Technical Article

Long-term Performance of Anoxic Limestone Drains

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Abstract. Ten anoxic limestone drains (ALDs), buried beds of limestone gravel that add alkalinity through dissolution of calcite, have been monitored for a decade. Influent and effluent water quality data have been analyzed to determine the long-term performance of each ALD for treating coal mine drainage. Alkalinity concentrations in the effluent of the ten ALDs ranged from 80 - 320 mg/L as $CaCO_3$ with near maximum levels of alkalinity being reached after approximately 15 hours of detention. ALDs that received mine water containing less than 1 mg/L of both ferric iron and aluminum have continued to produce consistent concentrations of alkalinity since their construction. However, an ALD that received 21 mg/L of aluminum experienced a rapid reduction in permeability and failed within eight months.

Key words: Passive treatment, acid mine drainage, ALD, calcite dissolution.

Introduction

Iron-laden water from abandoned coal mines contaminates thousands of miles of rivers and streams in the United States. Federal agencies, state and local governments, and grassroots watershed groups share the goal of restoring these waters to a quality sufficient to support fish and other aquatic life. Because the long-term care of any remediation technology eventually rests with the watershed groups, low-cost maintenance is a desirable feature. For this reason, passive treatment technologies are usually preferred.

The chemistry of a particular mine drainage dictates the steps necessary to restore water quality. Net

alkaline drainage requires only oxygen, sufficient time for oxidation and precipitation to occur, and a quiescent pool or pond to settle and collect the fine product. Traditionally, these requirements have been successfully met using aerobic wetlands. Typical aerobic wetlands consist of an aeration device, such as a rip-rapped ditch or waterfall, a deep (1.2 - 2.4 m) unvegetated pond, and a shallow (~0.15 m) wetland that usually contains cattails (typically *Typha latifolia*) that are either planted or invasive. The deeper pond collects the majority of the precipitated iron oxides. The cattail wetland is designed to remove the remaining iron. Experience shows that these systems remove 10 to 20 g of iron per square meter of wetted area (ditches, ponds, wetlands) per day (Hedin et al. 1994a). However, this is a conservative estimate; actual rates are dependent on iron concentration, dissolved oxygen concentration and pH. Removal of manganese can occur in these systems, but only after the iron is removed (Hedin et al. 1994a). Manganese removal is seasonal, with greater removal occurring at higher temperatures. Because of the much larger areas required for manganese removal (about 20 times the area needed for equivalent iron removal), and the generally non-toxic effects of manganese, except in very soft waters (Kleinmann and Watzlaf 1988), iron removal is the priority at many abandoned mine land (AML) sites. Manganese is typically removed to the greatest extent possible given the area and funding limitations for the project.

Net acidic drainage requires the addition of alkalinity prior to the aerobic wetland. A number of passive and semi-passive treatment technologies have been used to add alkalinity to net acidic waters. ALDs and reducing and alkalinity-producing systems (RAPS) are the most

$$H^+ + CaCO_3 \rightleftharpoons Ca^{2+} + HCO_3^- \qquad (1)$$

frequently used passive systems. RAPS (also known as successive alkalinity-producing systems (SAPS), vertical flow wetlands (VFW), or vertical flow systems (VFS)) consist of three layers that include standing water, organic matter, and limestone gravel (Kepler and McCleary 1994). The water first flows down through the organic layer (0.15 - 0.61 m thick). The purpose of the organic layer is to provide an environment suitable for the growth of sulfate reducing bacteria (SRB) which generate bicarbonate alkalinity. Further, this produces a reductive zone which removes dissolved oxygen and may convert ferric iron to ferrous iron. The extent to which the organic matter may directly remove the contaminates, such as by ion exchange or adsorption, has not been clarified. Many forms of organic material have been used; in and around Pennsylvania, spent mushroom compost has been the organic material of choice. The approximate composition of this type of compost includes horse manure (56% by weight), hay (22%), straw (10%), chicken manure (10%), and gypsum (2%). Variable amounts of crushed limestone are often added to the compost when the inlet pH would be too low to permit the establishment of the SRB without some prior neutralization. The water then flows through the limestone layer (0.6 -1.2 m thick), which adds additional alkalinity by the dissolution of calcite. The iron precipitates down-gradient after contact with the atmosphere. These systems have been found to produce 30-60 $gd^{-1}m^{-2}$ of alkalinity (Watzlaf and Hyman 1995; Watzlaf et al. 2000).

An ALD is a buried bed of crushed limestone engineered to intercept mine water while it is in an anoxic state (Turner and McCoy 1990). The ALD relies on the dissolution of limestone as the alkalinity addition technique. This is in contrast to RAPS, which also incorporate an additional microbial mechanism. ALDs are used for the sole purpose of generating alkalinity and, like RAPS, must be followed by ponds and aerobic wetlands to oxidize and remove the dissolved iron and manganese. Dimensions are typically on the order of 1 m deep, 1-7 m wide, and 25-100 m long. The limestone neutralizes acid in the mine drainage (Equation 1) and adds bicarbonate alkalinity.

Factors affecting the level of the resultant alkalinity include the contact time, the initial partial pressure of carbon dioxide, the initial pH, the stone size of the crushed limestone, the calcium carbonate content of the limestone, and the initial calcium concentration in the drainage. The first two factors, contact time and partial pressure of carbon dioxide, have been shown to significantly affect the final concentration of alkalinity in the effluent (Hedin et al. 1994b).

Field tests show that relatively high rates of limestone dissolution occur within the initial 15 hours of contact with mine water. After this contact period, the rate of limestone dissolution is much slower. For this reason, most ALDs are sized to have a 15-hour detention time at the end of its design life (25-30 years). Therefore, ALDs have significantly higher initial detention times (greater than 15 hours) to allow for the quantity of limestone that will dissolve during the 25- to 30-year life of the ALD (Hedin and Watzlaf 1994).

Metal removal must necessarily occur elsewhere to prevent clogging of the bed and premature failure. Inadvertent metal removal in the ALD will reduce the effective lifetime by lowering permeability and/or coating the stone (armoring), thereby reducing calcite dissolution rates. For this reason, ALDs are not appropriate for waters high in aluminum, because aluminum becomes insoluble at pH values between 4.5 and 8.5 (Stumm and Morgan 1970). Also, the ALD must be kept anoxic to prevent the oxidation of soluble ferrous iron to the insoluble ferric species. Air is excluded by keeping the ALD inundated with water and by capping the limestone with soil, clay, and/or plastic sheeting. Additionally, capping may increase the extent of calcite dissolution and alkaline addition by trapping evolved carbon dioxide, which promotes further calcite dissolution via equation 2.

$$CO_2 + H_2O + CaCO_3 \rightleftharpoons 2 HCO_3^- + Ca^{2+} \quad (2)$$

ALDs are self-buffering, providing a pH of about 6.5, so that it is essentially impossible to overtreat the water. Controlled pH and anoxic conditions are key elements in

the prevention of the precipitation and retention of ferrous iron and manganese in the drain. In practice, ALDs, RAPS, settling ponds, and aerobic wetlands should all be viewed as potential components of a total remediation system. For example, ALDs are followed by settling ponds and aerobic wetlands for oxidation, precipitation and settling of metals.

In this paper, we describe the results obtained from long-term monitoring of ten ALDs located in Pennsylvania and Maryland and estimate the longevity of those systems that are still functioning. In addition, we document failures where they have occurred, and attempt to ascertain the cause so that more robust systems might be designed for future application.

Methods

Grab samples representative of influent and effluent water quality were collected periodically, always during daylight hours but without regard to ambient temperature or precipitation events. For four of the ALDs, additional water samples were collected from wells placed along the flow-path of the drain. Alkalinity was measured in the field using either the Orion Total Alkalinity Test Kit and a calibrated pH meter or the Hach Digital Titration method. All pH measurements were made in the field using Orion 250A or 290A meters with standard pH electrodes. The pH meter was calibrated using standard buffer solutions prior to measurements at each site. At each sampling location, an unacidified and acidified sample (150 mL each) were collected. Samples containing visible particulate matter were filtered through a 0.2-micron syringe filter prior to acidification with concentrated HCl (2 mL). Acidification lowered the pH to below 1.0. Samples were transported to the analytical laboratory and analyzed using standard methods. Acidity was determined by adding H_2O_2 to the sample, heating, and titrating the solution to pH 8.2 with NaOH (American Public Health Association, 1998). If the sample was net alkaline, it was heated with H_2O_2, and then the solution was titrated with H_2SO_4 to a pH of 4.5. Net alkalinity was reported as a negative net acidity. Metal concentrations in the acidified samples were determined using inductively coupled argon plasma -

atomic emission spectroscopy (ICP-AES). Ferrous iron concentrations were determined by titration with $K_2Cr_2O_7$ (Fales and Kenny, 1940). Ferric iron was calculated as the difference between total and ferrous iron. Sulfate concentrations were determined using ion chromatography for samples collected before November, 1992. After this date, sulfate concentrations were determined by ICP-AES (as total sulfur) on water samples that had been acidified and boiled to remove any hydrogen sulfide. The agreement between these methods was found to be good (within 2%).

Flow rates were measured at the effluent of the ALDs by the time necessary to collect a known volume of water (bucket and stopwatch method). Typically, five measurements were averaged to determine each flow.

Tracer tests were conducted on two of the ALDs. Concentrated solutions of sodium bromide were added to the influent flow. Samples were collected at the effluent after selected periodic intervals (1-8 hrs) using automatic samplers. Bromide concentrations were measured using a specific ion electrode (in the field) and by ion chromatography (samples returned to lab) with suppressed conductivity detection using a standard anion column. In analyzing the tracer data, the effective (or mean) detention time (t_e) was calculated by $t_e = E[(C_t t)\Delta t]/E(C_t \Delta t)$, where C_t is the bromide concentration at time t, t is the time after tracer addition, and Δt is the time between samples.

Detention times (t_d) were calculated based on ALD volume (V) and average flow (Q), using $t_d = 0.49V/Q$. Porosity was determined using containers of known volume filled with the limestone used in the ALDs. The amount of water it took to fill these limestone-filled containers to the top of the limestone was measured. An average value of 49% for porosity was obtained.

Site descriptions

All sites are located in western Pennsylvania, with the exception of the Elklick site, which is located in northwestern Maryland. Discharges are associated with

Allegheny group coals (mainly the Kittanning and Clarion seams) formed during the Pennsylvanian period.

Howe Bridge 1 - Mine pool discharge, which occurs through an abandoned gas well, is captured and piped to the ALD. Influent water is sampled via a well prior to contact with limestone. Four sampling wells are evenly spaced along the length of the drain.

Howe Bridge 2 - Mine pool discharge, which occurs through an abandoned gas well, is treated in an S-shaped ALD. Influent water is sampled via a well as the water flows into the beginning of the ALD. Two sampling wells are located along the length of the ALD.

Morrison - Seepage is intercepted at the toe of the spoil of a reclaimed surface mine. After the ALD was built, another seep, similar in quality to the pre-construction water, was discovered, and is being used to represent influent water quality. Two sampling wells are located along the length of the ALD.

Filson (R and L) - Seepage is intercepted at the toe of the spoil. A seep, located between the ALDs, is similar in quality to the pre-construction raw water and is used to represent influent water quality.

Elklick -Water from an abandoned borehole is collected in a bed (7.0 m x 1.8 m x 0.9 m) of crushed, low-pyrite sandstone at the head of the ALD. Influent water is sampled at a well located in this sandstone. Three sampling wells are equally spaced along the length of the ALD.

REM (R and L) and Schnepp - ALDs were constructed downslope from collapsed underground mine entrances. Influent water quality is based on historical data. Use of historical data to represent influent water quality may overestimate contaminant levels since water quality elsewhere in the watershed has improved significantly over the past decade.

Jennings - An abandoned underground mine discharge was collected in an inert river gravel bed and piped to the system. Influent water was sampled prior to contact with limestone via a sampling well. The ALD consisted of a series of 6 buried limestone cells. Water flowed into the bottom of each cell and exited through the top before being piped to the next cell.

Additional details on the construction of each ALD are presented in Table 1.

Results and Discussion

Tracer Studies

To obtain information about the flow characteristics within the ALDs, tracer studies were undertaken at two of the sites in which a known amount of bromide in solution was injected into the ALD. The effluent from the drain was then monitored for the concentration of bromide emanating over periods of hours and days. The concentration profile obtained at the Howe Bridge site is shown in Fig. 1. The second experiment, at the Morrison site, produced a similar profile. The profiles are asymmetrical with rapidly rising concentrations at shorter times and gradually dropping concentrations at longer times. Such profiles may be the result of a number of factors, such as diffusion, channeling, back-mixing, adsorption, and mobile phase saturation, acting simultaneously. In the case of ALDs, the first three factors predominate.

In Table 2, a number of descriptive statistics that can be used to characterize the flow are compared to the detention time calculated using the drain volume and the aforementioned 49% void volume. In both cases, the maximum concentration occurred fairly soon after the first appearance of the bromide in the effluent. The time required for 50% of the material to exit the drain, the median detention time, was considerably longer than the time to peak and was the statistic that most closely matched the calculated detention time. The time-weighted average, or mean, or effective detention time

Table 1. Dimensions, stone size and quality, and source of influent water quality data for ALDs.

ALD Site	ALD Dimensions: Length x Width x Depth, meters			Limestone		Influent Water Quality Data Source
				size, cm	% CaCO$_3$	
Howe Bridge 1	36.6	6.1	1.2	5.1 - 7.6	82	Well
Howe Bridge 2	13.7	4.6	0.9	5.1 - 7.6	82	Well
Elklick	36.6	3.1	0.9	5.1 - 20.3	85	Well
Jennings[1]	228	1.0	1.0	15.2	90	Well
Morrison	45.7	0.9	0.9	5.1 - 7.6	92	Adjacent Seep
Filson - R	54.9	6.1	0.9	5.1 - 7.6	88	Adjacent Seep
Filson - L	54.9	6.1	0.9	5.1 - 7.6	88	Adjacent Seep
Schnepp	12.2	6.1	0.9	1.9 - 2.5	90	Historical
REM - R	13.7	7.6	0.9	7.6	82	Historical
REM - L	61.0	16.8	0.9	7.6	82	Historical

[1] The Jennings ALD is composed of 6 sequential cells, each cell approximately 38 m x 1 m x 1 m.

was longer yet. Of these statistics, we consider the median time to be the better measure of performance for ALDs. The ratio of the median (50% eluted) to the mean (effective) detention time is less than one. This indicates that a disproportionate amount of material is eluting at times earlier than expected for an ideally behaving plug-flow system and is interpreted as an indication of channeling (i.e., short-circuiting). In addition, concentrations of bromide above background levels continued to be measured in ALD effluent for several days after tracer addition, indicating that more material is eluting at times longer than would be expected ideally. This is taken as an indication that back-mixing or dead areas exist within the drain. Thus, the ALDs appear to provide both shorter and longer detention times than would be expected based on simple plug-flow. Channeling is of concern because it leads to inefficiencies in calcite dissolution. The longer residence times of some of the mine water is not necessarily beneficial, because the concentration of alkalinity in this water does not increase significantly after 15 hours of contact with the limestone (*vide infra*).

Limestone Dissolution and Alkalinity Production

Data describing the 10 ALDs in this report are listed in Tables 1, 3 and 4. These ALDs intercept flows ranging from about 10 to about 100 L/min. When possible, ALDs were designed to provide a detention time of at least 15 hours. The importance of detention time is seen in Fig. 2, where the amount of alkalinity in the effluent ALD water is plotted as a function of the time the water is in contact with the limestone (detention time). These data were obtained at four sites where sampling wells had been installed at regular intervals along the length of the ALD. The mine water increases in alkalinity as it travels through the ALD until it approaches a maximum after about 15 to 20 hours of contact. As can be seen by the shape of the plots in Fig. 2, the ultimate level of alkalinity addition varies from ALD to ALD but the rates at which the alkalinity level increases appear to be nearly first order with a half-life of about 5 hours. A minimum contact time of 15 hours ensures that at least 85% of the maximum achievable alkalinity is realized.

The variation in the level of alkalinity addition (Fig. 2) cannot be attributed to the size of the limestone because it was the same for all four ALDs. There is a trend of increasing limestone dissolution with decreasing pH for the data presented; however, the final concentration of alkalinity produced in an ALD depends on factors other that just the pH of the water to be treated. An empirical test has been developed to estimate the alkalinity concentration that will be produced in an ALD using the actual mine water and limestone in collapsible containers (cubitainers) (Watzlaf and Hedin 1993). With this, one can determine limestone consumption rates, the quantity of limestone needed for a desired design life, and whether the ALD will make the mine water net alkaline.

All of the ALDs successfully add alkalinity, increasing the effluent levels by 50 to 270 mg/L (Table 4). The smallest increases, observed at REM-R and REM-L, are undoubtedly due to the short detention times afforded by these ALDs (Table 2). At half of the sites, a single ALD was sufficient to convert net acidic to net alkaline drainage. In the other 5 cases, the acidity produced from iron concentrations in excess of 200 mg/L was greater than the amount of alkalinity generated in the ALD. The increases in the alkalinity measured between the inlet and outlet of each drain correlate with the increase in the calcium concentration. The average molar ratio of the increases in calcium and alkalinity, as $CaCO_3$, ((calcium out - calcium in)/(alkalinity out -alkalinity in)) was 1.02 for the seven cases for which all the data were available. This compares well with the expected ratio of 1.00. In general, ALDs receiving water with low aluminum and ferric iron concentrations, and designed with detention times greater than 15 hours, have generated alkalinity at a consistent rate throughout their existence (Fig. 3). The effluent concentrations of alkalinity in the ALDs indicate consistent performance over the past ten years. The significantly higher alkalinity values for the last sample points for Filson R and L in Fig. 3 were due to very high detention times reflecting very low flows

caused by a drought during that summer and into the fall. Detention times in these ALDs were increased by more than a factor of four during this low flow period. Flows at the other ALDs (Howe Bridge 1 and Elklick) shown in Fig. 3 were not significantly affected by the drought. It is also of interest to note that no seasonal variation was observed for these ALDs, presumably due to the fairly narrow range of influent water temperatures, typical of groundwater, and relatively consistent flow rates.

The amount of calcium carbonate remaining in these ALDs was calculated using the difference between the influent and effluent net acidity loadings over the period of time the system has been in use. Based on the quantity of limestone remaining and assuming that the volume of the drain collapses around the shrinking core of limestone (i.e., void volume remains at 49%), the current detention times were calculated. As would be expected, detention times become shorter as the limestone is consumed.However, most ALDs are still operating at near maximum efficiency because detention times remain in excess of 15 hours. As an estimate of expected longevity, the year in which the ALD detention time is expected to fall to the 15 hour minimum, was calculated from a linear extrapolation of the average rate of limestone consumption to date (last column of Table 3). Over half of the ALDs are still expected to meet or exceed their design life of 30 years. Three were undersized as built due to resource constraints at the site. The Jennings ALD is no longer in operation because of failure due to clogging and is described in more detail below.

Water quality changes

In addition to increases in calcium and alkalinity, changes in other effluent water quality parameters (pH, sulfate and metals) were observed and are discussed in this section. Influent and effluent water quality analyses

Table 2. Detention times of two ALDs based on tracer test data and calculated from volume and flow.

ALD	Time to first appearance, hrs	Time to peak, hrs	Time for 50% of tracer to elute, hrs	Effective detention time[1], hrs	Calculated detention time[2], hrs
Howe Bridge 1	7	16	30	40	25
Morrison	4	10	61	87	47

[1] Effective detention time (t_e) calculated by $t_e = E[(C_t t)\Delta t]/E(C_t \Delta t)$, where $C_{\bar{t}}$ = bromide concentration at time t, t = time after tracer addition, and Δt = time between samples.

[2] Calculated detention time (t_d), based on limestone volume (V) and average flow rates (Q) by $t_d = 0.49 V/Q$, using 49% for porosity.

for the ALDs are presented in Tables 4 and 5. For four of the ALDs (Howe Bridge 1, Howe Bridge 2, Elklick, and Jennings), influent samples could be collected immediately before the water flowed into the ALD. For three of the ALDs (Morrison, Filson-R, and Filson-L), seeps in the immediate vicinity were sampled to represent influent water quality. For the remaining three ALDs (REM-R, REM-L, and Schnepp), influent water quality was based on historical data.

In general, the pH increased as the alkalinity increased until a pH of about 6.4 was achieved above 160 mg/L. The seven pH measurements corresponding to alkalinities above 150 mg/L gave an average pH of 6.45 ± 0.20 s.u. Thus, the effluent of an ALD resembles a bicarbonate buffered solution, as would be expected for a mixture of mineral acid and carbonate alkalinity.

Sulfate concentrations are not affected by the ALDs. The first 4 entries in Table 3, which represent matched influent/effluent samples, never show more than a 15 mg/L loss of sulfate. Subsequent entries do show some larger sulfate loses but only historical or adjacent seep data are available for the influen and thus the apparent losses are suspect. Sulfate loses would not be expected in these ALDs. Chemical precipitation as gypsum is unlikely at these low calcium concentrations. There is no added organic matter in these ALDs to act as ion exchange material or to provide a source of carbon for sulfate-reducing anaerobes, such as occurs in RAPS. Although sulfate reduction does not appear to be active

in the systems studied here, it cannot be ruled out automatically for all ALDs. In some cases, mine drainage becomes associated with other pollution sources, such as feedlot run-off or contributions from leaking sewers or septic systems. In such cases, a source of organic carbon would be present, which could provide an acceptable environment for anaerobic, sulfate-reducing bacteria within the ALD. In those cases where matched influent and effluent samples were obtainable (Howe Bridge 1, Howe Bridge 2, Elklick, and Jennings), the iron balances (with the exception of Jennings) indicated that iron was not retained within the ALD. The influent water at Jennings contained both ferrous and ferric iron. At the other three sites, all (>99%) of the iron was in the ferrous form. As already discussed, at the sites where inlet concentrations were estimated from historical data, the listed "in" value probably overestimated the contamination actually entering these ALDs. Manganese balances across the ALDs indicated that little or no retention was occurring. Chemical precipitation as an oxide or hydroxide would not be expected in water having a pH of less than 7 under anoxic conditions. Although manganese carbonate precipitation is a possibility, there was no indication that this was occurring at the ALDs in this study.

Only three of the sites had water containing aluminum in excess of 1 mg/L. The highest aluminum concentration was observed at the Jennings site (21 mg/L) and is thought to be responsible for the premature failure of this ALD.

Table 3. Initial and current conditions of anoxic limestone drains. The term t_d represents detention time.

ALD Site	Year Built	Initial Conditions		Avg. Flow	Current Conditions		Year when
		Limestone	t_d^1		Limestone	t_d^1	$t_d = 15$ hours
		tonnes	hrs	L/min	tonnes	hrs	
Howe Bridge 1	1991	455	25	96.8	405	22	2021
Howe Bridge 2	1993	132	15	48.4	109	12	1993
Elklick	1994	165	22	37.1	153	20	2017
Jennings	1993	365	27	73.4	356	n/a	n/a
Morrison	1990	65	47	8.0	52	32	2019
Filson-R	1994	590	72	44.0	559	68	2078
Filson-L	1994	635	109	31.2	611	105	2114
Schnepp	1993	130	30	19.8	116	27	2023
REM-R	1992	125	6.8	112	88	4.8	n/a
REM-L	1992	125	8.1	96.2	80	5.2	n/a

[1] t_d based on limestone volume (V) and average flow (Q) using $t_d = V/Q$, assuming 49% porosity. n/a - not applicable
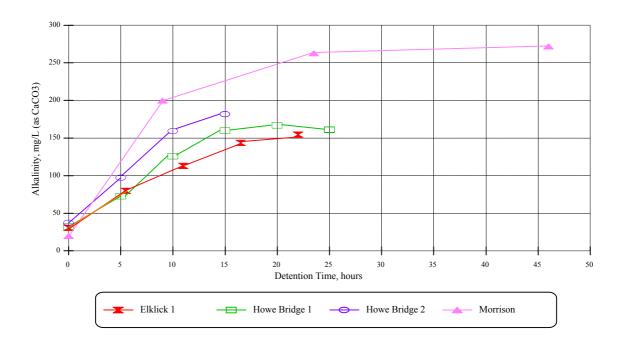

Figure 1. Alkalinity concentrations as water flows through selected ALDs.

Table 4. Average water quality before and after contact with the anoxic limestone drain.

ALD	Net Acidity,[1] mg/L as CaCO$_3$		Alkalinity, mg/L as CaCO$_3$		Calcium, mg/L		pH, s.u.		Sulfate mg/L	
	In	Out	In	Out	In	Out	In	Out	In	Out
Howe Bridge 1	472	352	32.6	155	115	223	5.74	6.30	1319	1314
Howe Bridge 2	411	274	35.3	163	157	209	5.40	6.48	1210	1211
Elklick	52.0	-63.0	33.8	159	258	232	6.06	6.73	334	327
Jennings	280	-33.5	0	139	ND	201	3.23	6.16	633	620
Morrison[2]	387	51.4	28.7	278	82.9	208	5.19	6.35	1256	1016
Filson-R[2]	100	-139	47.9	299	69.2	180	5.73	6.49	408	438
Filson-L[2]	104	-175	47.9	317	77.1	129	5.73	6.60	408	395
Schnepp[3]	307	-42.5	0	168	69.2	189	3.28	6.17	980	745
REM-R[3]	1148	835	0	54	258	206	4.28	5.45	2825	2394
REM-L[3]	ND	259	ND	113	ND	198	ND	6.00	ND	1256

[1] Negative net acidity values indicate net alkalinity.

[2] "In" concentrations based on water quality of a nearby seep.

[3] "In" concentrations based on historical water quality data of the untreated mine drainage prior to construction of the ALD. Numbers are not available for REM-L. ND = Not Determined
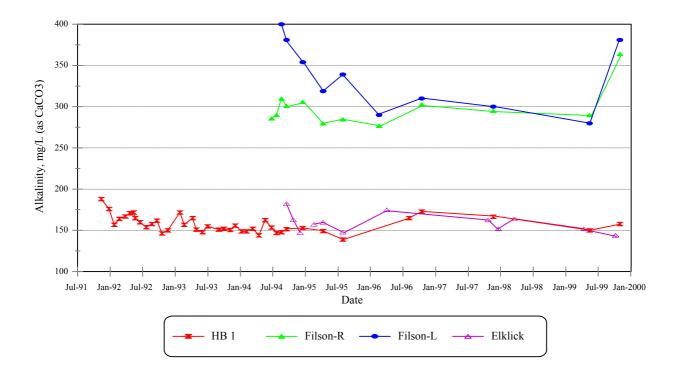

Figure 2. Effluent alkalinity concentrations of selected ALDs.

Table 5. Additional water quality parameters before and after contact with the anoxic limestone drain.

ALD	Iron, mg/L		Manganese, mg/L		Aluminum, mg/L		Cobalt, mg/L		Nickel, mg/L		Zinc, mg/L	
	In	Out	In	Out	In	Out	In	Out	In	Out	In	Out
Howe Bridge 1	276	275	41.5	41.5	<0.2	<0.2	0.48	0.48	0.51	0.50	0.62	0.55
Howe Bridge 2	250	248	36.6	35.9	<0.2	<0.2	0.39	0.39	0.40	0.40	0.42	0.39
Elklick	59.2	53.3	4.77	4.89	<0.2	<0.2	0.07	0.07	0.10	0.09	0.13	0.08
Jennings	75.6	59.3	8.39	8.33	20.9	1.1	0.13	0.15	0.40	0.40	0.66	0.54
Morrison[1]	207	156	48.7	40.9	0.5	<0.2	0.86	0.75	0.79	0.65	0.95	0.72
Filson-R[1]	59.3	55.5	19.9	19.8	0.4	<0.2	0.23	0.23	0.18	0.18	0.27	0.18
Filson-L[1]	59.3	68.6	19.9	15.9	0.4	<0.2	0.23	0.13	0.18	0.10	0.27	0.17
Schnepp[2]	92	61.5	28	26.3	6.7	<0.2	ND	0.27	ND	0.33	ND	0.34
REM-R[2]	589	447	136	126	4.5	3.2	ND	1.49	ND	1.54	ND	246
REM-L[2]	ND	185	ND	50.8	ND	<0.2	ND	0.60	ND	0.66	ND	0.76

[1] "In" concentrations based on water quality of a nearby seep.
[2] "In" concentrations based on historical water quality data of the untreated mine drainage prior to construction of the ALD.
ND - Not Determined

The ALDs receiving 5 and 7 mg/L of aluminum (based on historical water quality) at REM-R and Schnepp, have continued to operate since 1992 and 1993, respectively. Because the actual influent water samples were unobtainable, the average aluminum concentrations that these ALDs received is uncertain. Presumably, it is somewhat less than the 5-7 mg/L (based on historical data). The untreated mine water quality at other sites in this watershed has shown a general and significant improvement over the past ten years. Using historical data for the influent water quality biases the data with the more contaminated water samples collected and analyzed 7 or more years ago.

The concentrations of cobalt, nickel, and zinc were low in these waters and seldom exceeded 1.0 mg/L. Cobalt and nickel do not appear to be retained in the ALDs. Zinc appears to be diminished in all of the effluents but only by 0.1 mg/L or less. Some removal of zinc at higher concentrations (ca. 5-10 mg/L) within ALDs has been reported by Nuttall and Younger (2000).

Premature failure of the Jennings ALD

Construction of the ALD at the Jennings site was completed during April 1993; water treatment began on April 20. Although the ALD successfully reduced the acidity of the mine water, the amount of flow passing through it began to decrease after about 6 months, as seen in Figure 4. In September 1993, a small leak developed near the beginning of the third ALD cell. The flow from this leak progressively increased until it accounted for more than 80% of the total flow by January 1994.

Analysis of the water quality data provided insight into the reason for and possible mechanisms of failure. In addition to the flow data, Fig. 4 indicates the extent of metals retention in the ALD. Essentially 100% of the aluminum was retained within the ALD. Most of the ferric iron, which accounted for about 10% of the total iron in the mine water, was also retained in the ALD. Nearly 100% of these two species were retained with no loss in efficiency even as the flow deceased towards the end of 1993. Both of these species form stable

precipitates under the ambient conditions in the ALD, and are undoubtedly responsible for the decreasing permeability and eventual clogging of the drain. In addition to the constant removal of the two easily precipitated species, there is an initial retention of ferrous iron during the first few months of operation, probably due to oxygen scavenging by the ferrous species, adsorption on limestone surfaces or ion exchange on clay minerals in the limestone. The air present within the drain during construction contains oxygen, which is available for reaction if it is not flushed from the system prior to operation. Up to 40% of the iron retained in the drain may have resulted from the oxidation of ferrous iron and the subsequent precipitation of ferric hydroxide. The total quantity of retained material was calculated to be 581 kg of aluminum and 572 kg of iron. Thus, a combination of both iron and aluminum could be responsible for clogging the Jennings ALD; however, it might be argued that aluminum was more important for two reasons. First, given the assumption discussed above, that about 40% of the iron precipitate was due to oxidation, and that some of the rest was due to adsorption processes, it probably occurred throughout the ALD rather than in the one section where the actual plug developed. Second, the portion of the ALD where the clog was suspected was excavated, revealing the formation of a white gelatinous substance, similar to aluminum precipitates seen elsewhere. Aluminite has been reported as the priciple mineral phase responsible for the failure of at least one ALD. In that case, both Si and bacteria were also present (Robbins et al. 1996). Although aluminum is thought to be the major problem at this site, the lack of analytical data prevents firm conclusions. In the absence of reducing conditions, such as are generated in RAPS, ferric iron in the influent may also precipitate.

Conclusions

ALDs can effectively treat net acidic mine water. The ideal influent water quality for an ALD is net acidic water with a pH above 5.0. At this pH, neither ferric iron nor aluminum are soluble in significant quantities.
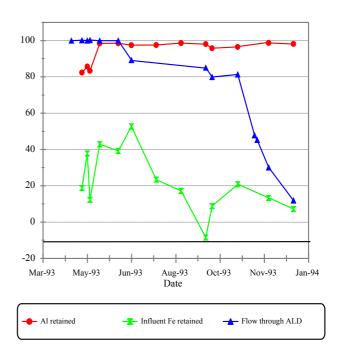

Figure 3. Flow of water through ALD and percent of influent aluminum and iron retained in the ALD at Jennings.

Intercepted ground water is typically low in dissolved oxygen, and often contains partial pressures of carbon dioxide higher that atmospheric levels, which allows for development of alkalinity concentrations greater than 100 mg/L as $CaCO_3$. Near maximum levels of alkalinity (usually between 150 and 300 mg/L) can be achieved with 15 hours or more of contact time. ALDs are tolerant of both ferrous iron and manganese because they remain soluble within the ALD. However, the presence of ferric iron and particularly aluminum can reduce permeability of the ALD by precipitation of these metals within the voids in the limestone. This has been documented in an ALD (Jennings) that received 21 mg/L of aluminum and clogged within eight months. In the absence of ferric iron and aluminum, ALDs have continued to perform well with no obvious seasonal variation nor long-term reduction in effectiveness.

Tracer studies indicated that while they approximate plug-flow systems, some short circuiting occurs and dead areas do exist. Calculated detention times, using

49% porosity, were in fairly good agreement with the median detention times of the tracer tests.

Characterization of influent water quality and quantity, including seasonal variation, is important prior to the development of a passive treatment design (see Hyman and Watzlaf 1995). The presence or absence of periodic events, such as spring flushes of deposited aluminum salts from within the mine, may favor using one technology over another. Water quality data will determine the applicability of an ALD and flow data will provide sizing criteria for an ALD that will remain effective for the desired design life. At mine sites where the ALD was appropriate and sized properly, effective treatment of mine drainage has resulted, provided the ALD was followed by ponds and/or wetlands for iron oxidation, precipitation, and settling. At these sites, it is projected that the ALD will be effective for the designed lifetime of 25 to 30 years and, in some cases, well beyond.

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