DEMONSTRATION OF A PULSED LIMESTONE BED PROCESS FOR THE TREATMENT OF ACID MINE DRAINAGE AT THE ARGO TUNNEL SITE, IDAHO SPRINGS, COLORADO[1]

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Abstract: Pulsed limestone bed treatment is a new technology for the processing of acid mine drainage that utilizes limestone in fluidized bed reactors for an economical method of neutralizing acidity, adding alkalinity, and removing metal contaminants from mining impacted waters. The technology was developed by the U.S. Geological Survey, at the Leetown Science Center in Kearneysville, West Virginia. Previous demonstrations of this technology have taken place at coal mining sites in the Appalachian region. In this demonstration project, funded by the Mine Waste Technology Program of EPA, the Pulsed Limestone Bed (PLB) technology is being demonstrated at the Argo Tunnel Water Treatment Facility, which currently treats metal mining impacted waters flowing into Clear Creek. A 230 liter per minute pilot treatment system was installed in a moving van trailer and transported to the site in summer of 2004. Untreated water at the Argo site typically contains about 600 mg/L acidity (as $CaCO_3$), due to the presence of hydrolysable metals including iron, aluminum, copper, zinc and manganese. Shakedown tests of the system were conducted by project cooperators from the Colorado School of Mines, and demonstrated an increase in pH from 3.0 to 7.0, nearly complete removal of iron and aluminum and an effluent alkalinity of about 100 mg/L as $CaCO_3$. Post-treatment of the process effluent was required for removal of Mn and Zn, but test results indicated a decrease in reagent costs, as well as decreased sludge volume, due to the replacement of lime or sodium hydroxide by limestone as the neutralization agent. Complete process testing is scheduled for summer 2005.

Additional Key Words: remediation, fluidized bed reactor, pilot plant, portable treatment system, metal removal and sludge volume

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Introduction

Background

Acid mine drainage (AMD) is an unintended consequence of coal and metal mining that adversely affects thousands of miles of streams in the U. S. Estimated costs of remediation for the state of Pennsylvania alone using current technology range upwards of 5 billion dollars (U. S. EPA, 2000). A novel AMD treatment process based on limestone neutralization has been developed and patented at the Leetown Science Center in Kearneysville, West Virginia (Watten, 1999). 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, Hedin et al. (1994) found that limestone ($CaCO_3$) was less than one third of the cost of hydrated lime ($Ca(OH)_2$), and less than one twentieth of the cost of sodium hydroxide (NaOH). 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 (all acidities and alkalinities in this report are in units of mg/L as $CaCO_3$) or 5 mg/L iron (Skousen et al., 1995). Recent research at the U. S. Geological Survey (Watten et al., 2004a) has shown that armoring can be avoided and the rate of limestone reaction increased by use of pulsed fluidized bed reactor technology, combined with addition of carbon dioxide (CO_2) to the reactor. Pulsing of the limestone bed allows for vigorous mixing of the limestone sand, resulting in high attrition rates, helping keep the limestone surface clean. Since limestone is a carbonate mineral, CO_2 has a large impact on its chemical behavior in water. The following reactions illustrate the mechanisms for dissolution of limestone (Plummer et al., 1978).

$$CaCO_3 + H^+ = Ca^{2+} + HCO_3^- \tag{1}$$

$$CaCO_3 + H_2O + CO_2 = Ca^{2+} + 2HCO_3^- \tag{2}$$

$$CaCO_3 + H_2O = Ca^{2+} + HCO_3^- + OH^- \tag{3}$$

These mechanisms were termed attack by acid, CO_2 and water, respectively. Under certain conditions of pH and $P(CO_2)$, one or another of these mechanisms may be predominant. The total dissolution rate is the sum of these three mechanisms, as shown in Equation (4) below (Sverdrup, 1984).

$$-\frac{dm}{dt} = \left[k_1[H^+] + k_2[CO_2] + k_w - k_b\left([Ca^{++}][HCO_3^-]\right)\right] * \left(\frac{3m}{\rho r}\right) \tag{4}$$

In Equation (4), k represents reaction rate constants, m is mass of particle, ρ is the density of the limestone and r is particle radius. Carbon dioxide attacks limestone directly through Equation (2) and also increases limestone dissolution through buffering of the pH to 5 or less, where the mechanism of Equation (1) is still effective. Inspection of Equation (4) also shows that the rate is inversely dependent on the limestone particle radius r, explaining why the pulsed limestone bed (PLB) system, with its sand size limestone, requires a much lower retention time than limestone drains, where the limestone particle size is much coarser. 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 PLB process. Thus far the technology has been tested at several coal mine drainage sites in Maryland and Pennsylvania, and has performed well, but has not been demonstrated at western U.S. hard rock AMD sites. Application of the PLB process to these areas could help alleviate acid and metal contamination on a wider scale than more expensive alternate sources of alkalinity.

PLB Technology Description

A schematic of the PLB treatment apparatus is shown in Fig. 1. A treatment apparatus sized to treat 230 liters per minute (L/min) of flow consists 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 CO_2 absorption into the water. Incoming water is routed to one set of two columns (columns 3 and 4, as depicted in Figure 1) containing limestone. The limestone particle size is roughly 0.1 to 1.0 mm. The flow fluidizes a single limestone bed for a period of one minute, and then the flow is diverted to the other column for one minute, while the bed in the first column settles. Water is discharged to the drain continuously.

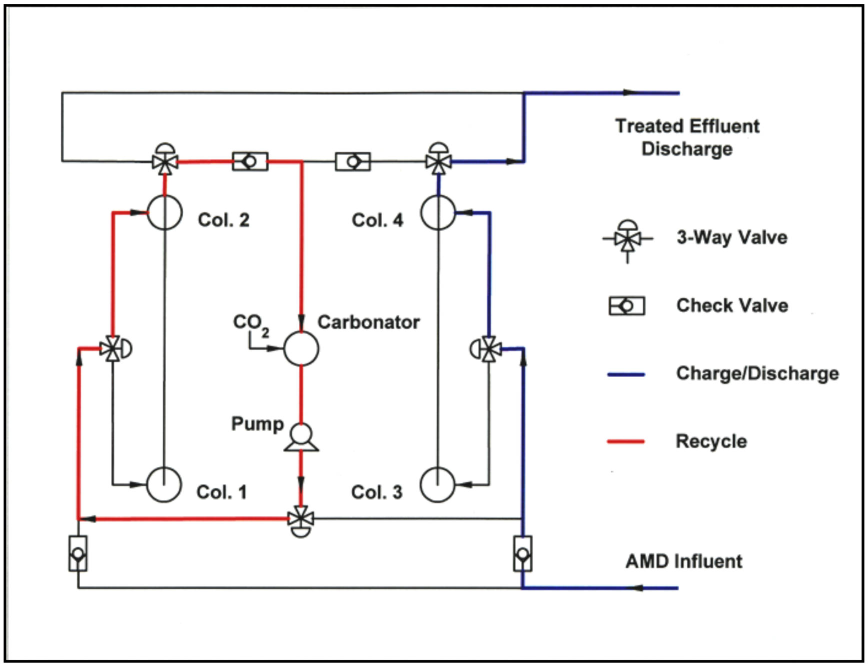

Figure 1. Pulsed limestone bed process schematic

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 is controlled by electrically actuated ball valves operating on a timer-controlled program. Meanwhile, the water in the other set of two columns (columns 1 and 2 in Figure 1) is recirculated through the carbonator, where CO_2 can be added to the water. This is termed the recycle mode, and the water is diverted back and forth between two limestone columns as before on one-minute intervals. The beds operate as described for a total of four minutes, then another set of ball valves is actuated, and the columns that had been receiving incoming water are switched to recycle mode, and the columns that had been on recycle are switched to charge and discharge water. The water that is discharged from the top of the reactor is predominately treated water, while fresh, untreated water is charged into the bottom of the reactor for another cycle of treatment. Thus, at any one time, one out of the four columns is receiving and discharging water, and one of the columns is receiving water recycled through the carbonator.

PLB Development

Initial laboratory testing of the PLB concept was carried out using a prototype unit treating about 8 L/min of acidified well water (Watten and Schwartz, 1996). Test data demonstrated that the process could increase limestone dissolution rates by a factor of 100, and completely neutralize H_2SO_4 acidities ranging between 30 and 1000 mg/L while providing effluent alkalinities in excess of 1000 mg/L. The required hydraulic retention time was just eight minutes. The prototype unit was transported to several AMD sites and successfully demonstrated performance on a short-term basis. At this point, a larger pilot scale system was built to treat up to 230 L/min of flow. This system was first tested at the Toby Creek site in Elk County, PA in May through June of 1999 (Sibrell et al., 2000). Total acidity at this site was about 300 mg/L. During the 30-day 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 CO_2 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 L/min 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 unit was conducted at the Friendship Hill National Historic Site from June 2000 through August 2001 (Sibrell et al., 2003). Process testing at this site included sludge handling, so that this aspect of the treatment could be evaluated. Based on a survey of AMD sites in Pennsylvania (Rose and Cravotta, 1998), the Friendship Hill site is among the most acidic coal mine drainages and was therefore considered an ideal place for testing of the resistance of the PLB process to armoring. Influent acidity at this site was about 1000 mg/L, with up to 200 mg/L Fe. Typical effluent alkalinity was 50 mg/L without CO_2 addition, and 300 mg/L with a limited addition of commercial CO_2. Over the 14 months of operation at Friendship Hill, 50 million liters of AMD were neutralized using 50 metric tons of limestone. The limestone utilization rate was in excess of 90%, much higher than most limestone neutralization systems, and no indications of armoring were observed under standard operating conditions for the system. Maintenance requirements were low, resulting in a 95% operability factor for the system. Total metal removal was above 80%, and essentially all of the Al and Fe^{3+} was removed. However, due to their higher pH precipitation range, some Fe^{2+} and Mn passed through the system. A laboratory comparison of neutralization of the Friendship Hill AMD with different reagents demonstrated that limestone showed a clear advantage in regard to sludge volume. Other neutralization reagents generated greater sludge volumes after 20 hours of settling, as follows: lime, 2.5 times as much sludge volume, i.e., 2.5X; sodium hydroxide, 5X; and ammonia, 6X (Sibrell and Watten, 2003). This is an important finding, given that sludge handling can represent 50% of the total cost of treatment.

Argo AMD Treatment Plant

Currently, the State of Colorado and the EPA are operating a plant to treat up to 2650 L/min of AMD discharging from the Argo Tunnel, in Idaho Springs, Colorado (part of the Central City/Clear Creek NPL site). Sodium hydroxide was initially used as the neutralizing agent, but plans have been made to convert the plant to use lime as the neutralizing reagent. Treatment consists of addition of either NaOH or lime to pH 10, settling and filtration to remove the resulting solids, and reacidification to pH 8 with carbon dioxide. Although the process results in good effluent quality and metal removal, the operating costs are high, about $1.1 million per year (Colo. Dept. Public Health and Env., 2000). Major factors in this cost are the expense of NaOH and the handling and disposal of the solid precipitate, which tends to encapsulate large amounts of water. Limestone neutralization is an attractive alternative at this site for two reasons. First, the low cost of limestone typically makes it the cheapest agent for acid neutralization. Second, the resulting solid precipitate is usually denser and settles more rapidly than lime or hydroxide sludges, so handling and disposal costs would be decreased.

Preliminary laboratory tests of the PLB process have already been conducted on samples of AMD from the Argo site. These laboratory tests were conducted at the Leetown Science Center in Kearneysville, West Virginia using a 0.5 L/minute apparatus to minimize required sample volume. The results showed that a PLB neutralization process could offer significant savings in operating costs for the treatment of Argo Tunnel AMD. Post-treatment of the limestone process effluent with NaOH was required to remove manganese and zinc, but savings arose due to a 70% decrease in NaOH requirements as well as an 80% decrease in overall sludge volume and associated handling costs. Some savings would be offset by CO_2 costs, so testing over a range of CO_2 additions was recommended. Recycle of CO_2 through the use of gas strippers and absorbers would also cut input requirements. In addition, CO_2 stripped from the limestone effluent could be used for reacidification of the filtered product water to pH 8 for discharge. These results were encouraging enough to warrant a larger-scale investigation of the use of the PLB process at the Argo Tunnel site. Funding was received in 2004 and the treatment system was installed in a moving van trailer and transported to the site in July. Preliminary shakedown tests of system performance were performed in late July and August. The purpose of this manuscript is to describe the results of this preliminary evaluation of the performance of the pilot-scale PLB process at the Argo Mine Water Treatment Facility in Idaho Springs, Colorado.

Materials and Methods

Modifications to Treatment System

Two major modifications were made to the PLB system based on operating experience from previous field tests. The first modification involved the water inlet system to the limestone reactors, which was redesigned to simplify the flow path and the cleaning procedure in case of plugging. Formerly, the inlet water was brought down from the top of the reactor to the bottom of the fluidized bed through a pair of U-shaped pipe assemblies with orifices drilled in the bottom to give a jetting action against the floor of the column to help scour the limestone surface and prevent armoring. Previous experience had shown that under certain conditions, a precipitate of iron and aluminum hydroxides had built up within the downleg system and necessitated disassembly of the reactors for cleaning. The inlet plumbing was modified to bring the inlet water through the side of the fiberglass reactor near the bottom, again with orifices directed towards the bottom of the reactor to give the scouring and attrition action. The new inlet system allowed flushing and cleaning of the lines without disassembly of the reactor.

The second modification involved carbon dioxide (CO_2) reuse and recycling. An innovative CO_2 recovery system was constructed with the objective of recycling as much CO_2 back to the limestone reactors as possible. Typically, CO_2 is stripped and absorbed into liquid streams using packed or spray tower technology, where the water and gas travel countercurrently in a vertical column (Perry et al., 1984). However, previous experience with packed towers coupled with the PLB system showed that CO_2 transfer efficiency was limited much of the time because of the small retention time of the water in the tower (Sibrell, et al., 2003). To increase retention time of water in the CO_2 recovery system, a horizontal absorber/stripper was constructed. The stripper was split up into eight compartments using plastic partitions, with the limestone column effluent (CO_2-rich) and column influent (CO_2-poor) water flowing countercurrently down the length of the stripper. Holes were drilled in the transverse partitions to allow water flow along the axis of the stripper, but no direct contact was allowed between the influent and effluent streams. A water jet spray in each compartment provided intimate contact between the gas and liquid phases for CO_2 absorption and stripping, and centrifugal fans directed the enriched CO_2 gas stream from the effluent side to be absorbed into the influent water.

System Layout

Due to space constraints within the Argo Water treatment plant, it was not feasible to situate the PLB test system within the plant. Therefore, the system was installed in a moving van trailer at the Leetown Science Center and then transported to the site. The PLB treatment system layout is shown in Fig. 2.

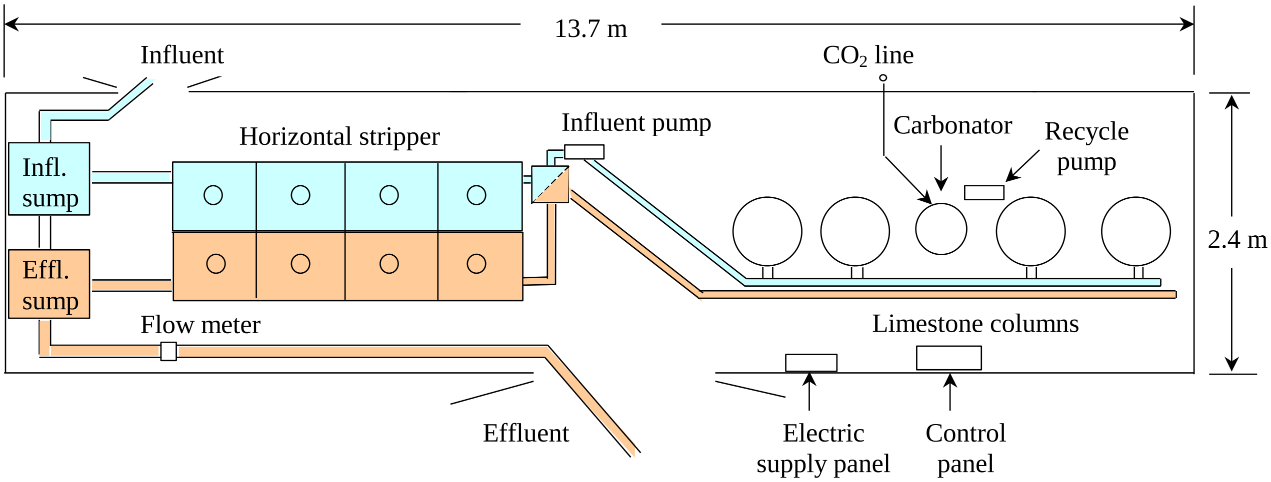

Figure 2. Layout of pulsed limestone bed system in trailer.

Water entered the trailer via a 10-cm flexible hose from equalization basins situated just north of the Argo treatment building. Due to the elevation difference between the basins and the trailer, water flowed by gravity to the trailer without any need for additional pumping. Influent water flowed into a 380-L influent sump, and then continued by gravity into the horizontal stripper. The influent, now fortified with recycled CO_2, was pumped using a 1.5 kilowatt (kW) centrifugal pump into the treatment feed lines for the limestone columns. Pumping for the recycle mode within the limestone columns was provided by a 1.1 kW centrifugal pump. Column effluent was directed back into a split sump and flowed by gravity into the effluent half of the horizontal stripper, and then into an effluent sump. A fountain aerator was placed in the effluent sump to help remove any CO_2 not recycled in the horizontal stripper. The sump drained into a recycle sump within the Argo treatment plant for recycle to the equalization basin. Carbon dioxide, if used, was directed from a manifolded pair of Dewar storage tanks through a mass flow meter and into the carbonator column of the treatment system. The mass flow meter gave CO_2 flow in standard liters per minute (SLPM), i.e., the gas volume was corrected to standard conditions of 273 K and 1 atmosphere pressure. The CO_2 cost was \$0.44 per kg.

The limestone in the reactors was consumed by neutralization of acid and by generation of alkalinity. The initial charge was about 230 kg of limestone to each reactor, and additions were made to each column before each test to maintain a settled limestone bed depth of about 53 cm. The limestone source was high calcium limestone from Colorado Lien's Owl Canyon Quarry, near Fort Collins, Colorado. The cost of the limestone was \$40.70 per metric ton, as delivered to the site.

Testing and Analysis

The trailer arrived at the test site on July 15 and testing began on July 26. Because of water quantity constraints during this period of low flow at the Argo plant, most tests were performed at flows of less than the typical 230-L/min capacity of the treatment system. A total of five test conditions were evaluated over the two-week test period. Samples were taken after two hours of equilibration, and, for four of the tests, sampling was repeated after four hours of operation to assess the effect of elapsed time on system performance. Major variables tested were treatment flow rate and CO_2 input. Water flow rate in the recycle portion of the PLB system was held constant, at 230 L/min. Water quality analyses were performed by Colorado School of Mines cooperators in accordance with standard protocols (APHA, 1995). Analyses performed on-site included pH, temperature, alkalinity (Method 2320B), and acidity (Method 2310B, with hot peroxide treatment). A duplicate of each effluent sample was vigorously air stripped for 7 minutes using a diaphragm pump to remove CO_2, and the pH again measured. Samples of untreated water, limestone column effluent and sump effluent were analyzed for metals content of the water by inductively coupled plasma atomic emission spectroscopy (ICP-AES) at the Department of Chemistry and Geochemistry at the Colorado School of Mines. Metals content was determined both before and after filtration with 0.45 μm membrane filters. Filtration and sample preservation (addition of nitric acid to $pH<2$) were performed in the field as soon as possible after sampling. The CO_2 concentrations in the horizontal stripper compartment headspaces were measured using an infrared CO_2 analyzer (CEA Instruments, Emerson, NJ, USA). The CO_2 concentration in the limestone column effluent was determined with a headspace analyzer (Watten et al., 2004b) coupled with the infrared CO_2 gas analyzer. Readings of $\%CO_2$ in the gas headspace were converted to mg/L CO_2 in the water through application of Henry's law at the specified temperature and pressure. Local barometric pressure was measured with a pressure transducer (Solomat Partners Ltd, Stamford, CT, USA). Samples of Argo tunnel feed water, and PLB product effluent (Test 4B) were also collected for laboratory testing of post-treatment neutralization. A 0.1 M NaOH solution was used to neutralize both samples to pH 10, and to hold at that pH for one hour. The neutralized samples were then transferred to Imhoff cones for determination of the settleable solids, and sub-samples taken for ICP analysis.

Results and Discussion

Alkalinity, Acidity and pH

Test conditions and resulting pH, alkalinity (Alk) and acidity (Acy) data are presented in Table 1. Tests 1 and 2 were conducted without commercial CO_2 addition, at treatment flowrates of 115 and 170 L/min, respectively. Effluent pH ranged from 5.6 to 5.8 before air stripping, and from 6.4 to 7.0 after air stripping to remove CO_2. Effluent alkalinities were in the range of about 70 to 130 mg/L. There was significant variation in effluent pH and alkalinity for the test 1 replicate, indicating that the system may take longer than two hours to reach equilibrium. Tests 3 through 5 show the effect of 25 SLPM CO_2 additions at 115, 170, and 230 L/min influent flow rate, respectively. Effluent pH before air stripping was typically less than that for the samples obtained without CO_2 addition, but after air stripping, the pH was usually higher, because of the additional alkalinity generated by the CO_2 attack on the limestone. Lower flow rate usually resulted in a higher alkalinity, because of the additional residence time that the water was in contact with the limestone. Test 3, at 115 L/min, showed the largest alkalinity achieved during the shakedown testing, at 224 mg/L leaving the limestone columns. Test 4, at 170 L/min, and test 5, at 230 L/min, showed corresponding decreases in effluent alkalinity because of reduced contact time with limestone in the reactors.

Table 1. Test conditions and field results for PLB shakedown tests at the Argo Water Treatment Facility. Water temperature was 20±1°C, influent acidity was 590±80 mg/L as $CaCO_3$, influent pH was 3.0±0.1, and limestone bed depth was 53±3 cm.

			Column Effluent				Sump Effluent			
Test #	Q(H_2O) (L/min)	Q(CO_2) (SLPM)	pH NAS	pH AS	Alk (mg/L)	Acy (mg/L)	pH NAS*	pH AS**	Alk (mg/L)	Acy (mg/L)
1A	115	0	5.75	6.68	72	ND†	5.81	6.32	45	ND
1B	115	0	5.70	6.35	134	ND	5.86	6.05	99	233
2	170	0	5.57	7.04	78	212	5.7	6.06	54	140
3A	115	25	5.41	7.50	162	48	5.74	6.91	99	131
3B	115	25	5.43	6.84	224	-15	5.84	7.08	147	96
4A	170	25	5.31	6.70	141	185	5.62	6.34	97	213
4B	170	25	5.35	6.71	167	134	5.77	6.87	119	77
5A	230	25	5.47	7.00	114	149	5.44	6.1	42	260
5B	230	25	5.48	6.68	121	59	5.61	6.51	90	65

* NAS= Not air stripped
** AS=Air stripped
† ND=Not determined

Because of the methodology of the hot acidity analysis, which is a measure of net acidity, alkalinity plays an important part in the acidity result. This explains the differences in acidity reported in Table 1, because alkalinity varied widely, depending on whether CO_2 was added. The main species responsible for the remaining acidity were Mn and Zn, and the pH was still not above that required for hydrolysis of those metals. As with previous tests, there was significant variation between the first sample typically taken after 2 hr of operation versus the second sample taken after 4 hr. Again, this is likely due to the large volume of the system, which requires a lengthy time of equilibration to stabilize to steady state.

Alkalinity always dropped between the limestone column effluent and the sump effluent, after passing through the CO_2 recycle part of the system. This is probably due to influent water short-circuiting the limestone columns in the split sump, where a 5-cm hole was drilled in the partition to allow water to equalize between the two sides of the sump in case of flow fluctuations. The extent of bypassing can be estimated using the Ca concentrations in the column effluent and the sump effluent because of the difference in Ca content between treated and untreated water. The average percentage of influent bypassing the limestone columns was 11% over all of the tests reported. This also accounts for the increase in acidity usually observed between the column and sump effluents.

Metal Removal

Metal removal is depicted in Fig. 3 for tests 1A and B, and for tests 5A and B, as a function of sample location. For test 1, metal content shows little variation between influent sump filtered and nonfiltered samples, indicating that all species are soluble at this point. The limestone column effluent shows the treatment effect. In the filtered samples, Fe and Al have been removed nearly completely. Zinc and Mn do not show significant changes in Figure 3 because the limestone treatment does not reach a pH high enough to precipitate these metals as hydroxides. Note also the increase in Ca from 300 mg/L to 500 mg/L. This corresponds to a 500 mg/L increase in $CaCO_3$, which agrees with the changes in acidity between the influent and treated water. The effluent sump samples show similar results to the limestone column, indicating the CO_2 stripping in the horizontal stripper did not have a major effect on metal removal. A slight decrease in Ca content is apparent, and indicates a small degree of bypassing of the limestone columns, as explained earlier. Although increased CO_2 flow resulted in increases in effluent alkalinity and pH, the effects of external CO_2 addition were minor for most metals, as can be seen by a comparison of the results for tests 1 and 5. As with test 1, results from test 5 show nearly complete removal of Fe and Al, but not Zn or Mn, regardless of the alkalinity achieved. About 10 mg/L of Fe remained in the filtered effluent samples, particularly in test 5, and is probably indicative of Fe in the Fe^{2+} form. Analysis of Fe speciation was not performed in this test series, but at pH 5.5 as was recorded in the column and sump effluents of test 5, any Fe in solution must be in the Fe^{2+} form because of the precipitation of Fe^{3+}. At about 10 mg/L, this represents only about 10% of the total Fe concentration, as would be expected for an oxic discharge as the Argo Tunnel water has been described (Wildeman, 1983). The Fe^{2+} may be further decreased by oxidation during air stripping, but will be removed in any case by adjustment to pH 10, which will be required for Mn and Zn removal. These findings corroborate the results seen for the PLB at coal mine drainage sites, although Zn was not present in significant amounts in the coal mine drainages tested (Sibrell, et al., 2000; Sibrell, et al., 2003), and confirm the ability of the system to remove the readily hydrolysable metals Fe^{3+} and Al.

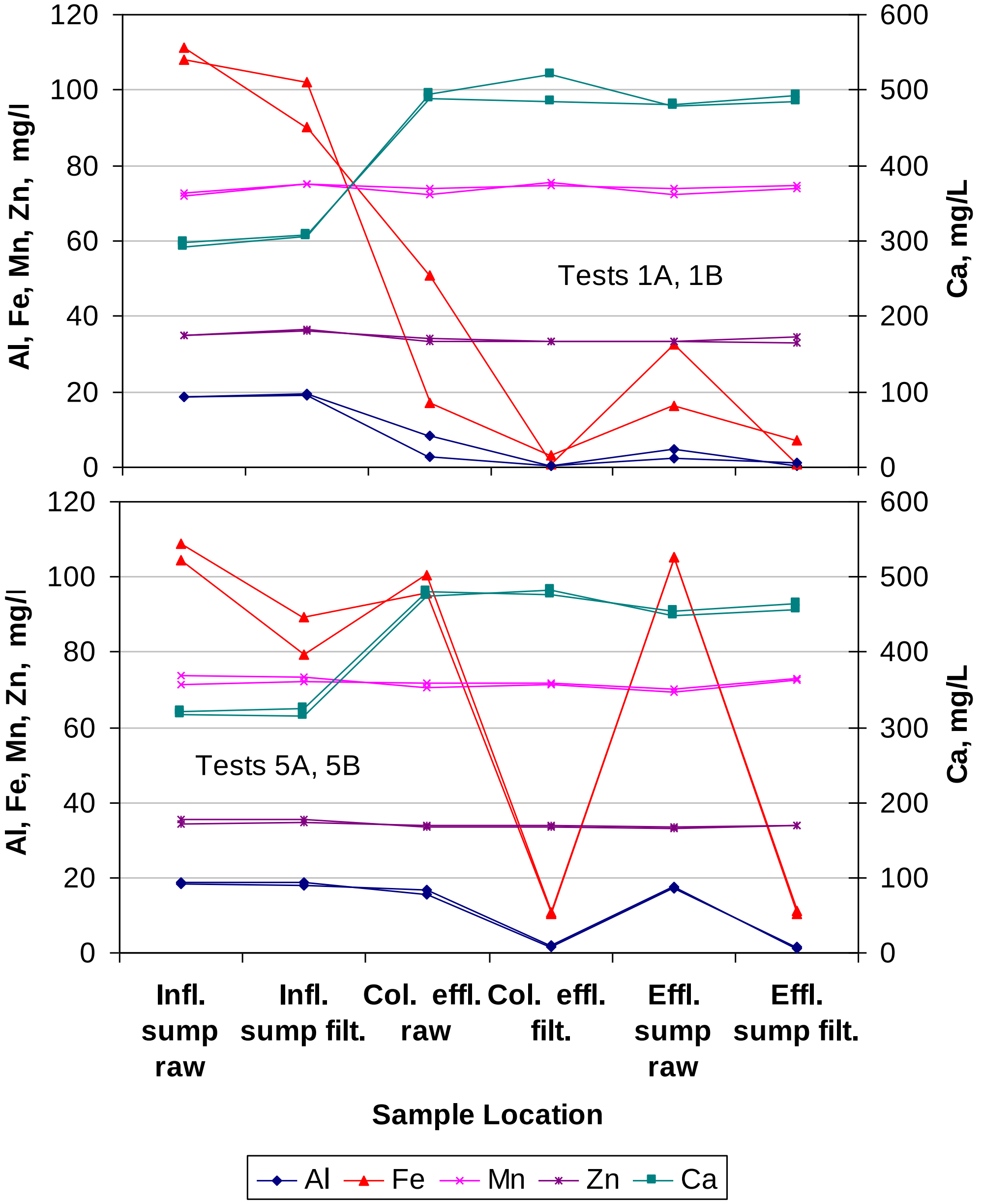

Figure 3. Metal concentration as a function of sample location and treatment, for tests 1A,B (115 L/min flow, 0 SLPM CO_2), and for tests 5A,B (230 L/min flow, 25 SLPM CO_2).

CO_2 Use and Recycle

Since CO_2 use is one of the greater operating expenses for the PLB system, the efficiency of the horizontal absorber/stripper is crucial for CO_2 recycle and process economics. Table 2 shows the performance of the horizontal stripper for each of the tests discussed in Table 1. Gas headspace measurements (% CO_2) were used to calculate CO_2 concentration in the water (mg/L) at the given barometric pressure (BP) and temperature.

Table 2. Performance of the horizontal absorber/stripper for PLB shakedown tests at the Argo Water Treatment Facility. (Influent for the horizontal stripper is the limestone column effluent. Same treatment conditions as in Table 1.)

Test #	$Q(H_2O)$ (L/min)	$Q(CO_2)$ (SLPM)	BP (mm Hg)	Stripper Influent (% CO_2)	Stripper Influent (mg/L CO_2)	Stripper Effluent (% CO_2)	Stripper Effluent (mg/L CO_2)	CO_2 Recycle (%)	CO_2 Recycle (SLPM)
1A	115	0	588.6	16.5	220	7.4	98	55.5	7.0
1B	115	0	585.0	13.0	172	7.2	96	44.6	4.4
2	170	0	586.2	14.5	192	6.3	84	56.6	9.4
3A	115	25	586.0	46.5	617	13.5	179	71.0	25.3
3B	115	25	585.4	54.0	716	17.5	232	67.6	28.0
4A	170	25	587.0	34.0	452	12.5	166	63.2	24.7
4B	170	25	586.8	49.5	658	15.0	199	69.7	39.7
5A	230	25	584.6	31.0	410	14.5	192	53.2	25.3
5B	230	25	584.0	31.5	416	14.5	192	54.0	26.1

For those tests where no commercial CO_2 was added, the CO_2 content of the stripper influent was about 200 mg/L, which arose through the reaction of acid in the water with the limestone. The CO_2 content of the stripper effluent was less than 100 mg/L, indicating a 40 to 60% recovery of the internally generated CO_2. This amounted to about 5 to 10 SLPM of CO_2 input, just from CO_2 generated by reaction of limestone with acidity. For those tests where CO_2 was added, recycle efficiency was in the range of 50 to 70%, and provided additional CO_2 input of 20 to 40 SLPM CO_2. As in Table 1, there were some variations between the replicate samples, indicating that steady state had not yet been reached, due to the limited time available for equilibration. The recycle efficiency also appears to depend on the treatment flowrate, with higher recoveries at low flow rates. This is probably due to the greater residence time of the water in the absorber/stripper at lower flow rates. The recycle loop results in a greater concentration of CO_2 in the limestone columns, where it is needed for alkalinity generation. For example, a recycle efficiency of 67% means that the concentration of CO_2 in the limestone columns is raised to three times what it would have been without recycle. Given the cost of CO_2 at the site, at about $0.44 per kg, the value of the horizontal absorber/stripper is apparent.

Post-treatment

Because of the high pH required for removal of Zn and Mn, the PLB effluent required post-treatment with lime or NaOH to pH 10 to complete metal removal. A laboratory post-treatment test was conducted on a sample of effluent (test 4B) using NaOH. The post-treatment decreased metal content to less than 0.05 mg/L for Al, Cu, Fe, Mn and Zn, thus meeting metal removal criteria for the Argo plant. As compared to the Argo plant feed, the NaOH requirement for treatment of the PLB process effluent was decreased by 36%, and the sludge volume was also decreased by 36% as well. Previous tests performed at the Leetown Science Center showed greater reductions in reagent requirements and sludge volume, of up to 80%. Some aging of the samples used in this experiment was apparent, and that may account for the differences observed. On-site investigations of post-treatment are planned for the upcoming test season.

Conclusions and Recommendations

A 230 L/min pulsed limestone bed AMD treatment system was assembled and transported to the Argo site in July 2004. Shakedown tests conducted at that time resulted in the following conclusions:

1. The treatment system effectively processed from 115 to 230 L/min of Argo water, added about 500 mg/L $CaCO_3$ (acidity neutralized and alkalinity generated) to the water, and boosted pH from below 3.0 to 6.5-7.0 after air stripping.
2. Metal removal was greater than 85% for Al and Fe, but was less than 10% for Zn and Mn, due to higher pH required for the precipitation of these species. Post-treatment of the PLB effluent would be required to remove Mn and Zn, but less lime or NaOH would be required to accomplish this than in the untreated water.
3. Carbon dioxide addition increased effluent alkalinity, but did not affect metal removal. However, since CO_2 may help prevent armoring and could be used for reacidification of the treated water before discharge, further testing of CO_2 effect should be conducted, while keeping in mind that CO_2 is a major component of operating costs.
4. The horizontal stripper recovered from 40 to 70% of the CO_2 in the limestone column effluent water, and recycled it to the incoming water, providing an equivalent of 5 to 10 SLPM of CO_2 with no external CO_2 addition, and 25 to 40 SLPM with CO_2 addition.
5. Laboratory tests conducted on the effluent from the PLB system showed that pretreatment of the Argo water with limestone decreased the final sludge volume after adjustment to pH 10, thus significantly reducing the sludge handling and disposal costs.

Based on the positive results regarding reagent use and sludge volume reduction, further testing of the system is justified and should be conducted in the summer of 2005. Further areas to be tested include on-site post-treatment testing with lime or NaOH, effects of decreased CO_2 additions, and longer-term tests to achieve steady state operation.

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Literature Cited

APHA (American Public Health Association). 1995. Standard methods for the examination of water and wastewater, 19th edition. American Public Health Association, Washington, DC.

Colo. Dept. Public Health and Env. 2000. Argo Water Treatment Plant, brochure for visitors to the Argo Tunnel Water Treatment Facility, Idaho Springs, Colorado.

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. http://dx.doi.org/10.2134/jeq1994.2361338x http://dx.doi.org/10.2134/jeq1994.00472425002300060030x.

Perry, R. H., D. W. Green, and J. O. Maloney. 1984. Perry's Chemical Engineers' Handbook, McGraw –Hill, New York.

Rose, A. W. and C. A. Cravotta III. 1998. Geochemistry of coal mine drainage. Chapter 1 in Coal mine drainage prediction and pollution prevention in Pennsylvania, M. W. Smith, K. B. C. Brady, and J. M. Tarantino, eds., Pennsylvania Department of Environmental Protection, Harrisburg, PA.

Sibrell, P. L., B. J. Watten, A. E. Friedrich, and B. J. Vinci. 2000. ARD remediation with limestone in a CO_2 pressurized reactor. In Proceedings, 5th International Conference on Acid Rock Drainage, Society for Mining, Metallurgy, and Exploration, Denver, Colorado, pp. 1017-1026.

Sibrell, P.L., and Watten, B.J. (2003). Evaluation of sludge produced by limestone neutralization of AMD at the Friendship Hill National Historic Site. Proc. 20th Annual Meeting American Society for Mining and Reclamation, Billings, Montana.

https://doi.org/10.21000/JASMR03011151

Sibrell, P.L., Watten, B.J., and Boone, T. (2003). Remediation of acid mine drainage at the Friendship Hill National Historic Site with a pulsed limestone bed process. In Hydrometallurgy 2003, C.A. Young, A.M. Alfantazi, C. G. Anderson, D.B. Dreisinger, and A. James, The Minerals, Metals and Material Society, Littleton, CO, pp. 1823-1836. http://dx.doi.org/10.1002/9781118804407.ch57.

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.

Sverdrup, H.U. (1984). Calcite dissolution kinetics and lake neutralization. Ph.D. thesis, Lund Institute of Technology, Lund, Sweden.

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.

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.

Watten, B. J. and M. F. Schwartz. 1996. Carbon dioxide pretreatment of AMD for limestone diversion wells. In Proceedings, 17th Annual West Virginia Surface Mine Drainage Task Force Symposium, Morgantown, WV, April 2-3, 1996.

Watten, B. J., Sibrell, P. L., and Schwartz, M. F. 2004a. Effect of acidity and elevated PCO2 on acid neutralization within pulsed limestone bed reactors receiving coal mine drainage. J. Environ. Eng. Sci., 21, 786-802. http://dx.doi.org/10.1089/ees.2004.21.786.

Watten, B.J., Boyd, C.E., Schwartz, M.F., Summerfelt, S.T., and Brazil, B.L. 2004b. Feasibility of measuring dissolved carbon dioxide based on head space partial pressures. Aquacult. Eng. 30, 83 –101. http://dx.doi.org/10.1016/j.aquaeng.2003.09.002.

Wildeman, T.R. 1983. Chemistry of the Argo Tunnel water, Idaho Springs, Colorado. Colorado School of Mines Quarterly, 78, 31-37.