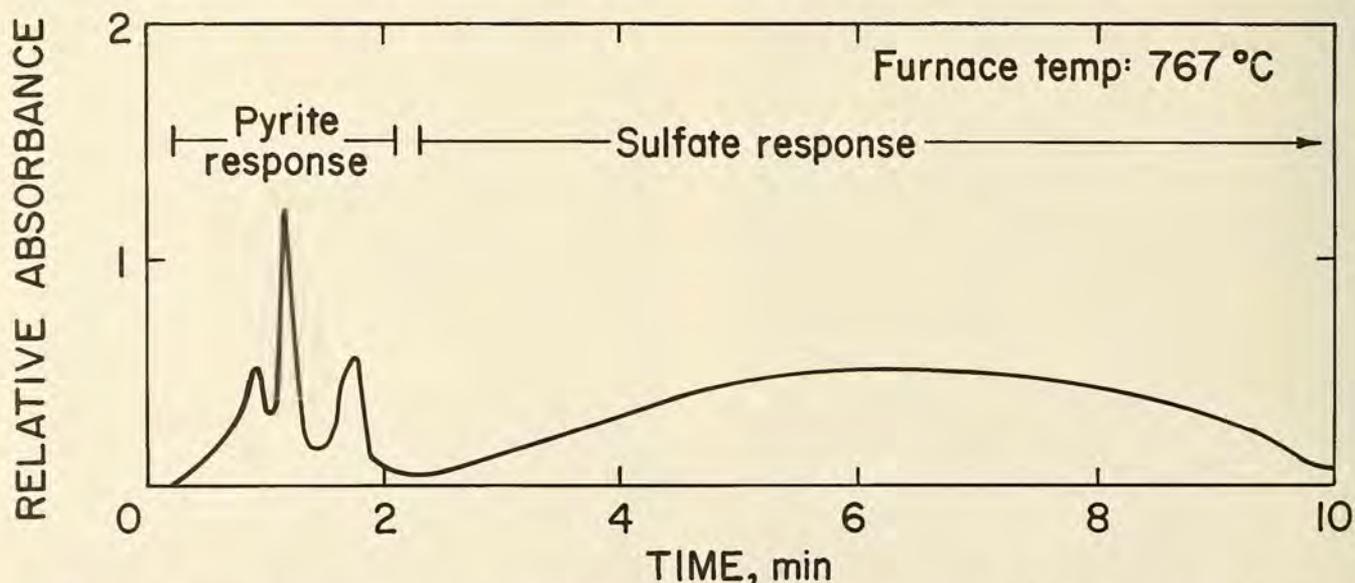[5]Reference to specific products does not imply endorsement by the Bureau of Mines.

FIGURE 1. - Time-resolved, evolved-gas analysis of a sample containing 0.20 g pyrite and 0.480 g $Fe_2(SO_4)_3 \cdot H_2O$.
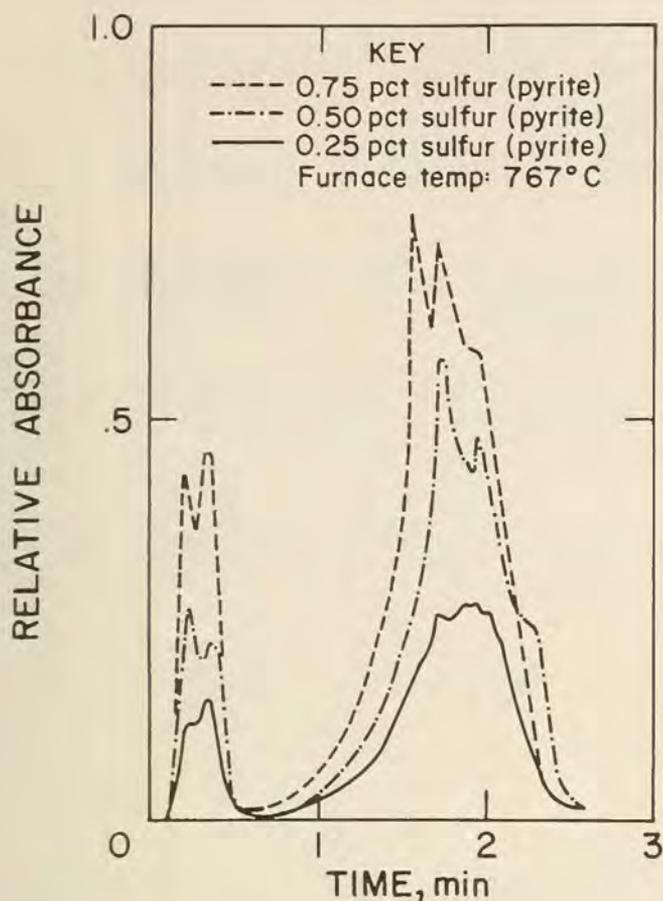
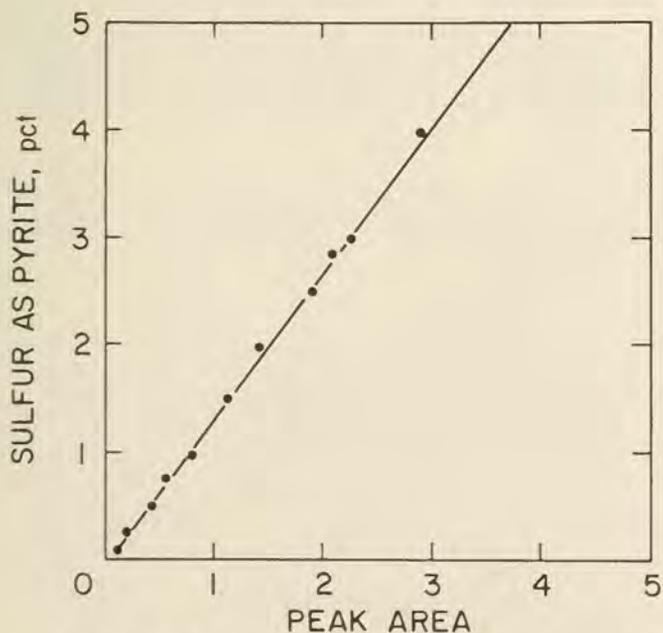FIGURE 2. - Time-resolved, evolved-gas analysis of pyrite standards.

FIGURE 3. - Plot of cumulative pyrite peak area versus sulfur content.
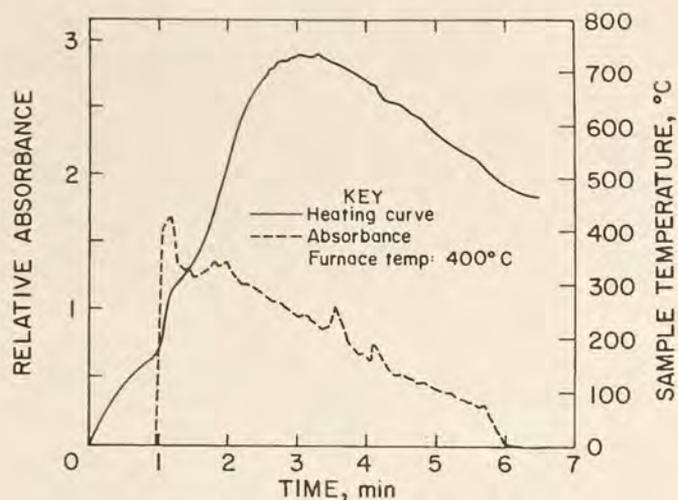

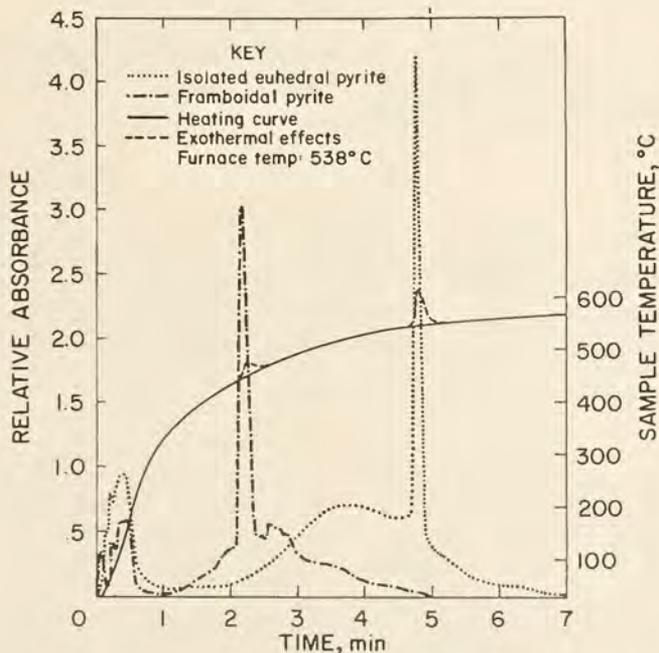FIGURE 4. - Evolved-gas analysis of carbonaceous sample.

FIGURE 5. - Evolved-gas analysis of isolated euhedral and framboidal pyrite morphologies.

standard of each form in a silica gel matrix (100- to 200-mesh). Framboidal pyrite was supplied by Dr. Alfred Stiller of West Virginia University, who confirmed its purity by Mossbauer spectroscopy. Framboidal and isolated euhedral pyrite standards were run individually at a furnace temperature of 538° C and at purge and lance flows of 4 and 1 L/min, respectively. The superimposition of the two thermograms (fig. 5) illustrates the

difference in thermal reactivity between framboidal pyrite and the more stable isolated euhedral pyrite. At this time, no thermograms have been run on samples containing both framboidal and isolated euhedral pyrite. Therefore, the amount of interaction between pyrite forms, if any, and the characteristics of the resulting thermogram cannot be predicted.

Although Bureau of Mines research into pyrite reactivity is still in preliminary stages, it can be concluded that--

1. Pyritic and sulfate sulfur in noncarbonaceous materials can be differentiated using a Leco SC-32 Sulfur Analyzer.

2. Pyritic sulfur can be quantitatively determined in noncarbonaceous matrices using evolved-gas analysis techniques.

3. Framboidal and isolated euhedral pyrite morphologies differ significantly in thermal reactivity.

4. Carbonaceous materials seriously interfere with the evaluation of sulfur species using evolved-gas analysis.

Future Bureau of Mines research into pyrite reactivity will include--

1. Investigations of the thermal reactivity of other pyrite morphologies.

2. The evaluation of evolved-gas analysis as a quantitative technique for determining pyritic and sulfate sulfur in noncarbonaceous materials.

3. The development of a technique for performing routine evolved-gas analysis of sulfur species in carbonaceous materials.

4. Correlation with contract research.

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