THE USE OF PRE-AERATION TO REDUCE THE COST OF NEUTRALIZING ACID MINE DRAINAGE[1]
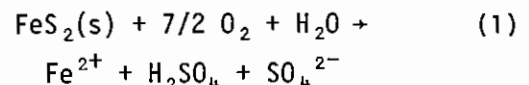
T. C. Jageman, R. A. Yokley and G. W. Heunisch[2]
Consolidation Coal Company
Research and Development Department
4000 Brownsville Road
Library, Pennsylvania 15129

Abstract.--Acid mine drainage (AMD) pumped from an underground mine can contain dissolved carbonates. When hydrated lime is added in the treatment process to neutralize the AMD, the dissolved carbonates react with the lime to form insoluble calcium carbonate. The presence of dissolved carbonates in the untreated water increases both the amount of lime required to neutralize the AMD and the amount of sludge formed during the treatment process. Laboratory tests show that dissolved carbonates can be removed as gaseous carbon dioxide by aerating the AMD prior to the addition of lime (pre-aeration). Field tests were conducted at three AMD treatment plants. The tests demonstrated that pre-aeration is an effective method of reducing treatment costs for an AMD containing dissolved carbonates. Pre-aeration has been permanently applied at each of the sites, and treatment costs have been substantially reduced, while strict compliance with environmental permits has been maintained. The chemistry of dissolved carbonates in the AMD treatment process, the results of the three field tests, and the specific modifications that were made to the treatment plants are discussed.

INTRODUCTION

Acid mine drainage (AMD) is formed by the weathering of pyritic materials, predominantly FeS_2, that are present in the waste found in strip mine spoil, coal refuse piles, etc., as well as from exposed pyritic surfaces in active and aba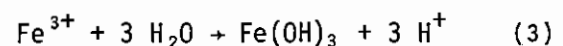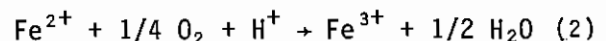ndoned underground mines. These pyritic materials are oxidized in the presence of air (oxygen), water, and certain bacteria to yield large quantities of iron, sulfate, and acidity (Reaction 1), according to Stumm and Morgan (1981).
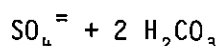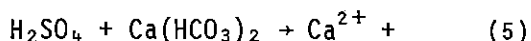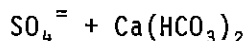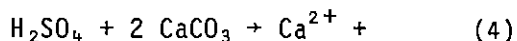
$$FeS_2(s) + 7/2\ O_2 + H_2O \rightarrow \qquad (1)$$
$$Fe^{2+} + H_2SO_4 + SO_4^{2-}$$

Sulfuric acid, one product of the oxidation reaction, is readily recognizable as an acid. The ferrous iron produced in Reaction 1 is also a source of acidity as shown in Reactions 2 and 3 (Stumm and Morgan, 1981). The abiotic oxidation of ferrous iron (Reaction 2) proceeds slowly in acidic solution. In the absence of significant bacterial activity the acidity associated with ferrous iron in many deep mine sites is not released until the water is pumped to the surface for treatment.

$$Fe^{2+} + 1/4\ O_2 + H^+ \rightarrow Fe^{3+} + 1/2\ H_2O \quad (2)$$
$$Fe^{3+} + 3\ H_2O \rightarrow Fe(OH)_3 + 3\ H^+ \qquad (3)$$

---

[1]Paper presented at the 1988 Mine Drainage and Surface Mine Reclamation Conference sponsored by the American Society for Surface Mining and Reclamation and the U.S. Department of the Interior (Bureau of Mines and Office of the Surface Mining Reclamation and Enforcement), April 17-22, 1988, Pittsburgh, PA.

[2]T. C. Jageman is a Research Chemist, R. A. Yokley is a Senior Research Chemist, and G. W. Heunisch is a Staff Scientist, Research and Development Department, Consolidation Coal Company, Library, PA.
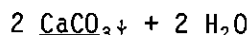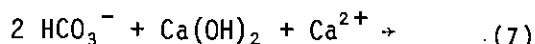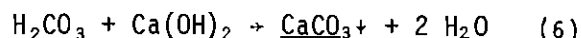
The water entering a deep mine does so by percolating through the overburden and surrounding strata. If the water passes through limestone, it will contain alkalinity in the form of calcium carbonate and/or bicarbonate when it enters the mine (Parizek and Tarr, 1972). When water containing alkalinity encounters the products of pyrite oxidation, neutralization takes place (Reactions 4 and 5).

$$H_2SO_4 + 2\ CaCO_3 \rightarrow Ca^{2+} + \qquad (4)$$

$$SO_4^= + Ca(HCO_3)_2$$

$$H_2SO_4 + Ca(HCO_3)_2 \rightarrow Ca^{2+} + \qquad (5)$$

$$SO_4^= + 2\ H_2CO_3$$

This neutralization moderates the pH of the AMD by consuming sulfuric acid and may limit the solubility of ferrous iron. However, the products of this neutralization, bicarbonate ion and carbonic acid, are weak acids. When AMD that has been partially neutralized in this fashion is pumped to the surface and treated with an alkaline material such as hydrated lime, the carbonic acid and bicarbonate ion react with the lime to form sparingly soluble calcium carbonate (Reactions 6 and 7). Because of these reactions, excessive amounts of alkaline material must be used to achieve a pH that is favorable for ferrous iron oxidation and manganese removal.

$$H_2CO_3 + Ca(OH)_2 \rightarrow \underline{CaCO_3}\!\downarrow + 2\ H_2O \qquad (6)$$

$$2\ HCO_3^- + Ca(OH)_2 + Ca^{2+} \rightarrow \qquad (7)$$

$$2\ \underline{CaCO_3}\!\downarrow + 2\ H_2O$$

Work performed in our laboratory demonstrates that the AMD pumped from most deep mines contains dissolved carbonates which can be removed from solution as gaseous carbon dioxide. The removal is accomplished by aerating the mine water prior to the addition of alkaline material (pre-aeration) and can result in a substantial reduction in the amount of alkaline material required for neutralization. The use of pre-aeration to reduce AMD treatment costs has been reported previously (Herman and Korb) for a mine drainage which was treated to a high pH (>10) to assure manganese removal. Our work indicates that pre-aeration is much more broadly applicable than previously reported.

Field Test

An AMD treatment plant located in western Pennsylvania was used to investigate the utility of pre-aeration. At this site (fig. 1), AMD containing 520 mg/L of dissolved carbonate (calculated as CO_2) is pumped from a flooded deep mine. A side stream is split from the main flow and is used to form a lime slurry. The slurry stream is recombined with the main flow of AMD in an open channel which leads to a series of two aeration basins.

In the first basin an aerator mixes the lime slurry with the main flow of AMD and initiates the ferrous to ferric iron oxidation reaction. In the second basin, aerators drive the oxidation reaction almost to completion.

The treated water discharges from the second aeration basin through an open channel into a large settling basin. Here, continued oxidation takes place, and the insoluble ferric oxyhydroxide sludge settles out. Clarified water discharges from the settling basin, and the solids are pumped from the bottom of the settling basin back into the mine.
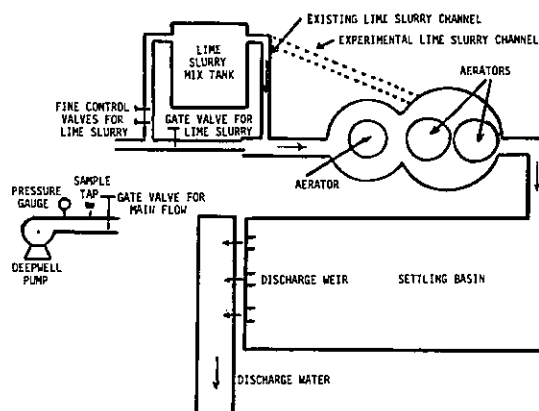

Figure 1.--Sketch of Site 1.

The field test consisted of a baseline test in which the plant was operated normally. A six-day pre-aeration test was then performed. The AMD was treated at the same flow rate and same pH (8.4) as the baseline test. Pre-aeration was accomplished by diverting the lime slurry to the second aeration basin (fig. 1). In this configuration the first basin was used to pre-aerate the unlimed AMD causing dissolved carbon dioxide to evolve to the atmosphere. Even though the residence time (~15 minutes) in the pre-aeration basin was too short for optimum removal of the dissolved carbonates, pre-aeration produced the following results:

o   38% of the dissolved carbonates were removed in the pre-aeration basin.

o   Hydrated lime use was reduced 27%.

o   The concentration of unreacted ferrous iron leaving the aeration basin was reduced from 55 mg/L to 5 mg/L.

o   The sludge settling rate improved dramatically, and the sludge volume was reduced by about 50% (fig. 2).

o   The discharge water quality was maintained with the concentration of total iron <2 mg/L and manganese <1 mg/L.

132

The treatment plant continued to operate as it was configured for the experiment for the next 18 months. As a result treatment costs were reduced by approximately $300,000/yr.
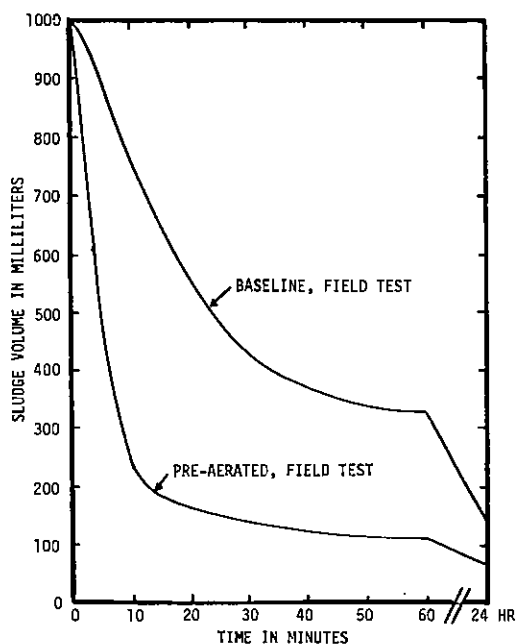

Figure 2.--Sludge Settling Data for Site 1.

Recently, the treatment plant was modified, and a permanent pre-aeration basin was constructed. Based on two weeks of operating data, chemical costs for the new plant are 62% less than the costs before pre-aeration (table 1). Approximately one-fourth of the savings is due to improved water quality in the flooded mine. One-half of the savings is due to preaeration. The remaining one-fourth is due to improved lime utilization.

Application to Other Sites

Field tests and modifications were made at two additional sites. At one of these sites (Site 2 shown in fig. 3) the treatment plant was built on a hillside with the lime handling equipment and mix tanks at a higher elevation than the aeration basin, which was at the base of the hill. The treatment plant was designed as previously described (Site 1) with a small side stream split off to form a lime slurry and then recombined with the main AMD flow.
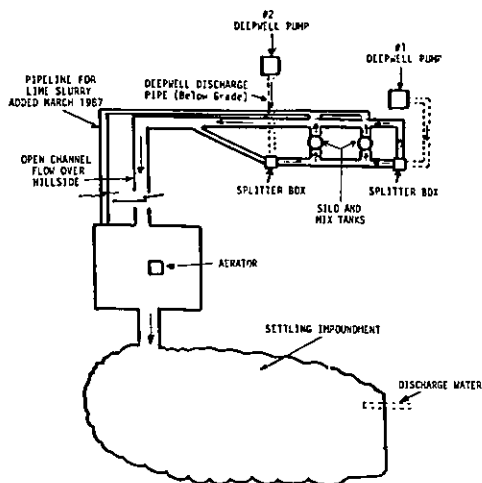

Figure 3.--Sketch of Site 2.

The AMD treated at this site has a pH of 4.6 and contains 200 mg/L of dissolved carbonates (table 2). Laboratory tests indicated, because of the low pH of the AMD, that the dissolved carbonate removal at this site would be rapid. Instead of installing a pre-aeration basin, it was decided to utilize the site topography. A pipeline was installed to transport the lime slurry to the aeration basin. The bulk of the AMD was allowed to flow over

Table 1.--Analysis of Site 1 AMD and the Effect of Pre-aeration.

AMD Sample	pH	Fe^{2+} (mg/L)	Total Dissolved Carbonates (mg CO_2/L)	Lime Requirement (ton/MM gal)
January 1986				
Raw	6.0	603	512	8.31
Pre-aerated	6.4	585	317	6.03
August 1987				
Raw	6.2	447	524	5.76[1]
Pre-aerated	6.5	368	189	3.19

[1] Theoretical value calculated from the concentration of ferrous ion and dissolved carbonates measured in the raw AMD.

the hillside in a rock-lined, open channel. The turbulent flow of the acid water resulted in almost complete removal of the dissolved carbonates.

The plant has continued to operate with pre-aeration for approximately 7 months. The use of pre-aeration at this site reduced lime use by approximately 40% and resulted in a modest improvement in sludge settling rate (fig. 4) and sludge volume. Treatment costs at this site could be further reduced by moving the lime handling equipment to the base of the hill next to the aeration basin. This would allow all the AMD to be pre-aerated in the open channel before contacting lime.
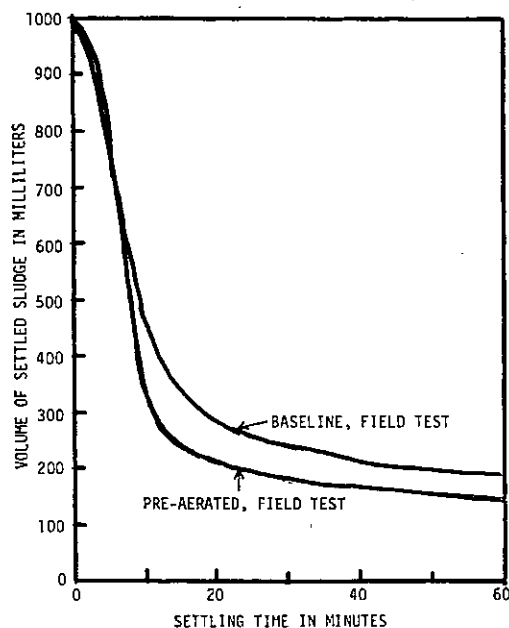
Figure 5.--Sketch of Site 3.

Figure 4.--Sludge Settling Data for Site 2.

At a third site, pre-aeration was accomplished by installing an aerator in an existing AMD holding pond (fig. 5). This pond was initially included in the treatment plant design to allow AMD, which is pumped to the plant from three different sources, to mix and equilibrate prior to treatment (table 3). The pond is an ideal site to retrofit a pre-aerator. Pre-aeration removes approximately 60% of the dissolved carbonates at this site, and the quantity of alkaline material used at the plant has been reduced by more than 50%.

DISCUSSION OF RESULTS

The chemical mechanism for the removal of dissolved carbonates can be explained as follows. Carbonic acid, one of the products of the reaction of calcium carbonate and sulfuric acid, exists in an acidic solution as a component of two chemical equilibria (Reactions 8 and 9).
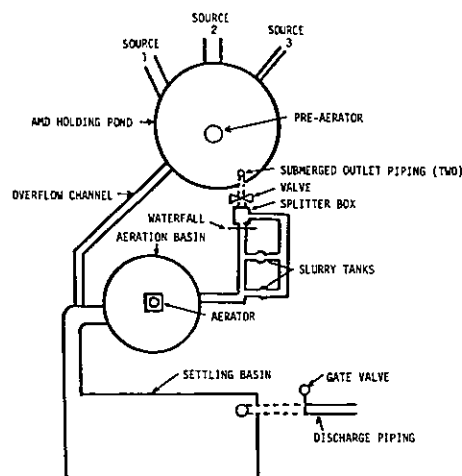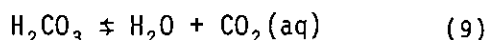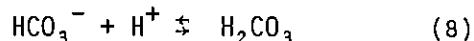
$$HCO_3^- + H^+ \leftrightarrows H_2CO_3 \qquad (8)$$

$$H_2CO_3 \leftrightarrows H_2O + CO_2(aq) \qquad (9)$$

The chemical reactions of these equilibria provide a pathway for converting bicarbonate ion to carbonic acid and ultimately for converting carbonic acid to dissolved carbon dioxide. Carbon dioxide has a very limited solubility (<1 mg/L) in an aqueous solution that is in equilibrium with the atmosphere (Cole, 1979). Aerating an acidic solution that contains dissolved carbonates causes carbon dioxide to be stripped from solution. This shifts the equilibria of Reactions 8 and 9, and more carbon dioxide is formed as the solution equilibria are re-established. In theory, carbon dioxide removal can continue in this manner until the dissolved carbonate concentration is <1 mg/L. In practice, complete removal of the dissolved carbonates is unlikely, and the pH of the untreated AMD determines how difficult carbonate removal will be.

As indicated above, prior to reaching equilibrium with atmospheric CO_2, the relative concentrations of the various carbonate species in AMD are governed by the equilibria of Reactions 8 and 9. The equilibrium of Reaction 9 lies far to the right, indicating that associated carbonic acid is always a minor component of the carbonate system (Cotton and Wilkinson, 1972). The equilibrium of Reaction 8 indicates that in strongly acidic solution (pH <4.5) dissolved carbon dioxide is the only significant carbonate species. At more moderate pH values (pH >6.4) bicarbonate ion becomes the predominate species.

The form of the carbonates in an AMD is critical to the design of a pre-aeration system because dissolved carbon dioxide is readily stripped from solution, but bicarbonate ion is not. In order to remove bicarbonate from solution the bicarbonate ion must react to form carbonic acid (Reaction 10) and then dissociate to dissolved carbon dioxide (Reaction 11). This sequence of reactions takes time, particularly Reaction 11 (Cotton and Wilkinson, 1972).
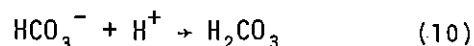
$$HCO_3^- + H^+ \rightarrow H_2CO_3 \qquad (10)$$

134

Table 2.--Analysis of Site 2 AMD and the Effect of Pre-aeration.

Sample	Flow Rate (gal/min)	pH	Total Iron (mg/L)	Dissolved Carbonates (mg CO_2/L)	Lime Requirement (ton/MM gal)
Pump #1	1,250	4.5	206	190	2.7
Pump #2	1,500	4.6	164	207	2.5[1]
Combined AMD After Pre-aeration	2,750	4.8	180	3	1.6

[1] Theoretical value calculated from the concentration of ferrous ion and dissolved carbon dioxide in the raw AMD.

Table 3.--Analysis of Site 3 AMD and the Effect of Pre-aeration.

AMD Sample	pH	Fe^{2+} (mg/L)	Dissolved Carbonates (mg CO_2/L)	Lime Requirement (ton/MM gal)
Composite Raw	6.4	306	546	3
After Pre-aeration	6.6	266	233	1.7

$$H_2CO_3 \rightarrow CO_2(aq) + H_2O \qquad (11)$$
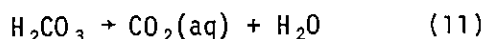
This pH dependent distribution of the carbonate species and the time required to remove the bicarbonate ion explains the differences in the performance of the three pre-aeration systems that were discussed. At Site 2, where AMD of pH 4.6 is treated, the carbonates are present as dissolved carbon dioxide, a rapid and nearly complete removal of the carbonates is accomplished by simply allowing the water to fall over a hillside. At Site 1, where AMD of pH 6.2 is treated, approximately half of the dissolved carbonates are present as bicarbonate. Agitating this water in a large basin with mechanical aerators removes only 65% of the carbonates. At Site 3 the pH of the water is also high (6.4), and only partial removal of the dissolved carbonates is achieved.

An additional point worth mentioning is that for some mine drainages, pre-aeration alone can effect neutralization and iron removal. For mine drainages where the molar ratio of bicarbonate ion to ferrous ion exceeds 2:1, the acid produced by iron oxidation (Reactions 2 and 3) is consumed by the conversion of bicarbonate ion to carbon dioxide (Reactions 10 and 11). Since this condition (high bicarbonate concentration) can only occur when the pH of the untreated water is high (>6), pre-aeration can cause the iron to oxidize and precipitate while the pH remains at a level that is suitable for discharge.

SUMMARY

Pre-aeration has proven to be a very effective means of treatment cost reduction for deep mine AMD. In addition to the three sites discussed in this paper, pre-aeration has recently been installed at one other site and has been recommended for several others. It is anticipated that pre-aeration will eventually reduce AMD treatment costs for Consolidation Coal Company by approximately one million dollars per year.

LITERATURE CITED

Cole, G. A., 1979, Textbook of Limnology, C. V. Moseley Co., St. Louis, MO, pp. 263-271.

Cotton, F. A. and Wilkinson, G., 1972, Advanced Inorganic Chemistry – A Comprehensive Text, John Wiley and Sons, Inc., New York, NY, pp. 296-297.

Herman, Stewart T. and Korb, Michael C., "The High Density Sludge Process -- An Improved Technology to Treat Coal Mine Drainage," Presented at the 1983 American Mining Congress Coal Convention, St. Louis, MO, May 1983.

Parizek, R. and Tarr, E., 1972, Mine Drainage Pollution Prevention and Abatement Using Hydrogeological and Geochemical Systems, In Proceedings, Fourth Symposium on Coal Mine Drainage Research, Pittsburgh, PA, pp. 72-75.

Stumm, W. and Morgan, J., 1981, Aquatic Chemistry, John Wiley and Sons, Inc., New York, NY, p. 470.