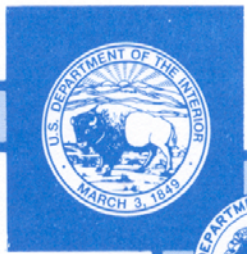# Cause of Floor Self-Heatings in an Underground Coal Mine

By Y. Miron, C. P. Lazzara, and A. C. Smith

UNITED STATES DEPARTMENT OF THE INTERIOR

BUREAU OF MINES

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UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

Btu/lb	British thermal unit per pound	mcal/(s·in)	millicalorie per second per inch
°C	degree Celsius	mg	milligram
cm	centimeter	min	minute
°C/min	degree Celsius per minute	mL	milliliter
cm³/min	cubic centimeter per minute	mm	millimeter
ft	foot	μm	micrometer
g	gram	pct	percent
h	hour	ppm	part per million
in	inch	vol pct	volume percent
m	meter	wt pct	weight percent
mcal/s	millicalorie per second		

CAUSE OF FLOOR SELF-HEATINGS IN AN UNDERGROUND COAL MINE

By Y. Miron,[1] C. P. Lazzara,[2] and A. C. Smith[3]

ABSTRACT

This report presents a U.S. Bureau of Mines study to identify the causes of self-heating events beneath the floor of a deep underground coal mine.

Mine samples from both heated and unheated areas were examined by various techniques, including visual, microscopic, thermal, chemical, and instrumental tests. The combined results led to the conclusion that pyrite (FeS_2) oxidation was the prime cause of the heatings. However, adiabatic oven tests of selected samples did not indicate the effect of the pyrite on the self-heating process, probably because of the experimental conditions.

A fast, simple procedure to assess the concentration of pyrite in the mine samples was developed, utilizing the reactivity of the sample with an aqueous solution of hydrogen peroxide (H_2O_2).

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INTRODUCTION

Self-heating events in underground coal mines are usually not detected until relatively high temperatures are attained and/or other phenomena, such as odor and haze, are observed. An increase in the concentration levels of carbon monoxide (CO) as a function of time is often the first signal that the temperature of the coal is increasing because of self-heating.

The propensity of coals to self-heat is rank associated. In general, low-rank coals are more susceptible to self-heating than high-rank coals. Thus, precautions against the occurrence of spontaneous combustion are more commonly practiced in low-rank coal mines. However, heatings and spontaneous combustion episodes can occur in mines of higher rank coals.

A deep coal mine that mines a low-volatile bituminous coal has experienced a series of floor self-heatings of various degrees of severity over a period of several years. All of the heatings have occurred in a section of the mine separated by a fault line, where an expanded seam exists beneath the floor. To date, 14 heatings have occurred, 7 of which were around the gob of a longwall panel extracted in this section. There is extensive folding and faulting in the coal basin in which the coal seam is located. Both normal and strike-slip faulting have occurred, and horizontal and vertical displacement is substantial. Floor heave is common throughout the mine entries, especially in tailgate roads and at four-way intersections. Yield abutment-yield pillar design is now employed and has helped to reduce floor heave to a great extent, but has not eliminated it completely. The ground heave exposes the material below the floor to a continuous supply of air and moisture. Because of the depth of the mine and the amounts of methane (CH_4) released, high-ventilation rates are prevalent throughout many of the mine areas, often resulting in high-pressure differentials across stoppings and other ventilation-control structures. To identify the causes of these floor heatings, the U.S. Bureau of Mines instituted a research study to evaluate samples from both heated and nearby unheated areas of the mine. The samples were collected by mine personnel and sent to the Bureau for analysis by several standard laboratory techniques, including thermal analysis, coal analysis, qualitative chemistry, instrumental analysis, and adiabatic oven experiments. The reactivity of many of the samples with aqueous H_2O_2 was also assessed. Finally, two samples were tested in a sealed flask test to measure their avidity for oxygen (O_2).

The conclusions reached as to the causes of the heatings, based on the cumulative evidence obtained by the analyses of all the samples, are presented.

MINE SAMPLES EVALUATED

SAMPLES FROM HEATED AREAS AND CORE SAMPLES

Five sets of samples, with each set and/or subset containing multiple samples, were collected in the heated areas of the mine at different times. Most of these samples consisted of mixtures of coal, shale, and/or rock, with the amounts varying from sample to sample, depending on the strata and the manner in which they were collected. Clays, silica, mica, and other similar compounds were intermingled in the samples. Set 2, which also contained wood cribbing, was from an area that sustained the worst heating. A sixth set, consisting of six cores, drilled at different times and in different areas in the mine, was also examined. Descriptions of all the samples in these sets are presented in the appendix, tables A-1 through A-5, for sets 1 to 6. The individual samples are designated by numbers for ease of identification. A few of the samples are shown in figures 1 to 4. A schematic map of the mine, with marked locations of some of the heated areas, shown in figure 5, indicates the extent of the problem, namely, that the heated areas were not localized but rather widely spread.
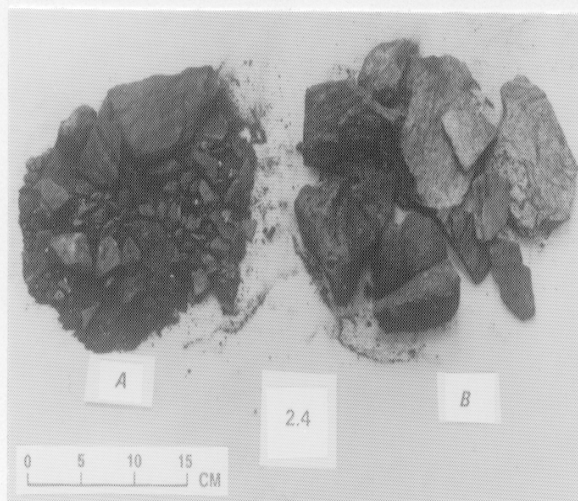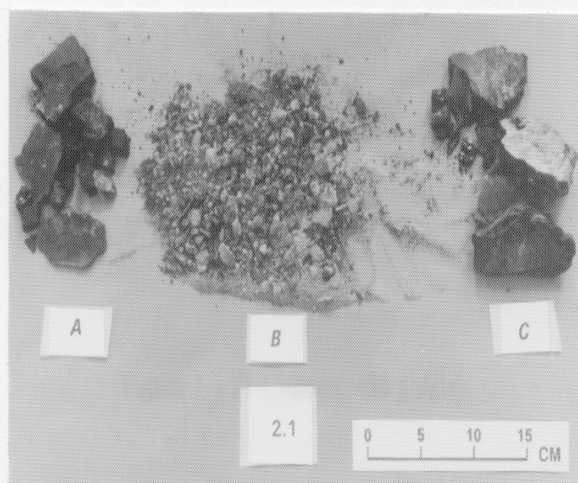
Figure 1.—Various samples of coal, shale, and rock dust from set 2. (See table A-2 for descriptions of each sample.)

SAMPLES FROM UNHEATED AREAS IN MINE

Five sets of samples from unheated areas were collected in floor channels, at different times, as detailed in table A-6. The individual samples are also desginated by numbers, for ease of identification. Sites where samples were collected are identified in the map in figure 5. Many of the samples contained large amounts of rock shale and clay compounds, in addition to coal, depending on the areas from which they were taken. Zone samples contained a mixture of coal, rock, and shale. Coal-rock interface samples contained less rock and shale than zone samples, while coal samples contained essentially coal only. As an example, figure 6 depicts the various zones from which the channel samples were collected on June 9, 1989.

Figure 2.—Sample 2.3 (partially charred wood-crib block) from set 2.

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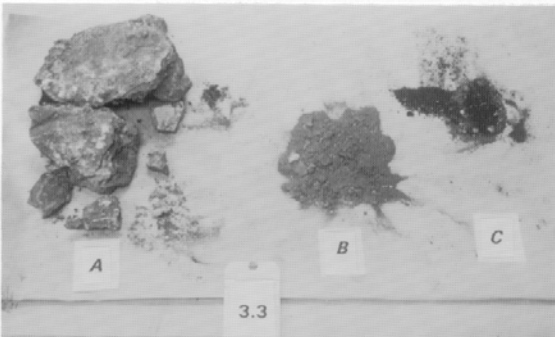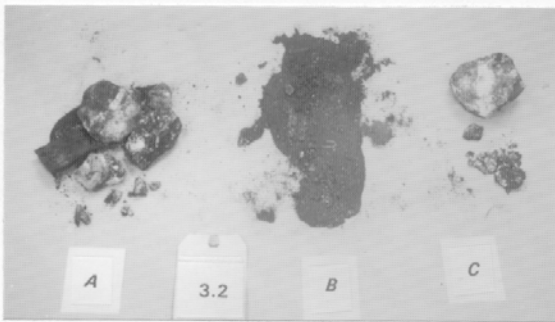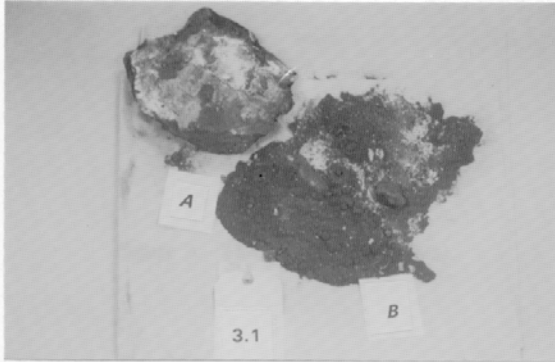
Figure 3.--Various samples of coal, shale, and rock dust from set 3. (See table A-3 for descriptions of each sample.)
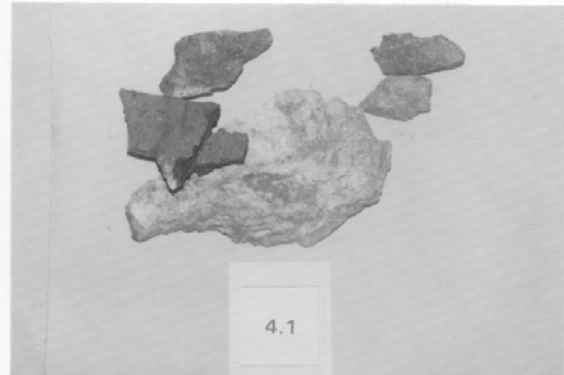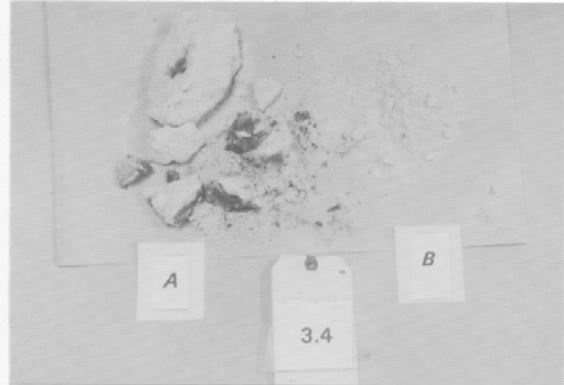
Figure 4.—Various samples of coal, shale, and rock dust from sets 3 and 4. (See table A-3 for descriptions of each sample.)

3-20-89
3-28-89

6-9-89

2-28-89

4-21-89

N

LEGEND

⊗ Date of collection and
location of samples
from unheated areas

▨ Heated areas

0   500   1,000
Scale, ft
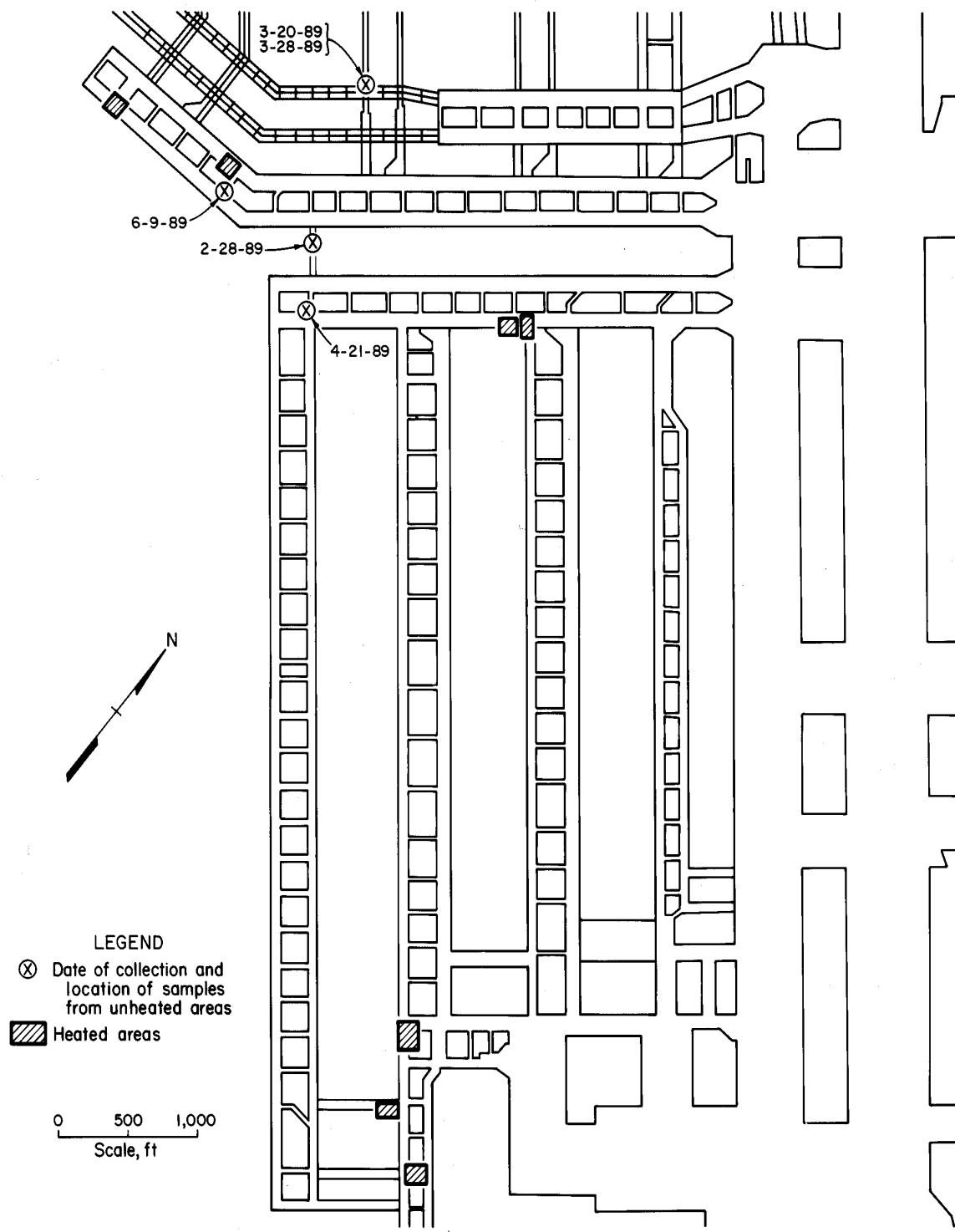
Figure 5.—Schematic mine map showing heated areas and locations of unheated areas from which samples were collected.

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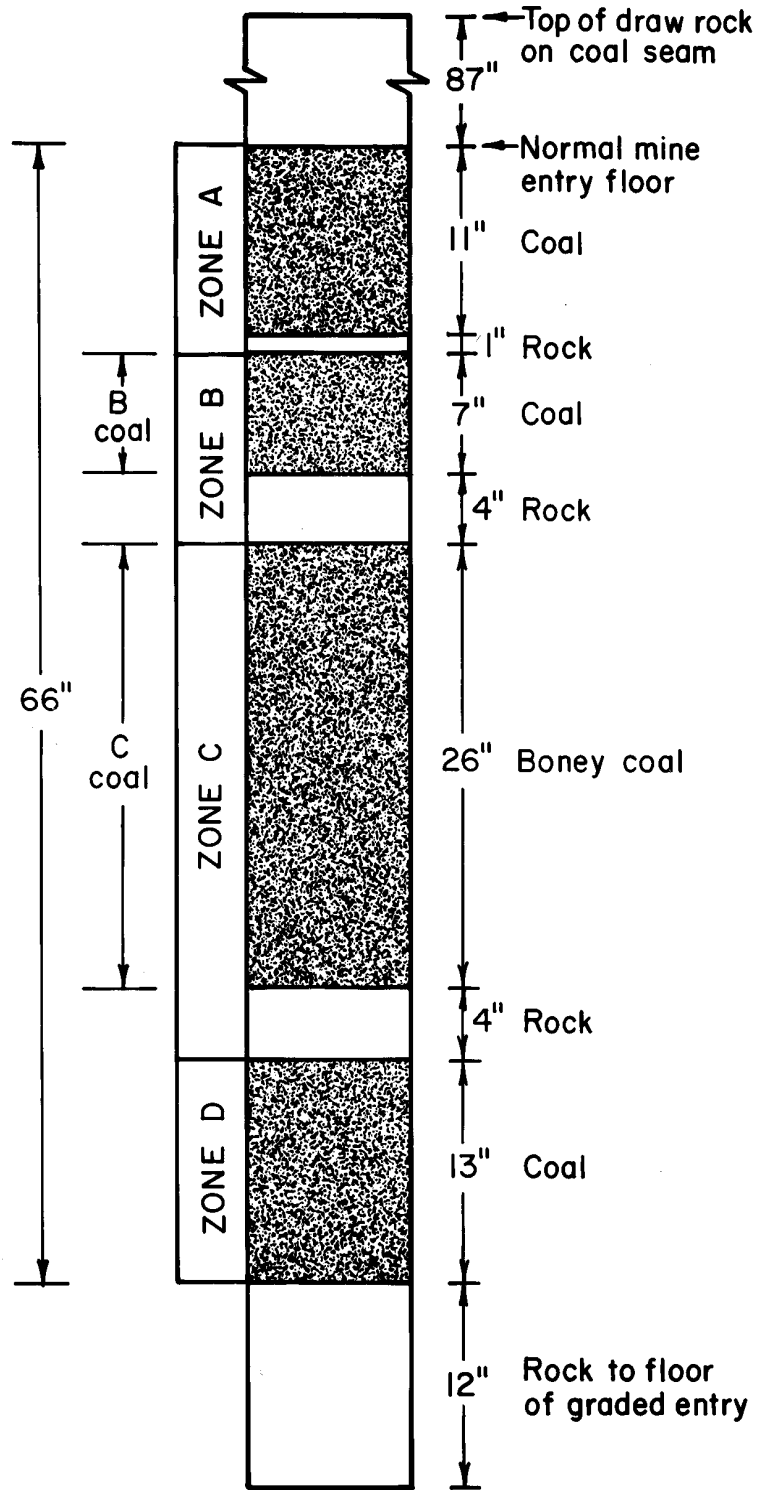
Figure 6.—Schematic of floor strata showing sampling zones for samples of set 11.

EXPERIMENTAL PROCEDURES

VISUAL OBSERVATIONS

All of the samples were visually examined and pertinent observations were noted. Optical microscopy was used intermittently to observe the samples and to aid in the selection of specific specimens for tests by thermal analysis, qualitative chemical analysis, or instrumental analysis.

THERMAL ANALYSIS

A Du Pont[4] 990 differential scanning calorimeter (DSC) was used to evaluate various portions from all the samples. Sample sizes varied from a few milligrams to about 75 mg. For the evaluation of bulk samples, larger amounts were used, whereas for specific samples of interest, carefully collected specimens were usually small in size. The samples were contained in covered aluminum pans and heated at 10° C/min in an initial atmosphere of static air, which changed to a self-generated atmosphere as the test progressed. In all tests but one, the sensitivity was set at 1 mcal (s·in). In the one exception, it was set at 2 mcal/(s·in). For additional insight into the identity of the compounds present in the samples, some of the heated samples were cooled in the pans and then reheated, usually at the same conditions.

CHEMICAL AND INSTRUMENTAL ANALYSES

Standard qualitative chemical methods were used to identify the presence of ferrous and ferric cations and sulfate and carbonate anions. These procedures are described in greater detail in the section "Experimental Results and Discussion." In a few cases, X-ray diffraction analysis and inductively coupled argon plasma (ICAP) atomic emission spectroscopy were used to identify select minerals, compounds, and elements.

COAL ANALYSES

Ultimate and proximate analyses, heating values, and forms of sulfur (sulfatic, pyritic, and organic) were obtained for many of the samples, mostly from the unheated areas.

ADIABATIC OVEN TESTS

Tests were conducted in an adiabatic oven to determine the minimum self-heating temperatures (SHT's) of many of the samples from the unheated areas. A detailed

description of the test is available in a Bureau publication (1).[5] The following is a brief description of the test procedure. The sample was pulverized and sieved, and the minus 100-mesh (minus 150 μm) fraction was dried in an oven at 67° C with a flow of dry nitrogen (N_2). A 100-g sample was placed in the adiabatic oven and brought to a preselected initial temperature under a 200-cm³/min flow of dry N_2. The sample was then exposed to an equal flow of humidified air. Usually, a series of tests is made, each test with a fresh sample, in 5° C increments, until a minimum initial temperature that produces a sustained exothermic reaction (thermal runaway) is determined. Not enough material was available to conduct all the tests necessary for the determination of the minimum SHT's of the samples. Accordingly, for some of the samples, tests were conducted at larger temperature increments, and the probable minimum SHT values were qualified to within a range of about 20° C. Still, for other samples, only an upper or lower limit (go/no-go) was established. The lack of sufficient material was also the reason for using the minus 100-mesh fraction rather than the minus 100- plus 200-mesh fraction prescribed for the tests. A schematic of the adiabatic oven is shown in figure 7.

HYDROGEN PEROXIDE REACTIVITY

H_2O_2 is a strong oxidizer and reacts exothermally with both inorganic and organic material. When mixed with coal that contains pyrite, it reacts with the pyrite and decomposes at a fast rate.

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[5]Italic numbers in parentheses refer to items in the list of references preceding the appendix at the end of this report.
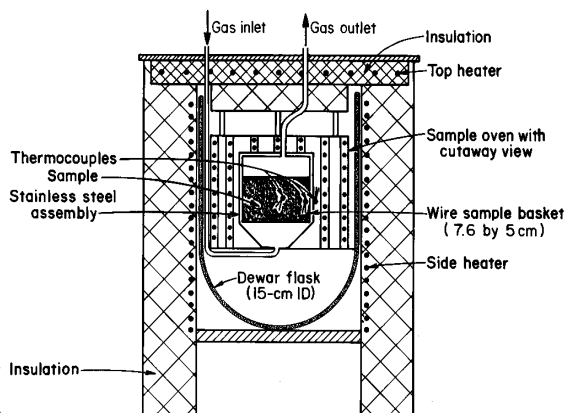
Figure 7.—Schematic of adiabatic oven.

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

For the tests, 5-g samples of the minus 60- plus 100-mesh fraction were used. A sample was placed in a Dewar flask (250 mL in volume), 35 mL of an 8.4 pct aqueous H_2O_2 solution was added, and the flask was stoppered loosely. The temperature of the reacting mixture was monitored with a type K thermocouple as a function of time until a maximum value was attained. Monitoring continued until the temperature fell a few degrees below the maximum value.

SEALED FLASK OXYGEN ADSORPTION TESTS

The ability of materials, such as coal, to adsorb O_2 and the quantity adsorbed over time is a good measure of their propensity to self-heat. Two samples were chosen to undergo this test, which is described in detail in a Bureau publication (2). As-received samples, 50 g each, were sealed in 500-mL flasks in ambient air. The samples were neither ground nor sieved prior to the test because their particle size distribution was similar to the size range prescribed for the test. Miniature pressure transducers monitored the pressure in the flasks as a function of time. A gas sample was taken from each flask after 10 days and analyzed by gas chromatography.

EXPERIMENTAL RESULTS AND DISCUSSION

SAMPLES FROM HEATED AREAS

Visual Observations

Many of the samples from sets 1 to 5 that were mixtures of coal, shale, and rock also showed evidence of extraneous material. This material was usually present on the surfaces in small quantities, but it was seen on a large portion of the samples. It varied in color from white to yellow-orange to red, and its physical appearance varied between dry and moist, and powdery and crystalline, suggestive of oxidation compounds commonly found on coals that have been exposed to air and moisture.

The dark red paste sample from set 1 was the only sample different in appearance, consistency, and texture from all the other samples. It felt like a clayey paste to the touch, but resembled iron oxide in hue.

The hard cores from set 6 showed a variety of materials, as described in table A-5. Only small amounts of extraneous material were seen here and there on a few of the surfaces. These observations were helpful in guiding the course of the study and in understanding the results of the tests.

Thermal Analysis of Coal-Shale

During tests in the DSC, thermograms are recorded. These thermograms indicate the release (exotherm) or absorption (endotherm) of heat by the sample. When heat is not exchanged, a straight baseline is recorded. The exotherms and endotherms are usually identified by the temperatures at which their peaks occur and, at times, by their onset temperatures as well. The shape and magnitude and the peak temperatures of a thermogram are a function of sample size and geometry, heating rate, composition of the sample, and the presence of impurities in the sample. The nature of the atmosphere in the DSC also influences the results. For instance, coal will undergo exothermic oxidative decomposition in an atmosphere of air or O_2, while in an inert atmosphere, it will pyrolyze endothermally.

Most of the samples from all the sets were mixtures of coal, shale, and/or rock. The resultant DSC thermograms depended on the relative proportions of these materials in a sample. When coal was the main ingredient, a typical coal thermogram was obtained. The first thermogram in figure 8 was obtained for sample 1.4 from set 1. This thermogram contains a very shallow endotherm extending from ambient temperature to near 100° C because of water evaporation, followed by two exotherms. The first, smaller and shallow exotherm, with a peak temperature of the plateau at about 350° C is overlapped by the second and much larger exotherm, with a peak temperature of about 560° C. The main determinant of peak
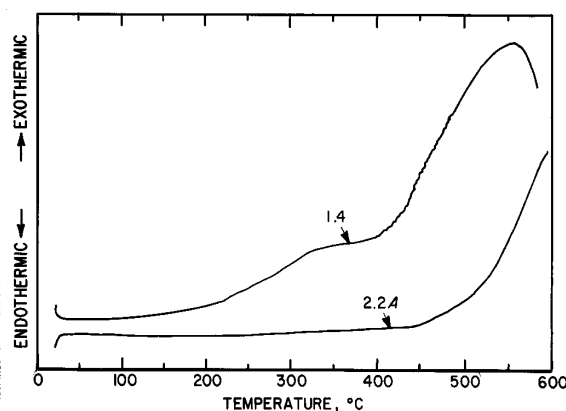
Figure 8.—DSC thermograms of sample 1.4 (unheated coal) from set 1 and sample 2.2A (heated coal) from set 2.

temperatures for the stated test conditions is the coal rank. Lower rank coals record lower peak temperatures, especially for the second exotherm. During the temperature range of the first exotherm, aliphatic portions of the coal decompose more easily and gaseous species, such as CO, carbon dioxide (CO_2), water, and other volatiles, are evolved. Tars are also released to an extent, and some char starts to form. Decomposition of aromatic groups and char oxidation are more prevalent during the temperature range encompassing the second exotherm, but the transformations detailed for the lower temperature range also continue. Thermograms for samples from the other sets, which contained mostly coal, were similar to the first thermogram seen in figure 8 for sample 1.4.

When a coal that has been previously heated to temperatures in the vicinity of 350° C is tested in the DSC, the first exotherm is either missing or largely reduced in size. And, if the coal has previously been exposed to high temperatures or has been heated for an extended period of time in the temperature range where it undergoes some decomposition and is then tested in the DSC, the second peak often shifts to a higher temperature. Both these effects are seen in figure 8 for sample 2.24, a floor sample collected from the second area to undergo a heating (heated area 2). The first exotherm is barely discernible, while the peak temperature of the second exotherm is higher than 590° C. The test was terminated at 590° C to prevent melting of the aluminum sample pan and cover. A few other samples from the other heated areas generated similar thermograms. Thus, depending on the sampling location, there was clear evidence that the carbonaceous matter had experienced high temperatures.

Thermal Analysis of Extraneous Matter

As was indicated previously, extraneous material was seen on many of the samples. In addition, set 1 contained a sample of pastelike red material (table A-1, sample 1.2). This consistency was probably a result of the flooding of the area with water soon after the discovery of the heating. A careful examination of the sample revealed the presence of both black and white particles in the paste. When some of the particles were sectioned, concentric layers of black, red, and white material could be seen. A sample of the red material that contained a few black particles was tested in the DSC, and the resultant thermogram, presented in figure 9, displays a variety of features. The presence of coal (probably some of the black particles) is evident by the exotherm with peak temperature at 540° C. The first exotherm usually associated with a coal's thermogram is much reduced in size, and it peaks at about 300° C, thus indicating that the sample has been heated
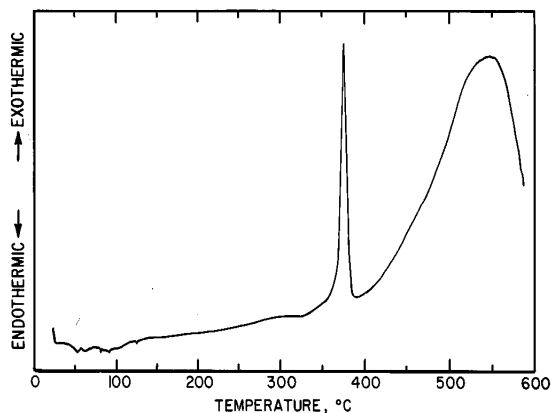
Figure 9.—DSC thermogram of sample 1.2 (red paste) from set 1.

prior to the test in the DSC. Various endotherms, at 55°, 65°, 85° to 90°, and 123° C, and a sharp exotherm with its maximum temperature at 377° C, are indicative of various phase changes being undergone by the constituents of the red material during the test.

The appearance of the many mine samples suggested the presence of a wide variety of oxidation products. Consideration was therefore given to those inorganic oxidation products generally associated with the oxidation of coal and its associated minerals as the source of the diverse endotherms and exotherm cited above. These distinct products include various kinds of iron oxides and hydrous iron oxides, for example, $Fe_2O_3 \cdot XH_2O$ or $FeOOH$ (3); iron sulfates and double salt compounds, such as jarosite [$KFe_3, \cdot (SO_4)_2 \cdot (OH)_6$] (4), and also gypsum ($CaSO_4 \cdot 2H_2O$). Hydrous calcium sulfates [$CaSO_4 \cdot 2H_2O$ and plaster of Paris ($CaSO_4 \cdot 1/2H_2O$)] form when calcium carbonate ($CaCO_3$) associated with the coal matrix reacts with sulfuric acid (H_2SO_4), which also forms during the oxidation process (5-6). As can be seen from the chemical formulas, these compounds contain varying amounts of water of hydration, which can be driven off by heat at relatively low temperatures in about the same temperature range in which the endotherms are clustered. Furthermore, hydrous or amorphous iron oxides undergo exothermic crystallization when heated, to form either alpha or gamma hematite (α- or γ-Fe_2O_3) (7). This phase change usually occurs at about 360° C, but in the presence of other material, the temperature can shift in either direction. The sharp exotherm in figure 9 is probably due to just such a change taking place in the red paste sample, partially confirming the assumption that it is a hydrous iron oxide, as also suggested by its hue.

Some of the white particulates found in the red paste were separated and then heated in the DSC to 145° C. Multiple endotherms were recorded, as seen in figure 10. When the sample was then cooled in the sample pan to ambient temperature and then reheated, most of the endotherms were gone, thus supporting the hypothesis of dehydration being the origin of these endotherms.

When the extraneous, varicolored (white, yellow, orange, or red) material was scraped from the surfaces of samples in all the sets and tested in the DSC, a similar variety of endotherms was obtained, as seen in figures 10 and 11. The second and third thermograms in figure 10 are also for samples that consisted mainly of white material scraped from surfaces. The second thermogram, with
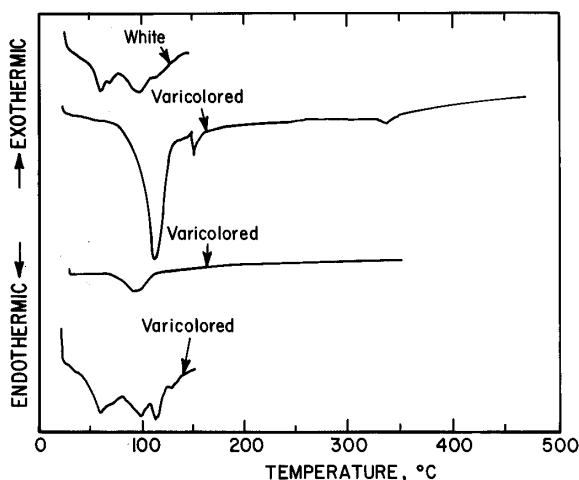
Figure 10.—DSC thermograms of white and varicolored materials found in samples from set 1.
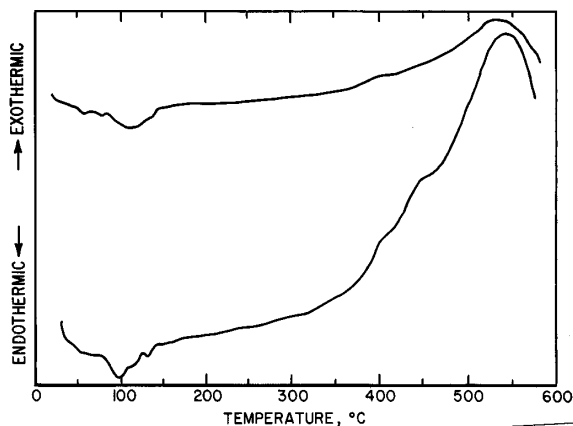
Figure 11.—DSC thermograms of both red and black matter found in sample 1.2 from set 1. First thermogram obtained at a sensitivity of 2 mcal/(s·in); the second at 1 mcal/(s·in).

the large endotherm peaking at 110° C and the two smaller endotherms at 150° and 335° C, can be the result of dehydration of sulfate compounds, such as $CaSO_4 \cdot 2H_2O$, $CaSO_4 \cdot 1/2H_2O$, melanterite ($FeSO_4 \cdot 7H_2O$), siderotil ($FeSO_4 \cdot 5H_2O$), and coquimbite [$Fe_2(SO_4)_3 \cdot 9H_2O$]. The iron sulfates lose some of their water of hydration at higher temperatures, above 150° C, as does $CaSO_4 \cdot 1/2H_2O$. Iron and calcium sulfates are known to be associated with coal and other carbonaceous materials that have been exposed to air and underwent oxidation (7).

The number of endotherms, their peak temperatures and relative sizes (or heights) differed for the different samples, as is expected when more than one compound is present, each in a different amount. Here, it is surmised that a suite of diverse hydrous salts is present in various proportions. The peak temperatures of the endotherms match many of the temperatures at which these compounds lose water. However, matching peak temperatures do not prove equal identities; they only imply that the probability exists. Based on many prior results of DSC analyses of known oxidation products in association with coal, this probability is quite high.

The two thermograms in figure 11 were obtained for samples that contained both black and red material; the black matter is probably either coal or shale and the red matter is one of the hydrous iron compounds. Pyrite could also be present in the black material. The second thermogram in figure 11 contains three exothermic peaks, at 400°, 440°, and 537° C, instead of the common two. This behavior has been observed at times for other coals, though infrequently. On the other hand, the peak at 440° C could be an indication of pyrite decomposition. The first thermogram in the figure, for a smaller sample, was obtained at a lower sensitivity (2 mcal/(s·in)) and therefore the sizes of the exothermic peaks are much smaller. Nonetheless, endotherms indicative of extraneous matter are clearly visible.

Thermal Analysis of Samples Containing Sulfidic Matter

Two other distinct features observed in the thermograms of many of the samples are described below:

First Feature.—This feature is a jagged or pulsing behavior superimposed on a portion of the exothermic rise, in the temperature range of 400° to 525° C. Various examples can be seen in figure 8 for sample 1.4, in figure 12 for samples 5.1 and 5.2, in figure 13 for sample 2.2B (rock, shale) obtained from the roof over the heated area, and in figure 14 for samples 2.6 and 2.7 obtained from the trench, 15 to 30 in and 30 to 45 in below the surface, respectively. Some of the samples from the other sets also displayed the same behavior.
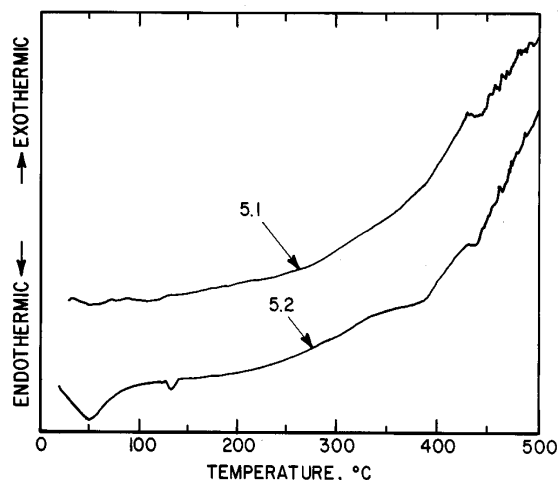
Figure 12.—DSC thermograms of samples 5.1 and 5.2 from set 5 showing jagged behavior.
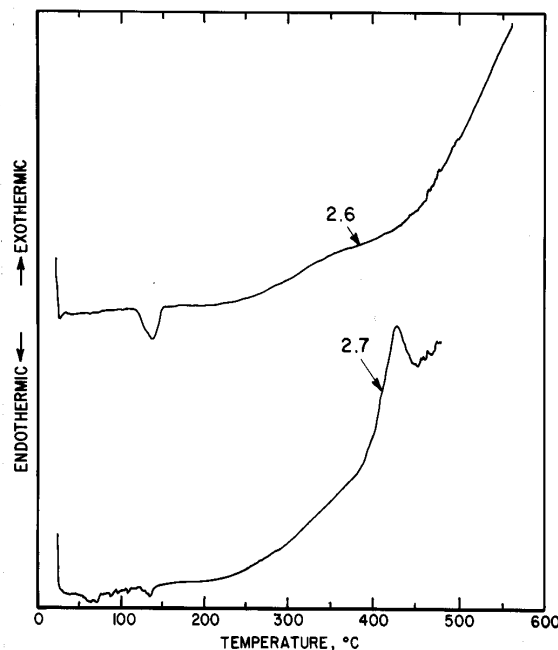
Figure 14.—DSC thermograms of samples 2.6 and 2.7 from set 2 showing jagged behavior.
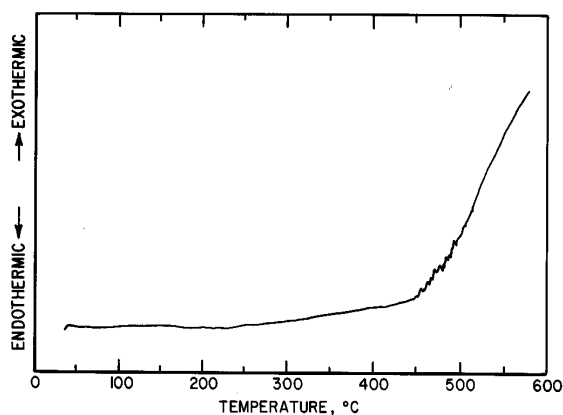
Figure 13.—DSC thermogram of sample 2.2B (rock, shale) from set 2 showing jagged behavior.

At times, this jagged behavior was preceded by an endotherm at about 440° C, as shown in the two thermograms in figure 12, the second thermograms in figures 14 and 15, and the last thermogram in figure 18. The cause for this endotherm is not known. It might be that some marcasite (also FeS_2) is present with the pyrite and is undergoing change. Marcasite, an isomorph of pyrite, undergoes a solid-phase transition to pyrite at 450° C (8). This transformation is kinetically slow; its rate increases with increasing temperature (9). In the presence of sulfur, marcasite can invert to pyrite at a temperature as low as 150° C, but in its absence, transformation does not occur below 400° C (10). However, it is more probable that

any pyrite present is undergoing decomposition at this temperature. The tests in the DSC are conducted in an atmosphere of static air. As the tests proceed and the coal decomposes, a self-generated atmosphere results, which contains CO, CO_2, and various hydrocarbons as the major gaseous products. In such an atmosphere, pyrite will likely undergo decomposition, releasing some sulfur, which in turn will react with the hydrocarbons and form hydrogen sulfide and other sulfur-containing compounds. Even some carbonates, such as dolomite, in the presence of coal, can decompose endothermally at this low temperature.

Thermograms with similar jagged behavior have been reported for pyrite particles heated in the DSC at a constant heating rate (11). The sizes of the jutting ridges and the spacings between them vary with particle size and heating rate, among other factors. This phenomenon is due to the initiation of oxidation reactions in individual particles or particle clusters at a temperature dependent on their surface properties, which in turn depends on the method of sample preparation (12). Extremely small active sites that are in poor thermal contact with the rest of the particles may reach a high instantaneous temperature during oxidation. In the present study, the size of these ridges is modulated by the major constituent of the sample, namely the coal, shale matrix with the reactive pyrite

or iron sulfide being a very small component, although the reactivity of the individual pyrite particles also plays a role. These active sites require only minute amounts of O_2 and can possibly be oxidized by the CO_2 present in the atmosphere.

Second Feature.—This feature is small exothermic peaks, at 400° C and at 440° to 450° C, that appear in a few of the thermograms, which are not presented in this report. These peaks are thought to be a result of the decomposition of sulfidic matter, such as pyrite, in the coal or shale matrix.

Thus, these two distinct features, manifest in the thermograms, point to the presence of iron sulfides and specifically pyrite in many of the samples collected from the heated areas in the mine.

Samples 5.1 and 5.2 were specifically collected by the mine personnel because they suspected the presence of large amounts of pyrite in these samples. Indeed, the thermograms of these samples displayed the unique features associated with pyrite, as described above. In addition, a specimen of sample 5.1, tested in the DSC to a temperature of 125° C, showed a variety of the endotherms associated with sulfide oxidation products (as explained in the previous section), as can be seen in the first thermogram in figure 15. The second thermogram in this figure was recorded for another specimen of the same sample. The endotherm, with a peak at 127° C, indicates the presence of $CaSO_4 \cdot 2H_2O$, which loses water of hydration at this temperature. This thermogram also contains the jagged ridges.

Portions of the coal in sample 5.2 contained small patches of yellow matter on their surfaces. The matter was scraped off the surface and heated in the DSC. The resultant thermograms for this material, which was thought to be sulfur, were different than all the other thermograms recorded during this study. Two of these thermograms (the third and fourth ones in figure 15) contain a large endotherm, which starts at about 325° C. Neither the melting nor the boiling points of sulfur coincide with the endotherms' initiation or peak temperatures. It is believed that these endotherms are due to evaporation of a relatively large amount of H_2SO_4 in the sample tested. Filtrates of aqueous suspensions of samples 5.1 and 5.2 were treated with barium chloride and found to contain large amounts of sulfate ions, indicating the oxidation of the pyrite and the formation of the acid, in addition to the formation of iron sulfates. When tested, the samples were found to be highly acidic. A similar endotherm at 335° C was seen in the second thermogram in figure 10; it may also be indicative of the presence of H_2SO_4.

Thermal Analysis of Other Mine Materials

Many substances undergo physical and/or chemical changes when heated. Thus, each substance has its own specific thermogram, which can serve as a fingerprint for identification. If such materials are exposed to heat prior to being tested in the DSC, the resultant, changed thermograms can be used to approximate the temperature of the earlier exposure. This has been shown previously for coal. The same phenomenon was found for a piece of wood-crib block (sample 2.3), one of the samples in set 2 from the batch collected after the second heating. Both uncharred and charred portions of the wood-crib block were examined. The first thermogram in figure 16, for the uncharred
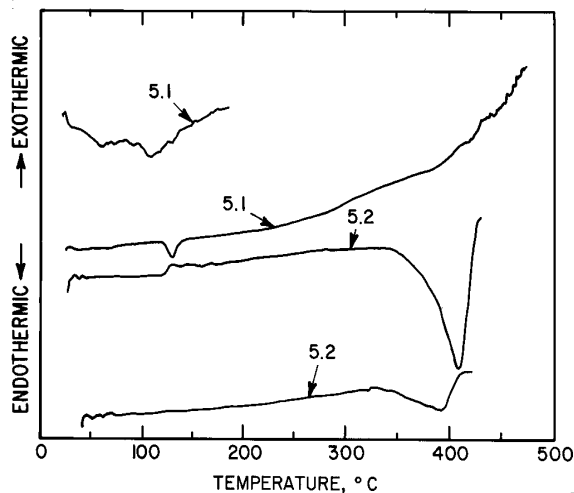
Figure 15.—DSC thermograms of oxidation products found in samples 5.1 and 5.2 from set 5.
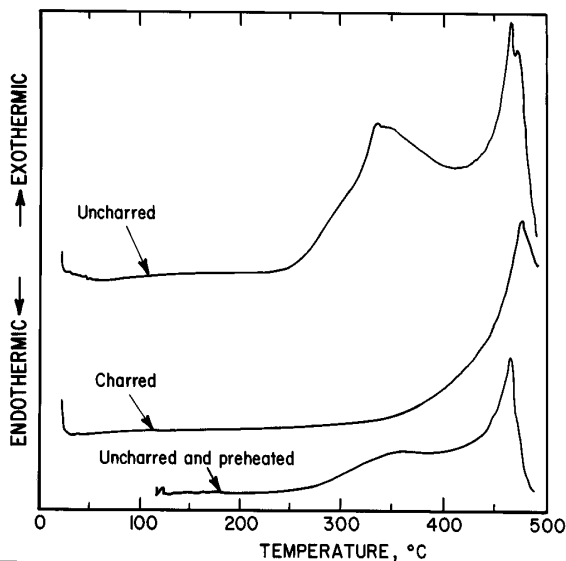
Figure 16.—DSC thermograms of sample 2.3 (wood-crib block) from set 2; uncharred, charred, and uncharred sample preheated in DSC to 340° C.

wood, contained two typical exotherms, while the second thermogram, for the charred portion, contained only one exotherm. When a sample of the uncharred wood was heated in the DSC to 340° C and then immediately removed from the DSC to cool and arrest further reaction, it was found to be charred. When reheated from ambient temperature, this sample still registered two exothermic peaks (third thermogram in figure 16). However, the first exotherm was more shallow. Ratios of the peak heights for the unheated and heated samples (first and third thermograms) were 1.7 and 2.5, respectively, indicating the reduction in size of the first peak of the thermogram for the heated sample. These results imply that the charred wood block sustained a temperature of at least 340° C, the same exposure temperature that was inferred for the coal sample from the floor of the heated area, as discussed in the "Thermal Analysis of Coal-Shale" section, for sample 2.2A, and more probably an even higher temperature.

Thermal Analysis of Cores

Small samples, which appeared of interest visually, were collected from surfaces of the various cores or from portions of the cores and were tested in the DSC. Only a few results will be cited; some of the resultant thermograms were similar to thermograms found for the samples from the other sets, while others were devoid of thermal features.

Core 6.1 was received with samples 5.1 and 5.2 (on September 29, 1988). It consisted mostly of dark gray sandy material and some limestone. Thermograms of two samples scraped from the core are presented in figure 17. The first thermogram is essentially representative of inert matter and does not contain any significant endotherms or exotherms, while the second thermogram indicates the presence of some carbonaceous matter.

Core 6.2 from heated area 1 was analyzed next. A very small sample, which was mostly soft coal, yielded the familiar coal thermogram (third thermogram in figure 17), while a sample scraped from a shale portion showed minimal thermal activity, as observed in the fourth thermogram in the figure. There was extraneous yellowish white material on one edge of the core. The material was removed, and a relatively large sample was tested in the DSC. The endotherm, with a peak at 132° C, as shown in the first thermogram in figure 18, is evidence of the presence of oxidation products. The second thermogram in the figure, of another specimen, from the shaley portion of the core, contained a small exotherm with its peak at 432° C. This is possibly due to the crystallization of a small amount of hydrous ferrous oxide to α-Fe_2O_3 and is likewise an indication of oxidation products being present. As mentioned previously, the temperature at which this phase change occurs can vary, depending on sample composition.
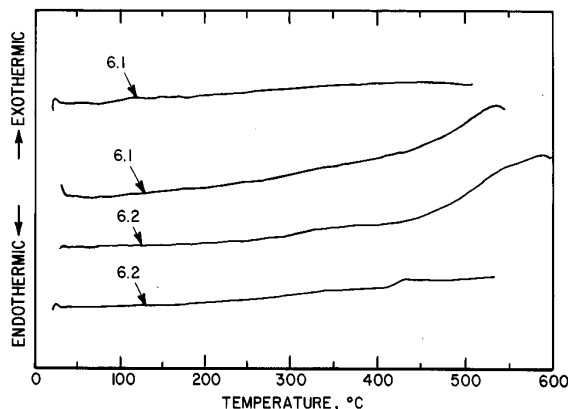
Figure 17.—DSC thermograms of cores 6.1 and 6.2 from set 6.
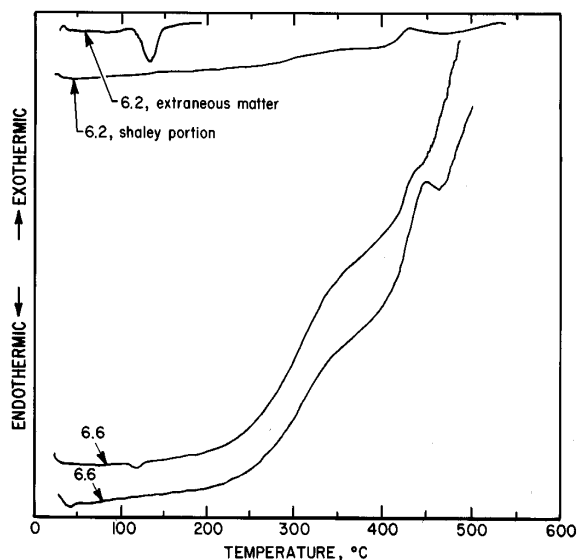
Figure 18.—DSC thermograms of cores 6.2 (extraneous matter and shaley portion) and 6.6 from set 6.

Three cores, 6.3, 6.4, and 6.5, were obtained from heated area 3. One sample, from core 6.4, showed the regular coal thermogram, while another sample was essentially without thermal features. These thermograms are not shown. Thermograms of a few samples from core 6.5 were also devoid of the exothermic behavior associated with carbonaceous material, although there was some endothermic activity, characteristic of the oxidation products, with endothermic peaks at 122° and 138° C. These thermograms are also not presented in this report.

Core 6.6, from heated area 4, contained both coal and shiny, metallic crystals, which were seen in the microscope. All of these samples gave thermograms similar to other thermograms of samples containing pyrite, with the jagged features and the endotherm at about 460° C, as observed in the third and fourth thermograms in figure 18.

Qualitative Chemical Analyses

Both the appearance of the samples and the thermal analysis results presented a strong possibility that, in addition to coal oxidation, or jointly with it, oxidation of sulfide compounds occurred in the mine. Ambient oxidation, or weathering, of pyrite has been studied in great detail, and much information is available in the literature. Major oxidation products include H_2SO_4 and iron sulfates, including ferrous sulfate ($FeSO_4 \cdot XH_2O$) and ferric sulfate [$Fe_2(SO_4)_3 \cdot XH_2O$]. It is easy to identify the anion (SO_4^{2-}) and cations (Fe^{2+} and Fe^{3+}) formed, as well as the strongly acidic conditions that result.

To test samples for the presence of the oxidation products, the samples were mixed with water and filtered. The pH values of the filtered solutions were determined, and various indicators were added to aliquots of the filtrates. Characteristic results, which were obtained for many of the samples from the different locations, are shown in table 1.

Table 1.—Identification of oxidation products by qualitative wet chemical analysis

Indicator	End result	Meaning
Aqueous barium chloride ($BaCl_2$) solution.	White precipitate of barium sulfate ($BaSO_4$).	Sulfate ions present.
Ammonium hydroxide (NH_4OH).	Gelatinous precipitate due to formation of hydrous iron compounds.	Fe ions present.
Hydrochloric acid (HCl).	Distinctive yellow color of iron chloride ($FeCl_3$).	Fe^{3+} ions present.
Aqueous ammonium thiocyanate (NH_4SCN) solution.	Distinctive deep red color of iron thiocyanate [$Fe(SCN)_3$].	Do.
Aqueous potassium ferricyanide [$K_3Fe(CN)_6$] solution.	Distinctive deep blue color of iron ferricyanide, $Fe_3[Fe(CN)_6]_2$.	Fe^{2+} ions present.

When oxidation products were present, the pH values of the water eliminate extracts were usually 2 or less; that is, they were highly acidic owing to the presence of H_2SO_4. The H_2SO_4 that forms during pyrite oxidation reacts with carbonates associated with the coal or shale. $CaCO_3$ converts to calcium sulfate or its hydrated form, $CaSO_4 \cdot 2H_2O$, the presence of which is therefore also associated with coal

pyrite oxidation. The ferrous and ferric sulfate products also form many hydrates, among which are szomolnokite ($FeSO_4 \cdot H_2O$), rozenite ($FeSO_4 \cdot 4H_2O$), $FeSO_4 \cdot 5H_2O$, $FeSO_4 \cdot 7H_2O$, and $Fe_2(SO_4)_3 \cdot 9H_2O$. Such hydrated salts lose their water of hydration when heated, usually sequentially, depending on the heating rate. These events were evident in the many thermograms of the various samples from the mine.

Reactions representing pyrite oxidation, such as

$$FeS_2 + 7/2O_2 + H_2O \rightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+, \quad (A)$$

$$Fe^{2+} + 1/4O_2 + H^+ \rightarrow Fe^{3+} + 1/2H_2O, \quad (B)$$

and

$$FeS_2 + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+}$$

$$+ 2SO_4^{2-} + 16H^+, \quad (C)$$
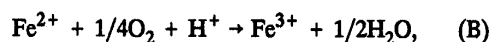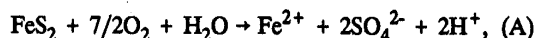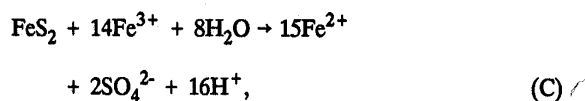
only describe the global events. Many more reactions are involved, and the kinetics and mechanism, although fairly well understood, are not known in detail. What is known, in addition to the fact that acid, iron sulfates, and hydrous iron oxides are the main reaction products, is that the process is highly exothermic, with the overall rate increasing with increasing temperature. If the heat cannot be dissipated, spontaneous combustion will occur.

Instrumental Analyses

A few selected samples, after suitable preparation, were analyzed by X-ray diffraction or by ICAP atomic emission to obtain additional data on their compositions and for verification of some of the results of the other tests. Some characteristic results of interest from sample sets 1, 3, and 6 are given here:

Set 1.—The red paste (sample 1.2) from set 1 was evaluated by X-ray diffraction and found to contain Fe_2O_3, $FeSO_4 \cdot 5H_2O$, $KFe_3 \cdot (SO_4)_2 \cdot (OH)_6$, and quartz ($SiO_2$). The three iron compounds are frequently found among the oxidation products of pyrite. The same red paste sample was treated with HCl, and the filtrate was analyzed by ICAP atomic emission. The relative amounts, in parts per million, of the main cations present in the filtrate were 204 Fe, 10 Al, and 5 each Ca and Mg, indicating that iron compounds were the major constituents. The presence of some clay was shown by the Al ions.

White and orange extraneous material from the various surfaces of the samples was collected, dissolved in water, and filtered. The clear solutions, analyzed in the same

manner, contained essentially the same cations. In the solution from the white material, the relative proportions, in parts per million, were 8.0 Fe, 5.5 Al, 0.8 Ca, 0.9 Mg, and 0.2 Na. For the orange material, the corresponding relative concentrations, in parts per million, were 2.6 Fe, 0.3 Al, 0.4 Ca, 0.1 Mg, and 0.8 Na. These results show that iron compounds were present in most of the samples, and especially in the oxidation products. The presence of clay in the samples is indicated by the aluminum ion.

Set 3.—The white material on the surface of the coal seen in figure 3, center (sample 3.2C), was dissolved in HCl and the solution was filtered. Analysis of the filtrate by ICAP atomic emission showed the presence of Ca (340 ppm), Mg (11 ppm), and Fe (4 ppm). The sample was probably rock dust, which was used by the mine to cover heated areas. The powder did not dissolve in water, and when it reacted with the acid, bubbles evolved, evidence of the presence of carbonate.

The dark orange material on the large chunk (figure 3, top, sample 3.1A) was similarly treated with dilute HCl and filtered. The solution contained the following relative concentrations, in parts per million: 170 Ca, 79 Fe, 7 Mg, and 5 Na. Based on the color and texture of the sample, its ease of solubility in HCl, and proportions of cations in the solution, this sample contained a mixture of rock dust and iron oxidation products.

Set 6.—Core 6.3 from heated zone 3 had green material on one surface. The material was scraped off and treated with acid, and the filtrate was analyzed. Iron was the most abundant ion found.

Coal Analyses

As the evidence for the presence of pyrite oxidation products and pyrite in many of the samples accumulated, it became desirable to quantify the amount of pyritic sulfur in at least a few of the samples. The samples analyzed included samples 5.1 and 5.2, samples from cores 6.3 and 6.5 (from the vicinity of the third heating), and a sample from core 6.6, which was obtained from the area of the fourth heating. Proximate and ultimate analyses of the samples were also obtained, to determine if the pyritic matter was associated with samples containing mainly carbonaceous matter or ash.

The results of the analyses are presented in table 2. Two of the samples, sample 5.1 and core 6.6, contained relatively large amounts of pyritic sulfur. The presence of pyritic sulfur in the mine was thus substantiated. Its absence from some of the samples could be a function of its distribution mode in the mine and sampling location and sampling for the chemical analysis. At least for these samples, it appeared that the pyritic matter was present mainly with the carbonaceous matter.

Table 2.—Coal analyses of as-received samples from heated areas

(Weight percent unless otherwise specified)

	Set 5[1]		Set 6		
	Sample 5.1	Sample 5.2	Core 6.3[2]	Core 6.5[2]	Core 6.6[3]
Proximate analysis:					
Moisture	3.15	5.53	0.25	0.23	0.90
Volatile matter	23.03	12.43	5.09	8.90	16.34
Fixed carbon	48.85	16.50	5.39	.00	29.75
Ash	24.97	65.54	89.27	91.27	53.01
Ultimate analysis:					
Hydrogen	3.68	2.33	0.88	0.48	2.57
Carbon	53.11	19.35	6.88	2.82	33.79
Nitrogen	1.03	0.47	0.13	0.10	0.64
Sulfur	7.97	2.05	0.72	0.06	7.58
Oxygen	9.24	10.26	2.12	5.27	2.41
Ash	24.97	65.54	89.27	91.27	53.01
Forms of sulfur:					
Sulfatic	2.62	1.09	0.03	NA	0.19
Pyritic	4.53	0.87	0.62	NA	7.02
Organic	0.82	0.09	0.07	NA	0.37
Heating value ... Btu/lb ..	9,534	3.169	1.035	NA	6.017

NA   Not analyzed.
[1]Collected in expanded seam zone.
[2]Drilled in heated area 3.
[3]Drilled in heated area 4.

Sealed Flask Oxygen Adsorption Tests

Samples 5.1 and 5.2 were used, as received, for the tests in the sealed flasks. The samples were neither ground nor sieved prior to the test because the amounts available were small and their particle size distribution was similar to the size range prescribed for the test, but somewhat coarser. They were weighed and sealed in the flasks, and after 10 days, gas samples were taken for analysis by gas chromatography. Pressures were read in each flask during the test period.

Results of the gas analyses are shown in table 3, together with results from similar sealed flask tests conducted with a coal obtained from the same area, from a seam located above the seam of the mine. Both coals have similar coal analyses. The sample from the higher seam was ground and sieved and immediately sealed in the flasks. Two different fractions were tested.

Samples 5.1 and 5.2, which were coarser than the other samples shown in the table, adsorbed some O_2 and emitted small amounts of CO_2 and much smaller amounts of CO; the amount of CH_4 evolved was minute. In all probability, these samples adsorbed some O_2 before the tests, whereas the coal sample from the upper seam was carefully packed, as large chunks, and sealed in plastic bags to minimize exposure to air. Also, samples 5.1 and 5.2 were not clean coal samples, but contained large amounts of inert material (ash), 25 and 66 wt pct, respectively, as compared with 12 wt pct for the sample from the upper seam. All the coal seams located in this coal basin contain large amounts of CH_4. The CH_4 from samples 5.1 and 5.2 was probably expelled prior to the tests. The quantity of O_2 adsorbed by the samples is representative of coals with low self-heating tendencies. The pressure drops and pressure drop rates measured in the flasks with miniature pressure transducers were likewise indicative of coals with low self-heating propensities. The quantities of CO emitted by samples 5.1 and 5.2 were smaller by an order of magnitude than the quantities emitted by the sample of the coal from the upper seam. Since the amount of CO emitted depends on the extent of coal oxidation, these results suggest that the samples were exposed to air prior to the tests. Also, it is not possible to determine from the results the fraction

of the O_2 that is adsorbed by the pyrite and the fraction that is adsorbed by the coal. Sample 5.1, which contained 4.5 pct pyritic sulfur and 53.1 pct C, adsorbed less O_2 than sample 5.2, which contained only 0.87 pct pyritic sulfur and only 19.4 pct C (table 2). However, sample 5.2 contained more moisture (5.5 pct) than sample 5.1. Tests with various pyrites in the sealed flask have shown that the presence of moisture is paramount for O_2 adsorption. Without sufficient moisture, the rate of O_2 adsorption by pyrite is nil.

Sulfur dioxide (SO_2) is not usually reported as one of the oxidation products of pyrite at ambient temperature. Braley [13] suggested its formation during oxidation of dry pyrite, as follows:

$$FeS_2 + 3O_2 \rightarrow FeSO_4 + SO_2 \uparrow. \qquad (D)$$
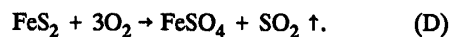
The gaseous atmospheres in the flasks were tested for the presence of SO_2. Only a trace amount (1 ppm) was detected in the flask with sample 5.1, while none was found in the flask with sample 5.2. These samples were not dried prior to the test; both samples contained moisture. SO_2 was not expected to be present, as indeed was the case.

SAMPLES FROM UNHEATED AREAS

Visual Observations

The samples were scanned visually for the presence of any unique features, such as pyrite, sulfur, or oxidation products. The samples were also observed in the optical microscope. In general, no outstanding features were seen.

Coal Analyses

Coal analyses were obtained for many of the samples from the unheated areas. Results of these analyses are summarized in table 4. In addition to ultimate and proximate analyses, many of the samples were tested for forms of sulfur. As can be seen in the table, each suite of samples contained at least a few samples with relatively large

Table 3.—Gas analysis results for sealed flask tests

(Volume percent unless otherwise specified)

Sample	Particle size, μm	O_2	CO_2	CO	CH_4	O_2 adsorbed
5.1	NA	17.4	0.18	0.0083	0.0043	3.6
5.2	NA	15.2	.56	.0025	.0027	5.8
Upper seam coal[1] . .	1,200 × 600	12.3	.23	.0240	16.21	8.7
	600 × 300	13.2	.21	.0268	13.22	7.8

NA   Not analyzed.

[1]A sample of coal from the upper seam was ground and sieved. The two designated fractions were then tested, each in a flask.

amounts of pyritic sulfur, as high as 10 wt pct (or 18.71 wt pct FeS₂). For example, samples 7.5 and 7.7 from the first group of samples (collected February 28, 1989) contained 4.60 and 4.39 wt pct pyritic sulfur (8.6 and 8.2 wt pct FeS₂, respectively), while samples 7.2 and 7.4 from the same group contained only minor amounts. In general, large amounts of pyritic sulfur were found in the same zones for all the sets of samples.

None of the samples contained noticeable amounts of sulfate (or sulfatic matter); that is, none of the samples have undergone appreciable oxidation. Many of the samples contained large amounts of ash; this is likewise reflected in the low heating values of many of these samples.

Many of the samples from the unheated areas were also examined by the Bureau's Twin Cities Research Center.[6] The sulfur content of these samples was measured and the results were in very good agreement with both the coal analyses and H₂O₂ test results reported here.

Thermal Analysis

The identification and quantification of pyrite was mainly done by chemical analysis. However, its presence in

various samples was also established by thermal analysis in the DSC. The main purpose of analyzing the samples from the unheated areas in the DSC was to rapidly identify the presence and thereby the location of oxidation products of pyritic matter.

All the samples from the first group of samples (collected February 28, 1989) were analyzed in the DSC. Very small samples, of the order of 1 mg in size, were used. The thermograms for samples 7.1 to 7.7 are presented in figure 19. None of the thermograms show evidence that oxidation products are present in these samples, as there are no endotherms. The first four thermograms, samples 7.1 to 7.4, contain the usual two exotherms associated with coal, while the other three, samples 7.5 to 7.7, have an additional plateau or shoulder, at about 475° C. Somewhat larger samples of 7.2 and 7.7 were then tested with the same results, as depicted in the thermograms in figure 20. Only the thermogram for sample 7.7 displays an endotherm at about 478° C, which is thought to be indicative of the presence of pyritic matter. These results, suggesting the presence of pyrite in samples 7.5, 7.6, and 7.7, as deduced from the DSC thermograms, agree with coal analysis results for 7.5 and 7.7. Likewise, the low pyritic content in samples 7.1, 7.2, 7.3, and 7.4, based on DSC thermograms, again parallel coal analyses for samples 7.2 and 7.4.

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[6]Letter reports prepared in 1988-89 by G. W. Reimers, Twin Cities Research Center; available from BuMines, Minneapolis, MN.

Table 4.—Analyses of as-received samples from unheated areas (sets 7 to 8, 10 to 11)

(Weight percent unless otherwise specified)

Set and date collected	Sample	Heating value, Btu/lb	Proximate analysis				Ultimate analysis					Forms of sulfur		
			Mois-ture	Volatile matter	Fixed C	Ash	Hydro-gen	Car-bon	Nitro-gen	Sul-fur	Oxy-gen	Sul-fatic	Py-ritic	Organ-ic
Set 7:														
Feb. 28, 1989 ..	7.2	8,189	0.49	17.28	38.78	43.45	2.92	47.74	0.91	0.39	4.59	0.03	0.08	0.28
	7.4	10,260	.67	20.42	47.67	31.24	3.57	58.64	1.13	.73	4.69	.02	.28	.43
	7.5	6,045	.55	15.73	29.01	54.71	2.57	34.49	.70	4.66	2.87	.04	4.60	.02
	7.7	6,260	.89	15.79	29.69	53.63	2.55	35.01	.78	4.45	3.58	.04	4.39	.02
Set 8:														
Mar. 20, 1989 ..	8.1	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	.06	.75	.30
	8.2	3,901	.75	13.12	19.52	66.61	NA	NA	NA	NA	NA	.18	8.42	.00
	8.3	5,274	.90	15.19	24.50	59.41	NA	NA	NA	NA	NA	.09	3.44	.00
	8.4	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	.03	1.31	.00
	8.5	3,536	.99	12.04	15.96	71.01	NA	NA	NA	NA	NA	.05	1.47	.04
Set 10:														
Apr. 21, 1989 ..	10.1	NA	.82	NA	NA	NA	NA	NA	NA	NA	NA	.03	.11	.20
	10.2	NA	.99	NA	NA	NA	NA	NA	NA	NA	NA	.05	.17	.47
	10.3	9,359	1.00	20.51	44.08	34.41	3.38	49.94	.68	10.70	.89	.27	10.07	.36
	10.4	NA	1.18	NA	NA	NA	NA	NA	NA	NA	NA	.20	7.03	.22
	10.5	NA	1.30	NA	NA	NA	NA	NA	NA	NA	NA	.01	3.02	.33
	10.6	5,631	1.43	14.90	26.78	56.89	2.56	31.87	.88	3.87	3.93	.16	3.63	.08
Set 11:														
June 9, 1989 ..	11.1	10,173	1.48	20.62	47.17	30.73	NA	NA	NA	NA	NA	.14	.43	.49
	11.2	11,413	1.66	22.52	54.64	21.18	NA	NA	NA	NA	NA	.49	8.08	1.08
	11.3	4,684	1.28	14.16	22.83	61.70	NA	NA	NA	NA	NA	.27	3.97	.12
	11.4	11,609	1.30	22.85	53.93	21.92	NA	NA	NA	NA	NA	.19	3.64	.86

NA   Not analyzed.

18
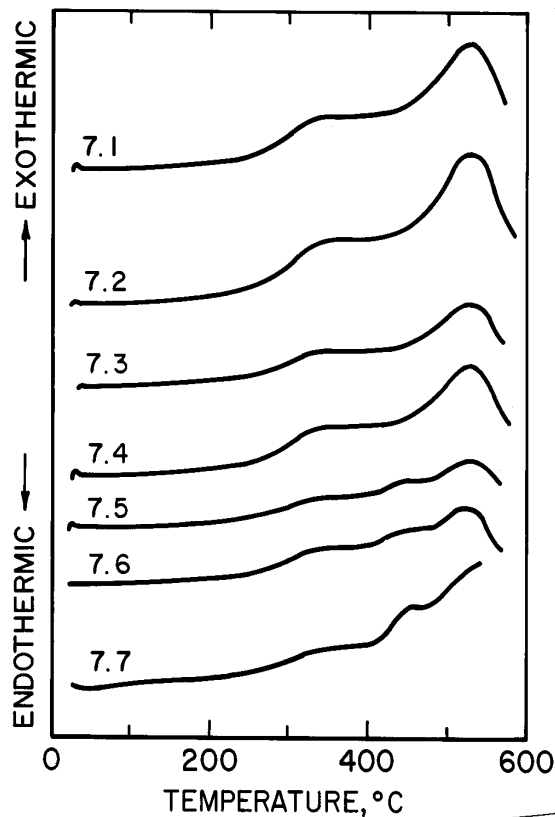
Figure 19.—DSC thermograms of very small amounts of samples 7.1 to 7.7 from set 7.

Figure 20.—DSC thermograms of samples 7.2 and 7.7 from set 7.

The results presented here indicate that the presence of sulfidic or pyritic matter may be identified even in small samples, by the presence of the plateau, at about 460° to 480° C, if the pyrite is well distributed throughout the sample, fine in size, and found in relatively large amounts. Larger samples are needed to see the jagged pattern, as well.

Adiabatic Oven Tests

The minimum SHT of a coal sample is determined in tests in the adiabatic oven. Previously tested coal samples, which were obtained from various seams from the same area, had minimum SHT values of 135° C (1).

The tests in the adiabatic oven were conducted with two goals in mind. The first goal was to see if the samples had about the same minimum SHT values as previously found. The second goal was to assess the effect of pyrite in the samples on the minimum SHT values. Since it was postulated that the presence of pyrite might reduce the minimum SHT values of those samples containing pyrite, tests

were at first conducted at temperatures much lower than 135° C. The first batch of samples (collected February 28, 1989) was tested at an initial starting temperature of 70° C, and none of the samples underwent thermal runaway. Because of the small increase in temperature (about 3° C) of the samples during the tests, the next test, with sample 7.5 from the same batch, was started at a temperature of 95° C, but the sample did not undergo thermal runaway. A fresh sample was then tested at a starting temperature of 130° C, and it did undergo thermal runaway. Temperature-time traces for the two tests, at 95° and 130° C, are presented in figure 21. These traces are typical for tests in which samples do and do not undergo thermal runaway. The O_2 and CO concentration profiles of the exit gas stream were also recorded for each test. The O_2 and CO concentration profiles in the self-heating test of sample 7.5, at the initial temperature of 130° C, are also shown in the figure. The O_2 concentration dropped slightly, while CO concentration showed a rapid rise at the start of the test and rose slowly thereafter.

Samples collected on March 20 and 28, 1989, were tested next in the adiabatic oven at a starting temperature of 100° C, while samples from the last two batches, April 21, and June 9, 1989, respectively, were tested at 110° C. Results of all the tests in the adiabatic oven are summarized

Figure 21.—Temperature-time traces for sample 7.5 from set 7 in self-heating tests in adiabatic oven at initial temperatures of 95° and 130° C (top), and O_2 and CO concentration profiles in self-heating test at an initial temperature of 130° C (bottom).

Table 5.—Results of adiabatic oven tests (sets 7 to 11)

Set and date collected	Sample	Initial temperature, °C	Maximum temperature rise, °C
Set 7:			
Feb. 28, 1989 ..	7.1	70	2.6
	7.2	70	2.5
	7.3	70	2.4
	7.4	70	2.8
	7.5	70	2.5
	7.5	95	2.0
	7.5	130	(^{1})
	7.6	70	2.6
	7.7	70	3.0
Set 8:			
Mar. 20, 1989 ..	8.1	100	2.5
	8.2	100	2.4
	8.3	100	1.6
	8.4	100	2.4
	8.5	100	1.8
Set 9:			
Mar. 28, 1989 ..	9.3	100	6.1
	9.3	120	(^{1})
Set 10:			
Apr. 21, 1989 ..	10.1	110	4.0
	10.2	110	3.1
	10.3	110	15.2
	10.4	110	3.1
	10.5	110	4.0
	10.6	110	4.0
Set 11:			
June 9, 1989 ...	11.1	110	7.0
	11.1	120	(^{1})
	11.2	110	(^{1})
	11.3	110	6.0
	11.4	110	(^{1})

[1]Sample underwent thermal runaway.

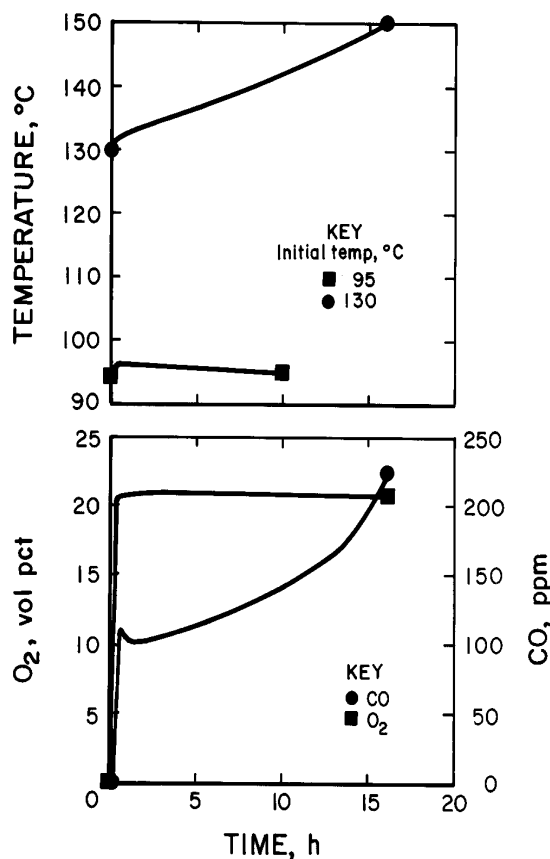in table 5. As can be seen from the data, none of the samples that were tested at 100° C, or at lower temperatures, underwent thermal runaway, and only 2 of 10 samples that were tested at 110° C achieved thermal runaway from this starting temperature. These two samples were samples 11.2 and 11.4 from the floor channel cut on June 9, 1989. These samples contained 15.1 and 6.8 wt pct FeS_2, and 21.2 and 21.9 wt pct ash, respectively. Of the samples analyzed by coal analyses, these two contained the least amounts of ash and the highest amounts of fixed carbon and volatile matter. Sample 11.1, from the same floor channel, with an ash content of 30.7 wt pct, but with little pyrite, self-heated at 120° C, and did not self-heat at 110° C. Temperature-time traces for these two tests, as well as CO and O_2 concentrations for the self-heating test at an initial temperature of 120° C, shown in figure 22, are similar to the traces in figure 21.

Sample 9.3 (collected March 28, 1989) self-heated and reached thermal runaway from a starting temperature of

120° C, whereas at 100° C, the maximum temperature rise was 6.1° C. The sample was not tested at 110° C. This sample was not analyzed; its fixed carbon, ash, and pyritic sulfur concentrations are not known. Thus, comparisons cannot be drawn.

Sample 10.3 (collected April 21, 1989), tested at 110° C, had the highest maximum temperature rise, 15.2° C, of all the samples tested at this temperature that did not undergo thermal runaway, as seen in table 5. Based on results from many other tests, the probability is high that this sample would have undergone thermal runaway at 120° C. Of all the samples in table 4, it had the highest amount of pyritic sulfur (10.07 wt pct) or pyrite (18.84 wt pct). Its ash content was 34.41 wt pct, while fixed carbon and volatile matter concentrations were 44.08 and 20.51 wt pct, respectively.

With the exception of sample 9.3 (collected March 28, 1989), whose composition was not known, the samples that
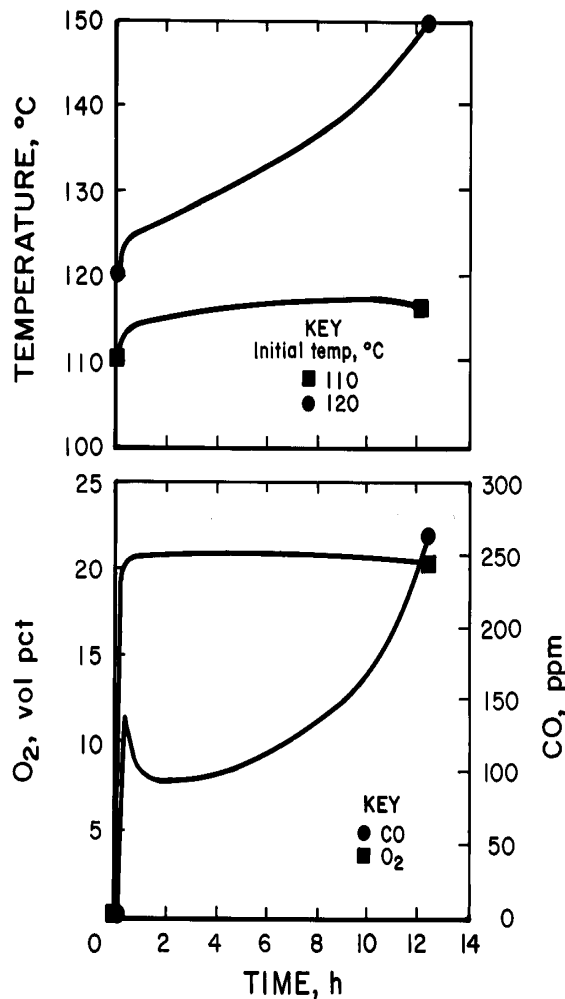
Figure 22.—Temperature-time traces for sample 11.1 from set 11 in self-heating tests in adiabatic oven at initial temperatures of 110° and 120° C (top), and O_2 and CO concentration profiles in self-heating test at an initial temperature of 120° C (bottom).

underwent thermal runaway had the higher heating values, fixed carbon, and volatile matter. More systematic experiments, however, are needed before the effects of ash concentration on the minimum SHT of a mine sample can be quantitatively determined. The standard test conditions in the adiabatic oven test are not conducive to the oxidation of pyrite. Pyrite oxidizes in humid air, initially at a slow rate. The ferrous sulfate that is formed oxidizes next, also at a slow rate, to ferric sulfate. Once ferric ions are present, they oxidize pyrite at an accelerated rate (see reactions A to C) and, concurrently, the temperature rises.

Large amounts of moisture are required for the formation of the sulfates, and most likely, sufficient moisture was not available in the adiabatic oven tests. Examination of the samples after the tests did not show any oxidation products. Specific experimental conditions must be devised that will facilitate pyrite oxidation and the quantitative identification of its effects on the minimum SHT of a mine sample.

None of the mine samples tested are considered to be highly reactive to self-heating compared with the self-heating of coal; coals that have minimum SHT's >100° C are considered as having a low spontaneous combustion potential (1). These results, then, give additional credence to the idea of pyrite itself being the primary or the initial material to self-heat in the mine. The results also indicate that adiabatic oven tests with the present experimental conditions and procedures are not able to assess the effect of pyrite on the self-heating process of the mine sample and will need to be changed.

Hydrogen Peroxide Reactivity

H_2O_2 is a strong oxidizer and reacts with both organic and inorganic materials. It has been used in studies of oxidation of coals of various ranks (14), as well as for the isolation of mineral matter from coal (15). In the presence of ferrous and ferric ions, H_2O_2 undergoes catalytic reduction and oxidation simultaneously; the combined reactions are identified as the Fenton reaction. When coal contains pyrite, the pyrite decomposes in the H_2O_2, and the iron ions, in turn, catalyze the decomposition of the peroxide. The rate of the overall reaction depends on the concentration of the pyritic matter, as well as on other factors, including particle size of the test sample and the pyritic matter in it, H_2O_2 concentration, and starting ambient temperatures.

The results of the tests with many of the samples from the unheated areas are given in table 6. Temperature increases were related to the concentrations of pyrite in the samples, but a better correlation existed between the time to reach maximum temperature and the concentration of pyritic sulfur in the sample, as determined in the coal analyses (shown in figure 23). The data can be expressed by the following formula of a power fit curve:

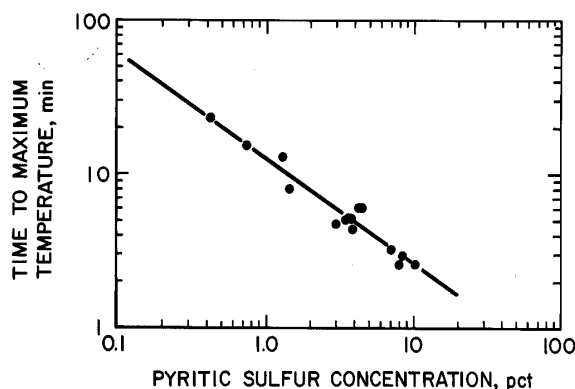$$T = 12.61 \times P^{-0.68}, \qquad (1)$$

Figure 23.—Pyritic sulfur concentrations in mine samples as a function of time to maximum temperature in H_2O_2 reactivity test.

where T = time to maximum temperature, min,

and P = pyritic sulfur concentration, wt pct.

The correlation coefficient was found to be 0.9399. This formula can be used to estimate the pyritic sulfur concentration of samples from other areas of the mine. Considering the large variation in the composition of the many samples, the results are quite satisfactory.

The results from the chemical analyses and the H_2O_2 reactivity tests show that pyritic matter was more prevalent in certain areas of the floor strata, such as zones B and C, of the samples collected during February and March 1989. Samples from zones C, D, E, and F, obtained April 21, 1989, and samples from zones B, C, and D obtained June 9, 1989, all contained pyrite to various degrees.

Table 6.—Results of H_2O_2 reactivity tests with samples from unheated areas (sets 7 to 11)

Set and date collected	Sample	Maximum temperature increase, °C	Time to maximum temperature, min	Pyritic sulfur concentration,[1] wt pct
Set 7:				
Feb. 28, 1989 ..	7.1	0	NA	NA
	7.2	0	NA	0.08
	7.3	0	NA	NA
	7.4	0	NA	.28
	7.5	63	6	4.60
	7.6	62	9	NA
	7.7	64	6	4.39
Set 8:				
Mar. 20, 1989 ..	8.1	56	15	.75
	8.2	67	3	8.42
	8.3	63	5	3.44
	8.4	60	13	1.31
	8.5	61	8	1.47
Set 9:				
Mar. 28, 1989 ..	9.1	48	60	NA
	9.2	65	4	NA
	9.3	64	3	NA
	9.4	60	7	NA
	9.5	58	15	NA
	9.6	58	15	NA
Set 10:				
Apr. 21, 1989 ..	10.1	0	NA	.11
	10.2	0	NA	.17
	10.3	67	2.7	10.07
	10.4	65	3.2	7.03
	10.5	61	4.7	3.02
	10.6	61	5.1	3.63
Set 11:				
June 9, 1989 ..	11.1	51	23.0	.43
	11.2	63	2.6	8.08
	11.3	60	4.4	3.97
	11.4	60	5.2	3.64

NA   Not applicable or not analyzed.
[1]Chemical analyses (see table 4).

SUMMARY

The samples that were collected after the first heating, especially the red, pastelike sample, gave strong indication that oxidation processes were of concern in the mine. The extraneous matter on the surfaces of the solid samples from the first heating and the hue of the red paste were the first visible evidence of the presence of oxidation products associated with oxidation of a coal that contains pyrite. Samples collected after the other heatings presented similar evidence.

Tests in the DSC revealed the presence of many hydrated compounds in the extraneous matter, as well as in other portions of the samples themselves. In addition, the unique features of the thermograms pointed to the presence of unoxidized, reactive pyrite in the samples. Since oxidation products of pyrite include many hydrated sulfate salts and hydrous iron oxides, the combined DSC results presented quite strong evidence, though indirect, that pyrite was present in areas of the mine and that in some of these areas it had undergone oxidation.

Qualitative chemistry tests were conducted next and showed conclusively the presence of relatively large amounts of sulfate, ferrous, and ferric ions in the samples, especially in the extraneous matter, all the resultant products of pyrite oxidation. Additionally, the high acidity associated with some of the samples was further witness to the same process. These results were also supported by the results from instrumental analyses of a few of the samples that showed iron cations to be the most prevalent.

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Finally, coal analyses verified the presence of large amounts of pyritic sulfur in at least some of the samples from both the heated and unheated areas.

Results from the adiabatic oven tests showed that the minimum SHT of the samples that underwent thermal runaway was >100° C, regardless of the pyrite content. Thus, the tests indicate that the carbonaceous matter in the samples is not highly reactive. Some of the samples tested, which had high percentages of pyritic matter, but also contained large amounts of ash, may not have had sufficient organic carbon for thermal runaway to occur in the adiabatic oven tests. Thus, at present, the role of pyrite in lowering the minimum SHT value of a mine sample has not been clearly established by these adiabatic oven tests.

Considering all the accumulated data, along with the low spontaneous combustion potential of the mined coal and the subfloor carbonaceous matter, the conclusion was reached that the expanded seams beneath the mine floor contain amounts of pyrite in such forms (size and morphology) that enhance their oxidation potential. Furthermore, the oxidation of the pyrite on exposure to the high flow of air and moisture, especially when the floor heaves, brings about increases in the temperature, such that the oxidation of carbonaceous matter in contact with the pyrite is accelerated.

Pyrite has been cited for many years as one of the factors capable of affecting the spontaneous combustion of coal. This is one case in which it has had a major effect. Other coal mines containing substantial amounts of pyrite may be worked in the future.

Procedures for easily identifying the presence of pyritic matter and for evaluating its approximate concentration, as well as assessing its effect on the self-heating tendency of the coal associated with it are needed. In addition to coal analysis, other procedures, such as careful visual observations, thermal analysis, and tests with H_2O_2, can help in this regard. These tests require the acquisition of samples ahead of mining so that locations rich in pyrite can be identified.

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APPENDIX.—DESCRIPTION OF ALL SAMPLES COLLECTED IN MINE

Table A-1.—Samples collected after first heating (set 1)

(Heating discovered November 1986)

Sample	Description
1.1	Mixture of coal, shale, rock.
1.2	Red, claylike paste.
1.3	Mixture of coal, shale, rock.
1.4	Do.

Table A-2.—Samples collected after second heating (set 2)

(Heating discovered February 1988)

Location and sample	Description	Depth below surface, in
Heated area 2:[1]		
2.1:[2]		
A	Coal	NAp
B	Rock dust with some coal ..	NAp
C	Coal, shale	NAp
2.2:[2]		
A	Rock, coal from mine floor ..	NAp
B	Rock from roof over area ...	NAp
C	Rock dust from area	NAp
D	Ashes from smoldering area[3]	NAp
E	Rock from roof over area, shale, coal.	NAp
2.3[4]	Wood-crib block	NAp
2.4:[2]		
A	Coal	NAp
B	Coal, shale; red patches visible.	NAp
Trench:		
2.5	Shale, coal, rock (hard shale).	0-15
2.6	Boney coal, rock (hard shale), coal.	15-30
2.7	Bright coal (reaction zone), shale.	30-45
2.8	Rock (shale), main moisture zone.	45-60

NAp   Not applicable.
[1]5,000 ft from area of 1st heating.
[2]See figure 1.
[3]Temperatures above 300° C were measured in two locations in the area.
[4]See figure 2.

Table A-3.—Samples collected after third (set 3) and fourth (set 4) heatings

(Heatings discovered August 1988)

Sample	Description	Location
SET 3[1]		
3.1:		
A	Large coal piece with oxidation products on surface. Coal-shale powder or dirt.	One crosscut away from location of 1st heating. Grab samples from trench, 24 in below surface.
B	Broken coal pieces and coal powder.	Do.
3.2:		
A	Small pieces of coal showing oxidation products.	Do.
B	Black coal powder	Do.
C	White powder on top of coal and rock pieces.	Do.
3.3:		
A	Large rock-coal pieces with oxidation products on surface.	Do.
B	Dark gray-black powder	Do.
C	Shiny coal powder scraped from back of large piece in A.	Do.
3.4:		
A	Coal pieces covered with rock dust.	Do.
B	Rock dust containing some coal and possibly other compounds.	Do.
SET 4[2]		
4.1	Coal pieces. One large shale-like chunk covered with white and purple-red matter.	About 1,800 ft from area of 1st heating.

[1]See figure 3.
[2]See figure 4.

Table A-4.—Samples collected from expanded seam zone in northwest part of mine (set 5)

(Heating discovered August 1988)

Sample	Description	Depth below footwall, in
5.1	Coal, shale, rock; 1- to 25-mm-diam particles.	15
5.2	Coal, shale, rock; moist	50

Table A-5.—Various cores from mine (set 6)

Sample	Mine designation	Date received	Description of various portions	Location
6.1	Core 1	Sept. 29, 1988 ..	Dark gray sandy fireclay; some limestone	NA.
6.2	Core A	Dec. 1, 1988	Dark gray-black layered shale, compact; dark gray massive, sandy shale, churned; broken pieces and thin discs in places along core; some surfaces partially covered with white-yellow-orange material.	Heated area 1.
6.3	Core 1A	..do	Dark gray-black massive, sandy shale, churned; dark-gray layered shale, compact, churned; light gray-beige sandy shale; massive shale with limestone; broken chunks showing mica flakes; a few surfaces partially covered with yellow oxidation products.	Heated area 3.
6.4	Core 2A	..do	Top edge consisting of thin layer of coaly material; dark gray massive, sandy shale; gray massive, layered shale; gray massive shale with a few coal streaks and not much breakup.	Do.
6.5	Core 3A	..do	Dark gray massive, sandy shale; dark gray layered shale; gray layered shale with limestone; mica flakes in some areas; a few surfaces partially covered with yellow-orange-red material.	Do.
6.6[1]	Core 6	Dec. 29, 1988 ...	Black shale; gray-black shale with coal streaks; black shale with white streaks (either interbedded sandstone or limestone); gray shale with limestone nodules; a few surfaces partially covered with red material.	Heated area 4.

NA   Not available.
[1]Collected after 4th heating.

Table A-6.—Samples collected from unheated areas beneath the floor (sets 7 to 11)

Set and date collected	Sample	Zone	Location[1]
7: Feb. 28, 1989	7.1	A1	Floor channel; spad 6670.
	7.2	A2	Do.
	7.3	A3	Do.
	7.4	B1	Do.
	7.5	C1	Do.
	7.6	C2	Do.
	7.7	D1	Do.
8: Mar. 20, 1989	8.1	A1	Floor channel; spad 6523.
	8.2	B1	Do.
	8.3	C1	Do.
	8.4	D1	Do.
	8.5	E1	Do.
9: Mar. 28, 1989	9.1	A1	Do.
	9.2	A2	Do.
	9.3	B1	Do.
	9.4	C1	Do.
	9.5	D1	Do.
	9.6	E1	Do.
10: Apr. 21, 1989	[2]10.1	A	Floor channel; spad 4908.
	[2]10.2	B	Do.
	[3]10.3	C	Do.
	[2]10.4	D	Do.
	[2]10.5	E	Do.
	[3]10.6	F	Do.
11: June 9, 1989	[3]11.1	A	Floor channel; spad 5759.
	[3]11.2	B	Do.
	[3]11.3	C	Do.
	[4]11.4	D	Do.

[1]See figure 5.
[2]Zone sample.
[3]Coal, rock interface sample.
[4]Coal sample.