CHEMICAL ASPECTS OF ACID MINE DRAINAGE

H. L. Barnes and S. B. Romberger

Water pollution by acid mine drainage has ruinous effects which have limited severely or destroyed the productivity of large parts of Appalachia and other areas. Lovell (1) has estimated that such drainage pollutes 5,000 miles (8,000 km) of streams in 10 states; Pennsylvania has 2,500 miles (4,000 km) of streams polluted by a daily influx of 1 bil gal (3.8 bil l) of mine drainage. The resulting losses are significant. Nevertheless, many pertinent chemical aspects of this serious economic and aesthetic problem have not been explored thoroughly. In this paper, a geochemical approach will be used to describe the generation of acid waters, prevention of acid formation, and treatment of acid waters.

Biesecker and George (2) have observed that the severity of the effects of acid formation in Appalachia depends primarily on two factors: damage increases with coal production and with lower concentrations of bicarbonate in diluting stream waters. Neither of these factors points to an answer to acid drainage. Decreasing production is obviously not in the best interests of the mining industry although it would lead eventually to a cure. High bicarbonate concentrations in local streams often are unattainable because such concentrations depend on the occurrence of quantities of carbonate-rich rocks at the earth's surface.

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Such rocks are not exposed where the problem is severe, as in many areas of Pennsylvania. Other more practical and economical answers to acid pollution are needed to preserve the future of the coal industry, segments of which are increasingly threatened by punitive legislation arising from this problem.

The chemical environment and causes of acid formation will be discussed first to establish a basis for considering techniques for either preventing the generation of acid or treating it once it has been formed.

Chemical Environment

The chemical environment under which acid waters are formed is best described by the two parameters oxidation potential, Eh, and acidity, pH. Figure 1 is an Eh-pH diagram showing the distribution of the predominant, stable aqueous species and solid phases of iron, carbon, and sulfur, for these are the most important in reactions involving the generation and neutralization of acid waters. A detailed discussion of the calculation of Eh-pH diagrams is given elsewhere (3). Figure 1 is calculated by assuming a total iron concentration in solution, ΣFe^*, of 1,000 mg/l and a ΣC of 1 mg/l in solution with contours representing 2 concentrations of ΣS, 10 and 1,000 mg/l (see Table I). Normal surface conditions (where mining and other

* ΣFe represents the sum of the thermodynamic activities of all iron-containing species in solution; ΣC and ΣS represent similar totals for carbon- and sulfur-containing species.

FIGURE 1.—Stabilities of minerals and aqueous species in solutions having maximum concentrations of 1,000 mg/l Fe, 1 mg/l C, and 10 or 1,000 mg/l S near 25°C. ——— = boundaries for water (fugacities of O_2 or $H_2 = 1$ atm) and for iron-containing species ($\Sigma S = 1,000$ mg/l); --- = boundaries for water in equilibrium with air (O_2 fugacity = 0.21 atm), for pyrite ($\Sigma S = 10$ mg/l) and for Eh-pH conditions when ΣS is 10 or 1,000 mg/l, respectively. Fields of sulfur species are limited by light solid lines except field of native sulfur where the boundary, at $\Sigma S = 1,000$ mg/l, is light solid line and, at $\Sigma S = 10$ mg/l, is light dashed line. Light dashed lines also represent the boundaries for carbon-containing species.

industries have little effect) lie approximately between pH's of 6 to 8 along the curve labeled f_{O_2} (oxygen fugacity, or, approximately, pressure) = 0.21 atm, or Eh's between +0.75 and +0.85 v. Pyrite and marcasite, both near FeS_2 in composition, are far out of equilibrium under these conditions, the stable iron species being the

oxidized ferric hydroxide.† However, in mine areas where acid is being generated, pyrite seldom is observed directly forming ferric hydroxide; this suggests that the conditions for acid

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† "Ferric hydroxide" represents the family of ferric oxy-hydroxide hydrates which form metastably within essentially the same Eh-pH region as $Fe(OH)_3$.

TABLE I.—Composition of Mine Waters before Dilution by Streams

Item	Common Range	Typical Value
pH	2.4–8.2	2.8
Fe^{2+} (mg/l)	10–2,000	100 ($10^{-2.75}$ molal)
Fe^{3+} (mg/l)	0–100	0
SO_4^{2-} (mg/l)	100–2,000	1,000 ($10^{-2.00}$ molal)
HCO_3^- (mg/l)	0–200	0
Ca^{2+}	10–1,000	200 ($10^{-2.31}$ molal)
Al^{3+}	0–150	50 ($10^{-2.73}$ molal)
Ionic strength	—	0.3

generation involve lower Eh and pH conditions. Barnes *et al.* (4) have measured both Eh and pH in 2 deep mines in the anthracite regions of Pennsylvania and found Eh's ranging from +0.08 v to as low as −0.04 v while the corresponding pH's ranged from 3.95 to 5.41. These conditions lie in the stability field of pyrite. In a third deep mine, waters with pH's of about 3.5 had Eh's of about +0.55. These conditions lie in the stability field of Fe^{2+}.

Figure 2 is an Eh-pH diagram calculated for assumed $\Sigma Fe = 1$ mg/l, $\Sigma C = 100$ mg/l, and $\Sigma S = 100$ mg/l. Under surface conditions, again at the top of the diagram, the stable carbon species are various forms of carbonate, depending on the pH. When present HCO_3^- buffers the waters near neutral pH's and the observed iron-containing species in the presence of such a solution will be, again, $Fe(OH)_3$.‡ Extensive deposits of ferric hydroxide are found in surface streams where neutralization and oxidation of acid waters have occurred. After such reactions, streams characteristically contain little dissolved iron. The mobility of iron depends on the distance between the point in a mine where the acid is generated and the point, usually along a stream, where oxidation and neutralization cause the solution to enter the ferric hydroxide stability field. Acid waters are apparently found with widely varying Eh values. The deep anthracite mines tested by Barnes *et al.* (4) have low values while

‡ After several thousand years, the mineral *goethite* may prove to be more stable but this is of no consequence here.

strip mines, in general, have high Eh values. Iron mobility apparently is generally much greater in the deeper mines.

Because the oxygen fugacity, f_{O_2}, (∼ pressure) varies over a range of about $1–10^{-83}$ atm where acid waters are found, either the generation of acidity is not simply oxygen-dependent or there is sufficient fluid circulation to carry to low Eh conditions the acid generated at higher f_{O_2} conditions. The following section will concern potential acid-generating mechanisms as a means of evaluating the two alternatives.

Acid-Forming Reactions

Organic Sources

Because the acid formed is predominantly sulfuric, it is commonly, but incorrectly, assumed that acid must be formed by the oxidation in water of any sulfide from either a mineral or organic source. The organic form may lead simply to the formation of sulfate ion with no effect on acidity.

$$S^{2-} \text{ (in organic solid)} + 2O_2(g) \rightarrow SO_4^{2-} \dots 1$$
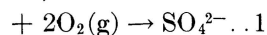
without freeing hydrogen ions. Oxidation of organic matter also is of little consequence in generating pH's below 3.5 because carbonic acid is predominantly un-ionized below a pH of about 6.4. For example, methane, on oxidation, frees no hydrogen ions to generate low pH's:

$$CH_4(g) + 2O_2(g) \rightarrow H_2O + H_2CO_3 \dots 2$$
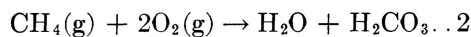
where

$$K \approx \frac{H_2CO_3}{(P_{CH_4})(P_{O_2})^2}$$

and concentrations are in molality (moles per kilogram of water) and pressures are in atmospheres, and

$$\log (K_{25°}) = +141.9$$

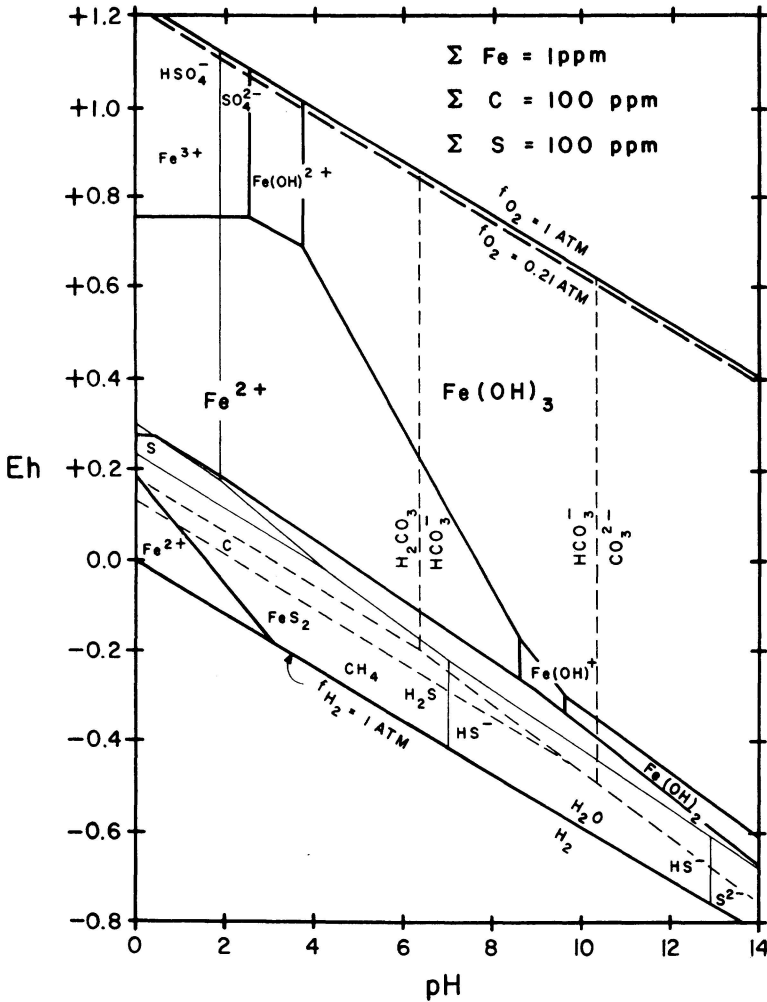In addition, this reaction takes place at insignificant rates at ambient tem-

FIGURE 2.—Stabilities of minerals and aqueous species in solutions having maximum concentrations of 1 mg/l Fe, 100 mg/l C, and 100 mg/l S near 25°C. ——— = boundaries for water (at 1 atm H_2 or O_2) and for iron species; - - - = boundary for water in equilibrium with air. Light solid lines limit fields of sulfur-containing species; and light dashed lines limit fields of carbon-containing species.

peratures, although the equilibrium constant indicates that complete reaction should take place even under slightly oxidizing conditions if sufficient oxygen is available.

Inorganic Sources

The principal source of acid in mine drainage is unquestionably the dissolving of the products of oxidation of the iron sulfides pyrite and marcasite. The total oxidation of these minerals in the presence of water can be represented by the reaction (K given for pyrite),
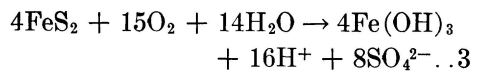
$$4FeS_2 + 15O_2 + 14H_2O \rightarrow 4Fe(OH)_3$$
$$+ 16H^+ + 8SO_4^{2-} \ldots 3$$
$$\log (K_{25°}) = + 829.4$$

in which the potency of pyrite or marcasite oxidation, as an acid-generating reaction, is emphasized by the fact that four moles of H^+ are released per mole of oxidized mineral. However, as already noted, the iron of pyrite or

marcasite generally forms Fe^{2+} but is not usually oxidized to the extent of forming $Fe(OH)_3$ at the same location where the sulfide is oxidized to form acid. The total reaction normally proceeds by at least two steps, with sulfur oxidizing by the first reaction,

$$2\,FeS_2 + 2H_2O + 7O_2(g) \rightarrow 2Fe^{2+}$$
$$+ 4H^+ + 4SO_4^{2-}\ldots 4$$
$$\log\,(K_{25°}) = +\,408.9$$
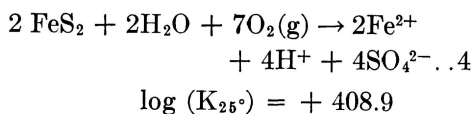
Formation of minor concentrations of metastable thiosulfate and polysulfide species, but not $S_2(g)$ as suggested by Clark (5), also is expected but is of little consequence here. Ferrous ion oxidation produces another increment of acid by the second reaction,

$$4Fe^{2+} + 10H_2O + O_2(g) \rightarrow$$
$$4Fe(OH)_3 + 8H^+\ldots 5$$
$$\log\,(K_{25°}) = +\,11.7$$
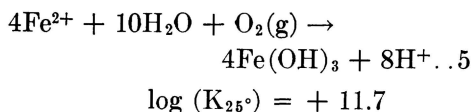
where the constants for reactions 4 and 5 are effectively the same for pyrite and marcasite. In Figure 1, the conditions where pyrite oxidizes to Fe^{2+} and SO_4^{2-}, as shown by reaction 4, are found at much lower Eh (and oxygen fugacity) than the oxidation to $Fe(OH)_3$ and SO_4^{2-}, the products of reaction 5. Both equilibrium constants are very large and given time, the reactions proceed to exhaust the reactants.

Kinetic Factors

Although these fundamental reactions for the oxidation of the iron sulfides are well known, problems arise in understanding both the sources of oxygen or other oxidizing agents for the reactions and the exact kinetic paths by which the reactions take place. Field observations have shown that, as expected, the rate of generation of acid increases where marcasite, the more reactive polymorph, is present instead of pyrite. The larger surface area provided by smaller grain size or high porosity of the sulfides also enhances the rate, as does also a higher

oxygen content (Eh) of the environment (5). This oxygen may be supplied by an air flow but is more effective if provided by an air-saturated solution because of the catalytic action of acid aqueous solutions. Bacterial action greatly increases the rate of oxidation both of the sulfur of pyrite in the initial reaction (Equation 4) and of ferrous ion in the secondary reaction (Equation 5). For example, in an antiseptic system at a pH below 5, the rate of oxidation of ferrous ions by dissolved oxygen is negligibly slow (6). Only in the presence of bacteria is this rate fast enough to generate important amounts of acid. Three species, *Thiobacillus thio-oxidans*, *Thiobacillus ferro-oxidans*, and *Ferrobacillus ferro-oxidans* have been described by Oborn and Hem (7) and by Hanna *et al.* (8) as these important biological catalysts for oxidation. The lower limit of common pH's in acid drainage, near 2.5, also may be fixed by the limit of endurance of these bacteria (8).

Substantial evidence compiled by Clark (5) suggests that ferric ion, whether produced biologically or inorganically, may react directly with pyrite by the reaction.

$$14Fe^{3+} + FeS_2 + 8H_2O \rightarrow 15Fe^{2+}$$
$$+ 2SO_4^{2-} + 16H^+\ldots 6$$
$$\log\,(K_{25°}) = +\,95.9$$
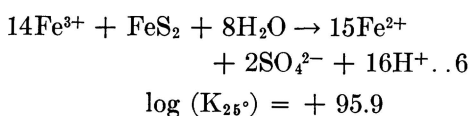
When the range of pH's and ferrous and sulfate ion concentrations of Table I are substituted into this equilibrium relation, the equilibrium constant is so large that the reaction goes effectively to completion and exhausts either the Fe^{3+} or FeS_2 supply. However, the stoichiometric relations also show that very large quantities of Fe^{3+} would be required to oxidize significant quantities of FeS_2. The concentration of ferric ion in acid drainage is typically well below 100 mg/l but such a solution, on complete reaction with pyrite, can lower the pH to only about 2.7. For this reason without an improbably

concentrated supply of Fe^{3+}, this mechanism is not likely to be a major contributor to acid formation.

In summary, optimum conditions for the generation of acid include circulation of well-aerated, bacteria-rich water over abundant fine-grained marcasite either in the coal or adjacent strata.

Sources of Oxygen

Kinetic studies of the variation in the rate of acid formation as a function of oxygen pressure, for example that made by Clark (5), have shown a direct dependence, proving that oxidation may take place through simple reaction with the oxygen of aerated solutions. However, Barnes and Clarke (9) have shown that air-saturated water, once isolated from the atmosphere, contains only enough oxygen to form, after complete reaction, somewhat less than 10 mg/l Fe^{2+} and a pH no lower than 3.5, in contrast to observed concentrations above 1,000 mg/l and pH's of 2.5. Therefore, dissolved oxygen alone cannot account for the generation of acid waters. Confirming evidence is found in measurements by Barnes et al. (4) of Eh, pH, and composition of waters in the shafts of anthracite mines. In the Storrs No. 1 Shaft, acidity increased from pH 5.41 at a depth of 300 ft (91.5 m) to 3.95 at 550 ft (168 m), although the oxygen pressure remained nearly constant at about 10^{-62} atm. If peculiar circulation and buffering of these waters are absent, oxidation and acid formation appear to be taking place although virtually no dissolved oxygen is present. Evidently, where available, dissolved oxygen accelerates both oxidation of pyrite and the formation of acid but its absence may not necessarily prevent these reactions from taking place.

Water has been suggested by Barnes and Clarke (9) as an alternative source of oxygen in acid-forming reactions; this possibility also can be tested thermodynamically. Products of such a reaction, besides Fe^{2+}, SO_4^{2-}, and H^+, may be either H_2 or an organic product formed by reaction of coal with H_2. Free hydrogen might be generated by the reaction suggested by Barnes and Clarke (9),

$$FeS_2 + 8H_2O \rightarrow Fe^{2+} + 2SO_4^{2-}$$
$$+ 2H^+ + 7H_2(g)..7$$
$$\log (K_{25°}) = -86.6$$
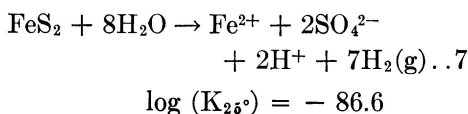
Although the magnitude of the constant appears reasonable for acid formation under the conditions of Table I, there is no evidence, such as escape of large volumes of gas from coal mines, that 3.5 moles of hydrogen are released for every mole of acid generated. At pH 2.5, this would amount to about 70 cu cm of hydrogen for each liter of acid water.

Reactions of pyrite, water, and coal could yield many possible organic products but the carbon in these products must be in a negative valence state if such reactions generate acid. For example, methane might be formed by

$$2FeS_2 + 7C + 16H_2O \rightarrow 7CH_4(g)$$
$$+ 2Fe^{2+} + 4H^+ + 4SO_4^{2-}..8$$
$$\log (K_{25°}) = -108.7$$
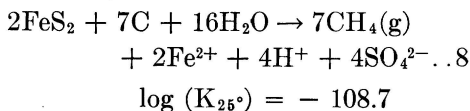
However, this constant, together with the observed concentrations of Table I, leads to the conclusion that pressures of methane approaching an upper limit as low as 10^{-10} atm would halt this reaction; therefore, it cannot contribute important quantities of acid. More acid might be formed by such reactions if (a) an organic compound exists which is more stable than methane under these conditions but which consists mostly of reduced carbon and has a ratio of more than 2:1 of H:O, (b) a highly soluble hydrocarbon were produced, or (c) the activity of Fe^{2+} (or SO_4^{2-}) were decreased significantly by complexing. No compounds have been found with the proper compositional characteristics that are more

stable than methane; this eliminates the first possibility.

If propane, a soluble gas, were formed by

$$8FeS_2 + 45C + 64H_2O \rightarrow 8Fe^{3+}$$
$$+ 15C_3H_8(g) + 16SO_4^{2-} + 8H^+ ..9$$
$$\log (K_{25°}) = -727.0$$
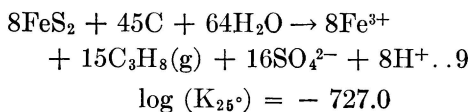
a pressure in excess of 10^{-40} atm of propane would be sufficient to stop the reaction; again, this is an unsatisfactory mechanism. Another possibility for organic reactions lies in complexing of Fe^{2+} by a stable organic ligand, such as oxalate,

$$2FeS_2 + 6H_2O + 13O_2 + 8C \rightarrow$$
$$2Fe(C_2O_4)_2^{2-} + 4SO_4^{2-} + 12H^+ ..10$$
$$\log (K_{25°}) = +724.6$$
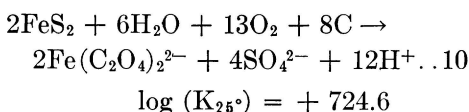
Here again, large quantities of oxygen are needed and the constant indicates that this complex is not stable enough to have a significant effect on acid formation. Examination of other humic acid complexes of iron, such as with tartaric $(C_4H_6O_6)$ or tannic $(C_{76}H_{52}O_{46})$ acids, leads to the same conclusion.

Although humic acid complexes are not stable enough to promote the oxidation of pyrite, they are likely to form by combining with either ferrous or ferric ions once these are released by oxidation. Because such complexes oxidize slowly (7) (10), they may be partially responsible for the slow rates of oxidation of Fe^{2+} and of deposition of $Fe(OH)_3$ in acid drainage, for example, where effluent may flow for tens of yards or meters in a shallow, turbulent stream before iron precipitates.

In summary, the mechanism of acid generation in the presence of oxidizing agents such as air is no longer in question although kinetic rate constants have yet to be measured for all important aspects of the reactions. For acid generation in the absence of dissolved oxygen (Eh's below about 0.3 v), no reaction product of coal with pyrite and water has been found suffi-

ciently stable to free oxygen from water to form sulfuric acid-rich waters whether the organic product is a gas, a soluble aqueous species, or a complexing agent. In fact, no thermodynamically reasonable mechanism has been found by which acid could be formed in the absence of dissolved oxygen or oxidizing agents. The evidence from the mines studied by Barnes et al. (4) may be misleading in its implication that acid waters can be formed at very low Eh's. However, the fact that Fe^{2+} is usually the first product of pyrite oxidation supports the contention that oxidation can take place in the absence of dissolved oxygen. This problem merits further study; particular attention should be given to the chemical conditions in flooded coal mines to extend observations to very low oxygen pressures.

Prevention of Acid Formation

Several techniques for discouraging the generation of acid in mines have been proposed and some of them have been tried experimentally. A summary of these, and their chemical limitations, follows.

Bactericides

The catalytic action of bacteria has been mentioned as being particularly important to the rates of oxidation of both the sulfur and iron of the iron sulfides. The rate of acid generation could be reduced significantly if active bacteria in the environment could be destroyed by chemical treatment of mine inflow. Attempts to use this technique have been unsuccessful (9) because local hydrology is usually too complicated to allow the treatment of the entire inflow system and also because these bacteria are self-inoculating in mines and recover rapidly from attempts at poisoning.

Mine Sealing

Excluding air from coal mines has become a popular engineering approach

to the control of acid formation. Because the rate of oxidation of pyrite is a function of oxygen pressure, if air can be excluded successfully the rate of acid formation should decrease. Results of mine-sealing experiments are largely negative, however. Braley reports little success in air-sealing of mines located above the drainage table (11); mines below the water table are already largely isolated hydrologically and thus sealing is of no practical value (12). The oxidation of pyrite may take place if the pressure of oxygen is about 10^{-60} atm or more, and evidence indicates that the rates of oxidation are adequate to reach pH's of 3 or less even at this very low oxygen pressure. Furthermore, the engineering problems become severe, with only expensive solutions, when air-sealing must reduce oxygen pressure to below 10^{-60} atm, while sealing has not been effective even in suffocating mine fires (11). Both theory and practice demonstrate that this method is not effective.

Passivation

Passivation, to prevent oxidation of exposed surfaces, by compounds particularly reactive with pyrite or marcasite, although not thoroughly explored as yet, is probably impractical. Neither pyrite nor marcasite is known to form with inorganic constituents solid solutions of as much as an atomic percent at ambient temperatures and the natural minerals are exceptionally pure, indicating inert surfaces; for these reasons high reagent concentrations would be expected if any surfactant were to be effective in treating even exposed mineral grains. Exposure of rock surfaces to passivating solutions would be needed over a considerable length of time in order to diffuse the reagent into near-surface grains. Nevertheless, caving and slumping would continually expose new, untreated sulfides, thereby negating the benefits of passivation. An additional problem is the method of application of any surfactant, particularly in mines above the water table.

Sulfate Reduction

The culture of sulfate-reducing bacteria has been discussed as a promising technique. Feeding of an organic nutrient might be required (8), but this could introduce another type of pollution from acid-pickled wastewater. There is the additional possibility that the bacteria might have a limited viability because of exhaustion of the sulfate. However, if the culture were found to be stable, this technique still would be only a partial cure in that the rate of subaqueous oxidation would be reduced greatly but the sulfide content of the effluent produced by the bacteria would release acid on exposure to oxidizing conditions in a stream. Again, this method of prevention is applicable only to flooded mines where other techniques also are feasible. In open mines, the bacteria have little chance to affect the moist but not inundated environment immediately around the sulfides where the initial oxidation takes place.

Carbonate Treatment

Where the hydrologic pattern is simple, the inflow to a mine may be treated with limestone or the less desirable Mg-containing dolomite to establish a buffering capacity against acid production and to reduce the rate of acid formation, because catalyzing bacteria are not as active metabolically at near-neutral pH's as under acid conditions (5). The pH of limestone or dolomite-saturated water is slightly above 8, (depending on grain size, carbon dioxide pressure, and water composition) and the bicarbonate content may approach a maximum of about 500 mg/l (13). Such water is capable of neutralizing the acid formed by complete reaction (3) when about 120 mg/l of iron is precipitated from so-

lution. Except under extremely un-favorable conditions, where the higher iron concentrations are found (Table I), this buffering capacity is adequate.

Hydrologic Control

Pollution by acid mine waters can be prevented absolutely only by hydro-logic isolation of a mine, a method unlikely to be practical in most open subsurface mines where the sources of mine water are many, entering through diverse channels and varying as min-ing progresses. Careful backfilling and compaction, to minimize the effects of pyrite oxidation on water composition by detouring surface drainage around stripping areas, is an obvious practi-cal application of this principle to surface mining, but detailed methods involve complex hydrologic problems (14). Beside reducing the water flow through a mine, rapid removal of mine waters by pumping or unimpeded drainage is also helpful because it reduces the time available for reaction with oxidizing sulfides (12). Aban-doned, flooded mines are apparently both self-beneficiating and nearly hydrologically isolated and present few problems (11) (12).

Summary

No method of general utility is pres-ently known for preventing the forma-tion of acid; under the hydrologic conditions where they can be used, isolation is effective or, as a second choice, mine inflow may be treated with carbonate rocks. For flooded mines, culturing of sulfate-reducing bacteria deserves testing to hasten beneficiation; the sealing of mines to forestall oxidation by excluding air is unlikely to produce results justifying the costs involved. At present, in typical circumstances, the liberation of acid and the drainage of mines cannot be prevented and the less desirable alternative of treating the acid water as industrial waste must be considered.
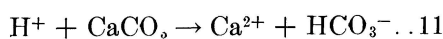
Treatment of Acid Waters
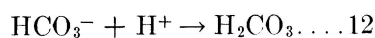
Neutralization with Carbonate Rocks

The most suitable material to use for the neutralization of acid waters is one which is available readily in large quantities, is inexpensive, and does not add harmful constituents to the water. The strong bases, such as sodium hydroxide or carbonate, are too expensive. However, calcium and magnesium carbonates occur as a ma-jor constituent in limestones and dolo-mites, and in minor amounts in cal-careous shales, sandstones, and some coals in many coal-producing regions. In addition, carbonate-rich rocks re-quire no preparation other than sizing, and therefore are inexpensive to pro-duce. The principal disadvantage, of course, is that the water is neutralized at the expense of added hardness.

Limestone is preferable to the less concentrated calcareous shales and sandstones because the necessary quantity of these is inversely propor-tional to the carbonate content. The use of dolomite as a source of carbon-ate produces undesirable quantities of magnesium salts, specifically $MgSO_4$ or epsom salts, dissolved in the water, with strong cathartic effects; in addi-tion, the magnesium is more difficult than calcium to remove from water if hardness must be treated for specific uses (13).
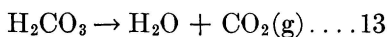
Limestone can be transported to the source of the acid drainage and added to the mine effluent in a crushed form for neutralization, or the acid water can be drained or pumped into wells in any nearby carbonate rocks. The lat-ter method will be discussed later. The three important reactions in the neutralization process are:

$$H^+ + CaCO_3 \rightarrow Ca^{2+} + HCO_3^- \ldots 11$$

$$\log (K_{25°}) = +2.0$$

$$HCO_3^- + H^+ \rightarrow H_2CO_3 \ldots 12$$

$$\log (K_{25°}) = +6.4$$

$$H_2CO_3 \rightarrow H_2O + CO_2(g) \ldots 13$$

$$\log (K_{25^\circ}) = + 1.5$$

The secondary reactions given in Equations 12 and 13 take place only below a pH of about 6.4, but reaction 11 can proceed at all pH's up to the point, slightly above pH 8, where solid $CaCO_3$ is stable with the solution in equilibrium with the normal atmosphere (pressure of CO_2 about $10^{-3.5}$ atm).

Figure 3 gives the minimum weight of $CaCO_3$ necessary to raise the pH from some given value to neutrality. This curve assumes complete reaction between the $CaCO_3$ and acid water. In practice, where the material being added is an impure limestone, the weight of $CaCO_3$ required according to Figure 3 must be divided by the fraction of $CaCO_3$ in the limestone to obtain the required weight of rock. Depending on the rate of flow of the water being treated, there may be incomplete reaction between acid and solid, and the coarseness and amount of $CaCO_3$ present for complete neutralization must be adjusted for these
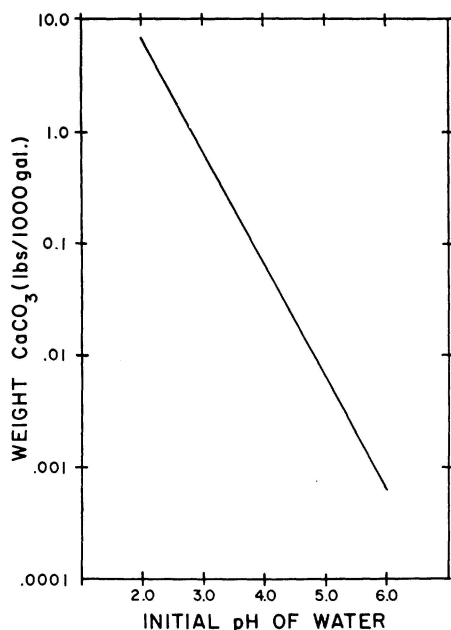

FIGURE 3.—Minimum weight of $CaCO_3$ necessary to raise the pH of mine waters from a given initial value to 7.0.

kinetic factors which can be evaluated only by empirical observations.

A difficulty in using carbonate rocks for neutralization of iron-rich waters is the precipitation of insoluble ferric hydroxide on reacting surfaces. This armoring effect prevents further reaction of the calcium carbonate with the acid, and the neutralization reaction stops after a short time. The reason for this precipitation can be seen by inspection of the Eh-pH relations in Figure 1 discussed earlier; in equilibrium with the atmosphere, the iron-rich phase deposited above pH 4 is the amorphous solid $Fe(OH)_3$. The problem of armoring can be minimized by the expensive expedient of fine grinding of the carbonate rocks and stirring during reaction. However, the use of limestone for neutralization offers a cost advantage of 2.5–3.0 ¢/1,000 gal (0.67–0.79 ¢/cu m) treated, as compared to the conventional lime method cost of 10–15 ¢/1,000 gal (2.6–4.0 ¢/cu m) (1).

Siderite is a common constituent of the host rocks of coal mines and it might inadvertently be considered as an acid-neutralizing agent because

$$FeCO_3 + 2H^+ \rightarrow Fe^{2+} + H_2CO_3 \ldots 14$$
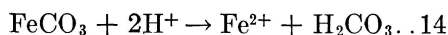
$$\log (K_{25^\circ}) = + 6.0$$

The constant, in conjunction with the data of Table I, indicates that siderite will neutralize temporarily some acid but, on oxidation of the ferrous ion (reaction 5), more acid is released than was neutralized through reaction 14. Siderite does not react rapidly with acid waters where the authors have observed it along streams affected by mine drainage. This mineral may magnify the acid-drainage problem slightly by addition of carbonic acid in some geologic environments.

Dilution

The pH of acid water can be raised both by simple dilution and by buffering when it is mixed with waters containing various concentrations of
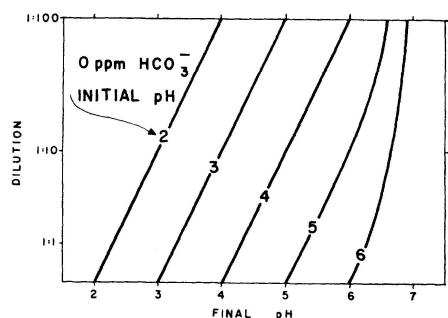
FIGURE 4.—Effect of dilution on the pH of mine waters when mixed with bicarbonate-free water with pH 7.

HCO_3^-. Figure 4 shows the pH change as a function of dilution when the diluent is free of bicarbonate and has a pH of 7. The equation for the curves at low initial pH's (linear segments of the curves) is:

$$pH_2 = pH_1 + \log(x) \ldots\ldots 15$$

where pH_2 and pH_1 are the final and initial pH's, respectively, and x is the ratio of the final to initial volume. For example, if 1,000 volumes of water of pH 3 are diluted to a final volume of 100,000 volumes, x is 100 and the final pH would be 5. The curves for higher initial pH are complicated by the contribution of H^+ by the diluent. Because the pH of the diluent is assumed to be 7, all curves will converge to a final pH of 7 at infinite dilution on Figure 4.

Water containing bicarbonate is much more efficient in neutralizing acid water than bicarbonate-free water; much less diluent is necessary for neutralization to take place. The important reactions in this case are those given in Equations 12 and 13. Figure 5 is a series of diagrams showing, for different concentrations of bicarbonate in the diluent, the initial and final pH relations as a function of dilution. The three equations describing these curves are:

$$(M_{H^+})_{final} = \left[(M_{H^+})_{initial}XD)\right] - \left[(M_{HCO_3^-})_{initial}X(1-D)\right] \ldots\ldots 16$$

$$(M_{H^+})_{final} = \frac{10^{-11.37}}{\left[(M_{HCO_3^-})_{initial}X(1-D)\right] - \left[(M_{H^+})_{initial}XD\right]} \ldots\ldots 17$$

$$pH = -\log(M_{H^+}) \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 18$$

where $(M_{H^+})_{final}$ and $(M_{H^+})_{initial}$ are the final and initial concentrations of H^+ in moles per 1,000 g of water, D is the dilution (the ratio of initial to final volume), and $(M_{HCO_3^-})_{initial}$ is the initial concentration of HCO_3^- in the diluent in moles per 1,000 g of water.

$$M_{HCO_3^-} = (1.64 \times 10^{-5})$$
$$\times \text{ mg/l } HCO_3^- \ldots 19$$

Equation 16 applies to the portion of the diagram where the final concentration of H^+ exceeds that of HCO_3^- after dilution, and Equation 17 to the portion where the final concentration of HCO_3^- exceeds that of H^+ after dilution. For example, with a diluent containing 10 mg/l HCO_3^-, an acid water of pH 3 must be diluted 1:10 to reach a final pH of 7. Slightly greater or smaller dilutions than those found from these curves might be required because of variations in activity coefficients and minor buffering reactions due to other components of natural waters.

There is a critical level of dilution for any initial pH and HCO_3^- content of the diluent that corresponds to the horizontal portion of the curves of Figure 5. Near this critical ratio, very small changes in the degree of dilution have major effects on the effluent pH. The critical ratio is caused by buffering by HCO_3^- and is important only above bicarbonate concentrations in the diluent of roughly 25 mg/l.

Reaction with carbonate rocks and dilution with bicarbonate-containing water are effective techniques for treating acid waters to raise the pH. How-
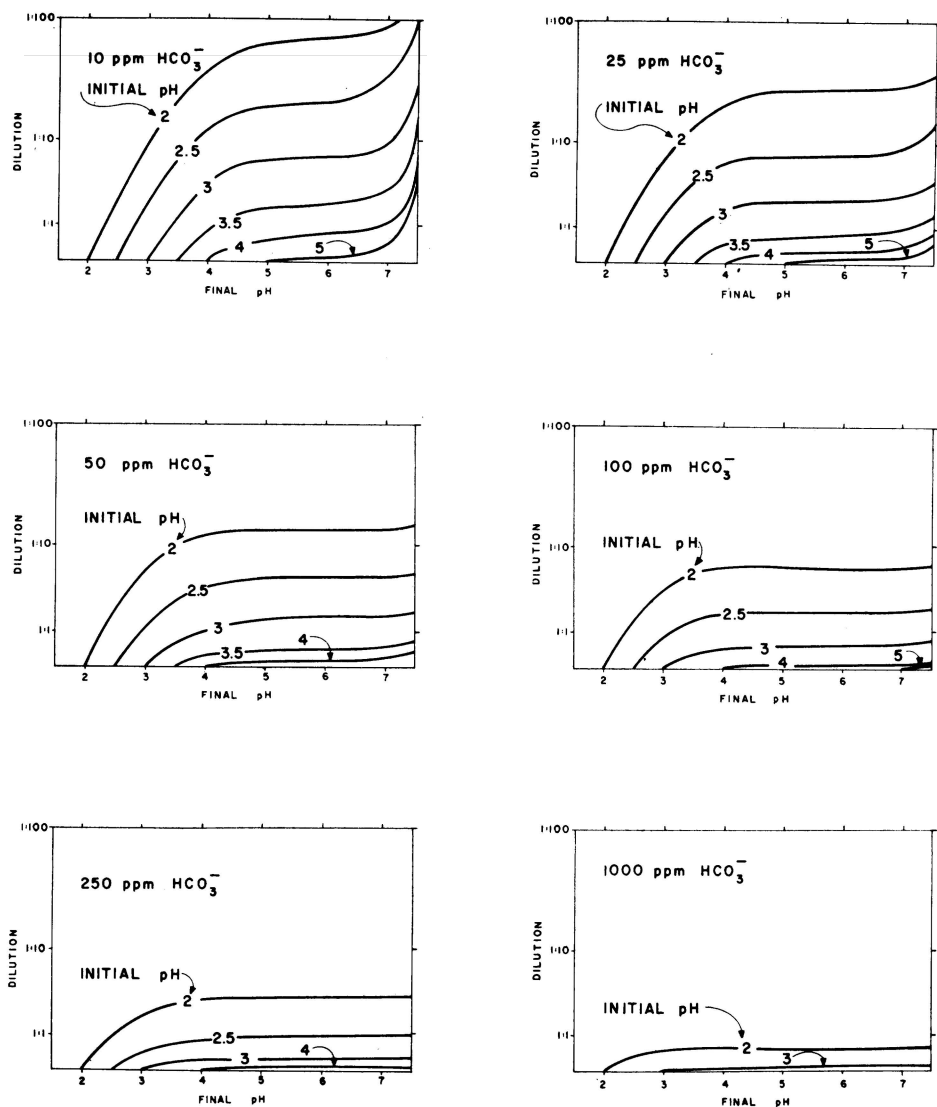
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FIGURE 5.—Combined effects on the pH of mine waters of dilution and buffering by mixing with bicarbonate solutions of six different concentrations.

ever, two consequences, the quality of the resulting water and the solids precipitated during neutralization, must be considered.

Precipitates

The principal problem after neutralization, and generally the most expensive part of drainage treatment, is the removal of precipitated, amorphous ferric oxyhydroxide hydrates from the treated water. Research is needed into more efficient methods of aggregation of this semigelatinous "yellowboy," including filtration as well as flocculation by surface-active agents. This research must be based first on an exact characterization of the precipitate, including grain size and chemical composition.

Other solids also may precipitate during neutralization. Gypsum ($CaSO_4 \cdot 2H_2O$) may precipitate if the product of calcium and sulfate concentrations, in parts per million, is about 10^6 (based

on an assumed activity coefficient product of 0.1) near 25°C or somewhat lower at mine temperatures. This product is exceeded only infrequently (Table I), but gypsum then may be found.

A white deposit is found occasionally where yellowboy precipitates, especially along streams. Melanterite ($FeSO_4 \cdot 7H_2O$) has been suggested as the primary mineral of this precipitate but its solubility, over 150,000 mg/l, is too great to permit this mineral to remain long in contact with aqueous solutions. This white deposit cannot be hydrated aluminum sulfate because it has a solubility of roughly 10^7 mg/l and also because it would be found at the point where sulfate and aluminum concentrations are maximized rather than near neutralizing reactions. An amorphous aluminum oxide hydrate is more likely; this solid becomes insoluble on raising the pH of acid waters to slightly above 5. (An activity coefficient of about 0.1 for Al^{3+} should be expected on the basis of sulfate complexing, giving a calculated solubility of 50 mg/l Al at pH 5, but this solubility decreases by 3 orders of magnitude at pH 6.)

Of the solids precipitated from acid waters, only ferric oxyhydroxide hydrate is a serious problem. An aluminum oxide hydrate is formed only in small quantities and gypsum appears only under exceptional circumstances.

Effluent Quality

Treated acid water may contain quantities of sulfate (over 250 mg/l), suspended solids (5 mg/l), magnesium (125 mg/l), hardness (over 200 mg/l as $CaCO_3$), and total dissolved solids (500 mg/l) (2) (13) that render it undesirable for domestic and industrial use. Nevertheless, typical concentrations in mine waters (Table I) indicate that after complete oxidation and neutralization have occurred, dilution by relatively clean water soon brings the quality of treated mine effluent within these compositional lim-

its. Of more concern are the methods of treatment of the acidity.

Conclusions

The leading problem in the chemistry of acid mine drainage is the question of reactions by which low pH's are reached at low Eh's where essentially no dissolved oxygen is available. Reactions involving organic species formed from coal are unlikely to cause oxidation. Further research with both field and laboratory studies is warranted here.

Methods of preventing the formation of acid are applicable only in optimum hydrologic situations where the mine may be isolated from major inflow or where the inflow can be carbonate-saturated with limestone or dolomite. Sealing to exclude air is probably impractical, in general, but the culturing of sulfate-reducing bacteria in flooded mines deserves investigation.

Because acid formation usually cannot be prevented, treatment of the effluent is necessary if pollution is to be minimized. Combined dilution and buffering by HCO_3^--containing waters is most effective and avoids the problem of armoring when carbonate rocks are used as neutralizing media. Only one precipitate is of importance during or after treatment and research is needed to explore methods of flocculating and removing this ferric oxyhydroxide suspension from effluent, because this is now a costly operation. Dilution of treated effluent, by even modest proportions of clean water, produces a useful resource for both domestic and industrial consumption.

A method of disposal of acid waters, injection into wells or abandoned mines, has been proposed and tested where neither carbonate rocks nor bicarbonate-rich waters are available at the surface (15). The wells were not successful because the selected horizons for injection were both too deep and too impermeable and the required pumping pressures too high. Because this method could succeed elsewhere,

the chemical aspects merit consideration. Possible contamination of groundwater reservoirs should be avoided in selection of stratigraphic horizons for injection. For maximum useful life of an injection site, armoring of neutralizing rocks should be avoided by the following steps to prevent both loss of active surfaces and hydraulic sealing of the area. If the iron of the acid waters is precipitated before injection, permeability of the rocks should be retained because the carbonate content of the rocks is dissolved by the acid while the iron suspension settles (but not preferentially on active surfaces). The iron first must be oxidized completely to the ferric state by a residence time of 0.5–1 hr in a shallow pond where oxygen is available and the bacteria *Ferrobacillus ferro-oxidans* are abundant (6). The concentration of dissolved iron then can be reduced to 1 mg/l [calculated as $Fe(SO_4)_2{}^-$ in the presence of 1,000 mg/l $SO_4{}^{2-}$] by adding enough neutralizing agent to raise the pH to 3.7. This treatment minimizes both the amount of lime or limestone used and the deleterious effects of injected effluent on groundwater. Both the slurry and the acid water then are ready for injection by gravity flow or by pumping.

Acknowledgments

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