

ARD Remediation with Limestone in a CO₂ Pressurized Reactor

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ABSTRACT

We evaluated a new process for remediation of acid rock drainage (ARD). The process treats ARD with intermittently fluidized beds of granular limestone maintained within a continuous flow reactor pressurized with CO₂. 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. Equipment performance was established at operating pressures of 0, 34, 82, and 117 kPa using an ARD flow of 227 L/min. The ARD had the following characteristics: pH, 3.1; temperature, 10 °C; dissolved oxygen, 6.4 mg/L; acidity, 260 mg/L; total iron, 21 mg/L; aluminum, 22 mg/L; manganese, 7.5 mg/L; and conductivity, 1400 µS/cm. In all cases tested, processed ARD 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. Processed ARD alkalinities were correlated to the settled 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 of 1136 L/min (five-fold dilution) of the combined three ARD streams entering the Toby Creek Plant. This side-stream capability provides savings in treatment unit scale as well as flexibility in treatment effect. The capability of the system 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 ARD.

INTRODUCTION

Acid rock drainage (ARD) is generated when sulfide minerals exposed to the atmosphere weather to produce sulfuric acid. The acid can then dissolve metals present in the host rock, most commonly iron (Fe), aluminum (Al), and manganese (Mn). Acid rock drainage is harmful to aquatic life and degrades stream quality. Over 7000 km of streams have been degraded in Pennsylvania and West Virginia alone (EPA, 1995). Traditionally, ARD has been treated with alkaline materials such as limestone (CaCO₃), hydrated lime [Ca(OH)₂], soda ash (Na₂CO₃), or caustic soda (NaOH). Limestone is the cheapest of these materials, but is also the least reactive and is readily degraded by metal precipitation (often referred to as armoring) on the particle surface (Evangelou, 1995). The USGS has recently patented a process (Watten, 1999) designed to circumvent problems restricting limestone use given its potential for reducing reagent costs, sludge volume and risk of overtreatment or handling.

The USGS process is based in part on the reaction of carbon dioxide with water and limestone to form calcium bicarbonate:



Carbon dioxide accelerates the dissolution of limestone while also providing high levels of alkalinity. This alkalinity can neutralize acid and hydrolyze dissolved metal species without reaction being required at the surface of the limestone particles. Also, since the limestone is dissolving more rapidly, there is less opportunity for metal hydroxide precipitation or armoring to occur on the limestone surface. Finally, the movement of the limestone particles in an intermittently fluidized bed of limestone results in scouring and

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attrition of the limestone surface, also hindering formation of an impervious coating. The USGS process has been tested in the laboratory with synthetic and imported ARD solutions, and has also been tested in the field at several ARD sites in Pennsylvania (Watten and Schwartz, 1996). Based on the positive results from the early tests, we constructed a scaled up version of the apparatus capable of treating 227 L/min of flow. This apparatus was transported to the Toby Creek acid mine drainage neutralization plant in Elk County, PA for testing. Here, the PA Department of Environmental Protection treats three separate ARD flows identified as "A", "B", and "C" in downflow limestone columns and with water wheel-driven rotating limestone drums. While pressures of up to 690 kPa were tested in early trials, tests at Toby Creek were held between zero and the pressure limit of the equipment, 138 kPa. A schematic of the ARD treatment apparatus is shown in Figure 1. The apparatus consists of four 61-cm diameter fiberglass columns containing limestone, and one 30.5-cm diameter column containing plastic packing (the carbonator) functioning as a packed tower for CO₂ absorption into the water. Column height was in all cases 213 cm. Water was directed into individual reactors near floor level using a lateral system described by Summerfelt (1996). Limestone bed depths were kept below 60 cm to prevent particle washout.

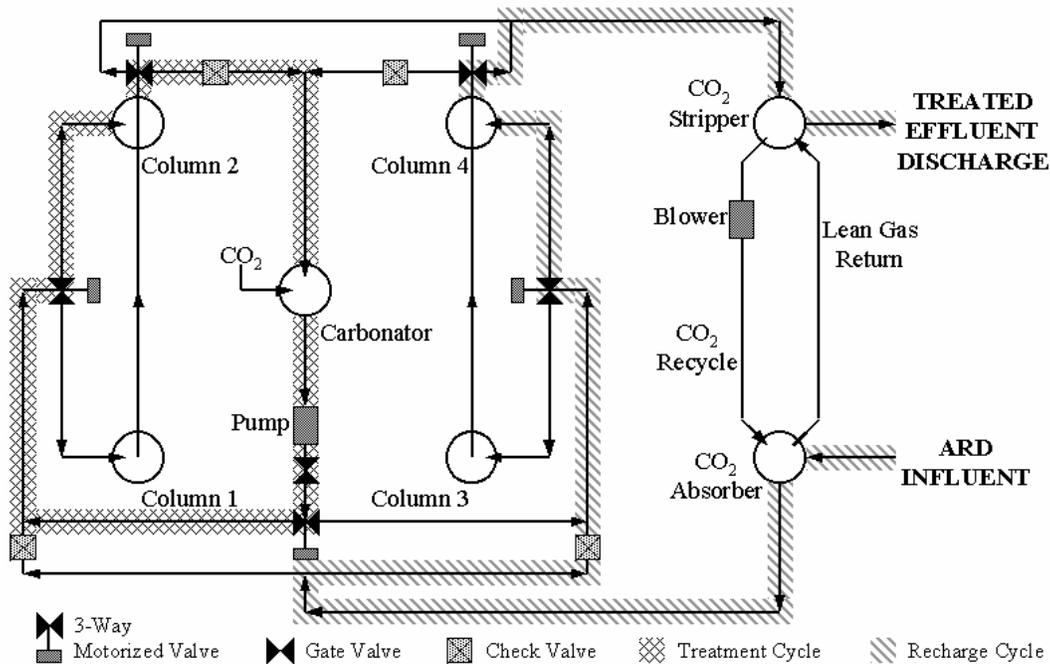


Figure 1 Generalized schematic of ARD treatment apparatus with CO₂ recovery system

The flow paths for the recharge and treatment cycles are highlighted in Figure 1. In the recharge cycle, ARD influent is routed to a CO₂ absorber, then to one set of two columns containing granular limestone. The flow fluidizes the limestone bed for a period of one minute, then is diverted to the other column for one minute, while the bed in the first column settles. Treated water displaced by incoming ARD is continuously discharged to the CO₂ stripper and then to the drain. The flow path is controlled by an electrically actuated three-way ball valve operating on a timer-controlled program. Meanwhile, in the treatment cycle, water in the other set of two columns is recirculated through the carbonator, where carbon dioxide gas is metered in and dissolved into the water. The water is diverted back and forth between the two limestone columns as before on a one-minute cycle. This continues for a total of four minutes, then a second set of ball valves is actuated, and the columns that had been in the recharge cycle are switched to the treatment cycle, and vice versa. Thus, at any one time, two out of the four columns are receiving water, and one of those columns is also discharging water to the CO₂ stripper and drain. The CO₂ stripper-absorber loop recovers and reuses some of the CO₂ dissolved in the discharged water. This is done using a pair of packed towers coupled in a closed loop with a regenerative blower as described by Watten (1999). The CO₂ is stripped from the discharged water in a stripping tower where air is passed countercurrently to the water through plastic packing. The CO₂-rich air is then recycled to the absorber, where CO₂ is dissolved in the incoming ARD.

PROCEDURES

Equipment performance was established over a 30-day period (May 10 - June 9, 1999) using ARD released from mine portal "A" located immediately adjacent to the treatment plant. Characteristics of this discharge were pH, 3.1; temperature, 10 °C; dissolved oxygen, 6.4 mg/L; acidity, 260 mg/L; alkalinity, 0 mg/L; total iron, 21 mg/L; aluminum, 22 mg/L; manganese, 7.5 mg/L; and conductivity, 1400 µS/cm. Prior to testing, reactors 1-4 were each charged with 180 kg of granular limestone. The limestone had an average size (D_{60}) of 525 µm and was purchased from the Bellefonte Lime Company, Bellefonte, PA as Bell Mine Glass Stone #1.⁴ The limestone was analyzed to contain 96.9% calcium carbonate. Carbon dioxide was obtained from an 18000-kg capacity liquid CO₂ tank coupled with a vaporizer and line pressure regulator. Equipment operating pressures were controlled by regulating CO₂ feed rates with a rotameter. Readings were corrected for the effects of line pressure and CO₂ density. ARD inflow and recirculation flows were held at 227 and 208 L/min as determined by paddlewheel type flow sensors. Over the 30-day test period, operating pressure was varied as follows: day 1-12, 82 kPa; day 13-14, 117 kPa; day 15-16, 34 kPa; day 17-28, 0 kPa; and day 29-30, 82 kPa. Carbon dioxide feed rates corresponding to these pressures were 117, 156, 45, 0, and 117 L/min, respectively. Limestone was consumed as the acidity of the ARD was neutralized. Settled bed depths were typically recorded twice daily. Reactors were taken off line as a group when bed depth dropped below about 35 cm. Limestone addition was recorded for each reactor. Treatment effect was established by comparing influent and effluent chemistry. Samples of the influent were analyzed directly whereas effluent samples were, in addition, analyzed following a seven minute air stripping step both with and without subsequent filtering through a Gelman Type A glass fiber filter (0.45 µm). Effluent samples were composites taken at a fixed rate during a randomly chosen 4-minute period. Analyses followed APHA (1995) and included temperature, pH, alkalinity, and acidity (hot peroxide treatment). Samples were also analyzed for metal content using standard EPA methods once per week by a private laboratory (Analytical Services, Inc., Brockway, PA) and once or twice a week by the PA Department of Environmental Protection, Harrisburg, PA. Dissolved oxygen and CO₂ content of the ARD were measured usually twice per day during the trial. Dissolved oxygen was determined polarographically (YSI Inc., Model 57). Carbon dioxide, measured as a percent of atmospheric pressure, was estimated using a head-space analyzer coupled with an infrared CO₂ gas phase meter (Boyd et al., 1994).

On day 8, system effluent was diluted 30, 40, and 50% with untreated ARD, then air stripped to establish mixture pH, acidity, and alkalinity. On day 10, system effluent was diluted 80 and 86% with an ARD mixture representing a combined treatment plant "influent chemistry," i.e. a proportional mixture of portal discharges "A", "B", and "C". Here analyses included pH, alkalinity, and acidity. Further, on day 28, equipment performance was established at elevated acidities through addition of sulfuric acid to the "A" source ARD. The acid was diluted 1:1 with tap water, then metered into the ARD influent line at rates that provided acidities of 5000, 1800, and 1200 mg/L during the five-hour test period. Carbon dioxide flows were adjusted to maintain an operating pressure of 82 kPa. Equipment performance was assessed based on measured changes in water chemistry across the reactor as described previously. Following completion of all performance trials, limestone samples were recovered from each of the four reactors as well as the CO₂ stripping sump. Samples were dried at 110 °C, then subjected to a screen assay to establish particle size distribution. This same procedure was used to evaluate unused limestone. Analysis of variance, least squares regression, and paired t-tests were used to test for factor effects and interactions. We used Systat® 8.0 statistical software to perform these analyses.

RESULTS AND DISCUSSION

The apparatus provided desirable changes in acidity, pH, and alkalinity under all conditions tested. Armoring of the limestone surface, as indicated by a color change, did not occur. Figure 2 gives effluent alkalinity as a function of time. At an operating pressure of 82 kPa (day 1 to day 12), alkalinity varied from about 150 to 300 mg/L. High alkalinity values were observed after recharging with limestone. Alkalinity then decreased steadily as limestone reacted away and settled bed depth dropped from about 60 cm to the minimum allowable depth of 30 cm. Bed depth was often difficult to determine while the apparatus was in operation because of the placement of the windows in the limestone columns. However, bed depth could be calculated at any time based on plumb line bed depth measurements made during recharge of the columns, coupled with limestone additions and run time -- at any given CO₂ pressure, the limestone consumption rate was constant, and therefore, the decrease in bed height due to consumption could be taken into account.

Figure 3 shows that alkalinities increased with CO₂ pressure and bed depth and that bed depth effects decreased at lower pressures. Statistical testing of these figures indicated that bed depth and pressure effects

⁴ Reference to specific products does not imply endorsement by the U.S. Geological Survey.

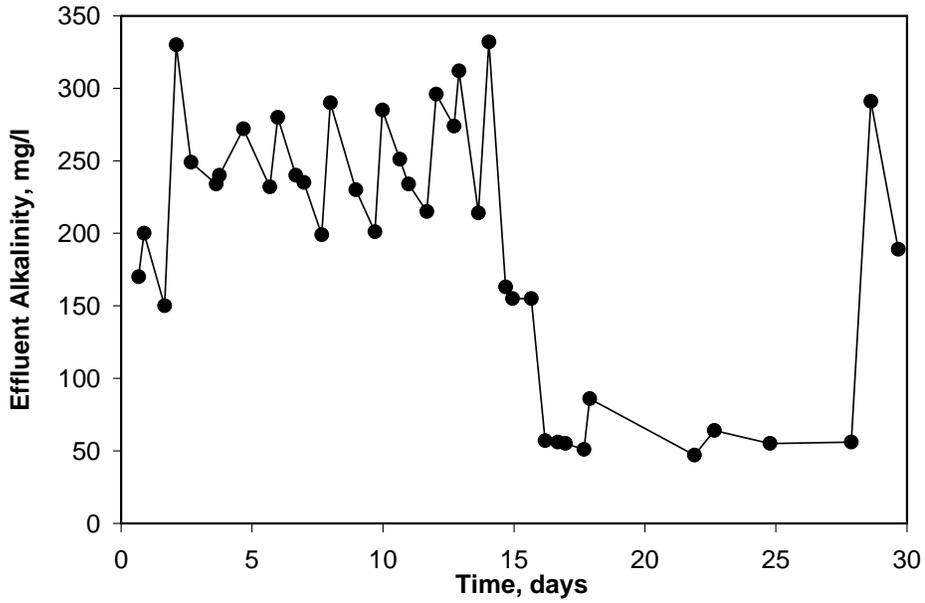


Figure 2 Effluent alkalinity (unfiltered) at various operating pressures during a 30-day trial

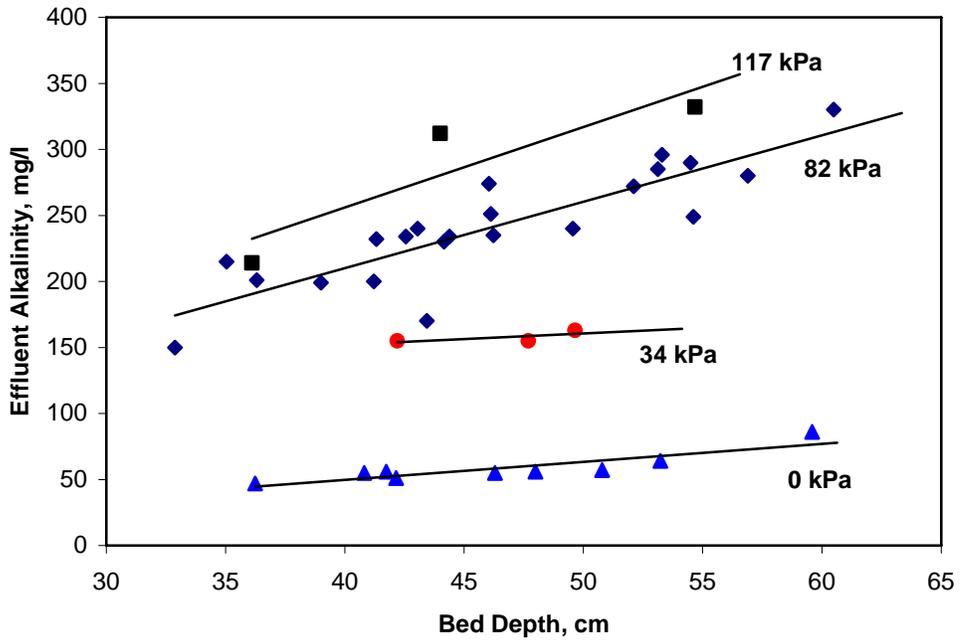


Figure 3 Correlation of effluent alkalinity with limestone bed depth at each of four test pressures

on alkalinity were significant, in that the probability of obtaining these results by chance was less than 0.1% ($p < 0.001$). Regression coefficients describing this interaction for the combined data set ($N=39$) are as follows: $R^2=0.934$; intercept, -138 ± 26 ; CO_2 pressure (kPa), 2.113 ± 0.099 ; and limestone bed depth (cm), 4.38 ± 0.54 . In a separate statistical test, we corrected alkalinity for bed depth effect then ran regression analysis to test for time effects during the two long term (>10 day) trials. Alkalinity increased with time at 82 kPa (line slope, 0.229 ± 0.052 ; $p < 0.001$) but had no effect at 0 kPa (line slope, 0.024 ± 0.023 ; $p > 0.05$). If limestone armoring had occurred, the alkalinity would be expected to decrease; therefore, these data show that limestone armoring did not occur.

The efficiency of the limestone use can be estimated by comparison of the total limestone added with the limestone dissolved into the ARD. The dissolved limestone corresponds to the sum of the acidity that was neutralized and the alkalinity that was imparted to the water. Over the 30 day course of the test, 4300 kg of limestone (96.9% calcium carbonate) was added to the reactor, and 410 kg was still present at the end of the test. A total of 10,045,000 liters of ARD were treated, giving an average concentration of 375 mg/L. The influent acidity averaged 260 mg/L, and the effluent alkalinity about 170 mg/L, for a sum of 430 mg/L. This is close to the calculated addition, considering the errors associated with sampling and analysis.

Table 1 gives examples of influent and effluent chemistry, including metals analyses, at operating pressures of 0 and 82 kPa.

Table 1 Influent and effluent analysis

CO ₂					
Pressure	Parameter	Influent ¹	Effluent ¹	Effluent ²	Effluent ³
82 kPa (Day 2)	pH	3.0	5.7	7.6	7.8
	Alkalinity	0.0	310	314	306
	Acidity	274	0.0	0.0	0.0
	Fe, total	21.8	20.8	20.6	0.59
	Fe, ferrous	1.44	1.74	0.68	0.10
	Mn	7.3	6.65	6.76	6.69
	Al	23.7	20.3	21.5	0.48
	Ca	104	364	373	341
	SO ₄	566	665	593	676
0 kPa (Day 16)	pH	3.2	6.0	6.6	6.6
	Alkalinity	0.0	62	58	56
	Acidity	228	0.0	0.0	0.0
	Fe, total	19.5	17.8	20.2	1.22
	Fe, ferrous	1.50	1.62	1.44	1.20
	Mn	6.4	6.3	6.3	6.3
	Al	18.9	16.9	19.3	0.2
	Ca	88	195	192	191
	SO ₄	507	600	585	593

¹ non air-stripped, unfiltered

² air-stripped, unfiltered

³ air-stripped, filtered

The unfiltered influent ARD stream as sampled on Day 2 had a pH of 3.0 and an acidity of 274 mg/L. In some cases, influent samples were filtered before analysis, and compared to the unfiltered samples. The results indicated that filtered and unfiltered influent samples were essentially identical. Over the course of the test, eleven influent samples were analyzed. The standard deviation for each of the parameters given in Table 1 was less than 10 to 20 percent of the mean value. After treatment, the influent acidity was neutralized, and an alkalinity of 310 mg/L was imparted to the water. The pH of the effluent was 5.7 before air stripping. Air stripping removed excess CO_2 dissolved in the water, resulting in an increase in pH, up to 7.6. Filtration generally increased pH, perhaps due to additional CO_2 stripping. The filtration process also decreased alkalinity, indicating that some of the unfiltered alkalinity was due to fine limestone particles swept from the reactor. However, the balance must necessarily be dissolved alkalinity, in the form of the bicarbonate species solubilized by the action of CO_2 on limestone. Filtered alkalinity over the course of the trial was on average ($N=33$) 15.5% lower than unfiltered alkalinity. This difference was significant ($p < 0.001$).

Metals Removal

The Fe content of the influent ARD stream was about 20 mg/L, most of it in the oxidized ferric form. Ferric Fe will generally undergo hydrolysis and precipitation by pH 5, but still appeared in the effluent unfiltered sample as the analysis reports total dissolved and particulate Fe content. The effluent contained essentially the same Fe concentration as the influent, indicating that metal precipitates which could lead to armoring or blockage of flow were not being held in the apparatus. The filtered samples show less than 2 mg/L Fe, a decrease of over 90%. The average iron removal efficiency was 96%. Ferrous Fe constituted less than 10% of the total iron in the influent. Since Fe(II) is not hydrolyzed and precipitated until pH 8 to 9, it would not be expected to be removed by pH adjustment with limestone. However, it is possible that siderite (FeCO_3) could be formed. When the effluent sample was air stripped and filtered, the Fe(II) concentration decreased slightly. This could be explained by formation of siderite, or by oxidation of Fe(II) to Fe(III), followed by hydrolysis and precipitation of the Fe(III). At this low concentration of Fe(II), it was not possible to determine whether siderite had been formed. Further research with ARD samples containing higher Fe(II) contents is planned for the future. Although the effluent contained about 1 mg/L Fe(II), more than enough alkalinity remained to neutralize any acid generated by subsequent Fe oxidation downstream.

For Al, hydrolysis and precipitation is generally complete by pH 5, but the solids were still present in the unfiltered effluent sample, as with Fe. After filtration, the Al content was less than 1 mg/L, a decrease of over 95%. Average Al removal efficiency was 99%. Manganese removal efficiency was much less, at 5%. This is because Mn hydrolyzes at a higher pH than Fe or Al, and generally requires a pH of 10 to 11 for complete removal. This is not possible with limestone; therefore, most of the Mn was still soluble after the treatment process. At elevated carbonate concentrations, Mn(II) can form the carbonate mineral rhodochrosite (MnCO_3), but since the Mn concentration was unchanged by treatment, little or no rhodochrosite could have formed. If Mn removal were required, a subsequent treatment step using a more alkaline reagent, such as lime or caustic, would be necessary.

The effect of CO_2 pressure on the percent of metals removal is shown in Figure 4. Regression analysis of the effect of CO_2 pressure on the percent removal of metals indicated that Fe removal was correlated ($p < 0.001$), but since Fe removal was above 93% in all cases, the effect was small. For Al and Mn, removal was independent of operating pressure over the range tested ($p > 0.05$). Evidently, even with no external CO_2 addition, the effluent pH was high enough that Fe and Al were hydrolyzed and precipitated, while Mn was not removed, despite CO_2 additions and effluent alkalinities.

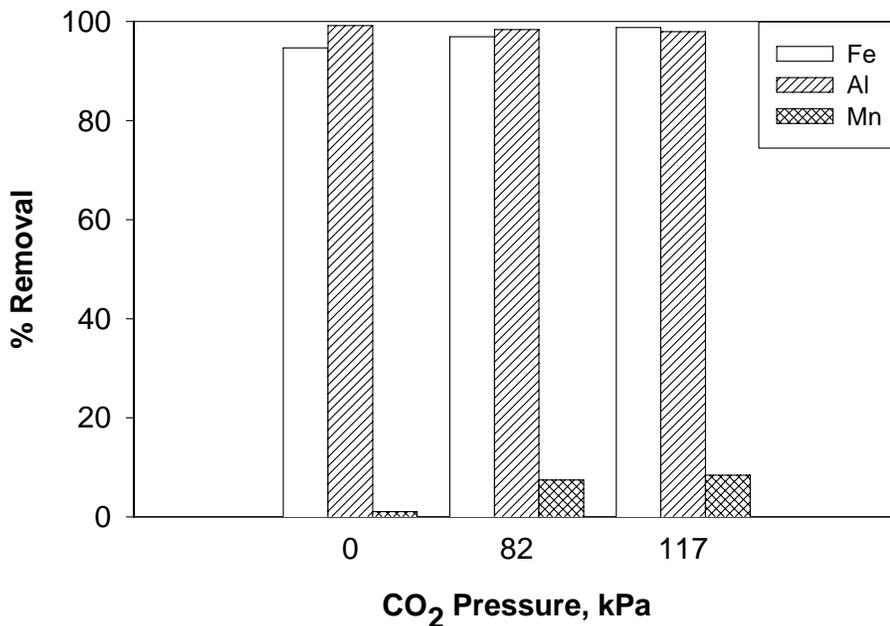


Figure 4 Effect of CO_2 pressure on metals removal

Mixing Tests

Effluent alkalinities ranged from 50 to 300 mg/L depending on the CO₂ addition to the system. This excess alkalinity could be mixed with other ARD flows to neutralize acidity and precipitate metals. Another possibility would be to use the apparatus in a sidestream treatment mode, where only a fraction of the flow is treated in the apparatus, and mixed with untreated flow to achieve a neutral endpoint. This would result in a significant reduction in equipment size and cost, since only a fraction of the total stream flow would be sent through the apparatus. The sidestream concept was tested by mixing treated effluent from our apparatus with additional ARD influent at various ratios. The results are shown in Table 2 for effluent generated at a CO₂ pressure of 82 kPa.

Table 2 Influent/effluent mixing tests

Sample	Acidity, mg/L	Alkalinity, mg/L	Calculated Alk., mg/L	pH
Influent	254	0		3.1
Effluent	0	224		7.0
70% Effluent/ 30% Influent	0	90	81	6.6
60% Effluent/ 40% Influent	0	54	33	6.4
50% Effluent/ 50% Influent	26	10	-15	5.8

The results from the PA Department of Environmental Protection laboratory were somewhat higher than would be calculated from the mixing ratios. However, even using more conservative calculated values, the results indicate that treated effluent could be mixed in a 60% effluent / 40% influent ratio, and still provide a near-neutral pH, with excess alkalinity. After filtration, Fe and Al were decreased to less than 1.0 mg/L at all mixing ratios. Therefore, by treating a 227 L/min flow in the apparatus and mixing with a 151 L/min flow, the apparatus at the Toby Creek site could neutralize a total flow of 378 L/min.

Results of mixing tests using other ARD flows available at the Toby Creek plant are given in Table 3. The alternate flows have lower acidities than the treated flow (A), so the percent of treated effluent mixed with the untreated water was decreased to 20% and to 14%. The 14% level corresponds to the ratio of the "A" stream to the total plant flow at the time of the field trial.

Table 3 Mixing tests with other flows at Toby Creek

Sample	Acidity, mg/L	Alkalinity, mg/L	Calculated Alk., mg/L	pH
Influent A	287	0		3.3
Influent B	119	0		3.8
Influent C	71	10		5.2
Effluent A	0	234		7.5
20% Eff. A /20% B /60% C	31	31	-14	6.7
14% Eff. A /22% B /64% C	42	17	-33	6.4

Again, the analytical results were somewhat higher than would be calculated based on mixing ratios. Results for the 20% effluent mixture show effluent from the apparatus could treat four times the original flow and still produce a stream at near-neutral pH. This would be equivalent to treating 1136 L/min of ARD with a composite acidity of 124 mg/L. Later metal analysis of the samples showed that influent "C" contained Fe in the reduced or ferrous state. This explains the presence of both acidity and alkalinity in the mixtures. Iron in this oxidation state is not hydrolyzed until the pH reaches 8.5, therefore, its acidity was not expressed in the mixing tests. However, the acidity due to the ferrous iron content was picked up by the acidity titration because of the hot peroxide pretreatment.

Acid Addition

The acidity of ARD treated at Toby Creek is representative of many coal mine drainages, but other hard rock mine drainages have acidities of several thousand mg/L. Early studies with limestone have demonstrated a rapid decrease in dissolution rates following exposure to water with acidities exceeding 8500 mg/L (Gehm, 1944). This response was attributed to gypsum (CaSO₄·2H₂O) formation. High levels of acidity also result in high rates of CO₂ release that in turn reduces hydraulic conductivity when fixed bed reactors are used. Results of our elevated acidity tests are given in Table 4. During the five-hour test period about 100 gallons of 1:1 sulfuric acid was added to the influent. Production of CO₂ within the reactor provided for a reduction in CO₂ feed rates required to maintain the desired 82 kPa (12 psi) operating pressure -- at the test acidity of

4940 mg/L, the required CO₂ feed rate was just 44% of the 117 L/min required when treating the unaltered “A” source ARD.

Table 4 Acid addition tests

Elapsed Time, hr:min	Influent pH	Influent Acidity, mg/L	Effluent pH	Effluent Alkalinity, mg/L
0:54	1.61	4940	7.39	289
1:15	1.83	4590	7.13	134
2:55	2.05	1755	7.41	195
3:55	2.11	1230	7.60	241
4:45	2.12	1270	7.61	241

These results show that, even at an influent acidity of about 5000 mg/L, the apparatus was able to produce an effluent at pH 7 or above, with 100 to 200 mg/L excess alkalinity, for a period of several hours.

Particle Size Distributions

The particle size distributions of the limestone feed material and the material remaining in the columns after the 30-day tests are shown in Figure 5. The data are plotted on a cumulative percent passing (probability scale) versus sieve opening in μm (logarithmic scale). In fluidized bed applications, the sand in the bed is often characterized by the size D₆₀, defined by the sieve opening which passes 60% of the material (Summerfelt and Cleasby, 1993). For our feed material, D₆₀ was 525 μm. For the limestone remaining in columns one through three, D₆₀ was 400 μm. The limestone in column four had a lower D₆₀ of about 320 μm.

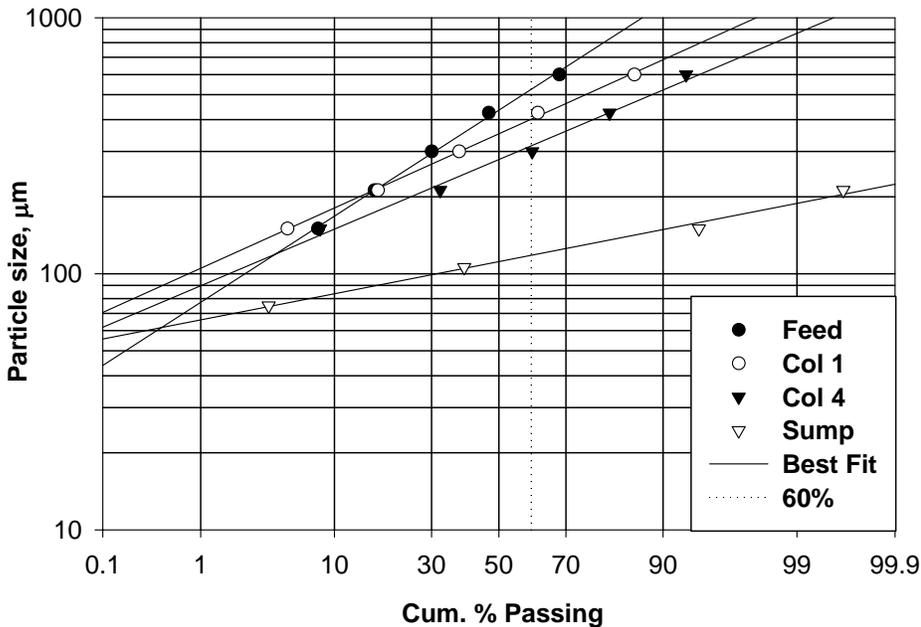


Figure 5 Particle size distributions

Also plotted in Figure 5 is the distribution for a sample of limestone grit carryover from the reactor that settled in the effluent sump. This material had a D₆₀ of 115 μm. Using a treatment flowrate of 227 L/min, and a column diameter of 61 cm, the fluidization velocity in the column was 1.3 cm/s. Data presented by Perry and Chilton (1973) suggest that particles sized 150 μm and smaller would be carried from the column at this velocity. This represents a loss to the system, but since the mass of a spherical particle is proportional

to the cube of the diameter, the percent loss for a 500 μm particle shrinking to 150 μm is $(150/500)^3$, or about 3%, which is negligible. In addition, although the limestone is lost from the column at this size, it would still be available in the effluent stream to provide some additional alkalinity.

Carbon Dioxide Use and Recovery

Treatment effect was easily regulated by changing CO_2 feed rates. This is desirable when treatment effect must change with varying inlet acidities. The partial pressure of CO_2 at influent "A" represented about 3.7% of the local barometric pressure. At 82 kPa, the CO_2 partial pressure was increased 3.7 fold to 17.7% by the CO_2 recovery system. This corresponds to a dissolved CO_2 concentration of 396 mg/L at 10 °C or a contribution of 102.4 kg/day. Given a system discharge CO_2 pressure prior to stripping of 62.3%, CO_2 recovery efficiency was 23.8%. Higher recovery efficiencies will reduce make-up CO_2 requirements further, and as such are desirable. This could be achieved through increases in packed bed height, staging or a combination of the two. The least cost combination will be related to amortized capital and variable costs as well as the CO_2 pressure in the discharge of the reactor.

As currently designed, CO_2 feed rates at 0, 34, 82, and 117 kPa correspond to consumptions of 0, 127, 331, and 441 kg/day, respectively. Bulk CO_2 costs vary with volume delivered but often range between \$0.099 and \$0.330 per kg. The CO_2 required per unit volume ARD will decrease when dilution of system effluent with ARD is feasible. For example, at 82 kPa our tests suggest treated source "A" ARD could be diluted 80% with the blended ARD entering the Toby Creek plant. This serves to lower the net CO_2 feed rate per unit volume treated while also reducing the scale of the treatment unit by a factor of five. Given that two moles of hydrogen ion acidity neutralized will generate one mole of CO_2 , feed rates and hence make-up CO_2 costs will drop as ARD acidity increases. We demonstrated this response during the elevated acidity test runs.

SUMMARY

The pressurized fluidized bed treatment system for ARD remediation performed well at the Toby Creek test site. The system treated ten million liters of ARD in the space of 30 days with no armoring of the limestone and no major system upsets. The influent acidity of about 260 mg/L was neutralized, and a net alkalinity of 50 to 300 mg/L was added to the ARD, depending on the CO_2 addition rate. The pH of the air stripped effluent never fell below 6.3. The effluent alkalinity was correlated to the limestone bed depth and the CO_2 operating pressure. The Fe and Al content of the ARD stream was decreased to 1 mg/L or less, a removal efficiency of over 95%. The treated effluent could be mixed with untreated influent at a ratio of 3:2, thereby increasing the effective treatment rate to 378 L/min. If mixed with other flows at Toby Creek, the effective treatment rate was 1136 L/min, with a near-neutral effluent. The major operating cost was the CO_2 reagent.

Further testing of the system is planned at the Friendship Hill National Historic Park, in southwestern PA. This will be a continuous long-term test to investigate other aspects of system operation, such as the sludge generation rate and disposal cost. Alternatives to the manual limestone feeding system will be investigated. Additional laboratory tests will be done with other ARD samples for testing of the process at higher acidities and metal loadings. The possibility of iron carbonate formation will be investigated for ARD sources rich in ferrous Fe as well.

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