THE USE OF INERT GAS TO ELIMINATE ACID PRODUCTION BY ABANDONED AND ACTIVE DEEP MINES

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The formation of acid mine drainage is a naturally occurring phenomena that results when pyrites are exposed to air and water. Pyrites, which are materials containing iron sulfide, generally occur in association with coal. The mining of the coal, either by surface or subsurface methods, exposes the pyritic materials which subsequently oxidize in the presence of moisture and air to form sulfuric acid and ferrous sulfate. These salts then dissolve in the ground or surface waters passing over the exposed pyrites to form dilute solutions of sulfuric acid and iron sulfate, commonly known as acid mine drainage. Acid mine drainage is well documented as a major source of pollution in the Appalachian states. Although the acid water can be neutralized with substances such as limestone, measures for preventing the formation of the acid are most desirable.

The primary technique for abating or preventing the oxidation of pyrites in deep mines is the elimination of oxygen from contact with the pyrites. Such elimination can be accomplished either by flooding the mine with water, or by sealing all its openings tightly to prevent the entrance of air. This latter technique was widely employed during the early 30's when more than 20,000 seals were constructed by the Works Progress Administration on abandoned deep mine entries (1). The results of this program were poorly documented in the literature, and thus no judgment can be made as to its effectiveness. Work conducted by S. A. Braley (2) at Mellon Institute of Industrial Research in Pittsburgh, Pennsylvania, documented the fact that a substantial reduction in the amount of acid formed by water in contact with pyrites could be achieved by controlling the oxygen content in the atmosphere contacting the pyrites. Braley's work indicated that no acid would be formed in an atmosphere consisting of 100% nitrogen and that any decrease in the oxygen concentration in the atmosphere in a mine should decrease the extent of acid formed.

Further work on sealing of mines and on the exclusion of oxygen from water pyrites mixtures was carried out by Shumate (3) at Ohio State University and by Bell (4) at Rice Company in Pittsburgh, under contracts supported by the Federal Water Pollution Control Administration and by Baker at Mellon Institute (5). Bell conducted a series of studies in the laboratory using columns of

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crushed pyrites where the composition of the atmosphere contacting the moist pyrites was varied. These latter studies showed that in columns developing a stable level of acid in the discharge under an air atmosphere, the sulfate in the discharge was decreased up to 95% in a relatively short period of time by changing the atmosphere from air to pure nitrogen. The short duration of these studies together with difficulties in preventing accidental air entry into the columns prevented learning the ultimate sulfate reduction that could have been achieved during extended operation on nitrogen alone.

Braley's earlier work had shown that when the oxygen was reduced to 0.4% or lower, the acidity developed in the water pyrites mixture was reduced approximately 97% over that in air. Bell's studies demonstrated quite clearly that momentary introduction of air into a column of moist pyrites previously operated on nitrogen resulted in an almost instantaneous increase in sulfate concentration in the effluent. This observation indicates that effective sealing of deep coal mines requires that air be excluded 100% of the time if effective abatement of acid production is to be achieved.

The foregoing requirement of complete air exclusion points up one of the key problems in mine sealing programs where fissures in the overburden, that result from roof falls or are present naturally, furnish passageways for the entry of air even though the main entries are sealed tight. The air entry through fissures is caused by the breathing of the mine that results from changes in the barometric pressure. The mine inhales when the barometric pressure is rising and exhales when it is falling. In Western Pennsylvania for example, typical barometric highs are 30.5 inches of mercury with lows of 29.85 inches. During adverse conditions, a complete change from a low to a high might occur within a 48-hour period. The maximum rate of change can be as much as 0.2 inches of mercury in a three-hour period. Supplying an inert atmosphere of nitrogen, for example, to a deep mine thus requires that the mine be slightly pressurized above the ambient atmospheric pressure and that the ability to supply such sealing gas must be at a rate able to keep up with the inhalation requirements associated with the maximum rate of atmospheric pressure change.

In a typical situation, going from the above mentioned low to high, approximately 4,000 cu. ft. of gas would be required per acre of mined out area to maintain the mine at a constant differential above atmospheric pressure. It is easy to see that for even a small mine of 100 acres, the cost of supplying pure nitrogen at 60 cents per 1,000 cu. ft. becomes prohibitive. It is for this reason that consideration of alternative inert gas sources led to the use of exhaust gases from combustion processes and, in particular, exhaust gases from internal combustion engines used to generate useful power.

Inert gas produced by combustion processes from natural gas costs approximately 7 cents per 1,000 cu. ft. based upon 50 cents per 1,000 cu. ft. for the gas. Where the inert gas is produced as the exhaust from an internal combustion engine driving an electric generator, power credit is substantial. In the general case

where inert gas is supplied only 50% of the time (the other 50% of the time the mine is exhaling), the power credit can reduce the operating costs, including amortization, by about 50%. If the inert gas can be supplied on a continuous basis 100% of the time, the power credit can cover operating and amortization costs completely.

Successful application of inert gas to deep coal mines has the obvious advantage, even at equal costs with other treatment techniques, of producing mine drainage of a quality approaching that of the natural ground water in the area of the mine. In order to determine whether the inert gas technique would be economic for either abandoned deep mines or active deep mines, it was necessary to embark on two separate experimental programs to determine the factors that would allow the required economic analysis.

ABANDONED MINE EXPERIMENTAL PROGRAM

The experimental program to determine the applicability of inert gas blanketing to abandoned deep mines was divided into several phases, the first phase of which involved the pressurization of a selected abandoned deep mine with air to determine the gas injection rate that would be required to maintain any desired positive pressure within the mine during normal atmospheric pressure changes. A subsidiary objective of the Phase I program was to develop methods for locating major leaks in an abandoned mine where the known entries have been sealed in a reasonably gas tight fashion.

The Phase I program was initiated in the summer of 1968 under contract to the Pennsylvania Department of Mines and Mineral Industries (6) with contract support from the Federal Water Pollution Control Administration. The mine originally selected for the start of the project was the Whipkey Mine located in Stewart Township, Fayette County, Pennsylvania. This mine was originally opened in 1938. An estimated 50 acres of coal was removed during its period of operation until its closure in 1964. The coal seam mined was in the lower Kittanning and has an average thickness of 36 inches in this area. The coal outcrops near the base of a steeply sloping hillside; the overburden of massive sandstone above the coal seam rapidly increases to an estimated 275 ft. It was hoped that the great depth and strength of the overburden would assure a reasonably tight mine with a minimum of potholes and fissures resulting from collapse of the roof.

The southern boundary of the mine where the coal outcropped along the hill had been stripped in 1960 and later backfilled and graded with a fill 4 ft. above the seam. At the time that the strip mine was backfilled, a wooden flume was installed in one of the original mine entries to provide drainage from the southeastern edge of the mine. The flow from this discharge point averaged 40 gallons per minute in the summer months and approximately 3 gallons per minute throughout the winter. The flow typically contained 1200 ppm total acidity and 500 ppm iron. It was estimated that drainage from the Whipkey Mine constituted approximately 80% of

the pollutional load on Cucumber Run in Ohio Pyle State Park. Three openings to the mine remain intact in the southwestern corner to the west of the end of the strip mine area. Masonry seals were placed in these three openings along with the necessary gas ducts and sampling probes to conduct the pressurization experiment.

On the basis of the mine maps and the observations that there had been very little roof fall, it was calculated that the mine contains approximately 4.6 million cu. ft. of void volume. Based upon maximum rate of change of atmospheric pressure of 0.2 inches of mercury in a 3 hour period, a volume change of 32,000 cu. ft. could be expected entering or leaving the mine, depending upon rising or falling barometric pressure. This requires a minimum air injection rate of 180 cu. ft. per minute during rising barometric pressure, in order that all of the breathing requirements of the mine are satisfied by the supplied injection air.

Air injection tests on the Whipkey Mine were run at 500 cfm. It was not possible to produce any measurable differential pressure within the mine, except during those periods when atmospheric pressure was falling. These results indicated that there were major leaks from the mine. Attempts were made to locate the leaks, using chemical smoke produced by titanium tetrachloride, but these attempts were not successful. Finally, the strip mine was excavated in the area of the three original mine openings on the southeast corner. It was found that these original openings had not been plugged but, in fact, had been simply closed over with a 5 ft. spoil cover. It was concluded that the porous spoil was in no way an effective seal and that, indeed, these old openings were the sources of the leakage of air from the mine and the reason for the inability to develop any positive differential pressures.

Operations were then switched to an adjacent though smaller mine, King Mine No. 2. This mine had been opened in 1951 and encompassed approximately 56 acres of which 15 acres had been mined. The coal seam was the lower Kittanning and outcropped near the base of a steeply sloping hillside with a dense sandstone overburden of up to approximately 170 ft. There were 5 entries into the mine; the lower two of these had had wet mansonry seals previously installed while solid seals were installed in the three upper entries. All 5 seals were intact at the time the experiment was begun. The two wet seals had a combined average flow of 25 gallons per minute in the summer and approximately 2 gallons per minute throughout the winter. Discharge from this mine also entered Cucumber Run approximately 1 mile above Cucumber Falls in Ohio Pyle State Park.

Air injection at the King Mine resulted in positive differential pressures being developed. Differential pressure varied from 0.20 to 0.28 inches of water for an air injection rate of 575 cfm. At 325 cfm, a differential pressure of approximately 0.06 inches of water was developed. It was possible to develop differential pressures during both rising and falling atmospheric barometric pressure. In the Whipkey Mine, it had been possible to develop

only a maximum of .06 inches of water differential pressure during a rapidly falling barometric pressure.

From the studies at both the King and the Whipkey Mines, it was noted that there were fluctuations in the differential pressure of from 0.02 to 0.08 inches of water, apparently resulting from variations in wind velocity and direction in the outside atmosphere.

In view of the fact that the calculated free breathing rate for the King Mine No. 2 was approximately 54 cfm during maximum barometric pressure change of 0.2 inches of mercury for 3 hours and since it was necessary to use a minimum of 325 cfm to gain a differential of only 0.06 inches of water, it was concluded that the King Mine likewise had unknown openings. In this instance, however, the records were good enough that it was known that the entries were all located and properly sealed. Thus, the unknown openings are probably either natural fissures or fissures resulting from collapse of the roof. Subsequent work on the King Mine at air injection rates of up to 2000 cfm revealed a leak from a pothole on the mine side of the seal at one of the three upper entries. Closure of this leak allowed development of differential pressures up to 1.0 inches of water at air rates of 2000 cfm compared to only 0.6 in. H2O before closure. Continuous injection of 150 cfm produced a steady 0.05 in. H2O differential even during very sharp frontal conditions. Even so, discontinuation of air injection resulted in a rapid fall of pressure within the mine which indicates still additional undetected leaks. Work is currently underway in the development of more sophisticated techniques for locating mine openings.

Based on the preliminary results with air pressurization of the King Mine, it is possible to calculate the relative costs for both capital and operations for lime neutralization of the acid mine drainage vs. application of inert gas from a simple inert gas generator as well as application of inert gas from the exhaust of a natural gas engine driving an electric generator. In the latter instance, the power so generated is assumed sold to the utilities serving the area for 7 mills per kilowatt hour. Table I shows the results of the calculations.

TABLE I
COMPARATIVE ABATEMENT COSTS FOR KING MINE

apital	Operating 3/
10,000 18,000 19,000	\$5,100/yr. 7,900 3,200
1	.0,000

^{1/} Basis 36,000 GPD, 500 ppm acidity mine drainage

^{2/} Basis 19,500 SCFH 50% of time

^{3/} Includes 10 year amortization, 7% interest

It should be noted that the King Mine represents what is believed to be an extreme comparison for the inert gas technique versus neutralization. This is so since the mined out area is very small compared to the length of the exposed outcrop. In other words, it is believed that the leak-off rate is closely related to the length of the outcrop line associated with the mined out area (a function of the square root of the area). Acid mine drainage production, on the other hand, is more nearly a function of the area of the working.

The result of the foregoing is that a tenfold increase in the worked out area of the King Mine would probably result in a five to tenfold increase in the flow of acid mine drainage and, hence, the capital and operating costs for neutralization while increasing by only two to three times the amount of inert gas required to maintain the mine in a sealed condition.

In view of the foregoing, it is obvious that it will be necessary to obtain gas leak-off rate data on a number of different abandoned mine situations in order to make useful approximations of the overall applicability of the technique. Even then, it is probable that application will be on a case by case basis. This latter circumstance should not detract from the method, however, since determination of the leak-off rate from any given abandoned mine is a relatively simple and inexpensive procedure, and substantial improvement of drainage quality appears possible at significantly lower costs than those associated with treatment. Both the Whipkey and the King Mines are to be resealed using the most effective techniques available. Pressurization measurements will be made as soon as these seals are completed.

ACTIVE MINE EXPERIMENTAL PROGRAM

An experimental program to determine the applicability of inert gases to an active deep coal mine was initiated in August, 1969, under a grant from the Federal Water Pollution Control Administration to Island Creek Coal Company (7). Cyrus Wm. Rice and Company of Pittsburgh was responsible under subcontract for the design of the inert gas and the life support systems with Island Creek's engineering staff being responsible for mine design. The application of inert gas to an active deep coal mine obviously poses many more problems than application to abandoned mines. Additional benefits accrue, however, in addition to preventing the production of mine acid, the elimination of oxygen from the mine eliminates fire and explosion hazards as well as any health problems resulting from continued inhalation of coal dust. A number of other possible benefits occur, among them being elimination of the major capital and operating costs for ventilation, elimination of the added capital costs for explosion-proof electrical equipment, elimination of rock dusting, possible capture and resale of methane, etc.

Since the purpose of the experimental program is to demonstrate the applicability of inert gas to deep coal mining for the abatement of acid mine drainage, the program was broken into four phases: Phase I - engineering feasibility study, in which

specifications for all of the components in the demonstration are developed; Phase II - shakedown testing of the major components of the life support system in an existing mine operated in an air atmosphere; Phase III - construction and operation of the demonstration mine in an inert atmosphere; and Phase IV - evaluation of the demonstration program results and projection to commercial mining conditions. Only Phase I - feasibility study, is funded under the current grant.

The initial bases used in the study were: (1) maximum use is to be made of equipment that is available as is or with minor modifications; (2) the demonstration mine is to be designed to allow use of all nitrogen, nitrogen plus methane, or all methane atmosphere with the oxygen content limited to a maximum of 0.1% v/v; (3) the demonstration mine is to be located adjacent to an existing active mine but not connected to it internally which will enable the use of the coal handling and coal preparation facilities of the active mine to handle the coal produced in the demonstration program; (4) a way station or refuge station is to be located in the demonstration mine near the working faces with the way station ventilated separately from the outside; (5) conventional rubber tired mining equipment is to be used throughout; (6) the demonstration mine is to be operated with a single complete mining crew for one section working a single shift per day.

Three alternative sites for the possible location of the demonstration mine have been selected. All three sites are in West Virginia, adjacent to new active mines of the Island Creek Coal Company. In each case, the portion of the seam selected for the demonstration mine is in virgin coal, and sufficiently separated from current and near future operations of the active mines that there is no possibility of any interconnection between the two. Seam heights of 50-60 inches are available at the selected sites. Samples of refuse from the three sites have been collected, ground, and loaded into test columns in the laboratory in order to determine the potential to develop acid mine drainage. addition, samples of mine drainage from each of the three active mines are being collected and analyzed to determine the amount of acid production that might be expected at the particular sites. None of the three sites is considered gassy and, hence, the design of the demonstration mine will be based on predominately nitrogen atmosphere.

One of the early decisions in the study was that the operators could not carry on their person the necessary life support equipment. The cramped operating conditions in the particular layout and dimensions of the operator seats and controls on the mining equipment preclude any back packs or chest packs of the size necessary to handle the breathing and cooling requirements of each individual for a reasonable period of time. A second decision made early in the study was that irritation and leakage problems ruled out the use of face masks and required instead a full helmet. An additional limit imposed by considerations of the maintenance of low oxygen in the mine atmosphere is a maximum leakage from each individual suit of 1 cu. ft. per hour. This limit effectively pre-

vents use of continuous purge breathing systems and necessitates the use of rebreather systems.

The basic decision to seal the mine produces still further restrictions on the selection of the life support system. In the sealed condition, the mine atmosphere will become saturated with moisture at whatever temperature is selected. The temperature of the mine atmosphere, particularly in the operating areas, is likely to be considerably higher than normal ground temperature because of the requirements to dissipate heat from the active mining equipment. The equipment chosen for the level of operations anticipated produces roughly 1,000,000 BTU's per hour, which will be transferred to the mine atmosphere during operation of the equipment. How much of this heat will be dissipated through conduction to the surrounding walls and roof of the mine, conveyed out of the mine by the coal, or removed by external cooling circuits remains In any event, it is obvious at the outset that to be established. some means of removing the normal 1200-1500 BTU's per hour of metabolic heat from each individual miner will be necessary since normal evaporative cooling and convective cooling from the body will not be practical at the anticipated temperature and 100% relative humidity in the mine atmosphere. These conditions quite naturally lead to the decision to provide full suit coverage for the miners and employ the rebreathing circuit for cooling as well as oxygen supply.

Since the temperature of air supplied to men working in full life support suits is established at approximately 72°F., the temperature of the mine atmosphere will have to be controlled within a fairly narrow range between the suit temperature and the normal ground temperature of 55°F., if excessive condensation of moisture on the suit and the face plate is to be prevented. Studies are currently underway on a heat balance of the mine and various means of controlling this mine temperature within the foregoing range.

With the decision made to use a full suit and helmet, consideration was given to the ease with which the miner himself could put on and take off all or part of the suit as this relates to both eating and relieving himself in the way station. As a result of these various considerations, it has been tentatively specified that the suit shall contain a removable helmet, with the helmet supported on the man's head, swivelling with his head movements. The suit is to be three-piece, separating at the waist, and is to consist of a porous undergarment, a light weight gas barrier of rubberized cloth, and an outside separate and replaceable heavy duty fabric coverall.

It should be noted that there is extensive experience in operations with life support suits and systems for ground support personnel servicing launching rockets and fuel storage and handling facilities at Cape Kennedy; upwards to a thousand men per week have been suited up with these suits and life support packs cleaned, serviced, and repaired in a routine manner. Techniques have been developed for

easy cleaning of suits internally after use since the same suit is not worn by the same individual successive times.

After consideration of many factors, not the least of which was the problem of compatability of individual body odors, it was decided to standardize on individual life support systems, mounting one or more units on the pieces of operating equipment as required. Consideration is being given to cryogenic oxygen, compressed cylinder oxygen, compressed oxygen nitrogen mixtures and to chemical oxygen as sources of supply of the maximum 0.2 lb. per hour per man requirement.

It has not yet been decided on whether the entire individual rebreather units will be taken in and out of the mine by the individual miner and serviced entirely outside the mine, or whether the unit will remain in its position on the operating equipment with the oxygen supply being replaced by the miner as he comes on shift.

Consideration has been given to the means for backing up the basic life support system during times of failure of the basic system or during times when the miner detaches from the basic life support unit mounted on his equipment and moves to the way station. During these backup periods, it is not planned to supply any cooling, but simply to take care of the requirements for oxygen supply and CO2 removal.

Communications between the miners individually and between the miners as a group to the outside control station must be provided. Simple radio transmission will not work except on line of sight, as transmission will not penetrate the walls of coal. The system tentatively selected involves a small very low powered transmitter receiver for each miner broadcasting to what is called a leaky cable system wherein a special antenna wire is strung along side of each passage and is coupled with a powerful transmitter rebroadcasting through the cable. Such systems have the required flexibility using multiple channels to allow miner to miner as well as group to group communication with a minimum of crowding. One problem yet to be resolved is how to meet the requirements of all miners in general but certain equipment operators in particular who must listen to the sound of the roof as it cracks and to the sound of a test probe or hammer as it is pounded on the roof to locate areas of loose rock. A separate contact microphone transmitter arrangement may be the answer. The muffling effect of the helmet is both a help and a hindrance in connection with the sounds generated by the mining equipment. The very high sound level generated by certain mining equipment during operation is in itself a health hazard, thus, muffling this sound is a definite benefit. On the contrary, the sound of a piece of equipment during operation is a quide to the operator both as to its mechanical condition and in some instances as to his operation of the controls. At present, it appears best to resolve this problem during Phase II shakedown operation.

Personnel and equipment will be admitted to the mine through gas locks at the entries and personnel will be admitted to the way station within the mine through a gas lock between the station and the mine. Makeup gas to the mine will compensate both for that lost through gas locking operations as well as that lost through leakage through any fissures. This makeup will be from a floating gas holder, which will maintain a constant differential pressure in the mine above surrounding atmosphere and will smoothe out the surges in inert gas requirements. Makeup to the gas holder for the demonstration project will be from an industrial inert gas generator employing natural gas as fuel. It is estimated that for one shift operation, the demonstration mine will use approximately 250,000 standard cu. ft. of inert gas per day. Gas quality control instrumentation will be employed to monitor the composition within the way station, the gas locks, and the mine proper.

Facilities will be provided outside the demonstration mine for suit and life support maintenance and for communications maintenance, in addition to the normal repair facilities for the mining equipment. A classroom, locker room, control room, and a timekeeper's office will be provided as well.

In summary, the feasibility study to date on the application of inert gas to active deep coal mining has not shown the existence of any significant technical obstacles. With the exception of the individual life support packs, all of the major required equipment is off-the-shelf, or off-the-shelf with minor modifications. The life support units themselves present only a simple combination of available components and do not appear to require a major developmental program. None of this is to say that there aren't many problems ahead. Not the least of these problems is going to be the effects of coal dust on the safe functioning of the connectors between the umbilical hoses supplying air to the suits and the life support packs, since such connections must be made and broken regularly in the mine as men come and go or leave their equipment for the way station. The control of dust in the mine also poses an unknown problem at present; due to the absence of large volumes of ventilating air, it is not known whether dust created by the mining operations will settle rapidly or will create visibility problems. All of these matters are under consideration at present; some of them can only be solved during the shakedown period; some won't be solved until actual operation in the demonstration mine.

REFERENCES

- Anon. "Substantial Progress Reported in Mine Seal Program," Coal Mining, 15 (2), 8-10, (1938).
- Braley, S. A., "Summary Report of Commonwealth of Pennsylvania (Department of Health) Industrial Fellowship No's 1-7 Incl.," Mellon Industrial Fellowship No. 326B, (1954), pp. 192-3.
- Shumate, K. S., and Smith E. E., 2nd Symposium on Coal Mine Drainage Research, Mellon Institute, May, 1968.
- Bell, W. E., "Studies of the Effect of Gas Atmospheres on Pyrite Oxidation," FWPCA Contract No. 14-12-404, Cyrus Wm. Rice Division, NUS CORPORATION, April, 1969.
- Baker, R. A., Mellon Institute, Carnegie Mellon University, personal Communication.
- "Gas Requirements to Pressurize Abandoned Deep Mines A Study of the Use of Inert Gases to Eliminate Acid Pollution from Abandoned Deep Mines," Commonwealth of Pennsylvania Project No. CR-81, FWPCA Project No. WPRD-227, 1968.
- 7. "A Demonstration of a New Mining Technique to Prevent the Formation of Mine Acid in an Active Deep Coal Mine," FWPCA Project No. 14010DZM, 1969.
- 8. "Space-Cabin Atmospheres, Part I-Oxygen Toxicity," National Aeronautics and Space Administration, SP-47, 1964.