Electrobiochemical neutralization of acid mine water

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When iron sulfides in a coal mine are exposed to water containing oxygen and sulfur-oxidizing bacteria, oxidation takes place, which results in the formation of sulfuric acid. The acid mine water so formed constitutes a formidable water pollution problem that seriously affects thousands of kilometers of streams and surface acreage in the U. S. In 1972, more than 3.5 billion kilograms (4 million tons) per year of sulfur acids were estimated to have drained from active and abandoned coal mines.[1] The additional strip mining for coal brought about by the energy crisis could result in even more serious pollution problems.

To cope with these problems, some water-treatment methods have been suggested by Koehrsen and Gandt [2] whereby acids are neutralized and iron is partially removed by adding lime or limestone to the water. This technique does not remove the SO_4^{2-} from the system; it produces a chemical sludge that must be removed periodically and it is costly to maintain. Other techniques such as reverse osmosis,[3] electrocoagulation,[4] and electrodialysis and distillation [5, 6] have been suggested but again the costs are high.

Campbell and Lind [7] have noted that it takes acid strip-mine lakes a long time to recover naturally. Randles [8] has summarized the early experiments on the use of sulfate-reducing bacteria to neutralize acid mine water, and Buttle *et al.*[9, 10] have called attention to their importance in the natural recovery of acid strip-mine lakes. They recognized the need of an energy-source material for these bacteria in order to hasten lake recovery and to reestablish essentially neutral water. The addition of wastewater was suggested as an energy source for the microbes. The lack of a carbon energy source in acid strip-mine lakes led King [11] to suggest this deficiency as a cause for the low algal productivity. Brochway *et al.*[12] have since shown that carbon as organic or inorganic compounds must be considered as a regulating nutrient for both heterotrophic and autotrophic populations. Decker and King,[13] assuming that the slow recovery of acid strip-mine lakes might be caused by the low flow of organic matter into the water, have shown that introduction of an organic energy source (wastewater sludge) into an acid strip-mine lake will substantially hasten the recovery of the lake. The bacteria removed the SO_4^{2-} and produced S^{2-} and CO_2. Some sulfur was removed as H_2S gas from the system at low pH, but as the pH increased, more of the sulfur was present as S^{2-} and HS^-. At higher pH, the sulfide ion was precipitated as FeS and thus reduced the sulfur concentration in the water.

In this paper we have combined the basic technique of Decker and King with the biochemical fuel-cell principle (described below) and have shown that by adding electrodes and a simple external circuit to the system, one can further increase the rate of acid neutralization and water quality. In addition, it may be possible to obtain a modest amount of electric power for plant operation, a practical means of disposal of sludge, and the recovery of some free sulfur.

PROPOSED METHOD

The addition of semi-solid organic matter such as wastewater sludge to acid mine water provides the energy source needed for the growth of sulfate-reducing bacteria such as *Desulfovibrio desulfuricans*. The mineralization of the organic matter $(CH_2O)_n$ and SO_4^{2-} can be generally represented by the following equation:

$$(CH_2O)_n + H_2SO_4 \rightleftharpoons H_2S + CO_2 + H_2O \quad (1)$$

Some years ago, Sisler [14] studied the anaerobic conditions at the bottom of the sea and took advantage of this reaction to produce a biological fuel cell. He was able to show that the reducing condition at the bottom of the sea, or in this case at the bottom of an acid strip-mine

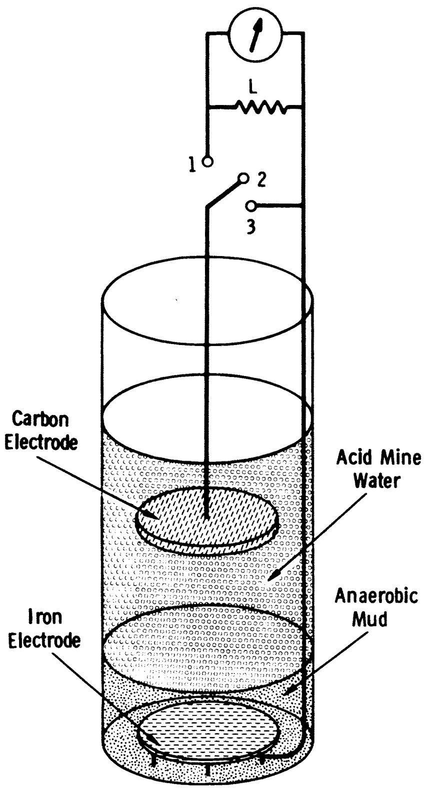

FIGURE 1. Sketch of cell showing relative positions of components. Electrodes can be connected through load resistor (L) for voltage determination (Position 1), be left on open circuit (Position 2), or be connected together (short circuited, Position 3).

lake, could be depicted by half-cells. The anaerobic half-cell contained organic matter, seawater containing SO_4^{2-}, and *Desulfovibrio.* At a pH of about 3 and higher, the hydrogen sulfide formed by the reaction is ionized and the sulfide ion formed is oxidized to S^0 at the electrode as follows:

$$H_2S \rightleftharpoons S^{2-} + 2H^+$$
$$S^{2-} \rightleftharpoons S^0 + 2e \text{ (at the electrode)} \qquad (2)$$

The anaerobic half-cell therefore represents the reducing conditions in the sea-bottom muds. The oxidizing half-cell represents the conditions near the surface of the water, which are given by the equation:

$$1/2\ O_2 + H_2O + 2e \rightleftharpoons 20H^- \qquad (3)$$

Excess H ions combine with hydroxyl ions produced in Equation 3 to form water:

$$2H^+ + 20H^- = 2H_2O \qquad (4)$$

By using platinum electrodes, Sisler was able to develop a potential of about 0.5 volt and a current in the 50-μamp range using a load of 10 000 ohms.

The same equations apply to the neutralization of acid mine water, which could have been used in this cell instead of seawater. After organic material is added to the acidic water in a strip-mine lake, the reactions in Equations 1 to 4 will tend to an equilibrium condition, and the anaerobic activity slows down. The reaction approaches equilibrium as long as the sulfide ion is concentrated in the mud. Moreover, the H_2S concentration increases with time and, as this substance is toxic to anaerobes, its presence inhibits a further increase in microbial activity. Decker and King found that it took 50 to 70 days to effectively neutralize acid mine water in experimental laboratory cells. It is conceivable that the reaction rate could be increased if the electrons on the sulfide ion produced in the anaerobic mud by the reaction of Equation 2 were allowed to discharge at an electrode buried in the mud in a manner similar to the fuel cell described above. Electrons could then flow through an external metallic conductor to the surface water to produce OH^-, as in Equation 3. Thus, if electrodes are placed in the bottom sediment and also near the surface in the overlying water and connected with an external conductor, the reaction rate would increase so as to neutralize the acid water in a shorter time. At the same time the concentration of H_2S would decrease, which would enhance the further growth and activity of anaerobes. Experiments were made to test the feasibility of using such a system to expedite neutralization of acid mine water.

LABORATORY TESTS

Experiments similar to those of Decker and King were repeated, except that electrodes were inserted in the top and bottom of the test cells. Two 40-l experimental cells were used to simulate acid strip-mine lakes and to determine whether acid waters could be neutralized by anaerobic activity at an accelerated rate by electrically connecting (short circuiting) the reducing and oxidizing regions of the cell.

Both test and control cells and electrodes were made as shown in Figure 1. The bottom 80 to 100 mm of the cells were filled with a sludge consisting of fire clay mixed with small amounts of agar, calcium lactate, and trace amounts of Na_2S, $MgSO_4$, $CaCl_2$, NH_4PO_4, and $FeCl_3$ to simulate a bottom mud with appropriate nutrients. In the upper layers of the sludge, bits of paper tissue and cardboard were mixed in as a carbon energy source. The sludge was then inoculated with a mixed enrichment culture containing *Desulfovibrio* commonly found in anaerobic sediments. Circular iron electrodes were inserted in the mud 10 to 20 mm below the top surface. About 12 days were allowed for incubation, after which massive black areas indicating anaerobic activity were noted throughout the sludge. Subsequently, sulfuric acid water of pH 2.0 containing a small amount of ferric iron to simulate acid mine water was slowly poured into the cell so as to prevent stirring and mixing with the sludge. Identical carbon plates as the second electrode were inserted below the surface of the water in each cell. Insulated leads were attached to both electrodes.

The electrodes in one cell were connected (short circuited), but in the control cell they were left on open circuit. Daily measurements were made of the pH of the water in both cells. The change in pH with time for the shorted and unshorted cells is compared in Figure 2. The data clearly show the faster rate of increase of pH in the shorted cell compared with the unshorted control cell. It should be noted that the rate of increase in pH was only moderate in the shorted cell initially but that the rate of increase became relatively high after the pH reached 3.5. This behavior conforms with the logarithmic nature of the pH scale and was also observed by Decker and King who showed that significant pH changes take place only after the acidity is reduced to about 100 mg/l of acid. At lower acidity, the buffering action is too weak to maintain low pH values, and the rate of neutralization increases.

In a second experiment, a 30-l cell with electrodes having a larger surface area than in the previous experiment was tested. During the day, the cell was left on open circuit; voltage, current, and pH measurements were made periodically. At night and on weekends, the cell was short circuited by the same method used in the previously described experiment. Significant reduction in acidity was found after the longer shorting periods, in agreement with the previous experiment. The power output was measured through a 10 000-ohm resistor connected across the same cell, and is shown as a function of time in Figure 3. During the first 24 h, the data were erratic because of mixing of the water and equilibration of the cell. Subsequently, the power dropped sharply after the shorted periods but tended to recover during periods of open circuit. Undoubtedly, the recovery of the acidity (decrease in the pH) is a local ion depletion phenomenon taking place in the region of the electrodes and caused partly by a buffering action.

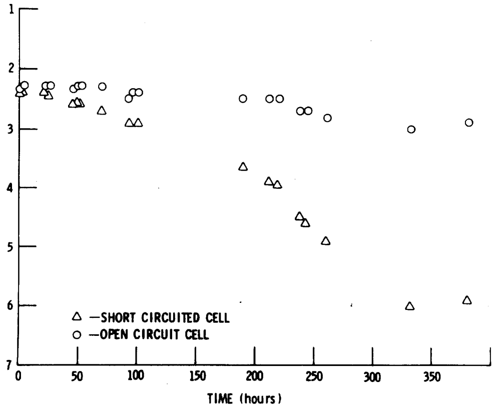

FIGURE 2. pH as a function of time for identical cells, one on open circuit and one shorted.

These experiments show that the neutralization of acid mine water by anaerobic activity can be accelerated by interconnecting or shorting of appropriate electrodes mounted in the cells. Other experiments carried out in the laboratory show that neutralization is a function of current and can be further accelerated by increasing the surface area of the electrodes. For instance, the cell current is almost linear with the carbon electrode area for one of the experimental cells. Also, the cell activity can be enhanced by keeping the ratio of the volume of acid water to the volume of anaerobic mud as low as practical. For a ratio of about 1:1, acid water of pH 2 was reduced to pH 7 in about 5 days in these model experiments.

It can be argued that the system proposed is merely a galvanic cell, as two dissimilar materials are used for the electrodes. Undoubtedly some initial loss of iron takes place in the anaerobic half-cell. However, an insoluble coating quickly forms on the surface of the iron electrode and prevents deterioration. The composition of this coating is not known; it may be ferrous phosphate similar to that found by Booth *et al.*[15] on well-preserved ancient iron nails buried in anaerobic mud. The authors have not observed any significant consumption

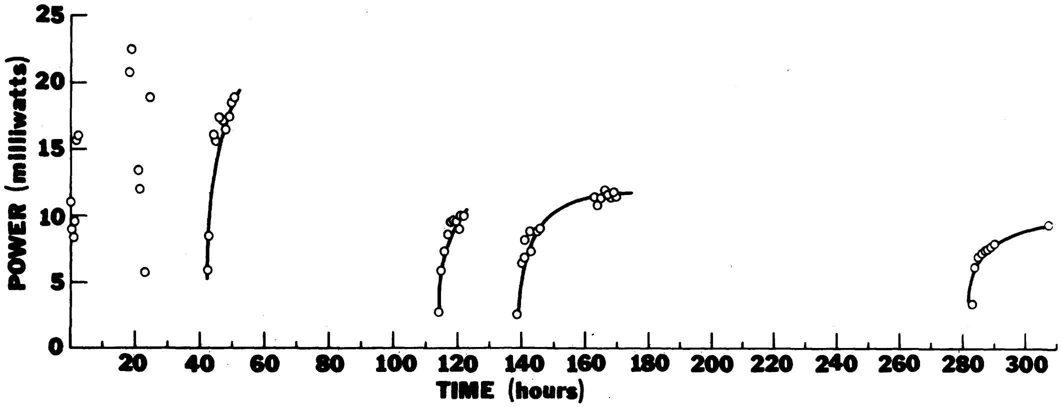

FIGURE 3. Power as a function of time for same cell shown in Figure 2 measured through 10 000-Ω resistor, when cell was on open circuit.

of either electrode and it therefore seems that the current flowing in the cells is primarily biological rather than galvanic in origin. Moreover, measurements with small test-tube cells using shorted platinum electrodes for both half-cells show very rapid neutralization of the H_2SO_4 in the anode side. This can be accounted for only by the production of hydroxyl ions by bacterial action as illustrated in Equations 1 to 3 .

As pointed out by Decker and King,[13] the process of acid-water neutralization also can be improved by algae production on the surface of the water. Algae take up CO_2 produced by the anaerobes and facultative bacteria and ultimately become a source of organic matter for the microorganisms to feed on. Decker and King mentioned that the photosynthetic oxygen produced by the algae inhibits the water-recovery process because it promotes acidity by the formation of SO_4^{2-}. However, in the shorted cell system, oxygen is also needed to form OH^- (Equation 3), which unites with excess H^+ to form water. Thus, in addition to being a good food supply, algae-produced oxygen will aide the neutralization of acid mine water in a pond or lake fitted with a shorted electrode system.

APPLICATION TO FIELD OPERATION

It should be emphasized at this point that the principle objective of this study is to accelerate the natural recovery processes of lakes, ponds, and streams such that they may satisfy environmental needs of a given region. These needs, of course, vary according to the intended uses, such as fishing, and provision of potable drinking water. In most situations, iron-carbon electrode sets placed in strategic locations in an acid pond or in the deeper basins of a flowing acid stream will hasten natural recovery through the mechanism of sulfate reduction by *Desulfovibrio* bacteria. In the instance of a holding pond where natural recovery from acid to neutral or slightly alkaline waters is to be augmented by the electrode system described above, it is important to recognize the hydrographic and other environmental conditions necessary for the activity of sulfate-reducing bacteria. These conditions must provide a basin where bottom circulation is poor, or dissolved oxygen from surface waters will prevent strict anaerobes from thriving in the bottom muds.

Each electrode set ideally would consist of a large-area iron electrode embedded in the sulfide-rich bottom mud and a carbon electrode suspended in the water above it. The iron electrode would also serve as an anchor for the upper carbon electrode, which is suspended from a buoy at an appropriate depth above the mud-water interface where the concentrations of dissolved oxygen and sulfur acids are optimum. The electrode set is completed by connecting both electrodes with an insulated shorting wire. Such an electrode set requires little or no maintenance.

Where large volumes of flowing acid water are to be treated near the mining area it may be more practical to consider a continuous flow system. The effluent from a mine could be allowed to flow by gravity through a series of biological holding ponds or tanks containing anaerobic sediment, electrodes, and an external circuit, so that the neutralized effluent from the last tank could be channeled directly into a public stream. More oxygen would be dissolved into the acid water flowing into the holding tanks than if a static system were used. In a flow system comprising several ponds in series, a higher capacity for neutralization may be available than in a single pond. Therefore, it may be desirable to divert some of this capacity to the generation of electric power for plant operation. To check the feasibility of this approach, a series of four 25-l cells containing anaerobic mud, a cardboard and paper diffusion membrane, and iron and graphite electrodes were arranged in terrace fashion in the laboratory so that each was gravity-fed by the preceding cell. A reservoir containing simulated acid mine water of pH 2 was fed into the first cell. The effluent from the last cell was found to be pH 7.0 and the flow rate was established at 6 l/d. Based on these laboratory observations one can project to a field-scale facility; assuming four holding ponds having a capacity of 1 400 m^3 each, the laboratory data can be scaled to yield a flow rate of about 336 000 l/d in a practical application.

In the aforementioned laboratory flow-through system, experiments were made in which small motors and timers continuously operated during the neutralization process. By scaling these experiments, one can approximate the amount of available power. For instance, if each of the 25-l cells were scaled up to a 300-m diameter pond equipped with the proper electrodes, it is not unreasonable to realize a power production of 2 to 4 kilowatts per pond. It should be noted, however, that if electrical energy is removed from the system, the effectiveness of acid neutralization is reduced.

As most biological processes are temperature-dependent, the residence time of acid mine waters for acid removal, whether in a holding pond (batch process) or a cascade system (continuous flow), will be inversely proportional to the temperature. The so-called Q_{10} effect, a doubling of reaction rate with each 10°C increase in temperature, roughly applies to our process. Therefore, the temperature of the season of the year must be considered in the above calculations. To circumvent the temperature problem, a more practical counter-current system using a continuous flow through concentric tubes could be designed to operate indoors or in a thermally insulated environment at the optimum temperature for bacterial growth. The authors have made preliminary experiments with such systems in the laboratory where a wire was mounted axially in a porous pipe that was in and iron pipe served as electrodes, and a much turn mounted inside an iron pipe. The wire and iron pipe served as electrodes, and a much larger volume of water could be processed in comparable time.

The cost of using this technique will depend on the complexity of the system used. If the goal is to clean up an existing acid mine pond (non-point source), scrap iron electrodes for the bottom and carbon electrodes attached to floats could be used which could cost as little as several hundred dollars per acre of pond. If large volumes of water from a point source require neutralization, the flow system previously mentioned is more desirable. This could take either one of two general forms: (a) water flowing successively through several ponds or holding tanks equipped with suitable electrodes, or (b) water flowing through a concentric tube counter-flow system. Both systems, (a) and (b), would cost more than the static system, but would be more efficient than a non-point source.

To date, experiments show that H_2SO_4 and some iron compounds are removed, but these methods do not constitute a complete system for water-quality renovation. An engineering study and a field demonstration are obviously required. Some effort has been made by the authors to further improve water quality. Various simple filter systems used at the final stages in the electrobiochemical treatment of acid mine water (sand and carbon filter columns) are now being tested. Vigorous air sparging greatly increases removal of residual organic matter by oxidation, chemical, and combined chemical and biological means.

Further studies are also being made on the application of magnetic fields to hasten ionic separation and neutralization of excess ions such as sulfur and iron, which are present in acid mine water and which may be considered undesirable pollutants. Previous studies by Sisler and Senftle[16] have discussed the possible influence of the earth's magnetic field on geomicrobiological processes in the hydrosphere. Within the past year, this concept has been applied on a laboratory scale in attempts to purify acid mine water by using both permanent and electromagnets. It was found that by circulating a simulated acid mine water containing sulfuric acid and iron chloride through the magnetic field, iron compounds could be precipitated in the side arms of a hollow glass tube fitted with positively and negatively charged electrodes.

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