

FINAL REPORT

ACID MINE DRAINAGE: REFINEMENT OF NEW TREATMENT TECHNOLOGY

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Executive Summary

Problem Being Addressed

Friendship Hill National Historic Site (FRHI), Point Marion, Pennsylvania, consists of 661 acres of land that lie adjacent to the Monongahela River in the southwestern corner of Fayette County. The Pittsburgh coal seams present within and adjacent to FRHI were mined extensively using both surface and deep mining methods. Highly acidic (pH 2.4) metal-laden water drains from the abandoned mine workings into Ice Pond Run which, in turn, traverses FRHI in a northwesterly direction as it flows 3 km towards the Monongahela River. Mitigation of the acidic mine drainage (AMD) at FRHI has remained the Park's highest natural resource priority since opening the site in 1978 given its devastating effect on stream ecology as well as the need to comply with State and Federal point source water quality standards.

Early investigations at FRHI by the Bureau of Mines identified the volume flow rate and chemistry of AMD sources impacting Ice Pond Run while evaluating the potential for mitigation based on passive treatment technology - constructed wetlands designed to exploit a combination of limestone dissolution and sulfide reduction reactions. The wetland technology evaluated was not adopted by the Park Service given projected treatment costs and excessive acreage requirements (61.8 – 96.5 acres) that resulted from the extreme acid and metal loading rates encountered, as well as observed seasonal variations in wetland performance. Alternative mitigation techniques considered but not adopted included active (chemical) treatment. Limestone has potential for reducing active treatment costs given that its market value, on an equivalent basis, is a fraction (0.03 to 0.26) of standard caustic reagents. Its use also reduces sludge volume and risk of over treatment while providing calcium ions needed to moderate toxicity of certain dissolved metals. These benefits have been offset by limestone's relatively slow dissolution rate and sensitivity to armoring by certain scale-forming reactions. However, in recent years, the pulsed limestone bed (PLB) process has been developed to circumvent both limitations. Here, a control system directs AMD intermittently into pressurized reactors charged with limestone sand to establish a repeating cycle of fluidization, bed turnover and contraction. During bed expansion, AMD is introduced at a high rate through nozzles designed to establish hydraulic shearing forces capable of abrading and carrying away solid reaction products. Further, a carbon dioxide pretreatment (absorption) step is used to accelerate limestone dissolution by forcing the reaction of carbonic acid with limestone and by minimizing, temporarily, the rise in pH that occurs during treatment. High dissolved carbon dioxide levels also elevate equilibrium concentrations of HCO_3^- and thereby allow for surplus acid neutralization capacity (alkalinity) in the reactors' effluent. In a final treatment step, CO_2 is stripped from solution forcing a desirable upward shift in equilibrium pH.

The objective of our study was to demonstrate, on a long term basis, the ability of the PLB process to neutralize acidity present in Ice Pond Run, and to refine operating parameters needed for future full-scale applications. Specific hypotheses tested include (1), limestone dissolution rates are accelerated by increasing CO_2 tension and inlet acidity and by decreasing reactor bed height, influent temperature and hydraulic residence time (2), intermittent fluidization decreases reactor sensitivity to the armoring of limestone surfaces by metal hydroxides (3), AMD sludges resulting from limestone-based acid neutralization have superior

settling, filterability and phosphorus adsorption characteristics when compared to alternate reagent types (4), recycling CO₂ present in the PLB system effluent can reduce gas feed rate requirements and (5), field application of the PLB process allows for enhanced rates of biological activity. Hypothesis testing required use of laboratory and pilot scale PLB reactors, numerical modeling (chemical reactor theory) as well as application of stream survey methods.

PLB Process Evaluation – Laboratory Trials/Modeling

Our initial laboratory scale testing of the PLB process (Tab 5) established the sensitivity of limestone dissolution (LD, mg/L), and effluent alkalinity (Alk, mg/L) to changes in the operating variables reactor pressure (P_{CO2}, kPa), influent acidity (Acy, mg/L) and reactor bed height (BH, cm). We used a PLB prototype capable of processing 10 L/min. when charged with high purity limestone (96.9% CaCO₃) having an effective size (D₆₀) of 600 µm. Limestone beds were operated with 60sec fluidization and contraction periods. The PLB process effectively neutralized sulfuric acid acidity over the range 6-1033 mg/L (as CaCO₃) while generating high concentrations of alkalinity (36-1086 mg/L) despite a hydraulic residence time of just 4.2-5.0 min. The decrease in HRT achieved provides for significant reductions in capital costs related to reactor volume when compared to alternate fixed bed reactors, such as anoxic limestone drains with required HRT's of 16-192 h. Alk and LD (mg/L CaCO₃) rose with increases in influent acidity and P_{CO2} according to the models: $Alk = 58 + 38.4 (P_{CO2})^{0.5} + 0.080 (Acy) - 0.0059 (P_{CO2})^{0.5} (Acy)$; $LD = 55 + 38.3 (P_{CO2})^{0.5} + 1.08 (Acy) - 0.0059 (P_{CO2})^{0.5} (Acy)$. Alkalinity decreased at an increasing rate with reductions in BH over the range 27.3 – 77.5 cm. These data suggested BH should be maintained above 50 cm through periodic limestone charging of the reactors. Carbon dioxide requirements (Q(avg)_{CO2}, L/min) increased with P_{CO2} following the model $Q(avg)_{CO2} = 0.858 (P_{CO2})^{0.620}$, resulting in a greater degree of pH buffering (depression) within the reactors, a rise in limestone solubility, and an increase in limestone dissolution related to carbonic acid attack. Corresponding elevated concentrations of Alk will allow for sidestream treatment particularly in applications with low to moderate levels of inlet acidity.

In a second laboratory scale test (Tab 3) we evaluated a PLB reactor of 15 L/min capacity operated using the same timing sequence and limestone source as in our initial test series (Tab 3). We established the effects of hydraulic residence time (HRT, 5.1-15.9 min), temperature (T, 12-22°C) and carbon dioxide tension (P_{CO2}, 34.5-206.8 kPa) on effluent quality when inlet acidity (Acy) was fixed at 440 mg/L (pH=2.48) with H₂SO₄. Inlet temperature can vary with AMD source or season. Temperature affects the solubility of PLB reactants, and products, as well as reaction kinetics. Again, the PLB reactor neutralized all H⁺ acidity (N=80) while concurrently providing high levels of effluent Alk (247-1028 mg/L as CaCO₃). Alk yields rose with increases in P_{CO2}, HRT and settled bed height and decreased with T following the relationship: $(Alk)_{non\ filtered} = -548.726 + 33.571 \cdot (P_{CO2})^{0.5} + 33.671 \cdot (HRT) + 7.734 \cdot (BH) - 5.197 \cdot (T)$. Differences between filterable and nonfilterable Alk (residuals) were small (4.15%) demonstrating that Alk is present in reactor effluent primarily as soluble CaCO₃. Limestone dissolution rates (LDR) corresponding to (Alk)_{filtered} were not influenced by T but did increase with P_{CO2}, and decreased with increases in HRT and BH, i.e., $LDR = 8.07E-7 + 8.73E-9 \cdot (P_{CO2})^{0.5} - 2.08E-8 \cdot (HRT) - 5.72E-9 \cdot (BH)$, where LDR in this case is expressed as mmol/cm²/s. We demonstrated LDR rises proportionally with increasing Acy given the associated increases in H⁺ loading on limestone surfaces. We also showed LDR rises exponentially with decreasing (Alk)_{filtered}. Thus while higher flow rates provide for increases in LDR, as well as reductions

in reactor volume, effluent Alk decreases lowering the potential for side stream treatment. CO₂ feed requirements (V_{CO2}) ranged from 1.9 to 66.7 L/4-min cycle with gas T and pressure standardized at 21.1°C and 760 mmHg. CO₂ feed requirements increased with (P_{CO2})^{0.5} and decreased with a rise in HRT and T as described by the regression equation: (V_{CO2}) = 13.602 + 4.632·(P_{CO2})^{0.5} - 0.910·(HRT) - 1.283·(T). These data demonstrate conservation of dissolved CO₂ often present in untreated AMD ([CO₂]_{AMD}, mg/L) will be important as well as selection of PLB operating pressure, and HRT, for the site specific T. Application of reactor theory also demonstrates (Tab 3 and 5) gas feed requirements (M_{CO2} / L, mg/L) are reduced as influent Acy rises and when CO₂ is stripped from PLB effluent then recycled at a rate R, where R represents recovery efficiency (varies from 0 to 1). For example effluent Alk, at steady state, can be calculated given selected values for R, Acy, [CO₂]_{AMD} and M_{CO2} / L through application of the following algorithms:

$$\text{Alk} = \frac{-b_2 \pm \sqrt{b_2^2 - 4a_2c_2}}{2a_2}$$

where the coefficients of the equation are:

$$\begin{aligned} a_2 &= \frac{1}{b_1^2} \cdot 7.52 \cdot \left(\frac{\beta}{A} \right)_{\text{CO}_2} \cdot (1 - R) \\ b_2 &= 0.44 - 2 \cdot \frac{a_1}{b_1^2} \cdot 7.52 \cdot \left(\frac{\beta}{A} \right)_{\text{CO}_2} \cdot (1 - R) \\ c_2 &= \left[\frac{a_1^2}{b_1^2} \cdot 7.52 \cdot \left(\frac{\beta}{A} \right)_{\text{CO}_2} \cdot (1 - R) \right] - 0.44 \cdot \text{Acy} - \frac{M_{\text{CO}_2}}{L} - [\text{CO}_2]_{\text{AMD}} \end{aligned}$$

Here A_i is the ratio 760/(1000K_i), K_i is the ratio of molecular weight to molecular volume, β_i is the temperature dependent Bunsen solubility coefficient in units of L gas/ (L·atm), and a₁ and b₁ are regression coefficients developed for a specific AMD source, e.g. (Tab 3 and 5), Alk = a₁ + b₁(P_{CO2})^{0.5}. Application of the algorithms showed that the PLB process will be favored at field sites with high levels of inlet Acy, like FRHI, given the potential for internal production of CO₂ that results from acidity neutralization with limestone, i.e., a net increase in CO₂ (mg/L) is established as described by the product 0.44·(Acy - Alk). In Tab 3, for example, we showed a rise in inlet Acy from 100 to 1500 mg/L increases effluent Alk from 99 to 266 mg/L without an external feed of CO₂. Effluent Alk was increased further to a high of 710 mg/L as recycle efficiency R was increased from 0 to 0.95. Accordingly, selection of the least-cost set of operating conditions for a target Alk will be related to the relationship between Acy, R and CO₂ recovery costs, as well as local costs of CO₂, power, and reactor capital (amortized). Tab 21 describes a CO₂ recovery system linked to a laboratory scale PLB of 9.5L/min capacity. CO₂ recovery was accomplished using a linked pair of packed towers (6.1 m of 1.6 cm plastic packing) for both CO₂ stripping and pretreatment of PLB influent. CO₂ rich gas generated in the stripping tower receiving PLB effluent was forced, by a compressor, through an absorption tower that received the untreated acidified test solution. CO₂ lean gas exiting the top of the absorber was redirected into the base of the stripper to complete a closed countercurrent gas recirculation loop that provided a recycle efficiency R of 0.64. R can be increased further through use of sequential treatment, or staging, and by control of pressure within individual stripper and absorber components. Use of the recovery step increased [CO₂]_{AMD} by about 600 mg/l when inlet Acy was fixed at 3250 mg/L.

Tab 4 describes a second PLB reactor (60L/min capacity) designed for use at atmospheric pressure so as to allow testing of certain design variables while operating in the single pass mode. Specifically, we evaluated the effects of intermittent fluidization (pulsing sequence), hydraulic loading rate and CO₂ dosing on effluent Alk. Further, we followed changes in water chemistry across the system when treating AMD from 3 different field sites both with and without CO₂ pretreatment. We showed effective removal of H⁺ acidity over the range 196 – 584 mg/L (CaCO₃) while concurrently generating surplus acid neutralization capacity. Effluent alkalinity rose with increases in CO₂ (DC, mg/L) according to the model Alkalinity = $31.22 + 2.97 (DC)^{0.5}$ where DC was varied from 11 – 726 mg/L. Alk represented about 58% of that predicted for the standard pressurized PLB configuration when operating at the same P_{CO2}. Altering fluidization and contraction periods did not influence Alk but did affect reactor hydraulics - - introducing the feed solution over a relatively short duration increases the pressure drop across the reactor orifices providing higher levels of energy dissipation/mixing in those cases where armoring or fouling is of concern. For example, the hydraulic loading rate with our test timing sequences (fluidization period/contraction period) of 10sec/50sec, 20sec/40sec and 30sec/30sec was, respectively, 2238, 1119, and 746 L/m²/min during the bed fluidization phase of the cycle with corresponding mean energy dissipation rates of 271, 68, and 30 w/m³ (Mott, 1979). Higher hydraulic loading rates also provided a greater degree of fluidization assisting in the displacement of dislodged solids from the reactor. Expanded bed height, as a percent of settled bed height, was correlated with timing sequence as follows: bed expansion (%) = $73.922 - (0.985 * (\text{sec fluidized}))$. Field trials with 3 AMD sources here, and with 2 sources using the conventional PLB configuration (Tab 5), demonstrated our limestone based process is capable of raising AMD pH above that required for hydrolysis and precipitation of Fe³⁺ and Al³⁺ but not Fe²⁺ and Mn²⁺. For example, (Tab 5) when evaluating AMD source A, the removal of Fe³⁺ and Al³⁺ was high and similar, ranging between 97.2 – 98.6%, and 80.1 – 85.0%. Removal of Fe²⁺ and Mn²⁺ was also similar but low ranging between 16.2 – 22.3% and 0 – 11.2%, respectively. These data suggest complete removal of Fe²⁺ and Mn²⁺ at FRHI will require a pre or post treatment oxidation step based on use of reagents or biochemical reactors.

The separation, dewatering and disposal of metal based AMD sludges can represent 50% of the total cost of AMD treatment. Sludge yield at FRHI is of particular concern given the extreme levels of Fe³⁺ and Al³⁺ present in the mine drainage entering Ice Pond Run. In Tab 7, sludges resulting from neutralizing FRHI AMD were tested as a possible low-cost amendment to reduce the loss of soluble phosphorus (P) from agricultural fields and animal wastewater. Sludges were prepared by neutralizing FRHI and synthetic solutions of AMD with limestone in a test PLB as well as with lime, ammonium hydroxide, and sodium hydroxide. P sequestration was tested in three distinct environments: water, soil, and manure storage basins. In water, sludges prepared from FRHI AMD adsorbed 10 to 20g P/kg dry sludge in equilibrium with 1 mg/L soluble P. Similar results were observed for both Fe-based and Al-based synthetic sludges. A local soil sample adsorbed about 0.1 g P/kg, about two orders of magnitude less. The AMD-derived sludges were mixed with a high P soil at 5 to 80 g sludge/kg soil, followed by standard water and acid extractions. All sludges performed similarly. About 70% of the water extractable P was sequestered by the sludge when applied at a rate of 20 g sludge/kg soil, whereas plant-available P only decreased by about 30%. Under anaerobic conditions simulating manure storage basins, all AMD sludges reduced soluble P by greater than 95% at a rate of 0.2 g sludge/g rainbow trout (*Oncorhynchus mykiss*) manure. These findings indicate

that FRHI AMD sludges could be an effective agent for preventing soluble P losses from soil and manure to the water environment, while at the same time decreasing the costs associated with AMD treatment. Further, elemental analysis of the FRHI sludge demonstrated the absence of toxic metals (< 0.5 mg/L) including arsenic, cadmium, chromium, lead and selenium that may have otherwise limited sludge application.

PLB Process Evaluation - Field Trials and Instrumentation Development

Operating characteristics of the PLB process, including sludge yield, were evaluated further in tests at FRHI based on application of a field-scale PLB reactor of 230 L/min capacity (Tab 10, 23-26). The reactor was operated over a 14 month period at a point adjacent to mine portal A, or D1, the major headwater source of Ice Pond Run. The treatment plant included a grit removal tank, a hydraulic surge tank, a 59 m² reactor/laboratory building, a limestone sand storage shed, an aeration basin (7.9 m³), effluent clarification tanks (4 x 15 m³), sludge thickening tanks (2 x 3.8 m³), an effluent lift station and a 20 kW back-up generator. Provisions were also made for pumping and treating AMD from a second mine portal (source B or D2). The PLB system tested incorporated a unique CO₂ recovery and reuse step based on packed column technology as well as PLB effluent recirculation. The latter was used to avoid hydraulic loading problems associated with seasonal variations in AMD flow rate. The aeration basin used provided additional dissolved oxygen and hydraulic residence time for Fe²⁺ oxidation prior to gravity removal of solid reaction products in the clarification tanks. Clarifier solids were intermittently directed into the systems thickening tanks so as to reduce water content prior to disposal off-site. A complete description of the treatment plant, as well as the operation and safety procedures developed, can be found in Volume 1, Tab 10, 13, 22, and Volume 2 and 3.

Our tests successfully demonstrated the utility and practicality of the PLB process at FRHI despite the unusually high levels of acidity and dissolved metals present in portal discharges (Tabs 9-13). Shutdowns for other than routine maintenance were rare, with a plant availability of over 95%. Over the course of operation, 50 million liters of AMD (pH 2.5) were neutralized to a pH of between 5.8 and 7.8. Limestone consumption was about 1g/L of AMD treated (T=12-15C), which worked out to a total plant requirement of about 50 metric tons over the test period (Tab 23). Over 96% of the limestone was consumed by neutralization, indicating that armoring of the limestone was minimized by the PLB treatment process. Sufficient CO₂ was generated by reaction of limestone with the AMD to give an effluent alkalinity of 50 mg/L as CaCO₃, thus verifying results of early laboratory scale tests conducted without a supplemental feed of CO₂. Tests conducted with addition of commercial CO₂ increased effluent alkalinity to a high of 300 mg/L, well above EPA requirements of 20 mg/L, again demonstrating the potential for sidestream treatment. The latter could be used at FRHI, as a plant management tool, to enable treatment of seasonally elevated AMD flows without increasing plant size. Recycling of CO₂ was achieved by the packed column equipment used, as well as through direct recycle of the liquid phase during low flow periods. CO₂ recoveries of up to 70% of the CO₂ feed rate were achieved illustrating the value, under field conditions, of this PLB process modification. However, extended use of the absorber resulted in bacterial fouling of the plastic packing designed to maintain the gas-liquid interfacial area required for gas absorption. The biological fouling problem was resolved by replacing the packing with a series of perforated trays common to the chemical process industry although this modification led to reduced potential for gas recovery given an associated decrease in the effective area-

volume ratio. As in laboratory scale tests, metal removal varied by element (Tab 10 and 25). Metal removal rates were about 95% for aluminum, 50 to 90% for iron (Fe), depending on the ratio of ferrous to ferric iron, which varied seasonally, and <10% for manganese (Mn). Ferrous iron and Mn removal were incomplete because of the high pH required for precipitation of these metal species. If treatment of AMD at FRHI is continued, iron removal could be improved by increased aeration following neutralization, and Mn removal could be enhanced through use of a post treatment settling/oxidation pond.

Despite problems with Mn and ferrous iron oxidation, over 450 metric tons of metal based sludge was removed from the PLB effluent by the clarifiers (Tab 10 and 26). Gravity separation of precipitated solids was rapid without the addition of any settling aids but some turbidity was observed in the product 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 were adjusted to 20 hours per week, annual variable costs would fall to about \$25,000, or \$0.51/m³ AMD. This is similar to the estimate of \$ 0.68/m³ calculated for the PLB system at FRHI by West Virginia University (Tab13), including amortized capital. Acid neutralization cost estimates here for the PLB process (Tab 13), excluding sludge handling (\$234.0/ton), compared favorably with those established for alternate active treatment reagents: anhydrous ammonia, \$413.6/ton; calcium oxide, \$300.45/ton; calcium hydroxide, \$362.7/ton; soda ash, \$596.4/ton; caustic soda, \$641.7/ton. The reductions in reagent costs associated with PLB use (22.1 – 63.5%) would increase further had the sludge handling component of the plant's operating budget been included in the estimates given the significant reduction in sludge yield that is associated with PLB use.

We established FRHI sludge characteristics including relative volume, composition, filterability, and settling rate in a series tests during the PLB system evaluation (Tab 11). Imhoff cone measurements showed a settleable solids content of 28-29 ml/L in the PLB effluent, and less than 0.5 ml/L in the clarifier overflow indicating a removal efficiency of 98%. Typical solids content of the sludge was 5-10%. Bulk x-ray fluorescence analyses showed FRHI sludge consisted primarily of aluminum and iron hydroxide, gypsum, and silica. All metal concentrations measured in a standard TCLP (Toxicity Characteristics Leaching Protocol) sludge leachate procedure were below regulatory limits, thus the sludge would be classified as non-hazardous. Comparative settling rate tests showed PLB use generated 50% less sludge than hydrated lime and 70-80% less than ammonium hydroxide or sodium hydroxide based treatments. A suite of seven polymeric flocculants were tested to increase settling and supernatant clarity. Sludge settling rates increased but high reagent costs and a near doubling of sludge yields would prevent their future use at FRHI. Subsequent vacuum filtration tests demonstrated the PLB based sludge was more readily filtered than sludges generated with sodium hydroxide or hydrated lime and that the solids content could be increased to 28%. Percolation tests with sand media provided a sludge solids content of 25% but would require a large foot print at the site as well as an extended treatment period (about 15-20 days). Alternatively, pressurized plate and frame filters for dewatering of settled solids are common in industry and so a sample of FRHI sludge was sent to a selected manufacturer for testing in their laboratory. The initial solids content of the sample was 5%. The press generated a filter cake with a solids content of 31%. The increase in solids content achieved represents an eight-fold reduction in water content, providing for a large savings in sludge disposal costs. The capital cost of the plate and frame filter sized for the FRHI operation was about \$35,000. Plate and frame filters offer lower maintenance costs than continuous vacuum

equipment and would, therefore, be an attractive option for the FRHI site should treatment be resumed.

The extreme concentrations of dissolved metals in AMD at FRHI lead not only to high sludge yields but also elevate the potential for passivation of limestone via scale development. We carried out studies (Tab 12) designed to document the chemical and physical processes that occur on the surface of limestone within the PLB reactors receiving FRHI AMD. Laboratory analysis of limestone samples included use of x-ray fluorescence, scanning electron microscopy, x-ray diffraction, electron microprobe and thermogravimetric methods. Limestone sand grains present in control columns not employing PLB technology (carbon dioxide pretreatment; intermittent fluidization) were coated with a rind of gypsum crystals and became almost completely encapsulated in a 10- to 30-micrometer thick Fe-Al hydroxysulfate armor within just 48 hours. Although the ochre armor readily flakes off upon drying, the gypsum coating under the armor appears to be more stable and prevents or retards further limestone dissolution - column effluent pH decreased from 7 to <4. Within PLB reactors, however, limestone grains completely dissolve leaving a residue of armored refractory minerals and rounded to partially reacted limestone grains. Partially dissolved calcite-rich limestone grains develop etched surfaces. The residual refractory mineral phases include dolomite, mica, quartz, and pyrite that are present in minor amounts as inclusions in the relatively pure limestone sand feed material. The modal abundance of armored grains from the reactor after 3 months of operation is about 30 percent armored grains. These particles have thicker more aluminous coatings and lack the gypsum rind that developed in the control column application. Aluminum-rich zones developed in the interior parts of armor rims on grains within both reactor types in response to pH changes at the solid/solution interface.

Our laboratory data (Tab 12) suggest the physical and chemical effects of CO₂ and pulsing in the PLB reactor effectively prevent armoring by gypsum and metal hydroxysulfate precipitates, and appear to maximize the ability of limestone to produce the alkalinity needed to provide an acceptable effluent pH. However, wetted surfaces outside of the limestone beds exposed to partially treated AMD were subject to fouling with hydroxysulfate precipitates. This included PVC piping used to mix and distribute treated and untreated AMD when portal flows dropped below the PLB flow requirement of 230L/min. Scales were removed physically at approximately 3 month intervals so as to reduce piping pressure drops. This procedure included the disassembly of the affected reactor components, including the inlet nozzles, and therefore required an interruption in plant operation, typically for 48-72 h. Inlet plumbing was subsequently redesigned, following completion of the field trial, so as to reduce affected piping and to simplify cleaning procedures, e.g., we used two short horizontal manifolds protruding through the bottom side walls of each reactor to replace the long, parallel u-shaped pipe assemblies that were drilled to provide the jetting action needed to scour limestone surfaces. We also modified the CO₂ recovery and recycle component of the PLB system to reduce the potential for biological fouling while also improving CO₂ recovery efficiency. Here we developed a unique horizontal absorber/stripper that incorporated enclosed surface agitators to provide the gas/liquid interfacial area required for CO₂ transfer. The horizontal reactor was divided into eight equal volume compartments using PVC partitions, with the limestone column effluent (CO₂-rich) and column influent (CO₂-lean) flowing countercurrently down the length of the recovery system, by gravity. Ports were cut in transverse partitions to allow water flow along the axis of the stripper, but no direct contact was allowed between the influent and effluent streams. Fractional kW centrifugal fans directed an enriched CO₂ gas stream from the

headspace of the stripping compartments to paired absorption compartments. Both PLB system modifications were tested successfully at an AMD portal (Argo Tunnel) located in Idaho Springs, Colorado (Tab 8), e.g., CO₂ recovery efficiency increased to a high of 71% providing an equivalent CO₂ feed rate of 5 to 10 L/min without external CO₂ addition and 25 – 40 L/min with CO₂ addition. Operation of the PLB system at the Argo site increased AMD pH (air stripped samples) from 3 up to 7, and provided near complete removal of iron and aluminum while generating an effluent alkalinity of 45-147 mg/L as CaCO₃.

Evaluation of the stripper/absorber at both the Argo and FRHI sites required use of instrumentation capable of measuring dissolved CO₂ (DC) in AMD containing high concentrations of iron and aluminum. These metals are known to express acidity during standard titrimetric CO₂ analyses which, in turn, exerts a positive and unacceptable error on dissolved CO₂ estimates. We developed and evaluated an instrument that measures DC without need for titration (Tab 6). DC is calculated based on Henry's Law, water temperature, and the steady state partial pressure of CO₂ that develops within the instrument's vertical gas-liquid contacting chamber. Gas-phase partial pressures were determined with either an infrared detector (ID) or by measuring voltage developed by a pH electrode immersed in an isolated sodium carbonate solution (SC) sparged with recirculated head-space gas. Calculated DC concentrations were compared with those obtained by titration over a range of DC (2 – 28 mg/L), total alkalinity (35 – 250 mg/L as CaCO₃), total dissolved gas pressure (-178 – 120 mmHg), and dissolved oxygen concentrations (7 -18 mg/L). Statistically significant correlations were established between head space (ID) and titrimetrically determined DC. Millivolt and titrimetric values from the SC solution tests were also correlated. The absolute and relative error associated with the use of the ID and SC solution averaged 0.9 mg/L DC and 7.0% and 0.6 mg/L and 9.6%, respectively. The precision of DC estimates established in a second test series was good; coefficients of variation (100(SD/mean)) for the head space (ID) and titration analyses were 0.99% and 1.7%. Precision of the SC solution method was 1.3%. The ID method was selected for use in measuring influent AMD and PLB process effluent DC given reduced system complexity and a required stabilization period of just 9 min.

Limestone requirements at FRHI were high (50 metric tons) requiring, in some cases, the daily addition of limestone to maintain acceptable bed heights (Tab 10 and 23). This was achieved by interrupting the process and manually loading the sand into each of the 4 reactors. This procedure required 1-2 h of intensive labor which added to the operating costs of the process as well as to the intermittent release of untreated AMD. To circumvent these problems, we developed a vacuum-assisted sand loading system powered by a 7 kW portable diesel engine (Tab 19). In operation, a rotary lobe blower maintains a vacuum of about 15.2 cm Hg within the PLB reactors that are tied, individually, to a vacuum hose assembly. The hose is used to transport the sand via air flow from a storage hopper to a point just above the settled bed/water interface. Our preliminary tests demonstrate a limestone delivery rate of about 39 kg/min was achieved. Had the system been implemented at FRHI, our high daily loading requirement of about 545 kg could have been achieved with a blower operating period of just 15 min, excluding set up.

PLB system capacity at FRHI (230L/min) exceeded the mean flow of the primary AMD source contaminating Ice Pond Run identified by the Bureau of Mines (source A, 203L/min, test period 5/12/89 to 9/4/90). While the plant successfully neutralized 50 metric tons of acid, and removed a substantial quantity of the associated metal contaminants (450 million liters of

metal based sludge), plant operation did not result in the restoration of Ice Pond Run as measured by an analysis of the structure of the fish and aquatic macroinvertebrate communities (Tab 14). Biological sampling was conducted at three sites on Ice Pond Run: just below the treatment system, in proximity to the mouth, and midway between the plant and the mouth. Sampling was also conducted on Dublin Run, a similar sized stream within the FRHI Park boundary that has a similar gradient but is not affected by AMD. Fish surveys were conducted using a backpack electrofishing unit over a minimum of 40 average stream widths. Invertebrate samples were obtained using replicate D-frame kick nets in accordance with US EPA's Rapid Bioassessment Protocols. Additionally, invertebrate recovery patterns were assessed by monitoring the colonization of 30 artificial substrates placed in each of the three Ice Pond Run sample sites. Sampling occurred before and several dates after plant start-up. No fish were collected from Ice Pond Run but fish were collected at the downstream (mouth) site only in Dublin Run during three of the four sample dates. The species collected (creek chub, *Semotilus atromaculatus* and bluegill, *Lepomis macrochirus*) are common in the Monongahela River and tolerant of habitat disturbances, including low pH. Aquatic invertebrate data from surveys conducted after initiation of limestone treatment indicated Ice Pond Run remained in a severely impaired state. Hence community composition was very different between sites on Ice Pond Run and corresponding reference sites on Dublin Run, e.g., the Jaccard Coefficient of Community Similarity, one of eight metrics used in the analyses, ranged between 0 and 0.18 out of a possible score of 1.000. Artificial substrates were colonized by a total of nine taxa. Two more taxa occurred at all sites following treatment but results here were inconclusive.

We believe the lack of recovery was most likely due to the fact that we did not treat all acid source waters. Clearly the acid load imposed by all sources of AMD, including source B, exceeded the reserve acid neutralizing capacity of the plant's discharge. Source B is located outside of the FRHI park boundary and so its treatment was pursued intermittently for research purposes only. Early surveys by the Bureau of Mines showed the mean discharge of this source was 50 L/min. with a calculated acid load representing about 29% of the sum of sources A and B. Flow measurements during our field test suggest source B now plays a more important role in the acidification of Ice Pond Run (Tab 24 and 25). Source B flow exceeded source A flow in some cases but overall averaged 68% of source A. Source B acidity was extremely high averaging 1719.8 mg/L, which exceeded our source A acidity mean (1122.7 mg/L) by a factor of 1.53. The net effect of the adjusted flow and acidity levels is an acid load imposed by source B that now represents 51.1% of the source A and B total. Further, a concurrent hydrological assessment of the site, conducted by the National Park Service, identified 8 additional minor sources of acidity located in the upper half of Ice Pond Run but positioned below source A and B, including seepage from riparian wetlands (Personal Communication, Connie Ranson, Natural Resource Management Specialist, FRHI, Point Marion, PA). Consequently, given the documented effectiveness of the pulse bed technology to improve water chemistry in the source water that was treated, we believe expanding our restoration efforts to include the use of either a number of distributed treatment sites, or construction of a single centralized plant sized to handle the total acid and metal load imposed by mine drainage would likely result in significant biological recovery. The latter could be positioned about mid-reach of the Ice Pond Run at a point below acid inputs or positioned at our original PLB test site if source-specific lift stations are employed to combine flows. Future use of the PLB process should include provisions for using standard chemical dosers during PLB recharge and maintenance operations and perhaps during the peak discharge (spring)

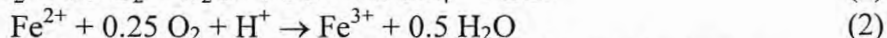
period of the year. Directing PLB product water through a constructed wetland prior to release into Ice Pond Run would also act as an additional hedge against short term reductions in water quality following planned or unplanned interruptions in active treatment.

I. Introduction

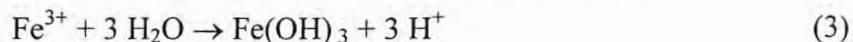
A. Background

Friendship Hill National Historic Site (FRHI), Point Marion, Pennsylvania, preserves the estate of Albert Gallatin, best known for serving as Secretary of the Treasury under Presidents Thomas Jefferson and James Madison. The site consists of 661 acres of land that lie adjacent to the Monongahela River in the Southwestern corner of Fayette County. The general public has access to the restored Gallatin residence, an information center, picnic areas and walking trails. Friendship Hill is one of more than 145 National Park System units affected by problems associated with abandoned mines. The Pittsburgh coal seams present within and adjacent to FRHI were mined extensively using both surface and deep mining methods. Mining began in the early 1900's and continued into the 1950's. Severely polluted water drains from the abandoned mine workings into Ice Pond Run which, in turn, traverses FRHI in a northwesterly direction as it flows 3 km towards the Monongahela River (Fig.1).

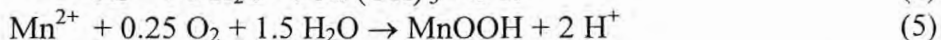
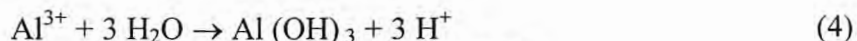
Concentrations of toxic heavy metals and acidity have decreased or completely eliminated biological productivity in Ice Pond Run. Accordingly, mitigation of the acid mine drainage (AMD) at FRHI has remained the Park's highest natural resource priority since opening the site in 1978. AMD is a major source of pollution in surface waters within the coal deposit regions of many parts of the world including Appalachia (CEQ, 1981; Maree et al., 1996). AMD often renders receiving waters unfit for domestic use and unable to support desirable plant or animal communities (Cole et al., 2001a,b; Starnes and Gasper, 1995). AMD is produced by oxidation of metallic sulfides, primarily FeS_2 , present with coal in mines or refuse piles (Evangelou, 1995):



Oxidation is followed by a hydrolysis reaction that generates an insoluble oxyhydroxide product:



Acidification provides for solubilization of certain base metals, including Al^{3+} and Mn^{2+} , that contribute acidity while undergoing secondary hydrolysis reactions (Evangelou, 1995):



Early investigations at FRHI by the Bureau of Mines (Hedin et al., 1991; Aljo and Hawkins, 1993) identified the volume flow rate and chemistry of AMD sources impacting Ice Pond Run while evaluating the potential for mitigation based on passive treatment technology - - constructed wetlands designed to exploit a combination of limestone dissolution and sulfide reduction reactions. These studies showed FRHI receives AMD primarily from two partially collapsed portals draining the Dulek (D1) and Winsted (D2) mines. Both portals are located in the headwater region of the 342 acre watershed that feeds Ice Pond Run (Fig.1). D1 and D2 discharge rates averaged 203 L/min. (range 68 -732) and 50 L/min. (range 14 - 147) respectively (Table 1) during the test period 5/12/89 - 9/4/90, with the highest flows occurring in the winter and spring months and the lowest flows occurring in the early fall. Acidity and

dissolved metal concentrations in both discharges were unusually high (Table 1). The acid load linked to D1 averaged 217.3 kg/d which represented, on average, 3.5 (range 2.7-4.9) times that provided by D2 (Table 2). Water quality improved slightly as AMD moved through the watershed towards the Monongahela River (Table 3), primarily as a result of dilution (Table 4).

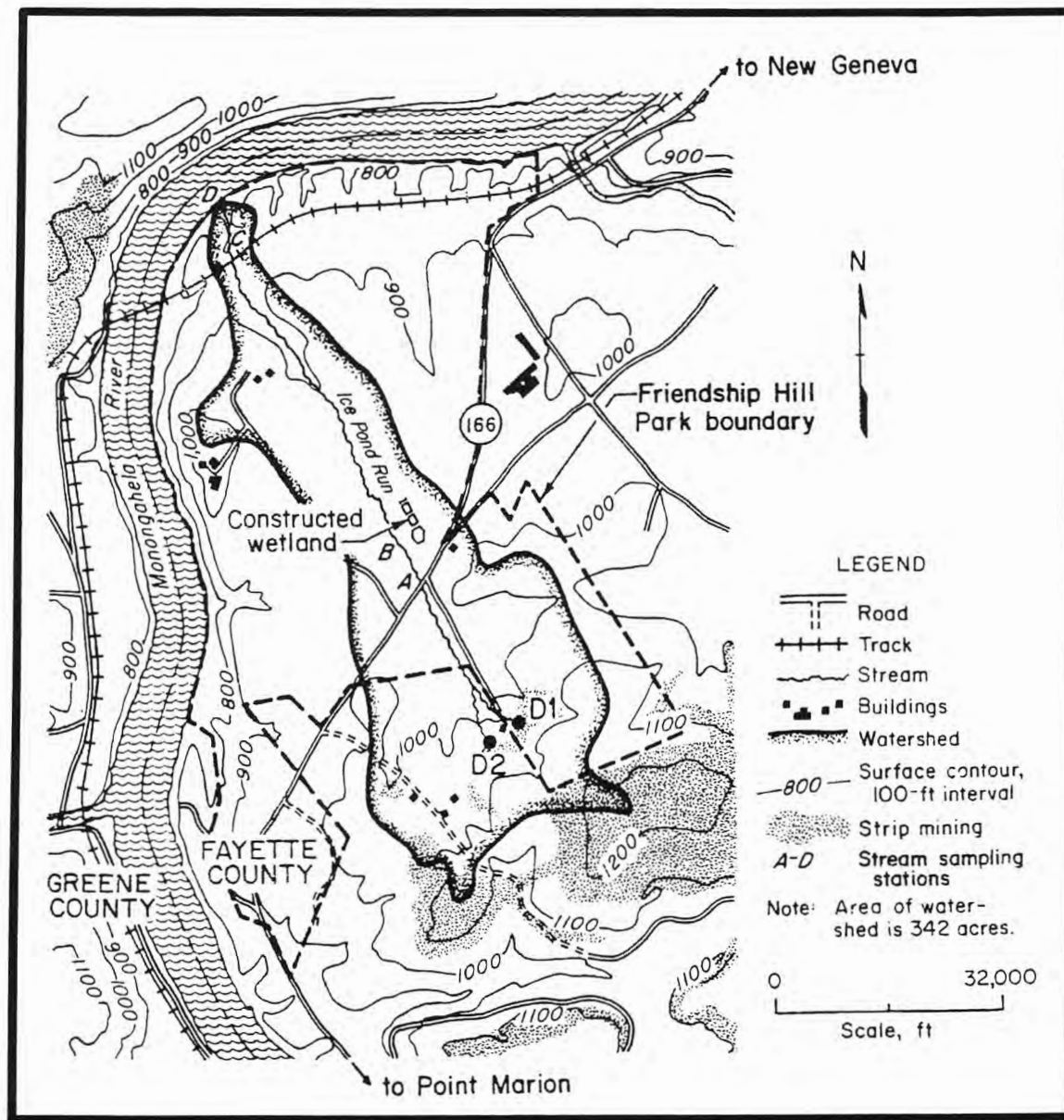


Figure 1. Ice Pond Run Watershed. D1 and D2 (source A&B) are points of primary and secondary mine water discharge (Hedin et. al. 1991).

The constructed wetland technology evaluated by the Bureau of Mines (Hedin et al., 1991) was not adopted by the Park Service given projected treatment costs and excessive acreage requirements (61.8 – 96.5 acres) that resulted from the extreme acid and metal loading rates encountered, as well as observed seasonal variations in wetland performance. Alternative mitigation techniques considered (Hedin et al., 1991), but not adopted, include: surface mining

of the abandoned deep mines to control oxidation of pyritic material; dilution using surface runoff from an expanded watershed; collection and piping to a point just above the confluence of Ice Pond Run and the Monogahela River; containerized passive treatment (spent mushroom compost contained in sealed, anoxic barrels) and chemical (active) treatment. Active treatment requires the direct addition of alkaline material followed by gravity separation of insoluble reaction products including those defined in Equations (3), (4) and (5). Alkaline materials used include anhydrous ammonia, sodium hydroxide, calcium oxide, and limestone (Skousen, 1998). Hedin et al.(1991) estimated the cost of treating 450 kg/d of acidity at FRHI with the reagent sodium hydroxide. The estimated total annual costs of the system, including sludge disposal, was \$190,000. Limestone has potential for reducing active treatment costs given that its market value, on an equivalent or acid neutralization basis, is a fraction (0.03 to 0.26) of the alternative reagents (Hedin et al., 1994). Its use also reduces sludge volume (Dempsey and Jeon, 2001; Sibrell and Watten, 2003) and risk of over treatment (Olem, 1991) while providing calcium ions needed to moderate toxicity of certain dissolved metals (Wilmoth, 1974; Ingersoll et al., 1990).

Table 1. - - Water chemistry and flow rate of the
two main mine drainage discharges impacting
Ice Pond Run, 5/12/89 – 9/4/90 (Hedin et al.,1991).

	Primary Discharge (D1)				Secondary Discharge (D2)			
	mean	sd	min	max	mean	sd	min	max
pH.....	2.8	0.1	2.3	3.0	2.5	0.1	2.4	2.8
Acidity	1178	94	977	1379	1883	196	1192	2292
Fe ^{tot}	245	29	140	296	403	18	354	436
Fe ²⁺	24	25	1	130	21	1	2	72
Fe ³⁺	221	23	124	255	381	20	350	416
Al.....	70	6	56	84	97	4	87	105
Mn.....	10	1	8	13	12	1	11	13
Ca.....	269	37	120	385	253	14	218	278
Mg.....	114	10	90	133	120	7	106	138
Na.....	5	1	4	7	4	<1	3	4
Cl.....	7	8	2	13	2	na	na	na
Sulfate.....	2277	190	1887	2650	2989	132	2675	3200
sum [+]......	45.2	4.0	35.5	53.2	57.5	2.2	51.7	61.9
sum [-]......	47.4	4.0	39.3	55.2	62.3	2.7	55.7	66.7
flow	203	124	68	732	50	39	14	147
(L min ⁻¹)...								
n.....	61 ¹				23 ²			

¹ except Cl, n = 2; and flow, n = 58

² except Cl, n = 1; and flow, n = 17

All units are mg L⁻¹ except pH (standard units) and flow rates which are L min⁻¹.

Sum [+] refers to the total milliequivalent charge of measured cations.

Sum [-] refers to the total milliequivalent charge of measured anions.

These benefits are offset, however, by limestone's relatively slow dissolution rate and sensitivity to passivation or armoring by certain scale forming reactions that inhibit transport of H^+ and its products at the solid-liquid interface (Lovell, 1973; Ziemkiewicz et al., 1997). Scales of particular concern include Fe, Al and Mn oxides as well as gypsum ($CaSO_4 \cdot 2H_2O$) (Pearson and McDonnell, 1975a; Sverdrup, 1984; Lovell, 1973).

Table 2. - - Comparisons of acidity and flow at the primary (D1) and secondary (D2) discharges when samples were taken from both discharges on the same day (Hedin et al., 1991).

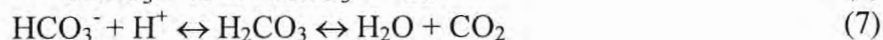
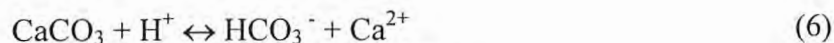
Parameter	Acidity ¹		Flow ²		Acidity Load ³		
	D1	D2	D1	D2	D1	D2	D1/D2
Average.....	1175	1864	126	25	216,273	65,234	3.5
sd.....	81	231	33	9	56,733	22,133	0.9
min.....	977	1192	93	14	143,474	42,175	2.7
max.....	1262	2293	182	36	323,547	96,632	4.9
n.....	14	14	8	8	8	8	8.0

¹ Acidity concentrations are $mg\ L^{-1}\ CaCO_3$ equivalent.

² Flow rates are $L\ min^{-1}$.

³ Acidity loads are $g\ day^{-1}$.

Dissolution rates of limestone impaired by scale have been diminished by a factor of 5 (Pearson and McDonnell, 1975b) reducing application to those sites that (1) can accommodate unusually long hydraulic retention times or (2), allow use of equipment designed to grind and abrade crushed limestone surfaces. The latter includes water powered tumbling drums (Zurbuch, 1963) and electric powered autogenous mills (Lovell, 1973). More recently (Sverdrup, 1984; Maree and du Plessis, 1994), fluidized bed technology has been adapted from early industrial applications (Ghem, 1944; Eden and Truesdale, 1950; Wheatland and Borne, 1962) so as to eliminate need for high torque drive components and associated power requirements. Here abrasion of the limestone surface is provided by interparticle collision forces generated hydraulically during bed expansion. Fluidized bed designs have been based primarily on the reversible first-order reaction of calcite, and its products, with hydrogen ions (Maree and du Plessis, 1994; Maree et al., 1996):



Plummer et al. (1978) identified two additional dissolution reactions that can occur simultaneously:

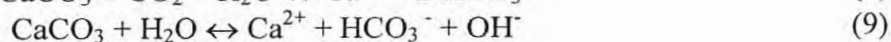
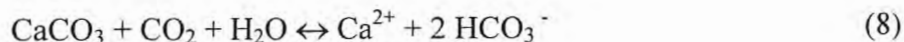


Table 3. - - Changes in Ice Pond Run water chemistry with flow toward Monongahela River, January 30, 1991(Hedin et al., 1991).

Sample Location	pH	Acid	Fe ^{tot}	Fe ²⁺	Ca	Mg	Al	Na	Mn	Sulfate
Primary discharge (D1) ...	2.49	1008	198	2	222	98	61	5	9	1925
Road Culvert (A)	2.60	582	110	3	110	48	34	4	5	1000
Wetland In (B)	2.72	484	85	3	90	39	28	5	4	800
Waterfall (C)	2.73	418	79	4	85	37	13	4	4	725
Monongahela River (D) ...	6.63	-9	1	1	23	6	1	8	<1	85

All concentrations are mg L⁻¹ except pH, which is standard units.

Table 4. - - Percentage change in concentrations of measured water Quality parameters (no pH) between sampling points, January 30, 1991.

Comparison	Mg	Acid	Fe ^{tot}	Ca	Al	Sulfate
Waterfall (C)/D1 Discharge	38*	41	40	38	21	38
Waterfall (C)/Road Culvert (A)	77	72	72	77	38	73

All concentrations are mg L⁻¹ except pH, which is standard units.

* Indicates that concentrations of magnesium at the waterfall station were 38% of concentrations at the primary discharge station.

Combining equations (6), (8) and (9), Sverdrup (1984) developed an overall kinetic expression for calcite particles > 10 microns:

$$-\frac{dm}{dt} = [k_1[H^+] + k_2[CO_2] + k_w - k_b([Ca^{++}][HCO_3^-])] \cdot \left(\frac{3m}{\rho r}\right) \quad (10)$$

where [] refers to the bulk solution concentration, k_1 and k_2 are first order reaction constants, k_w is a zero order constant for Equation (9), k_b is a constant for the backward reaction driven by the interaction of Ca^{2+} and HCO_3^- with calcite, m is mass of particle, ρ is the density of the limestone and r is particle radius. Certain rate constants are defined by hydrodynamic conditions and temperature, e.g., k_1 can be estimated with the relation (Sherwood et al., 1975):

$$k_1 = \frac{D}{r} \cdot (1 + 0.3Re^{1/2}Sc^{1/3}) \quad (11)$$

where D is diffusivity, and Re and Sc are the Reynold's and Schmidt numbers, respectively. Inspection of Equations (10) and (11) reveals calcite dissolution is accelerated under conditions of low pH, high free carbon dioxide concentrations (DC), high turbulence and when particle size (r) is small. However, reducing the particle size in a fluidized bed significantly lowers fluid flux rates required for bed expansion (Summerfelt and Cleasby, 1993). This response limits turbulence and interparticle collision forces (Cleasby and Baumann, 1977) resulting in excessive scaling of limestone surfaces (Ghem, 1944; Maree et al., 1992; Maree and du Plessis, 1994).

Watten and Schwartz (1995) described a pulsed limestone bed (PLB) process designed to prevent scale development at low mean flux rates. Here, a control system directs AMD intermittently into reactors to establish a repeating cycle of fluidization, bed turnover and contraction. During bed expansion, AMD is introduced at a high rate through nozzles designed to accelerate particle attrition. Expansion is interrupted prior to carryover of the limestone bed into the reactors' effluent. Further, a carbon dioxide pretreatment step is used to accelerate limestone dissolution by forcing Equation (8) and by minimizing, temporarily, the rise in pH that occurs during treatment (Equation (7)). High dissolved carbon dioxide levels also elevate equilibrium concentrations of HCO_3^- (Stumm and Morgan, 1996) and thereby allow for surplus acid neutralization capacity (alkalinity) in the reactors' effluent like that observed in anoxic limestone drains (Hedin et al., 1994; Mitchell and Wildeman, 1996). Dissolved carbon dioxide is stripped from the reactors' effluent, and then reused to minimize makeup CO_2 requirements (Watten, 1999ab). Decarbonation of effluent reduces acidity forcing a desirable upward shift in equilibrium pH (Pearson et al., 1982).

Short term field tests of the PLB process have demonstrated its ability to effectively treat AMD containing high levels of acidity, Fe^{3+} and Al^{3+} known to cause armoring within conventional limestone reactors. Table 5 gives performance data for a PLB reactor capable of processing 10 L/min (Watten, 1999ab). Samples of the AMD treated were trucked from Antrim Mine, Tioga County, Pennsylvania, then directed through the reactor while operating with a hydraulic residence time of 7 min. and a gage pressure of 137.9 kPa (CO_2). Operation resulted in significant increases in pH and alkalinity as well as reductions in dissolved metals. These changes provided for side-stream treatment with an effective blending ratio of 1 : 1. This operating mode, if adopted, could reduce plant capital costs by cutting, in this

case, the required reactor volume by 50%. This same PLB reactor was transported to and operated from the FRHI maintenance building in September 1996 (Watten, 1999a,b). Mine water originating from Ice Pond Run was pumped 845 m from a point near the test constructed wetland site (Fig. 1), then was directed through the reactor while operating with a gage pressure of 0 and 137.9 kPa. Table 5 shows changes in water chemistry when operating with supplemental CO₂ (137.9 kPa). As shown, unusually high levels of alkalinity were established during treatment despite inlet dissolved metal and acidity levels that exceeded those present in the Antrim mine samples by a factor of about 3.6. Iron and aluminum removal efficiencies were in excess of 98%. When operating without supplemental CO₂, the PLB process was still effective in raising the pH and alkalinity of the AMD beyond the minimum required changes - - pH increased from 2.57 to 7.34, acidity decreased from 1050 to 48 mg/L and alkalinity increased from 0 to 148 mg/L.

Table 5. - - Change in water chemistry across the test PLB reactor operating at 137.9 kPa with a cycle duration of 4 min.(September, 1996).

Variable	Water Chemistry	
FRHI Ice Pond Run	Influent	Effluent
pH	2.39	6.82
acidity, mg/L	903	0
alkalinity, mg/L	0	418
iron, mg/L	130	0.16
manganese, mg/L	9.3	8.6
aluminum, mg/L	59.2	0.7
Antrim Mine Discharge	Influent	Mixed Effluent
pH	3.18	7.61
acidity, mg/L	250	10.1
alkalinity, mg/L	0	137
iron, mg/L	25.5	0.7
manganese, mg/L	21.9	20.8
aluminum, mg/L	17.4	1.9

Larger scale field tests were performed over a thirty day period at the Toby Creek Mine Drainage Treatment Plant, Elk County Pennsylvania in cooperation with the Pennsylvania Department of Environmental Protection (Sibrell et al., 2000). PLB performance (Fig. 2) was established at operating pressures of 0, 34, 82, and 117 kPa using a PLB system capable of treating an AMD flow of 227 L/min. The AMD here had the following characteristics: pH, 3.1; acidity, 260 mg/L; total iron, 21 mg/L; aluminum, 22 mg/L; and manganese, 7.5

mg/L. In all cases tested, processed AMD was net alkaline with mean pH and alkalinities of 6.7 and 59 mg/L at a CO₂ pressure of 0 kPa, 6.6 and 158 mg/L at 34 kPa, 7.4 and 240 mg/L at 82 kPa, and 7.4 and 290 mg/L at 117 kPa. Effluent alkalinities were correlated with the settled limestone bed depth ($p < 0.001$) and CO₂ pressure ($p < 0.001$). Iron, aluminum, and manganese removal efficiencies of 96%, 99% and 5%, respectively, were achieved with filtration following treatment. No indications of metal hydroxide precipitation or armoring of the limestone were observed. The surplus alkalinity established at 82 kPa was successful in treating an equivalent flow of 1136 L/min (five-fold dilution) of the combined three AMD streams entering the Toby Creek Plant. The capability of the process to handle higher influent acidity was tested by elevating the acidity to 5000 mg/L with sulfuric acid. Net alkaline effluent was produced, indicating applicability of the process to highly acidic AMD.

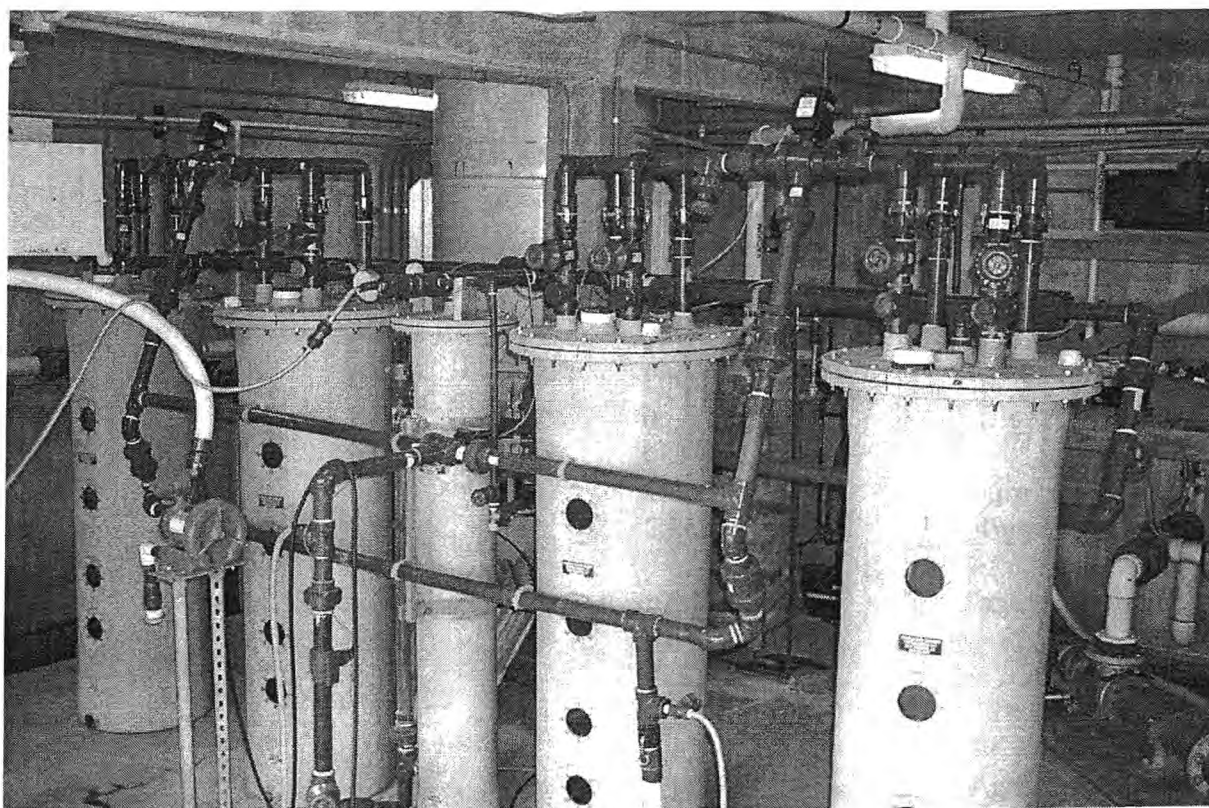


Figure 2. PLB treatment system evaluated at the Toby Creek Mine Drainage Treatment Plant, Elk County, Pennsylvania.

Further trials were conducted by Cole et al.(2001a) to evaluate the behavior and physiology of larval stoneflies (Plecoptera) to effluents produced by the PLB process both with and without CO₂ supplementation. Survival and ionoregulatory responses by nymphs of two species of stonefly (*Petersonarcys proteus* and *Acroneuria carolinensis*), and feeding and drift responses by *P. proteus* to treated and untreated AMD (Antrim Mine, Tioga County, Pennsylvania) were examined. Both species exhibited significant losses of whole body

sodium in exposures to untreated AMD. Nymphs of both species exposed to treated effluents experienced no loss of whole body sodium. *P. proteus* nymphs exposed to untreated AMD showed elevated drift rates and depressed feeding rates relative to those of nymphs exposed to treated AMD and to AMD-free controls. No significant differences in feeding or drift behavior occurred between nymphs exposed to treated AMD and AMD free controls. Therefore the PLB system operated with or without CO₂ pretreatment, provided water that was not toxic to the test animals, allowing normal behavior and physiological function. Cole et al. (2001b) also examined the physiological responses of stream fishes to effluents produced by the PLB process. Plasma glucose, plasma sodium, and leukocyte-count dynamics in response to exposure to treated effluents were examined in brook trout (*Salvelinus fontinalis*) and spiny sculpins (*Cottus cognatus*). Brook trout exhibited depressed plasma sodium and elevated plasma glucose concentrations in untreated AMD at both dilutions tested. Plasma sodium and glucose concentrations remained stable in treated AMD and in AMD-free treatments. Sculpins exposed to untreated AMD had elevated plasma glucose concentrations and depressed plasma sodium concentrations; these responses were not observed in treated AMD nor AMD-free water. Both studies indicated that the effluents produced by the PLB process are not toxic to the organisms tested and provided justification for field deployment of the PLB process at FRHI.

B. Project Objectives

FRHI is just one of 145 park units affected by abandoned mine problems; and one of 60 units with serious water pollution problems. Previous attempts to restore water quality at FRHI using passive (constructed wetland) treatment methods have been unsuccessful. Commensurate with the Parks need to comply with federal and State water quality requirements, this project sought to demonstrate, on a long term basis, the ability of the PLB process to neutralize acidity present in Ice Pond Run, and to refine operating parameters needed for future full-scale applications. Specific hypotheses tested include (1), limestone dissolution rates are accelerated by increasing CO₂ tension and inlet acidity and by decreasing reactor bed height, influent temperature and hydraulic residence time (2), intermittent fluidization decreases reactor sensitivity to the armoring of limestone surfaces by metal hydroxides (3), AMD sludges resulting from limestone-based acid neutralization have superior settling, filterability and phosphorus adsorption characteristics when compared to alternate reagent types (4), recycling CO₂ present in the PLB system effluent can reduce gas feed rate requirements and (5), field application of the PLB process allows for enhanced rates of biological activity. Hypothesis testing required use of laboratory and pilot scale PLB reactors, numerical modeling (chemical reactor theory) as well as application of stream survey methods. Table 6 gives the general research topic, specific test variables and location of results for each of the research products developed during the course of the study (Volume (1)). Volumes (2) and (3) of the report, developed at the request of the ALPO/FONE/FRHI/JOFL Park Superintendent, provide a detailed description of system components/operating procedures associated with the PLB reactor evaluated at FRHI as well as the health, safety, and laboratory procedures identified specifically for the FRHI test site.

Table 6. - - Summary of Volume (1) section tabs linked to specific research topics and test variables.

Topic Investigated	Test Variables	Reference Tab
PLB Process Performance		
Lab Scale, Water Recycle Loop Configuration	Temperature, Hydraulic Residence Time and PCO ₂	3
	Acidity, PCO ₂ , Bed Height AMD Source / Dissolved Metals	5, 21
	CO ₂ Recovery and Recycle	3, 5, 21
	Phosphorus Adsorption Capacity of FRHI AMD Sludge	8
Lab Scale, Single Pass Configuration	Acidity, PCO ₂ , Pulsing Sequence, AMD Source / Dissolved Metals, CO ₂ Recovery and Recycle	4
Pilot Scale, Water Recycle Loop Configuration	Extended Operation at FRHI, Water and CO ₂ Recycle, Economics	9, 10, 11
	Sludge Filterability, Settleability, Disposal	11, 20
	CO ₂ Feed Rate, Relative Sludge Yield and CO ₂ Recycle	8, 21
	Limestone Armoring Potential and Scale Composition, Automated Charging of PLB Reactors	12, 19
	Biological Assessment of Ice Pond Run	14, 22
Head Space Instrument Measuring CO ₂ Tension	CO ₂ Tension, Alkalinity, Total Dissolved Gas Pressure, O ₂ Tension	7

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