PREPRINT NO. 67F72

SOCIETY OF MINING ENGINEERS
of AIME
345 EAST 47T REET, NEW YORK 17, N. Y.

PRACTICAL ASPECTS OF MINE DRAINAGE CONTROL AND TREATMENT

G. L. Barthauer
Conservation Department
Consolidation Coal Company
Library, Pennsylvania

This paper is to be presented at the Annual Meeting of the American Institute of Mining, Metallurgical and Petroleum Engineers, Los Angeles, California, February 19-23, 1967.

These preprints are available only on a coupon basis. The coupon books may be obtained from SME headquarters for $5.00 a book (10 coupons) for members or $10.00 a book for nonmembers. Each coupon entitles the purchaser to one preprint. Mail completed coupons to PREPRINTS, Society of Mining Engineers, 345 East 47th Street, New York 17, N. Y.

***Preprint Availability List* is published periodically in MINING ENGINEERING.**

67F72

PRACTICAL ASPECTS OF MINE DRAINAGE CONTROL AND TREATMENT

by

G. L. Barthauer
Conservation Department
Consolidation Coal Company
Library, Pennsylvania 15129

It is a distinct privilege to have the opportunity of addressing this group today. Although I, myself, am not a mining engineer, I have always had profound admiration and respect for those of you who each day live and work according to the tenets of Murphy's Law. Murphy, as some of you may know, was an Irish philosopher whose sole contribution to his field was the observation, "In the mining industry, if anything can possibly go wrong, it will!"

You have heard this afternoon a variety of papers, touching on or describing in some detail imminent problems which presently face the coal industry. Many of these problems show no signs of diminishing. Actually, there is good reason to believe that they will intensify as governing bodies pass additional enabling legislation and regulatory agencies adopt more stringent "Rules and Regulations". In many cases, these groups are seemingly oblivious or indifferent to either cost factors or technical problems involved in achieving the desired goals.

I will direct your attention today to the subject of control and treatment of deep mine drainage, a problem which faces most coal operators throughout the Appalachian and Mid-Western coal fields. As all operators from these areas are acutely aware, many states have recently adopted standards which will require a major degree of treatment of such discharges.

Standards vary from state to state for reasons which I find impossibl to explain. For example, Pennsylvania has set an iron limit of 7 mg/liter (7 ppm) on the discharge from a treatment plant. West Virginia, on the other hand, has adopted 10 mg/liter (10 ppm) in the receiving stream as a satisfactor iron level, thus giving proper credit for the dilution effect of the stream. As you all know, public hearings are currently being held in all fifty states, attempting to develop stream standards which will be satisfactory to both the states and the Federal Water Pollution Control Administration. So, we still are aiming at a moving target.

Now, with this somewhat lengthy preamble, let's look at the "state of the art" of mine drainage treatment processes as we know them today. If I may beg the indulgence of those who are thoroughly familiar with the chemistry of formation of mine drainage waters, I would like to show Figure 1.

Figure 1 is the fundamental reaction which leads to the formation of acid and iron in mine waters. As you will note, pyrite (FeS_2) in the coal seam or in the adjacent strata reacts with water and air, producing acid (H^+) and divalent iron (Fe^{+2}). These materials are soluble and are carried away by the invading water, exposing fresh pyrite surfaces for further attack.

Now, let's consider the fate of the ferrous iron and the acid in the water as it moves--miles, in many cases--from its point of formation to its point of discharge. As all of you know, substantial amounts of limestone or calcium carbonate are associated with coal deposits. As our mine drainage water contacts these alkaline materials, certain specific reactions occur as shown on Figure 2.

The first reaction (Equation 1)--which occurs rapidly--is the reaction of the acid with, say, limestone. Bicarbonate ion is formed and acid in the mine water is neutralized.

After, or simultaneously with neutralization of the acid, another important reaction begins. You will remember that I stated that ferrous, or divalent iron, was formed as a result of the pyrite-water-air reaction which gave birth to our contaminants. One property of iron in this form is that it is quite soluble, even in neutral solutions. Another is its tendency to resist oxidation to the trivalent form (Fe^{+3}) in acid solution. However, by reaction with limestone, we have removed a major portion of the acid, thus raising the pH. Now, further oxidation of the divalent iron can and does proceed much more rapidly at these higher pH levels, resulting in the formation of ferric or trivalent iron hydroxide which is extremely insoluble in neutral solution. This is shown as Equation 2. Note that the ferric hydroxide precipitates from the water as the so-called "Yellowboy" so commonly seen in underground mines.

Also observe that more acid (or hydrogen ion) is produced as a result of this oxidation; however, this, too, will be neutralized by limestone or other alkaline rocks in the strata.

The sulfate formed by the initial pyrite-air-water reaction is unaffected and continues its "free ride" toward the point of discharge. Occasionally, the sulfate level will become sufficiently high to precipitate some calcium sulfate, but the major portion appears unchanged in the discharge.

Now, this picture of the formation and fate of the iron and acid in mine drainage water is predicated upon the availability of an almost unlimited supply of limestone or other alkaline rock in the strata and upon very long residence time of the mine drainage in the mine itself.

Let's now look at Figure 3 which shows schematically the overall process which I've been describing. Although this picture is somewhat oversimplified, it illustrates some of the difficulties which we may encounter.

Let's first use the Figure to explain the different types of mine drainage which we may have to handle in treatment plants. Looking at the extreme left of the Figure, we see one of the many ways in which water may enter the mine. Now, as it travels through, say, a gob area containing substantial amounts of pyrite and air, the reaction previously shown on Figure 1 occurs, i.e., ferrous iron, acid, and sulfate are produced.

Now, let's make the further assumption that the mine water in its passage toward its eventual point of discharge contacts alkaline rock in the presence of additional air. Ideally, a series of combined neutralization and oxidation reactions will occur and with long residence times, iron is oxidized from its ferrous form to the insoluble ferric form and is dropped out as ferric hydroxide or "Yellowboy". If residence time is sufficiently long, almost all of the iron will be removed and the discharge collected in the final sump will be essentially iron- and acid-free, although it may still contain large amounts of sulfate. For purposes of classification, I will call this "Type I" water. Table I shows a typical analysis of "Type I" water. Note the almost complete absence of iron and acid--but the high sulfate level.

Now, let's return to Figure 3 and suppose that we have, for one reason or another, a deficiency of "neutralizing" minerals or alkaline rocks over which the mine drainage can pass--or, alternately, aeration conditions are unfavorable, either due to the low partial pressure of air in the gob area or perhaps limited residence time for aeration. It may be necessary, for example, to pump the water to the surface prematurely to prevent interference with mining operations. In this particular instance, most of the original ferrous iron may have been oxidized to ferric ion and precipitated. However, as I previously pointed out, ferrous ion is relatively soluble in neutral solution and our discharge, although satisfactory from an acid standpoint, will still contain substantial amounts of iron, all in the ferrous form. This class of water, I'll classify as "Type II" water. A representative analysis is shown in Table II. Note that the pH is satisfactory but the iron content is relatively high. Note also that the remaining iron is in the ferrous (or divalent) form. If it had been oxidized, it would not be present in a discharge having this pH. Rather, it would have precipitated underground.

Let's return again to Figure 3 and now assume that no alkaline-type rock is present in the strata to accomplish these complete or partial neutralizations which we have just described. This can come about in several ways. The strata may initially be deficient in such materials, or, over a period of time, these neutralizing materials along flow channels of the percolating drainage are exhausted. In either case, the mine drainage becomes more and more acid as it passes over additional pyrite (in the presence of air) on its way to the discharge sump. If you recall, as the acidity increases, the rate of oxidation decreases so, after the pH reaches a low level of, say, 3.5-4.0, natural aeration is ineffective and the iron remains in the ferrous form. Little precipitates, and the net result is a discharge containing large quantities of acid and iron.

This, of course, is true "acid mine drainage" of the worst type. A typical analysis is shown in Table III.

All of the mining engineers in the audience--who have had far more experience in underground operations than I can ever hope to have--will recognize that I have oversimplified matters somewhat. Sumps are located in such a manner that seldom does all water entering the sump have the same prior history. Consequently, the sump may receive several different types of water and the discharge quality will be governed by the relative volumes of each.

At this stage, and after consuming the major portion of my allotted time, many of you are probably wondering when I plan to turn to the subject of mine drainage treatment processes. After all, this was the general title of my paper.

I submit to you that I have already discussed in detail, the major types of mine drainage treatment processes which industry presently plans to use to meet effluent or stream standards. Our problem--and it is a serious one indeed--is to carry to completion the reactions which, for one reason or another, have no been completed underground. However, instead of having available the huge underground volumes for sludge disposal (as it is precipitated from the mine water), we must in most cases provide these volumes on the surface. Instead of having shallow flowing underground streams with high turbulence to effect aeration and reaeration many, many times, we must depend upon natural oxidation of the ferrous ion in relatively quiescent deep ponds on the surface. Alternately, we must force-aerate with compressors. And, of course, in the case of acid discharges, we must supply our own alkaline materials to raise the pH to acceptable levels so that ferrous oxidation can proceed at a more rapid rate.

To illustrate my point, let's look again at Table II which illustrates "Type II" water. This type, you will recall, has a satisfactory pH level but contains excessive amounts of ferrous ion, having been insufficiently oxidized underground to precipitate all of the iron as "Yellowboy". Consequently, our problem is to complete the oxidation.

Figure 4, for example, is a schematic drawing of a treatment process which, at least in theory, will remove the iron from the discharge. The discharge is allowed to pass through the pond and subjected to natural aeration conditions, oxygen being supplied by a combination of preaeration over a "stair-step" aerator plus some additional aeration by diffusion of air into the pond surface. The reaction shown at the bottom of the slide (which you have seen before) occurs and iron is removed as the trivalent hydrated oxide or "Yellowboy".

Now, the rate of this reaction is not infinitely fast but is extremely susceptible to both pH level and water temperatures. Every case has its optimum solution. I realize that this is scant comfort for an operator who is looking for design parameters upon which to base a treatment plant. Frankly, he needs more than a bit of divine guidance, particularly since he cannot yet profit from the experience of others as would be the case if he were, say, designing a sewage disposal plant. However, build something he must, or face a shutdown of his operation.

Now, let's turn to the "acid mine drainage" type of discharge and review Table III for its composition. Using a similar analogy and recognizing the origin and prior underground history of such a discharge, our problem is both to neutralize and oxidize. Normally, operators who are building such plants plan to use hydrated lime rather than limestone as a neutralizing agent. Proposed treatment plants are shown on Figure 5.

We can follow one of two courses. We can, in the first case, neutrali to a pH level of 7.0 to 8.0 and oxidize the ferrous ion to ferric, under which conditions the iron will settle out as ferric hydroxide. In view of the large amounts of ferrous iron normally present in such discharges, force-aeration will probably be a necessity.

Another course is open to us, however, which, in some cases, may be more satisfactory. With lime, we can raise the pH of the discharge to approximately 9.0. At this high pH, no oxidation is necessary as the ferrous iron will cleanly precipitate and the overflow will be iron-free. However, this approach is not without drawbacks. For example, lime requirements will be higher. Even more serious is the relative volumes of sludge produced. The type of precipitate obtained is much more voluminous and gel-like than that produced by raising the pH to 7.0 or 8.0 and oxidizing the ferrous ion to ferric ion. Figure 6 illustrates this point. These are samples of the same discharge, treated in the two different manners. Note the higher sludge volume and the green color of the ferrous hydroxide precipitated at the high pH. Thus one must balance off the cost of a forced-aeration step against increased cost of lime and a more difficult sludge disposal problem.

I don't believe it is necessary to re-emphasize the tremendous problems of sludge disposal. Note the relative volume of sludge created by even the method which gives us the lowest sludge volume from acid mine drainage discharges. No one yet knows good practical methods of removing sludge from settling lagoons or the degree of compaction which such sludges will achieve upon standing.

We'll eventually find out--but it will be too late for many operators who will be forced to make unwise capital expenditures or must cease operations because they either cannot afford present processes or obtain sufficient land to meet present process requirements.

I have attempted today to draw parallels between underground reactions giving rise to various types of mine drainage discharges and the similar reactions which we must carry out aboveground to produce acceptable effluents.

The principal difference, I'm sure you realize, is that we do not have available to us on the surface the tremendous volumes and residence times available underground. For example, even if our treatment plant occupies 20 acres, it still represents a surface which is only a small fraction of one percent of the underground area. We must know more about the reaction kinetics, find more rapid ways for oxidizing ferrous ion to ferric iron and solve the acute problems of sludge disposal.

Two major universities are presently building full-scale treatment facilities, seeking answers to design problems which the industry needs today. I am familiar with at least a dozen other research projects having the same objective. Regulatory agencies, charged with enforcement of present laws, are equally interested in such answers. It is an anomaly, indeed, that operators in the Appalachian area are now being forced to build treatment plants with no more information than is presently available. The impact of unwise decisions will be less on high-tonnage mines with small volumes of mine drainage, but it is a "life or death" matter for those who are not so fortunate.

It would be much more constructive to insist that new mines be laid out in such a manner that drainage be controlled and treated to produce a satisfactory effluent. This would permit location of discharge boreholes at points where sufficient land is available, where such land can be purchased at less than exorbitant prices and not subject to strict zoning ordinances. After all, present outfalls were located to achieve maximum economy and these economies were enjoyed not only by the operator but also by the fuel-using public. At least, let's wait until the data are developed by West Virginia University and Pennsylvania State University on full-scale treatment plants so that we can do the best job possible at present outfalls.

Those who are charged with making our laws and those who have the responsibility for enforcing them must recognize that no industry can afford unwise capital investments on a wholesale basis. Laws are designed to meet goals which are in the public interest. Our industry will meet those goals--but technology cannot be created by fiat, and chemical and physical phenomena are completely indifferent to wishful thinking.

TABLE I

TYPICAL COMPOSITION OF "TYPE I" MINE DRAINAGE

pH	7.7
ALKALINITY	534 ppm* (as $CaCO_3$)
IRON	0
CALCIUM	302 ppm
MAGNESIUM	84 ppm
SULFATE	4570 ppm

*Parts per Million (ppm) = Milligrams / Liter

TABLE II

TYPICAL COMPOSITION OF "TYPE II" MINE DRAINAGE

pH	6.5
ALKALINITY	193 ppm* (as $CaCO_3$)
IRON	60 ppm
CALCIUM	205 ppm
MAGNESIUM	70 ppm
SULFATE	1750 ppm

* Parts per Million (ppm) = Milligrams / Liter

TABLE III

TYPICAL COMPOSITION OF "TYPE III" MINE DRAINAGE

pH	3.4
ALKALINITY	- 360 ppm* (as $CaCO_3$)
IRON	140 ppm
CALCIUM	150 ppm
MAGNESIUM	40 ppm
SULFATE	2106 ppm

*Parts per Million (ppm) = Milligrams / Liter

FIGURE 1

INITIAL WATER - PYRITE - AIR REACTION

$$2H_2O + \underset{\text{PYRITE}}{\underline{2FeS_2}} + 7O_2 \longrightarrow 2Fe^{++} + 4SO_4^{=} + 4H^{+}$$

FIGURE 2

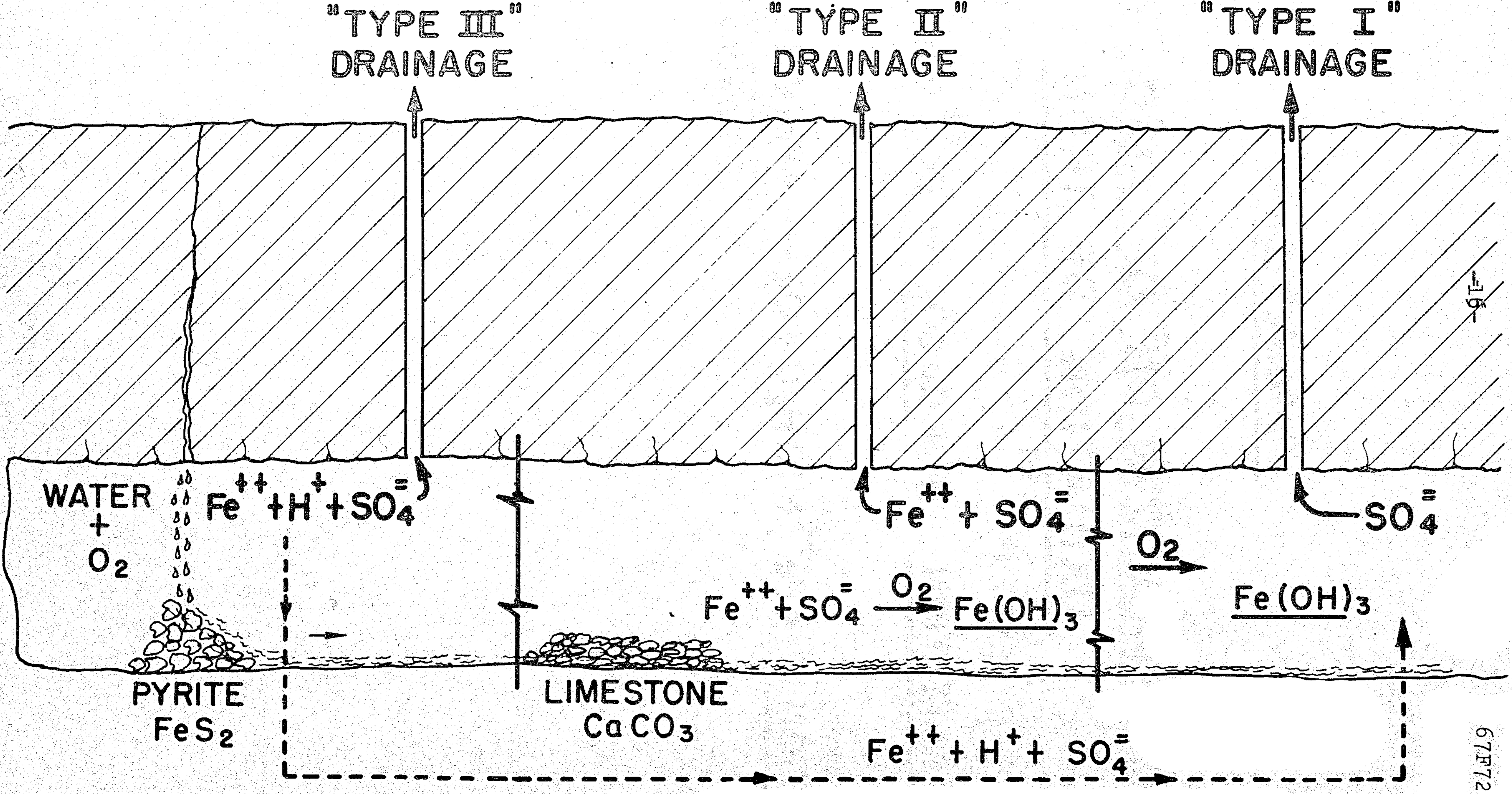
NEUTRALIZATION OF ACID AND OXIDATION OF IRON

NEUTRALIZATION $H^{+} + \underline{CaCO_3} \longrightarrow Ca^{++} + HCO_3^{-}$ (Eq. 1)

OXIDATION $4Fe^{++} + 10H_2O + O_2 \longrightarrow \underbrace{4Fe(OH)_3}_{\text{"Yellowboy"}} + 8H^{+}$ (Eq. 2)

FIGURE 3

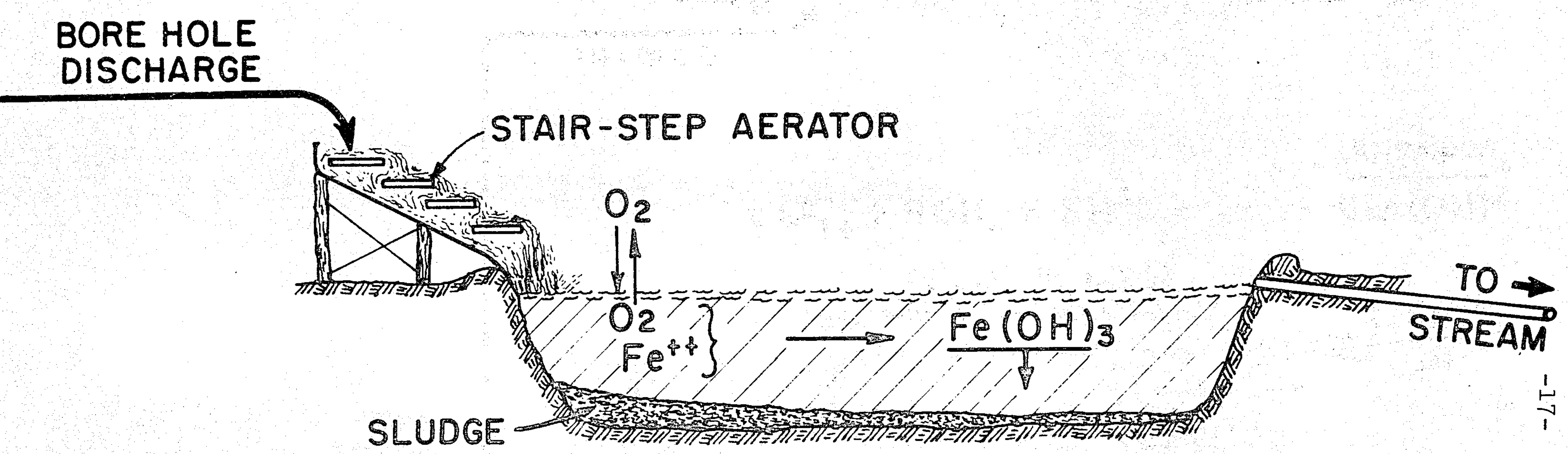
POSSIBLE UNDERGROUND FLOW PATTERNS



67F72

FIGURE 4

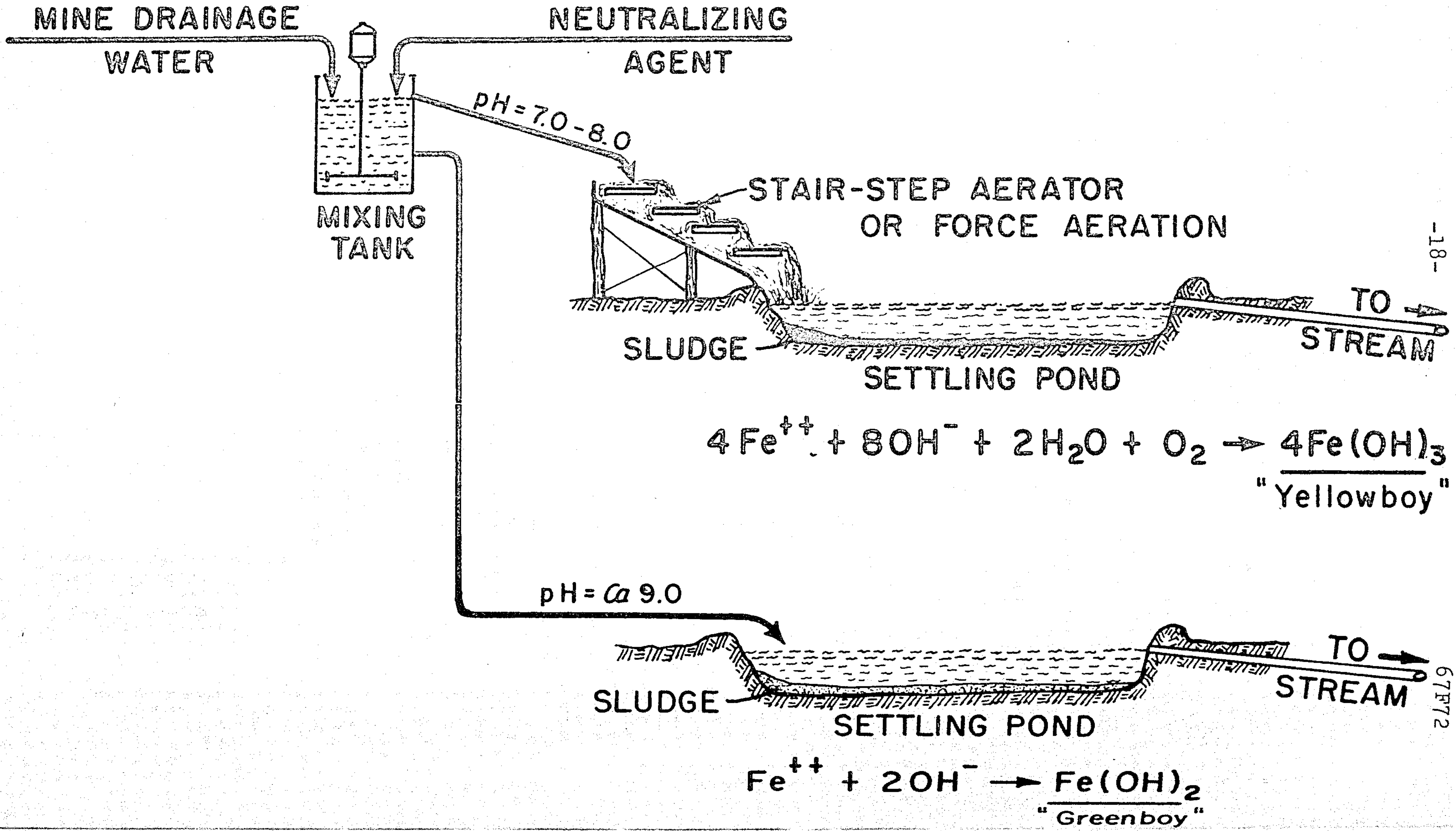
ALKALINE MINE DRAINAGE TREATMENT PLANT



$$4Fe^{++} + O_2 + 10H_2O \rightarrow \underset{\downarrow}{\underline{4Fe(OH)_3}} + 8H^+$$

FIGURE 5

ACID MINE DRAINAGE TREATMENT PLANT



$$4\,Fe^{++} + 8OH^{-} + 2H_2O + O_2 \rightarrow \underline{4Fe(OH)_3}$$

"Yellowboy"

$$Fe^{++} + 2OH^{-} \rightarrow \underline{Fe(OH)_2}$$

"Greenboy"

FIGURE 6

SLUDGE VOLUMES FORMED BY TWO TREATMENT PROCESSES