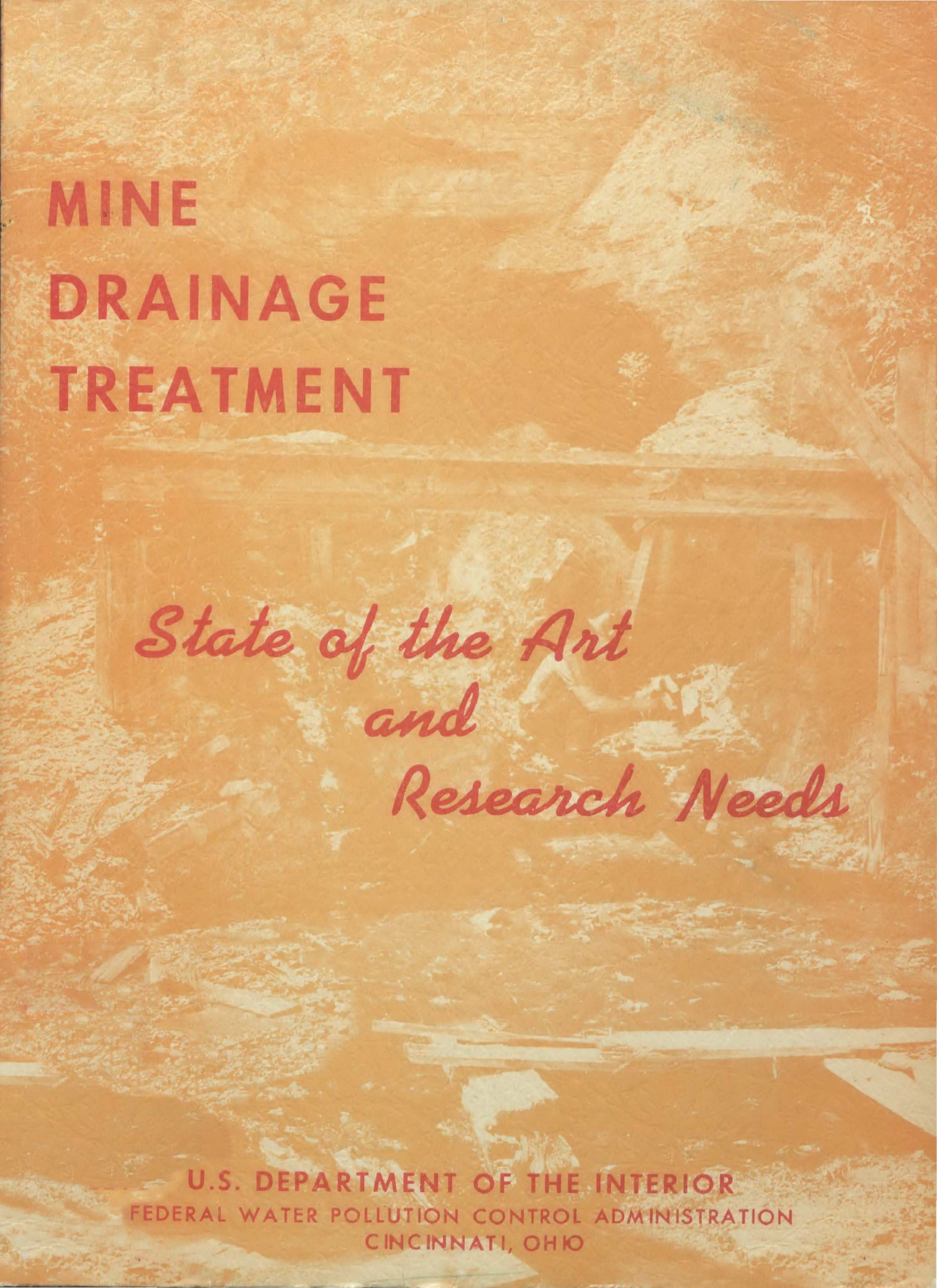

MINE
DRAINAGE
TREATMENT

State of the Art and Research Needs

U.S. DEPARTMENT OF THE INTERIOR
FEDERAL WATER POLLUTION CONTROL ADMINISTRATION
CINCINNATI, OHIO

MINE DRAINAGE TREATMENT
STATE OF THE ART AND RESEARCH NEEDS

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MINE DRAINAGE CONTROL ACTIVITIES
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December 1968

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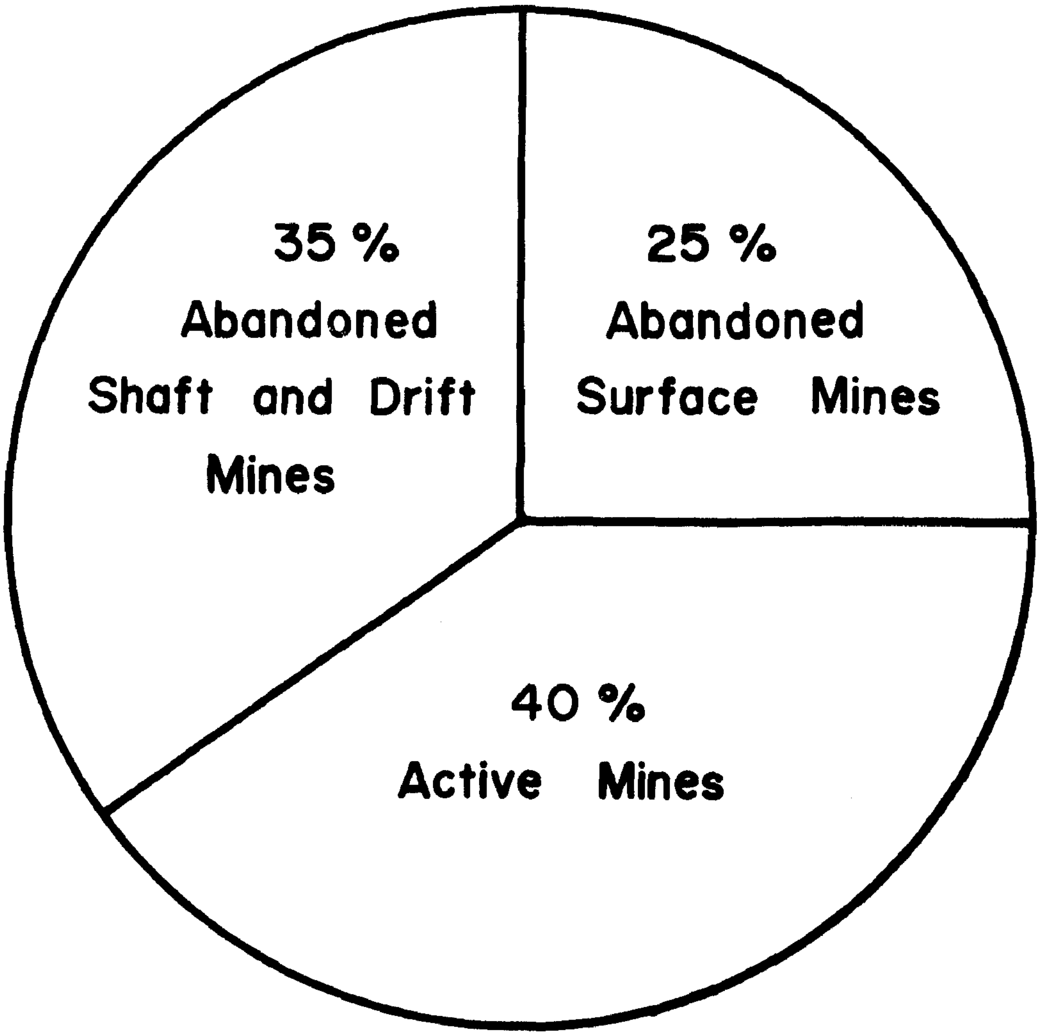
1. INTRODUCTION

Stream pollution resulting from mining operations is a serious problem in the United States. A U. S. Department of the Interior report (58) indicates that 4,800 miles of streams and 29,000 surface acres of impoundments and reservoirs are seriously affected by surface coal mining operations alone. Deep coal mining and other mining operations increase these figures several fold. Inventories of stream pollution magnitude and source have highlighted the seriousness of the problem. In Appalachia (55) during 1966, more than 6,000 tons of acidity per day were discharged to streams and over 10,000 miles of streams were polluted by all coal mining operations. Figure 1.1 indicates the approximate relative distribution of the mine drainage problem by source. About 40 percent of the mine drainage comes from active operations and the remainder from abandoned surface, drift, auger, etc., mines.

Methods of controlling mine drainage from surface mines are more advanced than those for deep mines. By utilizing preventive measures, such as good water control, mining techniques, and reclamation practices, pollution from surface mines can be held to a minimum. Strong state laws are being or have been enacted in most states to control pollution from surface mining.

Deep mine discharges present an entirely different situation than surface mines. Preventative control is not fully understood or developed. The major control measures used to date are water diversion to prevent water from entering the mine, flooding of the pyritic material to prevent oxidation, and sealing to prevent air from entering the mine and subsequently



Estimated Current Rate of Pollution :
3.5 Million Tons per Year to all U.S. Streams

Figure 1-1. Sources of Acid Pollution

oxidizing the pyrite. While each of these methods has been successful to some degree, documentation of the work performed and the results obtained is sketchy and inconclusive. A broad spectrum of research is needed to develop control methods for deep mine drainage.

At best preventative methods will not be 100 percent effective in every situation. Thus, another approach will be necessary to control the residual pollution from those measures. Further, there are many abandoned mine situations where preventative measures will not be applicable. Active mine operations also are usually not amenable to at-source control methods. In each of these situations, treatment of mine drainage appears to be the best method of pollution control.

This report reviews the current status of treatment methods for mine drainage and outlines those areas needing further research and development.

2. CHEMISTRY OF MINE DRAINAGE

The type of drainage produced by a particular mine is dependent upon the product mined and the nature of the surrounding geologic formation. In the case of coal mining, it is dependent upon the amount of sulfides present; the spatial distribution of these sulfides; the crystallinity of the pyrite; the size of the individual sulfide particles; the presence of bacteria associated with acid mine drainage; and the magnitude of the fluctuation of the water level within the mine, if the workings are below drainage. In addition, the presence or absence of calcium in the sulfide aggregates seems to have some effect upon the rate of sulfide oxidation and decomposition(8).

The sulfide content and distribution are dependent upon the nature of the paleo-environmental conditions which prevailed when the coals were being deposited. In general, those coals which were deposited in exclusively marine environments are more likely to produce acid waters than are those which were deposited in essentially continental environments. The Pennsylvania bituminous coal fields show an increase in sulfide content from east to west on the basal seams, reflecting the trend toward more marine conditions toward the west. Further, these same seams show a decrease in sulfur content upward in the stratigraphic column as progressively more continental conditions of deposition are encountered(37).

Emrich and Thompson(17) made an analysis of the data on file with the Pennsylvania Department of Health about the character of drainage from underground bituminous mines. They found that the younger coal seams

(Sewickley-Pittsburgh) have more alkaline discharges and the older seams (Clarion-Brockville) have predominantly acid discharges.

Hinkle and Kochler(23) who collected samples of mine waters, including roof drips of deep mines in West Virginia, reported as follows:

"The analyses of mine waters - - - - have shown that some mine drainage waters are decidedly acid and others are fairly alkaline. Roof drip waters so far collected have all been found to be alkaline; however, acid roof drips have been reported by others. The only significant difference between acid mine waters - - - - and alkaline drainage water and roof drips - - - - was that the acid waters contained essentially sulfates, whereas the roof drips and alkaline mine waters contained both sulfates and bicarbonates. The compositions of the alkaline mine drainage waters were dependent upon the composition of the roof drips. - - - - All three waters contained compounds of essentially seven metals: iron, aluminum, manganese, calcium, magnesium, sodium, and possibly some potassium. Chlorides were usually low in all waters. Silica (SiO_2) was relatively high in the acid mine water, but low in the alkaline mine waters and roof drops."

While wide variations exist in the chemical characteristics of mine drainage generally, acid mine drainage can be said to have a low pH, net acidity (acidity greater than alkalinity), high iron (iron (II) and/or iron (III), high sulfates, and significant amounts of aluminum, manganese, calcium and magnesium. Alkaline mine drainage generally can be said to have a pH near or greater than neutrality, net alkalinity, high sulfate, significant calcium, magnesium, and manganese, and low aluminum. Corbett and Growity (12) reported that the Zn, Cd, Be, Cu, Ag, Ni, Co, Pb, Cr, V, Ba, and Sr concentrations of mine drainage were less than 1 mg/l. Analyses of mine drainage samples collected in West Virginia and Pennsylvania by Federal Water Pollution Control Administration personnel revealed concentration of similar magnitude.

Although the exact mechanism is not fully understood, acid mine drainage results from the oxidation of pyrite (FeS_2) as illustrated in equation (1):

$$2FeS_2 + 2H_2O + 7O_2 \longrightarrow 2FeSO_4 + 2H_2SO_4 \qquad (1$$

(Pyrite) ⟶ (Ferrous sulfate) + (Sulfuric acid)

Subsequent oxidation of ferrous sulfate produces a ferric sulfate:

$$4FeSO_4 + 2O_2 + 2H_2SO_4 \longrightarrow 2Fe_2(SO_4)_3 + 2H_2O \qquad (2$$

(Ferrous sulfate) ⟶ (Ferric sulfate)

The reaction then may proceed to form a ferric hydroxide or basic ferric sulfate:

$$Fe_2(SO_4)3 + 6H_2O \longrightarrow 2Fe(OH)_3 + 3H_2SO_4 \qquad (3$$

(Ferric sulfate) (Ferric hydroxide)

$$Fe_2(SO_4)_3 + 2H_2O \longrightarrow 2Fe(OH)(SO_4) + H_2SO_4 \qquad (4$$

(Ferric sulfate) ⟶ (Basic ferric sulfate)

From the above equations, it can be seen that dissolution of one mole of iron pyrite ultimately leads to the release of four equivalents of acidity - two equivalents from the oxidation of iron sulfate and two from the oxidation of ferrous iron.

Pyrite oxidation also occurs due to ferric iron(52) as illustrated in equation (5:

$$14Fe^{3+} + FeS_2 + 8H_2O \longrightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+ \qquad (5$$

(Ferric iron) + (Pyrite) ⟶ (Ferrous iron) (Sulfate)

By either mechanism, an acid water is produced and the pH is lowered. At low pH's many metallic ions in the mine for example, aluminum and manganese become more soluble and enter into the mine discharge.

Mine drainage is a complex solution varying in quality from seam to seam, mine to mine, and even within the same mine. The water quality from mines low in pyrite may be alkaline and closely resemble ground water. Often mines produce water high in ferrous iron and acidity, indicating that reactions 1 and/or 5 are occurring. The discharge may have high ferric iron and acidity concentration, indicating that reactions 2 and 3 are occurring. The discharge may also have been partially neutralized within the mines thus reducing the acidity level.

Although there is no "typical" mine drainage, waters discharging from mines can be divided into four general classes as shown in Table 2.1.

The wide variations in mine drainage characteristics indicate that a number of treatment methods may be applicable. The best method for any one site will depend on the quality of the mine discharge and the ultimate use of the water. Treatment to meet stream water standards will be different from that needed to meet domestic and industrial water use standards. The following sections of this report review the current status of various treatment methods.

TABLE 2.1

MINE DRAINAGE CLASSES

	Class I Acid Discharges	Class 2 Partially Oxidized and/or Neutralized	Class 3 Oxidized and Neutralized and/ or Alkaline	Class 4 Neutralized and Not Oxidized
pH	2 - 4.5	3.5 - 6.6	6.5 - 8.5	6.5 - 8.5
Acidity, Mg/l($CaCO_3$)	1,000 - 15,000	0 - 1,000	0	0
Ferrous Iron, Mg/l	500 - 10,000	0 - 500	0	50 - 1,000
Ferric Iron, Mg/l	0	0 - 1,000	0	0
Aluminum, Mg/l	0 - 2,000	0 - 20	0	0
Sulfate, Mg/l	1,000 - 20,000	500 - 10,000	500 - 10,000	500 - 10,000

Source: In-house Studies, FWPCA

3. NEUTRALIZATION

Introduction

The neutralization of acid mine drainage with an alkali has been recognized as an acid mine drainage treatment method since the 1920's. In 1930 Carpenter and Davidson(7) reported on four lime treatment plants treating acid mine drainage. They conducted a number of studies themselves as did the U. S. Bureau of Mines(46). Investigators at that time concluded that the process was not economic for practical use. In addition, they pointed out the problem of handling and disposing of the sludge that was formed.

In recent years, with the advent of stronger laws enacted to prevent water pollution by acid mine drainage, interest in neutralization has been renewed, a number of laboratory studies have been initiated, and pilot plants and full-scale plants built.

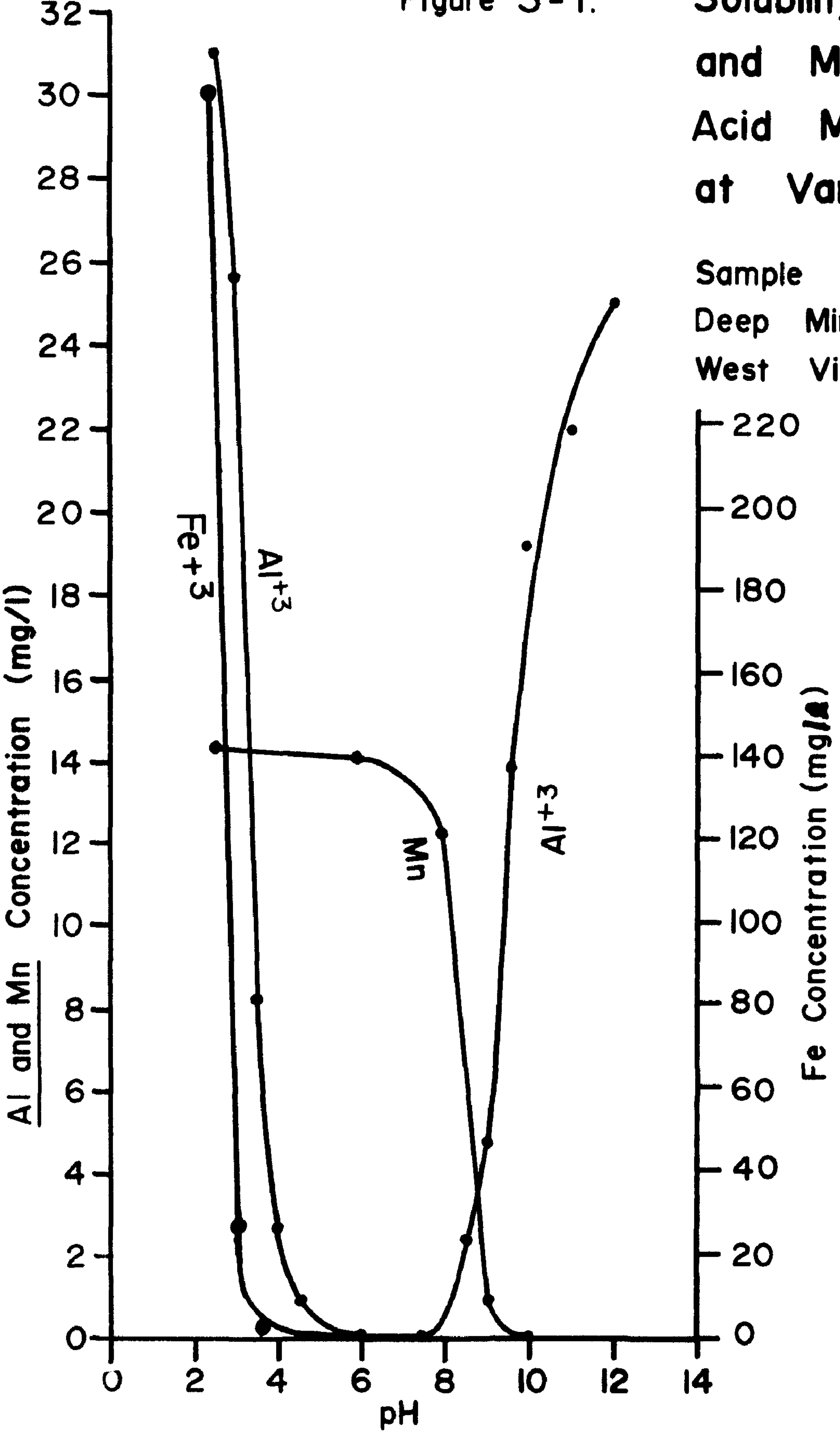
Principle of Neutralization

The principle of the neutralization processes is as follows: an alkali is mixed with acid mine waters to neutralize the acid and to precipitate the contaminating metal salts, which can then be separated by sedimentation and/or filtration. The metal salts commonly found in acid mine drainage are separated because they are less soluble at neutral or higher pH's than at lower pH's (Figure 3.1 and Figure 3.2).

The list of neutralizing agents suggested for acid mine drainage is presented in Table 3.1. While most neutralization work to date has utilized lime and limestone, other agents may be used successfully in some situations.

Figure 3-1. Solubility of Aluminum, Ir
and Manganese in
Acid Mine Drainage
at Various pH's

Sample Source:
Deep Mine, Elkins,
West Virginia



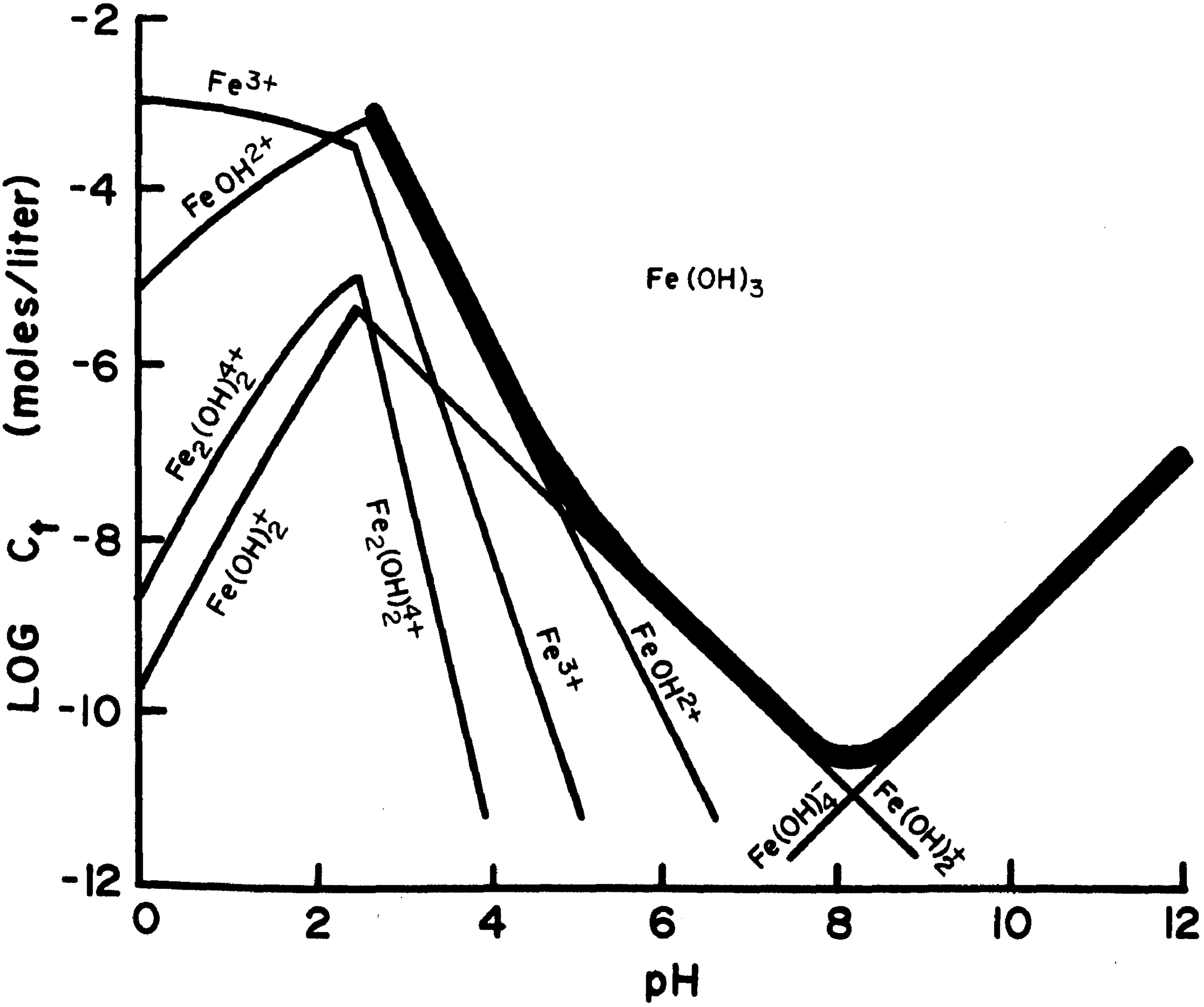


Figure 3-2. Solubility of Iron

(after O'melia & Stumm, 1967 (41))

TABLE 3.1

Neutralizing Agents		Basicity Factor (*)
Hydrated or calcined lime	CaO	1.78
Limestone	$CaCO_3$	1.00
Magnesium hydroxide	$Mg(OH)_2$	1.72
Dolomite	$Ca\text{-}MgCO_3$	1.006
Potassium permanganate	$KMnO_4$	-
Sodium hydroxide	$NaOH$	1.25
Potassium hydroxide	KOH	-
Ammonium hydroxide	NH_4OH	-
Sodium sulfide	Na_2S	-
Tri-Sodium phosphate	Na_3PO_4	0.915
Sodium cyanide	$NaCN$	-
Sodium carbonate	Na_2CO_3	0.94
Ammonia	NH_3	2.94
Magnesium oxide	MgO	2.482

(*) Grams of calcium carbonate equivalent per gram of agent.

The choice of an alkaline agent should be based on the following considerations:

Cost of Agent - The cheapest agent capable of fulfilling the requirements should be used.

Availability of Agent - Availability is partially reflected in cost. The availability of certain alkaline materials, such as a by-product of another industry, may not be long-termed.

Basicity Factor - The amount of alkali per unit weight of material varies among different alkaline agents.

Reaction Time - The reaction rates of alkaline agents vary over a considerable range and are important factors in the size of mixing tanks, etc.

Sludge Characteristic - The settling rate and properties of the sludge are important factors in the design of settling tanks and lagoons, and in the disposal of the sludge.

Basicity Factor

Basicity factor is defined as the grams of calcium carbonate equivalent per gram of alkaline agent. In Table 3.1 the basicity factors for some of the commonly used alkaline agents are given. These figures are slightly higher than those obtained in operation because of the purity of the commercial product and other factors. The basicity factor is a useful tool in comparing the cost of alkaline agents. Three alkaline agents are compared on the following page.

Agent	Basicity Factor	Price Dollars/Ton	Cost Dollars/Ton Basicity
Lime (CaO)	1.78	14	\$ 7.86
Limestone ($CaCO_3$)	1.0	5	5.00
Soda Ash (Na_2CO_3)	0.94	31	32.98

In this comparison, lime has the greater basicity factor, but is more expensive per ton of basicity than limestone.

Reactivity

Reactivity is defined as the rate at which the neutralization process occurs. Hoak, et al.,(24) reported the rate (in descending order) of the following agents in relationship to each other to be: NaOH, CaO, $Ca(OH)_2$, Na_2CO_3, and $CaCO_3$. In most cases, an increase in temperature from room temperature to 60° C increased the rate, as did aeration of the waste.

Sludge Settleability

Sludge settleability is defined as the characteristic of the sludge judged by the rate at which it settles and the final sludge volume. Hoak, et al.,(24) rated the sludge settleability of the following agents (descending order): Na_2CO_3, $CaCO_3$, NaOH, CaO, and $Ca(OH)_2$.

Caustic Soda

Caustic soda reacts rapidly, has a high settleability, reaction products are highly soluble, thus reducing scaling problems, and cause no increase in hardness. However, the cost of this agent is prohibitive for treating acid mine drainage except in special cases.

Sodium Sulfide

Care and Zawadzki(6) evaluated the treatment of synthetic acid mine water with aqueous sodium sulfide solutions. The following equations illustrate the reaction:

$Na_2S + 2H_2O \longrightarrow 2NaOH + H_2S_{(g)}$ (6

(Sodium Sulfide) + (Water) → (Sodium Hydroxide) + (Hydrogen Sulfide)

The pH of a 0.04 molar Na_2S solution is 10 to 11.

$4Na_2S + Fe_2(SO_4)_3 + FeSO_4 \longrightarrow Fe_2S_3(ppt) + FeS(ppt) + 4Na_2SO_4$ (7

(Sodium Sulfide) + (Ferric Sulfate) + (Ferrous Sulfate) →

(Ferrous Sulfide) + (Ferric Sulfide) + (Sodium Sulfate)

Fe_2S is a black precipitate and since the bulk of the precipitate is ferrous sulfide, the precipitate is black. The precipitate was easy to filter. At stoichiometric amounts of Na_2S, no H_2S odor was detected.

Upon addition of Na_2S solution the pH initially increased to between 4 and 5. The pH later increased to between 6.8 and 7.1, after the iron precipitated, and stabilized at this value.

Care and Zawadzki reported "- - - - essentially complete removal of both ferrous and ferric iron, neutralization of the acidity, and in addition, an innocuous sodium sulfate solution."

The major drawback was the cost of Na_2S (1965 price was $142 per ton of 100 percent Na_2S). Therefore, the agent cost of treating a 500 ppm total iron discharge would be $0.15 per 1,000 gallons of water.

Zawadzki and Glenn(62) conducted further tests on the use of sodium sulfide to neutralize mine drainage and remove iron (II). The addition of sodium sulfide at stoichiometric amounts to combine with the ferrous iron caused a rapid increase in pH. The rise in pH was accompanied by rapid reaction of the iron with sulfide. The reaction occurred best at pH's of 4 and above. At pH's below 4, there was insufficient sodium to neutralize the acidity.

Since treatment with sodium sulfide was dependent on pH control, Zawadzki and Glen(62) conducted their later studies on a limestone-sulfide system instead of a sodium sulfide system. The limestone-sulfide system is reported on in the iron removal section of this report.

<u>Limestone Treatment</u>

In equations 8, 9, and 10, the reactions of limestone with acid mine drainage are illustrated.

Limestone + Sulfuric Acid → Calcium Sulfate + Water + Carbon Dioxide (8

$$CaCO_3 + H_2SO_4 \longrightarrow CaSO_4 + H_2O + CO_2$$

Limestone + Aluminum Sulfate + Water → Calcium Sulfate + Aluminum Hydroxide + Carbon Dioxide (9

$$3CaCO_3 + Al_2(SO_4)_3 + 3H_2O \longrightarrow 3CaSO_4 + 2Al(OH)_3 + 3CO_2$$

Limestone + Ferric Sulfate + Water → Calcium Sulfate + Ferric Hydroxide + Carbon Dioxide (10

$$3CaCO_3 + Fe_2(SO_4)_3 + 3H_2O \longrightarrow 3CaSO_4 + 2Fe(OH)_3 + 3CO_2$$

Theoretically, one ton of limestone is required to neutralize one ton of H_2SO_4.

The process will occur as long as there is an excess of limestone available and the limestone surface is in an active state. Maintaining the limestone in an active state is a major problem. When high acid concentrations are treated, calcium sulfate, because of its low solubility (approximately 2,000 mg/l), will precipitate and coat the limestone. Ferric hydroxide also coats the limestone, markedly reducing its efficiency.

Limestone Treatment Studies

Braley(3) reported on a study in which acid mine drainage having both ferrous and ferric iron and 1,100 ppm acidity was passed through a flume 50 feet long containing 5 tons of limestone (1 to 2 inches size). The contact time was varied by changing the flow. The maximum neutralization of 50 percent was obtained at the lowest flow rate (180 gph) and greatest contact time (1 hour). The amount of acid neutralization increased with increased contact time. With continued use of the same limestone, the amount of neutralization decreased because the limestone became coated with gelatinous iron hydroxides, thus reducing the amount of reactive surfaces.

In a second series of tests by Braley, the above mentioned acid mine drainage was batch-treated with crushed limestone in a tank provided with an agitator. The agitator provided constant movement of the water through the limestone, but did not agitate the limestone itself. With new limestone, 5 hours were required to neutralize 135 gallons of acid mine drainage, or 4.02 hours per pound of acid. By the 39th test, without changing the limestone, 37.25 hours were required to treat the acid mine drainage. The increase in time was due to the coating of the limestone with iron.

Clifford and Snarley(11) reported similar limestone coating in their studies in which limestone was placed in cribs built in the bed of an acid stream and in a flume through which the acid waters passed. The limestone was coated not only with an iron deposit, but also with silt. Even when operating in a new condition, the limestone increased the pH only slightly because of the short contact time.

In his studies, Glover(19) confirmed that stationary beds of limestone grit soon became blocked with reaction products. In view of the large size of grit beds, he concluded that mechanical cleaning was not practical. Zurbuch(63) overcame the coating of limestone by placing the limestone in a drum turned by the streamflow. As the limestone revolved in the drum, the abrasive action between the particles wore off the coating and also helped the dissolution of the limestone. However, because of the short contact time provided, the increase in pH was small.

Wheatland and Borne(61) found that passing the waste upflow through a limestone or calcined magnesite bed did not reduce the particle coating problem.

Limestone can be successfully used to treat acid mine drainage only if the coating on its surface can be prevented or removed. Abrasion between the limestone particles or from an external force appears to be one method. The revolving drum mentioned earlier, if driven by motors and given sufficient contact time, might resolve the problem. A kiln or tumbler type reactor was found by Mihok and Chambalain(39) to supply the necessary abrasion. Another approach would be the use of finely ground limestone, such as that used for agricultural purposes.

The U. S. Bureau of Mines(40) conducted a series of tests using a 3-foot-diameter by 24-foot long tube mill driven by a 15-horsepower motor. The mill was charged with 3 x 1-inch limestone and optimum operation occurred when the limestone discharged passed a 400 mesh screen. It was found that the limestone generated having a size less than 400 mesh increased as the flow rate decreased. For example, at 7.2 gallons per minute (gpm), the limestone generated was 8.4 pounds per minute, while at 14.6 gpm only 5.1 pounds per minute was generated. These results indicated that instead of passing the entire flow through the mill, a portion should be split off and passed through the mill to make up the limestone slurry, then reunited with the main stream. Data were not presented in the report of the cost of grinding limestone by a mill as compared to buying ground limestone from the quarry.

Glover(19) in a series of tests using a tumbler reactor obtained good results in treating the free acid and ferric and aluminum salts and observed no apparent inactivation of the limestone. The rate of ferrous iron oxidation in the tumbler was no higher than in a stationary bed of limestone which was also tested. Glover, et al.,(20) have patented a mechanical attrition device in the form of a rapidly rotating impeller that operates in an upflow expanded limestone bed. This technique was reported to be very effective in maintaining the activity of the limestone.

Another approach to preventing limestone coating is the use of powdered limestone. Limestone in this state would have greater reactive surface area available and possibly would be solubilized before a coating formed. Glover(19) found that the limestone powder reacted rapidly with free acid and ferric and aluminum salts, but not directly with the ferrous salts. Hoak, et al.,(25) found pulverized limestone to be more effective than lump or crushed limestone because the fine particles reacted more completely. This approach warrants further consideration.

Limestone Reaction Rates

As mentioned earlier, the reaction rate of limestone is not as great as that of other alkali agents. The ferrous to ferric iron reaction is the limiting factor. The increase in pH and decrease in acidity usually occur in less than a minute, whereas the rate of ferrous oxidation is very slow in a limestone bed. When oxygen is supplied to a bed of limestone ferrous iron is oxidized. Under this condition, Glover(19) reported the oxidation rate to be 6 grams iron per liter per 24 hours (gFe/1/24) hours. He observed that the rate of ferrous oxidation was almost independent of the ferrous concentration and concluded that since oxygen and limestone were present in excess, the rate determining factor was probably the rate of stripping of the carbon dioxide product. In an aerated flow through a limestone bed, the oxidation rate ranged from 7 to 21 gFe/1/24 hours, suggesting that the moving water carried away the carbon dioxide. Deul and Mihok(13) also found carbon dioxide to be a limiting factor. In a limestone bed a terminal pH of only 6.0 to 6.5 could be obtained. However, in a rotary drum, with vigorous cascading agitation to introduce air, the CO_2 was driven off and a terminal pH of above 8 was reached. In these same studies, the investigator found that the pH of the acid mine drainage in a rotary drum with excess limestone could be increased to 6 or greater in less than a minute; however, ferrous iron oxidation required a much longer time. The final ferrous iron concentration after 20 minutes was dependent on the initial concentration, since the oxidation rate was relatively constant (ranging from 600 to 1,000 mg ferrous iron per liter per hour). The oxidation rate was greater when the ferrous iron concentration exceeded 400 ppm than when the concentration was less than 200 ppm. Hoak, et al.,(25) reported that the reaction rate was governed by the chemical characteristics, fineness, and a specific reactivity peculiar to a particular limestone which cannot easily be evaluated by trial.

Mihok and Chambalain(39) conducted studies on a continuous limestone neutralization pilot plant capable of handling 100 gpm. A rotary-kiln type reactor was used followed by aeration. They found that " - - - - - adequate treatment of acid waters containing less than 165 ppm ferrous iron can be achieved at normal mine water temperatures (10°C) with a reaction residence time of less than 5 minutes." The soluble ferrous iron concentration was reduced at a rate of 30 to 35 mg/l per minute and the pH was increased to between 6.5 and 7.5. The atmosphere within the reactor was found to have abnormally high amounts of carbon dioxide (0.16 percent), which may have surpassed higher terminal pH's. However, rapid precipitation of the ferrous hydroxide did not occur, even though an excess of very fine limestone was present. Subsequent aeration of the limestone-neutralized water reduced the residual ferrous iron at the rate of 1 to 4 mg/l per minute.

Calhoun(5) reported on a limestone treatment plant used to treat a mine discharge having the following characteristics: flow range 50 to 300 gpm, acidity 100 to 500 mg/l, and iron 20 to 120 mg/l (10 percent in the ferrous state). A rotating drum, 30 feet long and 3 feet in diameter, containing 5,000 pounds of 3 inch by 1 inch limestone, and rotated at 15 rpm, was used as a reactor. The water flowed from the drum to a settling basin. The first year's operation is summarized as follows:

effluent pH	6.2 - 7.3
effluent iron	0.4 - 5.3 mg/l
effluent alkalinity	4 - 26 mg/l

total operating cost	5 cents per 1,000 gallons
limestone cost	1 cent per 1,000 gallons
labor cost	2 cents per 1,000 gallons
limestone usage efficiency	65 percent

Advantages stated for limestone were: more economical, less volume of sludge and no danger of overtreatment.

Mihok, et al.,(40) conducted a series of field tests using a tube mill to grind limestone which was subsequently fed to mine drainage. They documented the importance of removing carbon dioxide from the process in order to increase the rate of neutralization. Table 3.2 presents a cost comparison for treating mine drainage with lime and limestone.

In summary, it can be concluded from the preceeding review that acid mine drainage can be neutralized with limestone in less than 1 minute of reaction time if the limestone is kept free of inhibiting coatings. Ferrous iron must be treated either in a separate step or the reaction time of the limestone treatment step must be extended. Possible methods of separate treatment of the ferrous iron are discussed in a later section. Limestone treatment may not reduce the hardness or sulfate concentration. In fact the hardness might be increased.

Lime Treatment

Quicklime (CaO) and hydrated lime ($Ca(OH)_2$) have been used in the treatment of acid mine drainage. These limes may be either high-calcium or high-magnesium (dolomitic). In equations 11 through 15, the reactions of lime with acid mine drainage are illustrated.

$$\text{Quicklime} + \text{Water} \longrightarrow \text{Hydrated Lime} \qquad (11$$

$$CaO + H_2O \longrightarrow Ca(OH)_2$$

TABLE 3.2

MATERIAL COST OF TREATING ONE MILLION GALLONS OF MINE DRAINAGE PER DAY WITH LIME AND LIMESTONE*

	Lime	Limestone
Material cost, dollars per ton	3	20
Material utilization, percent	50	100
Material required, tons	16.6	6.2
Cost per day, dollars	50	120

---

* Total Acidity - 2,000 mg/l as $CaCO_3$. From Mihok, et al., (40)

Hydrated Lime + Sulfuric Acid = Calcium Sulfate + Water

$$Ca(OH)_2 + H_2SO_4 \longrightarrow CaSO_4 + 2H_2O \qquad (12$$

Hydrated Lime + Aluminum Sulfate = Calcium Sulfate + Aluminum Hydroxide

$$3Ca(OH)_2 + Al_2(SO_4)3 \longrightarrow 3CaSO_4 + 2Al(OH)_3 \qquad (13$$

Hydrated Lime + Ferrous Sulfate = Ferrous Hydroxide + Calcium Sulfate

$$Ca(OH)_2 + FeSO_4 \longrightarrow Fe(OH)_2 + CaSO_4 \qquad (14$$

Hydrated Lime + Ferric Sulfate = Ferric Hydroxide + Calcium Sulfate

$$3Ca(OH)2 + Fe_2(SO_4)3 \longrightarrow 2Fe(OH)_3 + 3CaSO_4 \qquad (15$$

Besides increasing the pH and decreasing the acidity, lime treatment will remove many of the metallic salts. The aluminum and manganese will precipitate if the proper pH level is reached (Figure 3.1). Calcium sulfate will increase the hardness of the water until its maximum solubility is reached (approximately 2,000 mg/l), then it will precipitate. Ferrous hydroxide has a low solubility, which decreases as the pH increases. Ferric hydroxide is even less soluble than ferrous hydroxide and its solubility decreases at higher pH's. The oxidation of ferrous iron results in a decrease of the pH, which may result in an increase of the iron concentration because of the higher solubility of iron at lower pH's.

Hydrated lime is most widely used for the treatment of mine drainage, however, quicklime has been used in some cases. Quicklime is usually slaked before use by the addition of water, thus forming lime hydrate. Hoak, et al.,(27) reported that lime hydrate reacted more effectively than the hydrated lime. Quicklime is hazardous to work with and special hydrating plants must be constructed to prevent explosions and burns during mixing of quicklime and water. However, in some cases quicklime has a cost advantage.

Both high-calcium hydrated lime and dolomitic lime have been used to treat acid mine waters. The reaction rates of both types of lime are very rapid. However, since calcium sulfate is insoluble at higher concentrations, dolomitic lime may hold some advantages in treating highly acid water. Hoak, et al.,(27) found that the pH could be increased to 7 or greater in less than 2 minutes with both forms of hydrated lime. Similar results were reported by Dorr-Oliver(14).

The reaction rate of ferrous iron and lime is the limiting factor in treating acid mine drainage. This reaction goes very slowly and requires hours for completion even when the water is aerated. The process itself is not fully understood; however, it is apparent that the reaction is controlled by the pH of the system, the temperature, ion concentration, etc. The oxidation rate is low at low pH's, as shown in Figure 3.3.

Lime neutralization of acid mine discharges dates back to the early 1920's (Clifford and Snarely)(11). A common practice at that time, still in use today, was to apply the lime to the water and then pass the water through a pond or lagoon. Lime is either fed as a lime-water mixture (slurry) or as a dry chemical. Hydrated lime is reported to be difficult to handle in the dry form since it has a tendency to arch or bridge in storage bins and possesses poor flow properties.

Braley, et al.,(3) conducted studies on treating acid mine drainage with hydrated lime by batch treatment in an agitated tank. They reported the time of neutralization to be short and the treatment complete, although the gelatinous iron sludge settled very slowly. Approximately three-fourths ton of hydrated lime was required to neutralize one ton of sulfuric acid.

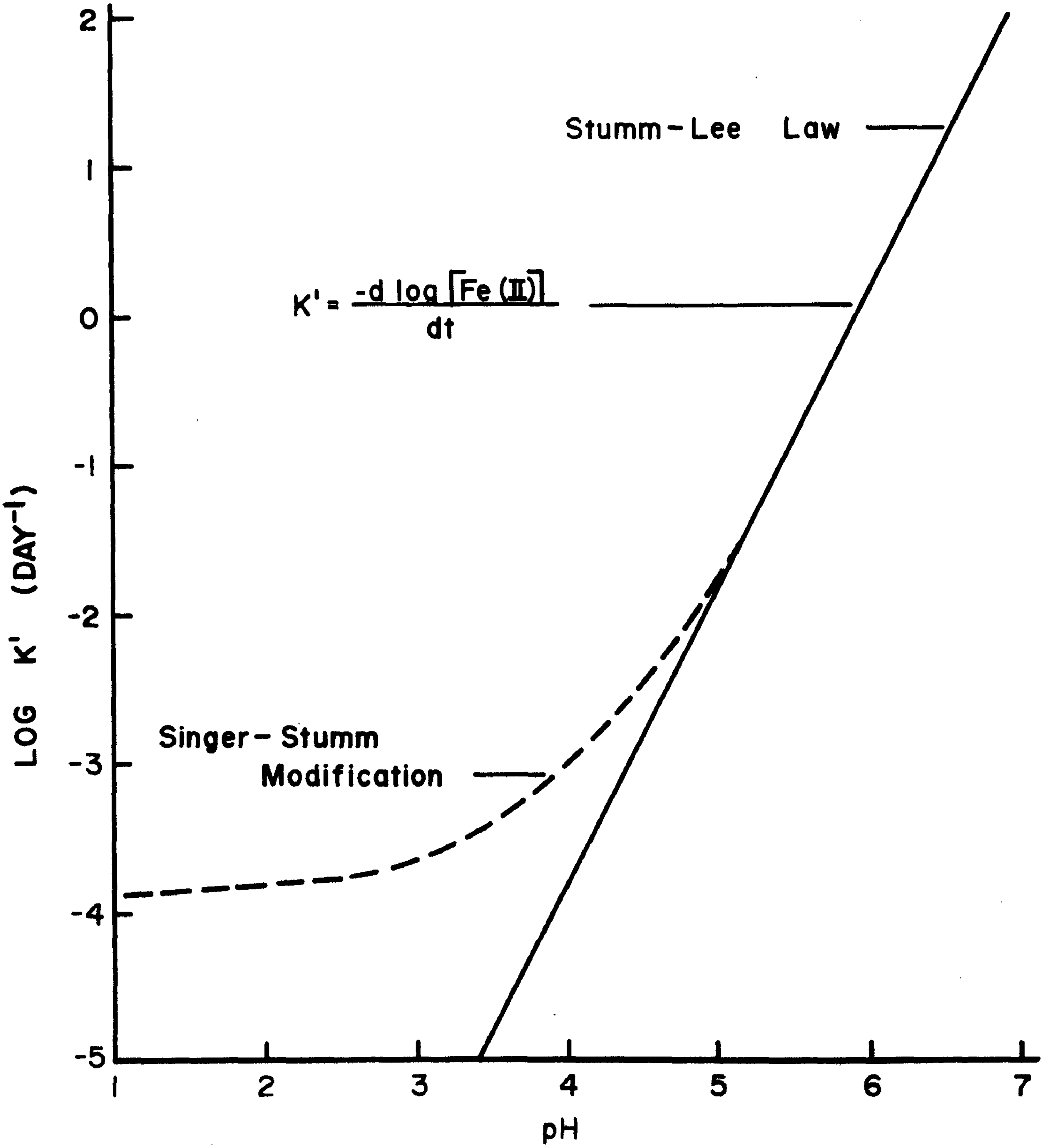


Figure 3-3. Iron (II) Oxidation Rate at pH 2-7

(after Singer and Stumm (51))

"Operation Yellowboy" was a program developed by the Pennsylvania Department of Mines and Mineral Industries(9) to demonstrate the treatment of acid mine drainage by lime neutralization. The treatment consisted of three steps in the following order: neutralization with lime in a flash mixer, aeration for iron oxidation, and clarification by a thickener. The sludge from the thickener was further treated by centrifuging. The pilot plant was mounted on a semitrailer and taken to six different mine drainage locations. Thus, the system was tested under a wide variety of conditions.

Results of this study showed that the acid mine drainage could be neutralized such that no acidity was present and the pH was greater than 6.5. Iron concentration could be reduced to less than 7 mg/l. However, the calcium and hardness concentration increased and the sulfate concentration remained relatively constant.

Approximately 30 minutes of detention time was necessary in the aeration tank, while the detention time in the thickener varied from site to site and ranged from 7.35 to 13.3 hours. The amount of detention time could not be related to the acidity or iron concentration of the raw water. Thickener-sludge solids varied from 0.9 to 4.98 percent. A drum filter was able to concentrate the sludge to between 12 and 26 percent solids. Gypsum was successful as a filter aid.

As part of the "Operation Yellowboy" studies(42) flocculating agents were tested. Although some flocculents increased the settling rate, they did not necessarily increase the solid concentration of the thickener underflow. Flocculents were also found to be pH sensitive. Centrifuge and filtration tests demonstrated that within a few hours after the floc was formed and settled it apparently went "stale".

In Figure 3.4 the cost data obtained from "Operation Yellowboy"(9) are reported. These data show that the unit cost increases as the concentration of acidity and iron in the raw water increases and decreases as the amount of water treated increases.

Deul and Mihok (13) treated acid mine drainage in a reactor (rotating drum) and found that neutralization took place very rapidly. The lime treated acid mine drainage did not produce a sludge that settled as rapidly or produced as dense a sludge as limestone treated acid mine drainage. Up to 15 hours were required to reduce the sludge solids volume to 10 percent.

Holland, et al.,(27) reported on the operation of a 230 gpm pilot lime neutralization plant treating a mine discharge with high acidity and ferrous iron concentrations. A lime slurry was fed to the water. A reaction time of 30 seconds in a pipe was sufficient for neutralization to occur. Enough lime was added to increase the pH to 10.5. According to the titration curves obtained by Holland, et al.,(27) a pH of this magnitude was necessary to assure complete removal of iron. Neutralization was followed by aeration to oxidize the ferrous hydroxide to the insoluble ferric hydroxide form. Following aeration, the water passed to a settling basin having 1.5 days retention time. Approximately 33 percent of the plant inflow remained as sludge in the settling basin and was pumped to a sludge basin. Here, the sludge was dewatered further by settling and decanting of the clear supernatant and by seepage and evaporation. In a three-week period the

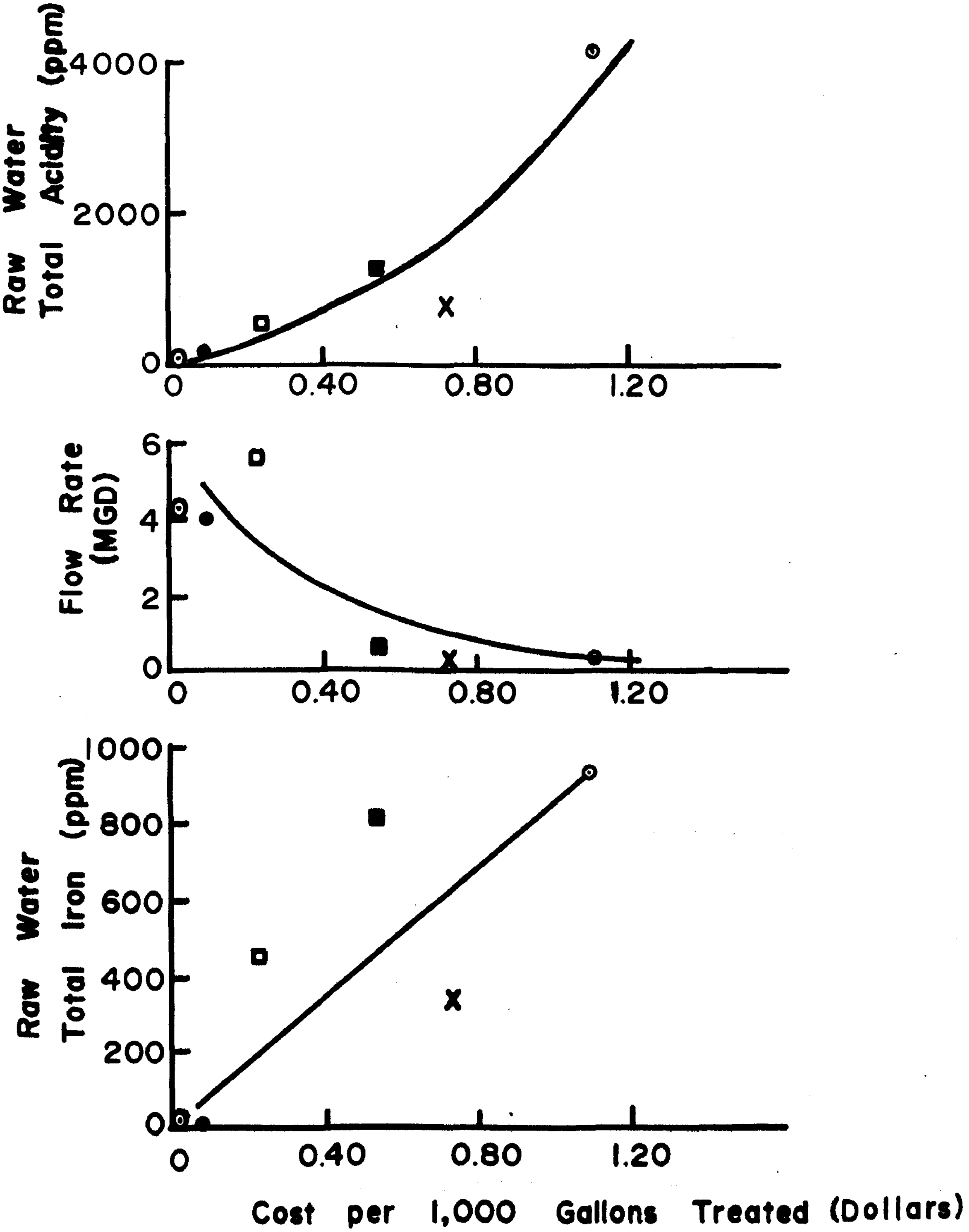


Figure 3-4. Cost of Treating Acid Mine Drainage

(Data from Charmbury, Maneval (9))

sludge had a solids content of about 20 percent. The final sludge volume in the sludge basin was three percent of the mine discharge pumped to the plant. Table 3.3 presents an analysis of the residual sludge. Based on the results obtained in this study, Holland, et al.,(27) estimated the cost of treating mine drainage to range from 18.9 to 62.5 cents per 1,000 gallons. Cost was dependent on plant capacity and the concentration of acidity and iron. In Figure 3.5 these data are plotted.

Birch(1) reported on laboratory bench tests conducted to determine the most efficient and economical oxidation-neutralization methods for different types of mine waters. He found that mine water that had aged in a holding pond had a faster reaction time and the iron precipitated out much more readily. The removal of carbon dioxide by loss to the atmosphere, in the holding pond may have been the reason for the improvement. Further, he found that sludge volume was about 10 percent of the original flow upon immediate settling and, after several days, would compact to five percent. When precipitated sludge was recycled to the influent water, the reaction and settling times were reduced about 50 percent and a larger and heavier floc was produced. Mihok, et al.,(40) conducted studies on the settling and compaction of mine drainage treated with lime and limestone to a pH of 6.9. As shown in Table 3.4 the sludge from the limestone treated water settled faster and compacted more than the sludge from the lime treated water.

Full scale lime acid mine drainage treatment plants are being placed in operation in increasing numbers. Tybout(60) reported 71 permits for the construction of such plants in Pennsylvania during 1967. In 1966, Jones

TABLE 3.3

ANALYSIS OF SLUDGE FROM MINE NEUTRALIZED AERATED TREATED ACID MINE DRAINAGE*

Item	Percent
Fe^{+++}	19.2
Al^{+++}	4.0
Ca^{++}	12.0
Mg^{++}	0.2
CO_3	3.9
SO_4	29.4
Insoluble	0.5
Water of Hydration	19.6
Specific Gravity	1.10
Total Solids	13.9

* From Holland, et al.,(27)

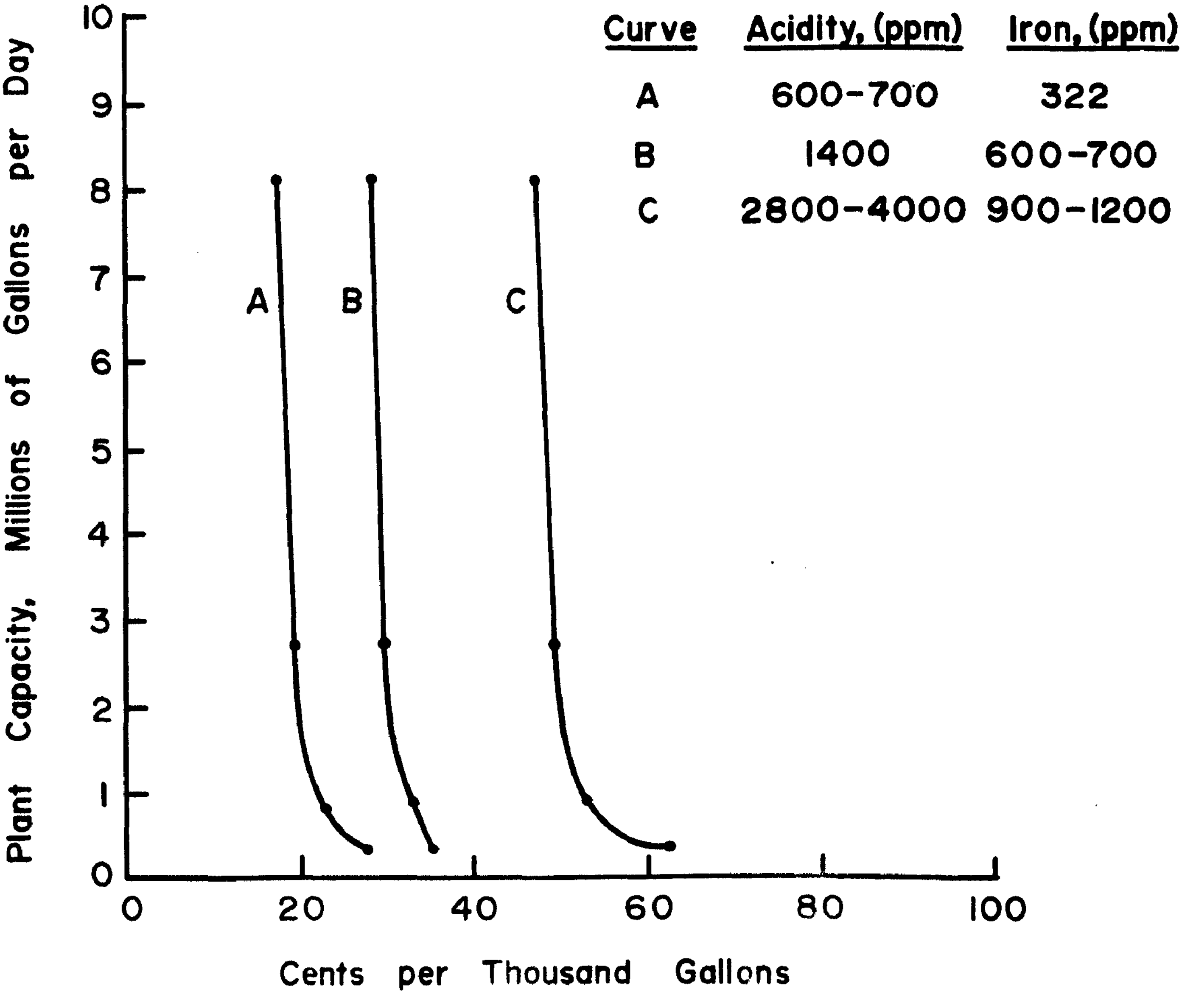


Figure 3-5. Estimated Cost of Lime Neutralization

(Data from Holland, et al.[(27)])

TABLE 3.4

HEIGHT OF SETTLED SOLIDS OF LIME AND LIMESTONE-TREATED WATERS*

Days	Percent of Total Volume[1]	
	Lime	Limestone
0	100.0	100.0
1	12.0	2.6
5	6.9	2.3
11	6.7	2.1
15	6.7	2.0
20	6.7	2.0
43	6.6	1.9

[1] As percent of total volume (pH = 6.9, no detectable iron in supernatant).

* After Mihok, et al.,(40)

and Laughlin(10), (29) began operation of a plant in Washington County, Pennsylvania. Mine drainage from a 10-inch borehole is placed in a 750,000-gallon raw-water surge lagoon (5 day storage). Considerable iron oxidation is reported to occur in the lagoon which reduces the lime requirements. Approximately 150,000 gpd are withdrawn from the lagoon and mixed with a slurry of hydrated lime. The treated water then flows through a small tank containing a pH probe. The pH probe is connected to equipment that controls the rate of lime feed and to a raw-water input valve that automatically shuts the system off if the pH is too high or low. Subsequently, the water flows to a 90,000-gallon settling lagoon where the sludge is removed. Once a week the sludge is pumped from the lagoon and hauled away to a bore hole, where it is discharged into an abandoned deep mine. Approximately 4,000 gallons per day of sludge are produced. Lime demand is two to five pounds/1,000 gallons for a raw water supply having a pH of 3.5, acidity 200 to 560 mg/l and ferrous iron 100 mg/l. A chemical analysis of the sludge resulted in the following: $CaSO_4$ - 40 percent, $MgSO_4$ - 5 percent, CaO - 3 percent, MgO - 1 percent, Fe_2O_3 - 15 percent, Mn_2O_3 - 4 percent, SiO_2 - 20 percent, and Al_2O_3 - 12 percent. The sludge contained six percent solids. Drying of the sludge increased the solids content to sixteen percent. Tests indicated that recycling the sludge and mixing it with the feed water did not increase the sludge solids content. Chemical flocculents did not increase the solids content either.

A 7,000,000 gpd discharge at a Jones & Laughlin(10), (29) mine in Pennsylvania is treated with slaked quicklime and passed to an aeration tank. Surface aerators are used. Overflow from the aerator is to two impoundment basins. The basins are used alternately to permit the sludge in the inactive basin to dry out for better compaction. Sludge is not removed from the basins and they were designed for 30 years of storage.

Only very limited work has been done on sludge handling and disposal. In "Operation Yellowboy"(9) studies were made on centrifuging and filtering the sludge. Johns-Manville(22) had some success with precoat filters. However, disposal of the thickened sludge is still a critical problem.

Lime treatment of acid wastes has been practiced for many years in the plating industry; and this experience is applicable to acid mine drainage in many cases. The major problems in lime treatment are the oxidation of the ferrous iron, the settling rate and density of the sludge, and the disposal of the sludge. Table 3.5 presents design considerations for a lime neutralization plant.

Limestone-Lime

Hoak, et al.,(25) found that neutralization could be accomplished better when a combination of limestone and lime was used than when either was used alone in treating pickle liquor. Pulverized limestone was used to neutralize the acid and precipitate part of the iron and lime to complete the treatment. The split treatment was found to be more economical than lime alone. Deul and Mihok(13) reported that, when using limestone alone, long reaction periods were needed to treat high ferrous iron waters, while with lime alone the same waters were rapidly neutralized but larger amounts of reagent were required to precipitate all the iron. When limestone and lime were used together the time required to oxidize the ferrous iron was reduced and the sludge settling rate and density of the settled sludge were better than for lime treatment alone and similar to limestone treatment.

TABLE 3.5

LIME NEUTRALIZATION DESIGN CONSIDERATIONS*

Reaction time (neutralization)	0.5 - 1.0 minutes
Sludge settling detention time	7.5 hours or more
Sludge volume	10 - 35 percent of plant influent
Sludge solids	1 - 5 percent
Sludge thickening in a basin (detention)	3 to 4 weeks
Sludge volume after thickening in basin	3 to 15 percent of plant influent
Sludge solids after thickening in basin	10 to 20 percent

* Ferrous iron to be removed in a separate operation.

Thus, split treatment had some advantage over single treatment.

Research Needs

Although more information is available on the neutralization of acid mine drainage than on any other treatment method, many areas need additional study. Some neutralization processes need further laboratory investigations; however, many are suitable for pilot plant evaluation or large scale application.

Needed neutralization research areas are:

Analytical tools to evaluate acid mine drainage and determine the amount of alkaline agent required, detention time to provide adequate settling, and improved sludge characteristics.

Methods for utilizing low cost alkaline agents to accomplish higher removal efficiencies e.g., limestone.

Methods of improving iron (II) oxidation and removal.

Methods for improving the settling and density characteristics of sludges resulting from chemical treatment.

Methods for concentrating sludge.

Methods for disposing of the sludge, e.g., to deep mines and surface mines for possible additional acid mine drainage control.

Byproduct recovery from sludges and/or sludge reuse.

Process analyses to determine how neutralization can fit in with other processes for higher quality water at lower costs to meet all water use requirements.

Optimization of neutralization process.

Cost analyses of the various neutralization processes.

FWPCA Research Program

The Federal Water Pollution Control Administration has the following research and development activities in the neutralization of mine drainage area:

Grant to the Pennsylvania Department of Mines and Mineral Industries and its subcontractor, Pennsylvania State University, for a project titled "Construction of Mine Water Treatment Plant at Hollywood, Pennsylvania." Grant Number WPRD-34.

Grant to the Pennsylvania Department of Mines and Mineral Industries and its subcontractor, Bituminous Coal Research, Incorporated, for a project titled "Optimization and Development of Improved Chemical Techniques for the Treatment of Coal Mine Drainage." Grant Number WPRD-63.

Grant to the Pennsylvania Department of Mines and Mineral Industries and its subcontractor, Johns-Manville Products Corporation for a project titled "Neutralization and Precoat Filtration of Concentrated Sludges from Mine Waters." Grant Number WPRD-150.

Grant to the Peabody Coal Company for a project titled "Lime/Limestone Neutralization of Acid-Mine Drainage." Grant Number WPRD-272.

4. IRON REMOVAL

Iron removal is an important aspect in the treatment of mine drainage. Iron must be removed to meet stream standards. Also, it is one of the major problem areas in treatment. Ferrous iron (Fe II) presents a number of problems to the neutralization of acid mine drainage; for example, oxidation of ferrous iron produces acid (see equation 2-4) and lowers the pH, thus increasing the amount of alkaline agent required. Fe (II) removal is a limiting factor in the neutralization process. Ferric iron (Fe III) presents problems in various other treatment processes; for example, it fouls the membranes of an electrodialysis unit and coats the exchange resin in an ion exchange process. Since iron removal is often a separate step in the treatment of mine drainage, and because it is a critical problem, it warrants a separate section in this report.

Chemistry of Ferrous Iron Oxidation

Stumm and Lee(56) reported that the rate of iron (II) oxidation at pH values of 6 and above depends on the pH, temperature, concentration of dissolved oxygen, and certain catalysts. The rate of oxidation was found to proceed 100 times faster at pH 7 than at pH 6. Catalysts such as Cu^{+2} in trace quantities, and anions which form complexes with Fe (III) increase the reaction rate significantly while small amounts of Fe (III), Cl^-, and SO_4^{-2} had no effect on the reaction rate.

The reaction of Fe (II) with oxygen generally leads to ferric oxides or hydroxides, the stoichiometric relationship being:

$$\text{Fe (II)} + \tfrac{1}{4} O_2 + 2\tfrac{1}{2} H_2O \longrightarrow \text{Fe } (OH)_3 \text{ (s)} + 2H^+ \qquad (16$$

Stumm and Lee concluded that the rate of oxidation was first order with respect to Fe (II) and independent of the Fe (III) concentration. Further, the rate was dependent on the partial pressure of oxygen to the first power. The rate increased as the pH increased due to the influence of the hydroxyl ions and as the temperature rose.

Singer and Stumm(51) conducted ferrous iron oxidation studies under conditions similar to acid mine drainage situations. One aspect of their study was to determine the effect of various material found in the mine environment on iron (II) oxidation. The Stumm-Lee rate law was found to be not applicable at pH's less than 4.5. Between pH 4.5 and 3, a transition occurs; at pH 3 and below, the rate is relatively independent of pH (Figure 3.3). The rate of iron (II) oxidation was found to be greater in sulfate free solutions than in solutions containing 10^{-3} to 10^{-5} M of sulfate. On the premise that clay surfaces might play a role in the oxidation of Fe (II), a study was undertaken to determine the effect of silica (SiO_2), aluminum oxide (Al_2O_3), bentonite and kaolinite on the oxidation kinetics. It was postulated that those surfaces may play a specific role due to their hydroxylated surface, Si-OH or Al-OH groups, or a general role resulting from surface absorption and localized increased reactant concentrations. Aluminum, silica and bentonite was found to catalyze the Fe (II) oxidation, but only at very large surface concentrations, which are not normally found in mine drainage, thus, these materials did not appear to be of significance in explaining the rapid Fe (II) oxidation rate observed in acid mine waters in the field. Kaolinite clay, although it gradually neutralized the acid, showed no catalytic influence. Colloidal ferric hydroxide and soluble Al (III) showed no catalytic effect. Powdered charcoal increased the rate only slightly. A series of tests was conducted to determine if the oxidation rate was greater in a dark environment, similar to the inside of an abandoned mine, or under normal light conditions. The oxidation proceeded at a rate two to three times faster in the light. In summary, Singer and Stumm were unable to explain on a chemical basis the high rate of iron (II) oxidation observed under field conditions. They did not evaluate the microbial aspects.

Kim(31) conducted studies of the effect of aeration upon the oxidation of ferrous iron in acid mine water. She concluded that the rate of oxidation increased until the solution is saturated with oxygen. Aeration beyond oxygen saturation does not increase the rate of iron (II) oxidation.

Removal of Ferrous Iron

Simpson and Rozelle(50), in a review of methods available for removal of iron from solutions, listed the following:

Precipitation of iron by the addition of an alkaline agent
Electrolysis of iron (II)
Aeration-filtration or aeration-settling
Ultrasonic energy
Ozone oxidation
Irradiation and photo-oxidation

Other methods could be added to this list, such as:

Chlorine oxidation

Potassium permanganate treatment

Biochemical oxidation

Precipitation by Addition of an Alkaline Agent

The addition of an alkaline agent such as hydrated lime, sodium carbonate or sodium hydroxide will result in the conversion of ferrous sulfate to ferrous hydroxide and increase in pH. At the higher pH iron (II) will oxidize rapidly to insoluble ferric hydroxide. Even where alkaline mine discharges with high ferrous content are found, an alkaline agent is sometimes added to increase the pH and thus increase the oxidation rate. Kosowski and Henderson(32) reported a situation in West Virginia where the mine discharge had a pH of 6.5, an alkalinity of 252 mg/l, and iron of 109 mg/l. The mine drainage was treated with lime to increase the pH for rapid oxidation and to prevent a depression of the pH as a result of the oxidation of the ferrous iron. Aeration and settling followed lime addition. Holland, et al.,(27) applied lime to an acid discharge high in ferrous iron to remove the iron. They found the pH had to be raised to as high as 10 to obtain iron removal.

Electrolysis of Iron (II)

Direct current electrolysis of iron (II) sulfate solutions causes the hydrogen ions to be discharged along with iron (II) at the cathode. Discharge of hydrogen ions causes the pH in the area surrounding the cathode to rise, resulting in the precipitation of iron (II) hydroxide. The electrochemical reactions at the anode are not well defined, but it appears iron (II) loses an electron to form iron (III) and that Fe (III) is hydrolyzed.(50) The reactions of this process are:

Cathode

$H^+ + e^- = \frac{1}{2}H_2$ (17

$Fe^{+2} + 2e^- = Fe$ (18

$Fe^{+2} + 2H_2O = Fe(OH)_2 + 2H^+$ (19

Anode

$H_2O = \frac{1}{2} O_2 + 2H^+ + 2e^-$ (20

$Fe^{+2} = Fe^{+3} + e^-$ (21

$Fe^{+3} + 3H_2O = Fe(OH)_3 + 3H^+$ (22

The electrolysis process has been studied in the laboratory but has not been evaluated on mine drainage in the field.

Aeration

A common method of iron (II) removal is aeration to oxidize the iron to the ferric form, followed by hydrolysis to ferric hydroxide, or the formation of the hydroxide followed by aeration, as in equation 23. The precipitated iron is then removed by settling or possibly filtration. According to equation 23, one mole of oxygen reacts with four moles of ferrous hydroxide to produce four moles of ferric hydroxide or one pound of oxygen will oxidize 9.1 pounds of ferrous hydroxide.

$4Fe\ OH^+ + 4\ OH^- + 6H_2O + O_2 \longrightarrow 4Fe(OH)_3 + 4H_2O$ (23

Ferrous Hydroxide + Water + Oxygen = Ferric Hydroxide + Water

As indicated earlier, the oxidation of iron (II) at low pH's is very slow, and therefore, it is advantageous to raise the pH by the addition of an alkaline agent.

Holland, et al.,(27) reported studies conducted on the aeration of acid mine drainage previously treated with lime. They listed the following three ideal conditions for aeration: maximization of the surface areas between air bubble and solution for a given quantity of air (minimize the bubble size), maximization of the amount of water which contacts the air, and maximization of the amount of time the air is in contact with the water. Three types of dispersion devices were evaluated for obtaining small bubble size. A large number of small dispersion devices produced a smaller bubble than a single large device because the velocity of air discharge was decreased. The geometric placement of the dispersion devices was also important.

Under field operation, Holland, et al.,(27) found that dispersion type aerators required daily cleaning with acid to remove the iron deposit which built up on the device. Surface aerators have also been used successfully to oxidize the iron (II) in holding ponds(32), (10).

Once the iron is converted to the ferric hydroxide form, it is usually removed by sedimentation in a settling tank or pond. The sludge usually settles slowly, has a low solid content, and presents a disposal problem.

Ultrasonic Energy

Ultrasonic energy has been used to oxidize iron (II) sulfate(50). Under the influence of ultrasound, hydrogen peroxide is generated which may oxidize the iron (II) through the formation of free radicals, for which oxygen is not needed, or the waves may catalyze the oxidation reaction. The rate of oxidation is a function of the intensity of the waves. This method is still in the research phase.

Radiation

Oxidation of iron (II) by alpha, beta, and gamma radiation is believed to occur by the same mechanism as ultrasonic oxidation. One major problem with inoxidation is the short depth of penetration of the water by the inoxidating particles. Steinberg, et al.,(53) studied the removal of iron from artificial mine drainage with high-energy radiation and found that the ferrous iron could be removed in a relatively short time from a mine water that had been treated by limestone neutralization to a pH of 5.7 and then exposed to Co^{60} gamma radiation. Iron removal was much slower in the non-irradiated water. Thus, radiation treatment appeared to act as a catalyst. The rate of ferrous iron removal was proportional to the square root of the intensity. An intensity of 4.3 megarads per hour obtained a rate of 45 ppm of ferrous iron removal per minute.

The authors suggest that a chain oxidation mechanism occurs which includes a biradical chain termination step. The chain carrier may be hydroxyl radicals. Sludge from the limestone-radiation process yields a readily separated crystalline particle, while the limestone treatment produced a flocculent precipitate which was difficult to handle.

Later studies by Steinberg, et al.,(54) with a sample of actual acid mine drainage resulted in the following conclusions: (1) G-values* ranging up to 285 were obtained at low intensities (130,000 rads per hour). The G-values decreased with decreasing temperature and were found to be three to five times less at 10° C. (2) At high intensities of 3.5×10^6

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*G-value is the radiation yield and is defined by the expression: G-value = 1.04 Q/I, where G-value is molecules (or atoms) of Fe^{++} oxidized to Fe^{+++} or removed from solution per 100 eV of radiation deposited, Q is rate of Fe^{++} removed (ppm/minute), and I is radiation intensity Co-60 gamma field (megarad per hour).

rads per hour, a G-value of 12 was obtained, and the rate of Fe (II) removal was 20 times higher than the control, and temperature had relatively little effect. (3) Increasing the pH and aeration increased the radiation yield and rate of Fe (II) removal and (4) the preliminary cost analysis indicated that if iron (II) could be removed at a rate of 10 ppm per minute with limestone treatment alone, then it would be difficult for the radiation treatment to compete on an economic basis solely.

Ozone

Ozone is a powerful oxidizing agent which is produced by passing an electrical discharge through oxygen. The reaction of ozone with iron (II) is:

$$2\ Fe^{+2} + O_3 + 2H^+ \longrightarrow 2\ Fe^{+3} + O_2 + H_2O \qquad (24$$

Simpson and Rozelle(50) reported that the rate of oxidation of iron (II) was independent of the concentration of iron (II) and temperature and dependent on the rate of flow of ozone through the solution. The oxidation of an acid mine drainage sample is illustrated in Figure 4.1. Terminal pH was approximately 2.8. The milliequivalent of iron (II) oxidized per milliequivalent of ozone was about 0.85 in acid mine drainage samples (Figure 4.1). Ozonation of iron (II) appears promising from laboratory studies, but has not been attempted on a pilot scale.

Oxidizing Agent

Oxidizing agents such as chlorine, iodine, and potassium permanganate have been used in the water treatment field for the oxidation of iron (II). The oxidation process is usually followed by filtration to remove the precipitated iron. These agents have had very little evaluation

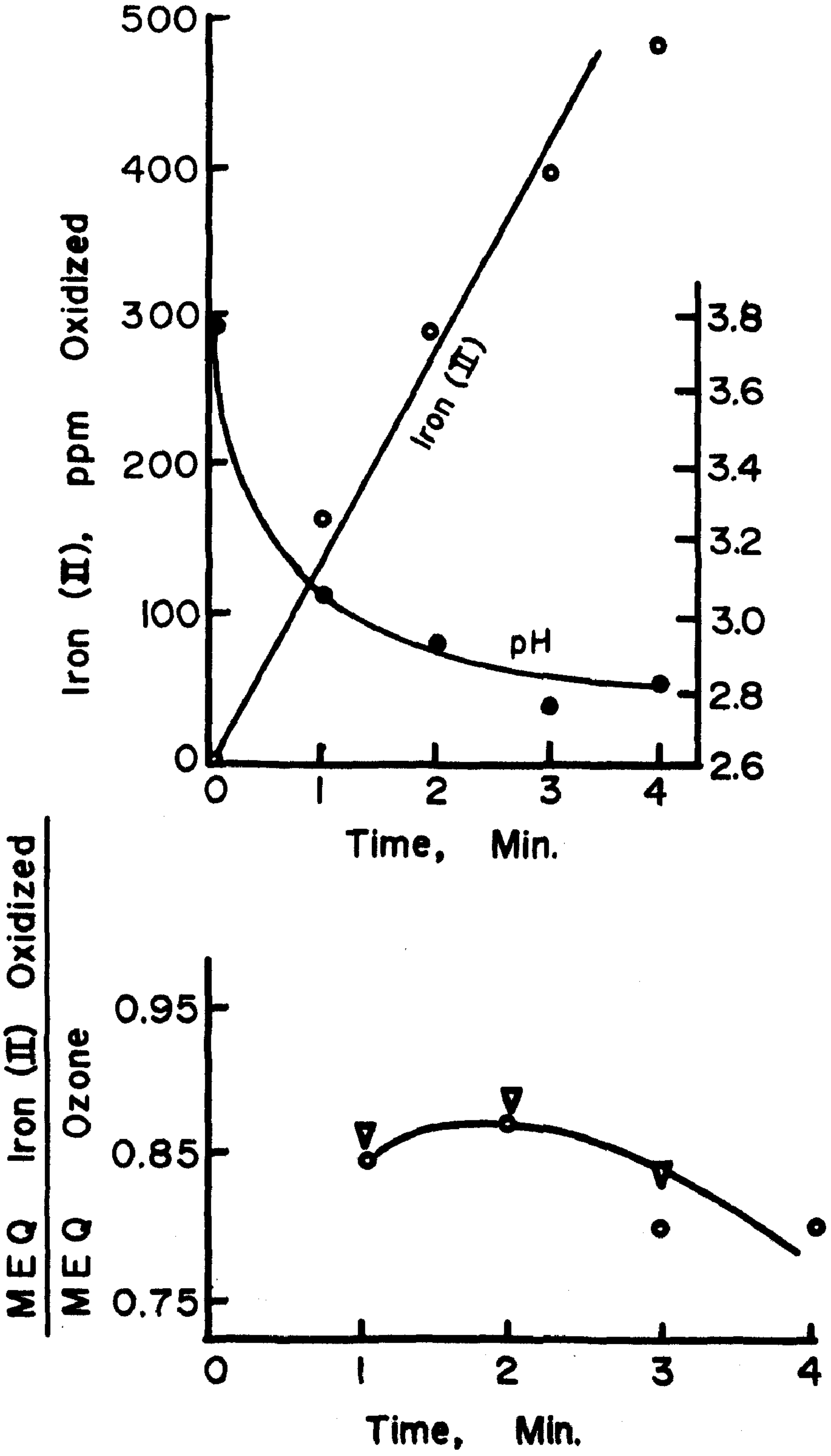

Figure 4-1. Ozone Oxidation of Iron (II) in AMD (after Simson and Rozelle(50))

for treating mine drainage. Birch(1) reported that studies were conducted on potassium permanganate and calcium hypochlorite. Potassium permanganate was found to react slowly in oxidizing the iron and was expensive. Calcium hypochlorite was found to do an excellent job of converting ferrous to ferric iron.

Biochemical Oxidation

Glover(19) has developed a biochemical oxidation process for ferrous iron removal. An autotrophic bacteria that derives its energy from the promotion of an inorganic reaction and its cellular carbon from carbon dioxide is used. These bacteria promote the oxidation of ferrous iron. An activated sludge type process is used. During startup, the acid mine drainage is seeded with an ochreous deposit from a mine and fed to an aeration chamber. From this chamber, the waste goes to a settling tank. The sludge is collected, recirculated, and mixed with the incoming acid mine drainage. Once the process is started, the seed is no longer necessary. The rate of oxidation was much greater in the activated sludge system than in a system of aeration alone. In general, the rate of oxidation was first order to the ferrous iron concentration. The quantity of activated sludge produced in a pilot plant remained adequate and a small surplus occurred only at temperatures in excess of 20° C. Chemical analyses of the influent and effluent showed that the ferrous iron was reduced from levels of 100 to 300 mg/l to less than 5 mg/l, and that a corresponding increase occurred in the ferric iron. The activated sludge process is followed by limestone neutralization to remove the ferric iron.

Sulfide Treatment

Zawadzki and Glenn(62) conducted studies on the removal of iron with sulfide. As indicated in equations 25 thru 27, both ferric and ferrous iron can be removed in this manner.

$3H_2S + Fe_2(SO_4)_3 \longrightarrow Fe_2S_3(ppt) + 3H_2SO_4$ (25

Hydrogen Sulfide + Ferric Sulfate → Ferric Sulfide + Sulfuric Acid

$H_2S + FeSO_4 \longrightarrow FeS(ppt) + H_2SO_4$ (26

Hydrogen Sulfide + Ferrous Sulfate → Ferrous Sulfide + Sulfuric Acid

$4Na_2S + Fe_2(SO_4)_3 + Fe\ SO_4 \longrightarrow Fe_2S_3(ppt) + FeS(ppt) + 4Na_2SO_4$ (27

Sodium Sulfide + Ferric Sulfate + Ferrous Sulfate → Ferric Sulfate +
Ferrous Sulfate +
Sodium Sulfate

The pH must be above 5 for the hydrogen sulfide to be effective. One disadvantage of the use of hydrogen sulfide is the formation of sulfuric acid. Thus, additional alkaline must be used to counteract this acid.

Research Needs

A number of the ferrous iron oxidation schemes considered have shown promise; however, the majority have not been tested on a pilot plant scale. Only aeration and precipitation with an alkaline agent have received any degree of testing. Each of these methods needs to be studied under field conditions to determine the system's efficiency, operating problems, factors affecting operation, best conditions for use, and its economics. The use of catalysis to increase the rate of iron removal needs to be studied further. Microbiological removal of iron requires study. The possibility of developing a magnetic sludge needs evaluation.

FWPCA Research Program

The Federal Water Pollution Control Administration has the following research and development activities in the removal of iron from mine drainage:

Grant to Bituminous Coal Research, Incorporated for a project titled, "Sulfide Treatment of Acid Mine Drainage," Grant Number WPRD-271.

Grant to Continental Oil Company for a project titled, "Microbiological Removal of Iron from Mine Drainage Waters," Grant Number WPRD-36.

Contract to Harvard University for a project titled, "Oxidation of Iron in Acid Mine Waters," Contract Number PH 36-66-107.

Grant to Pennsylvania Department of Mines and Mineral Industries and its subcontractor, Pennsylvania State University, titled "Construction of Mine Water Treatment Plant at Hollywood, Pennsylvania," Grant Number WPRD-34.

Grant to Pennsylvania Department of Mines and Mineral Industries and its subcontractor, Bituminous Coal Research, Incorporated, titled, "Optimization and Development of Improved Chemical Techniques for the Treatment of Coal Mine Drainage," Grant Number WPRD-63.

Grant to Pennsylvania Department of Mines and Mineral Industries and its subcontractor, Applied Science Laboratories, Incorporated, titled, "Feasibility of the Purification of Acid Mine Water by a Partial Freezing Process," Grant Number WPRD-265.

Contract to Syracuse University Research Institute titled, "Biological Treatment of Acid Mine Water," Contract Number WP-01460.

5. ION EXCHANGE TREATMENT

Ion exchange can be used to remove any number of undesirable constituents in mine drainage. In combination with neutralization, lime softening, and other processes, a highly refined water can be obtained. Ion exchange appears to be well suited to the removal of calcium and sulfate, which are not removed by neutralization processes. While a number of ion exchange schemes have been proposed for treating mine drainage, none have been tested on actual mine wastes.

Principles of Ion Exchange

Ion exchange has been defined as a reversible exchange of ions between two phases, usually a solid and liquid in which there is no substantial change in the structure of the solid. The solid is the ion exchange material or resin and is based upon a matrix composed of addition copolymers. This structure gives a maximum resistance to oxidation, reduction, mechanical wear and breakage, and is insoluble in common solvents.

The nature of the ionizable groups attached to the hydrocarbon network determines the chemical behavior of an ion exchange resin. In general, there are four major types of ion exchange resin; namely, strongly and weakly acidic (cation) resins and strongly and weakly basic (anion) resins. Of these resins, the weakly basic anion exchange resins appear best suited for mine drainage treatment because of their acid absorbing properties. The weakly basic resins are often used in the removal of free acids from solution and have ion exchange activity only below pH 7. However, schemes for using combinations of all the resins have been developed.

Although a variety of weakly basic exchanges are available, the more common of these contain mixtures of secondary and tertiary amine groups. The following characteristics have been reported for these resins(15)

Chemistry analogous to that of ammonia.

Free-base form of resin absorbs strong acid (HCl, H_2SO_4, HNO_3) to form hydrochloride, bisulfate, nitrate, etc.

Acid form of weak-base resins liberates free acid when in contact with water. The stronger the acid, the greater the tendency toward hydrolysis.

Acid forms can be interchanged; e.g., sulfate will replace chloride.

Complete regeneration to free-base form is achieved with nearly stoichiometric quantities of alkali.

Regeneration to free-base form can be carried out with ammonia or soda ash as well as with caustic soda.

Capacity to strong acid increases with the valence of the anion.

The weak-base resins can only form very unstable salts with weak acids; therefore, they cannot effectively remove carbon dioxide from water, though they do remove a limited amount. Illustrations of weak-base resin usage are shown in equations 32 and 37.

Strong-base resins have quaternary ammonium groups in their structure. They will remove salts by exchanging hydroxyl ions for other anions as in equations 28 and 29.

$$RN(CH_3)_3 + OH^- + NaCl \longrightarrow RN(CH_3)_3 + Cl^- + NaOH \qquad (28$$

$$(RNR^1_3)OH + H_2SO_4 \xrightarrow{\qquad} (RNR^1_3)2SO_4 + 2H_2O \qquad (29$$

Unless removed before ion exchange treatment, iron could cause a troublesome problem because of the exchange would result in ferric and/or ferrous hydroxide which would precipitate and coat the exchange resin. Removal of these precipitates would be difficult.

Weak-acid resins usually contain carboxyl groups in their structure. They cannot split neutral salts and are operable in the pH range above 7. These resins do not appear to be applicable to mine drainage.

Strong-acid resins are commonly composed of sulfonated styrene and divinylbenzene. In the hydrogen form they are used to remove cations from solution as in equation 30. Sulfuric acid in excess of the stoichiometric amount is required for good regeneration. Calcium and other metal ions can be removed as in equation 31. Sodium chloride is usually used for regeneration in this case.

$$RSO_3^-H^+ + NaCl \xrightarrow{\qquad} RSO_3^-Na^+ + HCl \qquad (30$$

$$3(RSO_3H) + Metal^{+++} \xrightarrow{\qquad} (RSO_3)_3\ metal + 3H^+ \qquad (31$$

These resins could be useful in removing the troublesome cations found in mine drainage.

Ion Exchange Treatment of Mine Drainage

A number of schemes for treating acid mine drainage by ion exchange have been suggested or seem feasible. These are reviewed on the following pages.

The weak-base anion resin can be used in the bicarbonate form by utilizing carbon dioxide during a carbonation step to produce $RHCO_3$. Once the resin is in the bicarbonate form, mine drainage is passed through it and the following conversion occurs:

$$Mx(SO_4) + 2RHCO_3 \longrightarrow R_2SO_4 + Mx(HCO_3)x \qquad (32$$

R = Ion Exchange Resin, M = Metal Ions

For example, the equation for ferrous sulfate would be

$$Fe(SO_4) + 2RHCO_3 \longrightarrow R_2SO_4 + Fe(HCO_3) \qquad (33$$

The resin once exhausted is regenerated with CO_2 and ammonium hydroxide (NH_4OH). Ammonium hydroxide is passed through the column first, then water saturated with CO_2; this results in the following conversion:

$$R_2SO_4 + 2NH_4OH \longrightarrow 2ROH + (NH_4)_2SO_4 \qquad (34$$

$$ROH + H_2CO_3 \longrightarrow RHCO_3 + H_2O \qquad (35$$

The waste is therefore, ammonium sulfate.

Pollio and Kunin(43) conducted studies on this process. In their scheme the ion exchange process was followed with aeration to expel CO_2, and to precipitate iron, aluminum, and manganese as the insoluble hydrous oxides. Some calcium and magnesium also coprecipitated or occluded with the hydrous oxides as $CaCO_3$ and $Mg(OH)_2$. After aeration a bicarbonate water with a pH of 8.0 to 8.2 containing calcium and magnesium hardness remains.

$$Ca(HCO_3)_2 + Ca(OH)_2 \longrightarrow 2\ CaCO_3 + 2H_2O \qquad (36$$

Pollio and Kunin(43) operated the ion exchanger as an upflow unit to prevent precipitation problems. Their study was on a small laboratory scale using a synthetic acid mine drainage water. The process worked successfully under this condition. Cost of the ion exchange process was estimated as 44 cents per 1,000 gallons for a 100,000 gpd plant and 38 cents per 1,000 gallons for a 1 mgd plant. The cost of ion exchange would increase as the anion content increased. They suggest that for economic treatment the ion exchange process should be limited to mine waters with an anion content below 4,000 ppm expressed as $CaCO_3$.

Disposal of the waste regenerant (primarily ammonium sulfate) from the ion exchange unit might present a problem unless the regenerant can be used as a fertilizer or put to some other use. A process could be developed where lime was added to the waste regenerant and NH_3 recovered and reused.

Another method would be to use the weak-base anion resin in the chloride cycle. Mine drainage as it passes through the resin is converted as follows:

$$Mx(SO_4) + 2RCl \longrightarrow MxCl + R_2SO_4 \qquad (37$$

The resin once exhausted is regenerated with NaCl as follows.

$$R_2SO_4 + 2NaCl \longrightarrow 2RCl + Na_2SO_4 \qquad (38$$

The effluent water from this process would contain high concentrations of ferrous chloride. With aeration the iron could be removed as ferric hydroxide. The chloride that remained would be somewhat difficult to remove.

The waste regenerant, which would be primarily sodium sulfate, would create some disposal problems.

The chloride cycle would be cheaper to operate than the bicarbonate cycle because of the lower cost of the regenerating agent.

Other ion exchange processes may have some merit. One process suggested(28) for sulfuric acid pickle liquor calls for the use of a cation exchange resin. The resin bed would remove the iron and produce sulfuric acid. During the regeneration step, the iron is removed from the resin as iron nitrate. Upon heating to 350° F, iron oxide is formed. The iron oxide and sulfuric acid are then marketable by-products. However, the concentration of iron and acid in acid mine drainage may not be sufficient to be economically recovered.

Use of ion exchange process to treat acid mine drainage and also to produce fertilizer can be visualized. The mine drainage would first be neutralized with NH_3, then settled. The sludge would contain the iron and aluminum while the effluent would be diluted $(NH_4)_2SO_4$. The ammonium sulfate would be passed through a cation resin bed to remove the ammonia and then through an anion resin bed to remove the sulfate. The cation bed would be regenerated with NHO_3 and the anion bed with NH_4OH. The waste regenerates would be NH_4NO_3 and $(NH_4)_2SO_4$ which could be used for fertilizer.

Care and Zawadzki(6) conducted studies using a strong anion resin in the sulfate form to treat acid mine drainage. The chloride form of the resin is converted to the sulfate form with sulfuric acid. When acid mine drainage is passed through the resin, the following conversion occurs:

$$R_2SO_4 + H_2SO_4 \longrightarrow RHSO_4 + RHSO_4 \qquad \text{(39}$$

By this reaction divalent sulfate ions on the exchange sites are converted to monovalent bisulfate ions. This conversion frees one of the two exchange sites initially required to hold the divalent sulfate ion. The newly freed site is now capable of accepting an additional anion.

The bed was regenerated with water as shown in equation 40(16).

$$RHSO_4 + RHSO_4 + H_2O \longrightarrow R_2SO_4 + H_2SO_4 + H_2O \qquad \text{(40}$$

Care and Zawadzki(6) regenerated the bed by downflow. They found that for every unit of acid mine drainage treated, three units of water were required to regenerate the resin. Iron fouling occurred when excess acid was not present to prevent the precipitation of ferric hydroxide.

Under conditions of 3:1 ratio of regenerant to feed, and flow rate of 4 gpm per square foot of bed cross section, a maximum of 90 percent of the iron was separated into a fraction containing only 20 percent of the acid. By this method the acid could be separated from the salt fraction. However, the acid fraction would have greater volume and be more dilute in sulfuric acid than the original feed solution because of the high ratio of regenerant to feed. Cost of treating 1 mgd was estimated as 30 cents per 1,000 gallons.

Schroeder and Marchello(49) describe the Nalco process in which three beds are used, that is, a weakly acidic bed, strongly acidic bed, and strongly basic bed. The raw water is filtered, then passed through the beds in the order listed above. Sulfuric acid is used to regenerate the cation bed and lime is used for alkali rinse regeneration of the acid-exhausted anion bed. The concentrated waste brine is acidic and underground injection is suggested as a disposal method. Schroeder and Marchello suggested the following possible difficulties: calcium, iron and manganese may greatly reduce resin life; calcium sulfate precipitating in the columns may plug them; and resin capacity may decrease markedly with continued use. The estimated costs for the Nalco ion exchange system are:

Plant Size, MGD	Capital Cost, Dollars	Dollars, Per 1,000 Gallons
0.1	254,000	$2.53
1.0	1,450,000	1.04
10	10,180,000	0.71
100	78,250,000	0.61

Another possibility would be a strong acid resin followed by a strong base. The first bed would remove the metal ions as shown in equation 29.

A barium-loaded strong-acid cation exchanger could be used to remove the sulfate and carbonates. The insoluble barium sulfate and carbonate formed would then be separated by precipitate. A method for recovering and reusing the barium has been developed(18). Studies to date using barium resin have been made with saline water where sodium is the predominant cation. Sodium levels are low in mine drainage and it would be necessary to determine if the process would operate with calcium and/or iron as the main cation.

Summary

A number of different ion exchange schemes have been suggested for treating acid mine drainage. Only two of these have been actually tested on mine waters, and in both cases a synthetic mine water was used. The various proposed schemes are summarized in Table 5.1. However, this list may not be all inclusive, and better and more economical methods might be developed.

Table 5.1 gives the estimated cost of ion exchange processes. Costs per 1,000 gallons vary from $0.30 to $2.53. The costs given by Schroeder and Marchello are probably close to the true costs, as they were quite inclusive, including such items as brine disposal.

Research Needs

Many problems still need to be investigated before the most economical and functional system can be developed. More than one system

TABLE 5.1

ION EXCHANGE SCHEMES

Ion Exchange	Estimated Cost Dollars/1,000 Gallons	Reference
Weak-base anion-bicarbonate cycle	0.38^b, 0.44^a	43
Weak-base anion-chloride cycle	——	——
Cation-nitrate cycle	——	28
Cation-anion-preceded by NH_3 treatment	——	——
Strong anion resin	0.30^b	6
Weak acid-strong acid-Strong base beds (Nalco Process)	2.53^a, 1.04^b 0.71^c, 0.16^d	49
Strong acid-strong base	——	——
Barium strong acid	——	18

a - 100,000 gpd plant
b - 1,000,000 plant
c - 10,000,000 gpd plant
d - 100,000,000 gpd plant

may serve to treat mine drainage and each will depend on such factors as the characteristics of the mine drainage, ultimate use of the treated water, and ultimate use or disposal of the waste regenerant. There is a definite need for ion exchange processes to be tested under actual field conditions. A partial list of areas needing investigation follows.

The advantages, disadvantages, economics, and application of each ion exchange process.

The upper limits of acid, iron (ferric and ferrous), sulfate, and other ions that can be treated economically.

The effect of calcium, magnesium and iron, on the life and activity of the resin.

The effect of bacteria, especially iron bacteria, found in mine drainage on the resin.

The effect of suspended solids, sediment and algae, found in mine drainage on the resin.

Best regenerant for resin efficients, and long life.

Possible marketable use of the waste regenerant.

Disposal of the regenerant.

FWPCA Research Program

At the current time, the Federal Water Pollution Control Administration is conducting no in-house or supporting any research on the treatment of mine drainage by ion exchange. The Commonwealth of Pennsylvania has announced that a full scale plant utilizing the process reported by Pollio and Kunin(43) will soon be constructed in Pennsylvania.

6. REVERSE OSMOSIS TREATMENT

Osmosis is defined as the transport of a fluid across a boundary which separates two solutions of differing solvent activity. The direction of solvent flow under an osmotic gradient is always from the dilute into the concentrated solution. Reverse osmosis is defined as the flow of solvent across a boundary from the more concentrated to the less concentrated solution as a result of application of pressure to the concentrated solution in excess of the osmotic pressure difference between the two solutions. In essence, the reverse osmosis process produces two discharges, one of concentrated solute, and one of "pure" water. The reverse osmosis process will remove acidity, sulfates, calcium, magnesium, iron, and other ions, from acid mine drainage and concentrate them as a brine. The product water has a low concentration of these constituents but the pH is raised only slightly. However, because of the removal of acidic components, only small amounts of alkalinity are required to increase the pH.

The reverse osmosis treatment process is in its early stage of development. The Office of Saline Water, U. S. Department of the Interior, has supported a variety of research on water desalination by reverse osmosis. One small study of mine drainage treatment has been made and another is in progress. A few pilot plants have been built for treating brackish water, but no full-scale plants. Reverse osmosis appears to be a promising process. It has the attractive feature of effecting the separation without change in state and therefore, there is a potential for utilizing energies close to the theoretical thermodynamic minimum.

Principles of Reverse Osmosis

In the reverse osmosis process, a membrane which is highly permeable to water and relatively impermeable to solutes, is used to separate product water from a feed solution. Water normally tends to flow through an osmotic membrane from the dilute to the concentrate solution. In the reverse osmosis process, the normal osmotic tendency is reversed by increasing the activity of the water in the brine by the application of pressure in excess of the osmotic pressure. The rate of flow through the membrane is proportional to the difference between applied pressure and the osmotic pressure.

The salt flow through a membrane is relatively independent of pressure and depends primarily on the gradient of the salt concentration, therefore, increasing the applied pressure produces not only in more water per unit time, but also water of higher quality.

The rate of water flow through a membrane is called the water flux and is defined by the following equation:

$$J = A(\Delta P - \Delta\pi) \qquad (41$$

The rejection properties of a membrane are called the salt flux and are defined by equation 42.

$$J_s = B(\Delta C) \qquad (42$$

Where J = product water flux, gpm/ft^2 of membrane

A = membrane constant, gpm/ft^2- psi

ΔP = the differential pressure across the membrane, psi

$\Delta\pi$ = the osmotic pressure, psi

Js = salt flux, g/cm^2 sec

B = salt flux coefficient, cm/sec

ΔC = difference in salt concentration between the brine and product, g/cm^3

As noted previously and as seen in the equations, the water flux is hydraulic-pressure dependent and the salt is pressure independent; thus, the product water quality improves as the applied pressure is increased.

The critical feature of the reverse osmosis process is the membrane. The membrane is required to discriminate between solute and solvent and to permit the passage of the solvent at a rate sufficiently rapid to render the process economically feasible at reasonable hydraulic pressure gradient. To date, the cellulose acetate membrane is the only proven one, but others are in the development stage.

Several different configurations of membranes have been developed. The "flat plate" membrane configuration is a membrane held flat by a frame. A "spiral-wound" membrane is essentially a "flat plate" wound into a cyclinder. A space is provided between the roll of membrane to provide movement of the brine and product water. The "tubular" membrane is in the form of a long tube made of fiberglass or some other material. Coating the inside of the tube is the membrane. Feed water and brine pass through the center of the tube and the product water passes through the tube to be collected on the outerside. A recently developed configuration is a hollow fiber. This membrane is still in the early stages of development.

Some terms used in reverse osmosis studies are not common to other treatment areas and are therefore, defined as follows:

> Water recovery is the ratio of product water to feed water expressed as a percent.
>
> Salt rejection is defined as the ratio of the specific conductance of the product water to the feed water expressed as a percent.

It has been observed(33) that after a period of time, the salt rejection of cellulose acetate reverse osmosis membranes decreases. This increase in salt flux can be ascribed to the hydrolysis of the cellulose acetate. Further, it has been shown that the hydrolysis is strongly dependent on pH and temperature. The hydrolysis rate is a minimum at a pH of 4.8 and a temperature of 23 degrees centigrade, and increases rapidly at higher and lower pH values. Mine waters directly from the mine usually have a temperature of 8 to 12 degrees centigrade, a level that would result in low hydrolysis. The pH of mine drainage varies widely from as low as 2.0 to above 7. However, the most troublesome waters have a pH of 2.5 to 5.5. Therefore, hydrolysis for some acid mine drainages may be near the minimum.

Merten, et al.,(38) reported that the performance of cellulose acetate membranes may have deteriorated as a result of rust (iron) deposits on the membrane. Acid mine drainage with its high concentration of iron may cause rapid deterioration of membrane performance. Larson(34) found that a reverse osmosis unit could remove 98 percent of the sodium and chloride ion and 99 percent of the calcium sulfate and bicarbonate.

Reverse Osmosis Treatment of Mine Drainage

Three studies have been conducted on the treatment of mine drainage. Two were field tests and the third a cost analysis.

Riedinger and Schultz(47) conducted tests using reverse osmosis to treat acid mine drainage at two mine sites near Kittanning, Pennsylvania. Their purpose was to explore the effectiveness of reverse osmosis in concentrating and reclaiming drainage containing acid and iron from coal mines. The tests were conducted on a 24-hour a day basis for about 10 days each. The modules used were of cellulose acetate membrane material in a spiral-wound configuration. Two types of membranes were used: a high-selectivity and a low selectivity, a high-selectivity membrane has greater salt rejection and less water recovery than a lower-selectivity membrane. Operating pressures of 400 and 600 psi were used. The mine drainage was pretreated with coarse screen and a five-micron cartridge filter.

Tests indicated that the osmotic pressure of the acid mine drainage at a conductivity of 1,040 micromhos/cm was 19 psi and was proportional to the conductivity(47).

The results of this test show that a high quality water can be produced from feeds with pH of 3.0 and lower, and containing 100 ppm or more of dissolved iron. Recovery ratios (product/feed) were in excess of 90 percent. The brine was highly concentrated, in fact, calcium sulfate, and magnesium sulfate were concentrated beyond saturation. Ferrous iron did not appear to cause problems, but ferric iron deposited on the membrane and reduced the water flux. The high-selectivity membrane produce the best results. The product waters were low in dissolved solids but had a pH of 5 or less.

Larson(34) reported that sulfate scale does not adhere as readily to membrane surfaces and tends to collect as large particles on brine channel spacers, whereas, carbonate scale tends to form at the membrane surface and adheres tenaciously. Sulfate scale causes a large increase in brine side pressure drop and carbonate scale a substantial reduction in product water flow. Calcium sulfate could be flushed from the module by increasing brine flow. Sodium tripolyphate was used to inhibit precipitation.

Cellulose acetate membranes in the spiral-wound configuration are being tested at the Federal Water Pollution Control Administration's Mine Drainage Treatment Laboratory, Norton, West Virginia. Results of one run are presented in Table 6.1. Salt rejection was high with all parameters, except acidity, reduced to less than one mg/l. Some difficulties with module failures occurred during these tests. No problems were encountered with iron precipitating on the membrane or with cleaning the modules following shutdown.

Schroeder and Marchello(49) estimated the costs of treating mine drainage by reverse osmosis and disposing of the brine by deep well disposal as follows:

Plant Capacity, MGD	Capital Cost, Dollars	Water Cost, Dollars/1,000 Gallons
0.1	248,000	2.57
1.0	1,407,000	1.09
10.0	10,120,000	0.77
100.0	81,250,000	0.68

TABLE 6.1

REVERSE OSMOSIS TEST RESULTS - NORTON, WEST VIRGINIA

	Feed Water	Product Water	Brine Water	Percent Reduction
pH	2.9	4.5	2.4	——
Acidity, Mg/l	504	4	2,050	99.2
Total Iron, Mg/l Fe	93	0.1	391	99.9
Iron (II), Mg/l Fe	3.8	0.1	5.1	97.4
Hardness, Mg/l $CaCO_3$	298	0	1,252	100
Calcium, Mg/l Ca CO_3	196	0	850	100
Sulfate, Mg/l SO_4	790	0.5	2,940	99.9
Specific Conductance	1,510	13	4,395	99.1
Aluminum, Mg/l Al	24	0.1	100	99.8

Salt Rejection - 99 Percent

Water Recovery - 76.5 Percent

Pressure - 560 psi

Experiments in reverse osmosis indicate the process has great possibilities for concentrating the dissolved solids in mine drainage and producing a high quality water, low in sulfate, iron calcium and acidity. The feed water requires prefiltration for removal of suspended solids and the disposal of the brine waste is a major problem.

Research Needs

Research needs for the development of reverse osmosis for the treatment of mine drainage are as follows:

Development of membranes best suitable for mine drainage treatment.

Determine the effect of acid mine drainage on deterioration of membranes.

Evaluation of membrane plugging problem due to iron, calcium, sulfate, and organisms.

Determination of membrane life under field conditions.

Development of methods of cleaning membranes.

Development of methods for reuse of brine material.

Development of methods of disposing of and treating brine waste.

Determine the cost of treating mine drainage by reverse osmosis.

FWPCA Research Program

The Federal Water Pollution Control Administration is conducting or sponsoring the following research on the treatment of mine drainage by reverse osmosis:

Cooperative research project between FWPCA and Office of Saline

Water at Norton, West Virginia, "Evaluation of a 10,000 gpd Reverse Osmosis Unit in the Treatment of Acid Mine Drainage."

Research project by FWPCA at the Mine Drainage Treatment Laboratory, Norton, West Virginia, on the treatment and disposal of brine from the reverse osmosis process.

Grant to the Pennsylvania Department of Mines and Mineral Industries and its subcontractor, Haven Industries, for a project titled, "Abatement of Acid Mine Drainage Pollution by Reverse Osmosis."

7. DISTILLATION

Distillation has proved the best method developed to date for the desalination of sea water. Many full-scale plants with capacities exceeding one mgd have been built throughout the world. Extensive knowledge is available on the construction of such plants. Two major advantages of distillation are: the process is relatively insensitive to the degree of contamination of the feed, and a water with 50 ppm of dissolved solids can be produced. The major problems of adopting distillation processes to mine drainage treatment are scaling and corrosion. Calcium sulfate which causes major scaling in all evaporators, is usually present in a high concentration in mine drainage and the acid nature of mine drainage makes it highly corrosive.

Principles of Distillation Processes

Distillation processes can be grouped into three main categories; (a) multistage flash evaporation, (b) long tube evaporation, and (c) vapor compression.

The multistage flash distillation process is based on the fact that water boils at progressively lower temperatures as it is subjected to progressively lower pressures. The feed water is heated (200° F) and then introduced into a chamber where the pressure is sufficiently low to cause some "flash" immediately into vapor, leaving the salt and other impurities behind. The vapor rises in the chamber and comes in contact with condenser tubes. As the vapor condenses against the cool tubes, droplets of water fall into a separator and are carried away as the product water. The brine produced in the first flash chamber, now lower in temperature, flows to a second chamber where the pressure is lower than in the previous chamber. The same process occurs again. Finally, the brine passes to a heat exchanger where the incoming water is heated and the brine condensed.

This method is most widely used in the largest of the desalination plants. It is an efficient system insofar as heat energy is concerned, since as much as 90 percent of the heat energy can be recovered.

The long-tube vertical distillation or full drop system is constructed of a series of bundles of long tubes. The feed water is heated to 250° F and is introduced at the top of the first series of long-tube bundles within a large cylindrical chamber. The first chamber or evaporator is a steam chest, and receives steam from an outside source. As the water pours down the sides of the tubes in a thin film, some of it vaporizes. Part of the vapor condenses and is drawn off as product water and the remainder is piped to the second chamber and acts as the "steam source." Unvaporized feed water is introduced at the top of the second chamber and the process is repeated. As many as 12 chambers may be used. The pressure in each chamber is progressively reduced to permit vaporization to occur at lower temperatures. The brine is collected after the final chamber. Scale control at high temperatures (250° F) has been a major problem. A one million gallon per day plant of this type is in use.

Vapor compression distillation depends on the fact that when the saturated vapor rising from a boiling liquid is compressed, it increases in temperature and in fact becomes slightly superheated. Since the vapor is at a higher pressure, its condensing temperature is correspondingly increased. Because its condensing temperature is now higher, this compressed vapor can transfer its heat of condensation to the boiling liquid. Water is evaporated at the cost of whatever power is required to compress the vapor. In single-stage vapor compression distillation, feed water is pumped upward through a bundle of tubes into a large spherical chamber. As the water travels upward, it is heated by steam condensing on the outside of the tubes. This transfer of heat causes some of the water in the tube to vaporize. When the mixture of vapor and brine leaves the tubes and enters the chamber, part of the brine is returned to the bottom and recirculated and the remainder is discharged. The vapor is compressed and conducted to the steam chest surrounding the tubes. Here it condenses, as noted above, and is withdrawn as product water. Two stage units of slightly different design are also used in saline water distillation processes.

The primary difference between this process and other distillation processes is in the method in which heat is added to the system. In other processes heat is added to the feed water, while in this process heat is added to the vapor by compressing it. Most of the energy is consumed by the motor which drives the compressor. Heat is added directly only during startup.

As in all distillation processes, vapor compression suffers from scaling and corrosion. The Office of Saline Water has one demonstration plant of this type with a capacity of one mgd. It has been plagued with scaling and hydraulic difficulties.

Distillation Treatment of Mine Water

Westinghouse Electric Corporation, under a contract with the State of Pennsylvania, studied the application of distillation processes for the treatment of acid mine drainage. Lemezis(35) reported that flash distillation was the most promising process because the plants are simple in construction, are easily designed to handle large volumes of flow, and do not involve boiling or a heat transfer surface. All contamination in acid mine drainage can be reduced and the product water would have approximately 50 ppm dissolved solids. The major problems were described as: "(a) The waste (brine) must be disposed of in such a way that it will not return to the streams or to the water table. (b) The mine water is acid from hydrolysis of its metallic sulfates and is, therefore, very corrosive."

Westinghouse Electric Corporation(57) studied the two aspects mentioned above for the State of Pennsylvania. They concluded that the best and cheapest way to handle the waste brine was to cast it into solid block. They failed to outline the method of casting the block and gave no costs for this process. Cost of hauling the brine to sea from Pennsylvania was estimated as 12-16 cents per 1,000 gallons of brine.

Laboratory tests by Westinghouse indicated, that if the temperature was kept near 200° F, no scaling occurs. At higher temperatures, a scale consisting mainly of calcium sulfate formed.

Corrosion tests were made to determine the best material for constructing the system. Titanium was found to be the most corrosion resistant material for use in acid mine drainage flash evaporators. The presence of free acid in acid mine drainage increased the corrosion rate on all materials.

It was concluded in the Westinghouse report that it was feasible to treat acid mine drainage by flash distillation and that a high quality water could be produced. Cost estimates for a five mgd plant were developed. Two types of plants were discussed. A single purpose plant just for treating acid mine drainage and a dual purpose plant for treating mine drainage and producing electrical power. The following cost figures were given:

	Single Purpose	Dual Purpose
Capital Cost (5 mgd plant)	$7,538,034	$9,570,444
Treatment Cost (cents/1,000 gallons)	81.31-95.36	33.3-51.3

Schroeder and Marchello(49) analyzed the cost of treating mine drainage by distillation methods. Since the cost of treatment by distillation is relatively independent of the feed water concentration, the cost figures developed should be applicable to most acid mine drainage situations. As noted earlier, because of the highly corrosive nature of acid mine drainage, special high cost material would be required to construct the reactors, etc. Schroeder and Marchello suggested as an alternate to high cost building materials that the acid mine drainage be neutralized first. They supported their contention with the following estimated costs for a one mgd multistage flash plant.

	Capital Cost, Dollars	Water Cost, Dollars/1,000 Gallons
Neutralized Raw Water Conventional Materials	$2,154,459	1.13
Unneutralized Raw Water Stainless Steel Construction	$3,712.540	1.50
Unneutralized Raw Water Titanium Construction	$3,257,720	1.38

Capital cost estimates, which included raw water intake, neutralization and settling facilities, process facilities and auxiliaries, fresh water storage, and brine disposal by underground injection, for the three distillation processes were as follows:

CAPITAL COSTS (DOLLARS)

Plant Capacity, MGD	Multistage Flash	Long-Tube	Vapor Compression
0.1	477,000	486,900	445,500
1.0	2,152,000	2,513,000	2,431,000
10	11,570,000	14,650,000	15,953,000
100	68,440,000	91,564,000	115,200,000

Schroeder and Marchello(49) noted that since a distillation plant produced water containing 50 ppm solids, (a higher quality water than usually required), costs could be reduced by mixing the product water with some neutralized raw water to produce a water with 500 ppm solids. Water costs for the 50 and 500 ppm solids content given on the following page, show that multistage flash produces the cheapest water, verifying Westinghouse's findings.

Water Costs (Dollars/1,000 Gallons)

Production MGD	Multistage Flash		Long-Tube		Vapor Compression	
	50 ppm	500 ppm	50 ppm	500 ppm	50 ppm	500 ppm
0.1	3.05	2.36	3.12	2.41	3.24	2.50
1.0	1.13	0.87	1.28	0.99	1.49	1.15
10	0.64	0.49	0.77	0.59	1.05	0.81
100	0.47	0.36	0.58	0.45	0.88	0.68

Summary

The distillation process can treat acid mine drainage and produce a very high quality water. The major problem areas are in scale control, corrosion, and brine disposal. Westinghouse Electric Corporation has developed some answers to the scale control and corrosion problems, and the neutralization of the acid mine drainage before distillation, as suggested by Schroeder and Marchello, will also reduce corrosion problems. No sound solution to the brine disposal problem has been developed. At this time, multistage flash distillation appears to be the most economical process. Suggested water costs are as follows:

Process	Water Cost, Dollars/1,000 Gallons	Reference
Flash - Single Purpose	0.81 - 0.95[a]	Westinghouse
Flash - Dual Purpose	0.33 - 0.51[a]	Westinghouse
Flash - Dual Purpose	0.40[a]	Pennsylvania
Flash	0.47[b], 0.64[c], 1.13[d], 3.05[e]	Schroeder & Marchello
Long Tube	0.58[b], 0.77[c], 1.28[d], 3.12[e]	" "
Vapor Compression	0.88[b], 1.05[c], 1.49[d], 3.24[e]	" "

Note: a - 5 MGD
b - 0.1 MGD
c - 1 MGD
d - 10 MGD
e - 100 MGD

Research Needs

The distillation processes are highly developed to a stage where full-scale demonstration plants are in order. The major area that requires further study is brine disposal and/or utilization. The Commonwealth of Pennsylvania has been evaluating various sites for the construction of a full scale plant.

FWPCA Research Program

The Federal Water Pollution Control Administration currently has no in-house research nor is supporting any research on the treatment of mine drainage by distillation.

8. ELECTRODIALYSIS

Electrodialysis for the treatment of brackish water has been developed to the point where a 650,000-gpd demonstration plant is in operation. Electrodialysis appears to be best adapted to desalination of waters of lower salt concentrations than sea water because the electric current required in this process varies directly with the amount of dissolved salt, rather than with the amount of water. For this reason, the treatment of acid mine drainage by this process may be feasible.

Principles of Electrodialysis

Electrodialysis, like reverse osmosis, utilizes membranes; however, electricity is used as the driving force in electrodialysis. The conversion assembly is essentially an electrolytic cell which contains two different types of ion selective membranes. One membrane will pass only negatively charged ions (anions), while the other will pass only positively charged ions (cations). Pairs of membranes are placed in an alternate pattern in a cell between two electrically charged plates. As feed water passes through the cell, the negative anions (such as sulfate) are attracted to the positive plate (anode), while the positive cations (such as iron, aluminum, etc.) are attracted to the negative plate (cathode). The anion-permeable membrane allows passage of the negative ions and the cation-permeable membrane allows passage of the positive ions, thus yielding fresh water between the membranes.

The amount of electric current required in the unit depends on amount of salt to be removed. Therefore, the cost of the energy consumed in the process depends on the concentration of salt in the feed water. Electrical power requirements might be lowered by operating the system at elevated temperatures, since high temperatures result in low electrical resistance of the electrolyte.

Membrane stacks are known to increase resistance to flow with time. The rate of resistance increases rapidly at the beginning of a run, then tapers off at a much lesser rate. This increase was found to result from deposition of suspended solids in feed waters on membrane surfaces, and not from any changes in the membrane properties(48). Brunna(4) reported the fouling of membranes by both turbidity and microorganisms. Therefore, acid mine drainage will probably require some type of pretreatment to remove suspended solids and control microorganisms.

Studies by the Office of Saline Water have indicated that the optimum pH needed to mitigate the stack resistance increase is between 5.5 and 5.1. Many acid mine drainages have pH's in this range or lower, and thus should be in a favorable range in many cases.

Waters of high hardness concentration cause scale problems as well as high treatment costs. The hardness of mine drainage waters is often high, a factor to be considered. The Office of Saline Water is conducting studies on pretreatment methods for high hardness waters.

Iron and manganese form deposits on membranes and thus increase membrane-stack resistance and power consumption. The recommended iron concentration for feed waters to an electrodialysis unit is less than one mg/l. Almost all acid mine drainage will have much higher concentrations than this, necessitating pretreatment to remove iron.

Electrodialysis Treatment of Mine Drainage

A small bench-scale electrodialysis unit was tested by FWPCA at its Mine Drainage Treatment Laboratory, Norton, West Virginia, in cooperation with the Office of Saline Water(45). When used on water receiving no pretreatment, the cathode cell quickly became fouled with iron. The current reversal technique showed promise of preventing flocculation in the membrane system. In those cases where the mine drainage was pretreated by lime neutralization for iron removel, the unit operated satisfactorily.

The 1966 Saline Water Conversion Report(48) states that a cooperative study between the Office of Saline Water and the Bureau of Mines was initiated on the use of the electrodialysis process to treat acid mine drainage. The purpose of this two-phase investigation was to determine methods of pretreatment of acid mine drainage to remove insoluble iron and other suspended solids, and to use these results in the construction and testing of a 10,000-gpd field unit. Results of this work have not been published.

Schroeder and Marchello(49) conducted a study on the estimated costs of treating acid mine drainage by electrodialysis. Their findings were as follows:

Plant Size (MGD)	Water Cost, Dollars/1,000 Gallons
0.1	$2.52
1.0	1.01
10	0.68
100	0.58

Research Needs

From the studies conducted to date, there is no reason to believe that the electrodialysis process could not be used for the treatment of acid mine drainage, providing pretreatment was included. The high hardness, iron, and low temperature of acid mine drainage will result in membrane problems. However, when pretreatment to remove these contaminants is included in the process, removal of the remaining dissolved solids should present few problems.

The electrodialysis process is highly developed, with a number of full-scale demonstration plants in operation. However, only limited laboratory and field studies have been made to test the procedure on actual acid mine drainage. Research and development effort should be placed on pretreatment, sludge disposal and/or utilization, and optimization of the process.

FWPCA Research Program

The Federal Water Pollution Control Administration is not conducting or funding work in this area at this time.

9. CRYSTALLIZATION (Freezing)

Introduction

Separation of salts from water by crystallization has been under study for a number of years by the Office of Saline Water. Several pilot plants are in operation. Crystallization processes have distinct energy advantages over many other methods of demineralization, since the separation of pure water from a salt solution requires the removal of only 144 btu per pound of water.

Principles of Crystallization Treatment

When mineralized water freezes, fresh-water ice crystals form, and the salts remain in solution in the unfrozen water. If the crystals are separated from the brine, washed, and melted, fresh water stripped of other substances is produced. The freezing (heat of fusion) of water requires only 144 btu per pound of water, or less than one-sixth of the heat of vaporization. Low temperatures also minimize scale and corrosion problems.

To further explain the crystallization process, when a feed water is cooled to below 32° F, ice begins to form. As more ice is formed, the salt concentration of the remaining solution increases. If the temperature continues to decline, a point is reached where the minerals in the solution begin to precipitate. This is called the eutetic point. For an NaCl solution, it is reached at a temperature of -6° F and a concentration of 23.3 percent.

Let us now consider an acid mine drainage water which contains inorganic ions such as Ca, Mg, Na, SO_4, and Fe. When water is removed from such a solution, the solubility of one ion is usually exceeded first, and it will precipitate with the ice. Soon a point is reached where the solubility of a second salt is exceeded. Further removal of water as ice precipitates salts and ice simultaneously until the solubility of a third salt is reached, and so forth. Calcium sulfate, which is commonly found in acid mine drainage at high concentrations, should be one of the first to precipitate.

Two methods of crystallization appear equally promising, i.e., the freezing method and the gas hydration method. In the freezing process, direct refrigeration is performed without transferring heat through a metal barrier. A portion of the precooled feed water is evaporated under reduced pressure, thus reducing the temperature, or a refrigerant such as n-butane is vaporized in direct contact with the feed water. The refrigerant is then separated from the water by a simple stripping process.

In the gas hydration process, a chemical reaction separates fresh water from a feed water by the use of hydrate-forming materials, notably propane. The hydrate-forming gas is used in its liquid phase. When introduced into the feed water, it combines with the water in complex crystals that reject ionic (salt) constitutents. These crystals are separated from, and worked free of, the mother liquor, and then melted into two immiscible liquids, i.e., the liquid hydrating agent, which is recycled, and fresh water.

In the freezing process, separating the ice crystals from the brine and precipitated solids is a major problem. However, techniques have been developed to make the separation effective.

Crystallization Treatment of Mine Drainage

The crystallization processes appear applicable to the treatment of acid mine drainage, although these techniques have not been tested on actual acid mine drainage. The Office of Saline Water has sponsored a number of research projects on these processes for the treatment of brackish water and a few demonstration plants are in operation.

Schroeder and Marchello (49) estimated the cost of treating mine drainage by vacuum freezing, secondary refrigerants (n-butane); and hydrate process as follows:

Production, Mgd	Water Cost, Dollars/1,000 Gallons		
	Direct Freezing	N-Butane	Hydrate
0.1	3.10	3.18	3.23
1.0	1.32	1.34	1.38
10	0.85	0.85	0.89
100	0.68	0.67	0.71

Cost would increase as the concentration of pollutants in the acid mine drainage increased.

Research Needs

The immediate research needs in the area of crystallization is a feasibility study to determine if the more troublesome ions found in mine drainage, such as iron (II), iron (III), sulfate, calcium, aluminum, magnesium and manganese can be removed efficiently and economically. An important aspect of the crystallization process would be disposal and/or utilization of the brine. Research is needed in this area.

FWPCA Research Program

The Federal Water Pollution Control Administration is sponsoring the following research on the treatment of mine drainage by freezing:

> Grant to the Pennsylvania Department of Mines and Mineral Industries and its subcontractor, Applied Science Laboratories, Incorporated, for a project intitled "Feasibility of the Purification of Acid Mine Water by a Partial Freezing Process."

Introduction

Biological treatment of mine drainage has been proposed as a method of controlling pollution from mines. As noted in Chapter 4 on iron removal, Glover(19) has developed a biochemical oxidation process for ferrous iron removal. An autotrophic bacteria that derives its energy from the promotion of an inorganic reaction and its cellular carbon from carbon dioxide is used to promote the oxidation of ferrous iron. Hanna, et al.,(21) suggested the use of sulfate-reducing bacteria to dispose of acid in acid mine drainage. Wood dust, sewage or sewage sludge could be employed as an inexpensive source of organic nutrients for sulfate-reducing bacteria. Various biological schemes are described in the succeeding text.

Sulfate Reduction

Tuttle(59) reported of finding the reduction of sulfate occurring naturally in a stream in Ohio. He observed a stream polluted with acid mine drainage flowing through a pile of saw dust. The stream below the wood dust pile contained less sulfate, and iron, and had a higher pH than above the pile. A strictly anaerobic gram negative mesophilic spore-forming sulfate-reducer of the genus Desulfotomaclum was isolated from the wood dust. Laboratory studies by Tuttle demonstrated that in wood dust-acid mine water cultures the sulfate could be reduced to sulfide with a concomitant removal of hydrogen ion and precipitation of iron and sulfide as FeS. Wood dust provided the oxidizable organic substrate for the sulfate-reducing bacteria and created the anaerobic conditions necessary for the growth of the microorganisms. Other organic material such as sewage sludge could be used in place of the wood dust.

The reactions occurring in the process are shown in equations 43 and 44.

$$Fe{+}{+} + SO_4 = +8H^+ + 8\bar{e} \longrightarrow FeS + 4H_2O \qquad (43$$

$$2Fe{+}{+}{+} + 3SO_4 = +24H^+ + 24\bar{e} \longrightarrow Fe_2S_3 + 4H_2O \qquad (44$$

Sulfate in the presence of hydrogen would be reduced to hydrogen sulfide, which would consequently react with ferrous and ferric ions to form insoluble ferrous and ferric sulfide. After the iron is depleted additional hydrogen would combine with the released oxygen to form water or with the excess sulfide to produce hydrogen sulfide. For these reactions to take place, a source of electrons must be present, which could be provided by organic compounds. Under anaerobic conditions the organic matter would be transformed to methane and carbon dioxide. It is anticipated that the above process would raise the pH of the water to at least 6.

A sulfate reducing process would include an anerobic reaction chamber to which the mine drainage and organic matter were fed. After sulfate reduction the water would pass to a settling tank where the insoluble matter such as ferric sulfide, activated bacteria, and residual organic matter would be removed.

Through further treatment the ferrous sulfide precipitate might be converted to a useable byproduct. For example the iron component could be converted to iron oxide and the sulfide to elemental sulfur.

Various studies(44) have been conducted that show that bacteria can reduce sulfate and many advances have been made in our understanding of the sulfate-reducing bacteria. The bacteria <u>Desulfovibrio desulfuricans</u> has been associated with sulfate reduction. However, the problem of putting these bacteria to work in a waste treatment process has been only superficially evaluated. Both laboratory and pilot plant studies are needed before full scale demonstration plants can be constructed.

Ferrous Iron Oxidation

In Chapter 4, the Glover process for the biological treatment of ferrous iron was discussed. Lundgren(36) has conducted extensive studies on the physiology of iron oxidizing bacteria. The bacteria *Thiobacillus thiooxidans*, *Thiobacillus ferrooxidans*, and *Ferrobacillus ferrooxidens*, have been associated with acid mine drainage. These bacteria have also been reported to play a role in sulfur oxidation. Except for the Glover process, only limited work has been conducted to develop full scale treatment plant for the biological removal of iron (II).

Research Needs

Biological treatment of mine drainage for sulfate reduction is a different process than that for ferrous iron oxidation. Thus the research needs have been listed separately.

Sulfate Reduction

Effect of pH on kinetics of reactions.

Optimum ratio of organic material to mine drainage.

Corrosion problems as a result of the acid water and hydrogen sulfide production.

Prevention of air pollution by hydrogen sulfide production.

Feasibility of sulfur and iron oxide recovery.

Optimization of a sulfide reduction process.

Evaluation of organic material sources.

Effect of such variables as sulfate concentration, iron (II) and iron (III) concentration, temperature, oxidation potential and organic solids.

Ferrous Iron Oxidation

Kinetics of the reactions and those factors that affect it, such as pH, iron and sulfate concentration and temperatures.

Development of laboratory and pilot systems for removal of iron.

Nutrient requirements of the iron oxidizing bacteria.

Optimization of the iron oxidation process.

FWPCA Research Program

The Federal Water Pollution Control Administration is sponsoring the following research on biological treatment of mine drainage:

Grant to Syracuse University for a project intitled, "Inorganic Sulfur Oxidation by Iron-Oxidizing Bacteria," Grant Number WP-01367

Grant to Syracuse University for a project intitled, "Biological Treatment of Acid Mine Water," Grant Number WP-01460

Grant to Continental Oil Company for a project intitled, "Microbiological Removal of Iron from Mine Drainage Waters," Grant Number WPRD-63.

11. SUMMARY

Mine drainage is a critical pollution problem in the Appalachian Region as well as other smaller areas of the United States. Over 10,000 miles of streams have been polluted by mine discharges in the United States. Although the ultimate control of mine drainage pollution lies in preventing its formation at the source, no proven method has been developed for underground and active mines. In the interim, treatment appears important in mine drainage control methodology, particularly in active mine situations, mine drainage not amenable to at-source control, and the control of residual pollutants from at-source control measures.

The type of treatment applied to mine drainage depends primarily on the quality of the water to be treated and the quality desired in the finished water. Table 10.1 outlines the treatment methods most promising for mine drainage. Neutralization, usually coupled with aeration, is the most commonly used method and removes acidity and iron but does not reduce the hardness or sulfate content. The remaining methods are essentially demineralization processes leading to pure water. Some of these processes require pre and post-treatment. The high quality of the product water would permit its use as industrial and municipal supplies.

Table 10.2 presents estimated efficiencies of the various treatment methods for removal of contaminants found in mine drainage. Table 10.3 compares estimated costs for the various acid mine drainage processes described in this report.

TABLE 10.1

TREATMENT PROCESSES FOR MINE DRAINAGE

Process	Comments	Benefits	Problem Areas
Neutralization	Process usually includes aeration and sedimentation. Lime and limestone used as alkaline agents.	Removes acidity, iron, aluminum, and manganese. Increases pH. Water less corrosive.	Does not remove hardness, sulfate. Sludge a major problem.
Reverse Osmosis	Three basic types of modules, i.e., spiral wound, plate, and tube.	Demineralization	Requires pretreatment for removal of sediment and control of organisms. $CaSO_4$ precipitation. Brine disposal. Resulting water has low pH and is corrosive and requires post-treatment for stabilization.
Electrodialysis	Has energy cost superior to distillation at low TDS.	Demineralization	Pretreatment to remove iron, manganese, sediment, and microorganisms required. Brine disposal. $CaSO_4$ precipitation.
Crystallization	Freezing process	Demineralization	Brine disposal. Ice separation.
Ion Exchange	Various schemes have been proposed. Each scheme has its own operating characteristics and removes different ions.	Demineralization Possible reduction of acidity.	Determination of best ion exchange scheme. Brine disposal, regeneration, iron fouling, precipitates.
Distillation	TDS of acid mine drainage often too low for economic removal.	Demineralization	Brine disposal. Corrosion problems.

TABLE 10.2

EFFICIENCY OF MINE DRAINAGE TREATMENT

Efficiency (Percent)

	Acidity	Iron	Aluminum	Sulfate	Manganese	Hardness	Water Recovery
Neutralization	98-100	90-100	95-100	0-5	95-100	0*	67-90
Reverse Osmosis	95-99	95-99	95-99	95-99	95-99	98-100	70-90
Electrodialysis	90-95	0**	95-99	85-95	0**	85-95	70-90
Crystallization	90-99	90-99	90-99	90-99	90-99	90-99	25-50
Ion Exchange	80-99	70-99	70-99	80-99	70-99	90-99	60-95
Distillation	95-99	98-100	98-100	98-100	98-100	98-100	60-80

* May increase
** Cannot operate at high iron and manganese concentrations

TABLE 10.3

ESTIMATED COSTS OF TREATING MINE DRAINAGE

Process	Dollar Cost per 1,000 gallons	Controlling Factors
Neutralization	0.05 - 1.10	Water quality, size of plant
Reverse Osmosis	0.68 - 2.57	Size of plant
Electrodialysis	0.58 - 2.52	Size of plant, amount of pretreatment, dissolved solids concentrate
Crystallization	0.67 - 3.23	Freezing process, size of plant
Ion Exchange	0.30 - 2.53	Size of plant, ion exchange scheme, dissolved solids concentration
Distillation	0.33 - 3.24	Size of plant, type of distillation unit

Research Needs

The demineralization processes have received considerable research support from the Office of Saline Water which has led to their refinement and illustrated their potential for use in mine drainage treatment. These processes need now to be modified to meet the criteria of mine drainage and to be demonstrated. Cost data are also needed.

Ion exchange probably requires the greatest development to ascertain the best schemes. Neutralization requires greater refinement to demonstrate cost and operational parameters. Ferrous iron removal needs to be optimized.

All of the processes need to be optimized to obtain maximum water recovery. Brine and/or sludge disposal is a major weak point of all the suggested processes. Thus the quantity of the waste materials should be held to a minimum. A major research program is needed in the area of the disposal and utilization of brine and sludges. The development or reuse of a useful byproduct would be an ideal solution. Mine drainage contains sulfur, iron and aluminum, which have commercial value. Of these materials, sulfur has the most promising price structure. Sludge and brine disposal techniques that lead to at-source control of mine drainage appear to be promising. Disposal to strip pits or to deep mines to coat and/or bury pyritic material is a possibility.

This report has examined those treatment processes which are most amenable to mine drainage. One purpose in reviewing the state of the art is to stimulate action in the development of other treatment methods.

The Federal Water Pollution Control Administration through its contract and grant program is prepared to help support research, development, and demonstration of new promising methods.

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In its assigned function as the Nation's principal natural resource agency, the United States Department of the Interior bears a special obligation to ensure that our expendable resources are conserved, that renewable resources are managed to produce optimum yields, and that all resources contribute their full measure to the progress, prosperity, and security of America - now and in the future.