

# Acid strip mine lake recovery

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**E**COLOGICAL PROBLEMS associated with runoff of acid water from coal strip mines are well known, and the papers documenting such deterioration of aquatic ecosystems are many. Many investigators have shown that the sources of this acid are the iron-sulfur pyrites and marcasites left on the surface after the coal has been removed. Oxidation products of these minerals are washed from the spoil banks by rain, and the resulting acid water collects in depressions to form acid strip mine lakes. Overflow from such lakes is of significant detriment to downstream areas, and in the acid condition these lakes are useless for water supply or recreation.

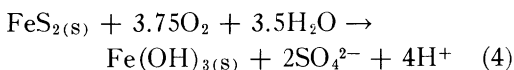
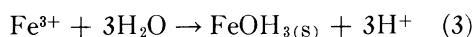
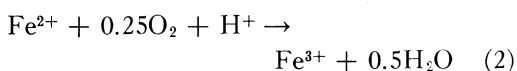
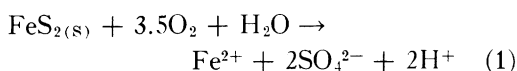
Campbell and Lind,<sup>1</sup> however, have shown that some acid strip mine lakes do progress naturally over a period of time to an alkaline state, where they are capable of supporting entire aquatic communities at a level characterized as early eutrophy. Considerable acidity reduction was noted by Tuttle *et al.*<sup>2,3</sup> when acid water was allowed to percolate through a sawdust pile. The authors suggested that the observed acid loss was related to the activity of sulfate-reducing bacteria that were responding to the availability of an organic substrate.

Campbell and Lind's<sup>1</sup> evaluation of the recovery pattern of lakes suggests that the rate of recovery from the acid condition is related to the acid production potential of the stripped areas relative to the availability and rate of accumulation of organic matter, such as leaves and grass, from undisturbed portions of the drainage basins of individual lakes. Wide variations in type and amount of metal cations in strip mine lakes<sup>1</sup> suggest a marked degree of interaction between the acid and minerals in individual spoils before the entrance of the runoff water into the lake. Thus it ap-

pears that the prognosis for natural recovery of any given acid strip mine lake is governed by some interaction between the amount of acid-bearing spoils exposed, the type and amount of various minerals in the spoils, and the amount of undisturbed land in the drainage basin.

## ACID FORMATION

Stumm and Morgan<sup>4</sup> presented a proposed sequence of steps in the oxidation of pyrite that leads to the formation of acid, and Singer<sup>5</sup> meshed research data with literature to give considerable credence to this oxidation scheme.



While bacterial activity seems to accelerate acid formation,<sup>6-8</sup> the net effect of this oxidation of pyrites is the formation of two equivalents of acid for every mole of sulfate formed.

Singer<sup>5</sup> found that data obtained from underground coal mines indicated roughly two equivalents of acid associated with each mole of sulfate, but that strip mine drainage yielded only 0.9 to 1.3 equivalents of acid per mole of sulfate. A survey of mid-Missouri strip mine lakes in various states of natural recovery,<sup>9</sup> including the lakes studied by Campbell and Lind,<sup>1</sup> indicated a range of from 0.01 to 1.53 equivalents of acid per mole of sulfate.

These values indicate considerable loss of acid between the point of formation at

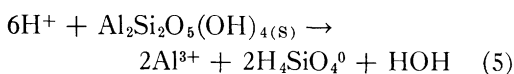
the pyrite crystal and the impoundment of the water in the strip mine lake, but little or no loss of sulfate. This acid loss, plus the significant accumulation of cations including aluminum, calcium, magnesium, manganese, sodium, and potassium noted by Campbell and Lind,<sup>1</sup> suggests a marked degree of interaction between the acid runoff water and the spoils it flows over before reaching the lake. In particular, the high clay content of the spoils and the high aluminum content of the more acidic strip mine lakes (Figure 1) point to the significant role of clay minerals in such alterations in acidity.

To evaluate some of the changes in acid water generated by clay minerals, highly acidic leachate from an abandoned waste coal settling pond was allowed to trickle through 1-m lengths of 2.54-cm diam Pyrex tubes half filled with selected minerals.<sup>9</sup> In each case an empty tube was used as a control, and change caused by contact of the acid water with the clays or other

minerals is represented as a difference in the quality of effluent from the two tubes in Figure 2. The minerals used in this investigation, gibbsite from the Alcoa bauxite mines in Bauxite, Ark., kaolinite No. 5 from Bath, S. C., montmorillonite No. 26 from Clay Spur, Wyo., and reagent-grade aluminum oxide powder, sorbed different amounts of water. The first data points in Figure 2 indicate the time at which the first water emerged from the tube containing the indicated mineral.

While Figure 2 shows that the ability of all minerals tested to alter water quality decreased with increased throughput of water, aluminum oxide, gibbsite, and montmorillonite indicated a marked ability to raise pH and decrease acidity, iron, and aluminum concentrations. These decreases in iron and aluminum seem to have been associated with elevations in pH, to the point where the solubility of these metals was significantly less than the concentrations present in the settling pond leachate used. Kaolinite, with its well defined crystalline nature, large particle size,<sup>10</sup> and low cation exchange capacity,<sup>11</sup> evidenced slightly increased pH, decreased acidity and iron concentration, and significantly increased aluminum content of the acid water.

From the data in Figure 2, it appears that clay minerals play a significant role in the determination of water quality in strip mine lakes. Much of the acidity loss noted probably is caused by sorption of hydrogen ions on the many interlayer crystalline sites of the clays, a process which is part of the natural weathering of feldspars and the various clay minerals.<sup>4</sup> Associated with this accelerated geologic weathering is some dissolution of clay minerals, which for kaolinite probably occurs as follows:



Because the oxidation products of pyrite in a strip mine spoil are in close contact with the clay minerals, Reactions 4 and 5 may be combined to show the potential inter-

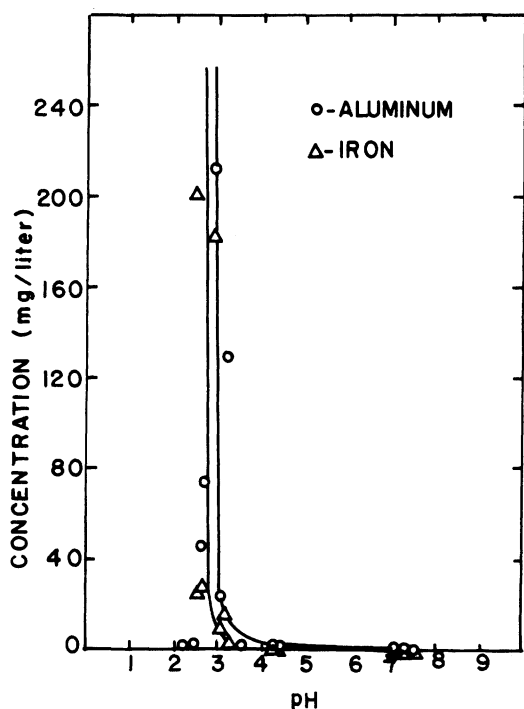


FIGURE 1.—Concentration of aluminum and iron as a function of pH in Missouri strip mine lakes.

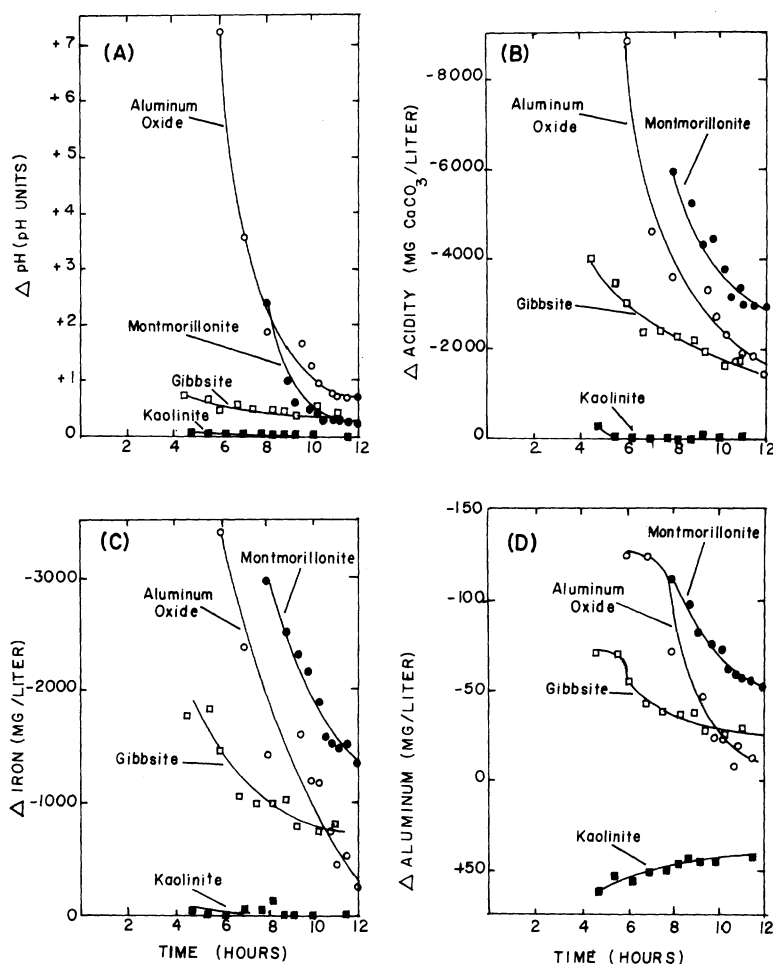
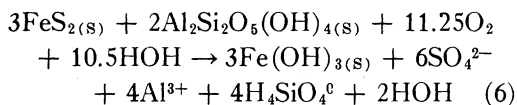


FIGURE 2.—Change in quality of acid mine water run through a glass tube containing 130 g of the indicated material: A, pH; B, acidity; C, iron; D, aluminum.

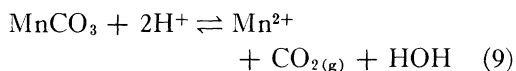
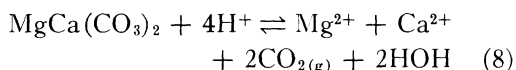
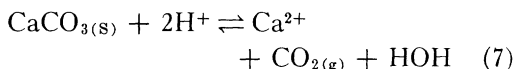
action as follows:



If the deprotonation associated with the dissociation of silicic acid has little effect on net acidity, Reaction 5 would seem to yield a pH increase with little change in total titratable acidity, because both  $2\text{Al}^{3+}$  and  $6\text{H}^+$  require six equivalents of base for neutralization. Some of the dissolved aluminum undergoes slow hydrolysis and eventual precipitation as gibbsite or bayerite,<sup>12</sup> but a large amount enters strip

mine lakes where it represents a significant acid buffer.

In addition to losses to clays by sorption and dissolution, some of the acid originating from pyrite oxidation is lost in the dissolution of the various alkali metal compounds commonly associated with strip mine overburden, as follows:



While such reactions would lead to the observed high cation concentrations noted in strip mine lakes,<sup>1</sup> cations such as  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{Mn}^{2+}$  are not titratable in the pH range used in a normal acidity titration. Reactions 7, 8, and 9 would result in increased pH and decreased acidity.

Differences in type and amount of both acid and nonacid soils that compose the overburden cast as exposed strip mine spoils determine the chemical composition of water entering strip mine lakes. Sorption and exchange of acidity by clays are determined by such characteristics as surface charge density, specific surface area, and number of exchange sites per area,<sup>13</sup> which in turn are determined by a complex interaction of physical and chemical variables.<sup>11</sup> This high degree of variability insures a significant degree of diversity in strip mine lakes. In all cases, however, the movement of acid water over the spoils results in some alteration in pH, acidity, and ionic composition. The degree of alteration is related to the contact time of the acid water with the particular soil types exposed at the surface of individual spoils.

Of the many alterations in water quality

that are generated by the contact of acid water with the exposed soils, increased aluminum concentration has the greatest effect on the rate of eventual recovery of the strip mine lake from the acid condition. A titration curve of water taken from an acid, mid-Missouri strip mine lake is presented in Figure 3, with a titration curve of distilled water adjusted to pH 3.0 with concentrated sulfuric acid and a titration curve based on a buffer intensity curve<sup>9</sup> calculated from measured sulfate concentrations.<sup>14</sup> Titration of dilute sulfuric acid approximates the titration curve calculated from sulfate measurements and theoretical considerations. The large difference in buffer intensity between these curves and that for strip mine lake water is believed to be caused by the elevated aluminum and iron concentrations characteristic of acid strip mine water (Figure 1). Because aluminum is roughly four orders of magnitude more soluble than iron in the pH range of interest (Figure 4), it has a much greater potential role as a proton donor. Aluminum may have been hydrated once, releasing between one-third and one-half of its potential acidity.<sup>12</sup> Over the pH range of 2.5 to 4.5, however,

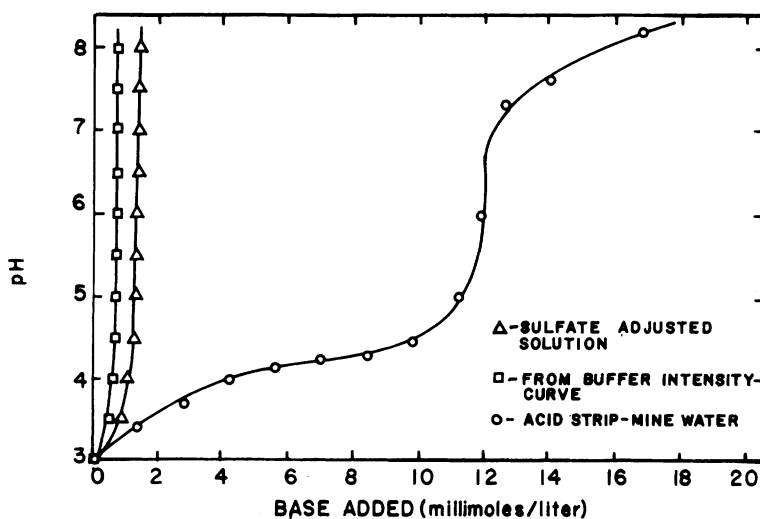


FIGURE 3.—Titration curve based on a buffer intensity curve derived from measured sulfate concentration compared with those of acid strip mine lake water and a sulfuric acid solution adjusted to pH 3.

aluminum can continue to act as a strong buffer as the remaining acidity is released gradually through hydrolysis as the pH rises.

It should be noted that Figure 4 is based on ideal laboratory equilibria at zero ionic concentration and 25°C. Such conditions are not common to strip mine lakes where similar solubility trends also reflect metal and ligand complexing agents. Representation of all iron and aluminum as hydroxides is an oversimplification, and oxides and oxy-hydroxides of both ferrous and ferric iron, as well as various polynucleic aluminum complexes, undoubtedly play a part in this extremely complex chemical system. But despite the complexity and the undoubted role of iron in the process, the sequential hydrolysis and eventual precipitation of aluminum appear to play a most significant role in buffering mid-Missouri acid strip mine lakes against increases in pH.

#### THE RECOVERY PROCESS

An evaluation of 25 yr of data led Campbell and Lind<sup>1</sup> to conclude that recovery of acid strip mine lakes is a natural succession resulting from gradual decreases in acid production by the spoils and leachate from unmined portions of the watershed. Leaves, grass, and other organic material in the runoff from unmined land eventually accumulate in such lakes to a concentration that is sufficient to allow the sulfate reduction noted by Tuttle *et al.*<sup>2,3</sup> All of the lakes studied by Campbell and Lind<sup>1</sup> that showed evidence of recovery had access to leaves and grass, while little terrestrial organic material was available to those lakes showing little recovery.

To evaluate the role of organic material in acid strip mine lake recovery, a series of microcosm studies, using a variety of different organic materials, was undertaken.<sup>9,14,15</sup> In each case, the selected organic material was added to containers of water taken from an acid, coal strip mine lake located about 15 miles (24 km) northeast of Columbia, Mo. Addition of the organic material was followed by

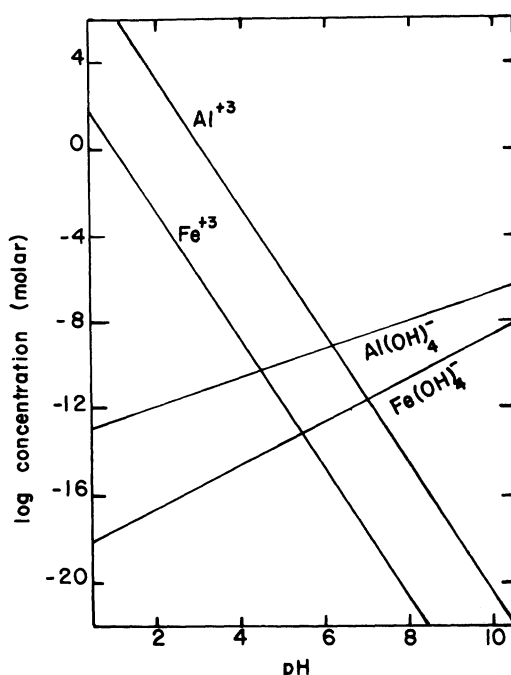
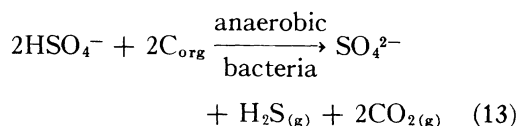
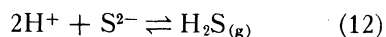
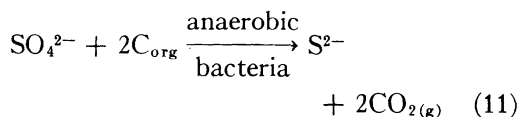
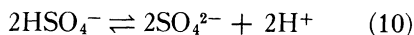


FIGURE 4.—Aluminum and iron solubility as a function of pH at 25°C.

marked improvements in the quality of the acid water. Results typical of the changes observed, from a microcosm in which the organic added was raw wastewater sludge, are presented in Figure 5.<sup>14</sup> Increased pH and decreases in sulfate, iron, and acidity all seem to be directly related to the activity of sulfate-reducing bacteria.

Sulfate reduction in acid mine water may be represented ideally as follows:



Loss of  $\text{H}_2\text{S}$  to the atmosphere represents a direct loss of acidity accompanied by an increase in the pH of the water. In-

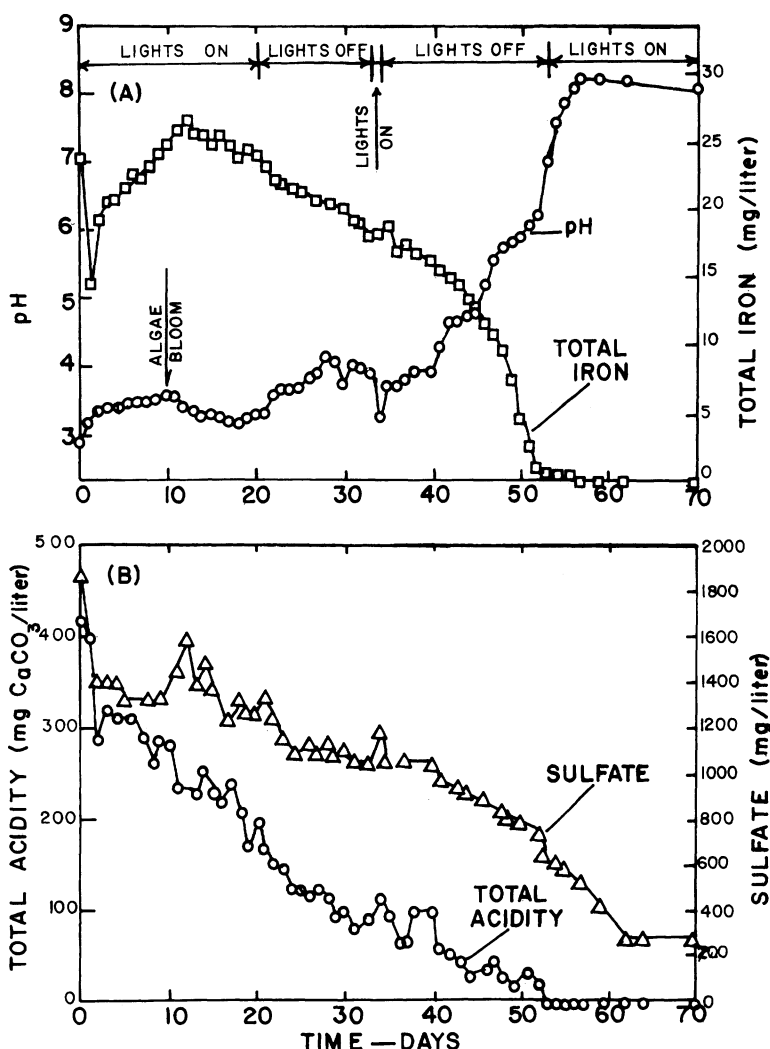


FIGURE 5.—Change in pH and iron, sulfate, and acidity concentrations with time in an acid strip mine lake water-wastewater sludge microcosm.

creased pH causes reduced solubility of metals in solution, and the precipitation of iron as an iron sulfide is accelerated by increased concentrations of sulfide in the water.

Establishment of reducing conditions is prerequisite to the initiation of sulfate reduction. Postgate<sup>16</sup> indicated that dissimilatory sulfate-reducing bacteria require an Eh of  $-150$  to  $-200$  mv, but Tuttle *et al.*<sup>3</sup> present data indicating significant sulfate reduction beginning at an Eh of  $-50$  mv. Despite possible pH-Eh considerations,

however, this higher value probably represents the Eh of the solution and not that found within the microenvironments where sulfate reduction occurred. Additional evidence of microenvironments is seen in the observation that pure bacteria cultures in artificial media did not reduce sulfate below a pH of 5.5, while mixed cultures of bacteria with a sawdust substrate showed sulfate reduction at a pH of 3.0.<sup>2</sup>

This suggests that other bacteria play a key role in establishing the required anaerobic conditions and providing metabolites



that serve as substrate for sulfate-reducing bacteria. Such preconditioning would be favored in protected microenvironments that allow buildup of the reduced products in amounts sufficient to overcome both the dissolved oxygen (DO) and the electron buffer imposed by the metals in solution.

In the microcosms used in this study, depth of organic material on the bottom was extremely critical. Initiation of sulfate reduction was related to the depth of organic material, rather than the ratio of organic material to acid water present in the microcosm. Increased organic depth allows rapid depletion of DO, and accumulation of reduced products in such bottom debris accelerates formation and maintenance by bacteria of an anaerobic zone significantly different from the overlying water. An example of such activity is seen in the data presented by Harp and Campbell,<sup>17</sup> which show increases in excess of 2 pH units from sediment surface to a sediment depth of 6 cm in recovering strip mine lakes.

Establishment of anaerobic conditions in the organic debris on the bottom allows gradual expansion of anaerobiosis. In addition, the iron in solution is gradually reduced from the ferric to the ferrous state, a process that markedly increases dissolved iron concentration in microcosms that contained iron-rich lake bottom soils before organic addition.<sup>14</sup> This reduction of the iron probably is accelerated by the increasing sulfide concentration, in which case it would be accompanied by formation of some elemental sulfur.<sup>18</sup> With continued pH and sulfide increases, the iron is precipitated as an iron sulfide.

Formation and release of sulfide from the microenvironment and its resultant loss to the atmosphere as H<sub>2</sub>S represent acidity loss with some increase in pH. These increases in pH, however, are counteracted to some extent by the concomitant gradual hydrolysis of aluminum. Dissolved aluminum retards rapid pH rise by supplying protons during hydrolysis while simultaneously serving as an electron buffer that tends to hold Eh in the bulk of the solution at a level above that required for

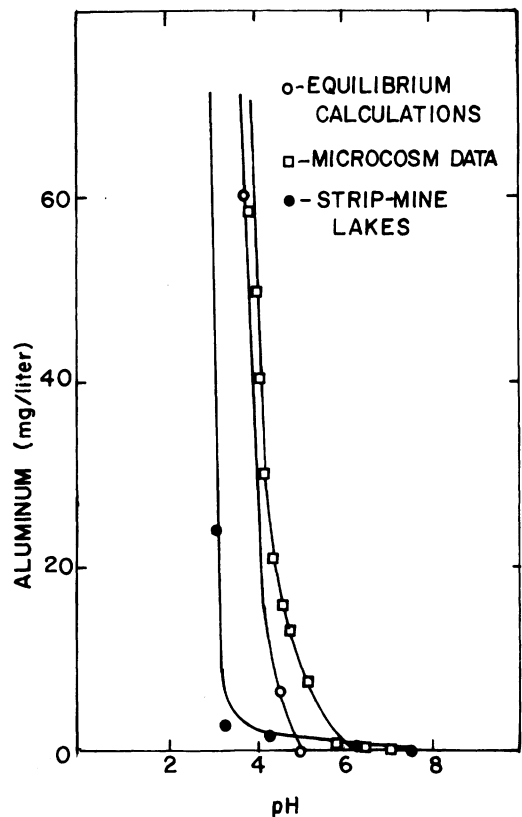


FIGURE 6.—Calculated aluminum solubility as a function of pH compared with measured aluminum concentration in a microcosm and in a series of strip mine lakes.

optimum sulfate reduction. Such retardation of the recovery of acid strip mine water continues until the aluminum is largely precipitated from solution. Comparison of measured aluminum concentrations with those calculated from a solubility product constant of  $10^{-32.6}$ <sup>12</sup> and pH data from a recovering acid strip mine water microcosm (Figure 6) indicates that, despite the buffering by aluminum, precipitation of the aluminum is also a function of the rising pH associated with H<sub>2</sub>S loss. Differences in the theoretical and microcosm data in Figure 6 seem to be caused by retarded settling of the hydrolyzed aluminum precipitate, while differences between these curves and the field data probably reflect various metal and

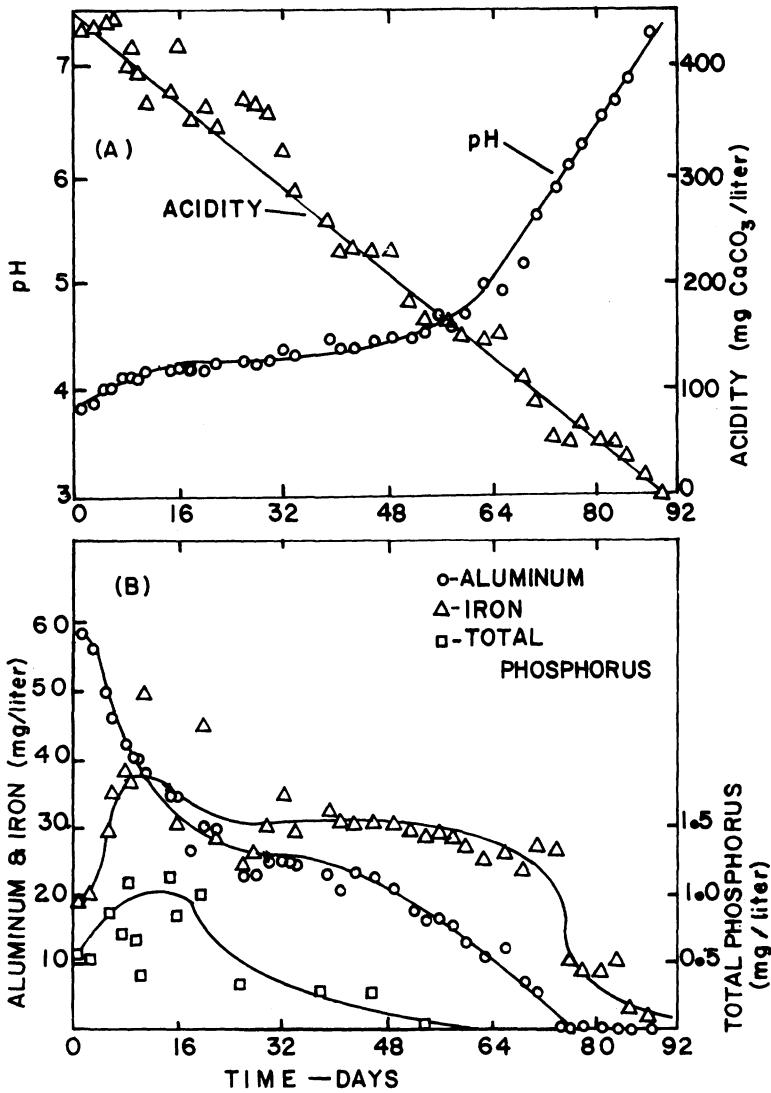


FIGURE 7.—Change in pH and acidity, aluminum, iron, and phosphorus concentrations with time in a microcosm fed raw wastewater sludge.

ligand complexes. Once aluminum is completely hydrolyzed, the proton and electron buffers associated with it are removed. Also, the acceleration of recovery noted above a pH of about 4.5 in Figures 5 and 7 seems to correspond with removal of most of the aluminum, as shown in Figure 7. The small number of strip mine lakes in mid-Missouri in the pH range of 4.5 to 6.0 suggests that, once recovery is initiated and a pH of 4.5 is reached, the

lake passes through this stage reasonably rapidly. Only 3 of the 19 acid strip mine lakes considered by Harp and Campbell<sup>17</sup> had a pH between 4.5 and 6.0.

Another factor tending to accelerate recovery is the formation of bicarbonate alkalinity. At pH levels above 4.5, the rate of sulfate reduction was accelerated and concentration of both sulfide and inorganic carbon increased rapidly, as shown in Figure 8. Continued pH increase would



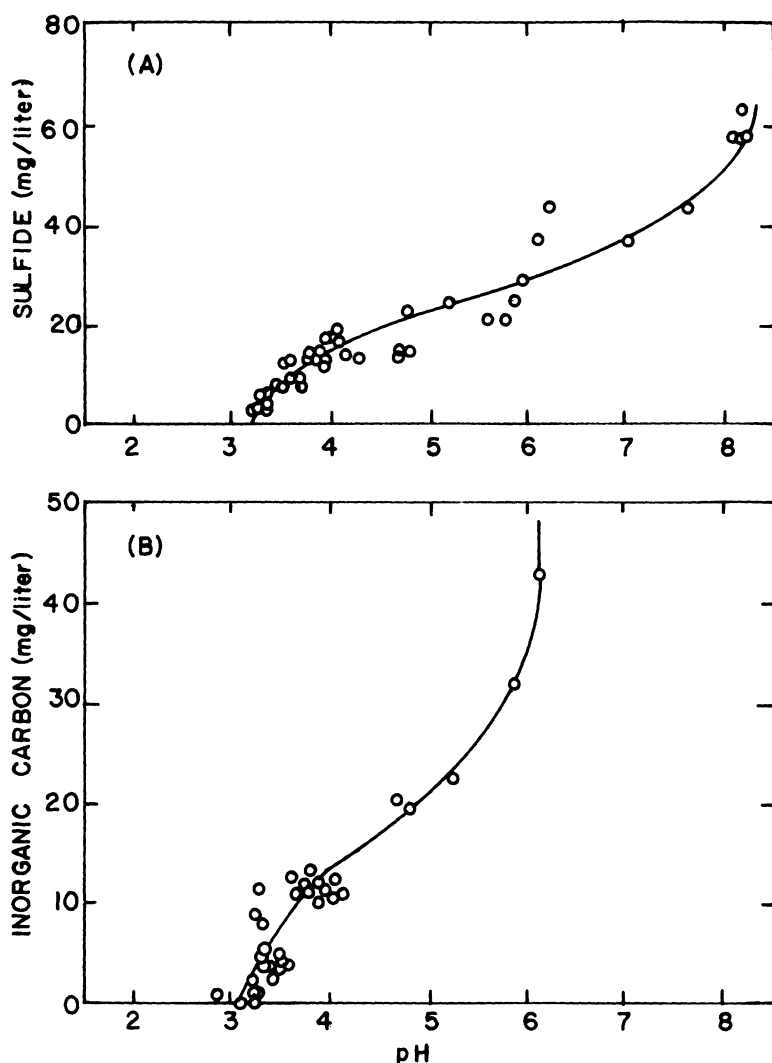
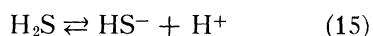


FIGURE 8.—Sulfide and inorganic carbon concentrations as functions of pH in a microcosm fed raw wastewater sludge.

be accompanied by bicarbonate formation from the carbon dioxide released by the bacteria as follows:

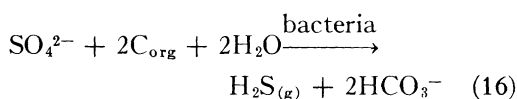


In addition to formation of a bicarbonate buffer, the buffering activity associated with the first dissociation of  $\text{H}_2\text{S}$  would begin to play the following role:



Because the  $\text{pK}_1$  for Reaction 14 is 6.4 and the  $\text{pK}_1$  for Reaction 15 is 7.0, these re-

actions favor continued formation and release of  $\text{H}_2\text{S}$  with concomitant bicarbonate increases. Each equivalent of alkalinity formed, however, would be accompanied by loss of an equivalent of acidity as  $\text{H}_2\text{S}$  and the reduction of an equivalent of sulfate, as follows:



The shape of the typical base titration curve of acid strip mine water in Figure

3 shows a good deal of similarity to the incremental pH change with time in the microcosms shown in Figures 5 and 7. This indicates that recovery of acid strip mine water is accomplished by a titration of the water caused by the bacterial sulfate reduction and the loss of  $\text{H}_2\text{S}$  to the air. Such similarity suggests that the point in the recovery sequence occupied by any existing strip mine lake could be determined from a single titration curve.

#### LAKE RECOVERY

While recovery to the alkaline state was very rapid in the laboratory microcosms, strip mine lakes are characterized by several factors that slow the rate of recovery in the field. Of these factors, the most important are related to the watershed that drains to the individual lake. The amount of acid spoils exposed determines the acidity of the lake, but significant changes in acid runoff may occur through interaction with the various minerals that compose the spoil. High rates of continued acid input obviously would slow the recovery of the lake.

The relative amount of vegetated land is of prime importance, because accumulation of organic material in amounts sufficient to allow bacterial generation of the reducing microenvironments necessary for sulfate reduction is the first step in the recovery sequence. Differences in the rate of accrual of terrestrial organics have a marked effect on the initiation and eventual rate of recovery of acid strip mine lakes; those acid lakes with a drainage devoid of vegetation show no recovery after periods of 30 yr or more.

Seasonal changes in temperature and wind-induced mixing of the water will tend to slow the recovery progression in the field, with the degree of retardation being related in part to morphology of the lake. Reoxidation of sulfide near the surface by atmospheric oxygen and the oxygen produced by algae, especially in the latter stages of recovery, also will slow the recovery rate.

Other than the time factor, the recovery

progression in acid strip mine lakes must occur in much the same complex manner as that in the microcosms and as that summarized in Figure 9. In both cases, the process is a bacterial mediated titration of acid buffers imposed by  $\text{HSO}_4^-$  and metal hydrolysis and the eventual formation of an alkaline buffer. The key to the process is the accrual of enough organic debris at the bottom of the lake to allow bacterial generation of suitably reduced conditions for sulfate-reducing bacteria. Export of hydrogen ions associated with loss of  $\text{H}_2\text{S}$  to the atmosphere represents acidity loss and allows pH increase. The rate of pH increase is a direct function of the metal content of the acid water, with aluminum playing a dominant role. But with the continued pH increase associated with continued  $\text{H}_2\text{S}$  loss, metals precipitate. Decreases in both cation and anion concentrations are reflected by decreased specific conductance of the water, as is shown in Figure 10, which is redrawn from field data presented by Campbell and Lind.<sup>1</sup>

While decreased cation concentration is associated with decreased metal solubility at increasing pH levels, decreased sulfate concentration represents the bulk of the anion decline. Once sulfate is produced at the pyrite crystal, there is little opportunity for sulfate loss to the exposed overburden soils. In fact, sulfate concentration may well be increased through interaction of acid water with the spoils if the spoils contain significant amounts of gypsum or another sulfate-rich mineral. Sulfate loss, and thus anion loss, occurs in lakes as  $\text{H}_2\text{S}$  is lost to the atmosphere, as metal sulfide precipitates to the lake bottom, and through conversion to elemental sulfur by chemical or biological means. In the latter stages of recovery, one of the microcosms developed a massive bloom of photosynthetic sulfur bacteria, which would represent biological conversion to elemental sulfur, while  $\text{H}_2\text{S}$  reduction of iron also would yield elemental sulfur.<sup>18</sup> But despite sulfide precipitates and formation of elemental sulfur, significant amounts of sulfate are lost to the atmosphere as  $\text{H}_2\text{S}$ .

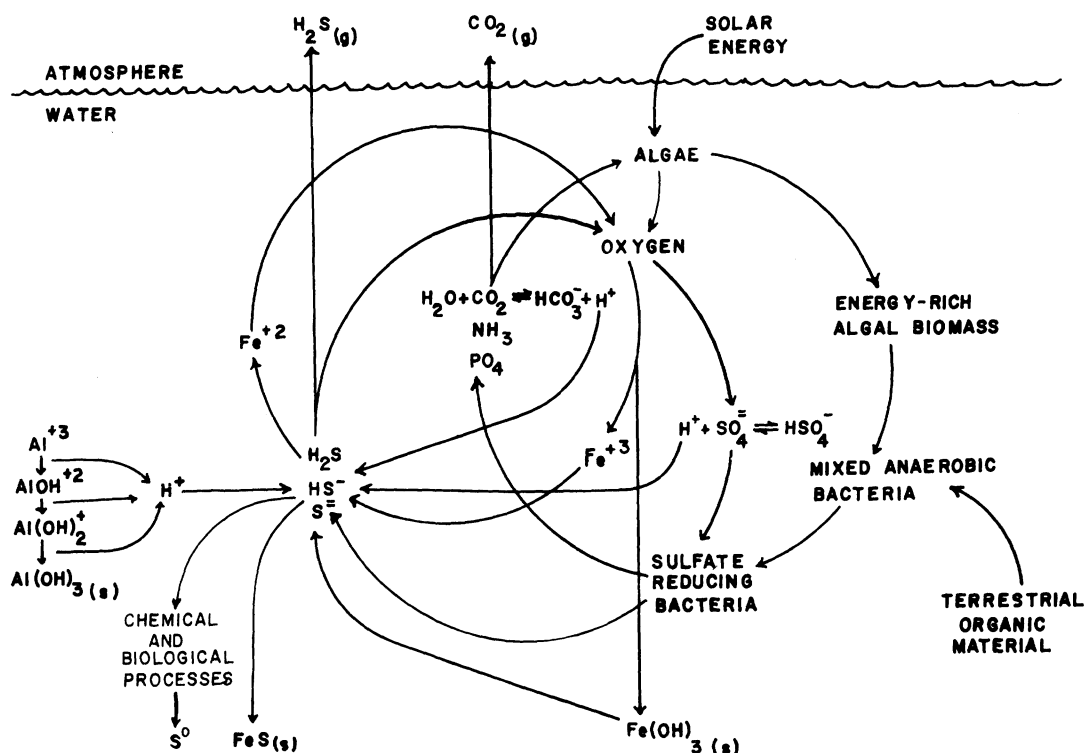


FIGURE 9.—Processes involved in acid strip mine lake recovery.

Bacterial use of organics at the lake bottom is accompanied by release of nitrogen, phosphorus, and other nutrients required for algal photosynthesis, but algal activity is limited by the availability of a photosynthetic carbon source under acid conditions.<sup>19</sup> Given the carbon dioxide, however, algae can develop to bloom proportions at pH levels as low as 3.5, as indicated by the microcosm data in Figure 5. Carbon dioxide concentration in this microcosm was elevated, because atmospheric exchange was somewhat limited and similar algal blooms would not be expected under field conditions at such low pH levels. Algal activity does increase, however, after recovery reaches the point where bicarbonate alkalinity is formed.

As shown in Figure 9, oxygen released during algal photosynthesis retards recovery through reoxidation of sulfide, but the resulting algal protoplasm serves as an additional organic source once the algae set-

tle to the lake bottom. This biological recycle of nutrients allows some continued supply of energy-rich algal biomass to the bacteria in those lakes receiving continued acid inflow. The large amount of organic material that must be mineralized to generate enough  $\text{H}_2\text{S}$  to allow recovery of an acid strip mine lake would seem to suggest that at recovery the lake would contain high levels of algal nutrients and would be highly eutrophic. Other factors associated, however, with the recovery process tend to minimize the degree of eutrophy.

Decline of total phosphorus concentration from 1.17 mg/l to an undetectable level in a microcosm (Figure 7) suggests significant phosphorus removal associated with metal precipitation. Continued bacterial use of the organics on the lake bottom after most of the metals precipitate, however, will continue to supply phosphorus and other nutrients. Thus the recovered strip mine lake would be expected

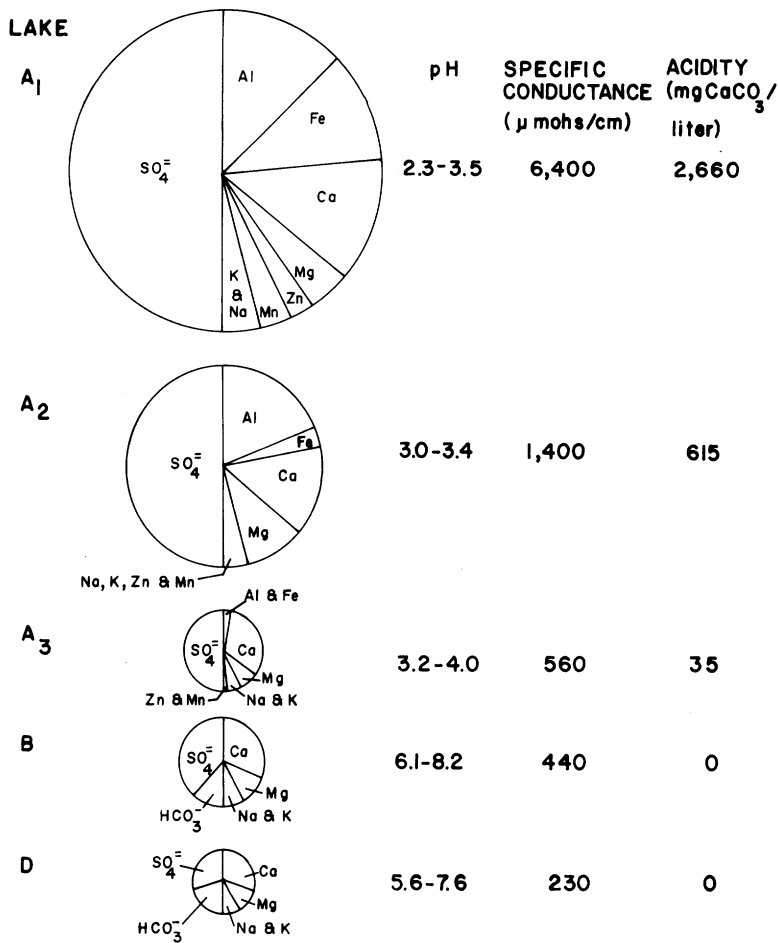


FIGURE 10.—Relative abundance by weight of major ions in strip mine lakes in various stages of recovery (redrawn from Campbell and Lind<sup>1</sup>).

to be in the state of early eutrophy noted by Campbell and Lind.<sup>1</sup>

Another factor that tends to limit algal production in the recovered strip mine lake is the availability of light. In the acid condition, strip mine lakes are extremely transparent, and clay turbidity entering from the denuded watershed is rapidly precipitated. Loss of metals and marked elevation of pH during the recovery process leave a water in which the clays are not rapidly removed. The high turbidity that is a characteristic of many recovered strip mine lakes must pose a severe light limit to algal photosynthesis.

The fate of a strip mine lake is determined by a complex interaction of many different physical, chemical, and biological parameters, each of which can alter the system. A sequential listing of the factors involved in formation and eventual recovery of a strip mine lake is given in Figure 11. Each strip mine lake will vary somewhat, depending on the type of soils exposed in the drainage, but the recovery from the acid condition is mediated by biological processes that respond to accumulation of terrestrial organics. Once this process is begun, the recovery includes reduction in acidity, increased pH, removal

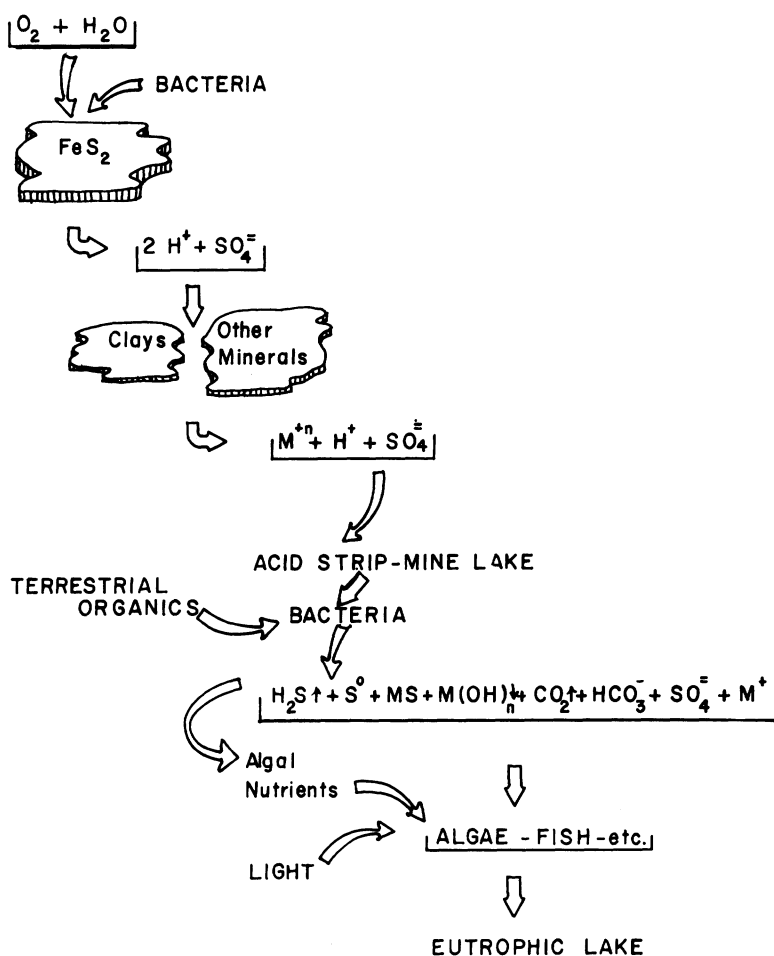


FIGURE 11.—Factors involved in formation and recovery of an acid strip mine lake.

of metals, and reduction in sulfate, leaving a water capable of supporting a complete aquatic community.

#### ACCELERATED RECOVERY

Because the precursor to recovery of acid strip mine lakes is the accumulation of organic material, it would seem that the recovery process could be accelerated by adding organic matter to such lakes. The bacteria do not require a specific type of organic, and any of a number of waste materials could be used. Sawdust, wheat straw, leaves, newspaper, cattle manure, and both raw and digested wastewater sludge all served as suitable substrate for recovery of acid strip mine water in mi-

crocosms.<sup>15</sup> When green leaves were used, the final state was a tea-colored water with many of the characteristics of bog lake water, including a pH of about 5 and a high organic acid content. The remainder of the organics used produced a clear alkaline water after the recovery process was completed.

Much of the future algal productivity of a strip mine lake is determined by the nutrient content of the original organic accumulation, and the carbon:nitrogen:phosphorus ratio is one consideration in the choice of the organic to be used to accelerate the process. Waste organics suitable for the bacteria vary markedly in nutrient content, as shown in Table I.

TABLE I.—Ratios by Weight of Carbon to Nitrogen to Phosphorus in Various Organic Materials

Substrate	Organic Carbon	Organic Nitrogen	Total Phosphorus
Raw wastewater sludge	26.2	2.85	1
Dried digested wastewater sludge	32.3	2.40	1
Pine sawdust	30,200	26.9	1
Newspaper	2,760	0.42	1
Wheat straw	915	5.97	1
Oak leaves	1,660	11.4	1
Sugar maple leaves	191	7.18	1
Cow manure	100	3.16	1

Where possible, it would be desirable to select an organic with a low nitrogen and phosphorus content. Some nitrogen and phosphorus are required, however, for successful bacterial utilization of the organic.

The major consideration in accelerating acid strip mine lake recovery is the rate of discharge of  $H_2S$  to the atmosphere. The corrosive and poisonous nature of  $H_2S$  would pose a potential hazard if the rate of discharge exceeded the rate of wind dissipation. The maximum rate of acceleration considered desirable would be dictated by the ability to evolve and dissipate  $H_2S$  in a problem-free manner. This would, in turn, be determined by several parameters, including local climatic factors and the use of the surrounding land.

The absolute amount of sulfur that could be discharged to the atmosphere during the recovery process would be determined by the acidity and sulfate concentration of a particular lake. For example, a strip mine lake 10 ft (0.3 m) deep with a sulfate concentration of 1,000 mg/l would contain 4.5 tons of sulfur/surface acre (10.1 metric tons/ha). Because recovered strip mine lakes are characterized by a high sulfate concentration,<sup>1</sup> the entire initial sulfur content would not be removed during the recovery process. Moreover, only a portion of the sulfate reduced would be evolved as  $H_2S$ , with the remainder remaining in the lake as precipitated metal sulfides and elemental sulfur.

A crude estimate of the amount of  $H_2S$  evolved during the recovery process may be obtained by considering only the acidity loss and the alkalinity formation. If the initial acidity of the lake were 500-mg acid as  $CaCO_3$ /l (10-meq acid/l) and the final alkalinity were 50-mg  $CaCO_3$ /l (1-meq/l), about 2.5 tons of sulfur, in the form of  $H_2S$ , would be lost to the atmosphere from each surface acre (5.6 metric tons/ha) of the 10-ft (0.3-m) deep lake during the recovery process. Bacterial activity would vary seasonally with temperature, and loss of this amount of  $H_2S$  to the atmosphere would take place over a period of years. In comparison, a coal-fired power plant burning 1,000 tons (907 metric tons) of 2 percent sulfur coal/month would have the potential of releasing 240 tons (218 metric tons) of sulfur/year.

Patty<sup>20</sup> lists 30 mg  $H_2S$ /cu m of air as the maximum average atmospheric concentration to which workers may be exposed, without injury, during an 8-hr working day. If a maximum  $H_2S$  concentration of 30 mg/cu m of air is assumed, one complete air exchange each day in a 10-m column of air, located just above the water surface, would allow dissipation of the 2.5 tons of sulfur/surface acre (5.6 metric tons/ha) in about 1,400 days. Greater wind velocity and more frequent air exchange would reduce this time period markedly, but such potential acceleration of the recovery process would be offset by slow sulfate reduction during the winter months.

Because the exact rate of  $H_2S$  formation during the warm summer months is unknown and a reducing microenvironment is required, the organic material added to acid strip mine lakes should be placed in piles rather than be spread evenly over the lake bottom. This would hasten development of the required reducing microenvironment and would allow a means of decelerating the process if evolution of  $H_2S$  exceeded the desired rate. Aeration and stirring of the organic piles would increase no and metal content in the microenvironments, and the resulting increase in Eh should slow the rate of sulfate reduction. If the rate of  $H_2S$  formation were too



slow, additional piles of waste organics could be placed in the lake.

The advantages of accelerating this natural process to recover acid strip mine lakes are that, in addition to the elevation of pH and loss of acidity and metals, which can be accomplished by adding lime, the process yields significant sulfate loss without creating a chemical sludge disposal problem. Another significant advantage is that organic wastes serve as the raw material for the process. The major disadvantage is the evolution of  $H_2S$  to the atmosphere, but this may be limited to reasonable levels by controlling the amount of organic wastes added to the lake. In addition to improving the quality of strip mine lake waters, this process also may be of value in treating sulfate-rich nonferrous mine and smelter wastewaters.

While it appears that this process will allow accelerated quality improvement of acid strip mine lakes, the entire complex biological, chemical, and physical interaction from acid formation to the recovered lake could be avoided by covering acid-producing materials with nonacid soil when coal is strip mined.

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#### REFERENCES

1. Campbell, R. S., and Lind, O. T., "Water Quality and Aging of Strip-Mine Lakes." *Jour. Water Poll. Control Fed.*, **41**, 11 (1969).
2. Tuttle, J. H., *et al.*, "Microbial Dissimilatory Sulfur Cycle in Acid Mine Water." *Jour. Bacteriol.*, **97**, 2, 594 (1969).
3. Tuttle, J. H., *et al.*, "Microbial Sulfate Reduction and Its Potential Utility as an Acid Mine Water Pollution Abatement Procedure." *Appl. Microbiol.*, **17**, 2, 297 (1969).
4. Stumm, W., and Morgan, J. J., "Aquatic Chemistry, an Introduction Emphasizing Chemical Equilibria in Natural Waters." Wiley-Interscience, New York, N. Y. (1970).
5. Singer, P. C., "Oxygenation of Ferrous Iron." FWQA Rept. No. 14010-06/69 (1970).
6. Temple, K. L., and Delcamp, E. W., "Autotrophic Bacteria and the Formation of Acid in Bituminous Coal Mines." *Appl. Microbiol.*, **1**, 5, 255 (1952).
7. Colmer, A. R., and Hinkle, M. E., "The Role of Microorganisms in Acid Mine Drainage: Preliminary Report." *Science*, **106**, 253 (1947).
8. Kuznetsor, S., *et al.*, "Introduction to Geological Microbiology." P. T. Brayner [Translator], McGraw-Hill, New York, N. Y. (1963).
9. Simmler, J. J., "The Chemistry of Acid Strip-Mine Lake Recovery." M.S. thesis, Univ. of Missouri, Columbia (1973).
10. Nalezny, C. L., and Li, M. C., "Effect of Soil Structure and Thriotropic Hardening on the Swelling Behavior of Compacted Clay." Highway Research Record No. 209, Publ. No. 1552 (1967).
11. Grim, R. E., "Clay Mineralogy." McGraw-Hill, New York, N. Y. (1953).
12. Hem, J. D., and Roberson, C. E., "Form and Stability of Aluminum Hydroxide Complexes in Dilute Solution." Geol. Surv. Water Supply Paper 1827-A, U. S. Govt. Printing Office, Washington, D. C. (1967).
13. Hillel, D., "Soil and Water, Physical Principles and Processes." Academic Press, New York, N. Y. (1971).
14. Decker, C. S., "Accelerated Recovery of Acid Strip-Mine Lakes." M.S. thesis, Univ. of Missouri, Columbia (1971).
15. Ogg, C. W., "Organic Wastes for Acid Strip-Mine Lake Recovery." M.S. thesis, Univ. of Missouri, Columbia (1972).
16. Postgate, J. R., "Recent Advances in the Study of Sulfate-Reducing Bacteria." *Bacteriol. Rev.*, **29**, 425 (1965).
17. Harp, G. L., and Campbell, R. S., "The Distribution of *Tendipes plumosus* (Linné) in Mineral Acid Water." *Limnol. & Oceanog.*, **12**, 2, 260 (1967).
18. Moody, B. J., "Comparative Inorganic Chemistry." American Elsevier, New York, N. Y. (1965).
19. King, D. L., "The Role of Carbon in Eutrophication." *Jour. Water Poll. Control Fed.*, **42**, 12, 2035 (1970).
20. Patty, F. A., "Industrial Hygiene and Toxicology." 2nd Ed., Interscience, New York, N. Y. (1958).