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In-Line Aeration and Treatment of Acid Mine Drainage

By T. E. Ackman and R. L. P. Kleinmann

UNITED STATES DEPARTMENT OF THE INTERIOR

IN-LINE AERATION AND TREATMENT OF ACID MINE DRAINAGE

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ABSTRACT

The Bureau of Mines has invented a simple, low-maintenance system to mix and aerate mine water in a pipeline. It consists of a jet pump, which entrains air by Venturi action, and a static mixer, which induces turbulent flow. The system has no moving parts and is designed to use the pressure generated by an existing mine water discharge pump.

The in-line aeration system has been field-tested at a mine site in Greene County, PA, where high ferrous iron (Fe^{2+}) concentrations were causing discharge problems. Discharge concentrations of Fe^{2+} were reduced from 10 to 20 mg/L to 0.2 to 0.9 mg/L by installation of the aeration system. At high influent Fe^{2+} concentrations (47 to 240 mg/L), the system also proved effective, despite low pH conditions (4.6 to 5.6).

Neutralization and aeration were combined into a single step by injecting sodium hydroxide (NaOH) into the port of the jet pump. This resulted in oxidation of the Fe^{2+} within a few seconds, indicating that combining neutralization and aeration optimizes reaction rates.

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[1] Mining engineer.
[2] Supervisory geologist.
Pittsburgh Research Center, Bureau of Mines, Pittsburgh, PA.

INTRODUCTION

Acid mine drainage (AMD) results from the exposure and subsequent oxidation of sulfide minerals (primarily pyrite) associated with coal and adjacent strata. The acidic reaction products are dissolved by infiltrating rainwater, eventually emerging in acid seeps or springs. Many factors influence the quantity and quality of water handled by a mining operation, but it is not unusual for a single mine to treat 1 million gal of acid water a day. Costs of treatment range up to $500,000 per year, with the entire industry probably spending over $1 million per day.

Conventional AMD treatment consists of four steps: (1) neutralization, (2) aeration, (3) settling and disposal of sludge, and (4) effluent discharge. A flow diagram for a conventional AMD treatment plant is shown in figure 1. Capital costs for such a facility range between $500,000 and $2 million (1).[3] Most treatment plants use lime for neutralization, but NaOH and limestone (2-3) may also be used.

Aeration requirements vary, based upon iron concentrations and flow volume. Iron dissolved in the acidic water is often in the reduced Fe^{2+} state. Before discharge, that iron must be oxidized to Fe^{3+} so that it will hydrolyze and

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[3] Underlined numbers in parentheses refer to items in the list of references at the end of this report.

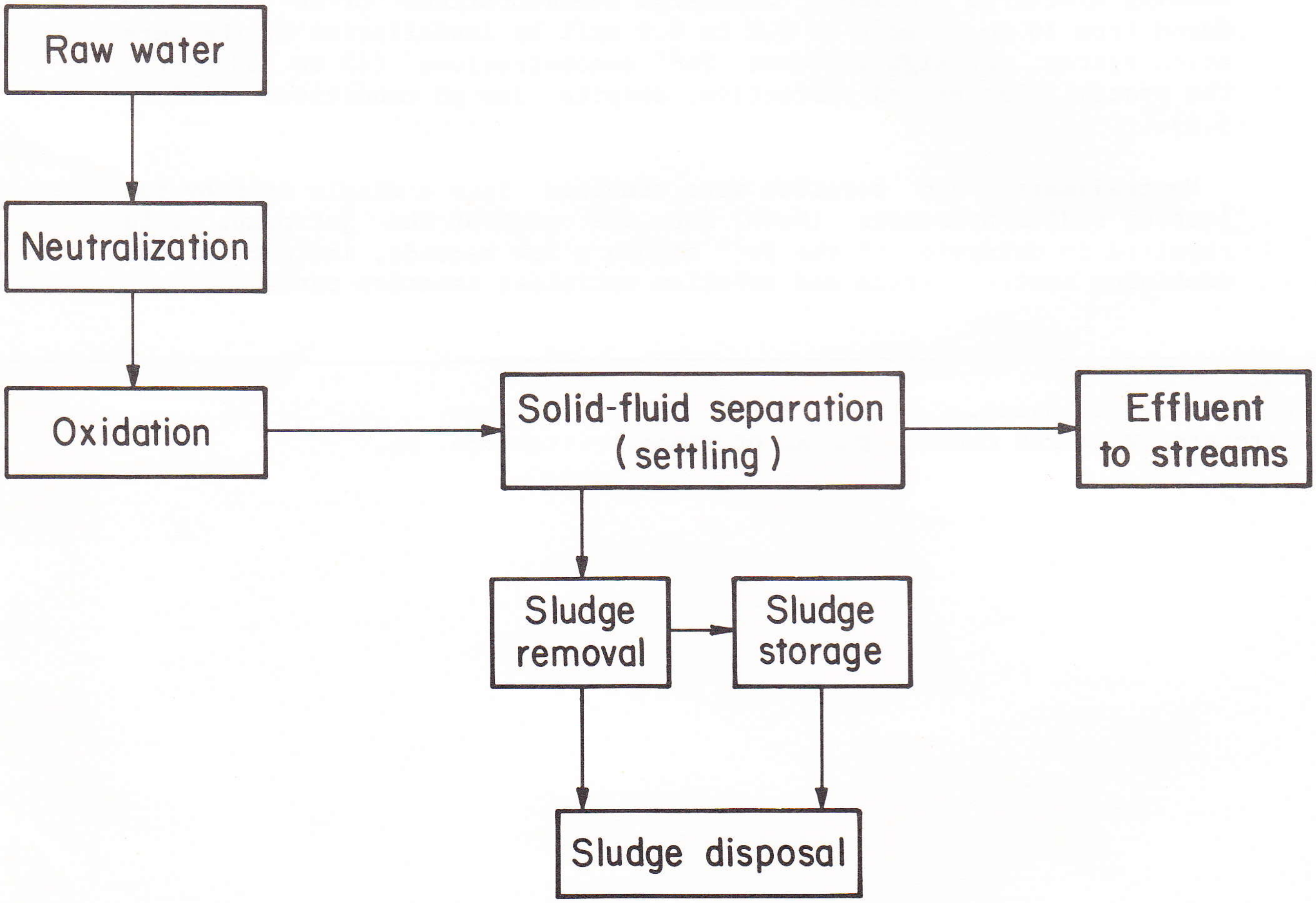

FIGURE 1. - Standard AMD treatment process.

precipitate as $Fe(OH)_3$, commonly known as yellowboy. The rate of Fe^{2+} oxidation is a function of dissolved oxygen (D.O.) and pH:

$$\frac{-d\ [Fe^{+2}, mol/L]}{dt} = k\ \frac{[Fe^{+2}, mol/L] \times (D.O., mg/L)}{[H^{+}, mol/L]^{2}}, \tag{1}$$

where $pH > 3.5$, and $k = (1.25 \times 10^{-14})\ h^{-1}\ mg^{-1}\ mol^{-2}\ L^{+3}$, or

$$\frac{-d\ [Fe^{+2}, mol/L]}{dt} = k\ [Fe^{+2}, mol/L] \times (D.O., mg/L), \tag{2}$$

where $pH < 3.5$, and $k = (1.57 \times 10^{-35})\ h^{-1}\ mg^{-1}\ L^{1}$.

Ferrous iron (Fe^{+2}) and H^{+} are given in mols per liter, whereas D.O. is given in milligrams per liter, and "k" is the rate constant obtained from the literature (4-6) and expressed in the appropriate units. Equations 1 and 2 can be integrated to yield relations for the amount of time ($t_{1/2}$) necessary for an initial Fe^{2+} concentration to decrease by 50 pct as a result of oxidation to Fe^{3+}, assuming constant pH and D.O., as follows:

$$t_{1/2} = \frac{(\ln 2) \times [H^{+}, mol/L]^{2}}{k\ (D.O., mg/L)}, \tag{3}$$

where $pH \geqslant 3.5$, and $k = (1.25 \times 10^{-14})\ h^{-1}\ mg^{-1}\ mol^{-2}\ L^{+3}$, or

$$t_{1/2} = \frac{(\ln 2)}{k\ (D.O., mg/L)}, \tag{4}$$

where $pH < 3.5$, and $k = (1.57 \times 1^{-35})\ h^{-1}\ mg^{-1}\ L^{+1}$.

It is obvious from equations 1 and 3 that pH plays an extremely important role above a pH of 3.5 in reducing iron levels. As can be seen from equations 1 through 4, D.O. is also important. Even if aerated, mine water contains only about 8 to 10 mg/L D.O., which is consumed at the rate of 1 mg/L for every 7 mg/L Fe^{+2} oxidized.

To replenish the D.O., settling ponds or lagoons are constructed wide and shallow to maximize diffusion of oxygen into the water and thereby increase D.O. transfer from the atmosphere. However, oxygen diffusion is relatively slow (7), so that at many sites supplementary aeration sources are necessary. For example, diffusion can be increased by increasing turbulence. This is typically accomplished by incorporating a series of open-channel drops in the flow path of the water, which increases the D.O. concentration. Mechanical aerators can also be used to continuously introduce bubbles of air into the water. This continuous replenishment of D.O. is effective in maintaining a rapid reaction rate, but it also has disadvantages: A separate aeration tank or basin is required; there are high initial capital costs; and there are operating costs associated with power consumption and maintenance, especially where gypsum precipitation is a problem.

This report describes a Bureau-designed treatment system, currently in full-scale operation, which has proven to have economic and environmental advantages over conventional treatment. The In-Line Aeration and Treatment System, or more simply, the In-Line System (ILS), functions in existing AMD pipelines using the energy of existing mine water discharge pumps. It offers reduced maintenance, operating, and capital costs, as well as improved reaction time.

ACKNOWLEDGMENTS

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FIELD TEST

UNIT DESCRIPTION

The ILS consists of two off-the-shelf components: a jet pump (8) and a static mixer (fig. 2). Both components can be described as aeration and mixing devices. Jet pumps are simply nozzles that entrain air by Venturi action (fig. 3). The jet pump used was made of polyvinyl chloride (PVC). Water enters under pressure generated by the existing mine water discharge pump and is converted by the jet pump into a high-velocity stream. This stream then passes through a suction chamber, which is open to the atmosphere. If the system is being used for neutralization as well as aeration, the suction chamber also serves as the injection point for the neutralizing material (e.g., lime, NaOH or potassium hydroxide (KOH), or finely ground limestone). Alternatively, the neutralizing material can be mechanically injected into the line by a metering pump anywhere before the ILS. After passing through the jet pump, the flow enters the static mixer (fig. 4). The static mixer consists of 1-ft sections of pipe made of copolymer polypropylene resins, laminated together end to end with fiberglass. Inside each section is a 1-ft helix that forces the water to follow a spiral path. Helixes are used routinely in sewage and industrial waste water treatment plants as vertical airlift aeration and mixing units, but that design was modified somewhat for this horizontal application. Each helical unit was rotationally offset 90° from its neighbor, thereby interrupting the corkscrew every foot and enhancing the mixing action. Eight 1-ft sections were used, which provided the

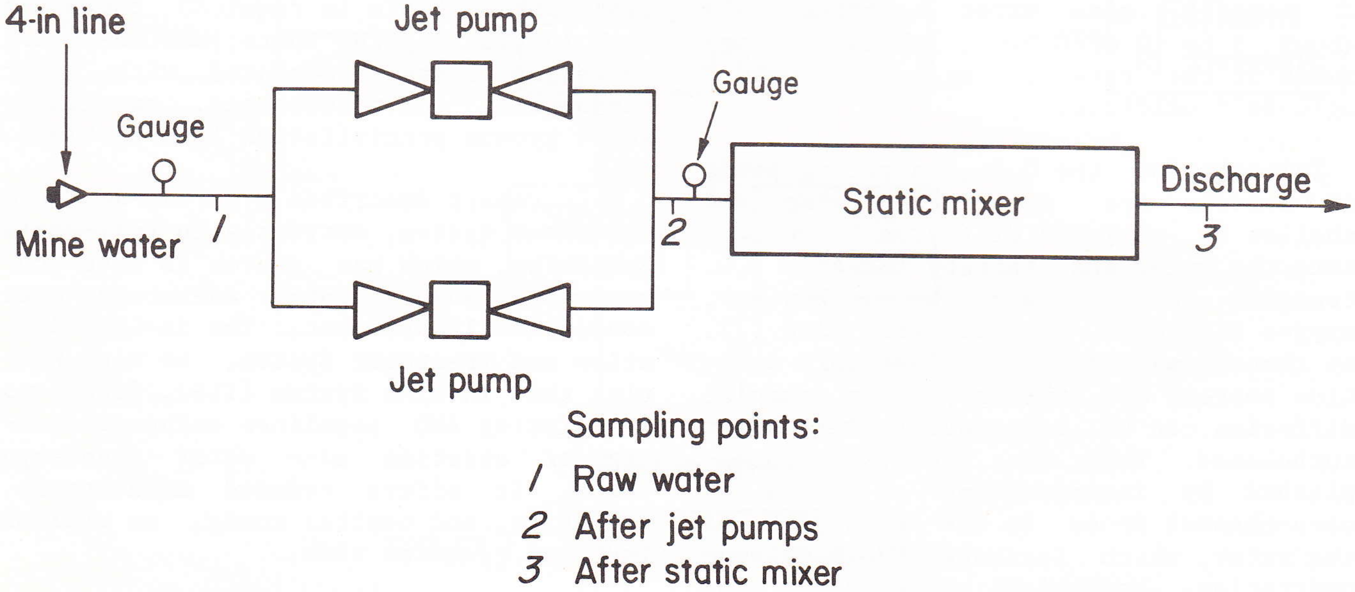

FIGURE 2. - Schematic of in-line aeration and treatment system (ILS).

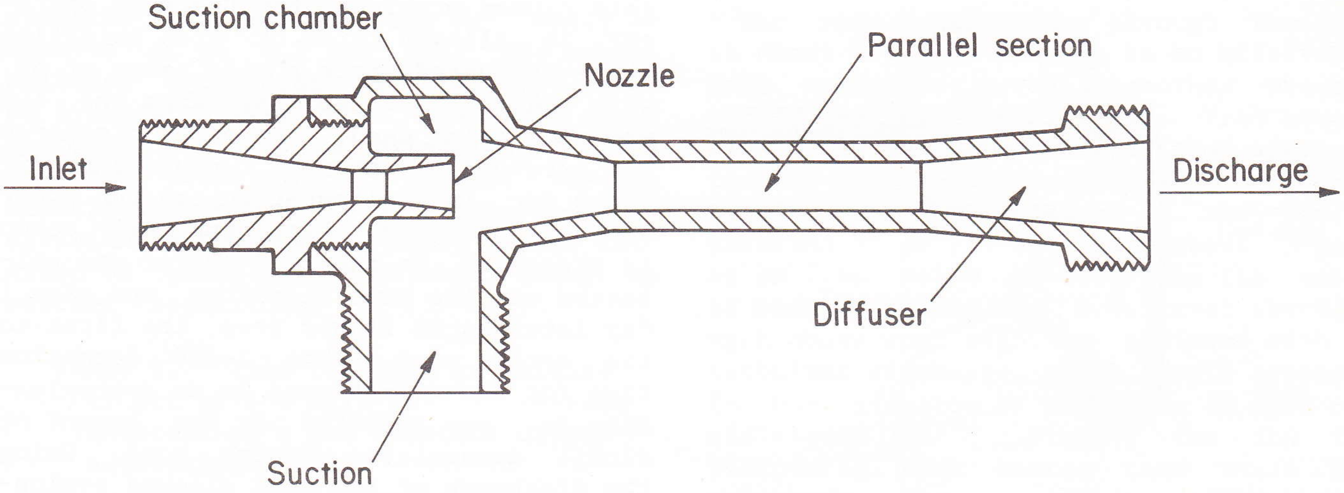

FIGURE 3. - Jet pump diagram.

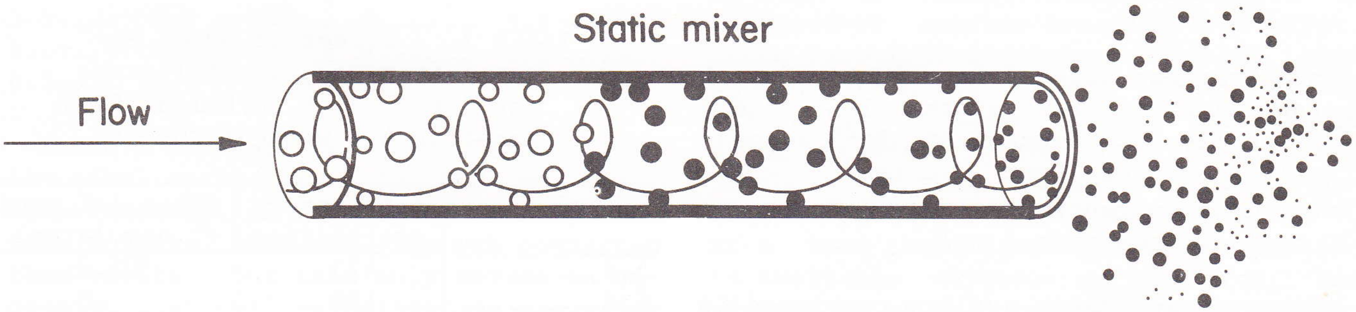

FIGURE 4. - Static mixer diagram.

contact time of a normal 32-ft pipe because of the induced spiral flow.

AERATION FIELD TEST

The ILS was tested and is currently in operation at a remote site in Greene County, PA. Historically, the mine water discharge from this site required no treatment. However, early in 1982, water quality began to deteriorate. In April 1982, the mine operator asked the Bureau of Mines for technical assistance because iron concentrations at the discharge end of the mine water settling ponds were exceeding legal discharge limits. Bureau investigators analyzed the water entering the settling ponds from the underground mine and found that Fe^{2+} levels were erratic but often exceeded 100 mg/L. D.O. was measured at 7.2 to 8.0 mg/L from the discharge pipe at the surface. Given the estimated detention time of the two settling ponds (about 4 days) and the influent pH (6.2-6.6), equation 1 was used to determine that sufficient oxygen was not available for complete Fe^{2+} oxidation and that additional aeration was needed to increase the rate of reaction and allow time for the $Fe(OH)_3$ to settle. As an alternative to mechanical aeration, the ILS was installed at the end of the discharge pipe from the underground mine on May 14, 1982 (fig. 5). It would actually have been preferable to splice the ILS in further up the pipeline to provide additional contact time. However, the operation of the jet pump has limitations in terms of back pressure from the discharge side of the line.

Monitoring of the discharge from the pond began on the fourth day after installation of the ILS. Ferrous iron

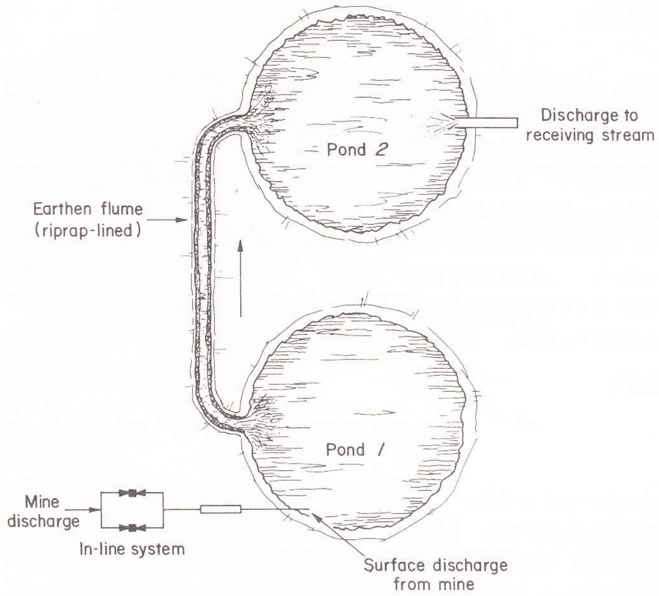

FIGURE 5. - Schematic of test site.

concentrations dropped from 10 to 20 mg/L before installation of the ILS to 0.2 mg/L on May 20. Subsequent Fe^{2+} concentrations ranged from 0.2 to 0.9 mg/L. Total iron concentrations fell from over 20 mg/L to less than 2 mg/L.

However, raw water quality continued to worsen during the summer of 1982 because of reduced pumping at an adjoining mine. Total iron concentrations in the effluent ranged from 2.1 to 20.8 mg/L because of higher influent Fe^{2+} concentrations (up to 240 mg/L) and declining pH (as low as 4.5).

Faced with the necessity of neutralization and yet reluctant to construct a conventional AMD treatment plant, the mining company decided to inject NaOH into the mine waterline. This would allow them to quickly meet acidity and pH standards in the effluent and would also provide water of sufficiently high pH for efficient Fe^{2+} oxidation in the ILS.

Injection of the NaOH (KOH during winter) into the mine waterline proved to be more difficult than the mining company first envisioned. Variations in water quality and flow and problems with the feed pump resulted in inconsistent and inefficient neutralization. Although this caused problems for the mine operator, it allowed rates of iron oxidation to be evaluated over a wide range of pH, with and without the ILS. When the ILS was not being used, the pipe discharge was arranged to provide turbulent conditions for initial aeration as the water entered the pond. Data for this setup is presented in table 1. Water was collected at the pipe discharge and also 1 day later as it flowed from the first to the second pond. This 1-day detention time for the first pond is an approximation and was affected by the amount of sludge accumulated in the pond. Using the discharge of the pond allowed evaluation of data despite the fluctuating water quality. It is important to note that the values in table 1 do not represent site discharge concentrations.

TABLE 1. - Effect of pH on Fe^{2+} concentrations, in milligrams per liter, with turbulent flow aeration but without the ILS

pH[1]	After neutralization	After 1st pond (1 day later)
5.6.........	473	305.0
6.4.........	199	.8
6.5.........	332	71.0
6.5.........	208	.6
6.6.........	351	86.0
7.5.........	208	1.6
8.7.........	320	.1
9.5.........	12.5	.7

[1] The pH was measured before the water flowed into the first pond.

Table 1 demonstrates satisfactory Fe^{2+} oxidation at a pH of 7.5 and above but inconsistent Fe^{2+} oxidation at pH 6.6 and below. The extent of iron removal that is occurring indicates that D.O. is being replenished in the pond by diffusion from the atmosphere. Assuming a fully aerated system and an initial Fe^{2+} concentration of 100 mg/L, one can calculate the minimum time it should take to reduce iron concentrations to an average legal discharge value below 3.0 mg/L at any pH (table 2).

With the approximate 24-h detention time of the first pond, it would be expected that most of the Fe^{2+} would be removed at pH 6.5 but that the amount oxidized would drop off rapidly below pH 6.5. With less D.O. present, as is the case in the pond, oxidation kinetics should be proportionally slower. The two occasions where Fe^{2+} oxidation remained efficient at pH 6.4-6.5 imply better aeration on these days, perhaps owing to weather conditions.

TABLE 2. - Time required to oxidize 97 pct of 100 mg/L Fe^{2+} at various constant pH's and constant oxygen saturation

pH	Time, h	pH	Time, h
4.5....	3.5×10^4	7......	3.5×10^{-1}
5......	3.5×10^3	7.5....	3.5×10^{-2}
5.5....	3.5×10^2	8......	3.5×10^{-3}
6......	3.5×10^1	8.5....	3.5×10^{-4}
6.5....	3.5		

Table 3 presents Fe^{2+} concentrations in the mine water when the ILS was used. Unfortunately, pH was lower during the time interval when the ILS was connected than earlier, but this only serves to emphasize that Fe^{2+} oxidation is occurring much faster than would be predicted.

TABLE 3. - Effect of ILS on Fe^{2+} concentrations, in milligrams per liter

pH	After neutralization	After ILS	After 1st pond (1 day later)
4.6..	185	188	4.1
5.3..	240	210	6.0
5.4..	55	52	5.5
5.5..	87	75	5.5
5.6..	141	141	11.0
5.6..	47	44	2.8

For example, at pH 5.5 and an initial Fe^{2+} concentration of 87 mg/L, a detention time of over 10 days should be required to reduce Fe^{2+} concentrations to 5.5 mg/L. Similarly, at pH 4.6 and an initial Fe^{2+} concentration of 185 mg/L, the detention requirements to reduce Fe^{2+} to 4.1 mg/L should exceed 400 days. Yet the Fe^{2+} is being oxidized, despite the low pH.

The mine water flows through the ILS in about 4 s and remains in an effervescent state for perhaps another minute before the bubbles disperse. From equation 3, it can be calculated that approximately half of an initial Fe^{2+} concentration would be oxidized in this short interval at pH 7.5 but only about 5 pct at pH 7.0. Below pH 7.0, the ILS unit is simply raising the D.O. level about 1 mg/L above what might be achieved with a turbulent discharge, which should account for the oxidation of only 5 to 10 mg/L of additional Fe^{2+}. Clearly the ILS is performing much better than would be expected.

The observed oxidation rates suggest that the ILS is either directly catalyzing the rate of iron oxidation in the pond or somehow creating a catalyst. Since turbulent discharge into the pond should mimic the direct effect of the ILS well, it seems that a catalyst is being created by the ILS. Tamura (9) demonstrates that amorphous ferric hydroxide catalyzes the oxidation of Fe^{2+}, at a rate that increases in proportion to available oxygen, surface area, and adsorption of Fe^{2+} on the $FeOH_3$, but decreases with pH. The crystalline phase associated with ferric hydroxide, lepidocrocite (γ-FeOOH), which consists of very small and very thin rectangular plates (5), has also been shown to catalyze Fe^{2+} oxidation (4-5), though again the effect diminishes with decreasing pH. It seems likely that the ILS must be increasing the rate of catalysis by $FeOH_3$ or γ-FeOOH by increasing the rate of particle formation, by altering the particle surface area, or by increasing the availability of oxygen.

IN-LINE NEUTRALIZATION AND AERATION

Because of the problems that the mine company was experiencing with injecting the NaOH into the pipeline, the Bureau suggested that the jet pumps of the ILS could also serve as an injection port. A pilot-scale test was conducted using a 55-gal drum of NaOH and a siphon hose, adjusting the feed rate by valve adjustment so that pH at the ILS discharge averaged about 7. Four sets of water samples were collected at three points in the ILS: before the jet pumps, after the jet pumps, and after the static mixer. The average values from the test are listed in table 4.

TABLE 4. - Effect of simultaneous in-line neutralization and aeration on water quality during flow through the ILS--pilot-scale tests

Parameter[1]	Before treatment	After jet pumps	After static mixer
pH[2]..................	4.5	6.7	6.9
Acidity or alkalinity[3]...mg/L..	-810	+45	+70
Ferrous iron...mg/L..	190	4.8	2.4
Total iron.....mg/L..	260	95	40

[1] All values are averages.

[2] Geometric averages (1).

[3] - indicates acidity; + indicates alkalinity.

Once again the Fe^{2+} iron is being oxidized much faster than would be predicted. Based on the average values shown in table 4 for pH and Fe^{2+}, very little Fe^{2+} should be oxidized during the 4 s of contact time in the ILS. Alternatively, one can look at the extent of Fe^{2+} oxidation and calculate that an apparent average pH of at least 8.5 must exist throughout the ILS, despite the measured pH. This apparent contradiction between anticipated and measured values is probably a result of the simultaneous aeration and neutralization. As the NaOH is injected, the instantaneous pH is extremely high (over 10) for a fraction of a second. For that instant, reaction rates are extremely fast, with a reaction halftime measured in microseconds and limited only by D.O., which is being continuously replenished by the jet pump.

If this hypothesis is correct, combining neutralization and aeration should consistently result in high Fe^{2+} oxidation rates. The point of injection for the NaOH was moved to the jet pump port, and samples were collected on randomly selected days over a 2-month period. The oxidation of Fe^{2+} was even more rapid than was observed earlier in the pilot-scale test (table 5). Iron levels in the discharge from the second pond consistently met regulatory requirements for site discharges. In many cases, virtually all of the iron was oxidized after passage through the ILS; on some days, the jet pump alone was sufficient to reduce Fe^{2+} to below detectable limits. This efficiency is attributed to the higher pH's in the system, which in turn reflects the fact that injection of NaOH no longer poses the problem that it did earlier.

TABLE 5. - Effect of simultaneous in-line neutralization and aeration on water quality during flow through the ILS--full-scale operation, Fe^{2+} iron concentration in milligrams per liter

pH after static mixer	Before treatment	After jet pumps	After static mixer	After 1st pond
7.2........	236	89.8	18.0	1.0
7.3........	148	33.7	ND	ND
7.7........	193	77.5	ND	1.0
8.4........	414	ND	ND	ND
8.5........	180	44.9	15.7	1.0
8.7........	274	137.0	80.9	2.2
8.7........	380	ND	ND	ND
9.5........	1,527	ND	ND	ND
10.0.......	420	390.0	ND	1.0
10.3.......	137	ND	ND	ND

ND Not detected.

COST ANALYSIS

The total capital cost of the ILS was less than \$3,000. Operating costs, based on an estimated 10 pct additional power consumption by the mine discharge pump, is about \$800 per year. By way of comparison, a mechanical aerator sized for this site would cost \$10,000 to \$20,000, with an estimated operating cost of about \$2,200 per year.

Since the ILS lacks moving parts, maintenance is much simpler for this system than for a mechanical aerator. Icing, a problem sometimes associated with spray from the mechanical aerator, should not pose a problem with the ILS; and gypsum scale, if it develops, can be dislodged simply by striking the ILS unit.

If the ILS is incorporated in a new AMD plant, space can be conserved by designing ponds that are deeper than normal, since diffusion of oxygen into the pond is no longer essential. This will allow detention requirements to be based solely on settling requirements. Increased pond depths can also reduce pond cleaning frequency, or alternatively, extend the life of a pond used for sludge disposal.

CONCLUSION

The ILS is a simple and inexpensive approach to aeration of mine water. It significantly increased oxidation rates above theoretical limits through the mixing and aeration action of the jet pump and static mixer. At a pH of 5.5, oxidation rates were 10 times faster than anticipated; at pH 4.6, oxidation rates were over 400 times faster than anticipated.

The rate of Fe^{+2} oxidation was further accelerated by incorporating neutralization into the ILS. When NaOH was injected into the injection port of the jet pump, the simultaneous aeration and neutralization maximized the Fe^{+2} oxidation reaction rates, so that almost all of the Fe^{2+} was oxidized as the water flowed through the ILS. The extremely high rate of Fe^{+2} oxidation observed can probably be attributed to the extremely high instantaneous pH in a portion of the flow, which reduced the reaction halftime ($t_{1/2}$) in that portion to microseconds.

The ILS is much more economical than conventional mixing and aeration devices. The total capital cost of the system, at this particular site, was less than $3,000--about one fifth of the price of a conventional aerator. Operating and maintenance costs for the ILS are also much lower than for the conventional mechanical aerator.

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