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ACID MINE DRAINAGE RESEARCH AT BITUMINOUS COAL RESEARCH, INC.

Edward A. Zawadzki
Project Scientist

Bituminous Coal Research, Inc.
Monroeville, Pennsylvania

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By
E. A. Zawadzki, Project Scientist

Bituminous Coal Research, Inc.
350 Hochberg Road
Monroeville, Pennsylvania

INTRODUCTION

The problem of pollution of water by mine drainage is at least as old as the mining industry itself. However, research on the formation, composition, treatment, and abatement of mine water is a relatively recent historical event.

At Bituminous Coal Research, Inc., acid mine drainage control has been an important area of work since 1944, at which time BCR began sponsorship of research at West Virginia University. The work at West Virginia University involved a detailed study of the acid mine drainage problem and led to the identification of iron oxidizing bacteria as important factors in the formation of acid mine water. The results of this research were summarized in 1954 by Temple and Koehler (1) who concluded that "no practical solution for the problem" of controlling acid mine drainage "is yet known."

BCR continued sponsorship of research by co-supporting the work of the late Dr. S. Braley.(2, 3) Dr. Braley's studies of the formation and control of acid mine water were significant contributions to our technology. Of particular importance are the results of Dr. Braley's work on the prevention of acid mine drainage by proper layout of drainage channels in active mines, his studies of the composition of mine water, and his identification of acid forming minerals.

In 1961, Bituminous Coal Research, Inc., moved into new laboratory facilities in Monroeville, Pennsylvania. Significantly, it was just after the move that "in house" research activities on controlling mine drainage were initiated. The work from 1962 to 1966 was exploratory in nature, but led to the development of an expanded program, discussion of which is the subject of this paper.

BCR recognized that there were many areas of the field of mine drainage control were research was needed, primarily research concerning the chemical and physical properties of mine water and mine water sludge, and research concerning the development of improved processes for the treatment of mine water.

Many facets of this research have been initiated and these will now be described.

1. Chemical and Physical Properties of Mine Water

In order to appreciate the intent of this work area, a brief review of the formation of mine water is necessary.

Acid mine drainage results from the dissolution of oxidation products of pyrite in normally alkaline ground water together with the subsequent dissolution of other minerals in the resulting acidic solution.

The mechanism of the chemical reactions involved in pyrite oxidation is complex. It has generally been represented by the following overall chemical reaction.

$$\text{(a)} \quad FeS_2 + 7O + H_2O = FeSO_4 + H_2SO_4$$

It is believed that the actual mechanism involves a series of simultaneous and consecutive chemical, electrochemical, and bacterially induced reactions which have not as yet been completely established. One hypothesis is that the initial reaction is a chemical oxidation as represented by reaction (a). It is believed that this initial reaction is dependent on such factors as pyrite properties, pyrite composition, and temperature. The formation of acid may then trigger a series of complex reactions as follows:(4)

$$\text{(b)} \quad 2\ FeSO_4 + O + H_2SO_4 \rightleftarrows Fe_2(SO_4)_3 + H_2O$$

in the presence of thiobacillus ferrooxidans and ferrobacillus ferrooxidans.

$$\text{(c)} \quad 7\ Fe_2(SO_4)_3 + 8\ H_2O \rightleftarrows 15\ FeSO_4 + 8\ H_2SO_4$$

acting on pyrite by electrochemical reaction.

$$\text{(d)} \quad Fe_2\ (SO_4)_3 + FeS_2 + H_2O \rightleftarrows 3\ FeSO_4 + 2S$$

another chemical reaction.

$$\text{(e)} \quad S + 3O + H_2O \rightleftarrows H_2SO_4$$

in the presence of thiobacillus thiooxidans.

The secondary reaction of H_2SO_4 produced by pyrite oxidation, with various minerals to form a complex solution of metal ions and sulfates in acid solution, is probably the reason for the presence of only a small quantity of "free sulfuric acid" in mine water.

Unravelling the complex chemistry of the aqueous solution known as mine drainage is part of BCR's research objective. More important, is the application of this knowledge to the treatment, control, and abatement of mine water, and to disseminate this information to those directly involved in treating mine water. Preliminary results in this area include an analysis of the properties of the principal ionic species present in mine water. Some of the results obtained are as follows:

a. Iron Content: Ferrous sulfate is the principal soluble oxidation product of pyrite. However, ferrous sulfate in solution is unstable, depending on pH and oxygen content of the water. At low pH <6, solutions of ferrous sulfate can be kept for long periods of time without change; above pH 6, in the presence of air, sunlight, and/or certain bacteria, ferrous iron oxidizes to ferric iron, the rate being dependent on the pH of solution. Mine water containing ferrous iron may be a clear solution, however, subsequent aeration, dilution with alkaline water, and/or bacterial action initiate the chain of reactions which lead to the formation of yellow to red precipitates which cause "red water." The formation of an iron precipitate from ferrous-containing water can be represented by the following reaction.

$$Fe^{+2} + O_2 + H_2O \rightarrow Fe(OH)_3 + H^+$$

Discussion of the mechanism of this reaction is beyond the scope of this paper, however, it is significant to note that in the formation of a ferric precipitate, which can be a chemical form other than $Fe(OH)_3$, the overall reaction includes the production of an excess of H^+ thus leading to an acid condition. The exact pH of mine water, either treated or untreated, depends on many factors and, therefore, a general statement concerning pH and stability of the solution cannot be made. However, it has been observed by many workers that a ferrous iron-bearing acid water which is treated with lime to precipitate ferrous hydroxide is not stable. This is due to the oxidation of the ferrous hydroxide precipitate to ferric hydroxide as shown in the following reaction.

$$Fe(OH)_2 + H_2O + O_2 \rightarrow Fe(OH)_3 + H^+$$

Thus, a water treated with lime may decrease in pH after treatment due to acidity generated by the oxidation of ferrous hydroxide.

Understanding of the complex chemistry of dissolved iron in mine water is of prime importance in development of useful and practical treatment processes.

b. Oxidation of Ferrous Iron: For the most part, the successful treatment of mine drainage concerns the efficiency of removal of iron from solution. In acid mine drainage, iron can occur both in the Fe^{+2} and Fe^{+3} forms. At pH above 3, but less than 9, Fe^{+2} is the stable form. Fe^{+3} hydrolyzes to completion at pH 3. The oxidation of Fe^{+2} to Fe^{+3} is rapid and complete at pH levels above 7; however, at a lower pH, or in the presence of complexing agent, Fe^{+2} is stable. Stumm, et al (5), Barthauer (6), Glover (7), and others (8, 9), have reviewed the problems associated with Fe^{+2} oxidation. Glover (7) has proposed a bacterial process for Fe^{+2} oxidation. Rozelle, et al (10) have proposed the use of ozone. Chemical oxidation has been considered, but only one full-scale treatment plant is known to be in operation and this on a water containing less than 50 ppm of Fe at a pH of 6.5-7.0.

BCR has been searching for a catalyst to assist in the oxidation of Fe^{+2} in acid medium. Working with simple solutions of H_2SO_4 and $FeSO_4$, various coal derived carbons have exhibited high catalytic activity. Data by Thomas and Ingraham (11) and the patent by Schumacher and Heise (12) support our observation that carbons in fact can act as oxidation catalysts. Considerable research is necessary, however, to find the best catalyst.

In addition to the catalyst research, an evaluation is to be made of various chemical oxidants such as permanganate, perchlorate, peroxide, and others. The cost and reactivity of these reagents is to be established and compared with oxidation by conventional aeration techniques.

c. Precipitate Formation: The problem of pollution of streams by mine water is twofold.

(1) Pollution from acid-forming constituents, and
(2) Pollution caused by the formation of insoluble metal precipitates.

The infamous sludge called "yellowboy" is notoriously familiar to all who have visited coal mining areas. The composition of this sludge is as variable as the source material itself. In its most idealized form it is a precipitate of ferric hydroxide. In reality, however, it is a mixture of hydrated metal oxides, hydroxides, and sulfates. The sulfates probably are present as adsorbed material since the hydrated oxides and hydroxides have active surfaces. Mine water treated with lime produces precipitates which may also contain calcium sulfate. Silica is also present in some precipitates treated with lime.

The formation of insoluble metal precipitates from mine drainage is primarily due to the formation and insolubility of various metal hydroxides with increasing pH. In untreated acid mine waters, changes in pH are due to dilution, reaction with alkaline water, and/or reaction with alkaline minerals, e.g., limestones, dolomites. In treated waters, the pH has been deliberately raised by adding a suitable reagent, such as lime. The influence of pH on the solubility of the metal hydroxides can be illustrated in Figure 1.

Figure 1 was prepared from published solubility data (13) and is a plot of pH versus the logarithm of the molar metal ion concentration. The designation, active or inactive form, on some of the lines, indicates a characteristic of the precipitate with time. Active forms are generally fresh precipitates produced under conditions of rapid formation and are more soluble than inactive forms. Of interest to this discussion is the relationship among Fe^{+3}, Al^{+3}, Fe^{+2}, and pH. In order for all of these ions to be present in mine water in significant concentrations, without precipitation occurring, a pH of 2 is required. Raising the pH to 3 causes most of the Fe^{+3} to precipitate. The pH must be raised to about 5.5 to assure the presence of only negligible amounts of Al^{+3}. Fe^{+2}, the principal pyrite oxidation product, can be found in significant quantity in solution, even at pH 8. The data in Figure 1 are calculated data and apply primarily to ideal systems, solutions in equilibrium with a particular hydroxide form and in the absence of substances which might form soluble complexes. However, information found in Figure 1 assists in understanding the complexity of mine water chemistry. Based on these data, the following observations can be made.

(1) The presence of significant quantities of Fe^{+3} in mine water above pH 3 indicates that the Fe^{+3} is present as colloidal $Fe(OH)_3$ or as a soluble complex which will be extremely difficult to treat.

(2) The presence of large quantitites of ferrous iron indicates a system which is unstable, difficult to treat with only lime since the pH must be raised above 8.

(3) $Al(OH)_3$ may be a component of mine drainage sludge.

(4) $Mn(OH)_2$ should not be found in mine drainage sludge.

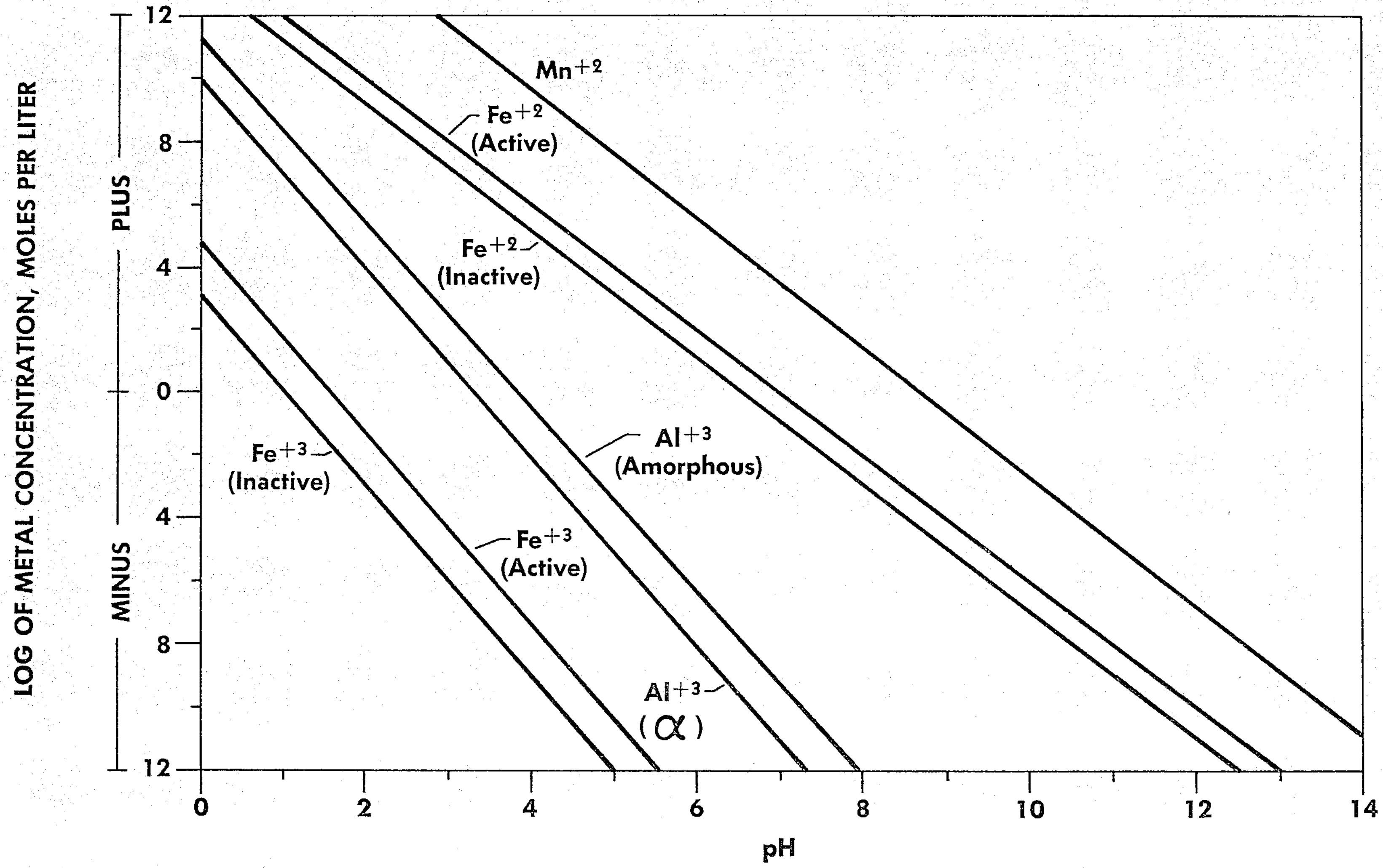

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Figure 1. Solubilities of Metal Hydroxides

To expand on these statements, it has been observed both in the laboratory and in the field, that the type, quantity, and even color of the precipitate produced by treating mine water is a direct function of the pH of the solution. In addition, the elemental composition of the precipitate is influenced by the physical properties of the sludge, including such properties as surface area and degree of hydration. For example, while $Mn(OH)_2$ is not precipitated, Mn^{+2} can be adsorbed from solution on the surface of the precipitate or occluded within the precipitate at the time of formation.

It is also known that practical treatment of mine drainage containing a large quantity of ferrous iron must include an oxidation step to produce ferric iron. This is due to the high solubility of Fe^{+2} at pH below 8. Without oxidation to Fe^{+3}, excessively and perhaps prohibitively large amounts of neutralizing agent will be required to precipitate $Fe(OH)_2$ and to decrease iron content to an acceptable level.

Our knowledge of the chemistry of sludge formation is far from complete, and BCR's investigation in this area has a high priority.

d. Acidity: One of the most talked about, but perhaps least understood, characteristics of mine water is acidity. The purpose of this paper is not to argue for or against any of the many analytical methods for measuring acidity; rather, an attempt is made to give an insight into the significance of acidity as it influences treatment of mine water.

The most widely used measure of acidity is pH. A workable definition of pH is the negative logarithm of the $[H^+]$ or

$$-\log [H^+] = pH.$$

Why measure $[H^+]$? For one reason, it is a simple measurement made without calculations and the equipment is amenable to field use. However, the $[H^+]$, or pH of a mine water, is a useful measurement only when used with other pertinent data. The following table relates pH to equivalent H_2SO_4 content.

pH	Equivalent Acidity as H_2SO_4, ppm
2	490
3	49
4	4.9
5	0.49
6	0.049
7	0.0049

The acidity of a mine water, however, is more than pH and in many cases does not involve H_2SO_4 at all. Acidity in mine water is contributed to by all metal ions which hydrolyze to form both stable and unstable species and which, in some cases, form insoluble hydroxides or oxides. The relative contribution of metal ions and H^+ to the acidity of a mine water is shown below.

H^+	1 ppm of H^+ = 49 ppm of acidity as H_2SO_4
Fe^{+2}	1 ppm of Fe^{+2} = 1.75 ppm of acidity as H_2SO_4
Fe^{+3}	1 ppm of Fe^{+3} = 2.635 ppm of acidity as H_2SO_4
Al^{+3}	1 ppm of Al^{+3} = 5.44 ppm of acidity as H_2SO_4
Mn^{+2}	1 ppm of Mn^{+2} = 1.78 ppm of acidity as H_2SO_4

The analytical measurement of acidity involves the titration with NaOH of a sample of water, which has been previously treated by heating to remove CO_2 and to promote oxidation of $Fe^{+2} \rightarrow Fe^{+3}$; treatment with H_2O_2 to complete Fe^{+2} oxidation is also required. The titration end point selected for use varies, however, since most of the early workers used an indicator, phenolphthalein, to detect the end point. Present techniques call for titration to pH 8.3, the pH at which phenolphthalein begins to change color.

e. Analytical Methods: Standardization of analytical methods for measuring acidity and other mine water properties is a major field of research in itself. BCR is participating in the development and standardization of mine water analysis. Current efforts include active membership on ASTM Committee D-19 Technical Committee on Industrial Water. In addition, BCR is developing analytical methods, an example is a spectrographic method for the analysis of metal ions in mine water.

2. Process Development Studies

While considerable work has been done in this country and abroad on the treatment of mine drainage by lime and limestone (6, 7, 14, 15) results achieved thus far indicate that many gaps exist in the data. Because of this lack of information, diverse opinions of the applicability of lime and limestone neutralization have been held by workers in the field.(15, 16, 17) Little systematic research has been conducted to resolve the differences in results achieved. The problems encountered in lime and limestone neutralization processes are both economic and technological; however, both types of problems are considered amenable to solution through research.

Most experimental work previously reported by others has involved large-scale exploratory research in which a particular mine water is treated with a particular reagent. In describing the results, little attention has been paid to the chemistry of the system being treated. Furthermore, only meager information is available on the effects of composition, chemical equilibria, temperature, oxidation potential, and on the treatability of a particular mine water by a specific process. Parameters for establishing the optimum combination of chemical techniques for treatment of particular mine waters are not available. It is the object of this phase of our work to establish these parameters. It is believed that data can be developed which will lead to the establishment of technology needed for optimizing the chemical techniques involved and for designing treatment plants for all mine waters.

a. Lime Treatment Process: The reaction of lime with acidic mine water can be represented by the following reactions:

$$Ca(OH)_2 + 2H^+ \rightarrow Ca^{+2} + H_2O$$

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

$$3\ Ca(OH)_2 + 2\ Fe^{+3} \rightarrow 3\ Ca^{+2} + 2\ Fe(OH)_3$$

$$3\ Ca(OH)_2 + 2\ Al^{+3} \rightarrow 3\ Ca^{+2} + 2\ Al(OH)_3$$

$$Ca(OH)_2 + Mn^{+2} \rightarrow Ca^{+2} + Mn(OH)_2$$

These are overall reactions and do not depict the mechanism of the formation of the insoluble hydroxides nor the interractions and complex compounds which might be formed during the neutralization of mine water with lime.

Depending on such factors as rate of addition of reagent, concentration of metal component, quantity of reagent added and maximum pH level attained, the above-described reactions will simultaneously or consecutively proceed all the way or only part of the way to completion. The influence of anions such as phosphates or the presence of organic chelating agents, for example, would tend to stabilize Fe^{+2} in solution.

The sludge formed by the neutralization of mine water with lime is large in volume and of such character that long settling times are required to provide clarification. The sludge formed is heavily hydrated and has a specific gravity near 1.0. This makes separation of the sludge from treated water difficult.

BCR is attempting to establish optimum conditions for the neutralization of mine water with lime in order to:

(1) Provide best conditions for neutralization of all acidic components of mine water, and

(2) Attempt to minimize, if possible, the formation of heavily hydrated sludges.

b. Limestone Treatment Process: Work on the utilization of limestone as a neutralizing agent has been conducted by many workers, including BCR. Most recently, the USBM,(18) Rochester and Pittsburgh Coal Company, (19) and the National Coal Board (7) have presented data. Widespread use of limestone as a reagent has not been accepted because of its reported non-reactivity. It is our belief that limestone can be used and that the reactivity of limestone has been under-estimated.

The reaction of mine water with limestone includes the following equilibria:

$$CaCO_3 + H^+ \rightleftarrows Ca^{+2} + HCO_3^-$$

$$HCO_3^- + H^+ \rightleftarrows H_2CO_3$$

$$H_2CO_3 \rightleftarrows H_2O + CO_2$$

If H^+ is the only reactant, the system will reach equilibrium rapidly and, depending on the concentration of the limestone, reach a pH of 6 to 7. At this pH level, the primary species present are dissolved CO_2 and HCO_3^-. H_2CO_3 is present, but only to the extent of about 3 percent of the CO_2 content. Unfortunately, other components are present which enter into the reaction. If sufficient quantity of limestone is added, all of the Fe^{+3} and Al^{+3} will precipitate. Fe^{+2} reportedly is unreactive.

Fe^{+2} removal can only be achieved by oxidation of the Fe^{+2} to Fe^{+3} or by aeration to strip out CO_2, thereby raising the pH to values high enough to precipitate $Fe(OH)_2$. The theoretical pH of a saturated solution of $CaCO_3$ is about 9.5, high enough to achieve reaction with all major acidic constituents of mine water.

The development of a practical limestone process for treatment of mine water is highly desirable. Limestone is cheaper than lime and readily available at most coal mining operations. Also, limestone neutralization produces a dense precipitate, as yet unidentified, which settles rapidly and in general is more desirable than the lime neutralization sludge.

BCR is evaluating the chemical techniques involved in limestone neutralization. Parameters being studied include the following:

(1) Limestone composition,
(2) Limestone particle size,
(3) Mine water composition,
(4) Agitation of limestone particles during reaction,
(5) Reaction rate, and
(6) Temperature.

Results of a preliminary statistical evaluation of the data obtained thus far indicate that the most significant variables are (1) limestone composition (high Ca more reactive than dolomitic) and (2) degree of agitation (highly agitated system is most reactive).

Data will be obtained on a wider range of naturally occurring basic minerals, including a wide spectrum of mineralogic forms of limestone which occurs in the coal mining districts. The objective of this study is to establish (1) the effectiveness of limestone as a neutralizing agent for mine water, (2) the type of mine water treatable with limestone, (3) the optimum design of the chemical techniques and unit operations involved in limestone neutralization, and (4) criterion for evaluating limestones in general as neutralizing agents.

c. Combined Limestone-Lime Process: Results of the above mentioned studies have led to an evaluation of a combined lime-limestone process. The combined lime-limestone process has been examined by Travers;(20) however, no systematic evaluation of the process has been reported. Results of the study to date are encouraging. The results indicate that the composition of the mine water, Eh of the solution at which the lime is added, and degree of agitation are important parameters in the process. The combined process has the advantage that the bulk of the reactions are between limestone and various acidic groups. Ferrous ion is precipitated, but due to the combined effect of limestone and lime, only small quantities of lime are required. The precipitated ferrous iron oxidizes rapidly and the resulting acidity is neutralized by excess limestone already in the system. The study is far from completion, the factors controlling the combined lime-limestone process need to be established. Such factors as (1) effect of mine water composition, (2) Eh, (3) pH, (4) quantity of reagents, (5) O_2 and CO_2 partial pressures, (6) agitation rate, and (7) aeration rate will be evaluated.

e. Sulfide Treatment Process: Under a grant from the Appalachian Regional Commission, BCR is investigating the use of sulfides as a reagent for treating mine water. The reaction between $S^{=}$ and mine water constituents is generally as follows:

$$S^{=} + \text{Metal ion} \rightleftarrows \text{Metal sulfide} \downarrow$$

The metal sulfide precipitates and can then be removed. $S^{=}$ reacts rapidly with Fe^{+2}, Fe^{+3}, and Al^{+3}. The current research will establish whether or not utilization of the above reaction can be made in mine water treatment. The program was initiated June 26, 1967.

CONCLUSION

This summary of BCR research efforts is presented to indicate both the type of research needed in the field of mine drainage and the extent to which the bituminous coal industry's research group is attempting to fill this need. BCR has initiated work in the following areas:

(1) The development of basic data on the chemical and physical properties of mine waters, both treated and untreated, and also on the precipitates produced in the treatment of mine water.

(2) Development and standardization of methods of sampling and analyzing mine water.

(3) The development of data to improve and optimize the lime and limestone neutralization processes now being installed as treatment facilities at many mines in Pennsylvania.

(4) Investigation of the utilization of the sludge or precipitates formed in the neutralization of mine water.

(5) The development of improved processes for the treatment of mine water.

It is hoped that the results of this work will assist in solving the difficult problems associated with mine drainage control.

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