

# EARTH AND MINERAL SCIENCES

THE PENNSYLVANIA STATE UNIVERSITY, COLLEGE OF EARTH AND MINERAL SCIENCES, UNIVERSITY PARK, PENNSYLVANIA

## Acid Mine Drainage

*Coal mining's persistent and complex problem is examined from the viewpoint of industrial dump leaching, and several approaches for solving it are discussed.*

LAWRENCE M. CATHLES, *Associate Professor of Geosciences*

In the first article of this series on sulfur and coal, Dr. Lasaga discussed the sulfur cycle, pointing out that sulfur is concentrated by bacteria in organic rich sediments. This occurs because the operative bacteria need to oxidize reduced material in order to

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**This is the fourth in a series of six articles on sulfur and coal. Yet to be discussed are sulfur in the burning of coal and sulfur's role in acid rain.**

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reduce oxidized sulfate to sulfide sulfur, the reaction from which they derive their life energy. The sulfide sulfur winds up either incorporated as part of the chemical structure of the coal or as a separate mineral, generally pyrite ( $\text{FeS}_2$ ). Sometimes, as illustrated by Dr. Davis in the second article of this series, "over eager" bacteria actually encase themselves in sarcophagi of pyrite. The

## Geography at Penn State—A Discipline of Spatial Analysis

*The geography faculty, recognized internationally for their expertise in a variety of areas, serve a growing number of graduate and undergraduate students.*

E. WILLARD MILLER, *Professor Emeritus of Geography, and Associate Dean Emeritus for Resident Instruction*

Geography at Penn State was first taught in the 1860s, but its development was sporadic for more than 60 years. The first course taught on a continuing basis was Physical and Commercial Geography, taught in the School of Mines in 1918. From 1918 to 1932, there were no professional geographers at Penn State, and the geography courses were taught primarily by geologists. The importance of the subject was, however, recognized for Deans Elwood S. Wood and Elmer A. Holbrook of the School of Mines taught geography on a regular schedule.

In 1928, when Edward Steidle became dean of the School of Mines (which he soon renamed the School of Mineral Industries) he broadened its program, particularly expanding the earth sci-

## Varied Program Planned for College Open House, April 24-25

There will be literally hundreds of things to see and do during EMEX 82—the 1982 Earth and Man Exposition—an open house in the College of Earth and Mineral Sciences.

EMEX 82 is scheduled for Saturday and Sunday, April 24 and 25, from 1 to 5 p.m., with exhibits, demonstrations, and open laboratories in all four of the college's buildings. Attendees are invited to begin self-guided tours in the lobby of Deike Building where programs will be available.

Sponsored by the Earth and Mineral Sciences Undergraduate Student Council in cooperation with the Dean's Office, the open house will feature activities planned by all of the instructional and research areas in the college—geosciences, geography, meteorology, materials science and engineering, mineral economics, and mineral engineering. General chairman of the event is Diane Nork, a senior in geosciences.

A major highlight of EMEX 82 will be the first public showing of  
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important point here is that the very property that makes coal a potential fuel—its reduced organic nature—tends to make it and the strata that enclose it rich in both inorganically and organically bound sulfur.

*Continued on next page*



*Hard at work on her map during a cartography laboratory session is Megan Lembach, 9th-term geography major. Watching her work is Gretchen Mortimore, a lab assistant and also a 9th-term geography major.*

ences, including geography. In 1932, Raymond Murphy came to Penn State as its first professionally trained geographer. During the 1930s, geography was accepted as an elective by many students on the campus, and, by 1940, there were three geographers on the faculty, and fifteen courses were being given, including three at the graduate level.

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## Acid Mine Drainage—

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As mentioned by all previous authors in this series, the sulfur associated with coal is a problem. When the coal is burned, the sulfur vents as sulfur dioxide (SO<sub>2</sub>) which, in high “smog” concentrations, can produce respiratory ailments and even be directly lethal to humans.

Photochemical processes convert SO<sub>2</sub> to sulfuric acid, and SO<sub>2</sub> emissions are one of the causes of acid rain, a topic to be discussed in a later article in this series.

In coal mining, pyrite present in the overburden that is disturbed, in coal fragments left behind in the mine, and in spoil piles left on the surface produces acid when exposed to atmospheric oxidation. This results in “acid mine drainage” that can kill fish and vegetation for many years after mining has stopped.

At Penn State, researchers have pioneered in efforts to understand and control acid mine drainage.<sup>1,3</sup> At the same time, workers in the mining industry have utilized the processes that produce acid mine drainage to develop processes for leaching and recovering metals from sulfide “waste.” Stated succinctly, industry hydrometallurgists have sought to *maximize* the rate of sulfide oxidation (and acid generation) in a *controlled* environment, while people concerned with acid mine drainage have sought to *minimize* sul-

fide oxidation in a *disturbed natural* environment.

In this article, we examine acid mine drainage produced as the result of strip mining from the viewpoint of industrial dump leaching—the process of dissolving copper from large piles of low-grade pyritiferous waste by deliberately recycling water through the piles. Consideration of the acid mine drainage problem from this viewpoint: (1) suggests that the acid generated during the mining process may be an important source of persistent acid drainage, and (2) provides a convenient framework for understanding the approaches that are being taken or that have been suggested to control acid mine drainage.

In concluding this article, we will briefly discuss a technique we are trying to develop to determine where acid is being generated in the field, and will mention efforts to use heap-leaching technology to remove fine-grained pyrite from coal. Drs. Aplan and Luckie discussed physical processes for cleaning pyrite from coal in the third article of this series that appeared in the previous issue of this bulletin.

### The Chemistry and Physics of the Leaching Process

Leaching pyrite or other metal sulfides from rock or coal involves both chemistry and physics. The chemistry is simple. One mole of pyrite is oxidized by the 3½ moles of oxygen dissolved in water. The products of reaction are one mole of dissolved ferrous sulfate and one mole of sulfuric acid. Most commonly, dissolved oxygen is not the direct oxidizing agent, but is utilized by bacteria to oxidize dissolved ferrous iron (Fe<sup>++</sup>) to ferric iron (Fe<sup>+++</sup>). The ferric iron is the agent that actually oxidizes and leaches the pyrite. The net result—whether ferric iron or oxygen is the oxidizing agent—is the same, but, as we shall see, the leach reaction proceeds more rapidly with ferric iron than with O<sub>2</sub> because more of it can be dissolved in the leach solution.

The physics of the leaching process is more complicated and of greater practical significance than the chemical processes because it is more susceptible to practical manipulation. The physical process of importance is the transportation of oxidant to the location of sulfide minerals (hereafter referred to as sulfide blebs) within the rock or coal. The ultimate source of oxidant is atmospheric oxygen.

The kinetics of the oxidation of individual sulfide blebs within the rock or coal could, in principle, be of importance (see Figure 2 for depiction of sulfide blebs in coal or rock fragments). Calculations from available kinetic data<sup>4</sup> and, more importantly, observations of outer layers of fragments of rock<sup>5</sup> or coal that are devoid

of pyrite indicate that the kinetics of sulfide bleb leaching is faster than the rate of oxidant supply. If the rate of sulfide bleb oxidation were the slow step in the oxidation process, all sulfide blebs in rock or coal fragments would leach at substantially the same rate and be removed evenly throughout the fragments—leached outer layers enclosing the coal or rock fragments would not form. (The leached outer layers of coal fragments were observed in recent coal-leaching experiments in our laboratory.)

The observation of leached outer layers and the recognition of their significance—namely, that sulfide bleb leach rates are fast compared to the rate of oxidant supply by diffusion of ferric iron through water-filled pores and cracks—are important because they lead to a major simplification—we need not be too concerned with differences in leach rates between different metal sulfides or forms of FeS<sub>2</sub> (such as pyrite, marcasite, framboidal pyrite, and euhedral pyrite). After an initial transient stage, when the form of the pyrite may be an influencing factor, the leach rate will be controlled by the effective diffusional porosity of the matrix (rock or coal) that encases the sulfide minerals and by the behavior of this matrix during leaching. The nature and character (e.g., size and form) of the sulfide minerals themselves is of secondary importance in determining the leaching characteristics of the spoil. This conclusion may still be a bit controversial, but it is increasingly supported by accumulating field evidence that acid production is not simply related to the types or morphology of pyrite (FeS<sub>2</sub>).

As suggested in Figure 1, transport of atmospheric oxidant to the locations of metal sulfide blebs within the rock or coal occurs by three processes: (1) diffusion of oxidant into spoil fragments through the water-filled cracks and pores in the fragments, (2) diffusion of oxygen into the spoil pile through the air-filled spaces between spoil fragments, and (3) air convection into the spoil pile. The rate of diffusive oxidant transport can be roughly estimated by using the physical constants given in Table 1 and assuming diffusion down a linear concentration gradient across a layer of rock or spoil. For example, the flux of oxygen across a water-saturated rock layer 0.3 cm thick with a porosity of 2% would be about  $6 \times 10^{-6}$  grams of O<sub>2</sub> per square centimeter per month ( $= 2.68 \times 10^6 \text{ DC}/0.3$ , where  $2.68 \times 10^6 = \text{seconds per month}$ ).

Since the chemical reactions discussed earlier required 0.94 gram of O<sub>2</sub> to oxidize one gram of pyrite (Table 2), if the rock layer contained 2 wt. % pyrite (about 0.054 gram per cubic centimeter or  $1.6 \times 10^{-2}$  gram per square centimeter surface area

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Symbol	Definition	Air	Water
$D'$ ( $\text{cm}^2/\text{sec}$ )	Diffusion constant	0.178	$2 \times 10^{-5}$
$\phi$	Formation or rock porosity	0.02 - 0.2	0.02 - 0.1
$D$ ( $\text{cm}^2/\text{sec}$ )	Effective diffusion constant $\approx D'\phi/5$	$7-71 \times 10^{-4}$	$8-40 \times 10^{-8}$
$C$ ( $\text{g}/\text{cm}^3$ )	Oxygen concentration	$2.8 \times 10^{-4}$	$8.6 \times 10^{-6}$
$\rho$	Density	$1.3 \times 10^{-3}$	1.0

Table 1. Parameter values used in calculations in Figure 1 and in the text are listed here.  $D$ , the effective diffusion constant for either individual spoil fragments or the spoil pile, is estimated from  $D'$  by multiplying by the formation porosity value and dividing by a tortuosity, assumed to have a value of 5, of the channels in which diffusion takes place.

Grams $\text{H}^+$ removed per unit surface area of a spoil layer by $20''/\text{year}$ infiltrated rainfall carrying out $10^{-5} \text{ g H}^+/\text{cm}^3$ .	$5.1 \times 10^{-4} \text{ g H}^+/\text{cm}^2/\text{year}$
Grams $\text{H}^+$ produced when one gram $\text{O}_2$ is consumed in oxidizing pyrite	$0.0179 \text{ g H}^+/\text{g O}_2$
Grams $\text{O}_2$ required to leach one gram of pyrite	$0.94 \text{ g O}_2/\text{g FeS}_2$
Grams $\text{H}^+$ produced when one gram of pyrite is oxidized	$0.0168 \text{ g H}^+/\text{g FeS}_2$

Table 2. Constants used in calculations for this article.

of the rock layer),  $1.5 \times 10^{-2}$  gram of  $\text{O}_2$  per square centimeter would be required to oxidize its contained pyrite, and it would be leached of that pyrite at an average rate of 0.04% per month under the diffusive oxidant flux of  $6 \times 10^{-6}$  gram of  $\text{O}_2$  per square centimeter per month.

Because the diffusive  $\text{O}_2$  flux decreases and the amount of contained pyrite in the layer to be oxidized increases proportionally with layer thickness, the average leach rate drops off sharply as the layer thickness increases. The case just discussed is shown by the line labeled A in the lower left corner of Figure 1.

In copper dump leaching, leach rates are commonly 0.1 to 1% per month—much greater than the 0.04% per month we just calculated. Fragment porosities are a few per cent, and the average waste fragment is about 3 centimeters in diameter. The explanation for the discrepancy between the observed and the calculated rates is that ferric iron in concentrations of about 1000 ppm is the oxidant in copper dump leaching rather than dissolved oxygen at concentrations of about 8 ppm, which was used for the calculations. Even taking into account the fact that 4 moles of ferric iron are oxidatively equivalent to 1 mole of  $\text{O}_2$  and that ferric iron is heavier than  $\text{O}_2$  on a molar basis, oxidant as ferric iron can diffuse into the interior of waste or spoil fragments about 17 times faster than oxidant in the form of dissolved oxygen.

In Figure 1, the second line, labeled B, in the lower left corner shows the leach rate for 1000 ppm ferric iron. This line passes through the range of leach rates (dotted area) observed in industrial copper leach dumps.

The oxidation of ferrous iron to ferric iron, generally a very slow process, is greatly speeded up in nature and in leach dumps by bacterial catalysis (*Thiobacillus Ferrooxidans*). Bacteria generate the ferric iron required for leaching and allow the leach rate to increase as indicated by the arrow labeled "bacteria" in the lower left of Figure 1.

Provided oxygen is available, bacteria produce ferric iron at a rate faster than it can diffuse into fragment interiors and be consumed in oxidizing and leaching metal sulfides. The area indicated by diagonal lines in the upper left corner of Figure 1 shows the rate at which bacteria could leach metal sulfides if their production of ferric iron were the rate-controlling step in the leaching process. Dump leaching experience indicates that, if anything happens to the bacteria, the rate of leaching is abruptly slowed. Leaching drops back down to the oxygen diffusion rates at the bottom of the "bacteria" arrow in Figure 1. Such drops in leach rate have been observed in dump-leaching operations when the bacteria have been inadvertently poisoned. The fact that the temperatures of copper waste dumps do not exceed 55 to 65°C is a consequence of the inability of iron-oxidizing bacteria to function at temperatures higher than this.<sup>5,6</sup> Bacteria are thus classic catalysts—their presence is necessary for effective industrial leaching; provided they are present (they always are) and the temperature of their environment is not too high, the rate of leaching is controlled by factors other than the level of their activity.

Diffusion of ferric iron into waste particles typically controls the rate of leaching in industrial copper waste dumps. The development around waste fragments of outer layers that are leached of sulfide minerals<sup>5</sup> accounts for the observed inverse-square-root-of-time decay of copper concentrations in the effluent streams of the dumps. Diffusion of oxidant into waste or spoil fragments is not the whole story, however. Oxidant must enter the dump in order to contact and leach the waste fragments. In general (Figure 1), atmospheric oxygen could diffuse into the dump or be carried in by air convection. Oxygen can diffuse through the air-filled spaces in a dump much faster than through the water pores of a waste fragment because the diffusion constant for  $\text{O}_2$  in air is four orders of magnitude greater than in water, and because the

concentration of oxygen in air is about 30 times that in water (Table 1). Since the average leach rate of a layer of spoil is proportional to the inverse square of the layer thickness,  $\text{O}_2$  diffusion in air can support leach rates comparable to those of aqueous  $\text{O}_2$  diffusion in waste layers about a thousand times thicker. Air diffusion could thus support leach rates observed in industrial practice in dumps up to about 10 feet in thickness, but not more (Figure 1). Industrial sulfide waste dumps are usually at least 70 feet thick, and can be many hundreds of feet thick.

Leaching in industrial dumps more than 70 feet thick is made possible by air convection. The dump piles must be quite permeable for air convection to take place. Provided they are, buoyant forces derived from the oxygen depletion, water vapor saturation, and heating of the air by the exothermic sulfide oxidation reactions can cause a significant convective supply of atmospheric oxygen to the interior of the dumps. As shown in Figure 1, it is really the combination of air convection and bacterial catalysis that allows leaching at industrial rates. As might be expected, dumps that contain unusual amounts of clay material, and are, therefore, relatively impermeable leach very poorly.

We are now in a position to apply Figure 1 to the acid mine drainage problem. Coal is generally strip-mined in steps as shown in Figure 2. The overburden is stripped and placed in spoil piles with the topsoil segregated, the coal is removed, the spoil piles are graded, and the topsoil replaced. The spoil piles are loose rock piles much like industrial waste dumps, and can be expected to have high enough permeability that their leaching will be assisted by air convection and occur at something like the industrial rates of Figure 1. When the spoil is graded into the reclaimed area and the topsoil replaced, the upper layers are compacted and are impermeable enough that air convection is no longer a factor. Continued sulfide leaching must rely on the diffusion of atmospheric oxygen through the soil layers into the spoil.



substantially reduce oxygen concentrations at depth. Nonetheless, it is clear that prevention of steady acid production will not always be an easy task. Still, it is an important one and has received much attention because, as shown by the 100% pyrite oxidation entry in Table 3, serious acid production could persist for a very long time. It is encouraging to recall that the pyrite associated with coal seams was not an environmental problem before the coal was mined. It is clearly not impossible to shield the pyrite from steady oxidation by reasonable thicknesses of vegetated overburden since nature has been able to do this routinely.

It is possible that most of the pyrite oxidation and acid generation occurs in the spoil-pile stage of the mining process. If this is true, several steps might be taken to greatly reduce the amount of acid generated. First, of course, the spoil should be buried and covered with topsoil as soon as possible, as is generally being done. Second, the spoil piles could be compacted as they are being constructed to eliminate air convection and reduce oxygen diffusion into the pile. Third, bacteriocides could be added to the spoil piles. These would greatly diminish the rate of pyrite oxidation (see bacteria arrow in Figure 1). Finally, in rare cases where it is economically and technically feasible, acid-neutralizing material could be mixed with the spoil to neutralize any acid generated.

How can we determine whether acid is presently being generated at a given site, or whether buried acid is simply being gradually flushed out? Holes could be drilled, their cores analyzed, their water levels (perhaps at various packed-off intervals in the wells) measured, and the chemistry of the water in the wells monitored over time. In principle, this could be done in enough holes so that the subsurface fluid flow pattern for the area could be determined, and acid anomalies traced to their source. Core analyses could then

determine if there is enough buried acid to act as the acid source, or if the level of observed acid production could be attained only with the help of steady pyrite oxidation. Study of even one area in this fashion would be a major undertaking, and hydrologic complexities are almost always such that uncertainties would probably remain even after this considerable effort was expended.

#### Determining Acid Generation by Voltage Measurements

We are trying to gain experience with another methodology. The tendency of a mineral to oxidize depends on the voltage (Eh) of its environment. In fact, oxidizing and reducing environments are characterized by an Eh (voltage) scale, just as the acidity or basicity of an environment is measured by the pH scale. We would expect the voltage at a site to be higher (more oxidizing) at the surface where atmospheric oxygen is available, and lower at depth where conditions become reducing. Where oxygen diffuses more effectively into the ground, the voltage should be higher at greater depths, and these may be the sites of pyrite oxidation and acid generation.

We have carried out voltage surveys (geophysicists refer to them as self-potential surveys) in two acid mine drainage areas. In one area, we have been able to make voltage measurements as a function of depth and verify the expected decrease in voltage with depth. We have extensive water-level and water chemistry data available to us from past work in this area by The USDA-ARS Northeast Watershed Research Center here at University Park, Pennsylvania. We have resurveyed the voltages eight times and have noted significant variations in voltages with time. Some of the changes appear related to periods of precipitation. Some are related to the season (summer versus winter). A good deal of work remains to be

done before we will understand the results we now have, but we are encouraged that the self-potential method may eventually help determine where and how acid is being generated at acid mine drainage sites. The surveys are relatively quick and inexpensive to make.

#### Using Heap Leaching to Remove Fine-Grained Pyrite from Coal

In another project we have been trying to ascertain whether heap-leaching techniques might be used to leach fine-grained pyrite from coal. In concept, coal piles could be leached much like industrial copper dumps while the coal is in inventory awaiting shipment or use in a power plant.

To assess the leach rate, we have measured the effective diffusional porosity of coal fragments, characterized the size and distribution of pyrite blebs in the coal, and run both batch and column leaching experiments. Results to date indicate that in the laboratory it is possible to leach about 90% of the pyrite out of ¼" coal fragments in about a year. The heat content (Btu value) of the coal is not degraded; in fact, by conventional measure, it is upgraded by the removal of pyrite. Whether the process is viable depends on the costs involved in implementing it and upon whether laboratory levels of pyrite extraction can be duplicated in field coal heaps. We are at present studying both these problems. With luck, they may be subjects of a future article in this bulletin.

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#### The Author

Dr. L. M. Cathles received his B.A. in 1965 in physics and his Ph.D. in 1971 in geophysics from Princeton University. From 1971 to 1978, he worked for the Kennecott Copper Corporation, carrying out research on copper dump leaching, in-situ leaching for copper, and the genesis of ore deposits. He joined the Penn State faculty in 1978, and, in addition to the areas mentioned in this article, is currently carrying out research on the in-situ leaching of uranium, the genesis of various kinds of hydrothermal ore deposits, and the plate tectonic setting of ore deposits.

Conditions of Pyrite Oxidation	Total Pyrite Oxidized	Time Required to Flush Acid Generated by Pyrite Oxidized
Oxidation by 20 vol. % air buried with spoil	0.11%	1.2 years
1 year's oxidation in spoil pile at dump leach rates	10.00%	108.0 years
100 % pyrite oxidized	100.00%	1080.0 years

Table 3. Estimate of the amount of pyrite oxidized and the time required to flush acid produced by pyrite oxidation during the mining process (assuming no acid is neutralized by reaction with the rock) is shown here. The pyrite-bearing spoil is assumed to contain initially 0.054 grams of pyrite per cubic centimeter (2 wt. %), and to be placed in a 20-foot layer in the reclaimed area. The acid is flushed by 20 inches per year of infiltrating rainwater that acquires a pH of 2.0 in passing through the spoil layer.