EVOLVED GAS ANALYSIS - A QUICK METHOD FOR IDENTIFYING TOXIC OVERBURDEN MATERIALS

By

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ABSTRACT

An evolved gas analysis technique that provides a quick and simple determination of pyrite availability has been developed by the Bureau of Mines, U.S. Department of Interior. This method employs a resistance furnace for the heating of overburden samples in an oxidizing atmosphere. The evolution of sulfur dioxide is monitored by an infrared analyzer and is recorded simultaneously with the sample temperature. Pyrite oxidizes to hematite and sulfur dioxide at temperatures ranging from 150^0 C to 550^0 C.

Twenty-five overburden samples were evaluated using evolved gas analysis. Comparison of thermal analysis results with laboratory weathering tests indicate that only those samples igniting below 220^0 C significantly affect water quality. Therefore, evolved gas analysis may offer some promise as a technique for discriminating between toxic and nontoxic overburden material.

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INTRODUCTION

-Pyrite, oxygen, and water react according to the following chemical expression to form acid mine drainage:

$$FeS^2 + (14/2)\ O^2 + (7/2)\ H_2O \dashrightarrow Fe(OH)_3 + 2\ H_2SO_4$$

The rate of acid product formation is dependent upon the-availability of pyrite, oxygen, and water. In order to predict the amount of acid that would be generated by the weathering of a specific overburden stratum, one would need to be able to estimate pyrite, oxygen, and water availability. The availability of oxygen and water is largely a function of material placement and reclamation technique and therefore is difficult to predict prior to mining.

However, pyrite availability is a property of overburden material that is only marginally affected by the diminution of particle size that occurs during mining and reclamation. Because pyrite availability or an estimate thereof is the only parameter that can effectively be measured prior to mining, it is commonly used as the basis for estimating acid potential in overburden analysis.

Pyrite availability is seldom equal to the bulk pyrite content. However, pyrite availability is a function of:

1. bulk pyrite content - generally, high pyrite contents result in high pyrite availability,
2. pyrite particle size - small pyrite particles exhibit increased surface area and hence, greater pyrite availability
3. pyrite morphology - certain pyrite forms such as framboidal pyrite display high surface areas and high pyrite availability,
4. coatings - the accumulation of oxidation products on the surface of pyrite particles inhibits the mass transfer of reactants to and products from pyrite surfaces, and
5. matrix characteristics - higher liquid and vapor phase permeability of the matrix results in increased pyrite availability.

A desirable method for determining pyrite availability would be sensitive to all five factors and would provide an accurate estimate of pyrite reactivity. The most obvious method for determining pyrite availability is to artificially weather a representative sample in the laboratory and monitor the formation of oxidation products with time. The weathering process can be accelerated by maximizing the amount of water and oxygen available for reaction. There are numerous and varied protocols for performing simulated weathering tests. Because these tests simulate actual weathering conditions, they are probably the most accurate means of determining pyrite availability. However, all suffer from one inescapable drawback. They are slow, requiring as long as 10 weeks to obtain meaningful data. They also occupy an inordinate amount of laboratory space and are labor intensive. Despite their inherent accuracy, simulated weathering tests are too expensive and time-consuming for routine overburden analysis.

In response to the need for a quick, relatively inexpensive method of overburden analysis, the acid/base account has gained widespread acceptance. This method employs whole rock analysis to estimate the maximum acid and alkaline loads that would be produced if all pyrite and carbonate in the sample reacted. The procedure is simple and relatively fast but has some serious drawbacks. The acid/base account tends to overestimate both the acid load and the alkaline load. Only the overestimation of the acid load will be addressed within the context of this paper.

The acid load is calculated from the total sulfur content based on the stoichiometry of complete pyrite oxidation. The overestimation arises from the fact that not all sulfur is pyritic sulfur and not all pyritic sulfur is available for reaction. Figures 1 and 2 illustrate the error that may be incurred by basing predictions of acid load on total sulfur content. Figure 1 is a plot of total sulfur content versus cumulative sulfate from humidity cell weathering tests for 25 overburden samples. Ideally, this should be a linear relationship with all points falling on the dashed line. The deviation of points is primarily due to the overestimation of pyrite availability although the neutralization potential also is not taken into consideration. Actually, pyrite availability as measured by humidity cell weathering tests is somewhat greater than it would be under field conditions because of smaller particle size and maximized weathering conditions. Therefore, the overestimation of field pyrite availability is greater than indicated in this plot. Figure 2 is a plot of acid/base account parameters versus cumulative sulfate (humidity cell weathering test) for the same 25 overburden samples. As in figure 1, this should approximate a linear relationship with all points falling on the dashed line. Because the neutralization potential is considered in the acid/base parameters, any deviation of points from the dashed line is directly attributable to the overestimation of pyrite availability. In some cases, this error is considerable and could conceivably result in a mining permit being denied where the post-mining water quality may not have been significantly degraded.

The Bureau of Mines has undertaken the development of new overburden analysis techniques that incorporate the accuracy of simulated weathering tests with the convenience of the acid/base account. Initial research has led to a potential method of quickly and directly determining pyrite availability. Like simulated weathering tests, this new technique monitors the oxidation of pyrite. However, in this case, the reaction is carried out at elevated temperatures and the monitored reaction is the anhydrous oxidation of pyrite to form hematite and sulfur dioxide.

$4\ FeS_2 + 11\ O_2 \dashrightarrow 2\ Fe_2O_3 + 8\ SO_2$

This reaction is reported in the literature (1,2,3)[2] to take place above 350^0C. During the course of this research, this reaction has been observed at temperatures as low as 150^0C for pyrite in overburden materials.

Pyrite also reacts through two less important pathways in an oxidizing atmosphere. Pyrite reacts with oxygen at about 300^0C to form ferrous sulfate and sulfur dioxide (2).

$FeS_2 + 3\ O_2 \dashrightarrow FeSO_4 + SO_2$

This reaction is much slower than the oxidation of pyrite to hematite and is not significant within the time frame of these tests. If the sample contains carbonaceous material, pyrite will react with carbon monoxide to form pyrrhotite and carbonyl sulfide.

$FeS_2 + CO \dashrightarrow FeS + COS$

We have only recently acquired the capability of continually monitoring carbonyl sulfide. However, preliminary results suggest that a significant amount of pyrite reacts via this mechanism.

EXPERIMENTAL

Equipment

The evolved gas analysis method employs a resistance furnace for heating samples in an oxidizing atmosphere. The evolution of sulfur dioxide is monitored using an infrared analyzer and recorded simultaneously with the internal sample temperature on a two-channel strip chart recorder. This technique is representative of a group of analytical techniques broadly termed evolved gas analysis (EGA).

2Underlined numbers in parentheses refer to items in a list of references at end of this paper.

Although not ideally suited for evolved gas analysis, a Leco SC-32 Sulfur Determinator[3] was used for these tests. This instrument was selected because it or functionally similar instruments are commonly available at labs specializing in coal and overburden analysis.

Minor modifications made to the SC-32 included:

1. A small, Type K thermocouple was inserted into the combustion boat and secured with high-temperature cement.
2. The lance flow was turned off.
3. The electronic integrator was bypassed by directly by connecting the infrared cell output (TP 3 on the A/D card) to a two-channel, strip chart recorder.

Sample preparation

Channel samples of 33 overburden lithologies from 10 surface mines in Pennsylvania, West Virginia, western Kentucky, Illinois, and Maryland were selected for the evaluation of pyrite availability by evolved gas analysis. These samples were collected by Engineers International, Inc. (Bureau of Mines contract J0328037) to determine the usefulness of three overburden analysis techniques for predicting post-mining water quality(4). During sampling, particular care was taken to insure that only unweathered material was collected. The samples were crushed to minus 6.35 mm (1/4 in.) by the contractor. In Bureau laboratories, the samples were pulverized to pass 250 um (60 mesh) and thoroughly mixed to insure homogeneity. Samples were evaluated as soon as possible after crushing.

3Reference to specific products does not imply endorsement by the Bureau of Mines.

Evolved gas analysis procedure

A known weight (300 mg) of each sample was spread uniformly in a ceramic combustion boat containing a small, Type K thermocouple. The combustion boat was then inserted into the combustion assembly of the Leco SC-32 Sulfur Determinator which was held constant at 540^0 C. The sample ignited as it heated in a 4 ml/min flow of 100 pct oxygen. The evolution of sulfur dioxide and internal sample temperature were monitored with respect to time.

Humidity cell weathering tests

Humidity cell weathering tests were performed by Sturm Environmental Services, subcontractors under Bureau of Mines contract J0328037. Samples were crushed to pass 6.35 mm and riffled to obtain a 100-300 g split. Each split was then weighed and placed in an inert, plastic container through which humidified air was passed. Each sample was leached on a weekly basis with 300 mL of deionized water. Leachate volume was measured and the leachate was analyzed for pH, specific conductance, acidity, alkalinity, and-sulfate. Each weathering cell was inoculated with acid mine drainage containing Thiobacillus ferrooxidans at the beginning of each test.

RESULTS AND DISCUSSION

The availability of pyrite in 33 overburden samples was evaluated by evolved gas analysis. Eight samples contained carbonaceous material; large exothermic effects resulting from the combustion of this material rendered EGA thermograms from these samples meaningless. EGA techniques and instrumentation capable of evaluating carbonaceous samples have been developed (5) but were not available for this study. Therefore, the results of this study are based on 25 noncarbonaceous overburden samples.

Figure 3 is an EGA thermogram of an overburden sample displaying thermal behavior typical of pyrite. The evolution of sulfur dioxide commences at about 370^0 C (Ti) and reaches a maximum at about 450^0 C (Tm). Thermograms of six samples showed significant evolution of sulfur dioxide at two temperature ranges indicating the presence of two forms of pyrite differing in reactivity. This is best exhibited in figure 4. Three temperature ranges of sulfur dioxide evolution were evident in one thermogram (fig. 5)

Peak maximum temperatures for overburden samples tested (fig. 6) ranged from 210^0 C to 480^0 C. All samples contained at least minor amounts of pyrite that demonstrated Tm's between 400^0 C and 480^0 C. Hydrothermal pyrite and marcasite (also tested) exhibit Tm's in this range. Seven samples contained additional pyrite with Tm's below 300^0 C. This pyrite is believed, on the basis of its lower evolution temperature, to be more available for reaction. Three samples contained pyrite displaying Tm's between 300^0 C and 400^0 C. These samples were originally thought to contain pyrite of intermediate availability. However, further study indicated that pyrite availability in these intermediate samples was less than would be expected from displayed Tm's. A plot of initiation temperatures (fig. 7) corroborates the breakdown noted in figure 6. In most samples, the evolution of sulfur dioxide initiated between 280^0 C and 440^0 C. Seven samples had initiation temperatures below 200^0 C. Again, there are three intermediates.

Conductivity (week 6) and cumulative sulfate (weeks 3-6) from humidity cell weathering tests were selected as most representative of water quality originating in each overburden material under field conditions. Plots of peak maximum temperatures versus humidity cell conductivity (fig. 8) and cumulative sulfate (fig. 9) exhibit two sample populations. One population with peak maximum temperatures above 400^0 C is tightly clustered. This high-temperature population does not significantly affect resultant water quality. The widely dispersed population that occurs below 350^0 C contains all samples which impact water quality. Both conductivity and cumulative sulfate are largely independent of peak maximum temperature in the low-temperature population.

In plots of initiation temperature versus conductivity (fig. 10) and cumulative sulfate (fig. 11), two discrete-populations can no longer be recognized. However, two observations can be made:

1. All samples that significantly effect water quality occur at initiation temperatures less than 225^0 C.
2. The water quality is independent of initiation temperature for initiation temperatures above 225^0 C.

Evolved gas analysis may provide a quick means of identifying overburden samples that effect water quality. Although no broad-based conclusions can be made from only 25 observations, it appears that samples with peak maximum temperatures above 400^0 C can be assumed to have little or no effect on resultant water quality. However, samples with initiation temperatures below 225^0 C will probably degrade water quality significantly. Because EGA requires only two minutes analysis time per sample, it can be used for the rapid prescreening of overburden samples. Samples with initiation temperatures below 225^0 C will require further analysis to determine the magnitude of the material's effect on water quality. Samples with initiation temperatures above 225^0 C may be ignored because they do not appear to significantly affect water quality.

The initiation and peak maximum temperatures of samples with especially reactive pyrite increase with exposure to air. This phenomenon was examined by exposing one sample (sample 5-4) to air for a period of eight weeks and monitoring the initiation temperature on a weekly basis. Figure 12 is a plot of two EGA thermograms. The thermogram labeled "metastable" represents sample 5-4 immediately after crushing. The stable thermogram is that of sample 5-4 six weeks after crushing with exposure to air. During the six weeks, the initiation temperature increased from 240^0 C to 410^0 C where it stabilized. Therefore, samples that are exposed to air prior to EGA analysis may not be thought to significantly effect water quality when in fact, they will. When performing EGA, it is necessary to analyze samples as soon as possible after crushing.

CONCLUSIONS

Although based on the results of only 25 observations, evolved gas analysis appears to offer some promise as a method for identifying overburden materials containing reactive pyrite. An analysis time of less than 2 min per sample makes EGA the most time- and cost-effective overburden analysis technique. Because EGA directly measures pyrite availability, it is inherently more accurate than techniques based on total sulfur content.

Evolved gas analysis does suffer from two disadvantages. EGA can only distinguish between samples that will or will not significantly effect water quality. The technique is not capable of determining the magnitude of water quality degradation. In addition, EGA cannot evaluate carbonaceous samples with the equipment described in this paper. The Bureau of Mines is currently developing an optimized EGA system that can analyze carbonaceous samples and may be able to estimate the magnitude of a material's effect on water quality.

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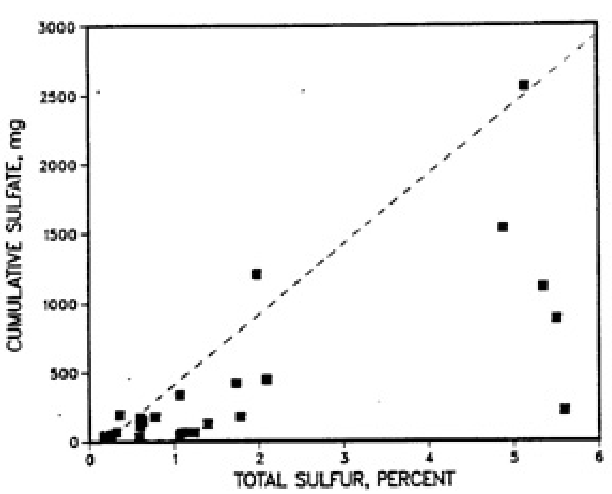

FIGURE 1. - The relationship between total sulfur content and cumulative sulfate in humidity cell leachates. Dashed line represents ideal relationship.

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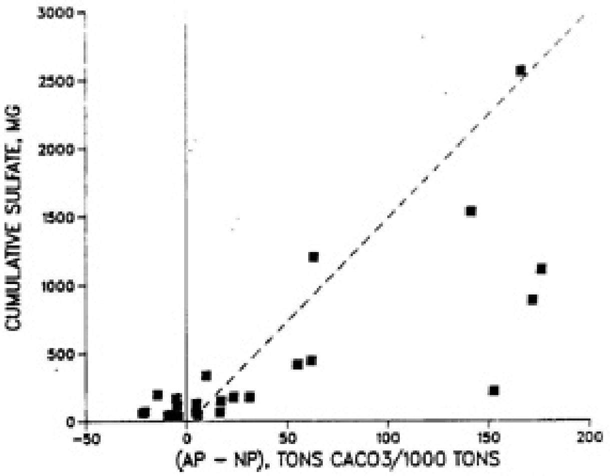

FIGURE 2. - The relationship between acid/base account parameters and cumulative sulfate in humidity cell leachate. Dashed line indicates ideal relationship.

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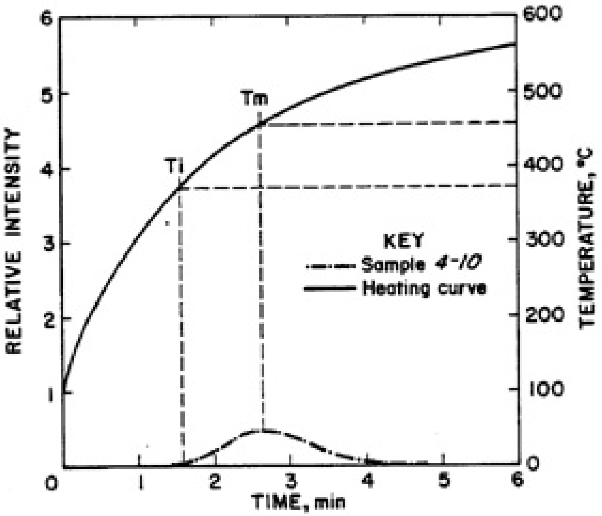

FIGURE 3. - Evolved gas thermogram of a typical overburden sample showing the sulfur dioxide initiation temperature (Ti) and peak maximum temperature (Tm).

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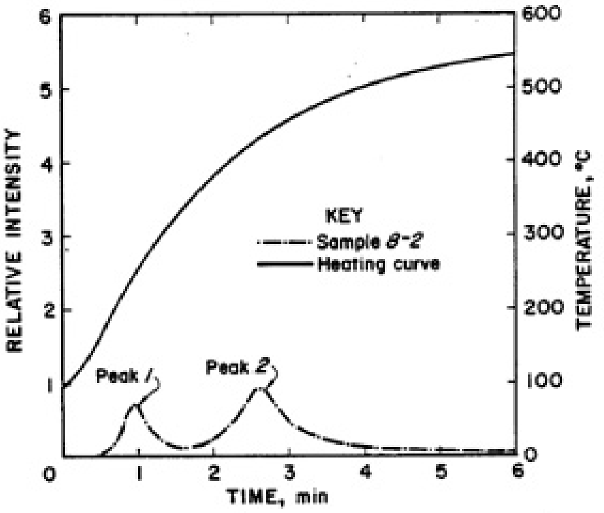

FIGURE 4. - Evolved gas thermogram of an overburden sample with pyrite displaying two reactivities.

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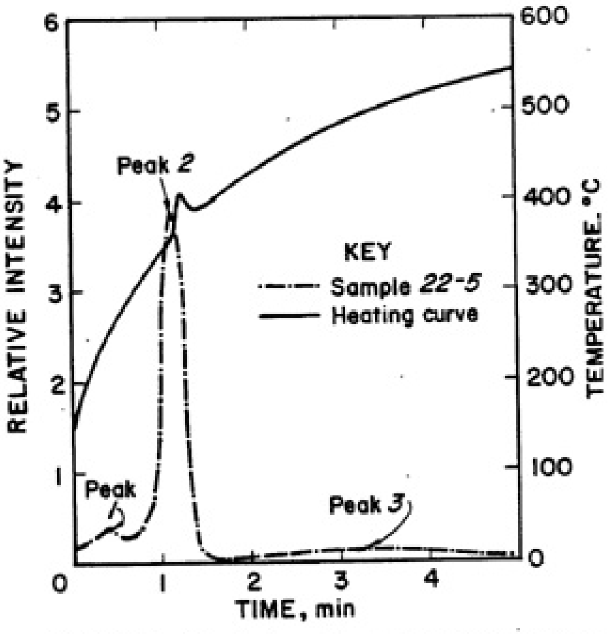

FIGURE 5. - Evolved gas thermogram of an overburden sample with pyrite displaying three reactivities.

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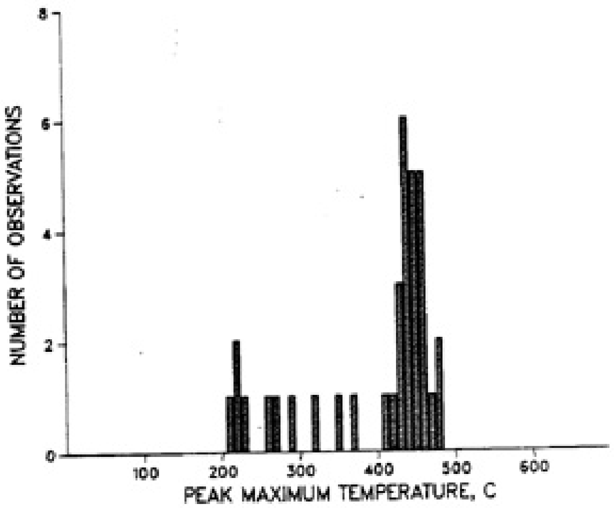

FIGURE 6. - Bar chart showing peak maximum temperature (Tm) distribution.

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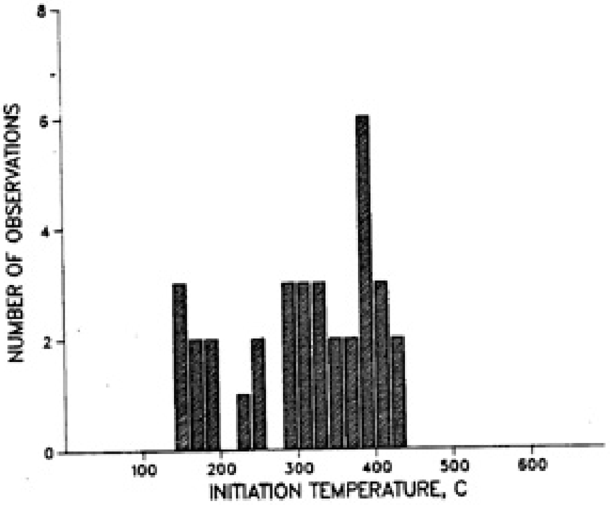

FIGURE 7. - Bar chart showing initiation temperature (Ti) distribution.

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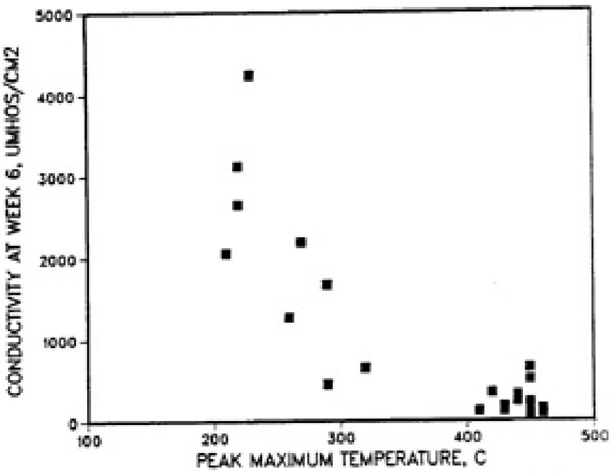

FIGURE 8. - The relationship of leachate conductivity to the peak maximum temperature (Tm).

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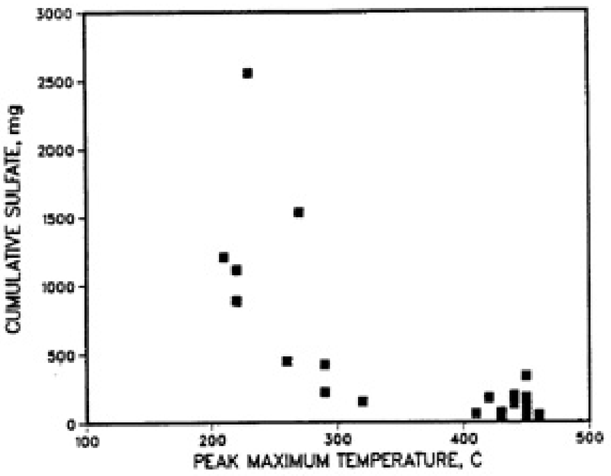

FIGURE 9. - The relationship of cumulative sulfate to the peak maximum temperature (Tm).

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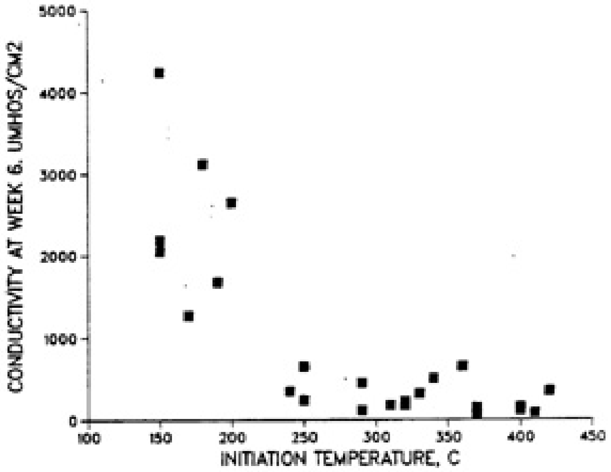

FIGURE 10. - The relationship between leachate conductivity and initiation temperature (Ti).

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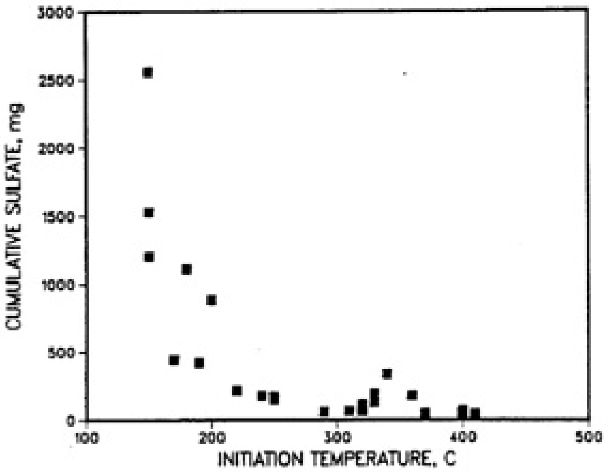

FIGURE 11. - The relationship between cumulative sulfate and initiation temperature (Ti).

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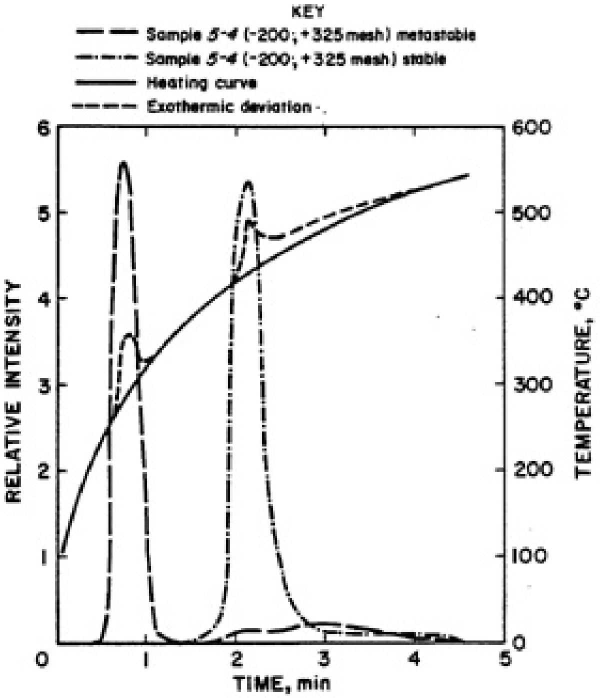

FIGURE 12. - Two evolved gas thermograms showing the difference in thermal reactivity between metastable and stable forms of sample 5-4.

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