



Analysis of Fundamentals of Acid Mine Drainage

A Basis for Future Investigations

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**Sponsored by
Ohio River Valley
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The Ohio State University
Columbus, Ohio

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Water Resources Center
Engineering Experiment Station
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A BASIS FOR FUTURE INVESTIGATIONS

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INTRODUCTION

The broad scope of the acid mine drainage problem has been well established by many previous studies relating it to both the basic and the applied sciences. Literature treating of the acid problem goes back some fifty years and contains a wealth of information. However, several specific areas remain in which knowledge is lacking. It is, therefore, considered timely to critically review the compilation of knowledge of acid mine drainage and establish its current status, in order that an intelligent appraisal can be made of the needs for research activities in this field.

For this purpose the Water Resources Center of the Engineering Experiment Station at The Ohio State University has pursued a project sponsored by the Ohio River Valley Water Sanitation Commission to attempt the following objectives:

1. To place in perspective the various factors related to the formation, measurement and control of acid mine drainage and its polluttional affects.
2. To indicate gaps in knowledge that should be filled in order to master comprehension of the problem, and advance the control efforts.
3. To chart a sequential method of research approach that will give proper emphasis to all factors and that will provide opportunity for efficient application of new knowledge as it becomes available.

Due to the diverse areas of participation necessarily involved in such a study, a task-force comprising individuals from each of the pertinent disciplines was assembled to pursue these studies.

The members of the team and their areas of specialization are as follows:

George P. Hanna, Jr., Project Supervisor, Associate Professor of Civil Engineering and Director, Water Resources Center; Engineering Experiment Station, The Ohio State University.

Russell A. Brant, Assistant Chief, Division of Geological Survey, Ohio Department of Natural Resources.

J. Richard Lucas, Assistant Professor of Mining Engineering, The Ohio State University.

Chester I. Randles, Professor of Bacteriology, The Ohio State University.

Edwin E. Smith, Associate Professor of Chemical Engineering, and Director, Chemical Engineering Research, Engineering Experiment Station, The Ohio State University.

FINDINGS AND RECOMMENDATIONS

It is intended that the results of this study will provide the framework for a broad plan of research, and will serve as a guide and reference for future studies of acid mine drainage to the end that reductions or abatements in this pollution problem may be realized.

The phenomena associated with the production and abatement of acid mine drainage is classified for simplicity into the four fundamental areas of chemistry, microbiology, mineralogy, petrology, and geology-hydrology. Figure 1 indicates the status of current knowledge, the proposed endeavors, and the goals to be achieved in each of these areas. The current knowledge indicates that generalizations are prevalent in defining the relationships of these fundamentals to the overall problem. The chemical end products and overall reactions are generally well defined. Some effect of microorganisms in the oxidation processes is acknowledged. The general description of pure sulfide materials is well established, as are techniques for defining the system geology and hydrology. Further intensive research to determine this relation to the oxidation of sulfuritic materials is recommended in:

1. The fundamental kinetics of the chemical reactions,
2. The exact role of bacteria in acid production,
3. Lattice structure and element arrangements in the reacting minerals.

The application of sound geological and hydrological principles and techniques is recommended to delineate the extent of both the sulfur bearing material and the water problem, and to provide a key to the solution by water controls and acid containment.

The narrative report cites in detail the current information status and indicates specific investigations to be pursued in order to fill voids in the existing knowledge. A section on applied studies is also included, with specific recommendations relating to mine seal studies including design and development of adequate seals, specific surface mining investigations, and general water controls.

The suggested planned program of research as indicated in Figure 2 requires a sound approach to define the problem area, select basic principles which apply, establish testing procedures, and employ these principles and procedures in both laboratory and field experiments. Discrepancies in correlated results suggest modification or revision of principles or procedures, and test replications until results fall within acceptable limits of error.

Basically this study deals with acid production and alleviation measures, and has therefore considered only those biologic organisms related to acid and acid formation. The effect of the acid mine drainage on biologic life has been intentionally excluded.

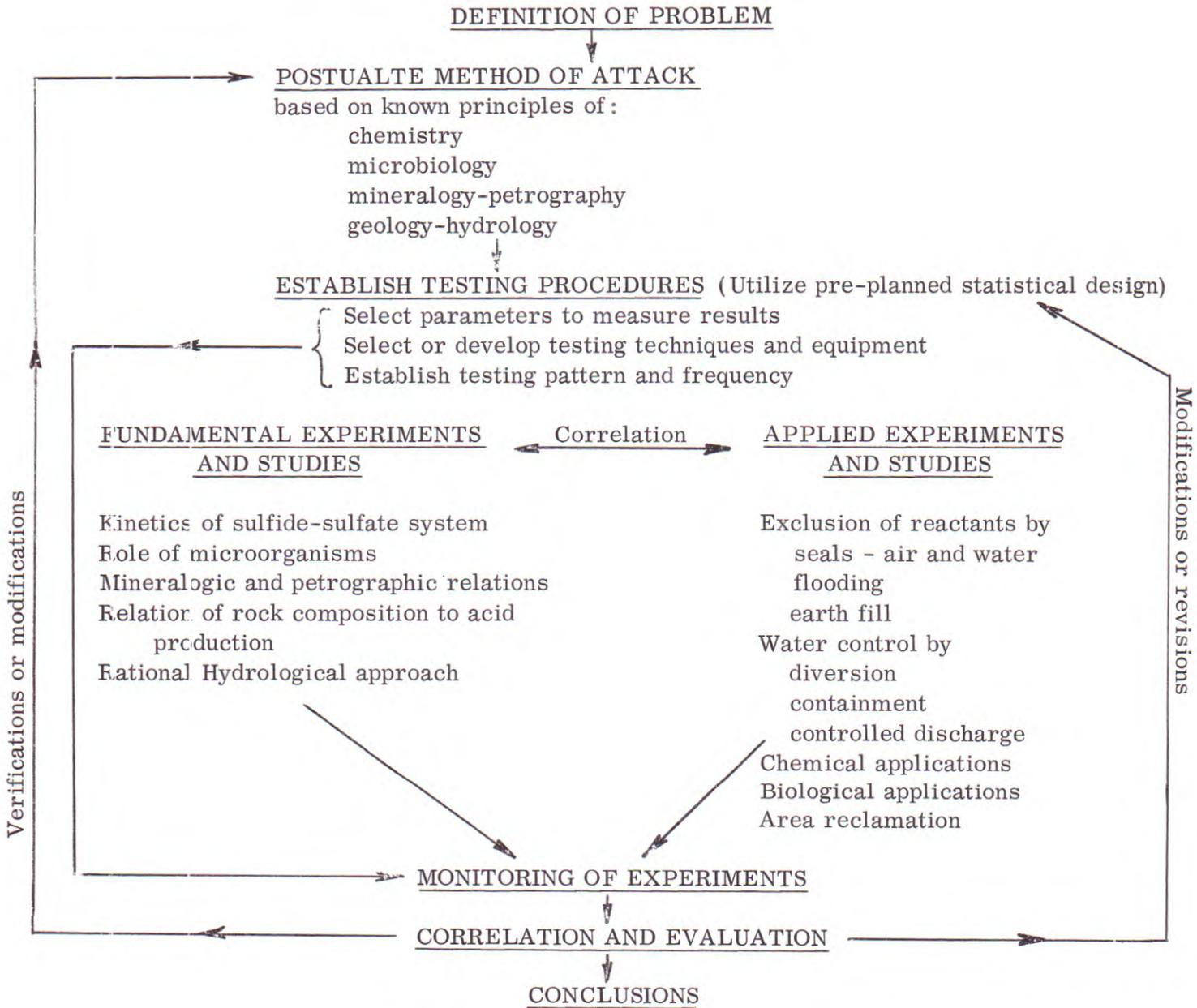
FIGURE 1

FUNDAMENTAL AREA RELATIONS TO THE ACID MINE DRAINAGE PROBLEM

| Fundamental Areas | Chemistry | Microbiology | Mineralogy - Petrology | Geology - Hydrology |
|--------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Status | <p>End products and general over-all reactions are well defined. Elementary reaction mechanism is unknown and intermediate reactants are not established. Several rate - mechanism concepts are postulated.</p> | <p>1. Microorganisms are "somehow" involved in sulfide oxidations. 2. Microorganisms can reduce $SO_4^{=}$.</p> | <p>1. General description of pure sulfide materials is well established. 2. Little is known of the mineral associations of sulfides in coal and associated strata.</p> | <p>General principles and overall effect are known.</p> |
| Proposed Endeavors | <p>Basic research on reaction mechanisms.</p> | <p>Basic studies of oxidation of $S^{=}$ and reduction of $SO_4^{=}$ by microorganisms.</p> | <p>Petrographic studies of sulfidic material in coal and associated strata.</p> | <p>Quantitizing and specific application of general principles pertinent to the "insitu" setting.</p> |
| Goals | <p>Determine kinetics of sulfide-sulfate system. Arrive at rate-controlling mechanisms on which methods of inhibiting or catalyzing reactions and evaluating acid potential may be based.</p> | <p>Determine qualitative and quantitative roles of various microorganisms in both oxidation of sulfides and reduction of sulfates.</p> | <p>Determine mineralogic relationship of sulfides in coal and associated strata.</p> | <p>Evaluate rock composition and mineral variation as a measure of acid potential. Determine the neutralization character of certain measures and their effect on the acid production. Develop a rational hydrological appraisal of the acid water production.</p> |

FIGURE 2

PLANNED PROGRAM OF RESEARCH - ACID MINE DRAINAGE



Effects of the overall abatement program of funda-
mental principles applied to the reduction of acidity
in mine waters as measured by specific parameters.

Effects at the sources of production
Effects in the receiving streams

OCCURRENCE AND SIGNIFICANCE OF ACID MINE DRAINAGE

OCCURRENCE

Acid waters originating from the exposure of sulfidic materials to degradation processes and weathering have resulted in one of the most serious water pollution problems now facing the coal producing regions of the Ohio River Basin. Sulfidic materials in their natural states of marcasite and pyrites may be present in the coal measures and adjacent strata. Removal of the coal with its attendant exposure of these sulfur bearing materials to air and water activates a reaction ultimately producing sulfuric acid dilutions in the tributary streams. Natural oxidation and hydrolysis results in the characteristic red or brown sludge deposits of iron hydroxides which accumulate and smother biologic life natural to the waterways. The acid water production is closely associated not only with the active coal mining operations, but also with the inactive and abandoned workings which continue to spill forth acid water. It has been variously estimated that some 2 1/2 million tons of sulfuric acid from active and abandoned workings pour into the Ohio River and its tributaries each year².

Active Mining Areas

The three general mining systems employed in the extraction of coal may be classified as follows:

- 1) Underground mines whose entrance is gained by shaft, inclined slope,

and downward sloping drifts.

- 2) Underground mines whose entrance is gained by horizontal or upward sloping drifts. Included in this group is auger mining of highwalls and coal outcrops.
- 3) Surface mining by progressive removal of the overburden rock formation in narrow strips.

While active mining operations are continuing, all three groups can produce acid mine drainage, since in each case sulfide minerals may be exposed to oxygen and moisture. During the active stages, mines in groups 1 and 2 usually produce more acid because of the extensive exposed coal surfaces, and fresh spoil bank and gob-pile deposits.

The amount of water inflow into a given mine and the subsequent handling of this water is another important factor in acid production. While the inflow is a function of many independent variables requiring further study, it is also a function of the mining system employed. If both water inflow to the mine and exposure of sulfidic materials can be reduced, the resulting acid contribution will be appreciably lessened. This possibility presents a challenge in incorporating these factors into the specific mine system planning and operations.

Underground Mining

The three necessary elements of acid production, the disulfide mineral, oxygen, and water, are usually present in large quantity in acid producing under-

ground mines. In strip mining some effort is made to dispose of the disulfide material, while in underground mining there is little or no opportunity for such disposal. In fact as mining progresses from the development stage to the pillaring or extraction stage, more disulfide material is exposed by the failure of the roof strata and supporting coal pillars. The failure of the coal pillars during extraction also produces finer size particles resulting in even more susceptibility to oxidation through increased surface areas.

Surface Mining

The mining of coal, by surface systems, is generally referred to as "strip mining" since a succession of narrow strips of overburden are removed from the coal seam during the mining process. After the uncovered coal is loaded out, mountains of fresh overburden are deposited in its place from uncovering the subsequent coal strip.

The extent of the problem in mines of Group 3 (Surface Mining) lies somewhere between Groups 1 and 2. The exposed surface area of the coal and overburden material is a minimum. However, this is aggravated by the high spoil banks, containing fractured and exposed sulfide minerals. These sulfide minerals, especially on the exposed surface will be continuously leached out until they are dissipated, and are a continued potent source of acid not only during the active period of the operation, but long after its abandonment. Grawe³ showed experimentally that two minerals associated with acid production are found on exposed spoil dumps.

These minerals are copiapite, a yellow hydrated ferrous-ferric sulfate, and starkeyite, a white tetrahydrate of ferrous sulfate. After an extensive period of time there will be a tendency toward a natural recovery of the abandoned areas. Some relief is experienced by covering the high sulfide materials and back-filling and damming the last strip cut for the partial exclusion of air and water. The system and sequence of removing the overburden is one of the most important independent variables that affect acid production in surface mining operations.

Abandoned Mining Areas

Acid production is significantly different when mining areas are abandoned due to depleting resources.

Eventually all operations in Group 1 abandoned mines will cease to produce acid due to natural "water flooding". The iron disulfide minerals are thus deprived of oxygen and their virgin state is unmodified by further oxidation.

Mining operations in Group 2 present the most serious long range problem. If these operations are abandoned without modification, they will continue indefinitely to produce acid mine water and form additional acid products from the sulfide minerals. It follows that some economical modification to the mines must be developed and applied at the time of abandonment in order to reduce the acid problem. Such modifications should receive high priority in any research effort directed at the whole problem of acid mine drainage.

Coal Preparation Plants

In the preparation process, coal impurities are more thoroughly separated from one another to upgrade the marketable product. The extent of preparation varies from little or none to extensive separation of the refuse from the run of mine (ROM) product. The refuse or spoil bank material as described above may run as much as 50 percent of the ROM product, but usually averages much less.

SIGNIFICANCE OF THE PROBLEM

Acid discharges destroying the natural alkalinity of the streams reduces the water suitability for recreational, industrial, and municipal use due to the increased acidities and total solids including sulfates and iron. The present day and future needs for increased water use and re-use and the corresponding increased valuation of suitable water supplies will place considerably higher dollar values on future damage estimates. At the mine sites the use of special acid resistant pipe and pumps is required in many cases to minimize corrosion effects⁴. Increased concrete and metal corrosion on river fixed structures and floating equipment is also attributable to the acid waters⁵.

Successful attraction of industrial development to supplement the economy in depressed areas depends in good measure upon the ability to furnish an adequate supply of clean water, relatively free of solids and scale producing or corrosion producing characteristics, to satisfy its cleaning, cooling, and product consumption requirements. The potential risk that acid waters may develop is a deterrent to

capital investment for either industrial or recreational expansion.

Much of the depressed area is forest oriented, and reforestation in many cases is a sound approach for area recovery, both from the standpoint of developing recreational facilities as well as the future aspects of a timber crop. However, the length of time required for productive return from new plantings does not offer the more immediate economic gain that can be realized from recreational development. The maintenance of acid free waters in the depressed areas such as Southern Ohio could be a strong motivation for expansion of recreational facilities to serve the nearby urban areas.

RELATION OF CHEMISTRY TO THE ACID MINE WASTE PROBLEM

CHEMISTRY OF THE SULFIDE-TO-SULFATE REACTION

As is the case in many commonplace "natural" reactions, gross changes which occur, as well as reactants and final products, are recognized and accepted with little thought as to the actual mechanism by which these changes are brought about. Two of the most common are the "rusting" (oxidation) of iron and formation of acid mine drainage. Only in the last several years has the mechanism by which iron oxidizes been closely examined. Since the "rusting" of iron has been recognized as a serious problem for many more years than has acid mine drainage, it is not surprising that the fundamental mechanism of the sulfide-to-sulfate reaction has been even less-studied than that of iron oxidation.

Kinetics As Related To Rate-Determining Reaction Mechanisms

It is a simple exercise in elementary chemistry to formulate balanced equations relating the reactants (sulfides plus oxygen) resulting in the sulfates (plus H_2S , sulfur, SO_2 , etc.) as end products of the sulfide-to-sulfate reaction. However, such general overall relations give no information regarding the elementary reaction mechanisms involved. The great majority of kinetic studies of the sulfide-to-sulfate oxidations made in the past have been based on overall reactions. Widely divergent reaction rates have been reported by different investigators. In view of the very limited range of temperature involved in the acid mine problem, there are probably

only a few (perhaps only one) reaction rate constants for the rate-determining steps in the overall reaction which would define the kinetics of mine acid formation. In order to determine these constants, first, the rate-determining steps must be defined, and second, all physical and chemical factors influencing these steps must be known and quantitatively related by the rate equations. Unfortunately these basic rate-determining steps are not as yet known.

Postulated Reaction Mechanisms

Within the last few years, several investigators have proposed reaction mechanisms thought to be part of the overall sulfide-to-sulfate reactions. McKay and Halpern⁶ made a kinetic study of the oxidation of pyrite in aqueous suspension at temperatures between 100 and 130°C. Although their interests and conditions were relative to the hydrometallurgical processes for leaching of sulfide ores, some of their conclusions are applicable to natural weathering phenomena.

They conclude that:

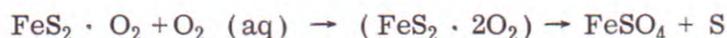
- 1) The rate-determining step in oxidation of pyrite is a heterogenous process on the pyrite surface which involves only an oxygen molecule. This is supported by the observation that the rate is first order in O₂, and independent of the solution composition.
- 2) The reaction: $4\text{FeSO}_4 + \text{O}_2 + 2\text{H}_2\text{SO}_4 \rightarrow 4\text{Fe}(\text{SO}_4)_{1.5} + 2\text{H}_2\text{O}$ determines the ratio of Fe(3+) to Fe(2+) in solution, but has no effect on the oxidation of pyrite.

- 3) The formation of elemental sulfur is favored principally by high acidities and low temperatures, while low acidities and high temperatures favor formation of sulfuric acid.
- 4) The simplest interpretation consistent with all their observations is that the oxidation of pyrite occurs predominately by the reaction:

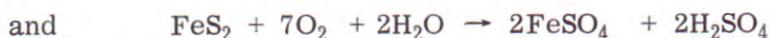


A plausible mechanism (although not the only conceivable one) for this reaction, consistent with the observed kinetics, might involve the following sequence of steps:

- a) O_2 is chemisorbed rapidly on the pyrite surface which is thus always covered by a monolayer of O_2 , comprised of one O_2 molecule on the O_2 - covered site; i. e.



- b) An alternative interpretation, also consistent with the observed kinetics is that S^0 is not an intermediate in the formation of H_2SO_4 but that S^0 and H_2SO_4 are produced by simultaneous competing paths corresponding to the reactions:



from a common intermediate which is, in turn formed in the rate-determining reaction between FeS_2 and O_2

Braley⁷ performed a series of extended laboratory tests involving continued exposure of sulfuritic materials and repeated water extraction therefrom. The ultimate sulfur to iron ratio of 2.00 from sample analyses indicated the validity of the second of the above equations.

Sato⁸ reports that results from measurements of single electrode potentials of sulfide minerals, when correlated with their electrode behavior indicates that the direct oxidation of a simple sulfide mineral is a process in which the metallic atoms move into the surrounding solution to become aqueous cations, accompanied by a stepwise decrease in metal-to-sulfur ratio of the remaining solid phase. When elemental sulfur is left over, it undergoes a series of oxidations to the sulfate ion. In the case of disulfides of iron, ferrous ions and S₂ molecules appear to be released simultaneously on oxidation.

A somewhat different conception of mechanism has been taken by Rosetti and Cesini⁹ who describe the oxidation as occurring by electrochemical reactions involving galvanic cell pairs between (for example) different metal sulfides in mine water solution. They state that, as a rule, compounds formed by the electrochemical reaction are minerals of lower stability and crystal symmetry, e.g. marcasite in place of pyrite. This concept adds the physical-chemical-structural relations and chemical environment of the system, or the mineralogical variable, to the search for the rate controlling mechanism.

Factors Influencing Kinetics of Reaction

It is possible that the kinetics of the sulfide-to-sulfate reaction is greatly influenced by the mineralogy of the system. Most laboratory studies have been made using "pure" crystalline samples of pyrite and marcasite, assuming in effect that these materials represent the solid reactants in the sulfide-to-sulfate reaction. It is likely that the sulfide minerals disseminated through a coal seam and adjacent strata are different in both physical and chemical properties from "museum-grade" samples of pyrite and marcasite. In addition, other minerals which may act as catalysts, or supply the galvanic couple, may be present.

One fact basic to the study of reaction mechanism can be stated with some degree of certainty: the rate-controlling mechanism, in normal temperatures and atmospheres, involves an interfacial (heterogeneous) mechanism in which a solid is one of the participating phases. It is implied from laboratory observations that the reaction rate is directly related to surface area of a solid reactant and that subsequent or intermediate reactions, which probably occur as liquid-phase ionic reactions, are relatively rapid^{10, 11}. The latter point is evidenced by the minor quantities of intermediate reactants present in the reaction system.

A number of variables, in addition to exposed surface area, are reported to influence overall reaction rate. Among these are water, oxygen partial pressure, pH of solutions, ferric ion concentration and other catalytic agents (bacteria, specific ions, etc.) and inhibitors (bactericides, phosphates, amines, ammonia, and other alkaline materials). In addition, the course of intermediate reactions

may shift product concentrations to alter the overall reaction rate. For example, ferric ion concentration and pH of solutions both may be fixed by products of intermediate reactions whose relative reaction rates are influenced by the factors (variables) listed above.

It is also conceivable that one of the rate-controlling mechanisms is physical rather than chemical in nature. Theoretically, one may postulate that, within the capillaries of sulfide minerals, a solution has reached chemical equilibrium and the rate of production of sulfates is dependent on how rapidly the reaction products within the capillaries enter the main body of solution where further oxidation may occur.

If the basic rate-determining mechanisms were known, it would be possible to deduce the factors which would influence the overall sulfide-to-sulfate reaction. Conversely, one method of determining the rate-controlling mechanism is to select one of the many mechanisms which may be postulated, then study the effects of those variables which theoretically should influence reaction rates. This indirect approach can lead to erroneous conclusions through misinterpretation of results or incomplete study of significant variables.

Any postulated mechanism must include consideration of several factors which have been well established by experience if not theory. Water is known to have a profound influence on the overall reaction rate. Just how water contributes to the reaction is not known. It may simply provide a media in which bacteriological or

ionic reaction occurs, or it may actually be one of the intermediate reactants involved in the overall reaction.

Microbiological influence on reaction rates has also been demonstrated. This aspect of the problem is discussed in the following section, but its importance as a part of the basic chemistry in the sulfide-to-sulfate reaction should be mentioned here. Basic chemical mechanisms postulated above may be catalyzed or directed by microorganisms; that is, while a reaction may be described as a chemical change, this change may well be influenced by bacteriological factors.

Importance of Knowing Reaction Mechanisms

The importance of an understanding of the basic reaction mechanisms in the study of acid mine drainage can be illustrated by reference to a proposed plan of attack on the problem. Suggestions have been made to examine different mining areas which differ greatly in the amount of acid they produce in the hope that some measure of "potential acid formation" could be made. At the present time such a study would require collection of all information which may be pertinent. Without some basis by which to select this "pertinent" information, the characterization of a mined area would be physically impossible due to the large number of possible contributing factors that could be suggested.

On the other hand, if the reaction mechanisms were clearly defined, the pertinent variables would be known, and characterization of a mine site with regard to "potential acid formation" as well as suggestions for abatement could be made in

RELATION OF MICROORGANISMS TO ACID MINE DRAINAGE

BACTERIA AND ACID FORMATION

Evidence of microbial participation

Direct Evidence

As long ago as 1919, Powell and Parr¹² stated that the oxidation of sulfides in coal seems to be hastened by the presence of bacteria or some catalytic agent. They based this statement on the finding that inoculation of fresh coal samples with well-oxidized coal samples speeded up the rate of sulfate formation from fresh coal. Davidson¹³ (1930) and Carpenter and Herndon¹⁴ (1933) arrived at a similar conclusion after comparing the activity observed with sterilized and unsterilized samples of coal.

Later a series of papers from the West Virginia Engineering Experiment Station described additional information regarding the action of bacteria on the oxidation of sulfides and reported the isolation of what were considered the two pertinent bacteria associated with acid formation: Thiobacillus thiooxidans and T. ferroxidans (see Colmer and Hinkle¹⁵, 1947; Temple and Delchamps¹⁶, 1953; Temple and Koehler¹⁷, 1954). Investigators at the Mellon Institute at about the same time were obtaining similar, but not entirely compatible results (see Leathen et al.^{18,19}, and Braley²⁰).

Results implicating microorganisms in the formation of coal mine acid have

also been obtained at The Ohio State University (see Moulton¹, 1957; and unpublished results of Randles²¹), and in the British Isles (Ashmead²², 1955).

Bryner and his co-workers in Utah have presented evidence that iron pyrite, chalcopyrite and molybdenite are oxidized biologically and have reported isolation of bacteria believed responsible for these changes (see Bryner et al.²³, 1954; Bryner and Anderson²⁴, 1957; Bryner and Jameson²⁵, 1958).

In addition, as Temple and Delchamps¹⁶ note, the oxidation of pyrite in soil has been associated with bacteria by several workers; in these cases the responsible organisms have not been definitely identified although T. thiooxidans has been suggested as the probable agent aiding the oxidation. Much of this work was done before it was realized that organisms such as T. ferrooxidans or F. ferrooxidans exist; this may in part explain some of the problems associated with demonstration of the nature of pyrite oxidation in soil. In this vein, Gleen²⁶ (1951) has shown that iron-oxidizing organisms are normal to soil. Divalent iron perfused through soil at pH 3 gave a soil enriched with iron oxidizing organisms. Such soils also oxidized thio-sulfate to tetrathionate, which would be expected if T. ferrooxidans were responsible for the iron oxidation. However, it is not clear whether this was the case or whether the accumulated ferric iron brought about the oxidation.

Indirect Evidence

It should be pointed out that other less direct but significant information is on hand that further implicates microorganisms in the production of mine acid.

1) The presence of significant number of both iron and sulfur oxidizing organisms in acid mine water is itself evidence that they are catalyzing oxidations of these materials in the mine. As Temple and Koehler¹⁷ rightly emphasize, the logical connection of these organisms with the oxidations has not always been appreciated. "It is not merely a matter of guilt by association." These organisms can live only by catalyzing these oxidations; their presence in such numbers means that they must be catalyzing these oxidations at least to the extent necessary for their proliferation.

2) The apparent lower limits of acidity that seems to develop normally in acid-mine waters (pH 2.5 - 3.0) may further suggest the significance of biological action. If responsible organisms have a lower limit of acid tolerance in this range a ready explanation for this pH limit is available. A Thiobacillus isolated from acid-mine water has such a limit (Nemeth and Randles²⁷, unpublished results) and it has been shown by Silverman and Lundgren²⁸, 1959) that the rate of oxidation of ferrous iron by F. ferrooxidans falls off rapidly below pH 3.0. Leathen et al.²⁹ (1956) give the optimum pH for growth of this organism as 3.5. On strictly chemical grounds an explanation for this pH limit is not apparent.

3) The extensive growth of a Pseudomonas and of Euglena in some acid waters also indicates that micro-organisms are involved in mine acid formation. Unpublished studies by Randles and Hrubant³⁰ show that the Pseudomonas growing as "streamer" required the B vitamin, thiamin, and organic material for growth. These must be present then in the acid mine water for such "streamers" to develop.

What would be the source of thiamin and organic material necessary for growth other than that produced by autotrophic bacteria in the mine?

Little information is available regarding the organic content of acid as opposed to normal water. One analysis reported by Temple and Koehler¹⁷ does point to a great increase in "volatile and organic material" in a Pittsburgh seam acid water as compared with roof drips from the same seam. Patrick ³¹(1958) reports a similar figure (Volatile matter 3,200 ppm) for acid water issuing from the air shaft of the abandoned Kempton Mine, compared with 20 ppm volatile matter from the non-acid Savage River reservoir.

The pH optimum for growth of this Pseudomonas "streamer" is about 7, so that the presence of "streamers" is clearly not due to any beneficial influences of acidity on growth of the organism. It is there in spite of adverse pH conditions. This clearly suggests that the organisms are growing in the acid water because the necessary nutrients are present. In contrast to normal waters, the effect of acidity on the polysaccharide produced by the organisms probably makes possible the formation of such streamers. The polysaccharide is sufficiently soluble in neutral water that such "streamers" would not be apt to develop even if necessary nutrients were present.

Euglena, which are prominent organisms in acid mine water, may also indicate a role for microorganisms in acid water in that the majority of these organisms require another B vitamin, B₁₂.

From the above evidence it seems conclusive that bacteria are involved in the natural oxidation of sulfide minerals. It should not be construed, however, that the oxidation would not occur unless bacteria are present. It only means that bacteria greatly accelerate the process. The nature of the organisms involved and their roles in the process of acid formation are not clear and need to be considered in more detail.

Nature of Bacteria That May Participate in Oxidations

There are three organisms described from acid mine water that need to be considered relative to formation of the acidity.

1. Thiobacillus thiooxidans
2. Thiobacillus ferrooxidans
3. Ferrobacillus ferrooxidans

Since these are important organisms in acid mine water, and are dependent upon reduced sulfur or iron for their growth, they must find these substrates somewhere in the mine environment and must catalyze their oxidation.

As a point of departure for the discussion the experimental results obtained in the three major studies of these organisms and their influence on the oxidation of, or acid formation from, insoluble metallic sulfides are briefly described.

Earliest in point of time were the series of studies conducted at the West Virginia Engineering Experiment Station between about 1930 and 1953 (Temple and Delchamps¹⁶, 1953, and Temple and Koehler¹⁷, 1954). The organisms they

isolated were Thiobacillus thiooxidans and T. ferrooxidans. The former, in agreement with all other reports showed no ability to oxidize ferrous iron; the latter oxidized ferrous iron rapidly but also grew on thiosulfate. However, after two years on ferrous iron media it failed to grow on thiosulfate.

T. thiooxidans showed no activity on pyrite, but was active on some sulfur ball material and on marcasite. T. ferrooxidans significantly increased the formation of sulfate from pyrite and sulfur ball material (marcasite was apparently not tried).

Studies begun at Mellon Institute in 1946 also led to the isolation of two microorganisms, T. thiooxidans and Ferrobacillus ferrooxidans. The latter differed from T. ferrooxidans in that no activity was demonstrable on thiosulfate (see Leathen et al.^{18,19}). However, some activity on sulfur has been reported for this organism by Silverman and Lundgren²⁸ (1959). Kinsel³² (1960) has just reported the isolation from acid mine water of Ferrobacillus sulfooxidans, an organism capable of oxidizing both ferrous iron and sulfur but not thiosulfate.

Leathen et al.¹⁸ concluded from their work that T. thiooxidans does not influence oxidation of sulfur ball material or pyrite but that some activity for marcasite existed. F. ferrooxidans, on the other hand, enhanced acid production from sulfur ball material as well as marcasite. No activity was demonstrated with pyrite. It may be noted that the particle size of pyrite employed was much larger in these experiments than in those the West Virginia group reported above.

The third group of workers (see Bryner and Jameson²⁵, 1958) involve a quite different locale - Brigham Canyon, Utah. Sulfur and iron oxidizing bacteria were

also isolated, one corresponding to T. thiooxidans and the other resembling most closely T. ferroxidans. The latter strain of organism, in addition to rapidly oxidizing ferrous iron, also oxidized sulfur at about half the rate of T. thiooxidans. No activity on pyrite or other sulfides was demonstrated by T. thiooxidans (marcasite not used). However, the strain of T. ferroxidans isolated, was active on pyrite as well as on chalcopyrite and molybdenite.

While these results may at first seem quite discordant, the differences are small enough to be largely explicable on the basis of different experimental procedures and strain differences, especially those arising during laboratory manipulation. The following table summarizes the activities of the organisms studied by these three groups.

Activities of Various Organisms Isolated From Acid Mine Waters

| Substrates | <u>T. thiooxidans</u> | | | <u>F. ferroxidans</u> | <u>T. ferroxidans</u> | |
|------------------|-----------------------|--------------|------------|-----------------------|-----------------------|------------|
| | Mellon Group | W. Va. Group | Utah Group | Mellon Group | W. Va. Group | Utah Group |
| Thiosulfate | | + | | - | + (later lost) | |
| Sulfur | + | + | + | (+ ; Silverman 1959) | | |
| Fe ⁺⁺ | - | - | - | + | + | + |
| Sulfur Ball | - | + | | + | + | |
| Pyrite | - | - | - | - | + | + |
| Marcasite | + | + | | + | | |
| Chalcopyrite | | | - | | | + |
| Molybdenite | | | - | | | + |

+ = activity shown

- = no activity

Blank = not done

The only discordant result with T. thiooxidans arises from the reported activity on sulfur balls. This may be a consequence of two differences: (1) the distinction between different sulfur balls and (2) the use of perfusion units rather than flasks for conducting the studies. By virtue of their greater efficiency, perfusion units may yield measurable change while flask experiments might not. It should be noted that the West Virginia and Utah groups used perfusion units for most of their studies while the Mellon group did not.

The failure of the Mellon group to obtain action of their iron oxidizing bacterium on pyrite may be a consequence of their use of relatively coarse pyrite (between about 0.04 and 0.095 inches) as compared with the ball mill ground pyrite of the W. Va. group.

There is inconsistency in relating action on sulfur ball material to that of marcasite and pyrite, in that pyrite was found in all four sulfur balls analyzed by Foster and Feicht³³ (1946) while no marcasite was found. Yet with T. thiooxidans (W. Va. group) and T. ferrooxidans (Mellon group) oxidation of sulfur ball material and marcasite but not pyrite is reported. Either the sulfur balls used did contain marcasite or the physical state of the pyrite in the sulfur balls made it much more reactive than the museum grade pyrite employed. (This "either or" statement, of course, neglects the possibility that other materials than the sulfide in the sulfur balls may be pertinent.)

Roles of Bacteria in the Process

Roles in Initial Oxidative Steps

What can be deduced from this work relative to the oxidation of sulfide materials and the bacteria isolated from acid-mine water?

1) T. thiooxidans shows no evidence of ability to oxidize ferrous iron, yet there is evidence that it can speed up the rate of oxidation of marcasite and probably certain sulfur ball material, this action will need to be related to action on the sulfur portion of the iron sulfide. Since several workers have demonstrated sulfur as a product of the chemical oxidation of iron sulfides, especially marcasite, it would be most logical to assume that oxidation of S by T. thiooxidans is responsible for its activity. Both speeding up the oxidation of this S and hastening development of an acid environment could be involved.

The suggestion would then be like that postulated by Quispel et al.³⁴(1952) to explain the oxidation of pyrite in reclaimed marine soils which was stimulated by T. thiooxidans: the oxidation of the surface ferrous iron chemically releases sulfur which can then be oxidized to sulfuric acid by T. thiooxidans. Marcasite would be affected more than pyrite by such a process because it is chemically less stable and apparently has a greater tendency to form sulfur.

On the other hand the possibility cannot be ruled out that T. thiooxidans can directly attack the sulfur in certain sulfides without waiting for sulfur to be released by a chemical oxidation. Possibly the mechanism whereby this organism attacks sulfur, which is insoluble, can also operate to some extent on insoluble sulfides. This mechanism is not known, but there is some support for the suggestion that

the reaction with sulfur involves reduced glutathione (GSH) :



Suzuki and Werkman³⁵ (1959) showed that cell-free extracts of T. thiooxidans oxidized sulfur only when reduced glutathione was present. They suggest two possible explanations for the results: "Elemental sulfur might enter the cell by forming -SS- bonds with the sulfhydryl groups of protein or glutathione located near the surface of the cell. It is also possible that sulfur is reduced to hydrogen sulfide by glutathione outside the cell and enters the cell in the form of the soluble sulfide ion." A comparable reaction would be possible with one of the sulfur atoms of the disulfide:



2) In line with the first suggestion above for the nature of the action of T. thiooxidans action, it is observed that the catalytic action of the iron-oxidizing organisms would hasten the formation of sulfur. In the presence of sulfur oxidizing ability in either the same organism (T. ferrooxidans) or another organism (T. thiooxidans) this would speed up the rate of acid formation if this reaction is limiting. It might also speed up the rate of the reaction by influencing the rate of oxidation of the second sulfur atom in the disulfide. (The sulfur atom indicated as remaining in the FeS of equation 2 above.)

With pure cultures of the F. ferrooxidans of the Mellon group, one of necessity needs to restrict the action of the organism to its effect on ferrous iron, and the oxidation of the sulfur portion of the molecule would need to be a strictly chemical process. This suggests that the iron in certain sulfides may be available for

oxidation by F. ferrooxidans. As with T. thiooxidans, however, we cannot be certain that some chemical process has not occurred (one that is not rate limiting) to make iron available to F. ferrooxidans.

In short there are alternative possibilities regarding the relation of chemical processes and biological processes in the oxidation of the iron disulfides by pure cultures of organisms whose action is restricted to either the iron or sulfur portion of the molecule. The catalytic action of these organisms on oxidation of iron disulfides would impose the major restriction that the chemical steps involved, whatever they might be, could not be the rate limiting reactions or the organisms would not exert a catalytic effect.

Since there are reasons to believe that the initial reactions of the iron disulfides are the rate limiting reactions, it seems most likely that the catalytic effects of the organisms involve the iron disulfide molecules rather than subsequent steps, with the possible exception of S itself if it is an intermediate.

3) With an organism capable of attacking both iron and sulfur, the initial processes in iron disulfide oxidation cannot be logically separated. Since the Utah group showed other sulfides capable of oxidation by their T. ferrooxidans it would seem most probable that the sulfur portion is initially oxidized (assuming a common reaction mechanism for the different sulfides); it does not seem probable that one organism could efficiently catalyze the oxidation of copper and molybdenum as well as iron. On the other hand copper and molybdenum are, like iron, metabolically important elements and thus not foreign to the metabolic machinery of the cell;

in fact they are involved in biological oxidations much as is iron.

There is no special compelling reason for assuming a common method of attack on the different sulfides; thus iron may be initially attacked in iron sulfides and sulfur in the other minerals. If attack of the sulfur portion of these sulfides is assumed, it must be explained why T. thiooxidans does not catalyze their oxidation. Two alternatives present themselves: (1) T. thiooxidans unlike T. ferrooxidans cannot directly use the sulfur of pyrite and the other sulfide minerals but must await the liberation of sulfur or some sulfur compound which can be used. (2) T. thiooxidans can only employ the sulfur in certain compounds (such as marcasite) while T. ferrooxidans has a broader spectrum of sulfur compounds from which it can remove and oxidize sulfur.

The action of T. ferrooxidans on the sulfides of copper and molybdenum cannot be a consequence of chemical reactions that liberate sulfur, such as suggested above for T. thiooxidans on marcasite and sulfur ball material, or T. thiooxidans would also be capable of catalyzing these oxidations. Thus it would be most logical that in these sulfides, at least, T. ferrooxidans can attack the sulfur in the sulfides while T. thiooxidans cannot.

It is now apparent, that the problem cannot be solved by this reasoning because there are alternatives that cannot be conclusively chosen. However, the reasoning is valuable in that it points up the problem by indicating the alternatives and what information would be required for resolution. It should also promote considerations of the problems of chemistry involved, particularly the limiting

reactions. Viewed in the light of the chemistry of sulfide oxidations these considerations may be most pertinent.

Roles in and Nature of Subsequent Oxidative Steps

Attention so far has been directed toward the initial processes that may be involved in sulfide oxidation. There is somewhat more information available or deducible regarding biological oxidation of hydrogen sulfide and of steps that may be involved in subsequent steps leading to sulfate. The nature of oxidations of hydrogen sulfide or sulfur may have importance in that they could be intermediates in iron sulfide oxidations.

Hydrogen sulfide oxidation

The oxidation of soluble sulfides will undoubtedly involve the HS^- ion or possibly the unionized H_2S in pH ranges of biological significance.

A number of organisms (filamentous and photosynthetic sulfur bacteria) in the presence of soluble sulfide yield visible accumulations of sulfur. In the absence of sulfide this sulfur disappears with the appearance of sulfate in the medium. In these forms, at least, we can with assurance call sulfur an intermediate in the oxidation of sulfide to sulfate. Thiobacillus thioparus rapidly oxidizes sulfide to sulfate without sulfur accumulation which means either that sulfur is not an intermediate or that it is oxidized as rapidly as it is formed. The latter alternative seems the most likely since T. thioparus can oxidize external sulfur quite rapidly.

The enrichment of S^{32} over S^{34} during biological oxidation of H_2S by T.

concretivorus (in contrast to abiological oxidation) observed by Kaplan and Rafter³⁶ (1958) points to sulfur as a possible intermediate and indicates that S formed in its culture was not primarily formed by chemical oxidation. Greater enrichment was observed in sulfate than in sulfur.

Sulfur oxidation

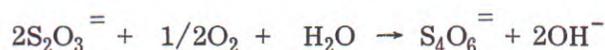
The mechanism of bacterial attack on elemental sulfur is not known. There is evidence that thiosulfate, tetrathionate and other polythionates are intermediates in oxidation of sulfur to sulfate. It has been suggested that sulfur reacts with sulfite to form thiosulfate, a known chemical reaction (Moeller³⁷, 1952); in somewhat acid media the reverse reaction occurs. (See above for suggested role of glutathione in sulfur utilization.)

Vishniac and Santer³⁸ (1957) reported unpublished experiments that demonstrate polythionates are intermediates in the oxidation of sulfide by T. thioparus. Thus if sulfur is intermediate in sulfide oxidation we would have confirmation that thiosulfate and polythionates are intermediates in sulfur oxidation. The work is worth quoting: "Resting cell suspension of T. thioparus have been incubated with radiosulfide for varying lengths of time, extracted with 30 per cent ethanol, and the extract chromatographed on Dowex-1 with increasing concentrations of ammonium formate. After one minute all radioactivity had disappeared from the sulfide peak and could be eluted with the thiosulfate and polythionate peak. On longer incubations the radioactivity of the combined thiosulfate and polythionate peak de-

creased and eventually could be recovered with eluted sulfate " Even if S is not an intermediate in sulfide oxidation this work demonstrates that thiosulfate and polythionates are intermediates in sulfide oxidation to sulfate.

Thiosulfate oxidation

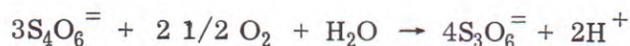
Quite strong evidence exists that tetrathionate is the first product of the bacterial oxidation of thiosulfate. The reaction can be best accounted for as:



Thiosulfate thus seems to be a key substance in the oxidation of reduced sulfur compounds, in that it is without much doubt formed during the oxidation of sulfide or sulfur (by a variety of organisms) and is further oxidized to sulfate by an even wider variety of bacteria. Incidentally, the oxidation of thiosulfate to tetrathionate by iodine in titrimetric methods is analogous to the above oxidation.

Tetrathionate oxidation

Tetrathionate is oxidized readily by several thiobacilli and by Chlorobium thiosulfatophilum, a photosynthetic sulfur bacterium. Manometric data is in agreement with the following equation for oxidation to trithionate:



A transient accumulation of trithionate was observed with T. thioparus.

Trithionate oxidation

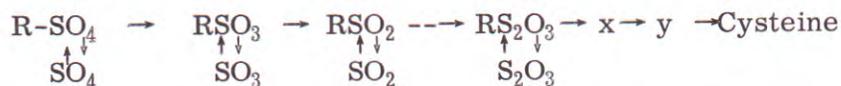
Some sulfur bacteria will and some will not oxidize trithionate. The inability

to oxidize an outside source of trithionate cannot be considered evidence that trithionate is not an intermediate since the cell may happen to be impermeable. The oxidation products of trithionate, other than the ultimate sulfate are unknown. Vishniac and Santer³⁸ hypothesize trithionate oxidation to sulfite by unknown mechanisms and subsequent oxidation of the sulfite to sulfate.

While it cannot be assumed that results of studies on the mechanisms involved in sulfate reductions are applicable to mechanisms involved in sulfide oxidation, the possibility must be considered that they may in part at least represent reversible processes. For example, several common heterotrophic bacteria possess an enzyme, tetrathionase, which brings about the reduction of tetrathionate to thio-sulfate (Pollock and Knox³⁹, 1943).

Many bacteria and molds can utilize sulfate as sole sulfur source which necessitates reduction to the sulfide level for amino acid synthesis. Studies of mutants of these organisms indicate that sulfite is the first product of reduction and that sulfite is reduced to thiosulfate. At least two genes (two steps) are involved in each of these reductions, (Davis⁴⁰, 1955).

Clowes⁴¹, (1958) has provided evidence of the following course of sulfate reduction to cysteine:



Sulfur and inorganic sulfides are apparently not intermediates.

The R refers to the probable association of the various sulfur compounds

with some other material, probably organic, during the actual reduction steps. This is not unusual in biological processes. There is no reason to rule out the possibility of similar associations in oxidation steps.

Enzyme preparations have been obtained from both yeast and Desulfovibrio desulfuricans that catalyze the reduction of sulfate to sulfite. This reaction:



has a standard free energy change of + 14 keal and hence it is not surprizing that a derivative with a higher free energy content than sulfate must be formed first.

Adenosine 5 phosphosulfate (or possible 3 - phosphoadenosine - 5 phosphosulfate with the yeast) obtained by reaction between adenosine triphosphate and sulfate is this intermediate which can then be effectively reduced to sulfite. At pH 7.75 only sulfite is formed by these preparations from D. desulfuricans, while at pH 6.0 hydrogen sulfide is the product. Sulfite reduction does not require energy; intermediate steps are not as yet known. Reduced triphosphopyridine nucleotide brings about the reductions with yeast preparations while reduced cytochrome C₃ is required with D. desulfuricans. Thiosulfate is reduced by this organism also with cytochrome C₃, although thiosulfate may not be on the main pathway of sulfate reduction (See Gregory and Robbins ⁴², 1960).

ROLES OF BACTERIA IN A POSSIBLE DISPOSAL PROCESS

Reduction of Sulfate to Hydrogen Sulfide

Biological treatment processes for alleviation of most water pollution pro-

blems are available but as yet none has been brought forth that is capable of dealing with acid mine water. A basic reason for this lies in the nature of the pollutant. Sulfate is already in the completely oxidized state, in contrast to the majority of pollutants, hence cannot be disposed of by an aerobic process. In addition, sulfate by itself cannot serve as a source of energy for microorganisms.

There is available, at least in theory, an anaerobic process whereby sulfate acidity may be reduced. This was pointed out sometime ago (See Moulton et al.¹, 1957) and certain experimental work has been conducted along this line. The process would depend upon the activity of anaerobic organisms capable of reducing sulfate to hydrogen sulfide in the presence of organic material. Desulforibrio desulfuricans is the most likely organism capable of affecting this reduction.

The major requirements for efficient reduction by this organism are:

- 1) An efficient and economical source of organic material which would supply the hydrogen for reduction of the sulfate to sulfide and
- 2) An effective treatment facility that would control the inflow of acid water to that which would be near optimum for the sulfate reducing bacteria.

Since a recent review (Postgate⁴³, 1959) covers very well the present information about sulfate reducing bacteria, the details will be omitted here. A few remarks are pertinent, however, regarding the ecology of the sulfate reducers since it bears on the feasibility of the process being considered.

Sulfate reducing bacteria are ubiquitous and will be found active in probably

any anaerobic environment containing organic material and sulfate. Under such conditions they meet with little competition because of their specialized physiology. This point is particularly important because it means that the primary task is to set the right conditions for their activity. It is not necessary to consider pure cultures or contaminating interference organisms inasmuch as this is a natural biological process.

The sulfate reducing bacteria can tolerate reasonable acidities, of about pH 4.5, and may well adapt to greater acid tolerance. Since their activities should result in decreasing the acidity of their environment, this level of acid tolerance should be adequate. These organisms can also tolerate high concentrations to sulfide so that this would not be a limiting factor in their activity.

Concerning the organic requirements of these organisms, a wide range of organic materials can be used either directly or indirectly. The natural substrates of the sulfate reducing bacteria are the products of fermentation or putrefaction by other microorganisms. In this way one should be able to employ whatever organic materials might be locally available and are essentially wastes, such as sewage, cellulose containing materials and so forth.

Of possible significance in this connection also would be the organic materials present in the acid water (mentioned above) that could contribute to the feeding of sulfate reducing bacteria. Laboratory studies¹ employed lactic acid as a carbon source, not because it is economically feasible but because it is a good carbon source for the sulfate reducers and is a main product of several fermentations that

might precede action of the sulfate reducing bacteria.

The second requirement listed above for efficient sulfate reduction, control of flow of acid water, involves essentially the design of equipment that would regulate the inflow of acid water within two limits. (1) The higher limit would be the rate which overtaxed the processes leading to reduction of acidity; under these circumstances too great an acidity would inhibit the active organisms. (2) The lower limit would be that rate which just failed to maintain the organisms in a highly active state.

Evidence from laboratory experiments⁴⁴ indicates that in some cases the rate of flow was too high, overtaxing the acid limit of the system, and in other instances too low so that the organisms were not maintained in an active state. In general the results are encouraging, but this problem of designing efficient equipment for laboratory study is, as of now, the crucial one.

Disposal of Hydrogen Sulfide

It needs to be understood that the reduction of sulfate to hydrogen sulfide, while the key process in this proposed disposal method, will not by itself solve the problem. If the hydrogen sulfide produced enters the stream it would be soon reoxidized to sulfate with the coincident increase in acidity. Some provision needs to be made for removal of hydrogen sulfide, or sulfur, from circulation.

There are several possibilities for eliminating the hydrogen sulfide (or sulfur) from circulation by either chemical or biological means. The most attractive at present, because of its simplicity, and the one currently employed in laboratory

trials, results when acid mine water is treated prior to the oxidation and settling out of the iron. In such cases the iron can effectively precipitate out the hydrogen sulfide as FeS. There should be enough iron in the water to remove as FeS about half of the hydrogen sulfide that would result from reduction of all the sulfate present. Thus this alone could lead to a fifty per cent reduction in acidity. If some disulfide were formed, more than half of the hydrogen sulfide would be removed.

VALID AREAS OF INVESTIGATION

The above discussion suggests that studies be advanced in the areas summarized below in order to secure more complete comprehension of the microbiological role in oxidation and reduction relations to acid mine drainage.

1. Although it is highly probable that microorganisms do catalyze the formation of acid from sulfides, more quantitative data on the relative rates of chemical and biological actions is required.
2. Clarification is needed of the problem of what organisms may be effective catalysts of sulfide oxidation.
3. The nature of the reactions whereby organisms exert their catalytic effects needs to be determined.
4. Relative to the process of acid formation in the mine are several related pertinent questions that require answering:
 - a. What is the content of organic matter in acid water compared with non-acid water?

- b. What is the source of this organic material?
 - c. What is the source of the thiamin required by Pseudomonas streamer organisms found in acid water?
 - d. Is Vitamin B₁₂ present in acid-water and does it explain in part, at least, the common occurrence of Euglena in such water?
 - e. Why does the pH of acid water appear to drop to 2.5-3.0 and not lower? Is there a biological explanation?
5. There is a paradox that needs to be resolved in that marcasite and sulfur ball material are reported oxidized by bacteria, while pyrite was not affected. Yet the form of iron sulfide in sulfur balls is reported to be pyrite.
6. How do the kinetics of biological oxidation compare with the kinetics of chemical oxidation?
7. Can biological sulfate reduction be developed into an efficient process for acid disposal?
- a. What are the rates of sulfate reduction and influence of pertinent factors, such as pH, on rate?
 - b. What organic materials can be used directly or indirectly in sulfate reduction?
 - c. How can the hydrogen sulfide produced be removed from circulation so that it is not reoxidized to acid again?

MINERALOGY - PETROLOGY

Many different approaches to the understanding of the fundamentals of acid production have been proposed and pursued. The mineralogic and petrologic approaches are considered appropriate areas of research that may provide inter-connecting links between various factors such as the distribution and quality of sulfuritic materials and the weathering effects of sulfur and non-sulfur bearing rocks and minerals on the overall acid production.

Occurrence of pyritic material in coals and adjacent strata is basic to the acid mine water problem. While wide-spread analytical work has produced considerable information with respect to sulfur content of coal, in both the coal and the overlying material the exact nature and composition of the sulfuritic materials (marcasite and pyrite) is unknown. Moreover, the relationship of the pyritic and sulfuritic products with other materials such as clay minerals, organic matter, or other matter associated with the crystallization is also imperfectly known.

HISTORICAL BACKGROUND

Stokes⁵⁰, as far back as 1901, described a method for quantitative determination of pyrite and marcasite in a mixture, based upon the estimation of iron dissolved when finely ground sulfide is treated with hot ferric alum solution. He also defined mineral "oxidation coefficients" or the ratio of sulfur oxidized to mineral decomposed as a definite characteristic of each mineral. Crystal form was regarded as a major aid for distinguishing between marcasite and pyrite. However,

density measurements were not regarded as trustworthy means of determining one mineral in the presence of the other.

Allen and Crenshaw⁵¹ evaluated the Stokes analytical method, indicating that errors occurred in not maintaining an excess of sulfide, and in the tendency of marcasite to flocculate and reduce its reactive surface.

Powell and Parr¹² concluded that sulfur occurs in coal in four characteristic forms, two of which are organic, and two inorganic. They also concluded that high results were obtained from early methods of analysis. Tucker⁵² reported variations of 23 to 51 percent pyrite from Ohio coals, based upon selected samples of "fair" quality from the several coal beds. The occurrence of "pyrite balls" at the top or base of the coal bed usually tangent to or intersecting the bedding plane between the coal and adjacent strata was described. Sulfuritic lenses were also described as occurring within the coal along the bedding planes.

More recent studies by Krumin⁵³ recognize three sulfur forms in coal - "(1) with iron as pyrite or marcasite and referred to as pyritic sulfur, (2) small amounts, especially in weathered coal, combined with calcium, magnesium, or iron in the sulfate form; and (3) with organic compounds as a part of the coal substance." Quantitative determination methods used by Krumin are modifications of procedures originally developed by Powell and Parr, and involve extraction of sulfate and pyritic sulfur from finely ground samples with dilute acids for long periods. Sulfur analyses are reported at selected depths of cores taken from the Ohio Meigs Creek No. 9 coal bed.

The oxidation and reaction products of pyrite and associated materials are known to produce a host of soluble sulfate minerals, many of which are described in literature and are particularly summarized in Dana's Mineralogy, Vol I, 17th Edition⁵⁴. Brant and Foster⁵⁵ described magnesian halotrichite as an evaporation product of an aqueous solution of ferrous and aluminum sulfates. They also indicated that many sulfate products are either mis-identified, or un-identified, thereby suggesting sulfate mineralogy as a fertile field for research. This is particularly significant inasmuch as these products are intermediates between the solid state non-contaminating sulfides and the ionically dispersed contaminants. It is with this in mind that the following categories are recommended as valid investigative areas. It will be apparent that many of these interrelate with other basic disciplines, particularly with chemistry.

LATTICE STRUCTURE AND ELEMENT ARRANGEMENTS

Structure and solid state occurrence of iron and sulfur in the marcasite or pyrite molecules can be described through a detailed study with modern techniques involving X-ray diffraction and electron microscopy. The resulting information regarding crystallinity, symmetry, and the dimensions of the unit-cell, or basic crystal unit will describe the structural relationship and bonding of iron and sulfur within the unit-cell, and will offer possibilities of correlation with the rates of oxidation and the relative degrees of stability of the sulfuritic materials. This should also assist in defining the sequence of chemical events in the oxidation of

pyritic materials. It also offers possibilities of correlation with chemical and bacteriological data to provide a better understanding of the basic mechanism rates. Once the mechanism is understood possible means of stopping or altering the reaction may be found. The nature of the "sulfur balls" or more properly, pyritic concretions, and the relationship between pyritic materials and other mineral matter could thus be more closely established.

PETROLOGY

Petrology treats of the relationships of minerals contained in rocks. Relationship of rock type and sulfuric materials requires both physical and chemical analyses in order to determine their mineralogic compositions. It is necessary to establish which minerals are present in order to determine if any interrelationships bear on the rate of oxidation. The detailed petrographic analysis of Meigs Creek Coal in Ohio made by Cady and Smith⁵⁶ may be applied to the estimation of pyritic materials in other rocks.

The nature of dissemination of pyrite through the coal and associated rock strata, the nature of and occurrence of the "sulfur ball", and the interrelationship of clay minerals, sulfides, and organic matter all are considered to have some influence on the rate of rock decay through exposure. A more comprehensive knowledge of these factors, their interrelationships, and their relations to the enclosing rocks, would better relate the resulting acid production to sulfuric material exposure through rock decay. In line with this thought, Braley⁵⁷ recently proposed

more comprehensive and integrated studies of the acid producing potential of the overburden.

It seems basic to understand the relationship of pyritic materials with coal, shale, sandstone, limestone, and clay, and to evaluate the overall contribution of these occurrences of pyrite to the production of acid or acid salts. Analyses for mineral sulfide and correlation of these data with chemical determinations of sulfur are important. Although petrographic analyses are slow and expensive, a sufficient number as determined by a statistical approach are necessary to give control to interpretation of chemical analysis for sulfide content. Sulfur determination by chemical means may then be interpreted in terms of pyrite or marcasite, and maps showing iso-sulfur lines (indicating rocks containing equal quantities or equal percentages of sulfur) may be compiled using either a coal-to-coal interval, or an arbitrary but significant number of feet of rock above the coal. The maps could then be correlated with other factors such as mining systems and ground water hydrology to provide a basis for estimating absolute quantities of acid potential in a given area.

DISAGGREGATION EFFECTS (WEATHERING)

Disaggregation is appropriate to consider as it applies to spoil banks of strip mines as well as gob piles and rocks exposed in underground mining. In a rock containing dispersed disulfides, it is postulated that the oxidation is selective at the disulfide site. It is further presumed that the oxidation is biochemical and that

it expands the oxidizable material thereby building up pressures tending to fracture the particle. This exposes more sulfuritic materials, and the process assumes chain-reaction characteristics continuing ad infinitum with resulting exposure of originally "interior" surfaces. Thus the disaggregation mechanism is dynamic in nature and appears to form soluble end-products from the sulfuritic material oxidations as long as such materials are exposed to the weathering factors. In addition, physical disaggregation of rock proceeds through:

- (1) Crumbling of the weakened rock structure due to the dissolution of its component minerals.
- (2) Swelling action of highly absorptive clays such as members of the montmorillonite group present in the rock composition resulting in cleavage and fracture of the enclosing structure.
- (3) Seasonal freezing and thawing.

All of the disaggregation processes tend to expose fresh surfaces to the weathering reactions. A limit of the reactive processes associated with weathering might be defined as the "acid potential" and would most certainly have a direct relationship to the total sulfur present in the exposed materials.

The rate of disaggregation, being a function of exposure to oxidizing factors has a direct relationship to the water problem as is more fully defined in the succeeding section on hydrology. Controls associated with water diversion and removal, and those associated with cover of freshly exposed surfaces will be effective in limiting the disaggregation rate of rocks enclosing sulfuritic materials.

GEOLOGY - HYDROLOGY

GEOLOGY

The various factors of composition, structure and exposure of coal and other rocks are considered under Geology. Thus geology may be considered an all inclusive basis for inquiry into the acid mine water problem. Previous discussions pertaining to mineralogy - petrology, and the subsequent section on hydrology all pertain to contiguous areas partially or totally embraced by the over-all geological concept.

Classically the main divisions of Geology are structure and stratigraphy. Structure is the attitude or dip and configuration of the various beds of the geologic column. Stratigraphy is actually the science of identification of rock layers and beds and the correlation and identification of rocks over small or large distances.

Structure of the sedimentary bed rocks is important to the acid problem because the "lay" of the rocks determines the direction of drainage in any particular stratum. In mining by the drift method, usually the heading of the mine is up dip so that any mine water will drain to the opening. In such a mine, acid drainage may continue for years after abandonment. Other types of mines are also influenced by structure in that it determines the natural drainage pattern. The cessation of pumping in an abandoned downward sloping drift or shaft operation usually results in flooding of the mine and either discontinuance or reduction of the acid drainage problem.

The science of stratigraphy is the correlation of rocks over reasonable distances. It includes the description of sedimentary changes that occur in rocks so that chemical, mineralogic and petrologic differences or variations may be explained in an orderly way. If it is apparent that there is lateral correlation then it should be possible to predict the conditions to be expected when new mining areas are developed in the same coal bed.

Brant and Moulton⁵⁸ have described in general terms the geologic basis of formation of acid materials and their transport to stream systems. Fruchey⁵⁹ made a detailed study of pyrite content of an interval between the lower Kittanning and Middle Kittanning coal beds. The area studied was relatively small, but it could be considered a pilot area and the principles used applied to wide range studies. His results demonstrate that the high sulfide content is centered principally in the shales immediately above the coal. Tucker⁵² also studied pyrite content of Ohio coals (Middle Kittanning) from the viewpoint of economic utilization of the sulfur.

The application of structure and stratigraphy to the acid mine drainage problem has been viewed in a cursory fashion by Central States Forest Experiment Station (Lindstrom and Merz⁶⁰) and through current work (unpublished) of the Ohio Reclamation Association. Some of the workers attempted systematic accounts of the character of overburden materials which become spoil piles in strip mining. However, these bear on toxicity to botanical recovery of the spoil piles or strip banks rather than on acid mine drainage directly. A current study organized by the Ohio Reclamation Association is attempting to show the curative effects of

knowledge of the hydrological conditions would assist in the selection of the most feasible means of reducing acid water production from inactive and abandoned workings.

It is fully realized that each operation is unique in certain characteristics, however, certain of these have similar features, and it is not unreasonable to assume that certain applications, within limits, would be adaptable to specific categories or groups of workings. It is therefore suggested that proper collection and analysis of hydrologic information, and the correlation of this data with the prevailing geologic characteristics will assist to establish ranges of hydrologic behavior applicable to the mine problems.

The following discussion attempts to point out the importance of the water problem in coal production and processing, and to suggest that hydrologic methods may be applied to assist in water quantity evaluations. It is not intended that all of the suggested factors be applied to each operation, for the economics of the problem may well dictate the balance between an extensive survey, and the minimum information necessary to adequately solve the problem.

Importance of Water in Coal Production and Processing:

With respect to the coal production and associated activities water behaves in a dual capacity:

It contributes to the problems associated with mining activities:

- 1) It is a solvent, and as such it dissolves mineral salts from the soils

- b. Another quality of the rocks, i. e. , neutralizing character needs to be studied. Calcium carbonate content is an apparent key to self neutralization of acids in a stream system. The overall importance of the limestone factor remains unknown. Although many local factors such as type of mining, hydrologic character of the mine and rate of oxidation may prove to far over-shadow the neutralization significance, the measurement and evaluation of this factor would be an additional tool in stream basin evaluation. Correlations of petrographic and geologic data of coal mine areas not producing significant quantities of acid with acid producing areas would also result in a better understanding of the significant mechanisms contributing to acid production.
- c. Structural and stratographic studies of new and old mining areas or drainage basin areas would relate general ground water occurrences and possible flow patterns. The structural study is a basic foundation upon which the framework of mining, past and future, can be constructed with respect to acid production and its conduction to the stream system.

HYDROLOGY

The ability to quantitatively evaluate and predict the occurrence of water in relation to mining would be of considerable economic value in planning and carrying out extensive operations. This would provide a basis for a rational engineering approach to the design and installation of water removal systems. A more thorough

knowledge of the hydrological conditions would assist in the selection of the most feasible means of reducing acid water production from inactive and abandoned workings.

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and strata. It also provides a suitable environment for, and in the presence of oxygen (air) reacts with, the metallic sulfides present in the strata to ultimately form sulfuric acid, metallic sulfates, and metallic hydroxides, as has been discussed in the previous sections relating to basic chemistry and bacteriology. It acts as a weathering agent, since the dissolution of certain mineral salts exposes more surface area, and subjects the material to an increasing degradation. This is a particular problem in the larger, older mines, where water discharges may increase through weathering of the formations.

- 2) It is a transporting agent for pollutants, and carries dissolved and suspended materials from the pollution source into areas where undesirable results accrue from the acid concentrations and from the accompanying metallic hydroxide precipitates.
- 3) It is an obstruction to the mining progress, and often necessitates the installation of heavy and costly equipment to remove the undesirable quantities entering the active operations.

On the credit side, water may assist in the control of the acid problem by:

- 1) Providing dilution for pollutants, and furnishing a means of controlled release in order to satisfactorily handle low acid concentrations.
- 2) Flooding of abandoned operations and thus inhibiting or "drowning" further acid production and reducing degradation by limiting contact with oxygen to the point where the acid production rate becomes

negligible.

- 3) Acting as a seal and a diluent where impoundments are constructed to inundate the last cut of strip mine operations. The impounded water is raised to a level to seal off the exposed coal and associated strata, and thus restrict further oxidation of the mineral sulfides. Continued precipitation and drainage into the impounded basin gradually dilutes the acid and dissolved mineral concentrations.

Water Quantity Evaluations:

Quantitative evaluations of water that may be encountered are desirable, and within limits, are predictable, based upon sound hydrological procedures involving selection of applicable parameters, collection of pertinent data, and its proper correlation and analysis. Seasonal variations of such information are usually required to establish maximum, minimum, and mean values.

Knowledge of the overall area hydrology is necessary for appraisal of the potential water quality and quantity.

- 1) Topographic surveys will delineate the specific limits of the basin, or the area contributing to surface runoff.
- 2) Installation of precipitation gages, or the extrapolation of precipitation gage data from established weather stations will furnish quantitative data for the area.
- 3) Streamlet, or stream flow measurements provide basin outflow infor-

mation, and define quantitatively the area runoff.

- 4) The relation of precipitation to runoff as established by measurements, or extrapolated data, and adjusted for reasonable evapotranspiration losses, will provide indications of groundwater variation.
- 5) Geologic information obtained from regional charts, and maps, and reinforced by local information available from workings can in general establish the geometry (position and extent) of the water bearing strata. The location and extent of aquifer outcrops, or projected outcrops, and characteristics of the overburden will assist in predicting the potential replenishment of the ground water supply.
- 6) Borings, or other subsurface samples will reinforce the information relating to types of strata, and sample examinations will give porosity data, indicating the potential water capacity of the formation.
- 7) Permeability, or the ability of the strata to transmit water can most easily be established through simple pumping tests on the aquifer, with simultaneous water level observations on nearby bore holes. Specific yield and specific retention of the strata in question can be estimated from the information on permeability and porosity.

Hydrologic data correlated with structural information and the geometry of a mine system is necessary to not only define the water problem, but also assist in indicating methods of water control. The removal of underground material from a given strata may result in excessive water production due to:

- 1) exposure of an interface of flow from an aquifer;
- 2) entry of water into the mine through rock joints or coal cleats, or
- 3) fractures, due to excessive overburden, intercepting an aquifer and permitting water escape.

The rate of flow from the formation will, in general, be a function of the surface exposed, the fluid pressure, the porosity, and the permeability. Porosity and permeability are of prime importance and are identifiable and mapable, particularly when related to the occurrence of sandstone bodies overlaying the coal beds. In most areas jointing is of secondary importance in water conduction at the depth of the coal seam.

An interrelationship exists between the effects of mine roof collapse and the consequent hydrological behavior of a mine system. Two effects are immediately apparent. First is the damming and consequent flooding that may reduce acid production. Second is the upward fracture projection which may intercept aquifers at some distance above the mine working, and result in more inflow through the newly created flow interfaces and fissures.

A logical analysis of correlated results may be useful in predicting

- 1) The amount of water production in the mine, and the direction of flow.
- 2) The amount of reactive surface that can be drowned by mine flooding, and
- 3) The potential head of water that must be developed in order to flood the mine either partially or completely.

Thus rational means may be provided for appraisal of the acid water production, and for establishing the feasibility of possible mine seals, plugs, or dams. Pumping data from existing mines correlated with the hydrologic information obtained as above may aid in developing generalizations or empirical relations of exposed mine roof area to the amount of water produced. Investigation of the features of roof collapse and correlation with available hydrologic data may shed further light on the frequency and characteristics of roof collapse, and its significance in the role of acid production.

Hydrology Related to Strip Mine Areas

The hydrology of the acid mine drainage problem as particularly related to the strip mining areas and coincident impoundments should be generalized by proper selection and evaluation of specific parameters.

- 1) In case of an impoundment, it is desirable to have some means of predicting the rate of reduction of acid concentration in the pool created. This concentration is a function of the total acidity by weight in the pool, and the volume of water in the pool at any one particular time.
- 2) The volume of the pool may be related to the average rate of rainfall, the average rate of runoff from the surrounding tributary area, the average rate of evaporation, and the average infiltration from the impoundment into the soils. This last factor will fluctuate with respect to the ground water table variation. It is also anticipated that the rate

of infiltration will be affected by pore clogging due to precipitation of iron and aluminum hydroxides in the impoundment.

It is postulated that some sulfate materials which will infiltrate will in time be reduced and will combine with metals present to again form natural metallic sulfides.

- 3) It is, therefore, considered entirely feasible that a quantitative hydrological approach can be applied to this phase of the problem, and when correlated with information to the potential acid production from, and the weathering characteristics of, acid producing formations, would result in predictions, within reasonable limits, of recovery of the impounded waters from the acid condition.

APPLIED STUDIES

All abatement measures must be conceived in relation to the process which is to be affected. In the acid production process, disulfide minerals, oxygen, and moisture are necessary ingredients. Transportation of the acid after it has been formed, from the mine to the stream system, requires, in addition, flowing water. If this water, which comes from the surface through adjacent strata, can be directed and controlled to avoid contact with the acid, then the acid will remain harmlessly in the mine. Therefore any effort for positive abatement must concern itself with one or more of the three necessary ingredients of acid mine production, and with the additional factor of acid transport to or in the stream systems. The association may be expressed in functional form indicating the relation of acid production to its major variables:

Acid Production = f (disulfides, oxygen, moisture, water transport), Two specific characteristics of disulfides, the reactive, or exposed surface area, and the disulfide nature as related to mineralogy affect the acid producing role. It is suspected that the amount of exposed surface area of the disulfide is rate-limiting to the acid production, and that the effect of oxygen and moisture on gross acid production may vary only as these factors are reduced to quantities such that they will become rate-limiting. It is anticipated that results from fundamental studies as outlined in the previous basic sections will establish relationships of the aforementioned variables in acid production. Water transport is a variable as it provides

a means of egress from the site of acid production. Its significance will vary as the water controls are established.

MINE SEALING

The objectives of a mine seal are to exclude oxygen from the disulfide minerals to prevent their oxidation, and to reduce the amount of water flowing through and out of the mine.

Surveys of the acid mine conditions in the 1920's and 1930's made by the U. S. Bureau of Mines⁶¹ followed by studies at the West Virginia University Experiment Station⁶² precipitated an extensive mine seal program under the Works Progress Administration. However, no systematic follow-up on the evaluation of this work has ever been made. Hence, little factual information is available regarding the effectiveness of seals. Spectacular individual cases of mine seal failures, due to lack of consideration of all factors affecting mine seal efficacy, have resulted in large economic losses. The present status regarding the effectiveness of new and old seals is controversial due to lack of operational data, and the fact that no maintenance has been applied to the seals.

As early as 1930, Leitch, Yant, and Sayers⁶¹ concluded from their field studies that mine seals are effective in abating the formation of acid in underground coal mines. Hodge⁶³ from his collected data in 1938 concurred with the same conclusions. More recently Braley⁶⁴ (1954) presented results of field studies of abandoned sealed mines over a five year period and concluded that sealing is

of doubtful value for control of acid formation unless the mine is below drainage level.

Air Sealing

Much of the misunderstanding and disagreement regarding the effectiveness of seals can be traced to the early emphasis and application of air seals. The objectives of these seals were to prevent air from entering the mine, and to permit the flow of water without interruption from the mine. The successful application requires that an effective and impervious air seal be developed at the openings. To achieve and maintain this condition at a mine opening over a period of time in strata related to the coal measures is an almost impossible task.

Complete Sealing

The process of complete mine sealing may offer some relief from acid formation within mines. Complete sealing would mean erecting a seal that would be a barrier to both air and water. Not only would the oxygen supply inside of the mine be depleted, but the rising water would also cover significant quantities of disulfide material on the floor and the coal ribs. This technique would also permit the flooding of mines with internally or externally generated water.

A study at this University on the McDaniels Test Mine in Southeastern Ohio^{2,44} has revealed some interesting data regarding complete mine sealing at this location. For a period of time before the seal was operating the mine was evaluated as to water quality, water quantity, structural condition, petrographic study of coal,

and the statistical sampling of sulfur burden in the coal as a function of elevation. In short, the prior history of the mine was established and studied for possible comparisons and judgements on the changes induced by the air-water seal.

Recent data (unpublished) indicates that the acidity is decreasing steadily over the past 1 1/2 year period. The atmosphere in the mine during this period has remained remarkably uniform, with oxygen at an encouragingly low level. The water level in the mine has also manifested a uniformity over the period while inundating over 60 percent of the sulfur burden in the mine. In summary the study has resulted in encouraging evidence to the fact that a "complete seal" may provide a means of minimizing acid formation within a mine.

Interior Sealing

The concept of interior sealing would stress the selection of the most desirable site location for the erection of a complete seal structure. This would preclude drift mine openings because of difficulties in both sealing and maintenance of the seal structures. The design of an interior seal can be varied and imaginative depending upon the conditions at hand. It might consist of a complete seal and an air seal structure; two complete seal structures separated by an air lock, debris barrier or a water barrier; or a complete seal and a barrier structure at the mine entrance to prevent vandalism access.

In abandoned portions of producing mines consideration should be given to the desirability of "complete sealing" of these areas with regard to water and air.

In the mining industry today, a running controversy exists on the pros and cons of sealing abandoned working areas because of the potential hazard in the buildup of explosive atmospheres, which may at any time be unexpectedly released or ignited. It is realized that the feasibility of interior sealing would depend upon resolving this controversy.

In active underground mining operations, considerable emphasis is placed upon efficient high volume ventilating systems to dilute the occluded gases released from the coal seam and nearby strata. As a result, considerable amounts of fresh air (oxygen) are available in quantity in all parts of the mine. Therefore, little can be accomplished in active portions of underground mines with respect to controlling two of the necessary elements for acid production, namely oxygen availability and disposition of disulfide material.

Additional mine seal studies are recommended in order to establish the effectiveness of this type of abatement. It is suggested that controls be established on the proposed mines prior to the seal installations in order to evaluate the several influencing factors as described for the McDaniels Test Mine Seal. It is further recommended that the mine seals be designed and developed according to the best available criteria, and that data taking be continued for several years after construction in order to properly evaluate the mine seal efficiency in terms of both the acid reduction obtained, and the required maintenance to the installation.

SURFACE MINING

Some efforts have been made with varying degrees of success to reduce acid production in strip mining. Braley²⁰ reported studies on several strip mine areas and indicated that significant acid reductions could be obtained through good operation based upon established principles.

Among the recommendations advanced for acid reductions from strip-mine areas are the following:

1. Segregate the disulfide containing material and bury it at the pit bottom after mining.
2. Backfill overburden into abandoned strip pits to prevent surface water from pooling above the disulfide material or in the pits.
3. Develop an adequate drainage system to keep the pits as dry as possible if they are well above the level of adjacent streams and permeable to water. If the pits are impermeable, they may be permitted to fill with water.
4. If the pits are below the water table or below the stream drainage system, then they should be permitted to fill with water to cover the disulfide material.

The basis for the above recommendations comes from the need to control the water flow, both inflow and outflow, in the pits areas and the need to develop economical and effective disposition of the disulfide materials in the pits. Certainly effort is needed to concentrate on the development of specific engineering recom-

mendations that will satisfy these two basic needs and thereby alleviate the acid production from surface mining operations. These recommendations will best result from the development of modified systems of surface mining, whose design considerations among others is restriction of acid production.

AUGER AND HIGH WALL MINING

Two other systems of mining are usually closely associated with strip mining and in fact each has an effect on the other. Auger mining consists of boring into the coal in a standing highwall with giant augers that may penetrate from 100 up to 200 feet into the seam. The holes are placed very close to one another with only a narrow barrier pillar, a few inches thick, between them.

The other system consists of driving mine entries from the highwall into the coal seam by utilizing underground mining equipment. The length of the entries are variable and they again are separated by a relatively narrow pillar between them. A very recent development called "Automatic Mining" utilizes a remotely controlled continuous mining machine and conveying system that will drive an entry to a thousand feet or more into the highwall.

The question is asked "What will be the effect of these mining systems on the production of acid mine drainage from the mining areas?" A marked increase in acid production is anticipated due to the increased exposure of surfaces containing oxidizable sulfidic materials. It is therefore recommended that a study be undertaken to evaluate these systems and determine their effect on and contrib-

ution to the acid mine drainage production.

It is hoped that the results of such studies would provide engineering recommendations which might be incorporated into the specifications of the mining system to aid in control of the acid production. It is expected that the amount of mining by these new systems will tend to consistently increase in the future. It must be stressed that the engineering recommendations should include considerations for physical modification at the time of abandonment of the mining area. This is the time during which these modifications can best be constructed and installed by the mining operator. The principle of abandonment modification is meant to apply not only to auger and highwall mining but also to the surface mining and underground mining systems.

WATER CONTROL

Control of the necessary third element for acid production offers the most potential for alleviation in active portions of underground mines. The control of water in mines is a fertile area for effort to be expended on the abatement of acid mine drainage. Water control covers a broad area of topics including water inflow from the surface into the overburden, into nearby strata and finally into the underground mine openings. It also includes the transportation and in-transit system of water handling while in the mine, and finally the disposition of the water when it leaves the mine.

A study in water control is presently being conducted in the Humphrey Mine, a new underground mine of the Christopher Coal Company in northern West Virginia. Water is being pumped at frequent intervals to the surface and mining conditions are being controlled during this investigation.

Much work still remains to be done in the design of efficient mine drainage systems. An example of the results of such a study are indicated from a sampling of the following recommendations for mining drainage systems:

1. Surface and ground water should be diverted to reduce water inflow through mine workings.
2. Water accumulations in working areas should be held to a minimum and pumped to the surface at frequent intervals through boreholes.
3. Reduced exposure of water to acid forming materials should be secured by the application of closed conduits instead of open conduits.
4. Surface reservoir capacity should be developed to prevent potent acid surges from entering an outside stream.
5. A program quantitatively regulating discharges into streams is desirable to eliminate undesirable potent accumulations and surges.
6. Development of a regular sampling program is recommended to establish quality values at important locations to aid in regulating the water control and drainage system.

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