

Passive Treatment of Acid Mine Drainage with Limestone

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ABSTRACT

The water treatment performances of two anoxic limestone drains (ALDs) were evaluated. Anoxic limestone drains are buried beds of limestone that are intended to add bicarbonate alkalinity to flow-through acid mine drainage. Both ALDs received mine water contaminated with Fe^{2+} (216–279 mg L^{-1}) and Mn (41–51 mg L^{-1}). Flow through the Howe Bridge ALD increased alkalinity by an average 128 mg L^{-1} (CaCO_3 equivalent) and Ca by 52 mg L^{-1} , while concentrations of Fe, K, Mg, Mn, Na, and SO_4^{2-} were unchanged. The Morrison ALD increased alkalinity by an average 248 mg L^{-1} and Ca by 111 mg L^{-1} . Concentrations of K, Mg, Mn, and SO_4^{2-} all decreased by an average 17%, an effect attributed to dilution with uncontaminated water. Iron, which decreased by 30%, was partially retained within the Morrison ALD. Calcite dissolution was enhanced at both sites by high P_{CO_2} . Untreated mine waters at the Howe Bridge and Morrison sites had average calculated P_{CO_2} values of 6.39 kPa ($10^{-1.20}$ atm) and 9.24 kPa ($10^{-1.04}$ atm), respectively. At both sites, concentrations of bicarbonate alkalinity stabilized at undersaturated values ($\text{SI}_{\text{Calcite}} = 10^{-1.2}$ at Howe Bridge and $10^{-0.8}$ at Morrison) after flowing through approximately half of the limestone beds. Flow through the second half of each ALD had little additional effect on mine water chemistry. At the current rates of calcite solubilization, 17.9 kg d^{-1} CaCO_3 at Howe Bridge and 2.7 kg d^{-1} CaCO_3 at Morrison, the ALDs have theoretical effective lifetimes in excess of 20 yr. By significantly increasing alkalinity concentrations in the mine waters, both ALDs increased metal removal in downstream constructed wetlands.

COAL MINE DRAINAGES in the eastern USA are commonly contaminated with dissolved Fe and Mn. The treatment of these polluted waters requires that the metal contaminants be precipitated and that the acidity be neutralized. In conventional mine drainage treatment systems, the water is treated with additions of highly alkaline chemicals such as NaOH, $\text{Ca}(\text{OH})_2$, CaO, Na_2CO_3 , or NH_3 (Skousen et al., 1990). These reagents promote metal removal reactions and neutralize the acidity, but are expensive, potentially dangerous, and when misused can result in the discharge of excessively alkaline water. Alternative passive processes that do not require regular chemical additions have attracted interest from mining, reclamation, and research groups (Brooks et al., 1985; U.S. Bureau of Mines, 1988; Hammer, 1989; Moshiri, 1993). Wetlands have received particular attention because of their tendency to decrease concentrations of Fe and Mn when the mine water contains bicarbonate alkalinity (Brodie, 1990; Hedin and Nairn, 1990, 1993). The circumneutral environment that is associated with bicarbonate ion (pH 4.5–8.3) promotes Fe and Mn oxidation processes that are rapid enough to make the wetland

approach cost-effective for mine drainage treatment. The bicarbonate ion also acts as a buffer to neutralize the proton acidity released when these metals hydrolyze (Hedin et al., 1994).

When mine water naturally contains sufficient alkalinity to offset the mineral acidity associated with dissolved Fe and Mn, passive treatment with a properly sized constructed wetland is sufficient. When mine water is acidic, successful passive treatment requires that alkalinity be added to the water. The most inexpensive alkaline source in coal mining regions is limestone (Table 1). In the past, however, limestone has been rarely utilized in either passive or chemical mine water treatment systems, because it has a low solubility under atmospheric conditions, and it tends to become armored with ferric hydroxide (Wentzler and Aplan, 1972; USEPA, 1983).

Recently, Turner and McCoy (1990) proposed that limestone could be used in passive mine water treatment systems if the Fe was in the ferrous (Fe^{2+}) form and the mine water contacted the limestone in an anoxic environment. Under this condition, no armoring of the limestone should occur. Turner and McCoy (1990) described two systems in which acidic mine waters contaminated with Fe and Mn were rerouted through buried, limestone-filled trenches. Both trenches had alkaline discharges that were then directed into wetlands where metal contaminants precipitated.

During the past 3 yr, dozens of limestone treatment systems, similar in concept to those originally described by Turner and McCoy (1990), have been constructed in the Appalachian coal field. Because of the emphasis on anoxic conditions and the similarity of the many systems to field drains, the systems have become known as *anoxic limestone drains* or ALDs. Surveys of the effluent chemistry of ALDs have documented that many systems successfully generate alkalinity; however, large variation exists in the amount of alkalinity generated and in the effects that ALDs have on metal concentrations (Brodie et al., 1991; Faulkner and Skousen, 1993; Hedin and Watzlaf, 1994). The causes of variability in alkalinity generation and metal retention are unresolved.

This paper reports detailed analyses of the performances of two ALDs constructed to treat mine water contaminated with ferrous Fe and Mn. Water quality at both sites was assessed at the ALD effluents and at wells placed within the two limestone beds. The water quality data collected during the 18- to 30-mo monitoring programs provide the most detailed analyses of ALD performance yet presented. The results are used to identify factors of the ALD construction and mine water chemistry that effect the generation of alkalinity, and the retention of metals at the two sites.

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Abbreviations: ALD, anoxic limestone drains; PVC, polyvinyl chloride; ICP, inductively coupled argon plasma spectroscopy; CV, coefficient of variation; SI, saturation index; ISE, ion-sensitive electrode; DO, dissolved oxygen; IAP, ion activity product.

Table 1. Comparative cost of limestone and alkaline chemicals commonly used in the treatment of acid mine drainage.

Material	Chemical composition	Cost per kmole of OH ⁻ equivalent†
Limestone	CaCO ₃	\$ 0.69
Hydrated lime	Ca(OH) ₂	2.64
Ammonia	NH ₃	5.61
Soda ash	NaCO ₃	15.16
Caustic soda	NaOH	21.56

† Chemical costs from Skousen et al. (1990). Limestone cost is based on a 95% CaCO₃ content at \$13 Mg⁻¹.

MATERIALS AND METHODS

Study Sites

Howe Bridge Anoxic Limestone Drain

The ALD at the Howe Bridge site treated acidic water that upwelled from an abandoned exploration well. In October of 1991, the well was capped and a PVC pipe was attached that transferred the mine water 15 m horizontally to the ALD. A sampling port was installed in this transfer pipe to allow sampling of the mine water before it contacted limestone. Mine water entered the ALD through a 15-cm diam. perforated polyvinyl chloride (PVC) pipe laid across the width of the limestone bed. The ALD was constructed of a rectangular bed of limestone gravel that was covered with filter fabric and buried under 60 cm of clay (Table 2). Four sampling wells, designated W1, W2, W3, and W4, were positioned evenly down the center of the ALD. Water discharged from the ALD through two pipes. Sampling of both discharges on three occasions early in the study indicated that the chemical composition of the discharges were within 3% for all ions analyzed. Since then, only the larger flow was sampled for chemical analyses. Flow rates were determined from the summed flow of both ALD effluent pipes.

Morrison Anoxic Limestone Drain

Contaminated mine water at the Morrison site discharged from the outslope of a reclaimed surface mine. The ALD was constructed in October 1990 and was intended to both intercept mine water within the spoil and treat it with limestone. The ALD was constructed by digging a narrow, 46-m long trench from the seepage point back into the mine spoil. The trench was filled to a height of 0.9 m with limestone gravel and then

Table 2. Construction and design characteristics of the Howe Bridge and Morrison anoxic limestone drains.

Parameter	Howe Bridge	Morrison
Dimensions (m)		
Length	36.6	45.7
Width	6.1	0.9
Depth	1.2	0.9
Limestone		
Weight (Mg)	455	64
Volume (m ³)	272	38
Source location	Bellefonte, PA	East Brady, PA
CaCO ₃ (g kg ⁻¹)	820	920
ALD pore volume (L)	133 000	19 000
Cover	Filter fabric and 0.6 m of clay†	Plastic and 1 to 3 m of spoil
Mine water input to ALD	Pipe	Seepage from spoil

† Type of clay unknown.

buried with spoil (Table 2, Fig. 1). Two wells, designated Y and Z, were installed in the ALD at points 37 and 23 m from the ALD effluent, respectively.

Water discharged from the Morrison ALD through a horizontal 30-cm diam. pipe that was laid on a clay berm at the end of the limestone bed. Flow rates were measured from the pipe outlet. Between October of 1990 and February of 1992, water levels in the ALD were controlled by the height of the bottom of this pipe, which was 0.6 m above the base of the limestone. The pore volume of the flooded limestone during this period was estimated as 12 500 L. In February 1992, a riser was connected to the effluent pipe that raised water levels in the ALD to the top of the limestone and increased the pore volume of the flooded limestone to an estimated 19 000 L.

Water Sampling and Analysis

Water samples were collected monthly from sampling wells placed within the ALDs and from the final effluent pipes of both ALDs. The sampling wells were constructed from schedule 40 PVC pipes that were perforated at the bottom. The perforated section of each pipe sat within the limestone bed, while solid pipe extended through substrate that covered both ALDs. All sampling pipes were capped. Water samples were collected from tubing that extended through the pipe caps and down into the saturated zone.

Temperature, pH, alkalinity, and dissolved oxygen were measured in the field. Temperature and pH were measured with a calibrated Orion SA270 or 290A pH/ISE meter.¹ Alkalinity (reported as mg L⁻¹ CaCO₃) was measured using the Orion Total Alkalinity Test Kit reagent and a pH meter. Results of the Orion method agreed well ($r = 0.99$) with results obtained in the field by the standard alkalinity titration procedure (APHA, 1985). In situ dissolved oxygen measurements were made potentiometrically with a Yellow Springs Instruments Model 57 portable meter or an Orion Model 820 meter. Acidity was determined by heating a sample with H₂O₂ and titrating the solution to pH 8.2 with NaOH (APHA, 1985). Solution concentrations of Al, Ca, Fe, K, Mg, and Mn were determined in acidified samples (2 mL of 12 M HCl per 250 mL of sample) using inductively coupled argon plasma spectroscopy (ICP). Ferrous iron concentrations were determined for acidified samples by titration with K₂Cr₂O₇ (Fales and Kenny, 1940). Ferric Fe was calculated from the difference of total Fe and ferrous Fe measurements. Sulfate concentrations in samples collected before November of 1992 were determined using a liquid chromatograph (Dionex 4500i series) coupled with a conductivity detector following adjustment of sample pH to 8 with NaHCO₃. After November of 1992, SO₄²⁻ was determined by ICP with the assumption that all the measured sulfur was present as SO₄²⁻. A comparison of SO₄²⁻ concentrations determined on 13 ALD samples using both methods verified this assumption. Sulfate concentrations determined by ICP were within 2% of SO₄²⁻ concentrations determined by liquid chromatography.

Total ion concentrations are reported as the results closely approximate dissolved concentrations. A comparison of unfiltered and filtered (0.22 μm) splits of 41 ALD water samples indicated that the cation concentrations of nonfiltered samples were within 1% of the cation concentrations in filtered samples. The mean cation/anion ratio for analyzed water samples was 1.02 (range of 0.91–1.13). Analyses of duplicate and spiked samples indicated an analytical error of less than 3% for all

¹ Reference to specific products does not imply endorsement by the U.S. Bureau of Mines.

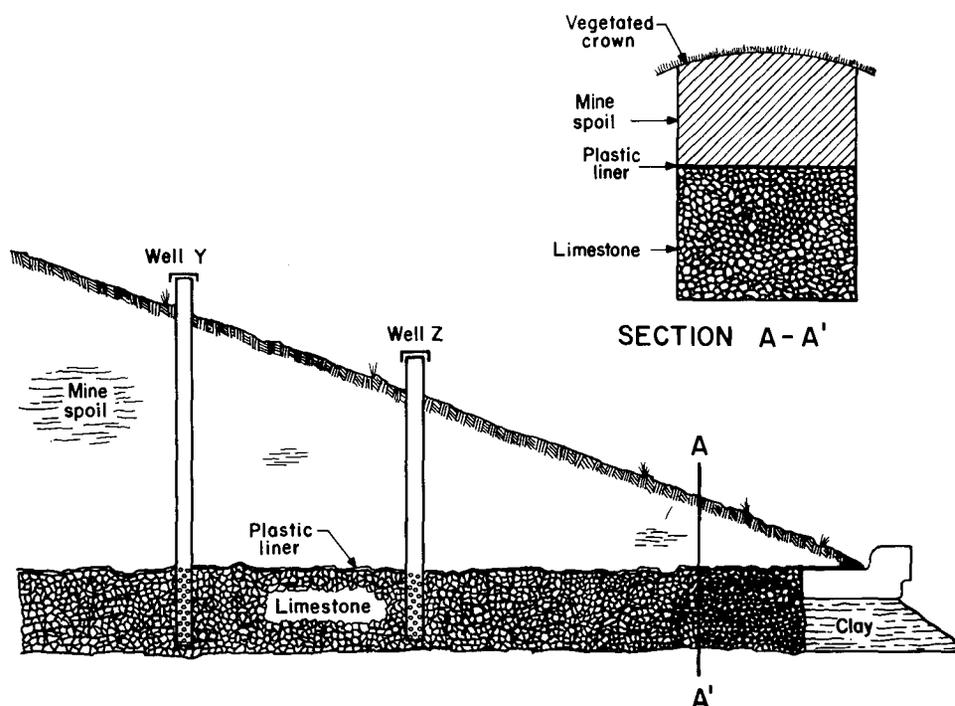


Fig. 1. Cross sections of the Morrison anoxic limestone drain. The figures are not drawn to scale.

parameters analyzed in the laboratory. Analyses of alkalinity standards indicated a maximum error of 10% for field alkalinity determinations.

Carbon dioxide partial pressures (P_{CO_2}) and mineral saturation indices (SI) were calculated from the results of water analyses using the computer model WATEQ4F (Ball et al., 1987). A bicarbonate input to the model was estimated by assuming that field alkalinity resulted entirely from HCO_3^- . This assumption was reasonable for the pH range (5.0–6.5) of samples collected in this study (Hem, 1985).

Flow rates were determined at the effluents of both ALDs by measuring the time necessary to collect a known volume of water. The retention times of mine water within the ALDs were estimated by:

$$t_R = 0.49V/Q \quad [1]$$

where t_R is the retention time in minutes, V is the ALD pore volume in liters, and Q is the flow rate in $L \text{ min}^{-1}$. The bulk

porosity value used in the calculation, 0.49, was based on average field measurements made on limestone gravel collected at both sites.

RESULTS

Performance of the Howe Bridge Anoxic Limestone Drain

The influent mine water at Howe Bridge was acidic and contaminated with Fe^{2+} and Mn (Table 3). Concentrations of Fe^{3+} and Al were less than 1 mg L^{-1} . The effluent flow rate averaged 96 L min^{-1} . Both the flow rate and chemical composition of influent mine water varied little during the sampling period. The coefficient of variation (CV) for the ALD flow rate was 7%. Coefficients of variation for major constituents of the ALD

Table 3. Mean concentrations of water constituents at the Howe Bridge ALD, January 1992 to May 1993. Concentrations as mg L^{-1} (alkalinity and acidity as CaCO_3) and flow as L min^{-1} . Dissolved oxygen (DO) was measured on a single occasion from the wells and on four occasions from the effluent. Samples size was 6 for K, and 18 for all other ions and flow. Standard deviations are shown in parentheses.

	Influent	Well 1	Well 2	Well 3	Well 4	Effluent
pH	5.6(0.2)	5.9(0.1)	6.1(0.1)	6.3(0.1)	6.3(0.1)	6.2(0.1)
Alk	33 (8)	78 (10)	132 (10)	164 (10)	171 (11)	161 (9)
Al	<1	<1	<1	<1	<1	<1
Ca	159 (10)	175 (11)	201 (12)	216 (12)	218 (11)	211 (11)
Fe^{2+}	279 (18)	278 (19)	278 (20)	279 (20)	277 (21)	277 (20)
Fe^{3+}	<1	<1	<1	<1	<1	<1
K	6 (<1)	6 (<1)	6 (<1)	6 (<1)	6 (<1)	6 (<1)
Mg	107 (8)	107 (9)	107 (10)	107 (9)	107 (9)	107 (9)
Mn	41 (4)	40 (4)	40 (4)	40 (4)	40 (4)	40 (4)
Na	11 (1)	11 (1)	10 (<1)	11 (<1)	11 (<1)	10 (<1)
SO_4	1323 (79)	1314 (114)	1339 (87)	1340 (84)	1339 (87)	1329 (76)
Acid	482 (36)	448 (33)	404 (39)	360 (32)	353 (35)	373 (42)
DO	<1	<1	1	<1	<1	<1 (<1)
Flow	NA†	NA	NA	NA	NA	96 (6)

† Data not available.

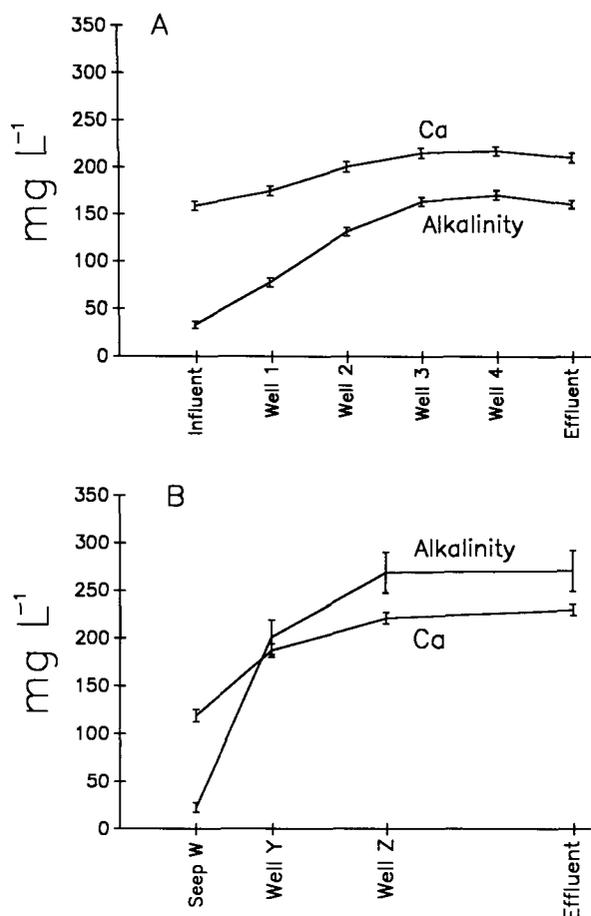


Fig. 2. Mean concentrations of alkalinity and dissolved Ca for sampling stations at the (A) Howe Bridge ALD, and the (B) Morrison ALD. The sampling stations are positioned on the x-axis to reflect their linear positions within the limestone bed. Vertical bars are 1 standard error of the mean.

influent (Ca, Mg, Fe, Mn, and SO₄²⁻) ranged between 5 and 9%.

As mine water flowed through the Howe Bridge ALD, pH increased by 0.6 units, alkalinity increased by 128 mg L⁻¹, and Ca increased by 53 mg L⁻¹. Most of the increase in both parameters occurred between the influent station and the third well (Fig. 2A), or after flow through approximately three-fifths of the ALD. Flow through the remaining two-fifths of the ALD had little additional effect on concentrations of Ca and alkalinity.

Effluent concentrations of alkalinity ranged from 147 to 176 mg L⁻¹ (Fig. 3). During the 18-mo study period, effluent concentrations of alkalinity showed a slight downward trend with time, but the trend was not significant ($r = -0.45, P > 0.05$). The average retention time for the Howe Bridge ALD was 23 h (± 2 h). There was a weak correlation between effluent alkalinity and retention time ($r = 0.58, P < 0.02$).

Dissolved oxygen concentrations in the effluent averaged 0.3 mg L⁻¹ (± 0.1). The ALD had no discernable effect on concentrations of ions not directly involved in calcite dissolution. The concentrations of Fe²⁺, Mn, Mg, Na, and SO₄²⁻ changed by less than 1% between the influent and effluent sampling stations. The lack of change

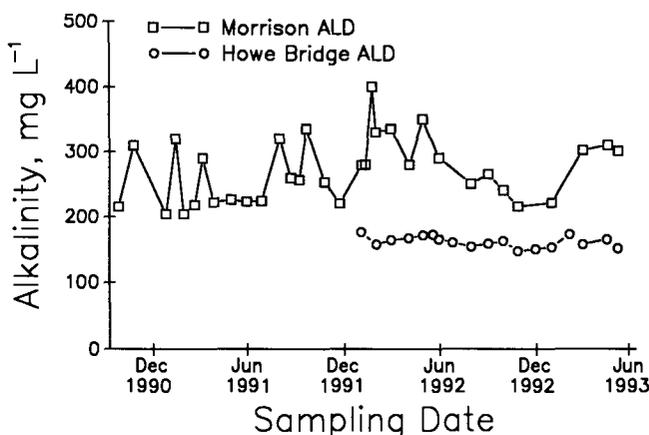


Fig. 3. Effluent concentrations of alkalinity at the Howe Bridge and Morrison ALDs. Data collection at both sites began within 2 mo of ALD construction.

in these parameters indicated that there was little dilution of mine water within the ALD by inputs of uncontaminated water.

Performance of the Morrison Anoxic Limestone Drain

Water samples at the Morrison ALD were collected from two wells within the limestone bed and from the ALD effluent. We were unable to directly sample mine water before it entered the Morrison ALD. An estimate of the chemistry of the mine pool (contaminated water unaffected by the ALD) was obtained from Seep W, a low-flow discharge of mine water located 10 m from the ALD (Table 4). Several aspects of the chemistry of Seep W indicated that it drained water from the same pool of contaminated mine water that supplied the ALD. The chemistry of Seep W was similar to the chemistry of the original seep that the ALD was designed to intercept (designated Pre-ALD in Table 4). Seep W was also compositionally similar to Well Y, the sampling well placed nearest to where mine water flowed into the ALD. Ion ratios for parameters unaffected directly by calcite dissolution were similar for the two sampling locations. The mean SO₄²⁻/Mg ratio was 10.8 for Seep W and 10.5 for Well Y. The mean SO₄²⁻/K ratio was 184.1 for Seep W and 177.6 for Well Y. These ratios would not have been so similar if Seep W and the ALD had drained different pools of mine water.

As mine water flowed through the Morrison ALD, its chemistry was affected by both dilution with uncontaminated water and reactions related to calcite dissolution. The dilution effect was estimated from changes in concentrations of Mg, K, and SO₄²⁻, because these parameters should be chemically and biologically conservative in the environments that existed within the limestone bed. Between the mine pool (Seep W) and the first ALD sampling station (Well Y), concentrations of SO₄²⁻, Mg, and K decreased by an average of 13%. Between the mine pool and Well Y, concentrations of Fe and Mn decreased by 13 and 12%, respectively, indicating that changes in metal concentrations were likely attributable to dilution with uncontaminated water.

Table 4. Mean concentrations of water constituents at the Morrison ALD, October 1990 to May 1993. Concentrations as mg L⁻¹ (alkalinity and acidity as CaCO₃) and flow as L min⁻¹. Standard deviations are shown in parentheses. *n* is sample size for all parameters in column, except K, *n* = 6, and dissolved oxygen (DO), *n* = 8.

	Pre-ALD†	Seep W	Well Y	Well Z	Effluent
pH	4.6(0.6)‡	5.3(0.2)	6.1(0.1)	6.2(0.1)	6.3(0.2)
Alk	5(6)‡	23(12)	201(42)	269(50)	271(50)
Al	NA§	1(<1)	<1	<1	<1
Ca	NA	119(15)	187(16)	221(14)	230(14)
Fe ²⁺	NA	216(32)	188(28)	169(44)	150(55)
Fe	199(127)	216(32)	188(28)	169(44)	151(55)
K	NA	7(<1)	6(<1)	6(<1)	6(<1)
Mg	NA	124(20)	107(16)	104(18)	102(21)
Mn	45(13)	51(8)	45(7)	43(8)	42(9)
Na	NA	48(8)	36(5)	35(6)	34(7)
SO ₄	1370(349)	1340(192)	1124(173)	1085(196)	1081(227)
Acid	432(128)	384(80)	185(65)	117(38)	99(36)
DO	NA	NA	<1(<1)	<1(<1)	2.6(0.9)¶ <1(<1)
Flow	NA	NA	NA	NA	6.8(3.5)
<i>n</i>	5	21	28	28	34

† Pre-ALD data provided by the mining company responsible for water treatment at the site.

‡ Laboratory measurements; field measurements were likely higher.

§ Data not available.

¶ First value represents samples collected from original effluent pipe. Second value represents samples collected from modified effluent pipe.

As mine water flowed from Well Y to the ALD effluent, concentrations of Mg, K, and SO₄²⁻ decreased by an average of 5%. Concentrations of Mn decreased by 6%, suggesting that concentrations of Mn were affected by dilution, not by retention of Mn within the ALD. Concentrations of Fe decreased by 20% between Well Y and the ALD effluent. Because this change was higher than for Mg, K, and SO₄²⁻, retention of Fe within the ALD was indicated.

Parameters directly involved in calcite dissolution were markedly affected by flow through the limestone bed. Between Seep W and the ALD effluent, pH increased by 0.9 units, alkalinity increased by 248 mg L⁻¹, and concentrations of Ca increased by 111 mg L⁻¹. All of the generation of alkalinity occurred between the mine pool and Well Z (Fig. 2B). Concentrations of alkalinity did not increase between Well Z and the effluent, a distance that accounted for one-half of the ALD. Most of the increase in concentrations of Ca also occurred by the time the mine water reached Well Z.

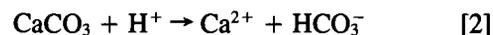
Dissolved oxygen concentrations in the Wells Y and Z averaged 0.7 (±0.7) mg L⁻¹ and 0.4 (±0.2) mg L⁻¹, respectively. Effluent samples collected early in the study contained 1.3 to 3.9 mg L⁻¹ dissolved oxygen. The elevated effluent DO values resulted from aeration of mine water within the horizontal effluent pipe. After this pipe was modified, so that no aeration of the mine water occurred between the ALD and the effluent sampling point (Fig. 1), dissolved oxygen concentrations were <1 mg L⁻¹.

Concentrations of alkalinity at the Morrison ALD effluent ranged from 204 to 400 mg L⁻¹ (Fig. 3). While there was a slight increasing trend in alkalinity concentrations during the 30-mo sampling period, the trend was not significant (*r* = 0.25, *P* > 0.10). The retention time of mine water within the Morrison ALD averaged 51 h (±35) and ranged from 16 to 192 h. This large range resulted from the highly variable Morrison flow rates (1.1–12.9 L min⁻¹) and also because modifications to the ALD effluent pipe during our study increased the

pore volume by 30%. Effluent concentrations of alkalinity were not correlated with retention times (*r* = 0.25, *P* > 0.10).

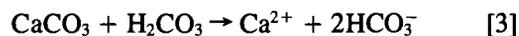
DISCUSSION

As mine water flowed through both ALDs, calcite dissolution caused the pH to rise and concentrations of Ca and HCO₃⁻ alkalinity to increase. The rise in pH occurred due to the reaction of calcite with hydrogen ion,



The alkalinity generated by this reaction was minor relative to the overall production of the alkalinity by the ALDs. The increase in pH at the Morrison ALD only accounted for a calculated generation of 0.2 mg L⁻¹ bicarbonate alkalinity (as CaCO₃). At Howe Bridge, where the influent pH was higher, the generation of alkalinity by Eq. [2] was 0.1 mg L⁻¹.

The principle bicarbonate-producing process at both ALDs was the reaction of calcite with carbonic acid,



Both mine waters sampled in this study had large calculated CO₂ pressures (Table 5) and, hence, large concentrations of carbonic acid. The influents of the Howe Bridge and Morrison ALDs had average calculated *P*_{CO₂} values of 6.39 kPa (10^{-1.20} atm) and 9.24 kPa (10^{-1.04} atm), respectively. These *P*_{CO₂} values were about 10 times greater than ones reported for uncontaminated spring and well waters in karst areas of the eastern USA (Langmuir, 1971; Shuster and White, 1971; Scanlon and Thrailkill, 1987). High CO₂ pressures for the two mine waters likely resulted from CO₂-producing processes within the mine spoil such as the neutralization of acidity by naturally occurring carbonates, the desorption of CO₂ from carbonaceous materials, and the oxidation of carbonaceous materials (Hem, 1985). The presence of high *P*_{CO₂} enhanced the alkalinity generating potential of the

Table 5. Carbon dioxide partial pressures (kPa) and saturation indices (IAP/ K_{sp}) for the ALD sampling stations. All values calculated using WATEQ4F (Ball et al., 1987).

Station	CO ₂ kPa(log(atm))	CaCO ₃ log(SI)	MgCO ₃ log(SI)	CaMg(CO ₃) ₂ log(SI)	FeCO ₃ log(SI)	MnCO ₃ log(SI)	CaSO ₄ log(SI)
Howe Bridge							
Influent	6.39(-1.20)	-2.65	-3.19	-5.91	-0.51	-1.39	-0.58
Well 1	7.51(-1.13)	-1.93	-2.51	-4.51	+0.16	-0.74	-0.54
Well 2	8.05(-1.10)	-1.45	-2.08	-3.60	+0.57	-0.32	-0.48
Well 3	6.39(-1.20)	-1.12	-1.79	-2.99	+0.86	-0.04	-0.46
Well 4	6.69(-1.18)	-1.10	-1.77	-2.94	+0.87	-0.02	-0.45
Effluent	7.87(-1.11)	-1.24	-1.90	-3.21	+0.75	-0.14	-0.47
Morrison							
Seep W	9.24(-1.04)	-3.22	-3.57	-6.86	-1.06	-1.74	-0.69
Well Y	13.05(-0.89)	-1.25	-1.86	-3.18	+0.61	-0.06	-0.55
Well Z	13.99(-0.86)	-0.94	-1.64	-2.65	+0.78	+0.14	-0.50
Effluent	11.37(-0.95)	-0.82	-1.54	-2.43	+0.83	+0.23	-0.48

ALDs by increasing the equilibrium concentrations of alkalinity (Hem, 1985) and by increasing the rate of calcite dissolution (Berner and Morse, 1974).

In both systems, calcite dissolution occurred predominantly in the first half of the ALDs. Little calcite dissolution occurred in the second half of either ALD (Fig. 2), despite the presence of mine waters that were still undersaturated with respect to calcite (Table 5). This asymptotic pattern of calcite dissolution was likely due to the large decrease in calcite dissolution kinetics that occurs as equilibrium is approached (Berner and Morse, 1974). The influents of the ALDs had SI_{Calcite} values of approximately $10^{-3.0}$, while the chemistry of both waters stabilized at SI_{Calcite} values of approximately $10^{-1.0}$ (Table 5). Laboratory studies by Berner and Morse (1974) suggest that the kinetics of calcite dissolution decrease by a factor of 10 over this range of SI_{Calcite} values. The decrease in calcite dissolution kinetics may have also been enhanced by the presence of large concentrations of Fe^{2+} and Mn. Calcite dissolution is inhibited by the presence of cations that form carbonate solids that are less soluble than calcite (Terjesen et al., 1961). Both Fe^{2+} and Mn form carbonates that are less soluble than $CaCO_3$.

Precipitation of Solids

The formation and precipitation of solids in an ALD is an important issue of ALD performance because of the possibility that solids will decrease the reactivity and permeability of the limestone bed. Equilibrium solubility calculations (Table 5) indicated that mine waters within both ALDs were supersaturated with respect to siderite ($FeCO_3$) and saturated with respect to rhodochrosite ($MnCO_3$). Despite these model results, little evidence for Fe or Mn retention was found. The Howe Bridge ALD did not effect concentrations of Fe or Mn. At the Morrison ALD, changes in concentrations of Mn were proportionally similar to changes in Mg, K, and SO_4^{2-} . Thus, dilution of Mn concentrations, not retention of Mn solids, was indicated.

The Morrison ALD did retain Fe. Concentrations of Fe at the Morrison ALD decreased from 216 mg L⁻¹ at the mine pool (Seep W) to 151 mg L⁻¹ at the ALD effluent. When the mine pool concentrations of Fe were adjusted downward by 17% to account for dilution,

the dilution-adjusted decrease in Fe concentrations was calculated as 28 mg L⁻¹. At an average flow rate of 6.8 L min⁻¹ and over the 30-mo study period, this change in concentration is equivalent to the retention of 249 kg of Fe. While we suspect that most of this retention resulted from siderite formation, we cannot discount the possibility that low-level inputs of dissolved oxygen resulted in the retention of Fe as an oxyhydroxide. There were no indications that retention of Fe was negatively affecting the performance of the Morrison ALD.

Long-Term Performance of Anoxic Limestone Drains

Over the course of this study, the Howe Bridge and Morrison ALDs dissolved calcite at mean rates of 17.9 and 2.7 kg d⁻¹, respectively (rates calculated from the difference of influent and effluent Ca and average effluent flow rates). The Howe Bridge ALD originally contained 373 000 kg of calcite (455 Mg of limestone with a 82% $CaCO_3$ content), which, at the current dissolution rate, would be exhausted in 57 yr. The Morrison ALD originally contained 59 000 kg of calcite, which would be exhausted in 59 yr.

Water within the Howe Bridge ALD did not reach a maximum alkalinity concentration until it reached Well 3, a distance that required an average 14 h of retention. Water within the Morrison ALD reached a maximum alkalinity value in the vicinity of Well Z, a distance that required an average 25 h of retention. As long as the retention times of mine water in the ALDs are greater than these plateau values, it is reasonable to expect that alkalinity concentrations will remain at current levels. However, when the loss of limestone through calcite dissolution causes retention time to decrease to less than 14 h, it is likely that concentration of alkalinity at the ALD effluent will also decrease. Assuming current dissolution rates and flow rates, retention times will decrease to 14 h in 23 yr at the Howe Bridge ALD, and in 42 yr at the Morrison ALD. These calculations do not account for changes in the structural integrity of the ALDs that will occur as calcite dissolution removes limestone mass. It is unknown at this time how long anoxic, porous conditions can be maintained in ALDs.

Table 6. Mean concentrations of water constituents at the Howe Bridge and Morrison passive treatment systems. Concentrations as mg L⁻¹ (alkalinity as CaCO₃). *n* is the sample size. All standard deviations were less than 50% of the mean.

Sampling point	<i>n</i>	pH	Alk	Ca	Fe	Mg	Mn	SO ₄
Howe Bridge								
ALD influent	17	5.6	33	159	279	107	41	1323
ALD effluent	17	6.2	161	211	277	107	40	1329
Pond effluent	17	5.6	23	182	195	96	39	1177
Wetland effluent	17	6.1	86	234	80	96	35	1053
Morrison								
Seep W	21	5.3	23	119	216	124	51	1340
ALD effluent	34	6.3	271	230	151	102	42	1081
Pond effluent	24	6.3	34	162	5	72	24	756
Wetland effluent	24	6.6	57	164	<1	70	11	717

Performance of the Total Passive Treatment Systems

At both study sites, the ALDs were one component of multicomponent passive treatment systems. The ALDs precede ponds and wetlands in which the bicarbonate alkalinity supplied by limestone dissolution facilitates the precipitation of metal contaminants. At the Howe Bridge site, the ALD effluent flows into two open water ponds, and then into a wetland constructed with an organic substrate that was underlain with limestone. Aerobic conditions in the ponds promote Fe²⁺ oxidation reactions and the precipitation of ferric oxyhydroxides. Bacterial processes and limestone dissolution in the wetland substrate continue to precipitate Fe and add additional alkalinity to the water. Before construction of the passive treatment system, water flowed untreated into the receiving stream. Since construction of the passive system, the Fe load to the stream has decreased by about 70% (Table 6).

At the Morrison passive treatment system, mine water flows from the ALD into a pond and then through two wetlands constructed with an organic substrate. Before construction of the ALD, water flowed through the same ponds and wetlands, but required the addition of alkaline chemicals to satisfy Pennsylvania Department of Environmental Resources effluent criteria (Fe < 3 mg L⁻¹ and pH 6–9). Since construction of the ALD, the wetland effluent has met effluent criteria without the addition of chemicals (Table 6).

SUMMARY

The Howe Bridge and Morrison ALDs both improved water quality by significantly increasing concentrations of bicarbonate alkalinity. Neither ALD showed an indication of deteriorating performance over the 18- to 30-month monitoring period. The Morrison ALD discharged water that contained 80% greater concentrations of alkalinity than the Howe Bridge ALD. Superior alkalinity generation by the Morrison ALD was not due to differential retention time, because both ALDs contained excessive amounts of limestone. The greater effluent concentrations of alkalinity were likely due to the Morrison influent mine water having greater *P*_{CO₂} and smaller *SI*_{Calcite} values. The findings indicate that while design and construction parameters can be manipulated to effect the theoretical lifetime of ALDs, the actual alkalinity generation of an ALD is strongly influenced by chemical characteristics of the influent mine water.

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