

REMEDICATION OF ACID MINE DRAINAGE AT THE FRIENDSHIP HILL NATIONAL HISTORIC SITE WITH A PULSED LIMESTONE BED PROCESS

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Abstract

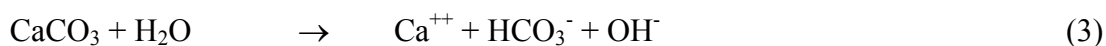
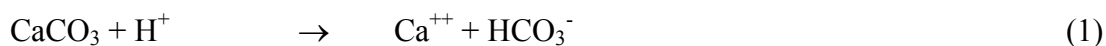
A new process utilizing pulsed fluidized limestone beds was tested for the remediation of acid mine drainage at the Friendship Hill National Historic Site, in southwestern Pennsylvania. A 230 liter-per-minute treatment system was constructed and operated over a fourteen-month period from June 2000 through September 2001. Over this period of time, 50 metric tons of limestone were used to treat 50 million liters of water. The influent water pH was 2.5 and acidity was 1000 mg/L as CaCO₃. Despite the high potential for armoring at the site, effluent pH during normal plant operation ranged from 5.7 to 7.8 and averaged 6.8. As a result of the high influent acidity, sufficient CO₂ was generated and recycled to provide a net alkaline discharge with about 50 mg/L as CaCO₃ alkalinity. Additions of commercial CO₂ increased effluent alkalinity to as high as 300 mg/L, and could be a useful process management tool for transient high flows or acidities. Metal removal rates were 95% for aluminum (60 mg/L in influent), 50 to 90% for iron (Fe), depending on the ratio of ferrous to ferric iron, which varied seasonally (200 mg/L in influent), and <10% of manganese (Mn) (10 mg/L in influent). Ferrous iron and Mn removal was incomplete because of the high pH required for precipitation of these species. Iron removal could be improved by increased aeration following neutralization, and Mn removal could be effected by a post treatment passive settling/oxidation pond. Metal hydroxide sludges were settled in settling tanks, and then hauled from the site for aesthetic purposes. Over 450 metric tons of sludge were removed from the water over the life of the project. The dried sludge was tested by the Toxicity Characteristics Leaching Protocol (TCLP) and was found to be non-hazardous. Treatment costs were \$43,000 per year and \$1.08 per m³, but could be decreased to \$22,000 and \$0.51 per m³ by decreasing labor use and by on-site sludge handling. These results confirm the utility of the new process in treatment of acid impaired waters that were previously not amenable to low cost limestone treatment.

Background

Acid mine drainage (AMD) is an unintended consequence of coal and metal mining that adversely affects thousand of kilometers of streams both in the eastern and western regions of the U. S. Exposure of sulfide minerals such as pyrite to air and moisture results in the formation of AMD. The sulfur is oxidized to sulfuric acid, which then solubilizes metals such as iron, manganese, and aluminum [1]. The resulting acidity and metal content is harmful to aquatic life and degrades stream quality until diluted to innocuous levels. Estimated costs of remediation for the state of Pennsylvania alone using current technology range upwards of 5 billion dollars [2].

A novel AMD treatment process based on limestone neutralization has been developed and patented at the Leetown Science Center in Kearneysville, West Virginia [3]. Limestone is an attractive candidate for acid neutralization because of its ready availability and low cost. In a cost comparison of reagents for acid neutralization [4], limestone was found to be less than one third of the cost of hydrated lime, and less than one twentieth of the cost of caustic (sodium hydroxide). Also, because of its less corrosive nature, limestone is less hazardous to handle, and the risk of overtreatment of impaired waters is low. Despite these advantages, limestone has not been used widely in the past due to limitations including slow dissolution rate and armoring (formation of an impervious coating on the limestone surface). Some researchers recommend that limestone be used only for AMD sources containing less than 50 mg/L acidity or 5 mg/L iron [5]. Recent research at the U.S. Geological Survey has shown that armoring can be avoided and the rate of limestone reaction increased by use of pulsed fluidized bed reactor technology, combined with pressurization of the reactor with carbon dioxide. Pulsing of the limestone bed allows for vigorous mixing of the limestone sand, resulting in high attrition rates, helping keep the limestone surface clean. In addition, the high flow of the pulsed bed flushes precipitated solids out of the reactor, preventing plugging and caking of the bed, as often occurs in static limestone packed beds. The carbon dioxide increases the rate and extent of limestone dissolution, decreasing retention time by a factor of 100 or more. This enhancement of limestone neutralization allows for much wider use of the more economical limestone than was previously thought possible. Waters containing up to 1000 mg/L acidity and 200 mg/L iron have been successfully treated with the process.

The kinetics of limestone dissolution have been explored in detail [6]. Three possible mechanisms are known:



These mechanisms were termed attack by acid, CO₂ and water, respectively. Under certain conditions of pH and (CO₂) pressure, one or another of these mechanisms may be predominant. These relations were combined with a general formula for dissolution of spheres settling through water to give the following [7]:

$$\frac{-dm}{dt} = \left\{ \frac{D}{\Delta r} \cdot [\text{H}^+] + k_2 [\text{CO}_2] + k_w - k_B \cdot [\text{Ca}^{+2}] \cdot [\text{HCO}_3^-] \right\} \cdot \frac{3 \cdot m}{\rho \cdot r} \quad (4)$$

In equation (4), m is the mass of the particle dissolving per time t, D is the diffusion coefficient for H⁺, Δr is the thickness of a boundary layer surrounding the particles, k is the reaction rate constant, ρ is the particle density, and r is the particle radius. This equation clearly demonstrates the enhancement of the dissolution rate by CO₂, not only directly, through reaction (2), but also as a consequence of the buffering of the solution pH at a lower value, thus increasing the concentration of H⁺, and thereby the rate of reaction (1) as well. The effect of the limestone particle size is also apparent.

A schematic of the AMD treatment apparatus is shown in Figure 1. The apparatus shown was sized to treat 230 liter per minute (lpm) of flow. It consisted of four 61-cm (24-in) diameter

fiberglass columns containing limestone, and one 46-cm (18-in) diameter column (the carbonator) functioning as a packed tower for CO₂ absorption into the water. The height of the

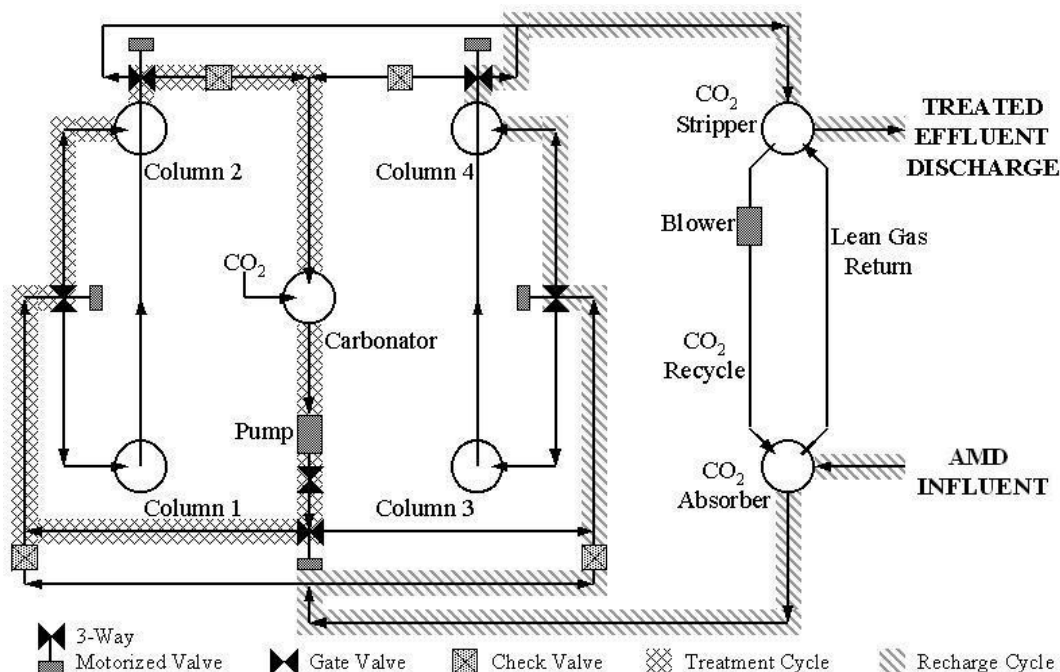


Figure 1. Schematic of pulsed limestone bed process.

limestone columns and the carbonator were 215 cm (84 inches). Incoming water was routed to one set of two columns containing limestone during a rinse/recharge cycle. The limestone particle size was roughly 0.1 to 1.0 mm. The flow fluidized a single limestone bed for a period of one minute, and then flow was diverted to the second column for one minute, while the bed in the first column settled. Therefore, water was discharged to the drain continuously. This pulsed-bed operation allows higher flow rates to be passed through the limestone bed, thus providing for better mixing and scouring of the particle surfaces. The flow path was controlled by an electrically actuated three-way ball valve operating on a timer-controlled program. Meanwhile, the water in the other set of two columns was recirculated through the carbonator, where carbon dioxide gas can be added to the water. This was termed the treatment cycle, and the water was diverted back and forth between the two limestone columns on a one-minute cycle as in the recharge phase. This mode of operation continued for a total of four minutes. A second set of ball valves was then actuated, and the columns that had been receiving incoming water were switched to the treatment cycle, and the columns that had been on treatment cycle were switched to receive and discharge water. Thus, at any one time, one out of the four columns was receiving and discharging water, and one of the columns was receiving water recycled through the carbonator. The system also recovered and reused some of the CO₂ dissolved in the effluent - after discharge from the columns, the effluent was sent to a 0.4 m diameter by 3 m tall stripping tower, where air was passed counter currently to the water through a packed bed. The CO₂ was stripped from the effluent with a counter current flow of air and recycled to a second paired packed bed reactor receiving incoming AMD.

This PLB system was first tested at the Toby Creek site in Elk County, PA in May through June of 1999 [8]. Total acidity at this site was about 300 mg/L. During a 30-day field trial, the unit neutralized 10 million liters of AMD without any evidence of performance degradation related

to armoring. Testing confirmed earlier results that effluent alkalinity depended on applied CO₂ pressure. Metal removal was excellent (>95%) for iron (Fe) and aluminum (Al), but manganese (Mn) was not removed (<10%). Mixing tests showed that the excess alkalinity in the treated effluent from the process could be used to neutralize other AMD flows at the site. Based on site flows and acidities, the pulsed limestone bed process could treat a total of 1150 lpm of combined AMD influent (five times the nominal treatment capacity), and still produce a net alkaline discharge. Sludge production and settling were not measured at this site as parallel processing was taking place concurrently, and treated waters were mixed in a common settling pond.

A long-term test of the treatment system was conducted at the Friendship Hill National Historic Site from June 2000 through August 2001. Based on a survey of AMD sites in Pennsylvania, the Friendship Hill site is among the most acidic coal mine drainages in the area [9] and was therefore considered an ideal place for testing of the resistance of the pulsed limestone bed process to armoring. One significant difference from previous configurations was the use of a water recycle loop. The discharge flow at Friendship Hill varied seasonally from about 75 to over 380 lpm. Since the process requires 230 lpm for proper fluidization of the limestone beds, a recycle loop was designed for recycle of treated water from the stripper sump to the absorber sump. Another difference was that process testing at this site included solids separation and management, so that this aspect of the treatment could be evaluated. This report discusses the results of testing at the Friendship Hill site.

Methods

The plant was designed to run with infrequent monitoring and adjustment requiring about 20 hours per week labor. However, since the plant was still in demonstration mode, a full time operator was assigned to the plant for the duration of process testing. The operator not only checked and adjusted plant variables, but also sampled and analyzed process streams to develop a database of plant operating characteristics.

The aeration and solids separation section of the plant at the Friendship Hill site consisted of an aeration basin followed by settling tanks and sludge holding tanks. Treated water exiting the CO₂ stripper was directed into an aeration basin measuring 1.2 m deep by 1.2 m wide by 6.1 m long, with an effective fluid volume of 7.9 m³. Here, twenty-four 0.6 m long Dacron sleeved diffusers mounted at floor level received air from a 0.75 kW regenerative blower. Gas-liquid contacting increased dissolved oxygen concentration while concurrently stripping residual dissolved CO₂. Water exiting the aeration basin flowed by gravity into four solids settling tanks operated in parallel. Each tank measured 1.2 m deep by 2.4 m wide by 6.1 m long with an effective volume of 15 m³. Individual settling tanks were periodically taken off-line, decanted and cleaned of accumulated AMD solids. Solids were held in two independent 3.8 m³ volume tanks prior to removal from the site to provide for additional sludge thickening. Supernatant exiting the solids settling tanks was pumped into the receiving stream at a point just down stream from the abandoned coal mine portal where it had been diverted to the treatment plant.

Process flows were monitored using paddlewheel flow sensors for the influent, mixed influent and recycle streams. Sampling of the plant influent and process effluent was done three to five days per week. Effluent samples were taken at the apparatus discharge, prior to air stripping. Four-minute composite samples were taken to even out the variability between different columns. The samples were analyzed for pH, then air stripped for seven minutes, and the pH measurement repeated. The air-stripped samples were then titrated in duplicate for alkalinity,

using purchased 0.02N H₂SO₄ solution. Because of the recycle loop, mixing of treated and untreated water alters the conditions that the limestone in the columns is exposed to. Therefore, a sample of the mixed influent was always taken for analysis in addition to the raw plant influent. Raw and mixed influent samples were analyzed for pH, air stripped, analyzed for pH again, then titrated for acidity according to standard methods [10], using purchased 0.1N NaOH. All alkalinities and acidities discussed in this report are in units of mg/l as CaCO₃. Samples of the limestone column effluent, aeration basin effluent, and clarification tank effluent were also analyzed for settleable solids according to standard procedures [10]. Additional samples of plant influent and clarifier supernatant were taken approximately every three weeks for outside analysis, for confirmation of in-house results. These samples were put on ice and transferred to Geochemical Testing, in Somerset, Pennsylvania for analysis for pH, alkalinity, acidity, iron, aluminum, manganese and sulfate.

The limestone in the reactors was consumed by neutralization of the acid and by reaction with CO₂ to form alkalinity. The rate of reaction also depended on the water treatment flow rate. The initial charge was about 270 kg of limestone to each reactor, and periodic additions were made to each column to maintain a settled bed depth of about 76 cm. At Friendship Hill, recharging was required every day during high spring flows, to as little as once per week at low flow conditions in the fall and winter months. Recharging of the system took about one hour. The AMD flow was stopped, the columns depressurized and opened, and limestone added by means of a large funnel inserted into a port in the top of the column. The depth of the limestone bed in each reactor was measured before and after recharge using a metal tape measure. The weight of limestone required to bring the bed height back to the target level was measured using a digital balance with an accuracy of 0.2 kg.

In April of 2001, the effect of the AMD flow pattern in the limestone columns was tested. Instead of an alternating pulsed bed arrangement as described previously, AMD was introduced into each reactor continuously at a rate of 58 lpm, to give an overall treatment rate of 230 lpm. No pulsing or CO₂ introduction was used during this period. This flow pattern was maintained for one week, and served as a control test for comparison to the pulsed bed mode.

Previous testing at the Friendship Hill site had indicated that the average flow rate of AMD was 230 lpm. As mentioned above, the flow was seasonally affected, with spring high flows of over 380 lpm, and winter flows of 75 lpm. Water temperatures were 12 to 15 °C, depending on the time of year, and were not affected by the treatment process. Based on earlier work, the primary AMD discharge was portal A, about 100 meters upstream on Ice Pond Run from the treatment plant. However, as testing progressed, it became apparent that a second source, Source B, was affecting a branch of Ice Pond Run, and causing reacidification where it met the treated water from the plant. Therefore, in March of 2001, a temporary pump station was installed at source B to transport this water to the inlet sump for the treatment plant. Since the acidity and iron levels in source B were greater than in Source A, this resulted in a jump in influent acidity and metals loadings.

From February 2001 through August 2001, the effect of CO₂ addition on process performance was measured. The CO₂ was supplied as a refrigerated liquid in an insulated tank truck. The flow rate of CO₂ into the carbonator was monitored using a Dwyer rotameter calibrated for air. Correction factors were applied to convert readings into standard liters per minute of CO₂. The gas pressure in the carbonator column was measured using a pressure gauge. The concentration of dissolved CO₂ in the feed and effluent streams was monitored by means of a gas headspace apparatus that stripped the gases from the water. The resulting gas mixture was analyzed for CO₂ content using a CEA GD444 portable CO₂ analyzer. Process streams were also analyzed

for dissolved oxygen and temperature, using a YSI Model 57 dissolved oxygen meter, with corrections for altitude and barometric pressure. Barometric pressure measurements were taken with a Solomat MPM 2000 with a pressure sensing modometer. In addition to the usual monitoring of pH and alkalinity, an extra set of process water samples were taken for analysis for metal content by inductively coupled plasma atomic emission spectroscopy (ICP-AES). This analysis was performed by the Department of Horticulture ICP analytical lab at Cornell University, in Ithaca, New York.

Results and Discussion

Influent and effluent pH

The AMD treatment plant at Friendship Hill began continuous operation in late June of 2000. With periodic shutdowns for plant maintenance and cleaning, the plant operated until August 31 of 2001. During that time, plant performance was monitored in-house through determination of pH, acidity and alkalinity of influent and effluent water samples. Figure 2 shows influent and effluent pH over the 431 days of treatment.

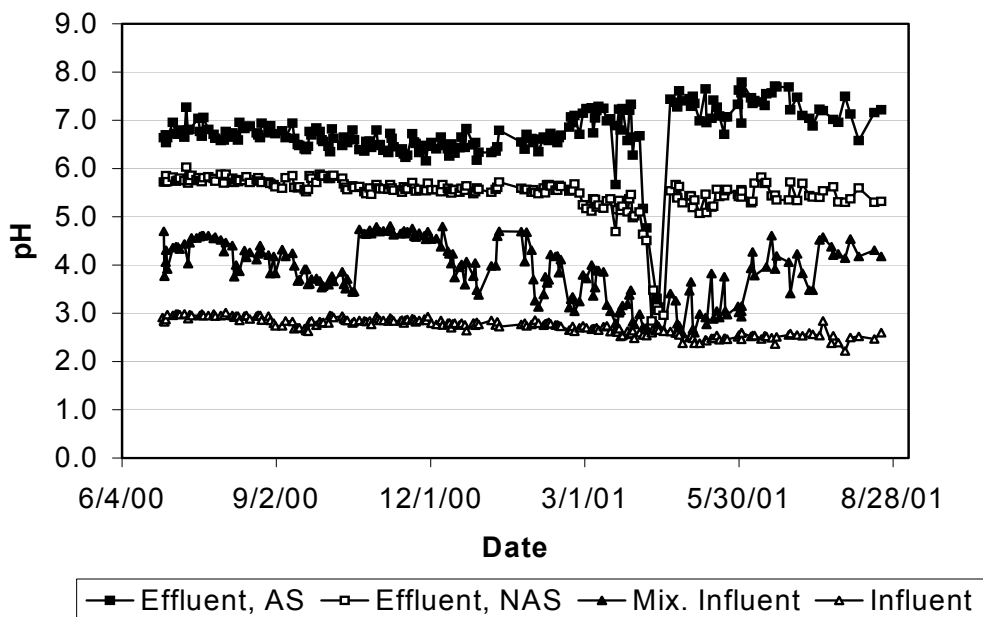


Figure 2. Treatment plant operation - Influent and effluent pH

The influent pH ranged between 2.5 and 3.0. The pH of the mixed influent reflects the amount of treated AMD recycled back into the feed, and so varied, depending on plant operating conditions, between 3 and 5. One consequence of the recycle of treated effluent through the system was the formation of iron hydroxide coatings in the inlet pipe distribution system. This coating required disassembly and cleaning of the reactor down flow inlet lines about twice yearly. Should the plant be operated further under these conditions, maintenance downtime could be decreased by changing the water inlet system to a pair of through-the-wall pipes at the bottom of the reactor. Effluent pH was measured both before and after air stripping. Air

stripping removes excess CO₂ that was added to increase limestone solubility and dissolution rate. Non-air stripped pH ranged from 4 to 6, and air stripped pH ranged from 6.0 to 7.5. Thus, despite the high acidity and metal content of the AMD at Friendship Hill, the plant effluent was continuously in the neutral range, except for a brief period in April 2001. A special test was performed at this time, where the AMD was introduced at a constant rate into all four columns at once, instead of the preferred pulsed bed operation described earlier. Under these circumstances the flow in each column was not sufficient to thoroughly mix the bed, and armoring of the limestone was observed. Thus, this test demonstrated that without the special features of the pulsed bed process, limestone neutralization would not work at Friendship Hill. When plant operation was returned to normal at the conclusion of this test, effluent pH was again neutral, and no evidence of limestone armoring was observed.

Acidity and metal removal

Beginning in October of 1999, stream sampling was undertaken at the Friendship Hill site to characterize acidity and metal loadings. Once the neutralization plant came online, samples of the plant influent and effluent were also analyzed. The average concentration (\pm standard deviation) for Al, Fe, and Mn in the influent AMD was 61 ± 8 , 200 ± 39 , and 11 ± 1 mg/L, respectively, over fourteen months of sampling. Figure 3 shows pH and acidity of the plant influent and effluent.

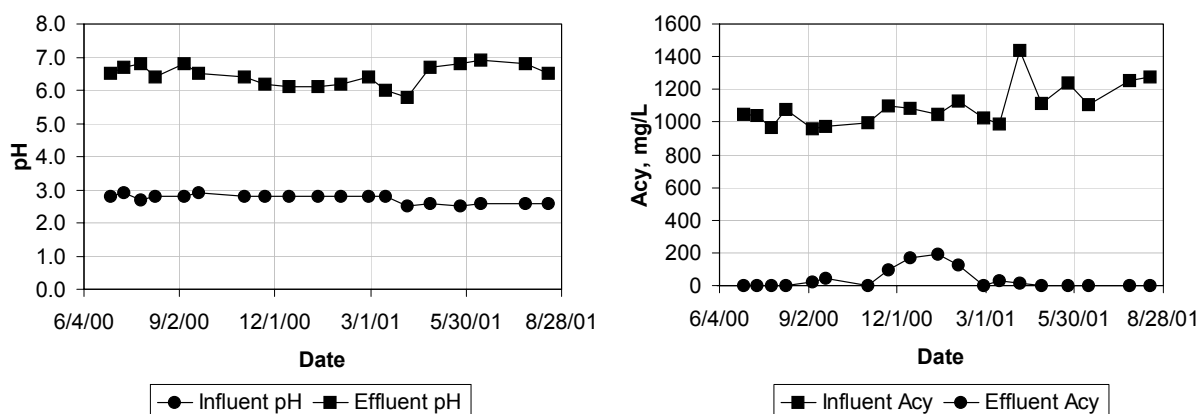


Figure 3. Treatment plant influent and effluent pH and acidity

Confirming the in-house results presented earlier, the plant effluent pH was consistently in the range of pH 6 – 7, despite an incoming pH of about 2.5. Acidity removal was good for most of the 14 months of treatment. However, in the winter of 2000-2001, effluent was net acid due to ferrous iron content of the incoming feed. This was an unexpected event, since earlier analyses of the AMD at the Friendship Hill site indicated that less than 10% of the total iron content was in the reduced ferrous [Fe(II)] state. Once the significance of the Fe(II) content was realized, extra samples were taken for analysis. The samples showed that except during the springtime high flow period, a significant portion of the total iron content was in the Fe(II) state. This has an impact on the neutralization plant because Fe(II) is not removed by pH adjustment until a pH of 8-10, which is not realized in limestone based processes [11]. If Fe(II) can be oxidized to the ferric state [Fe(III)], removal occurs at pH 3-4. The oxidation can be done by air, but reaction rates are slow below pH 7. Analysis results showed a Fe(II) removal rate of up to 50%. Better

performance of the aeration basin would help oxidize Fe(II) and decrease effluent acidity. Air stripping performance in the aeration basin was often limited by buildup of sludge and limestone fines in the basin as well as clogging of the diffusers. Periodic removal and cleaning of the diffusers was required, which was a time-consuming job. A possible solution to this problem would be the use of a different type of surface agitator to provide aeration. Also, recent investigations have shown that the oxidation of Fe(II) proceeds more rapidly in the presence of suspended ferric oxide particulates [12]. The concentration of these particulates in the aeration basin could be increased simply by recycling some of the settled sludge from the clarifying tanks. These changes should enable removal of more of the Fe(II), resulting in decreased acidity in the clarifier supernatant.

Effluent analysis results also indicate that manganese (Mn) was not removed by the treatment plant. This was not surprising, because the hydrolysis and precipitation of Mn does not occur until pH 9-10, which is not reached by limestone-based processes [11]. It may be possible to remove Mn in a downstream passive treatment system such as an oxidation pond or wetland. Sufficient alkalinity was imparted to the water to neutralize any acid released by oxidation of Mn, which would correspond to 20 mg/L, based on a solution concentration of 10 mg/L Mn. The toxicity of Mn has not been studied in detail, but it has been suggested that Mn is not as harmful as other base metals, especially in hard waters [13].

Total metal and acidity removal by the treatment plant is shown in Figure 4. Here, the metal and acidity load is a function of both the metals concentration and the flow rate into the plant. The average metal removal from the incoming water was 83%, or 30 kg of metal per day, while the titratable acidity removal was 97%, or 115 kg (as CaCO₃) per day.

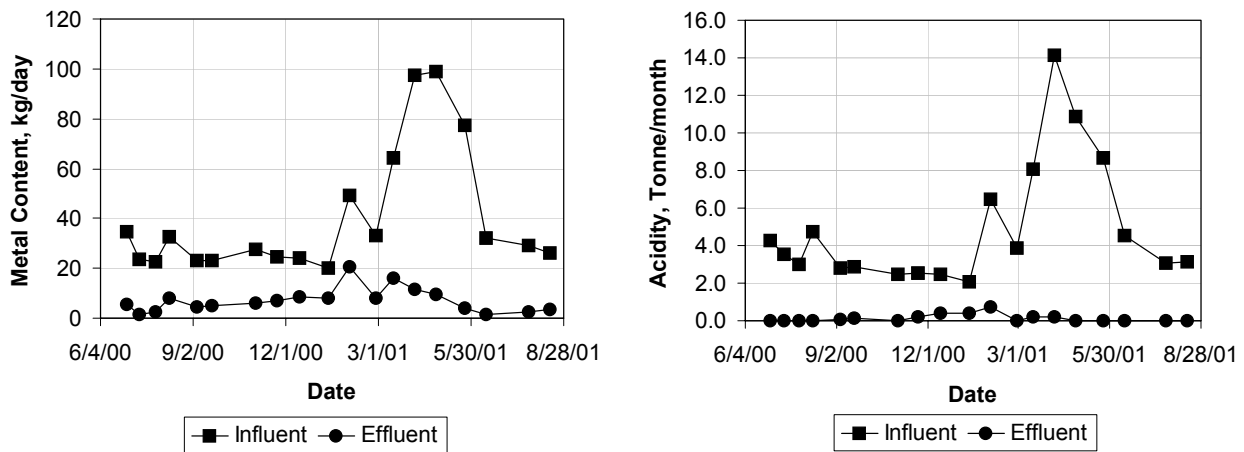


Figure 4. Treatment plant operation - metal removal

CO₂ addition and recycling

Previous studies using the pulsed bed limestone system have shown that effluent alkalinities can be increased by addition of CO₂ from outside sources. Some CO₂ is generated internally by the reaction of limestone with acid, and so sites such as Friendship Hill with high influent acidity can be operated without additional CO₂ input, as was done for the first eight months of operation. However, addition of CO₂ provides a method of controlling effluent alkalinity, which can be useful in times of high flow, for extra neutralization capacity. Therefore, a

commercial source of CO₂ was procured for testing in the spring of 2001. The CO₂ was contained as a liquid in an insulated truck-mounted tank delivered to the site in February of 2001. Flows of up to 120 standard liters per minute (SLPM) could be withdrawn from the tank and input into the carbonator, providing up to 138 kPa (20 psi) of pressure for increased limestone dissolution. The effect of CO₂ input on effluent alkalinity is plotted in Figure 5. Also shown in Figure 5 are calculated and experimental equilibrium alkalinities as a function of CO₂ pressure, as well as data from a previous field trial of the PLB process. The curve labeled PHREEQC was calculated using the PHREEQC geochemical modeling software, and shows the predicted alkalinity of water in equilibrium with CO₂-containing atmospheres at 15 °C. The calculated values are seen to be in good agreement with experimental values given by Lovell [14]. The data values for the operation of the PLB fall below the equilibrium values as would be expected due to the limited contact time of the water with limestone and CO₂ in the reactor. As expected, increasing CO₂ pressure increased effluent alkalinity. The Friendship Hill system gave higher alkalinities than observed at Toby Creek. This is probably due to recycle of the treated effluent back to the feed sump, thus increasing residence time in the PLB system. As stated earlier, the operation of the pulsed bed reactors at Friendship Hill require a steady continuous flow of 230 lpm. When influent flows were less than this, some of the reactor effluent was recycled to the feed sump via a pipe connecting the stripper and absorber sumps. Recycling of treated effluent has several effects on the operation of the neutralization system. First of all, recycling effectively increases the residence time of the water in the system, which should allow a closer approach to equilibrium alkalinity based on CO₂ pressure. Secondly, recycle of treated water also recycles some of the CO₂ contained in the water, which results in higher CO₂ concentrations.

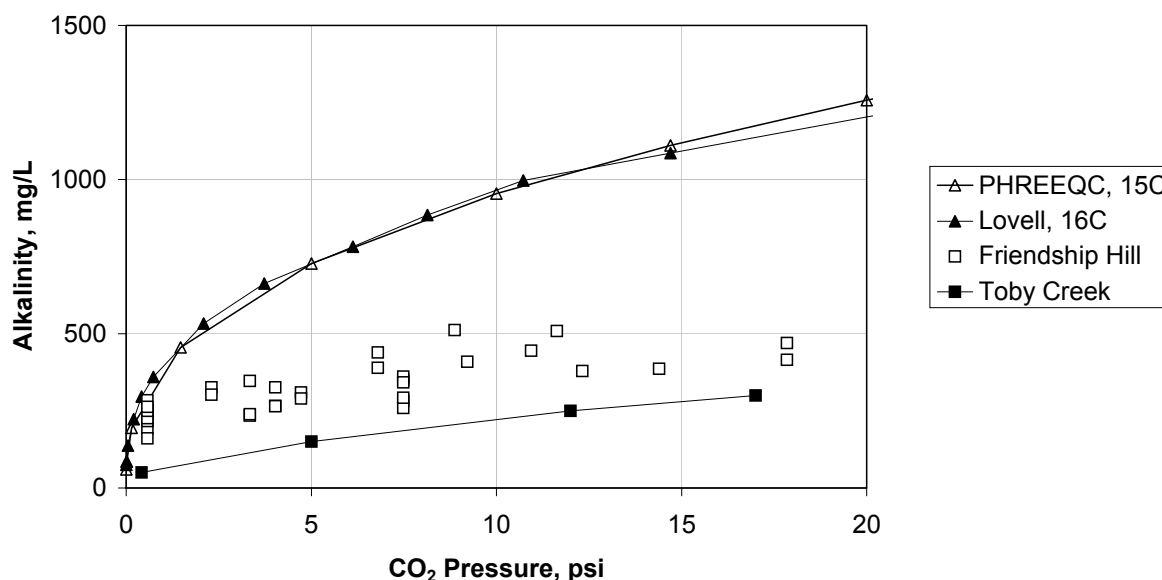


Figure 5. Effect of CO₂ addition on effluent alkalinity

As the effect of recycle was observed to impact the operation of the PLB system, further examination of the recycle process was undertaken. In the PLB process as implemented at Friendship Hill, recycling of CO₂ was accomplished either through the gas phase, using the stripper and absorber, or through recycle of the liquid phase. Several measurements of CO₂ concentration at selected points of the plant were periodically made in an effort to develop a mass balance for the CO₂, and assess the efficacy of recycling. These measurements were

performed using a gas headspace apparatus, coupled with an infrared CO₂ analyzer. A limitation of this measurement is that it is performed at atmospheric pressure, which means that CO₂ will be evolved from samples that had been at greater than atmospheric pressure, thus understating the CO₂ content of those particular samples. Nevertheless, we believe that the trends observed here are valid. The efficiencies of the gas and liquid recycling steps are shown in Figure 6. As expected, the efficiency of the liquid recycle rate was directly tied to the amount recycled. However, the efficiency of the gas recycle step was found to depend on the recycle ratio R (the ratio of recycle flow to the total flow into the reactor) as well, decreasing as R increased. This may be because less incoming AMD is flowing through the absorber, thus limiting the amount of CO₂ that can be taken up. Therefore, gas recycle predominated at low liquid recycle rates, and liquid recycle predominated at high liquid recycle rates. The net result is a much weaker dependency of the total amount of CO₂ recycled on the recycle ratio than would have been expected for a constant gas recycle rate, as observed in Figure 6.

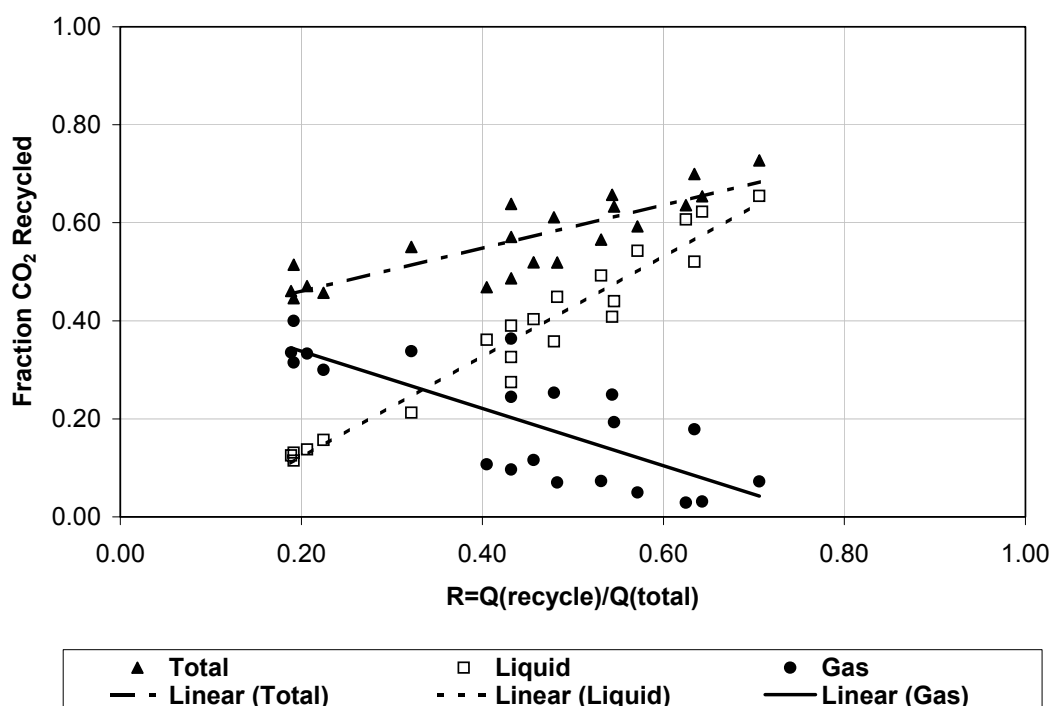


Figure 6. Effect of liquid recycle ratio R on CO₂ utilization

Limestone Utilization

The particle size distribution of the limestone used in the PLB is shown in Figure 7. Particle size ranged from 100 to 1000 μm . The effective size (D_{10} , corresponding to the screen size passing only the smallest 10% of particles) of the sand was 200 μm , and the uniformity coefficient D_{60}/D_{10} was 3.3. Analysis of the settling velocity of sand particles indicates that given the flowrate and reactor diameter at Friendship Hill, limestone particles of size 150 μm and smaller will be swept from the reactor, assuming the particles are spherical. This was observed in practice, as beds of limestone grit were found to accumulate in the stripper and absorber sumps and in the aeration basin. However, since limestone weight is proportional to the cube of the particle diameter, most of the limestone mass will have been converted to

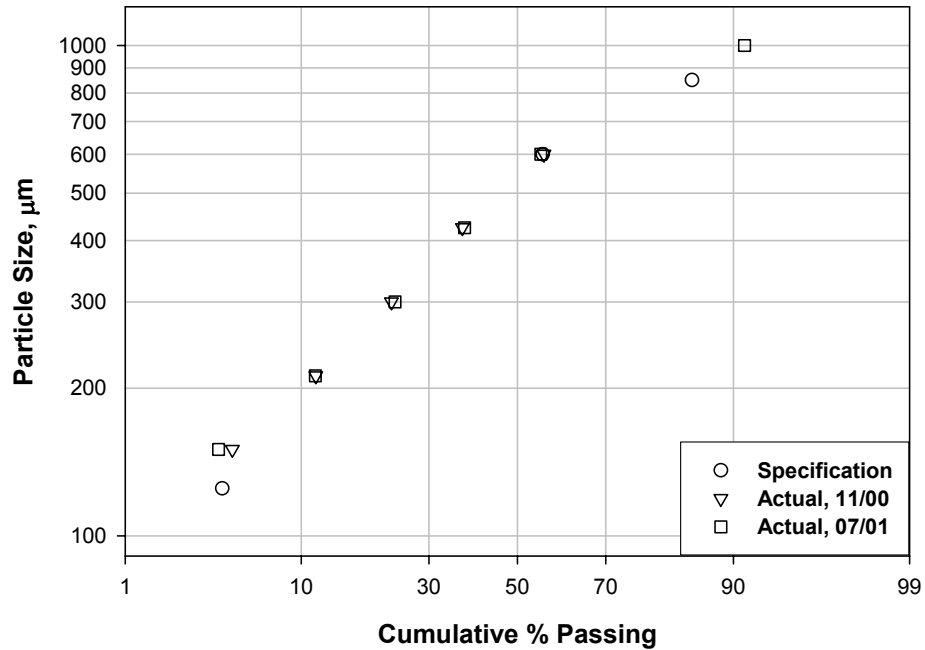


Figure 7. Limestone particle size distribution.

alkalinity before the particle is swept out. For example, particles with a diameter of 500 µm will contribute over 97% of their weight before being swept out at 150 µm.

Figure 8 shows the frequency and amount of limestone recharged to the reactors over the 400 plus days of operation of the plant. During the spring high-flow period, recharging was required every day of from 300 to 800 pounds of limestone. At low flow periods, recharging once to twice per week was sufficient to maintain the required bed depth of 76 cm of limestone in the reactors.

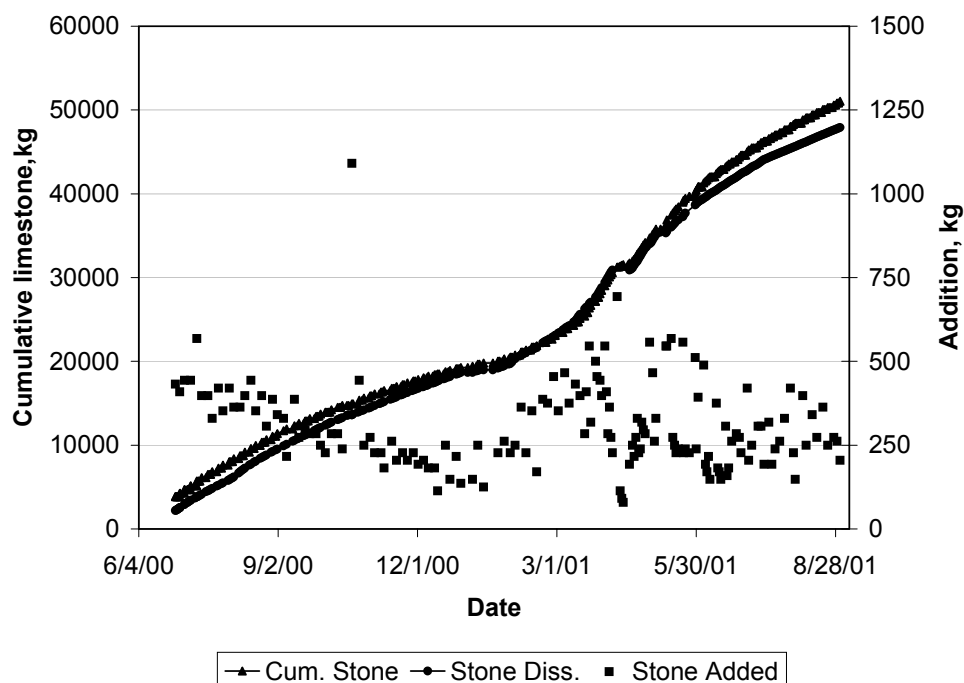


Figure 8. Limestone addition and consumption

Also shown in Figure 8 are the cumulative limestone addition and the calculated cumulative limestone consumption, based on flow, incoming acidity and effluent alkalinity. The results show that limestone utilization is nearly complete, that is, all of the limestone added is consumed by reaction with acid and in generation of alkalinity. This is a strong indication that armoring of the limestone is not occurring, as armoring would encapsulate limestone and prevent dissolution. Further work on the formation of armor coatings at Friendship Hill has been discussed [15].

Sludge handling

The AMD neutralization plant was run continuously, except for maintenance shutdowns, from July 2000 to September 2001. In that period of time, 50 million liters of AMD were treated, and over 450 metric tons of metal hydroxide sludge removed from the water. The typical solids content of the settled sludge was 5 to 10%. This compares favorably with many lime or caustic based sludges where the maximum settled solids is 3% or less. Plant effluent samples were periodically analyzed for total suspended solids (TSS) and showed from 30 to 150 mg/L TSS, based on influent chemistry. This indicates good solids removal efficiency for the plant, with as little as two hours settling time, and without the addition of any settling aids. Due to aesthetic concerns, the sludge was removed from the property and disposed of offsite by a contractor. The sludge was removed and transported to a filtration/disposal site using a septic system-type pumping truck, with a capacity of 3500 gallons. Thirty-three sludge pickups were made, at a total cost of \$17,475. This cost could be reduced by further sludge treatment on site [16]. The main components of the dried sludge were aluminum and iron hydroxide (oxyhydroxides), gypsum, and silica. The sludge was also tested to determine its status as a

hazardous waste, using the Toxicity Characteristics Leaching Protocol (TCLP) at a commercial laboratory. The results of this test showed that the waste was non-hazardous.

Costs

Table 1a shows a breakdown of the annual operating cost of the neutralization plant during the research phase of operation by categories.

Table 1a. Operating cost breakdown for PLB system at Friendship Hill-Research Mode

Item	Use per Day	Unit Cost	Annual Cost	Cost per m ³	% of Total Cost
Limestone	118 kg	\$38.50/tonne	\$1660	\$0.04	3.9
Electricity	133 kWh	\$0.06/kWh	2915	0.07	6.8
Sludge	0.98 m ³	\$40.00/m ³	14,300	0.36	33.2
Labor	8 hr	\$11.63/hr	24,200	0.61	56.2
Total			43,075	1.08	100.

The total estimated annual operating cost was about \$43,000 per year, or on a volume basis, \$1.08/m³ (\$4.09 per thousand gallons). Consumption rates were based on actual plant operating experience over the period from June 2000 to September 2001. Over that period of time, a total of 50 million L of AMD was treated, resulting in an average treatment flow rate of 80 lpm. If the flow were to be increased up to the maximum 230 lpm capacity of the plant, the limestone consumption and sludge disposal costs would roughly triple. The electrical and labor costs would not be expected to depend on treatment flow rate.

No account was taken for CO₂ costs, since the plant has been shown to be capable of operating without an outside CO₂ source. Use of CO₂ could be desirable in certain circumstances if an elevated effluent alkalinity were needed. A CO₂ flow of 24 SLPM increased alkalinities significantly, and would consume about 80 kg per day of CO₂. The monthly cost would be about \$1500, using the cost of \$0.44/kg CO₂, plus a tank rental cost of \$500/month. (Carbon dioxide costs are dependant on the size of truck used to deliver the gas, and could be decreased to about \$0.22/kg CO₂ if site access were improved to allow for tractor-trailer rigs.) This could be a strategy for coping with high spring flows, by using CO₂ only during these periods. Typically, high flows were encountered during March, April and May, so an outlay of \$5000 would cover CO₂ use during this period.

It is apparent from these results that limestone and electricity are a minor part of the plant operating cost. Sludge disposal costs could be decreased by using a plate-and-frame pressure filter to decrease the volume of sludge to be removed. Although not considered at the Friendship Hill, a settling pond could decrease sludge handling costs. Another option would be to find an alternate disposal site. In some cases AMD neutralization sludge is pumped into abandoned underground mines. Another possibility is to use the sludge as a component for topsoil to be land-applied. Labor costs were the major component of the plant operating cost. We believe the plant could be operated by a part-time operator, at 4 hr/day. However, since the Friendship Hill site is a research plant, additional time is required for data gathering and analysis, and this is why the plant has been staffed full time. If labor requirements decreased to

4 hr/day, and sludge disposal costs were decreased by two thirds to 13.30/m³, then yearly plant operating costs would drop to \$21,500, and on a volume basis, to \$0.51/m³ (\$1.93 per thousand gallons), as shown in Table 1b.

Table 1b. Operating cost breakdown for PLB system at Friendship Hill-Operation Mode

Item	Use per Day	Unit Cost	Annual Cost	Cost per m ³	% of Total Cost
Limestone	118 kg	\$38.50/tonne	\$1660	\$0.04	7.8
Electricity	133 kWh	\$0.06/kWh	2915	0.07	13.6
Sludge	0.98 m ³	\$13.30/m ³	4760	0.11	22.2
Labor	4 hr	\$11.63/hr	12,095	0.29	56.4
Total			21,430	0.51	100.

Conclusions

Test results from 14 months of continuous operation of the AMD neutralization plant at the Friendship Hill site have demonstrated the utility and practicality of the pulsed bed process. Effluent pHs were always in the neutral range and metal and acidity removal was nearly complete. Over the course of operation, 50 million liters of AMD were neutralized to an average pH of 6.5. Shutdowns for other than routine maintenance were rare, with a plant availability of over 95%. Due to the elevated acidity of the influent AMD at Friendship Hill (1000 mg/L), enough CO₂ was generated by reaction of the limestone with the water to give an effluent alkalinity of 50 mg/L. Addition of commercial CO₂ increased effluent alkalinity to as much as 300 mg/L. Recycling of CO₂ was accomplished by a gas/liquid scrubber absorber, as well as direct recycle of the liquid phase, and recovered up to 70% of the CO₂ added to the apparatus. Additions of CO₂ could be a useful process management tool for certain conditions such as high flow, where temporary CO₂ addition could enable treatment of higher flows without increasing plant size. Metal removal varied by element. For Fe(III) and Al removal was essentially complete. In the fall and winter months, as much as 60% of the Fe was in the reduced Fe(II) form, and was not removed by the PLB process. Better aeration would help alleviate this problem, and is recommended should treatment at the site continue. Manganese was not removed by the PLB process due to the high pH required for Mn precipitation. If Mn removal was required, passive treatment methods may be the best course of action, including oxidation ponds or bacterial remediation. Limestone consumption was 1000 mg per L of AMD treated, which worked out to a total of 50 metric tons over the 14-month operating period. Over 96% of the limestone was consumed by neutralization, indicating that armoring of the limestone did not occur under the PLB operating conditions. Settling of precipitated solids was rapid without the addition of any settling aids. Solids contents of the sludge were about 5 to 8%, much greater than usually achieved for chemical precipitation plants. Over 450 metric tons of sludge were removed from the water. Sludge removal and labor costs were the major operating costs for the plant. If sludge costs were decreased through on-site pressure filtration, and labor costs adjusted to 20 hours per week, yearly operating costs would fall to less than \$25,000, or about \$0.51/m³. If treatment is to continue at the site, several process modifications should be tested. These include addition of a settling/oxidation pond for removal of suspended solids and

oxidation of Fe and Mn, improvement of the air stripping step through alternate stripping equipment, and filtration or settling of sludge to reduce disposal handling costs.

References

1. Evangelou, V.P. and Y.L. Zhang. 1995. A review: pyrite oxidation mechanisms and acid mine drainage prevention. *Critical Rev. Environ. Sci. Tech.* 25:141-199.
2. U. S. Environmental Protection Agency. 2000. National Water Quality Inventory, 1998 Report to Congress: Washington, D. C. EPA Office of Water, EPA 841-R-00-001, p. 355.
3. Watten, B. J. 1999. Process and Apparatus for Carbon Dioxide Pretreatment and Accelerated Limestone Dissolution for Treatment of Acidified Water. Washington, D.C.: U.S. Department of Commerce, U.S. Patent No. 5,914,046.
4. Hedin, R. S., G. R. Watzlaf, and R. W. Nairn. 1994. Passive treatment of acid mine drainage with limestone. *Journal of Environmental Quality*, 23(6):1338-1345.
5. Skousen, J., Politan, K., Hilton, T., and Meek, A. 1995. Acid mine drainage treatment systems: Chemicals and costs, *in* Skousen, J.G. and Ziemkiewicz, P.F., compilers, *Acid Mine Drainage – Control and treatment*: West Virginia University and the National Mine Land Reclamation Center, Morgantown, West Virginia, p. 121-129.
6. Plummer, L. N., T. M. L. Wigley, and D. L. Parkhurst. 1978. The Kinetics of Calcite Dissolution in CO₂-Water Systems at 5 °C to 60 °C and 0.0 to 1.0 Atm CO₂. *Amer. Jour. of Science* 278:179-216.
7. Sverdrup, H. U. 1985. Calcite Dissolution Kinetics and Lake Neutralization. Doctoral Dissertation for the Dept. of Chemical Engineering, Lund Institute of Technology, Sweden.
8. Sibrell, P. L., B. J. Watten, A. E. Friedrich, and B. J. Vinci. 2000. ARD Remediation with Limestone in a CO₂ Pressurized Reactor. In *Proceedings, 5th International Conference on Acid Rock Drainage*, Society for Mining, Metallurgy, and Exploration, Denver, CO, pp. 1017-1026.
9. Rose, A. W. and C. A. Cravotta III. 1998. Geochemistry of Coal Mine Drainage. In *Coal Mine Drainage Prediction and Pollution Prevention in Pennsylvania*, M. W. Smith, K. B. C. Brady, and J. M. Tarantino, eds., PA Department of Environmental Protection, Harrisburg, PA.
10. American Public Health Association. 1995. Standard methods for the examination of water and wastewater, 19th edition. American Public Health Association, Washington, DC.
11. Stumm, W. and J. J. Morgan. 1996. *Aquatic Chemistry*, 3rd Edition. Wiley Interscience, New York.
12. Dietz, J. M. and B. A. Dempsey. Innovative treatment of alkaline mine drainage using recirculated iron oxides in a complete mix reactor. *Proceedings, 2002 National Meeting of the American Society of Mining and Reclamation*, Lexington, KY, June 9-13, 2002.
13. Kleinmann, R. L. and G. R. Watzlaff. 1988. Should the effluent limits for manganese be modified? *Proceedings, 1988 Mine Drainage and Surface Mine Reclamation Conference*,

Amer. Assoc. for Surface Mining and Reclamation and U. S. Department of Interior, Pittsburgh, PA, pp. 305-310.

14. Lovell, H. L. 1973. An Appraisal of Neutralization Processes to Treat Coal Mine Drainage. Environmental Protection Agency Report EPA-670/2-73-093.

15. Hammarstrom, J. H. and P. L. Sibrell. 2002. Characterization of limestone reacted with acid mine drainage in a pulsed limestone bed treatment system at the Friendship Hill National Historic Site, Pennsylvania, USA. Submitted to Applied Geochemistry in October 2002.

16. Sibrell, P. L. and B. J. Watten. 2003. Evaluation of sludge produced by limestone neutralization of AMD at the Friendship Hill National Historic Site. Proceedings of the 2003 Natl. Meeting of the Amer. Soc. of Mining and Reclamation, Billings, MT, June 3-6, 2003.