

Acid Coal Mine Drainage. Truth and Fallacy About a Serious Problem

by Douglas Ashmead

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In his paper Mr. Braley makes no mention of the bacteriological aspects of the problem. It is now quite well established that certain bacteria play a major role in formation of acid mine waters, and it is a simple matter in the laboratory to show that under sterile conditions the rate of acid production from a pyrites suspension is only about one quarter of that obtained from a similar suspension inoculated with drainage from a mine producing an acidic pit water. Under sterile conditions the oxidation is due to direct chemical action and, from the evidence just given and from much other evidence, this increase under nonsterile conditions is due to certain bacteria.

Experiments recently completed, and shortly to be published, have shown that this bacteriological oxidation can be prevented by the maintenance of pH conditions above 4. It was found that to raise this pH above 4 at the beginning of the experiments was not sufficient but that, due to the continuing chemical oxidation, alkali had to be added daily to maintain the pH conditions above 4. The amount of alkali added, however, over a fixed period, was only about one quarter of the alkaline equivalent of the acid produced when pH conditions were not controlled over an equal period. The opinion expressed by Mr. Braley that sodium hydroxide has little or no effect on the rate of oxidation of pyrites is not substantiated by the above experiments.

The writer does not claim that these results show a practical solution to the problems, especially in abandoned workings, but feels that the application of an alkaline coating, such as lime wash, to exposed accessible workings might be well worth trying.

S. A. Braley (*author's reply*)—In 1919 Powell and Parr¹ suggested that bacteria, or some catalytic agent, hastened the oxidation of pyritic or marcastic sulfur in coal. Carpenter and Herndon (1933)² attributed the action of *Thiobacillus thiooxidans*. Colmer and Hinkle (1947)³ observed an organism similar to *T. thiooxidans* and another organism that oxidized iron. Leathen and Braley⁴ first discovered this organism in 1947 in a sample of water from the overflow of the Bradenville mine (Westmoreland County, Pennsylvania). They characterized the organism in 1954⁵ and gave it the name *Ferrobacillus ferrooxidans*. Although Temple and Colmer (1951)⁶ had suggested the name *Thiobacillus ferrooxidans*, since they claimed it oxidized both ferrous iron and thiosulfate, we have found that pure cultures of the organism do not oxidize thiosulfate, hence the name *F. ferrooxidans*. In 1955 Ashmead⁷ isolated an organism, similar to the one called *Thiobacillus ferrooxidans* by Temple and Hinkle, from acid mine water in Scotland. It is probable that this organism was *F. ferrooxidans*. In 1954 Bryner, Beck, Davis, and Wilson⁸ reported microorganisms in effluents from copper mine refuse. These organisms appeared to be similar but were not in pure culture.

In view of this history of bacterial investigation of acid mine water and our own ten years of experience, we do not agree with Mr. Ashmead that bacteria play a major role in acid formation. We do not find that any of these bacteria will directly oxidize pyritic material. They do, however, augment the chemical formation of sulfuric acid by atmospheric oxidation. In two papers

in 1953⁹ Leathen, Braley, and McIntyre discuss the role of bacteria in acid formation and postulate the mechanism through which they operate.

Mr. Ashmead in his discussion of my paper has assumed that this work was carried on in the presence of acid mine water in which bacteria would be present. This was not the case. Strictly sterile conditions were not maintained, but the organisms present in mine drainages were definitely absent in these experiments. We believe that we have demonstrated that alkalis do not inhibit the chemical oxidation of pyritic material. This is also indicated by Mr. Ashmead's discussion in which he says that alkali must be added daily due to the continuing chemical oxidation.

It is interesting to note that Mr. Ashmead finds that maintenance of pH above 4.00 decreases the activity of the bacteria. We have found also that a decrease in pH below 2.8 also inhibits its activity. Table XIII of published data¹⁰ illustrates the decrease in activity with increased acidity, although pH values are not given.

Table XIII. Increase in Acidity Attributed to Iron-oxidizing Bacteria

Culture	Acidity Increase for Periods, Pct		
	10 Weeks	22 Weeks	29 Weeks
111	161	356	84
1V	129	232	47
V	144	338	98

These values are in comparison with uninoculated controls and show the marked increase in acidity up to 22 weeks but a decline at 29 weeks, at which time the experiment was terminated. It is probable that after a longer period only chemical oxidation would have continued.

From our studies⁹ we have postulated that the iron oxidizing bacterium (*Ferrobacillus ferrooxidans*) oxidizes the ferrous iron, resulting from chemical oxidation, to ferric iron. The ferric iron then aids the atmospheric oxidation of the sulfuritic material and is itself reduced to ferrous iron, which in turn acts as food for the autotrophic bacteria.

Study of the physiologic properties of *F. ferrooxidans* shows that its preferred pH is about 3.00 and its activity decreases with variation in either direction. It is extremely inactive above pH 4.00 and below 2.5. This inactivity above 4.00 is indicated by Mr. Ashmead's observations.

These properties of *F. ferrooxidans* then correlate perfectly with our hypothesis. Ferrous iron is oxidized very slowly by atmospheric oxygen in highly acid solution and since the bacteria become inactive, acid is formed only by atmospheric oxidation. At a pH of 4.00 or above iron is more readily oxidized by atmospheric oxygen, but the bacterial activity is decreased. However, with a pH above 4.00 the ferric iron is removed from the field of activity since its soluble sulfate hydrolyzes and precipitates the iron as ferric hydroxide or a basic sulfate. As we have shown in the paper under discussion, the alkali does not inhibit the chemical oxidation, and thus the acid formation continues. This

continuation would eventually reduce the pH to the active range of the bacteria, and they would augment the chemical oxidation until the pH became so low that they would become inactive and again only the chemical oxidation would prevail.

We are indeed appreciative of Mr. Ashmead's discussion calling to our attention a point which we did not mention in the paper. We believe that these facts substantiate our hypothesis of the role of bacteria in formation of coal mine acid.

As Mr. Ashmead states, regardless of the fact that alkali retards the activity of bacteria it does not indicate a solution to the problem, because of the inaccessibility of area of abandoned workings and the necessity for renewal of the alkali at intervals. Rock dusting constitutes such a procedure. Due to rapid removal of water from haulageways very little acid develops in these dry areas. Fresh working faces which are also rock dusted do not produce acid water. Evidence of the continuing acid formation in rock dusted areas is shown by the brown streaks of precipitated iron showing through the coat of rock dust. Such areas, once

abandoned, lose the rock dust coat by neutralization and spalling, and its effect is soon lost.

References

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Discussion

Low-Temperature Carbonization of Lignite and Noncoking Coals in the Entrained State

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R. G. Minet—The authors' description of the remarkable progress made in the last few years in applying the fluidized solids technique to the problem of lignite drying and carbonization clearly demonstrates that engineering techniques available today may make many processes practical and profitable which a few years ago were considered otherwise. As pointed out in the article, the future of the carbonization step hinges on the value and utilization of low temperature tar. On paper, at any rate, this tar looks like a valuable raw material for the chemical industry to use. Some 50 to 60 pct may be converted to pitch for electrodes, roofing, road tars, and other valuable products; the 25 to 30 pct tar acids could conceivably form a basis for a new low cost resin or plastic of the phenolformaldehyde type. Yet these materials are so new and dissimilar from available sources that much work must be undertaken by the chemical industry before they will be accepted. Now that the work of Dr. Perry and his colleagues has made a large supply of low temperature tar a real possibility, I would expect the chemical industry to accelerate its work in this field.

On the basis of certain data available in the literature it appears possible to produce a more aromatic tar, although in smaller yield, by operating at temperatures in the range of 1300° to 1500°F. Operating a fluidized bed process for lignite at these conditions should be technically possible, at least, and could produce a tar having more familiar characteristics. I wonder if Dr. Parry would care to comment on such a possibility.

Incidentally, in our own work on carbonizing coking coals in fluidized beds, using Ohio, Pennsylvania, and West Virginia high volatile bituminous coals, we have obtained yields which agree with the correlation given for tar yields vs moisture and ash-free volatile Btu. Our data are slightly under the line, but certainly in the range of the correlation. We have also obtained evidence in support of the authors' statement as to the effect of air on the process. In our pilot plant all the

heat required for carbonizing is released by internal combustion of char in the fluidized bed in normal operation. We are also equipped to obtain all carbonization heat by external electric heaters on the shell of the carbonizer while introducing only an inert gas to the process. We note no difference in tar yield or characteristics between the two operations. In the case of the gas, however, it appears that some hydrogen is consumed by the air combustion.

We would be interested in hearing in a little more detail about the hot dust and char handling problems at Sandow. Have the authors found char subject to spontaneous combustion? Have they ever tried a coking coal in their pilot plant?

V. F. Parry (author's reply)—Production of a more aromatic tar by operation of the carbonizer at 1300° to 1500°F does not appear to be economical. 1) The capacity of a reactor operating at 1500°F would be 30 to 50 pct less than the capacity at 932°F and the cost of processing would increase materially. 2) The cracking of tar vapors in a reactor requires appreciable time to complete the reactions and it is doubtful that considering the very short time of residence of tar vapors within the reactor (4 to 10 sec after evolution) the basic character of the tar would be changed significantly. This is indicated from the data reported in Table XIV. 3) General studies have shown that it is advisable to operate at the minimum temperature to produce the maximum tar and minimum gas. 4) Operating problems and the maintenance of vessels and reactors, and the hazards of handling hot char, increase with the temperature of carbonization. It is technically possible to operate at temperatures as high as 1500°F, but in my opinion it is not economical or desirable. We believe that the primary tar must be won in the simplest way and then processed alone to change its character for production of desired products.

It is interesting to have confirmation of our observations on the reaction of air with the products of carbonization. The major reaction is with the char, fol-