Mines Branch Information Circular IC 227

NEUTRALIZATION AND AERATION OF ACID MINE WATERS
(A Literature Survey)

by

V.F. Harrison*

ABSTRACT

Research and development work performed in the United States during the past twenty years or more on the neutralization of waste solutions containing sulphuric acid and dissolved iron is reviewed. The chemistry of mine water is explained, and the chemical properties of various types of limestone and lime are discussed. Also, methods of applying these reagents to coal mine drainage and industrial effluents to obtain clean water, and of disposing of the precipitated sludge, are outlined. It is suggested that mine water from some Canadian mines might be amenable to a limestone treatment process.

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Direction des mines

Circulaire d'information IC 227

NEUTRALISATION ET AÉRATION DES EAUX DE
MINE ACIDES

(Enquête documentaire)

par

V.F. Harrison*

RÉSUMÉ

Le présent rapport passe en revue les travaux de recherche et de
développement entrepris aux États-Unis depuis vingt ans et plus dans le
domaine de la neutralisation des solutions résiduaires contenant de l'acide
sulfurique et du fer dissous. Il examine la composition chimique des eaux
de mines et étudie les propriétés chimiques de divers genres de calcaires
et de chaux. De plus, le rapport fait un exposé général des méthodes
d'application de ces réactifs aux eaux de houillères et aux effluents
industriels en vue de leur épuration, ainsi que des méthodes d'évacuation
des sédiments accumulés. Il a été proposé que l'eau de certaines mines
du Canada pourrait se prêter à un traitement au calcaire.

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CONTENTS

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TABLES

FIGURES

INTRODUCTION

A major problem facing Canada's mining industry at the present time is the potential pollution of drainage waters with sulphuric acid, ferrous and ferric iron, copper, zinc, molybdenum, and nickel. In addition to such dissolved metals, these drainage waters carry sulphur as anions of sulphite, sulphate, thiosulphate and polythionate. Mine effluents, which sometimes may appear clear and colourless, can seriously damage equipment such as car rails, pipes, pumps, electrical switches, etc., and also can kill natural growth such as vegetation, animals, fish, etc. The obvious answer to the handling of these waters is to render them harmless before pumping them to the surrounding drainage courses.

Contamination of water at a mining site arises from the oxidation and dissolution of sulphide minerals, either underground or in tailings ponds. In the mine, these actions generally occur in worked-out areas and indeed are initiated by the mining operation itself, which exposes pyrite to air, moisture, and iron-oxidizing bacteria. Pyrite, contained in the materials discarded from the pre-concentration and leaching steps, is also amenable to bacterial oxidation, thus releasing acid and iron into neighboring streams. The acidity of these waters, both from the mine and from the waste dump or tailings pond, may vary from as low as pH 1.5 up to 4.5, depending on the concentration and fineness of the pyrite in the host rock, the temperature and humidity of the environment, the degree of aeration, and the availability of inorganic nutrients (N, P, K, Ca, Mg, etc). Unfortunately, drainage waters usually become more destructive as the life of the mine is extended, because additional fresh pyrite, either in the ore or in the tailings, is continually being exposed to biological and chemical activity. As yet, there is no known effective remedy to retard or stop the production of mine acid while the mine is functioning.

The only method found to control water pollution in the industrial regions of the United States was to neutralize the water with an alkali. Because oxidation plays an important role in the removal of acid and iron, water treatment is usually accompanied by aeration. A study of published information on the subject of neutralization revealed that it is much more complex than one might at first suspect. The various types of limestone, lime and dolomite, which are readily attainable, and are also the cheapest forms of agents available on the market, all have their own special problems. For example, limestone and lime not only have different physical characteristics, but they react differently toward sulphuric acid and dissolved iron. For this

reason, selection of a compound or compounds for the neutralizing
process must be based on laboratory studies, including chemical
analyses of the solution, techniques for incorporating the alkali
with it, pH control, and disposal of the final precipitates. Such
an evaluation makes it possible to design and build a full-scale
plant for effectively converting mineral-bearing acidic waters
to those of acceptable quality for discharging into rivers and streams.

This information circular has been prepared to provide
a useful reference to the present knowledge on neutralization
and aeration of the mine and tailings waters that generally result
from Canadian mining operations.

ACID MINE WATER

Mine acid, an industrial waste, results in the extraction
of mineral sulphides from the mining of coal, copper and uranium.
Pyrite is the chief source of sulphuric acid and of ferrous and
ferric sulphates which enter waters of underground operations
and ultimately find their way into the surrounding waters.
Chalcopyrite, although less reactive to decomposition than pyrite,
does supply the mine water with acid and iron salts. The following
reactions are assumed to take place in the presence of bacteria
when these sulphides are exposed to air and water[1][2]:

$$2\ FeS_2 + 7O_2 + 2H_2O \longrightarrow 2FeSO_4 + 2H_2SO_4 \quad \dots\dots\dots \quad (1)$$

$$Cu\ FeS_2 + 4O_2 \longrightarrow CuSO_4 + FeSO_4 \quad \dots\dots\dots\dots \quad (2)$$
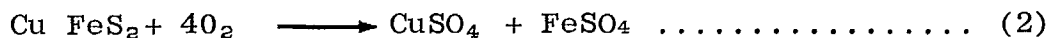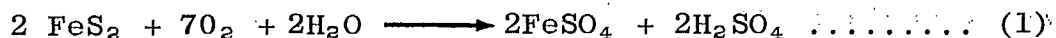
After a time, with aeration, the ferrous sulphate becomes oxidized
to ferric sulphate, which is kept in solution by the sulphuric
acid, until it comes into contact with these same sulphides[3].
This is shown in the following equations:

$$4\ FeSO_4 + 2H_2SO_4 + O_2 \longrightarrow 2Fe_2(SO_4)_3 + 2H_2O \quad \dots\dots \quad (3)$$

$$FeS_2 + Fe_2(SO_4)_3 \longrightarrow 3FeSO_4 + 2\ S \quad \dots\dots\dots\dots \quad (4)$$

$$CuFeS_2 + 2Fe_2(SO_4)_3 \longrightarrow CuSO_4 + 5\ FeSO_4 + 2S \quad \dots\dots \quad (5)$$
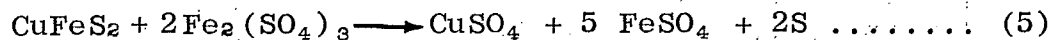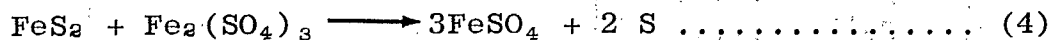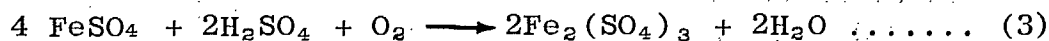
When mine drainage is diluted with water, either in
the mine or on the surface, the pH rises and the ferric sulphate
hydrolyses to ferric hydroxide and sulphuric acid as shown by
the following equation:

$$Fe_2(SO_4)_3 + 6H_2O \longrightarrow 2Fe(OH)_3 + 3H_2SO_4 \quad \dots\dots\dots \quad (6)$$
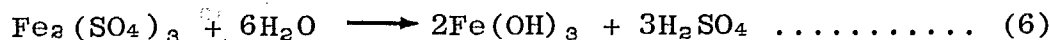
The iron precipitate, sometimes referred to as "yellow boy", causes rivers to flood, and the sulphuric acid, which renders water hard, kills all forms of wild life.

Other metal sulphides that are soluble in biologically oxidized iron sulphate are: covellite (CuS), chalcocite (Cu_2S), bornite (Cu_5FeS_4), tetrahedrite ($Cu_8Sb_2S_7$), sphalerite (ZnS), molybdenite (MoS_2), and millerite (NiS)[4][5]. Ferric sulphate also dissolves uraninite (UO_2) and the more refractory mineral, brannerite (UTi_2O_6)[6].

Autotrophic bacteria of the ferrobacillus-thiobacillus group play a major role in the production of mine acid. They catalyse the oxidation reactions of Equations 1, 2 and 3 at temperatures of from just above freezing to 40°C and at an acidity varying between pH 2.2 and 3.0[7]. Oxidation of ferrous sulphate in acid medium (Eq. 3) by air alone is extremely slow[8]. Since these micro-organisms are most active in an environment of 35°C and a pH of 2.2, the greatest production of acid and iron salts can be expected to occur under these conditions. However, an abundant supply of air and proper inorganic nutrients are also essential to maximum bacterial activity. Extraction of iron from pyrite increases with decreasing particle size, but is optimum when it is all minus 325 mesh.

A summary analysis of various coal-mine waters typical of Pennsylvania is given in Table 1.

TABLE 1

Summary Analysis of Coal-Mine Waters[12]

Constituent	Range in Analysis, g/1
(pH	2.8 - 4.6)
Fe^{++}..........	Trace to 0.75
Fe^{+++}........	0.0 - 0.30
Cu	0.006
Mn	0.012
Zn	2.10
Ca	0.188 - 0.495
Mg	0.002 - 0.66
P	0.003

In addition to the sulphuric acid and dissolved metal values, mine water contains complex sulphur compounds. These are generally in the form of polythionic acids, which are understood to be of the composition $H_2S_xO_6$ where x has mostly the values of 3 to 6 [9]. Polythionic acids and their salts are formed when hydrogen sulphide and sulphur dioxide react with each other in aqueous solution as represented by the following equation:

$$3SO_2 + H_2S \longrightarrow H_2S_4O_6 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (7)$$
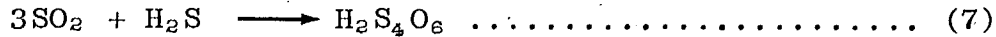
The optimum rate for polythionate formation is $3SO_2:1H_2S$. However, with a ratio of $1SO_2:2H_2S$, all the sulphur is precipitated as elemental sulphur:

$$SO_2 + 2H_2S \longrightarrow 3S + 2H_2O \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (8)$$
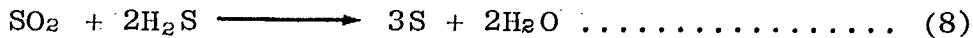
Polythionates are formed by the oxidation of thiosulphuric acid or thiosulphates with the aid of bacteria and of such agents as copper, dichromate, and persulphate ions. The following example uses copper ions as a catalyst:

$$S_2O_8^{--} + 2S_2O_3^{--} \longrightarrow S_4O_6^{--} + 2SO_4^{--} \quad \ldots\ldots\ldots\ldots \quad (9)$$
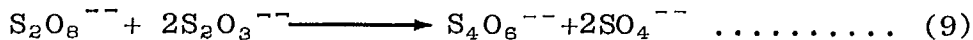
Although the stability of the polythionate ion $S_xO_6^{--}$ in aqueous solution varies with pH, it gradually disintegrates into sulphate and sulphite ions. For example, the trithionate ion, $S_3O_6^{--}$, decomposes in acid and weakly alkaline solutions, as shown by the following reaction:

$$S_3O_6^{--} + H_2O \longrightarrow S_2O_3^{--} + SO_4^{--} + 2H^+ \quad \ldots\ldots\ldots\ldots \quad (10)$$
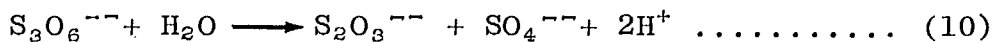
NEUTRALIZING AGENTS

One of the most effective ways to purify mine water is to neutralize it with an alkali, the most common of which are limestone, lime, magnesia, ammonia, sodium carbonate, and sodium hydroxide. Table 2 presents the comparative costs and the chemical affinity for sulphuric acid of the more common alkali agents [10].

TABLE 2

Alkali Requirements and Costs for Acid Neutralizations[10]

Reagent	Approx. Cost, cents/lb (Oct. 1968)	Approx. Dosage, lb/lb H_2SO_4
High-calcium limestone	0.2	1.06
Dolomitic limestone	0.2	0.95
High-calcium lime	0.5	0.60
Dolomitic lime	0.5	0.53
Anhydrous ammonia	4.0	0.35
Sodium carbonate	1.5	1.10
Sodium hydroxide	2.5	0.80

Limestone is the cheapest compound known to exist for neutralizing mine waters that contain sulphuric acid and iron. It is a standard commercial product that can be obtained from stone quarries, presents no industrial hazards, and can be stored indefinitely without precautions. The material may be used in its natural state, either in lump form or in the pulverized state, but each requires specialized equipment for applying it to acid waste. The per cent composition of a typical Pennsylvania limestone used in treating coal-mine water is presented in Table 3.

Chemically, pure lime is calcium oxide, CaO, but the commercial product contains impurities such as iron oxide, alumina, and silica. It is a totally different material from limestone in its handling and feeding characteristics. Lime cannot be stored satisfactorily if exposed to air, but must be stored in an airtight bin to prevent recarbonation. In this respect, it can be kept for a reasonable length of time in paper bags. It is fine enough to be applied through a feeder, and to react quickly with sulphuric acid and dissolved iron. However, utilization of lime requires certain facilities for proper hydration before it can be used effectively for neutralizing purposes. If the powder is hydrated with an excess of water at a temperature below the optimum of 95°C, hydration is incomplete, resulting in large agglomerates which do not react quickly with sulphuric acid[10].

TABLE 3

Chemical Analysis of Pennsylvania Limestone

Constituent	%
$CaCO_3$	– 92.8
$MgCO_3$	– 2.1
Metal oxides, R_2O_3	– 0.74
Acid insoluble	– 4.2
Moisture at 120°C	– 0.05

Neutralization of acid drainage with ammonia, sodium carbonate or sodium hydroxide was not observed in the literature searched, and therefore these reagents are not discussed in this review.

PROPERTIES OF LIMESTONE

Limestone rock varies in physical characteristics, depending on the deposits from which it was quarried, so that fine grinding in crushers can result in some differences in screen analyses. These differences can alter the relationship between particle size and neutralizing ability for limestones of similar composition when they are from widely separated localities. Geological history of the stone, its crystal structure, and the type and quantity of impurities all probably have a significant effect on limestone reactivity.

Because limestone represents the lowest basicity available, it must be finely pulverized to get full value of this factor. When it is desired to treat acid waste, and there is ample time to develop a minimum pH, slow-acting limestone might be seriously considered. However, the amount of agent required for neutralization will depend largely on the quantities of acid and iron present in solution. The following reactions occur when limestone is added to sulphuric acid and iron sulphates:

$$CaCO_3 + H_2SO_4 \longrightarrow CaSO_4 + CO_2 + H_2O \quad \dots \dots \dots \dots \dots \quad (11)$$

$$3CaCO_3 + Fe_2(SO_4)_3 + 3H_2O \longrightarrow 2Fe(OH)_3 + 3CaSO_4 + 3CO_2 \dots \quad (12)$$

$$CaCO_3 + FeSO_4 + H_2O \longrightarrow Fe(OH)_2 + CaSO_4 + CO_2 \quad \dots \dots \dots \quad (13)$$
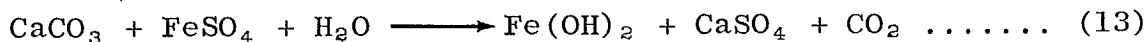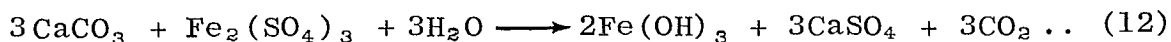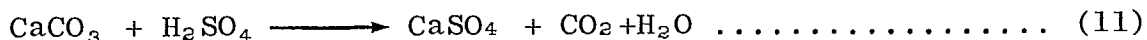
The diagram shown in Figure 1 relates the pH to what may be expected of limestone which is both high in calcium carbonate and magnesium carbonate[11]. The relationship denotes calcium and magnesium types of limestone having a terminal pH of 6.0 to 6.5. However, this condition is not maintained continuously, because the reactivity of calcium carbonate decreases gradually. This is a result of calcium sulphate coating its surface and the evolution of carbon dioxide. This gas is non-toxic, but its accumulation leads to formation of carbonic acid, which would tend to defeat the alkalinity of the limestone and the retardation of surface activity. If the carbon dioxide is not partially removed by aeration, satisfactory neutralization will not be accomplished. The air will also serve the purpose of hastening the formation of ferric hydroxide, by oxidizing the ferrous iron as the pH rises. Carbon dioxide is advantageous in limestone beds because the gas evolved would help to scour the limestone lumps of calcium sulphate, slime and oil contaminants. Although limestone activity improves with fineness of size, the corresponding increase in gas production that results will, if not properly vented, decrease the efficiency of neutralization. Long reaction periods are required of limestone if the water is high in ferrous iron as this does not start to precipitate until the pH is nearly 6. In such instances, a dual treatment using both limestone and lime would hasten the action. Lime could be used alone, but the water would become neutralized quickly and consume large amounts of the reagent to precipitate all the iron[12].

The pH range over which neutralization and precipitation occur is illustrated in Figure 2[13]. When mine acid is treated with a relatively strong alkali, ferric iron precipitates in the pH range of 2.5 to 5.0, and ferrous iron in the pH range of 5.0 to 9.0. During the early stages of the reagent addition, most of the free sulphuric acid becomes neutralized, and none remains in solution on reaching pH 7.

Sufficient limestone must be present for the reactions of Equations 11, 12 and 13 to go to completion. If only enough limestone is added to neutralize the free acid, an almost true basic ferric sulphate precipitate results. However, with excess calcium carbonate present--that is, after the free acid has been removed--the ferric sulphate is further reacted upon and decomposed
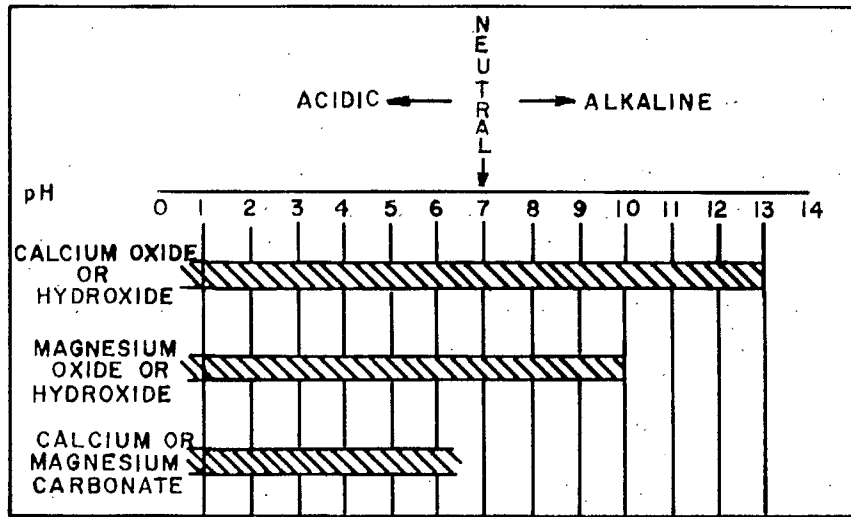
Figure 1. Relation between pH and calcium and magnesium carbonates.
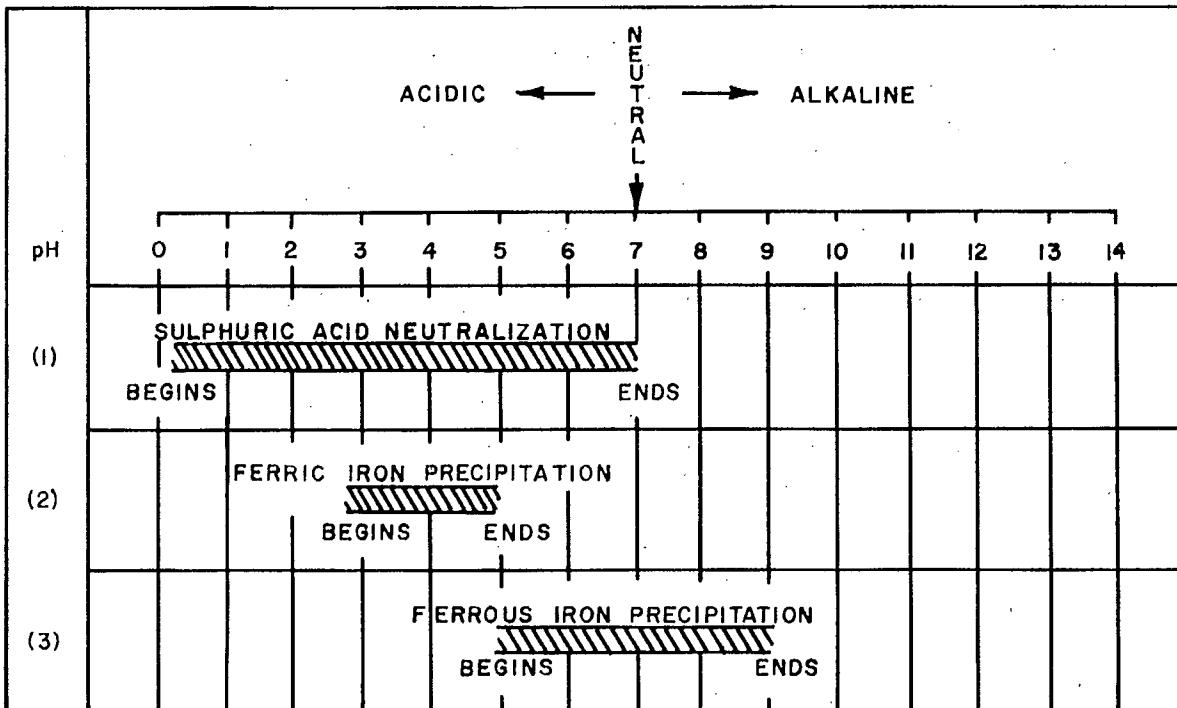
Figure 2. pH range for acid neutralization and iron precipitation.[13]

into ferric hydroxide and calcium sulphate. The calcium sulphate will remain in solution until the acidity is further decreased by additional calcium carbonate, after which calcium sulphate precipitates along with ferrous hydroxide. Theoretically, 341 lb of pure limestone will neutralize 80,000 U.S. gallons of water containing 0.5 g H_2SO_4/l. It is estimated that for every ton of ferric oxide produced, three quarters of a ton of minus-1/2-in.-mesh limestone is required.

To avoid long reaction times when using limestone, the sulphuric acid strength should not exceed 0.5%. A higher concentration of acid tends to coat the limestone particles with calcium sulphate and thereby decrease their ability to neutralize. The reaction between sulphuric acid and limestone is generally slow, especially when it contains appreciable quantities of magnesium carbonate. This is exemplified in Figure 3 where neutralization rate curves are plotted for limestone samples A, B and C[14].

Figure 3. Reaction rate curves for some limestones.

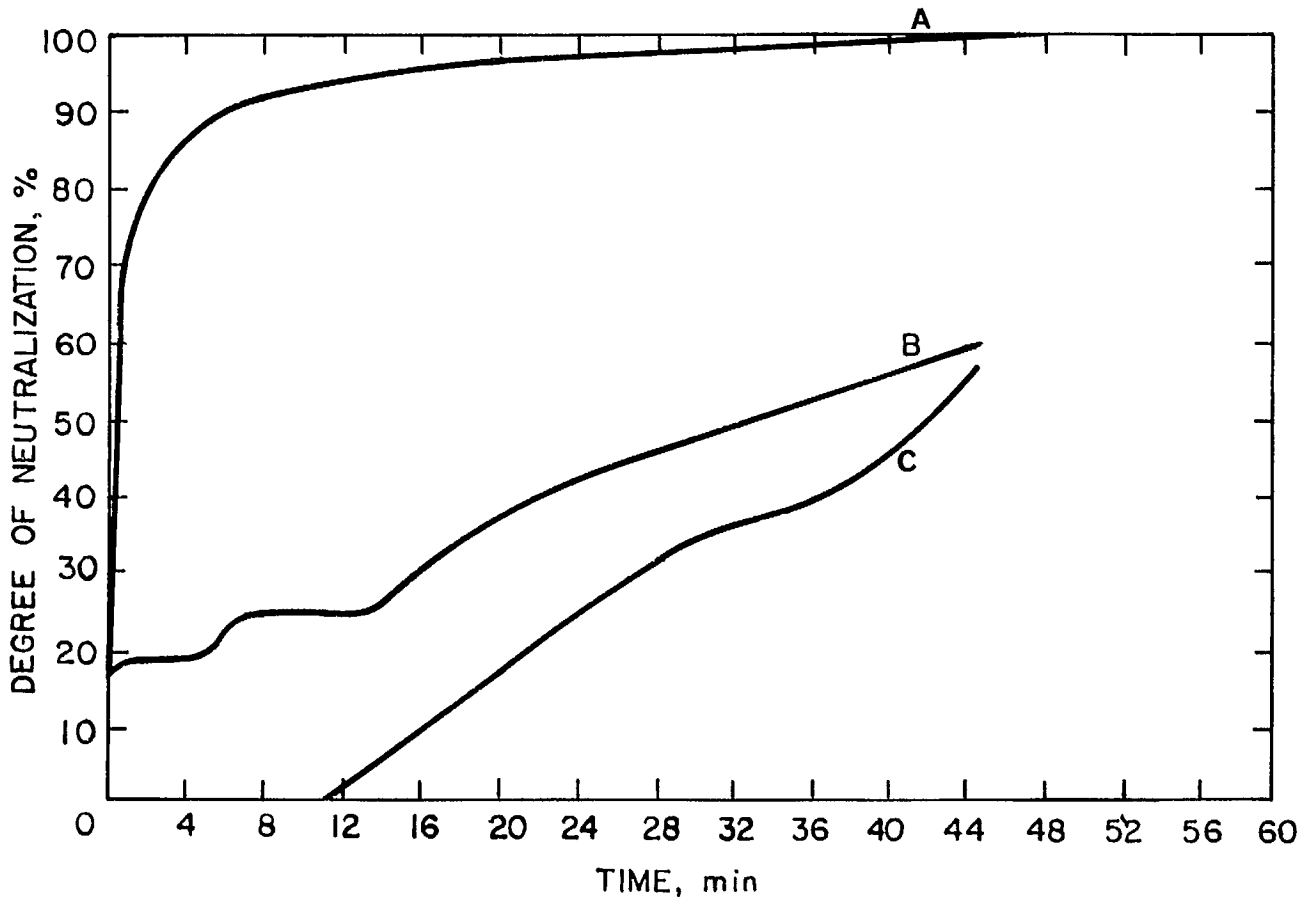In spite of the similar neutralizing power of these three limestones, the curves show the reaction rates to be different. Samples B and C contain greater quantities of magnesium than sample A, and their curves are typical of the reaction rates of dolomitic limestones. Other tests conducted on limestone, dolomitic limestone and dolomite showed that their activity decreased with increased content of magnesium carbonate and insoluble matter[15]. Furthermore, dolomite is said to have a pronounced effect on limestone; its rate of reaction is roughly inversely proportional to the percentage of magnesium carbonate if this constituent exceeds 2%. On the basis of these facts, it is essential to select a high grade of limestone for rapid and efficient neutralization. A good quality of limestone for neutralizing mine acid is suggested to be one containing at least 95% $CaCO_3$ and not more than 1% $MgCO_3$. For practical purposes, limestone can be assessed only through laboratory experiments using synthetically prepared acid solutions.

APPLICATIONS OF LIMESTONE

Reactor

A modified cement mixer of 1/4-cu-yd capacity was used in exploratory investigations as a reactor to treat coal-mine acid batchwise and on a continuous basis[12]. The chamber, with baffles and lifting plates, was set on an angle of 20° from the horizontal, and revolved at a constant speed of 22 rpm. Its inside surface was coated with epoxy resin to prevent extraneous iron from being dissolved by the acid water. The vigourous agitation afforded by the circular motion and the use of coarse limestone provided abrasion which removed the precipitated calcium sulphate solids from the neutralizing particles. This action was considered to re-activate their surfaces continuously, and to provide a large aeration surface for oxidizing ferrous iron to ferric iron and for removing carbon dioxide from the mixture.

Limestone used in this equipment was 1 1/2-in. size, and it analysed 94.3% $CaCO_3$, 0.21% $MgCO_3$ and 0.3% Fe. This material was reacted with three typical mine waters from a Pennsylvania coal field in a ratio of approximately 1 part water to 3 parts limestone, or 10 U.S. gal liquid to 150 lb solids. For experimental purposes, the mine waters were designated as B-1, B-2 and B-3 and were analysed as shown in Table 4. Each of these samples was mixed with the limestone at 12°C temperature for arbitrary periods of up to 30 min.

TABLE 4

Analysis of Raw Mine Waters Used in Reactor Experiments

Acidity and Iron Analysis, g/l	Water Sample		
	B-1	B-2	B-3
pH	3.20	4.55	3.25
Fe^{++}	0.00	0.748	0.470
Fe_{tot}	0.050	0.748	0.492

Figure 4 shows how the pH changes with time as limestone was added. It can be seen from these curves that the rate of neutralization for the three mine waters was quite rapid, but that it decreased somewhat with increasing Fe_{tot} content.
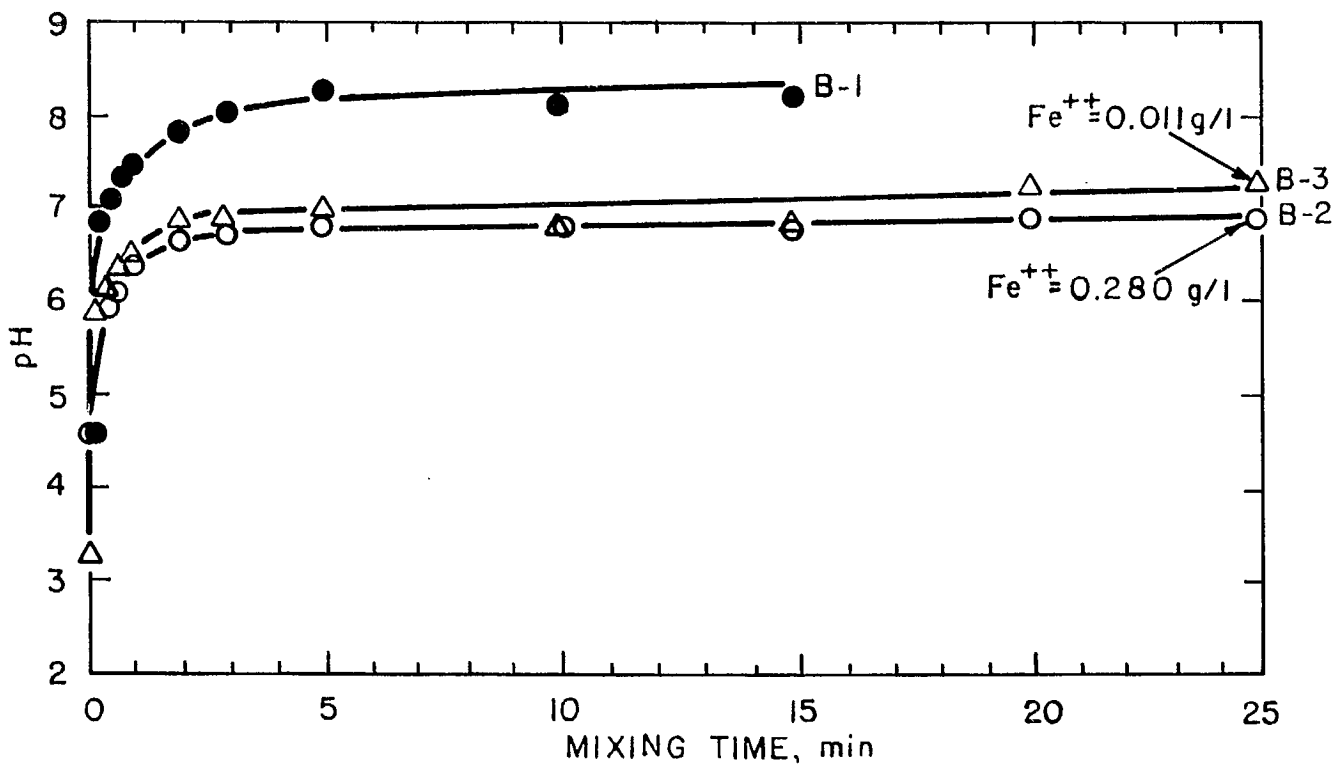
Figure 4. Limestone neutralization of B-1, B-2 and B-3 mine-waters.

Figure 5 illustrates how the concentrations of ferrous iron diminished with reaction time in three tests, 150 lb. limestone and 10 gal B-2 water, 250 lb limestone and 10 gal B-2 water, and 150 lb limestone and 10 gal B-3 water. The lower and upper curves show that when limestone is used, longer reaction periods are required with the mine water higher in ferrous iron. The middle curve indicates that an excess of limestone retards the removal of ferrous iron from solution.

Figure 5. Ferrous iron depletion with limestone treatment of various mine waters.

With water having a high iron content, the reaction time with limestone alone may be excessive. Therefore, a primary treatment with limestone to pH near 7, and a secondary treatment with lime to complete the precipitation of the remaining iron, may be necessary. This procedure was tried in the reactor, in which samples B-2 and B-3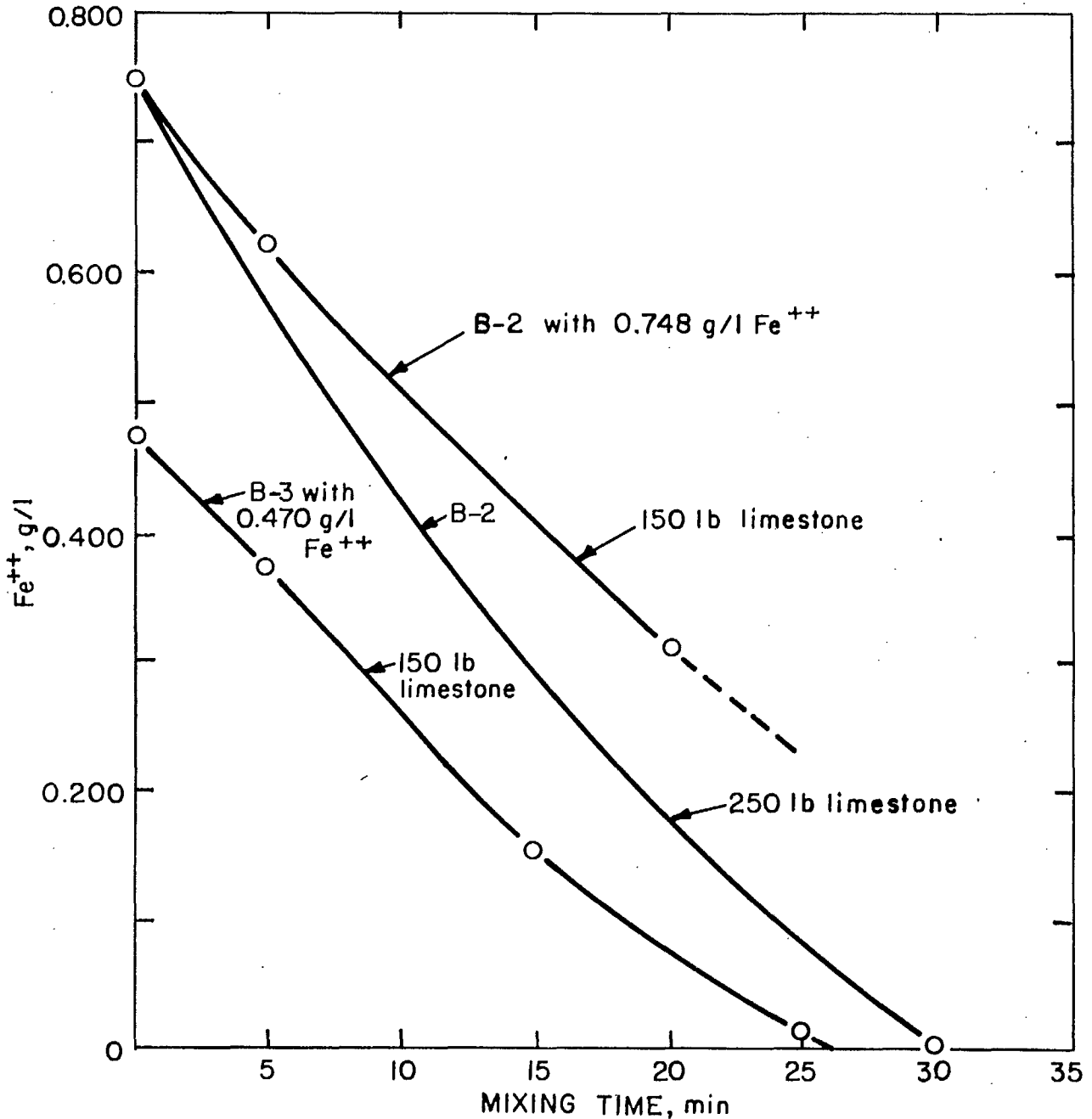 were mixed with the coarse limestone for 2 min and 5 min respectively, and then lime was added in small dosages until the solution pH reached between 8 and 9. The trend to ferrous iron depletion of the two mine waters in this study is shown in Figure 6.

Continuous neutralization was carried out in the cement mixer by introducing the mine water through a pipe submerged in the coarse limestone and allowing it to discharge near the opening of the vessel. Settling containers were provided for collecting the concentrated solids and the clear effluent. In one test, 700 gal of raw water, of pH 5.8, of 0.07 g Fe^{++}/l and at 12°C, was treated with 150 lb of 1/2-to-1-in.-size limestone over a period of 10 hours. The final discharge was measured at pH 7.3, and was analysed at no more than 0.003 g Fe^{++}/l.

Bed

One arrangement for neutralizing acid mine-water is to pass it through a bed containing coarse limestone, as shown in Figure 7[16]. This unit offers distinct advantages over other methods of neutralization because it is of simple design and requires little maintenance. The upward flow of solution through the interstices of the bed permits maximum utilization of the limestone. While solution flow is easily controlled, it imparts a washing action by keeping the limestone free of precipitates. It is recommended that the bed should be large in cross-sectional area and volume relative to the quantity of solution being processed, to keep the deposits of calcium sulphate and iron hydroxides on the limestone particles to a minimum and thereby obtain the most effective results. Furthermore, the system gives the minimum of trouble with respect to choking of the bed and to plugging of the false bottom.

The neutralizing power of minus-4-plus-6-mesh limestone of 98% $CaCO_3$ in a solution of 0.200 g/l H_2SO_4 is shown in Table 5[15]. The speed of neutralization suggests that limestone of approximately 1/4-in. size would be practical for treating acidic wastes in beds.
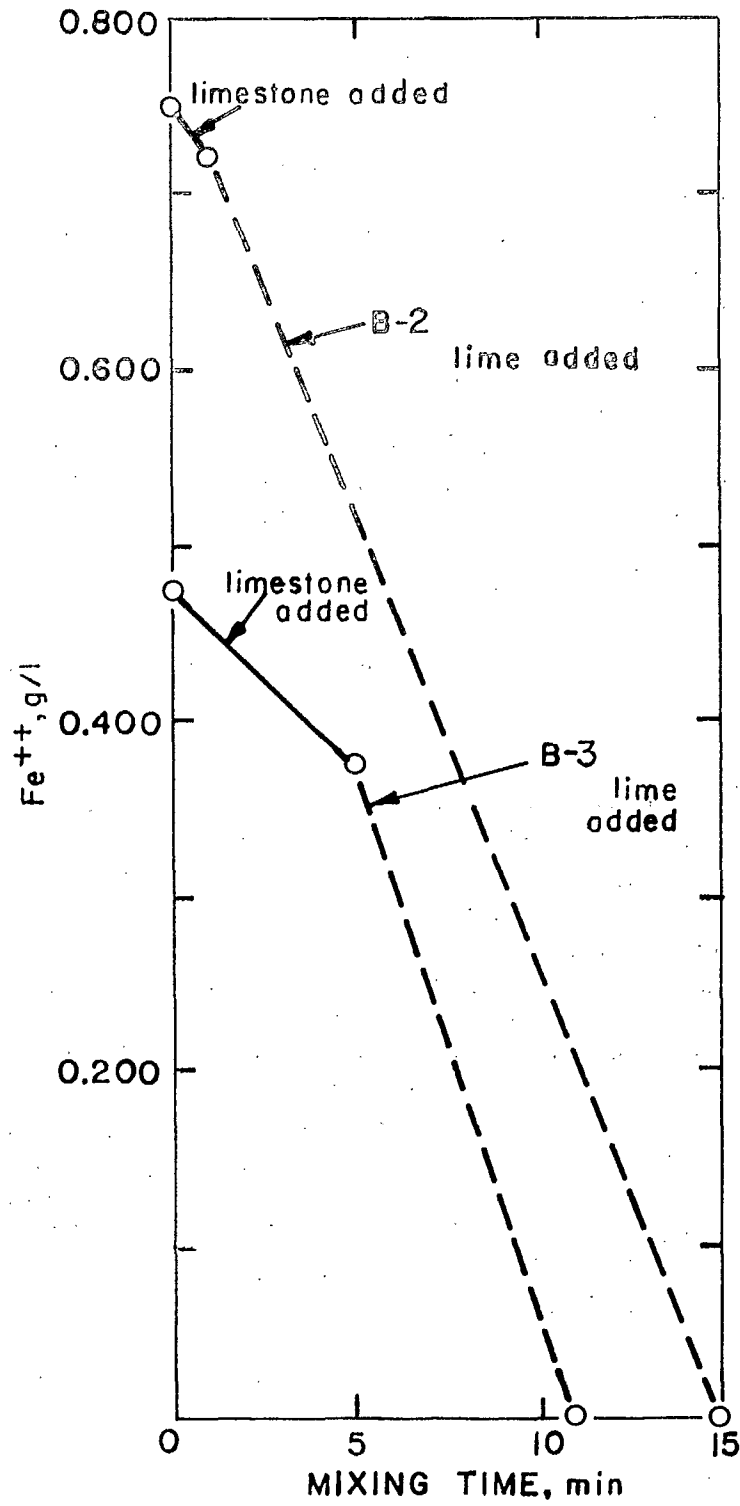
Figure 6. Ferrous iron depletion with limestone-
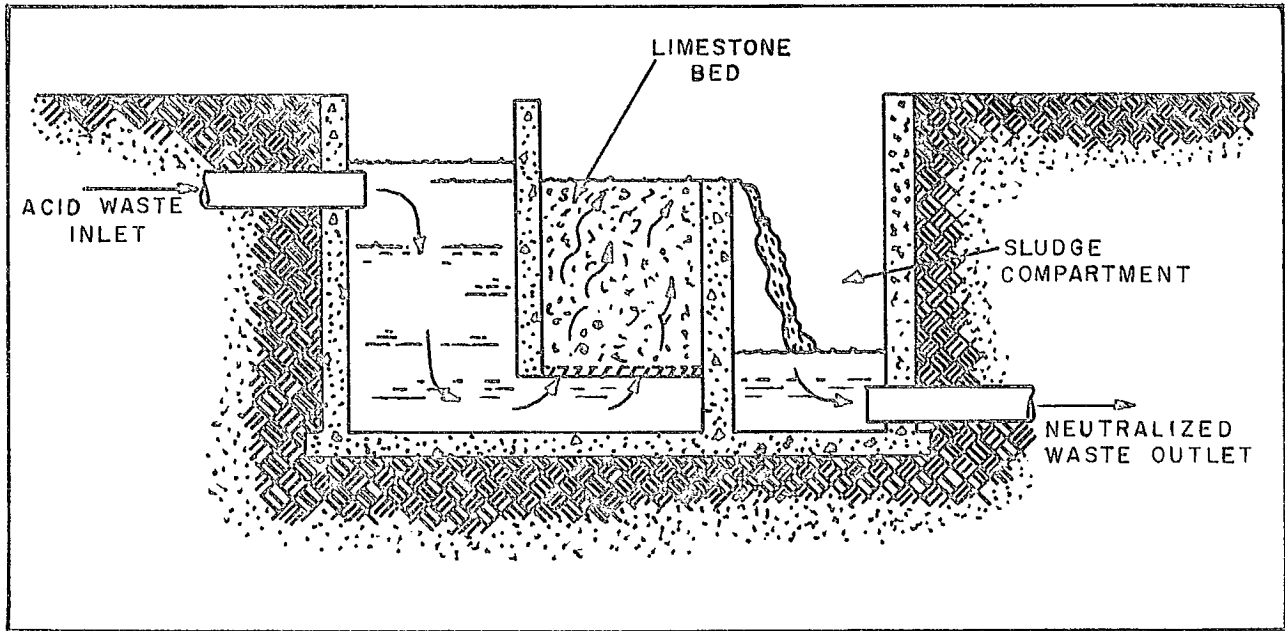lime mixed treatment.

Figure 7. Limestone bed for neutralizing acid waste.

TABLE 5

Neutralization of Free Acid by a Limestone Bed [15]

Cumulative Time of Contact, sec	pH	H_2SO_4, g/l
0	3.0	0.20
11	5.5	trace
19	6.0	trace
27	6.3	trace
45	6.9	trace
57	7.1	none

A series of experimental limestone beds has been used successfully to neutralize waste from acid-dipping and plating operations in a U.S. plant[17]. The reaction is carried out in a concrete box designed to handle approximately 200 gal of plating room effluent per minute. It consists of, as illustrated in Figure 8, a diluting and storage area divided into three chambers, and a neutralizing compartment containing two beds of 1/8-in.-size limestone supported by a layer of large trap rock. The first chamber acts as an accumulator for oil, grease and floating matter, and the second chamber for collecting all sludge and foreign material heavier than water. The suction line for the eductor is placed in the last chamber. The limestone beds varied in depth from 18 to 24 in., and were constructed to give uniform pressure and flow over the entire area, thus preventing channelling and yielding best results. Because of the shallowness of the sewer at Philadelphia where the unit was installed, it was necessary to lift the solution to give the head required for gravity flow through the beds to the sewer.

Acid waste, discharged from the plating room at a rate of 200 gpm, was mixed with from 1 to 2 parts neutralized water to keep its pH to a minimum value of 3 before going into the first limestone bed. Values lower than pH 3 had a tendency to coat the limestone with calcium sulphate. With the solution on the incoming side of the bed having a pH of 3, its acidity was easily raised to a figure of 5 or 6. However, to achieve this result, 200 gpm of the neutralized water were returned to the head of the circuit and aerated to drive out the carbon dioxide gas.

Slurry

In an actual working plant, limestone of minus-20-mesh size is slurried in water and fed to a sewer line carrying industrial waste of 0.5% H_2SO_4 or less[14]. Figure 9 shows a schematic view of the installation. The sewer line carrying the limestone-acid mixture was maintained at a minimum velocity of 3 ft/sec in order to keep the unreacted limestone in suspension. Optimum conditions for the neutralizing reaction was about 30 min. The effluent was finally released into an open ditch where it flowed rapidly for at least one mile into a settling basin where the unreacted limestone was removed. Provisions were made to create aerating conditions on the spillway of the dam to assist in the removal of dissolved carbon dioxide.
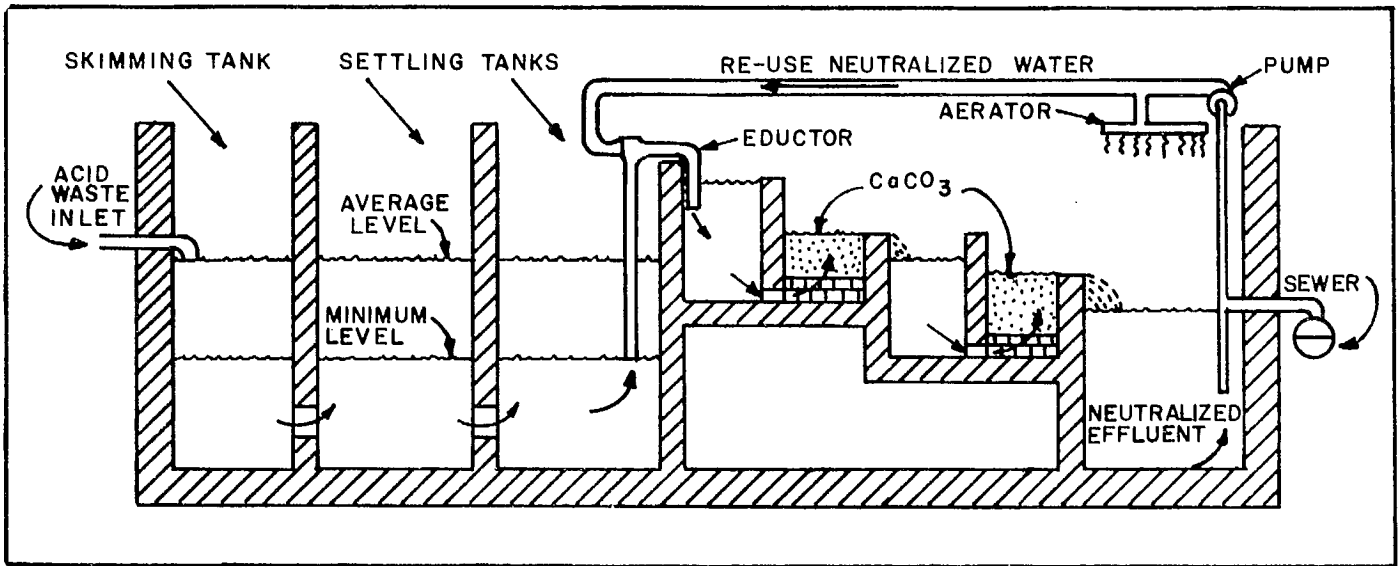
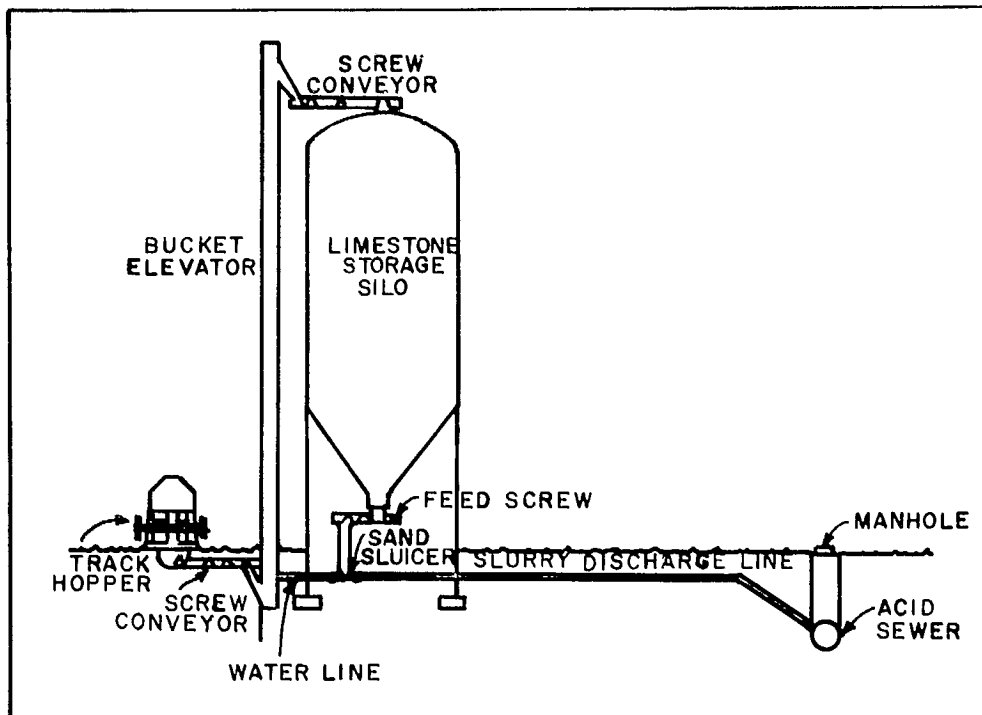Figure 8. Limestone beds for treating plating effluent.

Figure 9. Acid neutralization with limestone slurry.

The acid sewer line shown in the diagram collected all
the plant acid wastes, together with wastes from other sewer
lines, at a point ahead of limestone addition. The resulting
dilution decreased the acid strength to the desired level
(see page 9) of 0.5% H_2SO_4 before neutralization. Although the
slurry was abrasive, all that was found necessary was to renew
the piping at the bends once every two years.

The only trouble encountered in handling the fine
limestone was in obtaining a reasonable flow of the material
from the railroad car[14]. This was due to its becoming
thoroughly packed in transit, which was over a distance of 12
miles, and the result was difficulty in breaking it loose and
starting it flowing to the screw conveyor. Also, it was stated
that for good feeding properties the limestone must contain less
than 1% moisture.

A plant at the Calumet mine in Pennsylvania using minus-
200-mesh limestone for the continuous treatment of acid coal-mine
water is presented in Figure 10[18].

The pulverized limestone used to neutralize the acid
mine water is delivered to a mixing tank by means of a screw
conveyor. While the amount of powdered limestone used depends
on the quantity of sulphuric acid and dissolved iron, it can be
varied by adjusting the speed of the conveyor. Limestone and
water are thoroughly mixed as the water enters the tank and
passes over and under a series of baffles. Specially designed
flumes conduct the limestone-mine water mixture, at 1.5% grade,
to the centre of a Dorr thickener (varying in depth from 7 ft to
12 ft) 200 ft away. The flumes impart an undulating motion,
which completes the mixing of the solids and liquid commenced in
the mixing tank. This motion also aerates the slurry to help
liberate carbon dioxide and promote oxidation of the iron. A
flow of 1,000,000 gallons of mine water through the thickener
every 24 hours allows a settling period of 4 hours. During
this time, the suspended ferric hydroxide settles to the bottom
of the thickener and the clarified overflow is carried away to
storage for disposal. The underflow, consisting of compacted
sludge, is pumped out and fed to rotary driers from which the
iron powder is scraped off and shipped away.

Table 6 shows the content of the Calumet mine water
before and after neutralization with fine limestone. Table 7
shows the composition of the ferric oxide as it comes from the
drier.
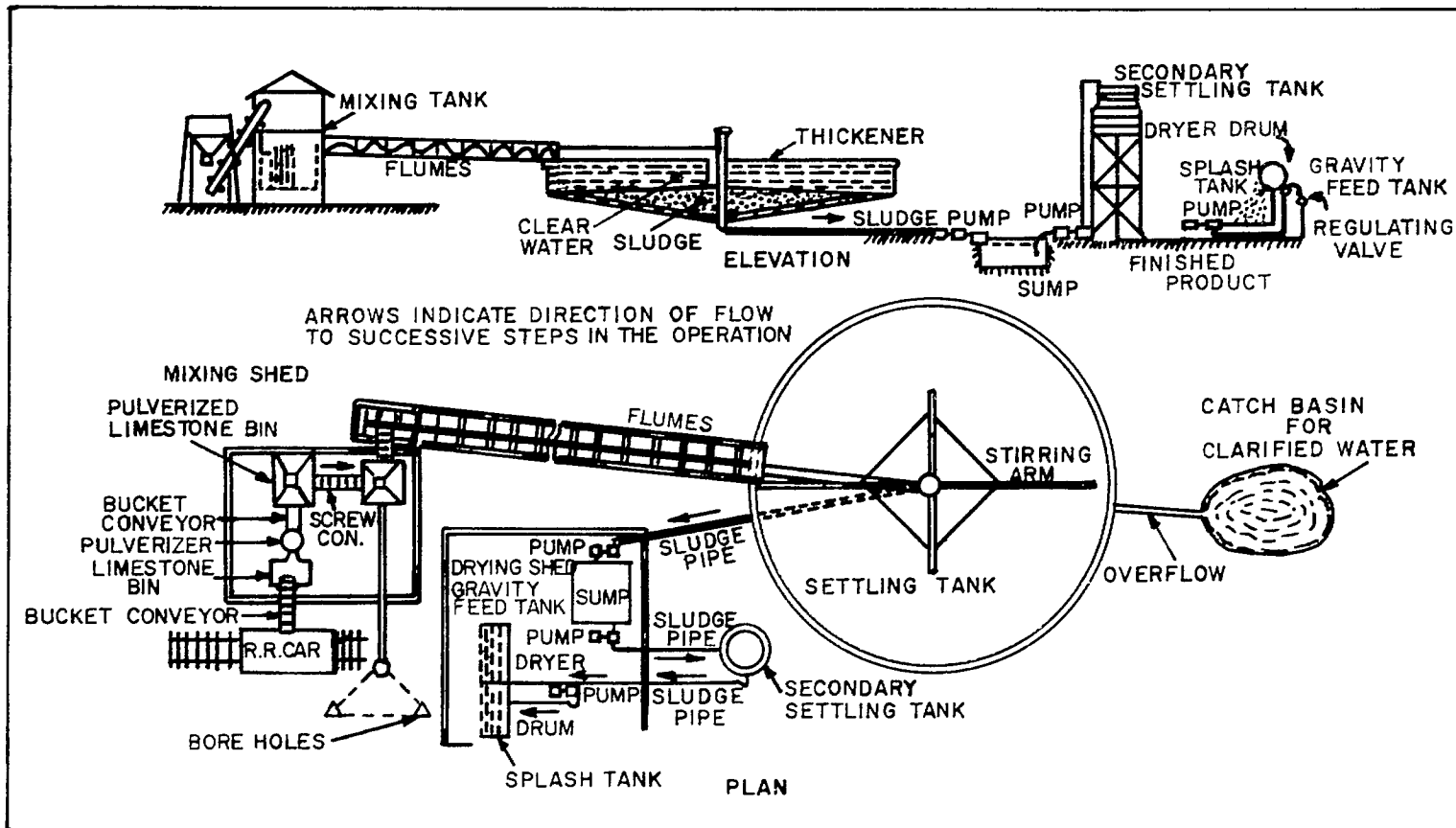
Figure 10.   Plan and elevation of acid neutralization plant.

TABLE 6

Analysis of Calumet Mine Water

Constituent	Before Limestone Treatment	After Limestone Treatment
Free H_2SO_4, g/l	0.36	0.012
Fe^{++}, g/l	0.035	0.004
Fe^{+++}, g/l	0.28	0.00

TABLE 7

Analysis of the Dried Ferric Oxide Product

Constituent	% Weight
SiO_2	13.0
TiO_2	0.3
Al_2O_3	10.3
P_2O_5	1.0
Fe_2O_3	37.0
CaO	13.2
MgO	0.6
K_2O	1.0
Na_2O	0.7
SO_3	11.6
H_2O (combined) above 105°C	4.8
CO_2	6.4
Total	100.0

A new concept in limestone treatment of acid mine-water, and proven to be highly successful in pilot-plant tests, is illustrated in Figure 11[19]. Briefly, the process consists of:

(1) producing a fine limestone slurry in an autogenous mill,

(2) contacting it with the mine effluent in a mixing trough,

(3) aerating the resultant mixture in a large pond,

(4) separating the solids from the liquid in another but smaller pond, and

(5) discharging clean water from it to the main lagoon.

Preliminary tests indicated that initial neutralization occurs faster with micron-size limestone than with lime. Analyses of the limestones and mine water involved in the plant study are shown in Tables 8 and 9, respectively.
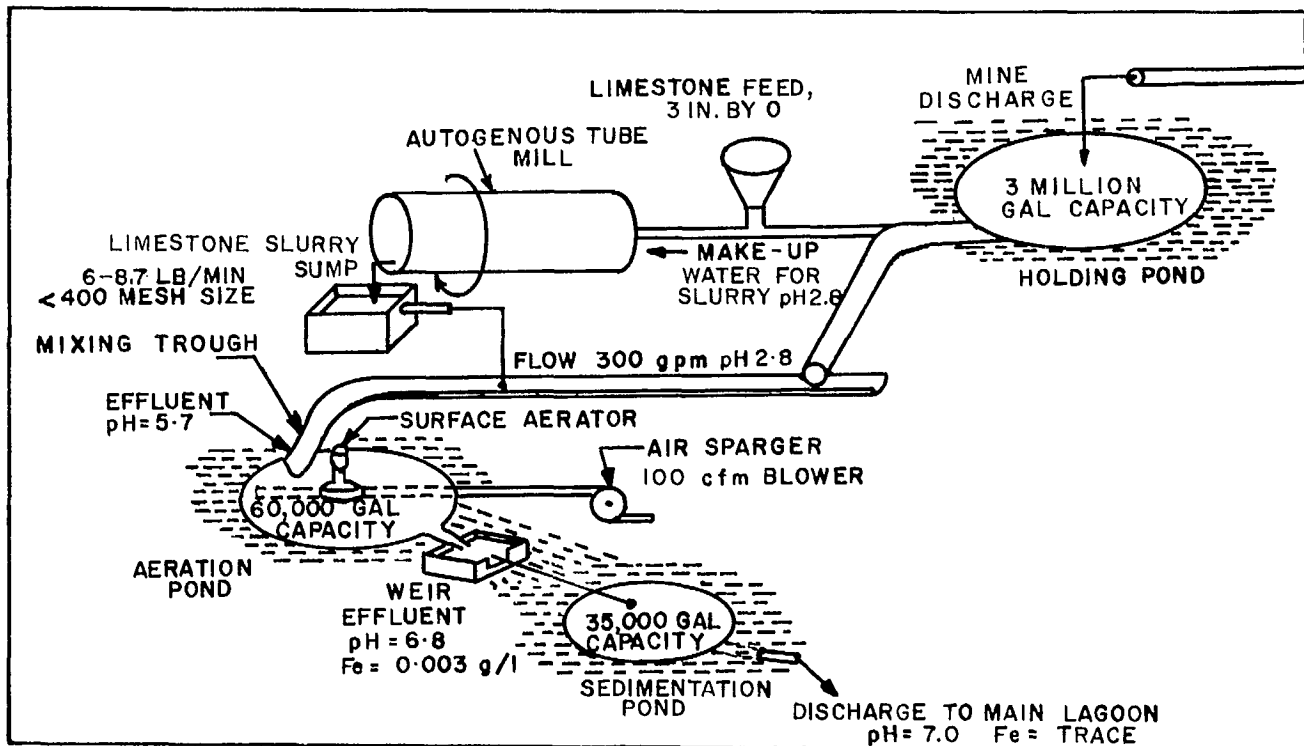

Figure 11. Pilot-plant flowsheet for neutralizing mine water with limestone slurry.

TABLE 8

Analysis of Limestones

	Limestone	
	Pennsylvania	West Virginia
Size, in.	3 x 1	1 x 0
Constituent	%	%
$CaCO_3$	72.0	82.0
$MgCO_3$	5.6	2.4
Fe_2O_3	1.6	1.7
Al_2O_3	4.5	1.3
SiO_2	14.6	8.0

TABLE 9

Analysis of Mine Water

Temperature, °C	-	15
pH	-	2.84
Acidity*, g/l	-	1.60
Sulphate "	-	3.90
Fe^{++} "	-	0.35
Fe^{+++} "	-	3.35
Ca "	-	0.25
Mg "	-	0.60
Al "	-	0.11

* As determined by hot phenolphthalein
  solution.

As indicated in Figure 11, crushed limestone and water
are fed to a 3-ft-diam by 24-ft-long tube mill, from which the
ground material is discharged into a sump. Here the solids are
classified, so that only the very fine particles (90% minus-400-
mesh size) are permitted to overflow into the 2-ft-diam by 60-ft-
long semi-circular trough. Mine water is fed by gravity from
the holding pond to the tube mill and feed trough, but only a
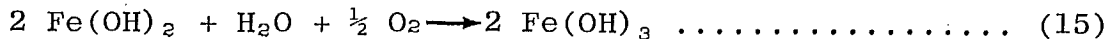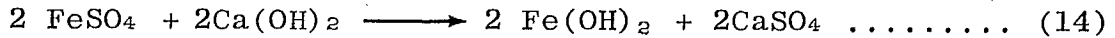small portion of the water to be treated is diverted to the mill

for autogenous grinding. The mine water meets the fine limestone slurry in the 60-ft trough, but the resultant mixture travels only a distance of 30 ft before it discharges into the aeration pond. Five seconds after the mine water and limestone make contact in the trough, the acidity changes from pH 2.8 to > 5.0. A further increase to pH 6.8 was observed in the aeration pond, where sparged air also conditions the slurry for settling in the sedimentation pond. The overflow discharging into the lagoon is considered of acceptable quality by the Pennsylvania health authorities.

Slurried limestone is easily prepared in a simple tube mill, because it requires a minimum of maintenance and control. Power to generate fine limestone in this type of mill is comparable to that required for commercial grinding devices. The cost of producing one ton of fine limestone is approximately 67¢ based on power at the rate of 1.5 ¢ per kilowatt hour. Furthermore, the ease of handling coarse limestone and limestone slurry permits low-cost techniques and efficient operation. Because it is impossible to overtreat to a pH greater than 8.4, expensive precision controls are unnecessary. For aerating the final effluent, standard equipment was found to be adequate.

At a rate of 1 million gallons per day, mine water analysing 2.0 g/l total acidity would require nearly 17 tons of limestone per day (assuming 50% utilization based on inert material and excess $CaCO_3$), costing $50 per day. These figures compare with 6 tons hydrated lime (assuming 100% efficiency), costing $120 per day. The savings in cost of neutralizing agent alone is equivalent to at least $25,000 per year. Furthermore, limestone yields more rapid settling rates and better sludge compaction than does lime, thus minimizing sedimentation.
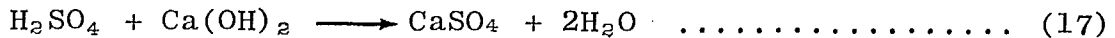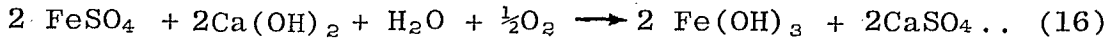
PROPERTIES OF LIME

Lime (CaO) is used widely in the treatment of acid drainage in the anthracite regions of Pennsylvania because ferrous iron is relatively high. The alkali agent is most effective when it is slaked with water to form hydrated lime ($Ca(OH)_2$), which reacts as follows[20];

$$2 FeSO_4 + 2Ca(OH)_2 \longrightarrow 2 Fe(OH)_2 + 2CaSO_4 \quad \ldots\ldots\ldots \quad (14)$$

$$2 Fe(OH)_2 + H_2O + \tfrac{1}{2} O_2 \longrightarrow 2 Fe(OH)_3 \quad \ldots\ldots\ldots\ldots \quad (15)$$

Adding Equations 14 and 15:

$$2 FeSO_4 + 2Ca(OH)_2 + H_2O + \tfrac{1}{2}O_2 \longrightarrow 2 Fe(OH)_3 + 2CaSO_4 \ldots \quad (16)$$

$$H_2SO_4 + Ca(OH)_2 \longrightarrow CaSO_4 + 2H_2O \quad \ldots\ldots\ldots\ldots \quad (17)$$

The reaction rates of high-calcium hydrated lime and of dolomitic lime, although very rapid, are slightly retarded by insoluble calcium sulphate. However, the formation of calcium sulphate is less when dolomitic lime is present, because magnesium sulphate is soluble in water. As was shown in Figure 1, lime (CaO) or hydrated lime $Ca(OH)_2$ is effective over the entire pH range, and magnesia (MgO) or hydrated magnesia ($Mg(OH)_2$) is effective in the entire pH range below 10. Retention times for these compounds, and the corresponding carbonate to reach various pH values in sulphuric acid, are demonstrated in Figure 12[13]. The curves show that the reaction rates of CaO or $Ca(OH)_2$ differ sharply from those of MgO or $Mg(OH)_2$. Furthermore, the reaction rates of these oxides and hydroxides differ sharply from their carbonates.

If it is desirable to treat acid waste to a pH of 7 or higher, and its rate of flow is high and space is limited, high-calcium lime may be the wisest choice. However, if the waste contains sulphuric acid, which is often the case, and sufficient reaction time is available to efficiently achieve a pH of about 7, dolomitic lime is preferred in order to take advantage of the solubility of magnesium sulphate. Figure 13 shows the quantities of slurried dolomitic quicklime that developed pH values of 6.0, 6.5 and 7.0 at the rates indicated. The curves suggest that when using 12.0 lb lime per 1000 gal of 0.25% sulphuric acid solution, pH values of 6.0, 6.5 and 7.0 can be attained in 4.5, 6.0 and nearly 9 min, respectively. Similar results can be obtained with lesser amounts of reagent, but longer retention times will be required.
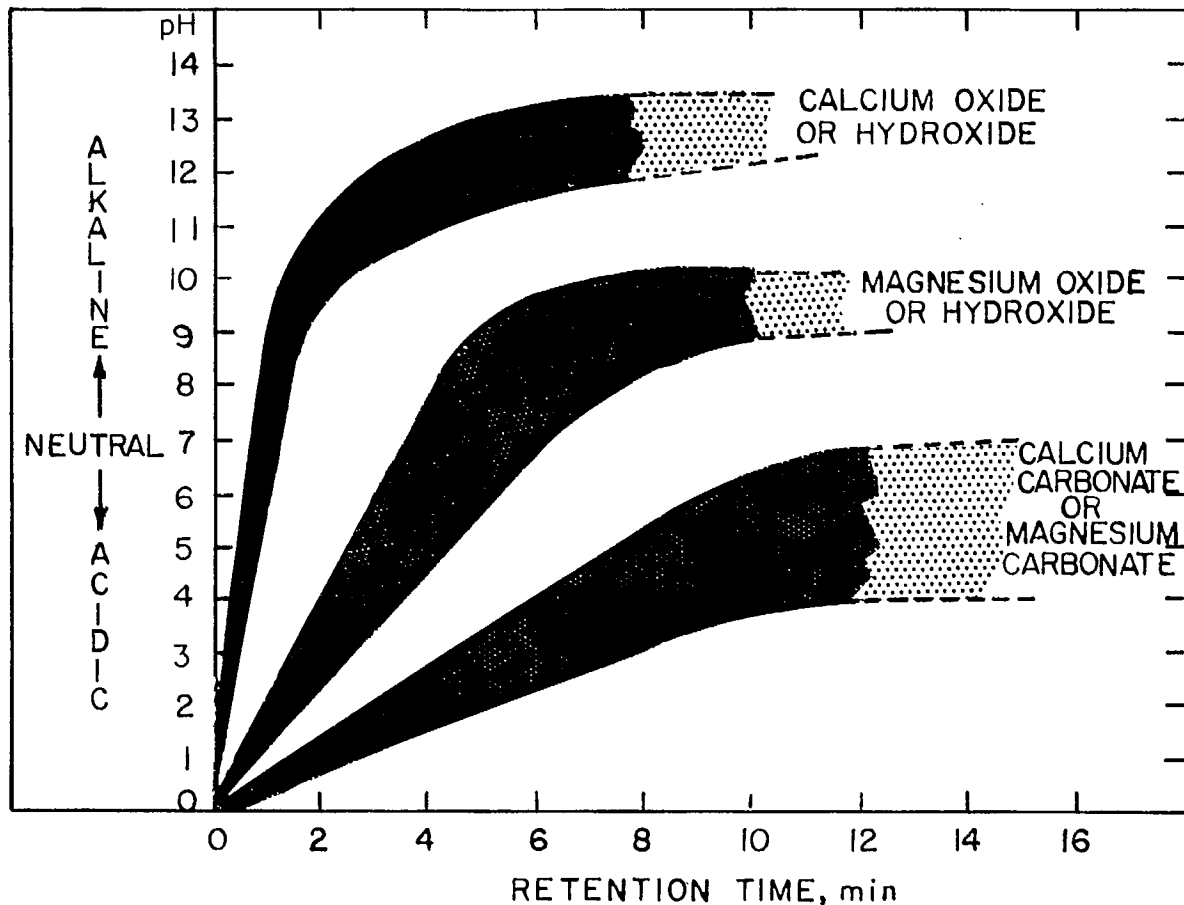
Figure 12. Generalized reaction rates for calcium and magnesium hydroxides and for corresponding limestones.

First attempts to neutralize acid waste with dolomitic lime were unsuccessful, for the reason explained in Figure 14[11]. The pH was controlled in terms of flow rate one minute downstream from the point of lime addition. Therefore, in one minute of neutralizing to pH 6.5, excess lime was being added. Calcium oxide reacted with the sulphuric acid, and since lime was in excess, there was never enough acid available to react with the magnesium oxide, thus leaving this component of the lime in the sludge. The relatively high calcium-sulphate and low magnesium-oxide contents of this sludge are not indicative of poor lime efficiency, but rather, as apparent from Figure 12, of a need for a longer retention time. When the pH control unit was placed 8 min downstream from the point of lime addition, complete utilization of the calcium and magnesium components of the dolomitic lime resulted. Also, the amount of calcium-sulphate sludge formed was substantially lowered because of the small but useful solubility of calcium sulphate. The only solids
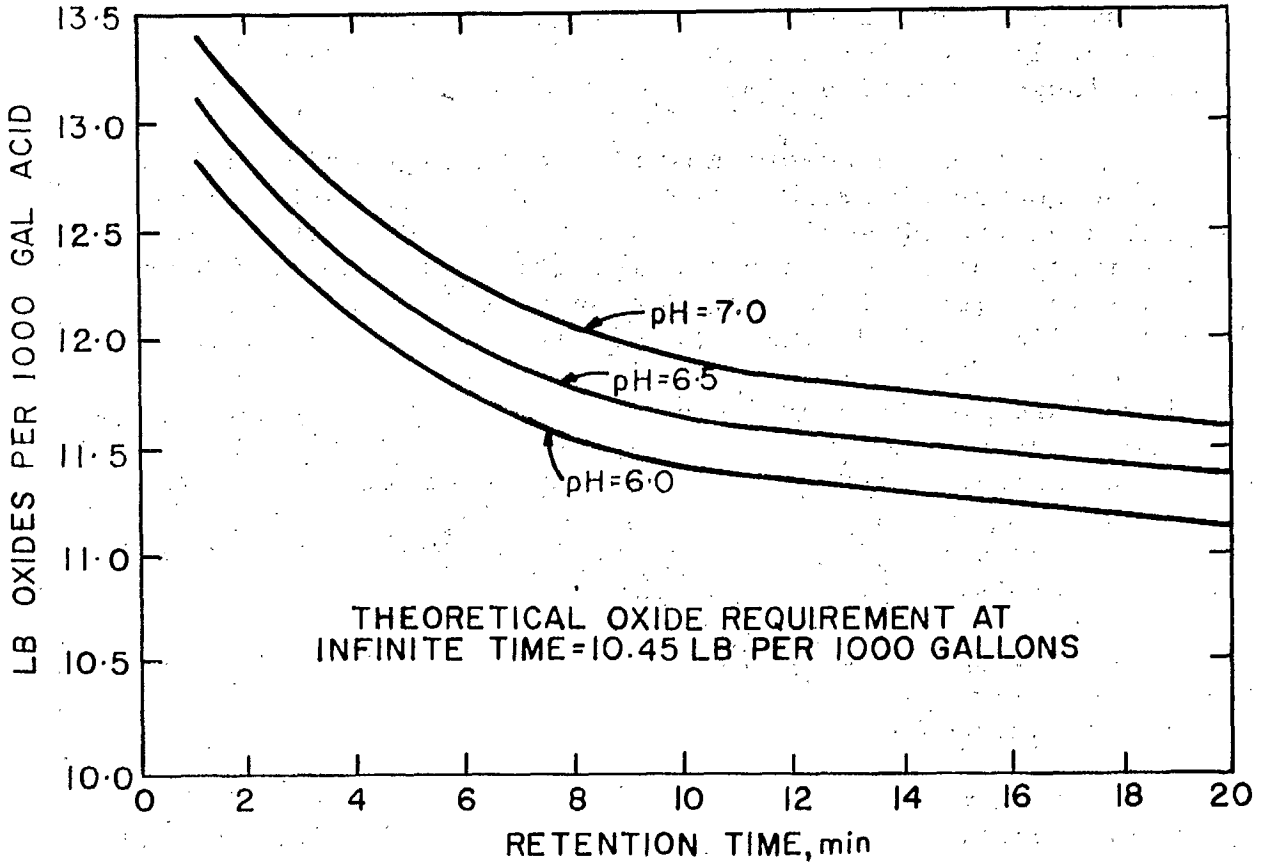
Figure 13.   Lime required to neutralize 0.25% sulphuric acid solution, using dolomitic quicklime.
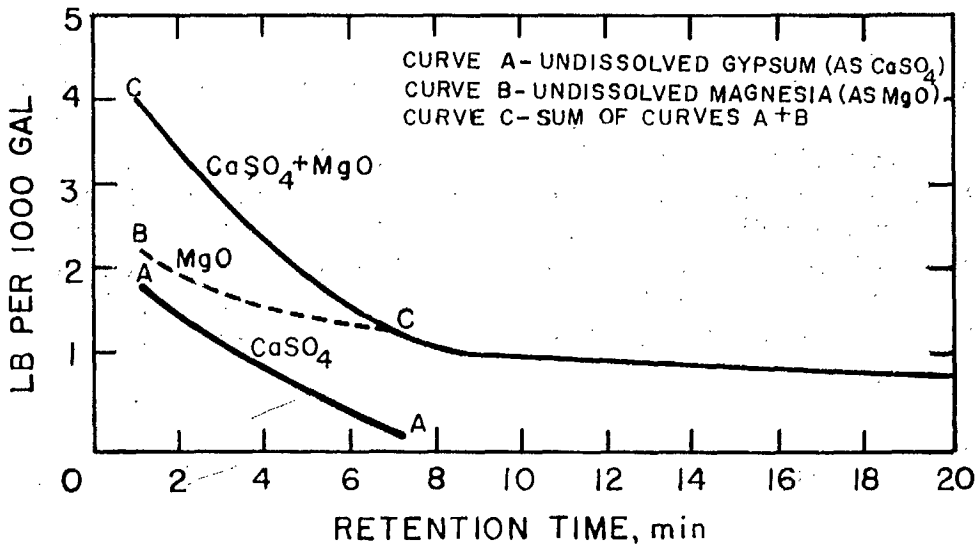

Figure 14.   Theoretical composition of sludge when neutralizing acid waste to pH 6.5 with dolomitic quicklime.

remaining, except for impurities, were a small amount of unreacted magnesium oxide representing the slight excess of lime used. Therefore, lime efficiency was considered to be almost 100% under a longer reaction time.

In treating waste solution with high-calcium lime, the three components H_2SO_4, $FeSO_4$ and $Fe_2(SO_4)_3$ behaved as indicated on the pH scale of Figure 2. Besides completely neutralizing the liquor and precipitating all the iron from it, high-calcium lime left a solution saturated with calcium sulphate. Dolomitic lime will do likewise but it begins to lose its efficiency on the alkaline side. What happens is that in the earlier stages of lime addition, magnesium sulphate goes into solution, but in the later stages, when the pH is on the alkaline side, the calcium-oxide portion of the dolomitic lime reacts with the soluble magnesium sulphate to precipitate magnesium hydroxide and gypsum. When the volume of pickle liquor is large and the flow rate is rapid (leaving no opportunity to oxidize the ferrous iron to ferric with air), high-calcium lime is preferred. However, if the waste liquor happens to be near a source of dolomitic lime, it is still, even with its reduced efficiency, an economic reagent.

When waste pickle liquor, which originates from steel mills and contains mostly ferrous sulphate and sulphuric acid, is treated with lime, it reacts as indicated in Equations 14, 15, 16 and 17 (see page 24)[20]. In Figure 2, it can be seen that it is not necessary to treat beyond a pH of 8.5 if the ferrous iron can be converted to ferric iron. This is possible because iron oxidizes readily under alkaline and aerating conditions. Small volumes or low flow-rates will favour such an oxidation reaction. When lime or limestone is added to the waste liquor and the mass is blown with air while kept within the pH range over which ferric iron precipitates, 2.8 to 5.0 (see Figure 2), ferrous iron will oxidize to ferric iron and precipitate. This relieves the pickle liquor of all dissolved iron and mineral acid without exceeding the neutral point of pH 7. Effluent from lime treatment will be saturated with gypsum and that from dolomitic lime treatment will contain soluble magnesium sulphate. If the resultant iron slurry is well agitated, it can be discharged to a lagoon where the dissolved iron in the supernatant will oxidize quickly and that in the solids will oxidize slowly. The latter action might take several years to complete. Under aerating conditions, the rate of oxidation of ferrous salts increases rapidly as the liquor pH is increased by the addition of lime. The action tends to leave an excess of calcium hydroxide over the stoichiometric requirement of the liquor because anions,

which would otherwise combine with calcium ions, are removed
from solution. Consequently, it appears possible to successfully
treat acid pickle liquor with less lime than its acid value
would indicate.

A neutralization nomograph, which is presented in
Figure 15, gives a rapid method for determining the weight of
lime required to completely neutralize a definite volume of waste
pickle liquor[21]. Although this liquor is essentially an aqueous
solution of sulphuric acid and ferrous sulphate, the nomograph
can be readily applied to other acidic waste solutions.

In order to assess the quantity of alkaline agent
required, the acid value of the liquor and the basicity factor
of the lime must be known. These figures can be obtained by
carrying out the following procedures:

Acid Value. Add 25 to 30 ml 0.5 N NaOH in excess of
that required for complete reaction to 50 ml distilled water con-
taining a 5-ml pipette sample of acid liquor. Heat to boiling
for 3 min to convert the precipitate to black iron oxide. Cool
and transfer the mixture to a 250-ml volumetric flask and make
up to the mark with distilled water. Pipette a 100-ml portion
from the flask and titrate with 0.5 N H_2SO_4, using phenolphthalein
as an indicator. The sulphate is calculated from the formula:

$$12 \text{ (ml NaOH - ml } H_2SO_4) = g \ SO_4/l$$

Basicity Factor. Weigh accurately into a porcelain
crucible about 1.3 g lime. Place the crucible in a 250-ml
beaker containing 15 ml water, cover, and heat to boiling and
tip the crucible to fill it with the hot water. Allow several
minutes to slake the lime completely, scrub the crucible inside
and out with a rubber policeman, wash and remove it, run in
enough 0.5 N H_2SO_4 to react with the lime, and add 30 to 35 ml
in excess. Now wash the mixture into an Erlenmeyer flask, boil,
cool, and titrate with 0.5 N NaOH using a phenolphthalein
indicator. The basicity factor is calculated as follows:

$$\frac{0.028 \text{ (ml } H_2SO_4 \times N) - \text{(ml NaOH} \times N)}{g \ sample} = g \ CaO/g \ sample$$

When figures have been obtained for acid value and
basicity factor, pounds of alkaline agent required per gallon of
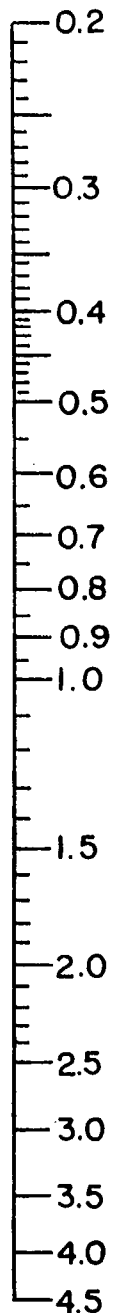acid liquor can be assessed from the nomograph, Figure 15.

BASICITY FACTOR
Grams equivalent
CaO per g sample
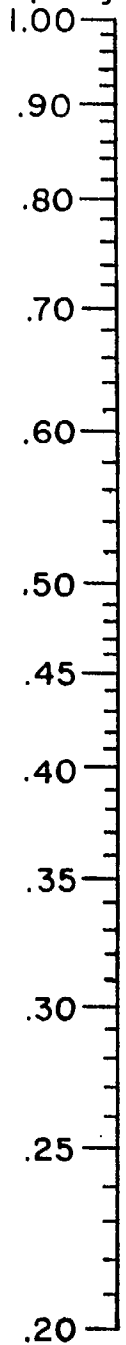
ALKALINE AGENT
Pounds per gallon

ACID VALUE
Grams SO$_4$
per litre

Connect Scales A and B with straightedge and read the result
on Scale C

Figure 15. Chart for determining alkali requirement in
acid waste neutralization.[21]

While the reaction time between slurried lime and
pickle liquor is completed in 15 min under well agitated
conditions, it is the usual practice, when using lime for
neutralization, to add an excess of about 3%.

APPLICATIONS OF LIME

Agitated Tank

An installation that uses ordinary hydrated lime for
neutralizing sulphuric acid is shown in Figure 16[14]. The lime
is removed from bulk storage to a hopper below by a positive-type
feeder but, since the material has a tendency to pack, agitators
or vibrators must be applied. After the lime is slurried, it is
transported through a 2 1/2-in. rubber hose to the down pipe of
the mixing tank through which the acid waste solution is introduced.
The mixture is well agitated for a retention time of about 2 min,
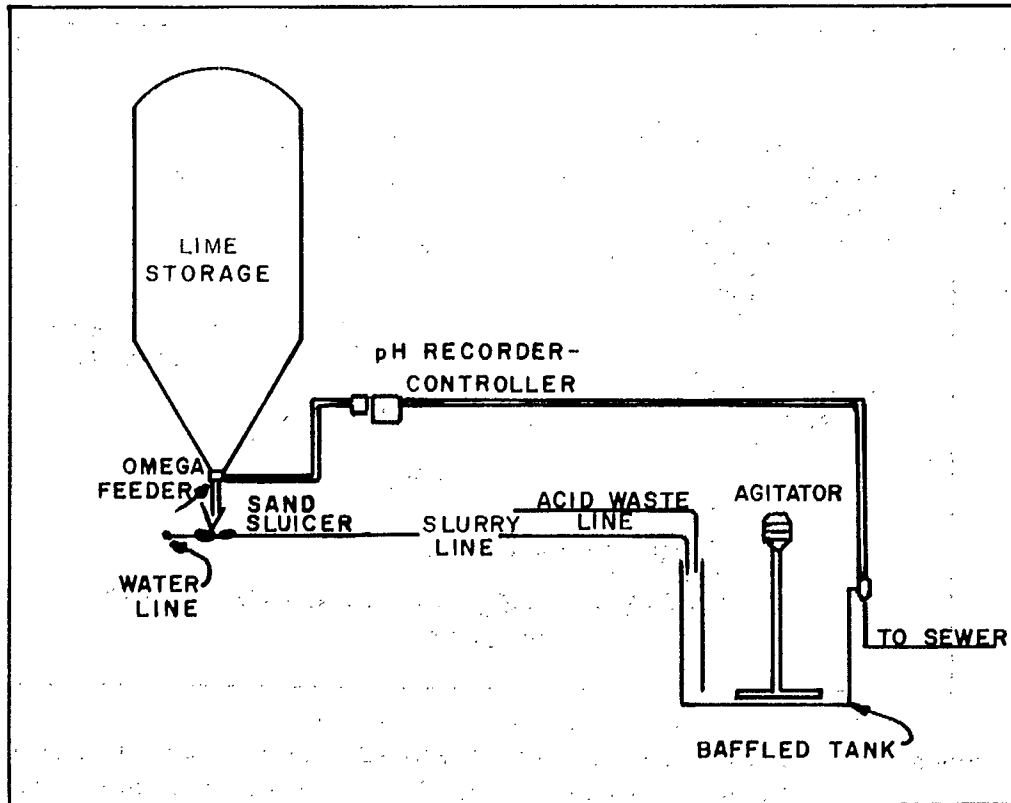and the overflow containing the precipitates goes directly to
the sewer.

Figure 16. Acid neutralization with lime.

Mobile Plant

A mobile plant designed by Dorr-Oliver Inc., using a lime neutralization-aeration-sedimentation-dewatering process, is outlined in Figures 17 and 18 [22]. The unit was fabricated on a float so that it could be moved to various coal-mine sites in Pennsylvania for obtaining engineering data on mine-water treatment. Mine drainage water, which contains mostly sulphuric acid and ferrous sulphate, is stated to be the largest single source of pollution to some 3,000 miles of rivers in the state.

Operation of the pilot plant is relatively simple. Acid water is pumped to a flash mixer, where it is combined with slaked lime and then flows into an aerator. Aeration introduces oxygen into the mixture to oxidize the iron and form an iron-bearing colloidal sediment. The neutral slurry is pumped to the thickener for settling, from which purified mine-water is drawn off at the top and the iron sludge discharged at the bottom. Separation of the insoluble solids is accomplished by filtration or centrifugation. Since no technological advances have been made for reprocessing the recovered iron, it is returned to the mine or buried in the ground.
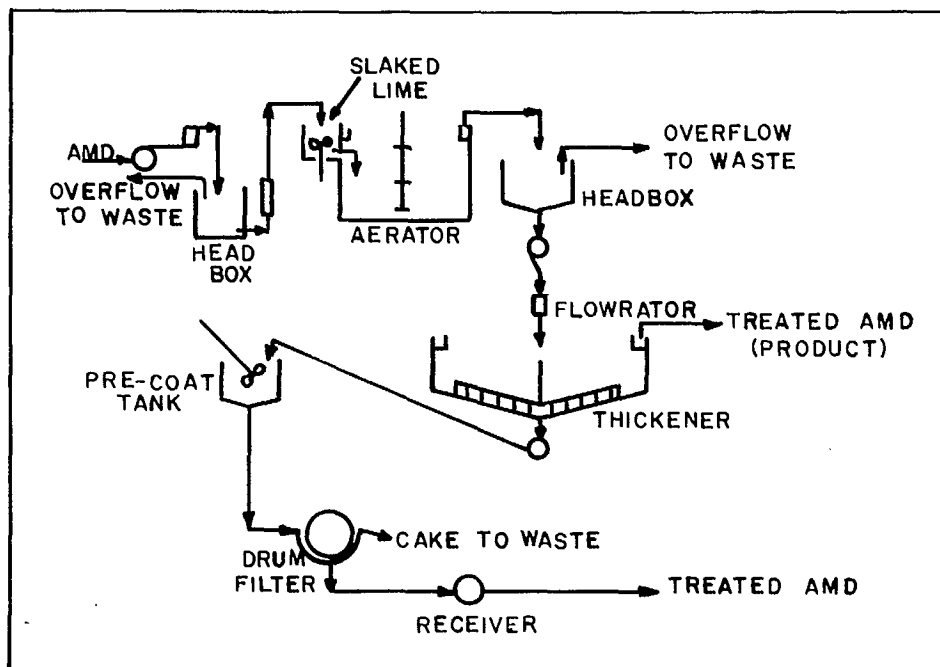

Figure 17.   Treatment of acid water with lime involves flash mixing, aeration, settling, dewatering, and reprocessing.
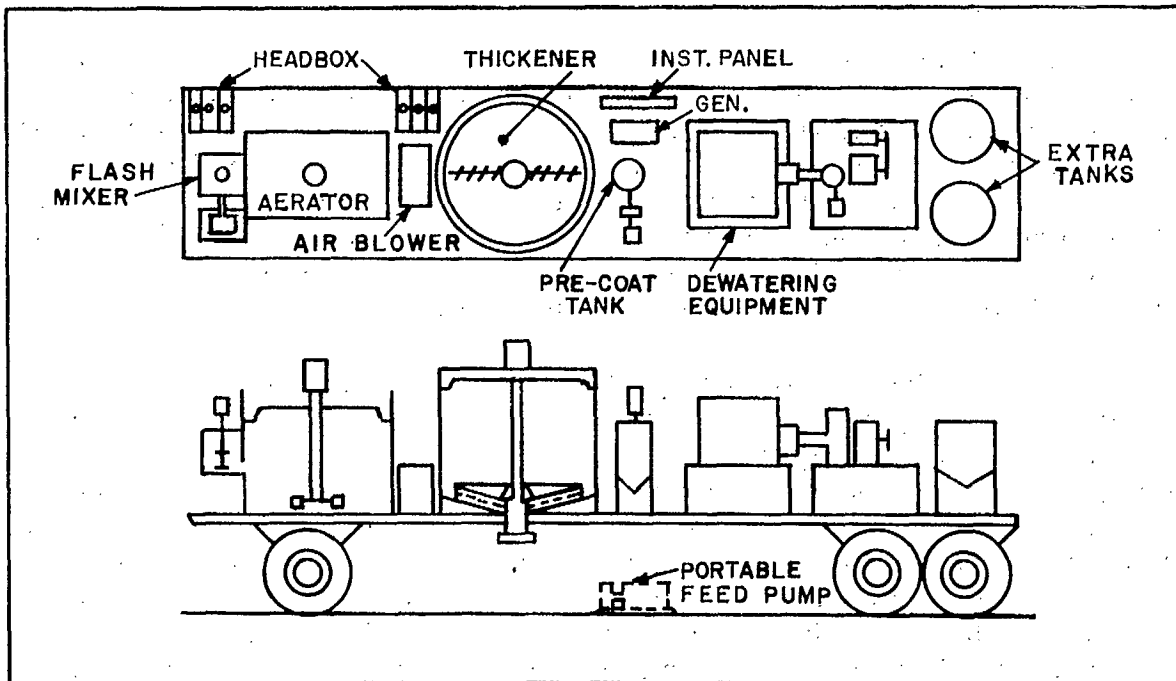
Figure 18. Treatment plant is located on a flat trailer 40 ft
long, 8 ft wide and 4 ft above the ground.

Automatic Limer

An automatic limer operated entirely by water power
continuously feeds lime to raw mine-water as it flows from a
gathering pond[23]. Schematic arrangement of the plant is given
in Figure 19. The rate of water flow through the device regulates
the quantity of lime fed into the mixing chamber. No attention
is required other than periodic refilling of the hopper, which
holds 150 lb lime. The machine is capable of treating flows of
from 0.5 to 100 gpm, and it raises the pH from 2.6 to 7.5 by
feeding 0.13 oz of lime per 100 gal water. A flow of 50 gpm
requires the hopper to be refilled every 24 hr. A full flow
through a 4-in. pipe requires refilling every 5 hr. Two of
these limers have been in service at a coal property in Pennsylvania
for nearly a year. They have performed well, and on one occasion
operated continuously for several weeks even when the temperature
was below zero every night. The device can be disassembled easily
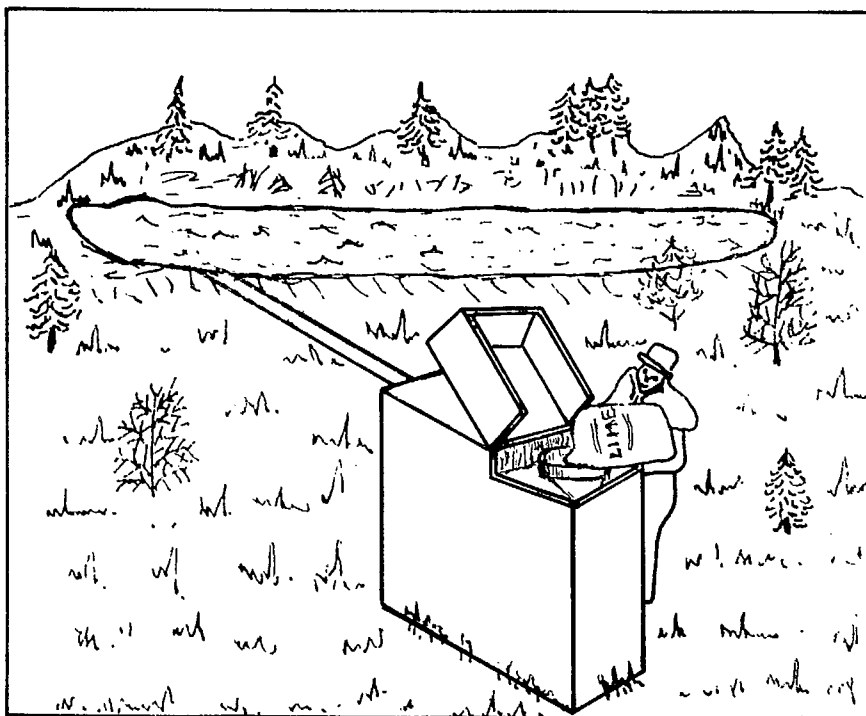for transportation by truck to a new site.

Figure 19.   Automatic limer installation.

Surface Plant

In Pennsylvania, U.S. Steel solved its acid-water problems by treating raw mine-water with lime[24]. Water having a pH of 2.9 to 3.3 and an iron content of 0.5 to 1.6 g/l is pumped from the mine into an 8-million-gal storage pond. The treatment plant, as indicated in Figure 20, incorporates a 100-ton lime bin equipped with a lime feeder, a slurry mixing chamber, and an aerator basin equipped with a mechanical aerator. A conventional pH recorder-controller sets the rate of lime fed to the acid water, with the pH electrodes immersed near the discharge of the aerating tank. During operation, the plant treats 2,500 to 3,000 gpm, a flow which is controlled automatically by a motorized valve. Water discharges from the settling lagoon at a pH of 7.3 to 8.5 and a total iron content of 0.002 to 0.004 g/l.
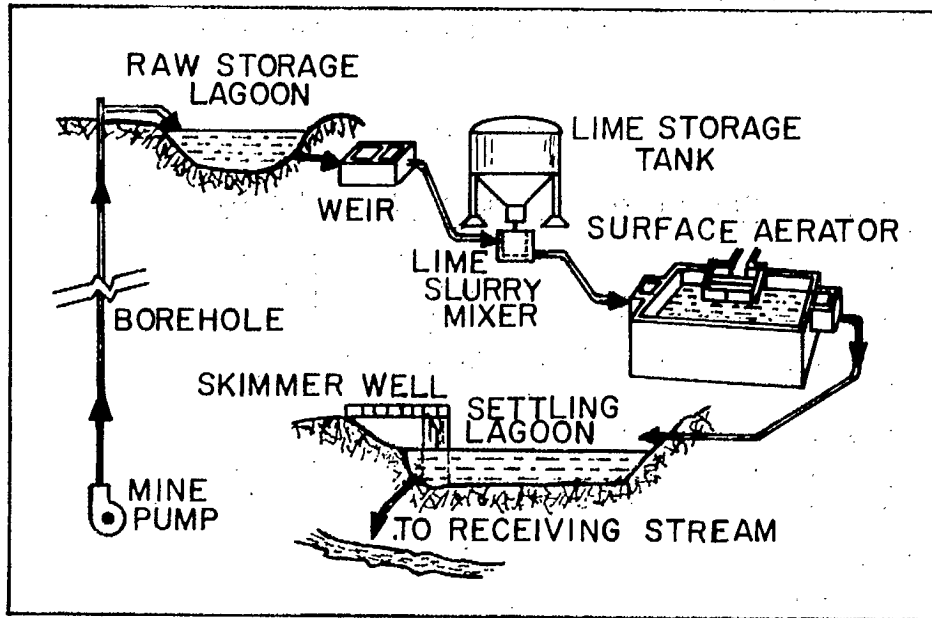
Figure 20. Lime treatment plant for neutralizing
acid mine-water.

AERATION OF MINE WATER

Atmospheric oxidation of pyrite and chalcopyrite and
of ferrous sulphate in the presence of water, as shown by
Equations 1, 2 and 3, is catalysed by bacterial activity.
Although the stoichiometric quantity of oxygen required in these
reactions is relatively small, it is insufficient to keep the
bacteria alive. Since an abundant supply of fresh air is
essential to growth, the degree of aeration will have a
significant effect on the overall composition of drainage. As
coal-mine water flows away from the areas of exposed sulphides,
or when it is pumped to the surface, nearly all of its iron is
in the form of ferrous sulphate, varying from 0.1 to 2.0 g Fe^{++}/l [15].
The relatively low ferric iron content is usually accompanied by
a low free-acid value at a pH of between 4.5 and 5.0. However, on
exposure to the atmosphere for a few hours and in the presence of
bacteria, the ferrous iron immediately starts to oxidize to
ferric iron, which then hydrolyses to ferric hydroxide and free
acid, thus lowering the pH to about 3. Fifty per cent of the acidity
in acid mine drainage of Pennsylvania, Ohio and West Virginia is due
to the oxygenation of ferrous iron, and the remainder to the
oxygenation of sulphide sulphur [25]. The formation of acid by

natural aeration may inhibit the self-purification of a stream
by providing an unfavourable environment for anaerobic micro-organisms.
Results of aerating mine water is shown in Table 10.

TABLE 10

Effect of Aerating Mine Water

Time	pH	Fe^{++}, g/l
At mine pump	5.1	0.312
After 48 hr in contact with air	3.1	0.170

Natural aerating conditions, in which mine water is
allowed to stand in contact with air, or to flow over assorted
sizes of rock, permit a limestone treatment for the removal of
free acid and ferric iron. Additional aeration will oxidize more
of the ferrous iron and generate more free acid for the
neutralization process to be repeated. This action can be
effected in actual practice by (1) percolating mine water upward
through a porous bed of limestone; (2) giving the limestone-water
slurry an undulating motion; and (3) introducing air into a
limestone aggregate mixture. These methods of aeration have
already been described in some detail.

HANDLING OF PRECIPITATED IRON SLUDGE

A general concept of a neutralization plant, in which
the pH is raised with limestone or lime to precipitate all the
iron, followed by aeration and settling, is shown in Figure 21[26].
The resultant colour of the solids may vary from deep green to
orange, depending on the ratio of ferrous to ferric iron in the
raw water and on the degree of oxidation. However, the quantities
of sludge that would be generated from operating such a plant can
sometimes be tremendous.

The magnitude of the problem that can be expected in
handling iron sludge is explained in settling and compaction tests
performed on mine water neutralized with limestone and lime[19].
Water treated by both alkalis to pH 6.9, with no detectable iron
left in solution, was placed in glass cylinders and allowed to
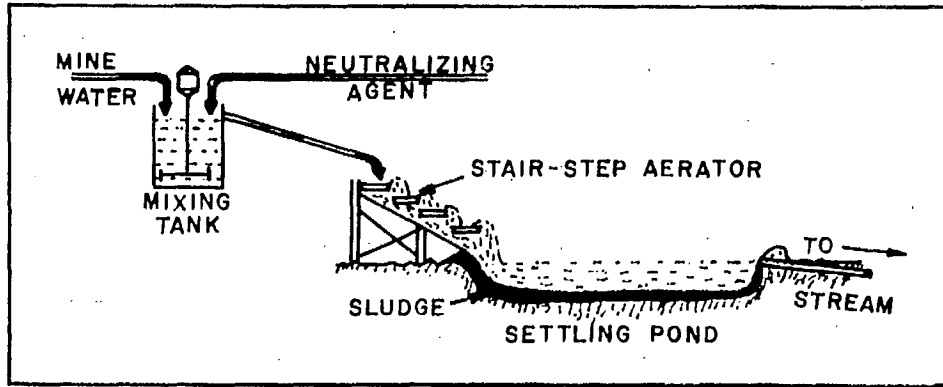settle. The results are illustrated in Figure 22, where after

<Figure 21. View of a generalized neutralizing plant.

the first day the sludge volume from limestone neutralization was less than one-fourth the volume produced from the lime process. After 43 days, the volume from limestone was less than one-third the volume from lime.
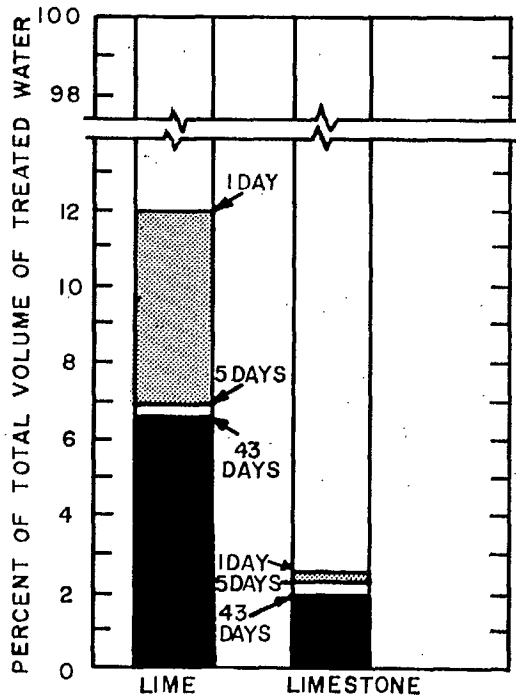

Figure 22. Volumes of precipitated sludge from limestone and lime neutralization of mine water.

In a similar test, limestone and lime sludges were
allowed to settle for 5 months. At the end of this period, the
volume of sludges was 1.2% and 5.3% of the volume of water
treated by limestone and lime, respectively. The dry solids
content of the sludges was 14.4% for limestone and 3.4% for lime.
These data are significant in designing a neutralization plant
and in reducing the volume of sludge to be disposed.

Iron sludges, which are formed when spent pickle
liquor is neutralized with pulverized limestone or hydrated lime,
have settling rates similar to those of these agents in water
alone[27]. Figure 23 gives curves based on results obtained by
treating equal volumes of liquor with limestone and lime and
allowing the precipitates to settle in a 100-ml graduated
cylinder. It was found in this work that the resultant slurry
from limestone settled more rapidly and to a smaller volume
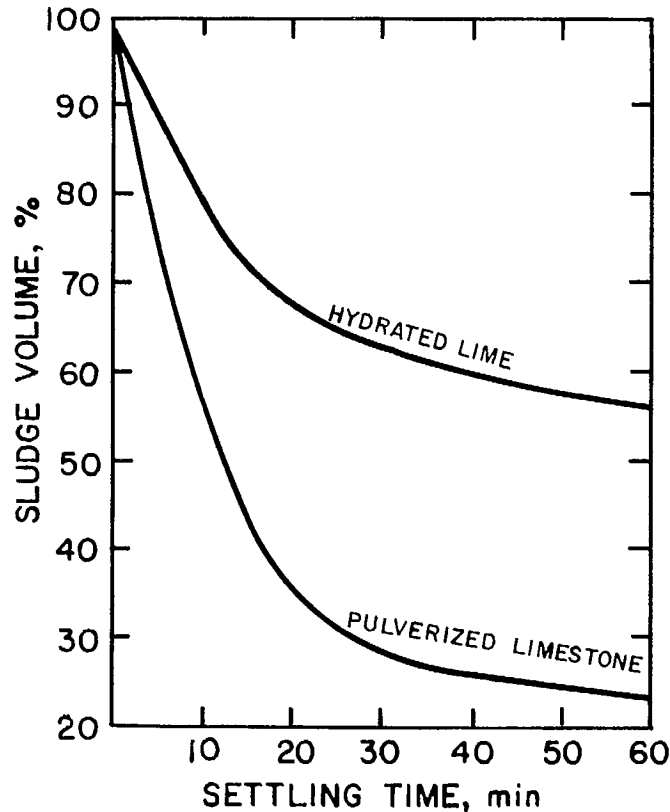than that produced from lime.

Figure 23. Effect of alkali agent on sludge
settling rate.

Calcium sulphate, formed from the interaction of limestone or lime with sulphuric acid and dissolved iron, is an important constituent of the iron precipitates. In the neutralization procedure, enough time must be allowed for the calcium sulphate to crystalize and settle out in the water. It has been estimated that if there is a settling pond for 3 days' flow of treated water, as much as 0.1 g/l $CaSO_4$ will separate with the sludge.

DISCUSSION AND CONCLUSIONS

Studies involved in the neutralization of contaminated mine-water revealed that limestone is satisfactory for weak acids containing mostly ferric iron and that lime is satisfactory for strong acids containing mostly ferrous iron. These agents are readily obtainable from local sources at a relatively low cost, and they yield waters of potable quality and precipitates that settle reasonably well.

In building a plant to neutralize acid waste, the following facts must be considered in formulating its size and design:

1. Chemical composition of the acid solution.

2. Information on the alkali agent, relating to its handling characteristics, reagent consumption, neutralizing efficiency and final products.

3. Volume and flow rate of the water to be treated.

4. Topography of the area in which the plant is to be erected.

5. Disposal of the sludge.

Waters discharging from several uranium and base-metal mines in Canada are acidic and contain some dissolved iron as well as trace amounts of other metals. The solutions are usually bacteria-bearing, and therefore can be expected to have a pH of approximately 2.5 and Fe^{+++} values of up to 0.5 g/l. In Ontario and Quebec, sulphuric acid and ferric sulphate cause excessive damage in the form of corrosion to mining equipment such as steel cables, car rails, skips, electrical gear, etc. The relatively low acid and iron contents of the water would make it amenable to a limestone treatment process, and thereby

reduce corrosion activity underground. A series of limestone beds installed near the source of the acid is suggested as an inexpensive means of implementing this reduction.

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REFERENCES

1. J.R. Hoffert, "Acid Mine Drainage", Ind. and Eng. Chem., 39, No. 5, 642-646 (1947).

2. D.W. Duncan and P.C. Trussell, "Advances in the Microbiological Leaching of Sulphide Ores", Can. Met. Quart., 3, No. 1, 43-55 (1964).

3. K.L. Temple and W.A. Koehler, "Drainage from Bituminous Coal Mines", West Virginia University Research Bulletin 25, 1-35 (1954).

4. L.C. Bryner et al., "Micro-organisms in Leaching Sulphide Minerals", Ind. and Eng. Chem., 46, No. 12, 2587-2592 (1954).

5. P.C. Trussell et al., "Recent Advances in the Microbiological Leaching of Sulphides", Trans. Soc. Mining Eng. AIME, 238, 122-128 (1967).

6. V.F. Harrison, W.A. Gow and M.R. Hughson, "Factors Influencing the Application of Bacterial Leaching to a Canadian Uranium Ore", J. Metals, 18, 1189-1194 (1966).

7. M.P. Silverman and D.C. Lundgren, "Studies on the Chemoautotrophic Iron Bacterium, Ferrobacillus Ferrooxidans", J. Bacteriology, 77, 642-647 (1959).

8. J.W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry" (Longmans, Green and Co., London, 1947), Vol. 14, pp. 265-266.

9. M. Goehring, "Die Chemie der Polythionsauren", Fortschritte der Chemischen Forschung, 2, 444-483 (1952).

10. F.N. Kemmer and K. Odland, "Chemical Treatment in Water Pollution Control", Chem. Eng., 83-88 (October, 1968).

11. C.J. Lewis, "Some Practical Suggestions on Waste Acid Treatment", Rock Products, 117-119, 149-150 (June, 1949).

12. M. Deul and E.A. Mihok, "Mine Water Research Neutralization", U.S. Bureau of Mines Report No. RI-6987, 1-24 (1967).

13. S.H. Ash et al., "Treatment of Acid Waste and Waters", U.S. Bureau of Mines Bulletin 508, 56-72 (1951).

14. H.L. Jacobs, "Acid Neutralization", Chem. Eng. Prog., 43, No. 5, 247-253 (1947).

15. A.B. Campbell, W. Howes and W.H. Ode, "Salts in Tri-State Mill Waters", U.S. Bureau of Mines Report No. RI-3149, 13-24 (1932).

16. F.N. Kemmer and K. Odland, "Chemical Treatment in Water Pollution Control", Chem. Eng., 83-88 (October, 1968).

17. A.L. Reidl, "Limestone Used to Neutralize Acid Wastes", Chem. Eng., 100-101 (July, 1947).

18. L.D. Tracy, "Six Tons of Ferric Hydrate Secured Daily from Water at a Connellsville Mine", Coal Age, 18, No. 1, 13-16 (1920).

19. E.A. Mihok, "Limestone Neutralization - a Low Cost and Effective Treatment for Acid Mine Waters", Coal Age, 73, No. 12, 65-70 (1968).

20. R.D. Hoak, C.J. Lewis and W.W. Hodge, "Treatment of Spent Pickling Liquors with Limestone and Lime", Ind. and Eng. Chem., 37, No. 6, 553-559 (1945).

21. R.D. Hoak, "A Neutralizing Nomograph", Water and Sewage Works, 360-361 (August, 1951).

22. D.R. Maneval and H.B. Charmbury, "Acid Mine Water Mobile Treatment Plant", Min. Cong. J., 69-71 (March, 1965).

23. Editor, "Automatic Limer Prevents Pollution", Coal Age, 71, No. 2, 120-121 (1966).

24. Editor, "U.S. Steel Solves Acid-Water Problems", Coal Age, 74, No. 5, 64-68 (1969).

25. W. Stumm and G.F. Lee, "Oxygenation of Ferrous Iron", Ind. and Eng. Chem., 53, No. 2, 143-146 (1961).

26. G.L. Barthauer, "Mine Drainage Treatment, Fact and Fiction", Coal Age, 71, No. 6, 79-82 (1966).

27. R.D. Hoak, C.J. Lewis and W.W. Hodge, "Basicity Factors of Limestone and Lime", Ind. and Eng. Chem., 36, No. 3, 274-278 (1944).

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