

**REPORT OF INVESTIGATIONS/1991** 

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# Applying Atmospheric Status Equations to Data Collected From a Sealed Mine, Postfire Atmosphere

By Robert J. Timko and R. Lincoln Derick

UNITED STATES DEPARTMENT OF THE INTERIOR



**BUREAU OF MINES** 

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**Report of Investigations 9362** 

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UNITED STATES DEPARTMENT OF THE INTERIOR Manuel Lujan, Jr., Secretary

BUREAU OF MINES T S Ary, Director

Library of Congress Cataloging in Publication Data:

Timko, Robert J.

Applying atmospheric status equations to data collected from a sealed mine, postfire atmosphere / Robert J. Timko and R. Lincoln Derick.

p. cm. - (Report of investigations; 9362)

Includes bibliographical references (p. 23).

Supt. of Docs. no.: I 28.23:9362.

1. Mine fires-Colorado-Paonia Region. 2. Combustion gases-Analysis. 3. Coal mines and mining-Colorado-Paonia Region. 4. Numerical calculations. I. Derick, R. L. II. Title. III. Series: Report of investigations (U.S. Bureau of Mines); 9362.

TN23.U43 [TN315] 622 s-dc20 [622'.4] 90-20193 CIP

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## UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

°F	degree Fahrenheit
ft	foot
ft <sup>3</sup> /min	cubic foot per minute
gal	gallon
h	hour
in	inch
in <sup>3</sup>	cubic inch

ų

lb	pound
lb/min	pound per minute
min	minute
pct	percent
ррт	part per million
S	second
st	short ton

## APPLYING ATMOSPHERIC STATUS EQUATIONS TO DATA COLLECTED FROM A SEALED MINE, POSTFIRE ATMOSPHERE

By Robert J. Timko<sup>1</sup> and R. Lincoln Derick<sup>2</sup>

### ABSTRACT

In early June 1986, an underground fire of unknown origin erupted in one of several entries of a coal mine located in southwestern Colorado. For a time, mine personnel aggressively fought the fire. However, control of the fire was later lost. To prevent further damage and reduce the possibility of an explosion, all portals and shafts to the mine were sealed.

The mine operator requested the U.S. Bureau of Mines' assistance in obtaining and analyzing mine fire gases taken from sampling ports placed through the mine seals, as well as down boreholes drilled after the fire. This report recounts activities within the first 2 years of the mine being sealed. It includes a description of gases analyzed and mine atmosphere status equations generated from the analyzed gases. The gases were analyzed by chromatography and included standard atmospheric gases as well as higher hydrocarbons that are found in postfire atmospheres. Nine equations were used to evaluate what was occurring within the sealed mine. Following a description of the rationale behind each equation, the 2-year trend is briefly analyzed.

<sup>1</sup>Physical scientist, Pittsburgh Research Center, U.S. Bureau of Mines, Pittsburgh, PA. <sup>2</sup>Manager, Safety and Loss Control, Cyprus Empire Coal Corp., Craig, CO. The Orchard Valley Mine, an underground coal mine, is located 5 miles north of the town of Paonia, CO. It was operated by Colorado Westmoreland, Inc. (CWI), Denver, CO, at that time a wholly owned subsidiary of Westmoreland Coal Co., Philadelphia, PA. In late 1988, the property and mineral rights were sold to Cyprus Coal Co., Denver, CO. The mine produced steam coal, which was primarily used for electric power generation. Approximately 2,200 st of coal were produced daily from two unit shifts.

The coal seam being mined is known as the D seam. It is a highly friable bituminous coal, has a vertical cleat, and a thickness varying from 8 to 26 ft. The seam slopes downward toward the north, and is interlaced with numerous vertical fault zones that have limited the practicality of mining in several sections. The seam is prone to spontaneous heating.

All mining was by the room-and-pillar method, using electrically powered continuous miners. Primary coal haulage and ancillary vehicular services were provided by diesel-powered equipment. Because of the diesel equipment and the propensity of the seam to heat spontaneously, a mine-wide carbon monoxide (CO) monitoring system continuously measured CO concentrations. This system had monitors and data storage centers located at the mine bath house and at a security guard house at the entrance to the mine property. Security personnel were responsible for CO monitoring during idle mine periods,

Mining was begun in 1976 with main entries driven north-northeastward from an intake portal and a belt portal (fig. 1). According to a previously completed Mine Safety and Health Administration (MSHA) mine ventilation survey, the mine layout was described as;

"a 9-entry mine with the beltline in the center entry. Main and panel entries were designated by sequential numbering either left or right of the beltline. Inby crosscut 9 the 9-entry system was separated into a 4-entry system and a 5-entry system extending in parallel. Separation was provided by a pillar which was approximately 200 ft wide and the 4-entry and 5-entry systems were connected together at about every 200 ft (every other crosscut). These connecting crosscuts had been left open at 5, 19, 31, 43, 71, 77, 80, and 81 crosscuts to provide for a balancing of airflows between the intakes. The return entries (3rd Left, 4th Left, 3rd Right, and 4th Right) were connected by overcasts at 44 crosscut. The belt entry was maintained on a neutral split and was the first entry on the right (east) side of the pillar.

Submains for panel development were either 5-entry of 4-entry systems" (1).<sup>3</sup>

An intake shaft and a fan shaft were sunk on the right side of the main entry, approximately 500 ft northeast of the belt and intake portals. Two 8-ft-diameter  $Joy^4$  axialvane fans pulled return air from the left and right sides of the mine.

Individual sections were developed on either side of the main entries on advance, creating mined-out abandoned areas or gobs, which required bulkhead structures to

<sup>4</sup>Reference to specific manufacturers does not imply endorsement by the U.S. Bureau of Mines.



Figure 1.-Orchard Valley Mine portal area affected by fire.

<sup>&</sup>lt;sup>3</sup>Italic numbers in parentheses refer to items in the list of references at the end of this report.

isolate them from the active mine. Four sealed gobs abutted the left mains; eight sealed gobs abutted the right. In addition, an active east-west submain extended southeast from the main entry about 1.25 miles inby the portal. This submain led to the only working section, located approximately 3.3 miles from the intake portal.

The U.S. Bureau of Mines was involved in a long-term research project which examined the relationship between the sizes of abandoned, sealed volumes and the potential for air-gas exchanges during atmospheric pressure fluctuations. Previous work had shown that explosive gas mixtures could readily accumulate immediately inby bulkheads which separated the abandoned volume from the active mine. The objectives of this research were to enable mine engineers to more effectively predict where these potential problems could occur and to develop methods to limit the potential for these emissions to accumulate.

## THE FIRE

At 4:40 a.m., Sunday, June 1, 1986, CO measurements being monitored at the guard house suddenly began to increase rapidly at three underground locations. No mine personnel were on mine property at that time. According to a preexisting emergency checklist, responsible individuals who were on-call were immediately notified. When they arrived at the mine 15 min later, they could already see large quantities of smoke pouring from the fan shaft. Power in the mine was lost shortly thereafter, eliminating several CO sensors. To limit the flow of air across the fire, one of the two fans was immediately shutdown.

Initial underground exploration was begun (fig. 2). By 5:30 a.m. the belt entry to crosscut 6, the return overcasts in crosscut 4 and 2, and the 1 left intake to crosscut 6 had been examined.

Smoke was seen entering the belt at crosscut 6 from a mandoor separating the belt from the 1 right intake entry. Smoke was also accumulating in the crosscut 5 sump area and was backing against the airflow in crosscut 4 at the 2 right overcast. Air moving through the return in crosscut 4 overcasts ordinarily flowed from west to east, to the exhaust fan. At approximately 6:10 a.m., rescue personnel, each now using self-contained breathing apparatus, noticed that the air had reversed and was now moving away from the fan in a westerly direction.

At the same time, two men rode down the intake shaft in a rescue-escape hoist to explore the 1 right intake up to crosscut 5 (fig. 3). There, smoke and heat were discovered. The men heard sounds of fire and felt heat, but could see nothing. They returned to the intake shaft to explore the 2 right entry, but conditions in this entry became impassable at crosscut 4. The men then returned to the intake shaft and were hoisted to the surface.

Mine management personnel, the mine rescue team, and the president of CWI were contacted. While the initial exploration was taking place, MSHA subdistrict inspector, the local sheriff, a Colorado Division of Mines representative, and two local mine rescue teams were notified. By 7:00 a.m., high expansion foam from a  $24,000 \text{ ft}^3/\text{min}$  diesel powered generator (fig. 4) was being produced at the intake shaft collar and poured down the shaft. Rescue crews were moving down the belt entry and examining, through mandoors, the 1 right intake to determine the progress of the high expansion foam and to identify possible locations for other foam generators. The mandoor in crosscut 6 was shut, reducing the smoke in the belt entry. At 7:30 a.m., MSHA issued a control closure order restricting personnel permitted in the mine.

Four other mine rescue teams were notified. Three were called to the mine, but because of their distance from the mine, they were not expected for some time. The fourth team was placed on standby at their home location. Two of the three enroute teams had foam generators.

At 9:00 a.m., one CWI crew repeated the examination of the 1 right intake entry (fig. 5) from the belt entry and found foam at crosscuts 5 and 6, and evidence of fire at crosscut 7. In an attempt to isolate the right side of the



Figure 2.-5:30 a.m.: Initial underground exploration.



Figure 3.-6:10 a.m.: Exploration from intake shaft.



Figure 4.--7:00 a.m.: High expansion foam being produced, intake and beit explorations continue.

mine, another crew began to set up a second high expansion foam generator in the belt entry at crosscut 3. This foam generator was borrowed from a neighboring mine.

To further restrict air to the right side of the mine, the intake shaft was covered with brattice cloth, except for an opening for the high expansion foam. At 10:15 a.m., the operating fan overheated and stopped, which required the mine to be immediately evacuated. The parallel fan, shutdown earlier, was restarted and crews were permitted to reenter the mine at 10:30 a.m.

Since the overcast in the 1 left intake entry at crosscut 4 was becoming warm, two teams attempted to enter the 2 left return (fig. 6) to block crosscut 2, which would again force air from west to east through crosscut 4. The first team went to crosscut 3, but was unable to enter the return because of excessive smoke and heat. The second team went to crosscut 7, entered the 2 left return, then



Figure 5 .--- 9:00 a.m.: Repeating the 1 right intake examination.

proceeded outby to crosscut 4, where they encountered heat and smoke in the reversed airflow from the right side of the mine.

At the same time, an 8,000-ft<sup>3</sup>/min foam generator began producing foam at crosscut 3 in the belt entry (fig. 7). Fifteen minutes later, a team detected foam in the belt entry at crosscut 6. After 45 min, foam was detected in crosscut 8 of the belt entry.

Shortly after noon, a meeting was held to plan for the exploration of areas further into the mine. The participants decided that a crew would advance down the 1 left intake entry to a temporarily sealed ventilation equalizer at crosscut 19, open it, and then proceed to the right side of the mine to examine conditions. Because of time restrictions agreed upon before the exploration, the crew was only able to proceed as far as crosscut 15 (fig. 8). The team stopped at each belt entry mandoor to check conditions. At crosscuts 11, 13, and 15, the belt atmosphere was smoky and very humid. There was evidence of condensation, possibly due to the high expansion foam reacting with the fire. They also examined the 2 left return at crosscut 12, where clear air was found. A second team was attempting to erect a curtain in the 2 left return just inby crosscut 4 to force combustion products out of the mine. As the curtain was being erected, the expandable plastic pipe, used to secure the brattice, as well as the brattice itself, began to melt, rendering the brattice worthless.



Figure 6.-10:30 a.m.: Attempting to reroute ventilation air at crosscut 4.



Figure 7.-10:30 a.m.: Foam being generated in belt entry.

While the inby explorations were taking place, firefighters reported that less than one barrel of foam remained at the intake shaft collar. Fire-fighting had begun with fifteen 55 gal barrels. Foam had also been obtained from several other mines in the area, from a local vendor, and from a surface-stored supply originally designed to be used by small foam generators located at the belt drives.

When all foam concentrate at the intake shaft was consumed, the methane concentrations at the fan, recorded by handheld detectors, began to increase and to become more oscillatory. CWI officials decided to evacuate the mine when methane concentrations reached 4 pct at the fan. Shortly after that decision, the foam generator in the belt entry ran out of concentrate. It was stopped and the mine was evacuated. Subsequent methane concentrations reached 6 pct.

Approximately 1 h after the depletion of foam at the intake shaft, a new supply arrived, and the generator was restarted. Methane readings at the fan had climbed to 8.2 pct. Bearings on the operating fan were overheating, so the area was again evacuated, and the fan was shutoff. Methane concentrations then began to slowly recede at the fan.

To restrict air to the fire, two metal fire doors on the 1 left intake portal were closed at approximately 2:30 p.m. High expansion foam continued to be pumped down the intake shaft. Methane concentrations fell to 3 pct at the fan.

Because the mine had to be evacuated quickly, crews were unable to remove the foam generator located in the belt entry. A decision was made to recover the generator if methane concentrations remained low after reopening the fire doors. At 3:23 p.m., the doors were reopened. Shortly thereafter, the methane concentration began to rise at the fan. The new foam supply at the intake shaft was depleted at 3:42 p.m. Methane concentrations rose to 9.9 pct requiring the reclosing of the 1 left doors. In the next hour, methane concentrations varied from 3.5 to 8.2 pct at the fan.

MSHA gave a rescue team permission to enter the mine and activate water to protect components of the foam generator at crosscut 3 in the belt entry. This permission was based on the provision that methane concentrations could be stabilized below 4 pct at the fan. When concentrations finally stabilized at 3.5 pct, the team entered the mine through a door in the belt entry and started water at the generator. These people were subjected to CO concentrations of 700 ppm from the portal to crosscut 3. After turning the water on, they exited the mine at 6:14 p.m.

A third diesel powered high expansion foam generator, this one having an 18,000 ft<sup>3</sup>/min capacity, was erected in the belt entry at the portal and began operating at 7:45 p.m. A load-haul-dump vehicle was driven inside the mine and stopped in the 1 left intake entry. The driver exited the mine, and the intake portal doors were reclosed to enable methane concentrations to continue stabilizing. At 8:00 p.m., a rescue team entered the mine through the 1 left fire doors to recover the generator at crosscut 3. They measured 700 ppm CO at crosscut 1, 115 ppm inby

. 1

crosscut 2, and 1,360 ppm at crosscut 6. High expansion foam, generated at the belt portal, was seen on the floor of the belt entry at crosscut 3 as the team was dismantling the foam generator. At 8:45 p.m., the team exited the mine with the generator.

Because of the inability to fight the fire by direct methods underground, officials decided to install foam generators in all portals and shafts. They also decided that, if fire fighting with foam was ineffective, the entire mine would be sealed. The belt entry generator continued operating while the generator at the intake shaft collar was restarted at 8:47 p.m. About 30 min after starting this generator, the airflow in the intake shaft reversed and began to outgas. After a short time, the airflow corrected itself and began intaking again. At 9:55 p.m., a third foam generator began operating in the 1 left intake portal.

At 10:04 p.m., the generator at the intake shaft collar was shutdown because of concern that the fire was being pushed toward the portals. It quickly became apparent that fire fighting from only the surface was ineffective, that hazardous gas concentrations restricted any underground efforts, and that only limited quantities of foam were presently available to fight the fire. Sealing the entire mine had become necessary.



Figure 8.-12:00 p.m.: Attempting to explore inby fire.

The belt entry was first sealed 100 ft inby the belt portal. A second seal was built at the portal face. The intake portal was sealed by closing the fire doors and pouring sand and rock dust against them. Portal sealing (figs. 9-10) was completed at 1:30 a.m., Monday, June 2, 1986.

Officials initially planned to have the intake and fan shafts sealed simultaneously. Some dirt fill was poured into the shafts, but was discontinued before the air was cutoff because the explosion doors on top of the fan housing had to be opened. This proved difficult because the fire in the fan shaft was now out of control (fig. 11). The entire bench had to be evacuated until conditions became more safe. Finally the fire subsided, the doors were opened, and shaft filling resumed.

The intake shaft was sealed first by dumping rock, dirt, and gravel into the shaft to a total depth of approximately 140 ft. Sand was poured on top of the fill to more effectively block the flow of air. The fan shaft was sealed in the same manner. Both shaft seals were finished at 4:30 a.m., Tuesday, June 3, 1986.



Figure 9.-Intake portal seal.



Figure 10.-Belt portal seal (right) and intake portal seal (left).



Figure 11.-Coal tars burning in fan and intake shafts.

The status of a postfire sealed mine atmosphere is usually monitored by an MSHA technical support group. Since all instrumentation from the support group nearest this mine was being used in another mine emergency, it was suggested that the Bureau could relate this work to other sealed gob research already completed in this mine and perform the required gas analyses. The request was formally made on June 3, 1986.

Representatives of the Bureau arrived at the minesite on Wednesday, June 4, 1986. A remote sampling strategy was developed to analyze mine fire gases. Before sealing both portals, the rescue teams had hung a 0.25-in-ID copper gas sample line inby the seals of both the intake and belt entries. An empty water pipe in the fan shaft ran from the fan shaft collar to the mine level. A 0.25-in-ID semirigid sample line was lowered within the pipe to the mine level. The pipe was then sealed to prevent ingassing from the surface.

Initially, samples were taken twice daily from each of these three positions. CWI and their mine fire consultant determined that at least two boreholes were needed to obtain more information on the location and state of the fire. A 250-ft-deep borehole (L-2) was drilled in the 2 left return at crosscut 3 on June 13, 1986. A second 1,100-ftdeep borehole (L-25) was drilled into the mine on June 18 at crosscut 33, near an old borehole, and intersected the mine in the 1 left intake entry. Sampling at this borehole was at two levels, the mine level (L-25-1) and approximately 6 ft below the borehole collar (L-25-2). Upon completion of the boreholes, semirigid sample tubing was inserted into the boreholes for gas sampling.

Gas samples were only taken when the atmospheric pressure was falling and the mine was outgassing. The pressure differential across the seals was found by connecting a Magnehelic differential pressure measuring instrument to the end of the sampling line and recording the value. Sampling only during an outgassing episode eliminated the potential for air-diluted samples caused by atmospheric air mixing with mine gases (2).

All gas sampling was done with 1.2 in<sup>3</sup> evacuated glass sample tubes. These tubes were closed at one end and

sealed with a rubber septum at the other and were similar to laboratory blood collection tubes. The tubes are more than 95 pct air evacuated, rather than the 50-60 pct air evacuation in standard blood tubes. The higher vacuum greatly reduces any problems with air dilution.

Sample lines were normally closed to the atmosphere between sampling periods. To prepare each location for gas sampling, the line was reopened and allowed to breathe for a short time before the pressure was measured. At times, a pump operating at a known flow rate was connected to the line to more effectively draw a sample from the mine. Since the length of sample line was known, operating the pump for a specific time ensured that the gas sample originated in the mine and not in the sample tubing. A plastic sample tee was located just upstream of the pump. Gas sampling took place through a rubber septum, which was placed over the third leg of the tee.

As the sampling line was being purged, a sample tube was placed into a plastic syringe containing axially aligned internal and external hypodermic needles. The septum end of a glass sample tube was placed into the syringe, so that the septum was in contact with the internal needle. At the completion of sample line purging, the external needle was forced into the septum on the plastic tee. The sample tube was then pushed into the syringe, where the internal needle punctured the rubber septum on the sample tube. The pressure differential between the sample line and the sample tube forced mine air into the tube. The tube typically remained open for 5 s before retraction from the syringe, which was then removed from the tee. The sample tube and sample tee septums were self-sealing upon removal of the needles.

Sample tubes were then packaged and returned to the Bureau's analytical laboratory via overnight air express. Two types of gas chromatographs were used: flame ionization detectors for low concentration gases, and thermal conductivity detectors for high concentration gases.

## **MINE FIRE GAS ANALYSIS**

The gases measured were divided into two general categories: atmospheric gases, and byproducts of oxidation or combustion. The atmospheric gases were those typically found in an atmospheric gas sample and included nitrogen  $(N_2)$ , oxygen  $(O_2)$ , carbon dioxide  $(CO_2)$ , and argon (Ar). Oxidation or combustion byproducts included CO, hydrogen (H<sub>2</sub>), and the alkane (C<sub>N</sub>H<sub>2N+2</sub>), alkene (C<sub>N</sub>H<sub>2N</sub>), and alkyne (C<sub>N</sub>H<sub>2N-2</sub>) series of hydrocarbon gases.

Alkanes, known as the methane series, are the end products of the anaerobic decay of plants. They are sometimes referred to as paraffins. Alkanes are saturated aliphatic hydrocarbons. Each available carbon atomic bond is taken by an individual hydrogen atom, thus all carbon bonds are single bonds. In aliphatic compounds, the carbon atoms form open chain molecules, rather than rings. The alkanes examined were methane (CH<sub>4</sub>), ethane  $(C_2H_6)$ , propane  $(C_3H_8)$ , butane  $(C_4H_{10})$ , and pentane  $(C_{1}H_{1}).$ 

Alkenes are unsaturated aliphatic hydrocarbons. They contain less than the maximum quantity of hydrogen atoms. Carbon atoms are double bonded, while all hydrogen atoms surrounding carbon are single bonded. Heating must occur for alkenes to form. The alkenes examined were ethylene or ethene  $(C_2H_4)$ , and propylene or propene  $(C_{1}H_{6})$ . Alkenes can form from alkanes in coal mine fires through the loss of hydrogen atoms by pyrolysis:

Large alkanes --HEAT 
$$\rightarrow$$
 Smaller alkanes + alkenes + H<sub>2</sub>

The alkyne series are highly unsaturated aliphatic hydrocarbons. Carbon atoms are triple bonded, while

hydrogen atoms surrounding the carbon atoms are again single bonded. The only alkyne examined was acetylene  $(C_2H_2)$ . Two common ways in which acetylene can be produced in coal mine fires are as follows:

Coal →(heat) →coke  

$$\downarrow$$
  
 $\rightarrow$  (2,000°F) → CaC<sub>2</sub> + H<sub>2</sub>O → C<sub>2</sub>H<sub>2</sub>  
/  
nestone →(heat) →CaO (A)

Limestone →(heat) →CaO

$$4CH_4 + O_2 \rightarrow (1,500^{\circ} \text{ F}) \rightarrow C_2H_2 + 2CO + 7H_2$$
 (B)

Both processes involve very high temperatures. In a mine fire where the burning area continues to be ventilated, it is possible that there will be enough oxygen to permit the temperatures to reach the above values.

## **MINE FIRE EQUATIONS**

Several equations have been developed to aid in establishing the status of a mine atmosphere. These predictive models are used to determine:

1. if a fire exists,

- 2. what is burning,
- 3. what quantity of coal is burning,

4. if the fire continues to burn after sealing the affected area. and

5. if the atmosphere is explosive.

All the models described in this section were used to evaluate the sealed atmosphere in the Orchard Valley Mine. A brief description of each model is given, along with an analysis of values obtained for 2 years of sampling. These models are used to develop trends, not measure individual values. Only through long-term analysis can a realistic picture of the mine atmosphere be created.

#### **IS THERE A FIRE?**

#### Index of Carbon Monoxide

The index of carbon monoxide (ICO), or Graham's index (3), is a dependable indicator of conditions underground, even if sample dilution exists. The ICO is temperature dependent, i.e., its concentration rises with increasing temperature. The index must have a ratio of O<sub>2</sub>-to-inertgas of 0.265. Inert, in all cases, is a combination of  $N_2$ and Ar:

 $ICO = CO/([0.265 \times {N_2 + Ar}] - O_2)$ 

CO = carbon monoxide, in pct

and  $(0.265 \times [N_2 + Ar]) - O_2 =$  oxygen deficiency, in pct.

The ICO can signify a fire or at least increasing temperatures if, after stabilizing for a time, the value begins to rise. ICO concentrations will rise with increasing temperatures until actual ignition takes place. With combustion, the rate of increase then begins to slow and, in many cases, will actually stabilize. Once a mine is sealed and the oxygen available for combustion is reduced, ICO levels again begin to climb and will remain elevated until temperatures fall to near ambient levels.

Inherent problems exist for the ICO during conditions where the CO levels decrease and O<sub>2</sub> concentrations increase. This can occur when combustion has slowed. Values in the denominator are forced toward zero because  $O_2$  is no longer being consumed. This phenomenon tends to reduce the inert gas concentration. If CO levels are decreasing at a slower rate, then the ICO may actually increase, indicating continued combustion. Fortunately, this error will always be on the conservative side, suggesting that conditions underground are worse than they actually are.

When the mine atmosphere approaches ambient gas levels, other indicators should be monitored along with the ICO, since very small quantities of CO can be produced by normal oxidation and mineral desorption. This occurs as

the sealed area goes from smoldering combustion at slightly elevated temperature to ambient temperature oxidation. During this time, CO values change very little. Therefore, the transition during which ambient oxidation is reached usually goes undetected.

Other difficulties exist with the ICO. There is no single CO value, ratio, or index that can be uniformly applied to all mines. At times, small concentrations of CO continue for extended periods. On the other hand, an absence of CO does not guarantee that the fire will not reignite once air flows past it (4). As in most equations relating to the status of a mine atmosphere, it is important to develop a trend by obtaining a reliable data base of ICO values and noting if successive values deviate from the trend.

#### Analysis Using the ICO Equation

If combustion is moving away from the sample location or decreasing in intensity, the ICO should decrease. In all six sampling locations (fig. 12), the values rapidly went to zero. However, it appears that reactions at the intake, borehole L-2, and fan shaft locations routinely generated small quantities of CO during late fall or early winter. This may have been caused by the increased frequency and amplitude of barometric pressure changes during that particular time of year.

With the information presented in the ICO analyses alone, one could conclude that combustion has ceased and CO generation in the sealed mine is no longer a problem.



Figure 12.--Analysis of carbon monoxide index.

#### Index of Carbon Dioxide

 $CO_2$  is a gas formed underground in a variety of ways.  $CO_2$  is a major product of combustion. It can be liberated by microorganisms oxidizing the coal or formed by mixing acidic mine water with calcium carbonate, which is found in either the surrounding strata or in rock dust. Samples may therefore contain more  $CO_2$  than is actually being generated by combustion. On the other hand,  $CO_2$  is soluble in water, therefore samples may contain less  $CO_2$ than is actually being evolved.

A carbon dioxide index  $(ICO_2)$  (5) has been developed to monitor elevated  $CO_2$  levels:

$$ICO_2 = (CO_2 - 0.03)/(100 - O_2)$$

This equation indicates elevated  $CO_2$  values in an oxygenfree atmosphere. In a normal atmosphere, where only ambient  $CO_2$  is generated, the  $ICO_2$  index provides the proportion of  $CO_2$  to total inerts and should approach zero. In a mine fire atmosphere, elevated  $CO_2$  would be compared with total inerts and gaseous byproducts of combustion.

If  $CO_2$  is a product of combustion, an  $ICO_2$  versus temperature plot will closely parallel an ICO versus temperature plot. Where no temperature information exists, an ICO-ICO<sub>2</sub> ratio can be developed.

 $ICO_2$  values increase once ignition occurs and continue to increase as long as the temperature or fuel quantity increases. In sealed areas having no combustion, the  $ICO_2$ value will also rise, but then stabilize with time.

#### Analysis Using the ICO<sub>2</sub> Equation

The intake and belt entry  $ICO_2$  (fig. 13) show an immediate decrease in the postfire sealed atmosphere. All sampling locations, except for the fan shaft, had similar, stable values for the 2-year sampling period. Results from the fan shaft fluctuated continuously. Mine personnel theorize that the water pipe, into which the sample tube was inserted, was not completely sealed and, at times, ambient air flowed into the pipe. The maximum fan shaft  $ICO_2$  value appeared to parallel the other sampling locations.

The intake, belt, and borehole L-2 locations exhibited a change in the quantity of  $CO_2$  being generated during the late fall and early winter months. This change tended to drive the ICO<sub>2</sub> toward zero, which indicated a more stable sealed mine atmosphere. Again, the rationale behind the changes was that they were caused by fluctuations in barometric pressure during that time of the year.

The long-term stability exhibited by the  $ICO_2$  at each sampling location infers that combustion has at least slowed and, more probably, has been halted.



Figure 13.—Analysis of carbon dioxide index.

#### WHAT IS BURNING?

#### **Jones-Trickett Ratio**

The Jones-Trickett Ratio (JTR) (6) is used only to determine sample reliability. The equation:

JTR = 
$$(CO_2 + [0.75 \times CO] - [0.25 \times H_2])/([0.265 \times \{N_2 + Ar\}] - O_2)$$

is based on the principle that the molecules of matter consumed in a fire are proportional to the volume of gas produced. It was originally developed to help researchers differentiate between the causes of explosions, whether gas or dust. It has since been adapted, with mixed success, to mine fire situations.

The JTR varies with the type of fire, depending on the fuel. If the JTR is less than 0.4, there is no combustion. When the JTR is between 0.4 and 0.5, methane is the fuel. JTR values between 0.5 and 1.0 indicate that the fuel is coal, oil, conveyor belting, insulation, or urethane foam. If the JTR is between 0.9 and 1.6, wood is burning. Although values more than 1.6 are possible under controlled laboratory conditions, when JTR results above 1.6 are obtained during a possible fire episode, the gas chromatograph should be checked for proper calibration.

#### **Analysis Using Jones-Trickett's Ratio**

Because of their sampling proximity, a good correlation existed between the intake, belt, and borehole L-2 sampling points (fig. 14). These three positions initially showed a JTR value decreasing to below 0.4, which indicated that combustion has ceased. After approximately 1 month, the JTR value at these three sampling positions reversed. This was finally followed by a stabilizing of the values at about 0.5.

The fan shaft data initially showed no combustion at this location. Over time, results also showed an increased tendency toward combustion. The JTR value steadily increased until a loss of data occurred after approximately 1 year. When sampling was restored, the values here also stabilized near 0.5.

Large JTR value swings were initially recorded at borehole L-25 top and bottom locations. JTR values at these two positions then began reacting like other sampling locations and finally reached similar stabilized values. The large fluctuations in JTR quantities obtained early in the postfire examination may have been influenced by other parameters, such as gases being liberated from an oxidizing rider seam or the differing buoyancy of the various gases.

Since the two boreholes were drilled in remote locations, data acquisition was more difficult and has not been obtained as consistently as the other positions. This is the reason for gaps in these three sampling positions.

The data presented in the JTR graphs exhibited values leading one to conclude that combustion had restarted and that methane or materials such as coal, urethane foam, conveyor belting, oil, or insulation were being consumed in the fire.

### WHAT QUANTITY OF COAL IS BURNING?

#### **Theoretical Quantity-of-Combustion Equation**

Once it is determined that there is a fire, it is useful to know how large the fire is (7). This equation enables personnel to estimate the quantity of coal burning:

$$\mathbf{F} = (\mathbf{O}_2)(\mathbf{k})$$

where F = quantity burning, lb/min,

and k = 0.03 (coal), 0.08 (wood).

$$O_2 = Q(O_2' - O_2'')$$

where  $Q = airflow across fire, ft^3/min,$ 

 $O_2'$  = intake oxygen concentration, pct,

and  $O_2^{"}$  = return oxygen concentration, pct.

This equation requires a knowledge of air quantities and oxygen concentrations that may not be available once the mine has been sealed. It is important that adequate sample lines are placed in the mine prior to sealing, so that gas sampling can be performed remotely and coal combustion quantities can be generated.

#### Analysis Using Combustion Equations

Coal combustion rates (fig. 15) remained slightly above 100 lb/min as long as the high expansion fire fighting foam was being generated and applied. Within 30 min following the initial depletion of foam, the quantity of burning coal increased to approximately 250 lb/min. After foam was exhausted, the combustion rates were never reduced to the values found while foam was initially being applied.

15



Figure 14.--Analysis of Jones-Trickett ratio.



Figure 15.--Projected quantity of coal undergoing combustion.

#### IS THE FIRE CONTINUING TO BURN?

#### **Relative Intensity and Relative Efficiency**

The relative intensity (RI) (8) equation is used by power industry engineers to determine boiler and fuel efficiency, oxygen excess or deficiency, water vapor production, and heat losses. In its adaptation to mine fire analysis, RI is used as a tool to determine the proximity of the sampling location to the fire. It performs best when many sampling locations, spread throughout the mine, are available. RI measures the quantity of air available to burn a unit mass of fuel (11.6 lb of air are required to completely burn 1 lb of coal), the percentage of oxygen consumed, and the effect of combustion on temperature. 
$$RI = ([1 - {3.83 O_2}]/[N_2 + Ar])(ICO)$$

The relative efficiency (RE) (9) equation was also developed for the power industry. It was derived from basic fuel combustion equations. In mine fire analysis, it is an effective indicator of thermal reactions in the earliest and latest stages, which are of greatest interest immediately after a mine is sealed.

$$RE = ([0.262][{N_2 + Ar} - {3.83 O_2}])/(CO_2 + CO)$$

Both the RI and RE equations are designed to show the location of the sampling point relative to the fire. If RI or RE increases, then the fire is either growing or moving closer to the sampling location. Conversely, if the RI or RE decreases, the fire is being throttled, or is moving away from the sampling location.

#### Analysis Using RI and RE Equations

All sampling locations exhibited a visible decrease in RI since the beginning of gas analysis (fig. 16). Lack of measurable CO in certain samples resulted in the collapse of the RI equation, which is the reason for gaps in the RI graphs.

RE values displayed an immediate increase, followed by a general flattening of the curve (fig. 17). Five of six sampling locations displayed autumnal fluctuations during the second year of sampling.

The slope of the RE curve showed that combustion efficiency was gradually being reduced over time. Referring back to the RE equation, when oxygen is consumed through combustion and replaced by  $CO_2$  and CO, the equation will be driven toward zero.  $CO_2$  and CO are generated by progressively higher temperatures. This also would tend to drive the equation toward zero. If, on the other hand, conditions had stabilized and no additional oxygen was introduced into the mine, the curve should remain stable at some previously defined value. In fact, this does occur at all sampling locations after many months.

The slope of the mine is downward away from the sampling locations. After the fire, a tremendous volume of undisturbed atmosphere remained in the lower elevations of the mine. Since most sampling locations are at the highest elevation, the oxygen remaining could continue to support low-level combustion. In other words, the mine could be simulating a partially capped exhaust stack slowly emitting fire byproducts. The only way to prove this hypothesis would be to sink a borehole well inby any potential fire areas and determine oxygen concentrations there.

#### RATIO

This equation was developed (10) to monitor a scaled mine atmosphere. It was designed to eliminate the potential for reignition of a mine fire when the mine is reopened and oxygen is reintroduced into the mine. Only four gases are required to be monitored to successfully obtain results: oxygen, carbon monoxide, methane, and ethane. The atmosphere is divided into three parts: air, methane and ethane, and residual gas.

Air = 
$$a(O_2)$$

where a = (100.000/20.946) = 4.774.

Residual gas  $(R_g)$  is the volume percent of gas within a sealed coal mine after air, methane, and ethane have been subtracted from the sample.  $R_g$  contains excess nitrogen (not part of air), products of combustion (CO, CO<sub>2</sub>, H<sub>2</sub>, and hydrocarbons), along with products formed by chemical processes not related to combustion.

$$R_g = 100.0 - Air - CH_4 - C_2H_6$$

The concentration of CO in parts per million of air within the residual gas is:

$$(CO)_{R_{\pi}} = ([CO]_{s}/R_{g}) \times 100$$

where  $[CO]_s$  = sampled CO, in ppm.

From these values the R-Index  $(R_1)$  is developed:

$$R_{I} = ([CO]_{R_{g}}/R_{g} = ([CO]_{s}/R_{g}^{2}) \times 100.0.$$

If  $R_I$  remains constant, one of two things is occurring: sustained low-temperature combustion, or a sustained low rate of ambient CO production. If combustion is taking place, the average  $R_I$  value will be higher than if ambient CO production is occurring, because CO production increases as temperatures increase.

In deriving a ratio, the actual measured  $R_I$  is referred to as  $(R_I)_{act}$ . A second  $R_I$ , known as the maximum equilibrium value  $(R_I)_{eq}$ , is also obtained:

$$(R_{\rm I})_{\rm eq} = 300 (Rg/O_2)^{-1/2}.$$

 $(R_1)_{eq}$  represents the maximum equilibrium value of the R-Index for a gas sample, if only ambient temperature processes are responsible for CO production.



Figure 16.—Analysis of relative intensity.

An equation, referred to as RATIO has been created to determine the state of a sealed area:

RATIO = 
$$(R_I)_{act}/(R_I)_{eq} = 1/3(CO)_s(R_g)^{-3/2}(O_2)^{-1/2}$$
.

If the RATIO is greater than one, ambient temperatures have not been reached. There is either smoldering combustion or above ambient temperature oxidation. This condition is considered unsafe for reentry.

If the RATIO is less than, or equal to one, it is possible that ambient temperatures have been reached. However, equilibrium exists only if the RATIO stabilizes at a value less than one. The minimum time for the value to remain stabilized at less than one has been established at 30 days. If the value remains below one for a time and then rises to a value greater than one, the 30 day period must begin anew.

#### **Analysis Using RATIO**

After about 2 months, the RATIO at all locations fell to below one (fig. 18). Two years of autumnal fluctuations are evident in the intake, belt and borehole L-2 sampling positions. Again, breaks in the data were caused by a lack of measurable carbon monoxide. The equilibrium of most values indicates that conditions in the mine atmosphere



Figure 17.-Analysis of relative efficiency.

have stabilized and that combustion is no longer taking place.

#### **Hydrocarbon Ratio**

The hydrocarbon ratio (R1) was developed (11) after researchers (12-14) showed that the desorption of low molecular weight hydrocarbon gases from coal was directly related to temperature. Primarily methane is liberated at ambient temperatures. If coal is heated, other gases begin to be desorbed, starting with carbon dioxide, then carbon monoxide, hydrogen, ethylene, propylene, and acetylene with increasing temperatures. In effect, all hydrocarbon concentrations increase with rising temperature.

Knowing this direct relationship between hydrocarbon concentrations and temperature, the Hydrocarbon Ratio equation was developed. It is defined as:

$$R1 = ([1.01{THC} - CH_4]/[{THC} + c])(1000),$$

where THC = total hydrocarbon concentration, in ppm,

$$CH_4$$
 = methane concentration, in ppm,

This equation was designed to equal zero when no hydrocarbons were detected, 10 when methane was the only measured hydrocarbon, and about 1,010 at the upper limit. The only limiting factor is that the methane concentration must be greater than 20 ppm.

For bituminous coal, the R1 values obtained are closely dependent on temperature. Because of this, limits have been derived to aid in determining the temperature of coal being analyzed. R1 values from zero to 50 indicate that only normal temperature oxidation is occurring. Values from 50 to 100 indicate possible elevated temperatures. Above 100, the coal is undergoing elevated temperature oxidation. This equation, like all others, is designed to be examined over time, so that a trend can be established.





### Analysis Using Hydrocarbon Ratio

R1 values at the intake sampling position (fig. 19) rapidly fell from the elevated oxidation range to normal temperature oxidation values. A large deviation, which occurred not long after the fire, was caused by a large increase in measured total hydrocarbons. Seasonal

changes in the sealed mine atmosphere appeared significant enough to drive the R1 values back into the elevated temperature oxidation range. During much of the sampling program the values remained below the elevated temperature oxidation threshold, indicating only ambient temperature oxidation was occurring.



Figure 19.---Analysis of hydrocarbon ratio.

#### IS THE ATMOSPHERE EXPLOSIVE?

#### Explosibility

Once an area is sealed and combustion begins to slow, the gas components of the contained atmosphere change. It is important to determine whether the atmosphere is explosive or if it has the potential to become explosive. If combustion restarts and the atmosphere is explosive, then an explosion will likely result. This problem is frequently encountered during mine recovery, when the mine is reopened and oxygen is reintroduced.

A diagram has been developed (15) to monitor the explosibility of mine atmospheres having a maximum hydrogen concentration of 5 pct (50,000 ppm) and a maximum CO concentration of 3 pct (30,000 ppm). The diagram has three major elements: effective inerts (EI), effective combustibles (EC), and the ratio of methane (CH<sub>4</sub>) to total combustibles (<u>R</u>):

$$EI = excess (N_2 + Ar) + (1.5 \times CO_2)$$

where excess  $N_2$  = sample ( $N_2$  + Ar) - (3.8 × sample  $O_2$ )

$$EC = CH_4 + (1.25 \text{ x } H_2) + (0.4 \text{ x } CO)$$

and

(The values 1.25 and 0.4 are the lower explosive limit ratios, respectively, of  $CH_4$  to  $H_2$  and CO).

**R** = 
$$CH_4/(CO + CH_4 + H_2 + other alkanes + alkenes$$

+ alkynes).

These values can then be diagrammed (fig. 20) to determine the potential for explosibility. EI is plotted along the horizontal axis, and EC is found on the vertical axis. The <u>R</u> value varies between 0.0 and 1.0. Data fit into one of three areas, explosive, explosive when mixed with air, and nonexplosive. The area into which the sample fits depends directly on <u>R</u>. Continually plotting results on this graph enables one to determine if the atmosphere is progressing toward or away from an explosive mixture.

To determine when the atmosphere could become explosive, a graph plotting explosibility (E) versus time is generated:

$$E = EC(O_2/MAO)$$

where MAO = Maximum allowable oxygen =  $5 + 7\underline{R}$ 

and 
$$R = 5 + 7(CH_4/[CH_4 + H_2 + CO])$$
.



MAO is the lower threshold value of oxygen required for flame propagation; an  $O_2$  sample below the calculated MAO means that insufficient oxygen is present for ignition, and the mixture is either nonexplosive or explosive if mixed with additional oxygen. If the oxygen concentration exceeds the MAO, then the explosibility diagram should be used to determine if the mixture is explosive.

#### Analysis Using Explosibility Equations

Explosibility values from the intake, belt, borehole L-2, and fan shaft sampling locations increased over time (fig. 21). Methane and nitrogen concentrations at these locations steadily rose while oxygen, carbon monoxide, carbon dioxide, hydrogen, and all higher hydrocarbons decreased. The methane concentration increased more rapidly than the oxygen decreased, thus the reason for the apparent increase in explosibility.

Borehole L-25 bottom and L-25 top gas samples behaved differently. Carbon monoxide, an early indicator that combustion was taking place, was lower at these locations than at other positions. On the other hand, hydrogen, an indicator of even higher temperature combustion, was more prevalent here than anywhere else. The reason for the elevated hydrogen concentration was unclear.



Figure 21.--Analysis of explosibility trend.

Methane concentrations at borehole L-25 bottom and L-25 top were sometimes 10 times greater than at any other sampling position. These concentrations appeared to be cyclic, fluctuating from very high values to values similar to other sampling locations. When methane concentrations were depressed, they were replaced by atmospheric gases, principally nitrogen and oxygen. One explanation proposed was that air was leaking through surface faults to the mine elevation during periods of rising barometric pressure.

Examining the results of the explosibility data, one would conclude that the atmosphere within the sealed mine was becoming increasingly unstable and, if air is reintroduced to the mine during reopening, conditions would trend toward an increasing likelihood of an explosion.

## DISCUSSION

A fire of unknown origin occurred in a coal mine in southwestern Colorado. After successfully combating the fire for a time, control was lost, and the mine had to be sealed. The Bureau was requested to monitor and analyze the atmosphere in the mine. Several different atmospheric and combustion gases were monitored. In addition, the status of the mine has been continuously followed by applying equations developed to analyze various postsealing mine problems. This report details information from the first 2 years of gas sampling following the sealing of the mine. There were six sampling locations. The results over a 2-year period indicated that seasonal changes influence the status of the atmosphere. Overall, the results tend to show that combustion has abated. The results of 2 years of data show that individual values of any equation are worthless, trends must be developed to obtain a realistic picture of the sealed atmosphere, and no one equation can provide all the answers regarding the sealed mine atmosphere.

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