LONG-TERM PERFORMANCE OF ALKALINITY-PRODUCING PASSIVE SYSTEMS FOR THE TREATMENT OF MINE DRAINAGE[1]

George R. Watzlaf, Karl T. Schroeder and Candace Kairies[2]

Abstract. Ten passive treatment systems, located in Pennsylvania and Maryland, have been intensively monitored for up to ten years. Influent and effluent water quality data from ten anoxic limestone drains (ALDs) and six reducing and alkalinity-producing systems (RAPS) have been analyzed to determine long-term performance for each of these specific unit operations. ALDs and RAPS are used principally to generate alkalinity. ALDs are buried beds of limestone that add alkalinity through dissolution of calcite. RAPS add alkalinity through both limestone dissolution and bacterial sulfate reduction. 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 20 mg/L of aluminum experienced a rapid reduction in permeability and failed within five months. Maximum levels of alkalinity (between 150 and 300 mg/L) appear to be reached after 15 hours of retention. All but one RAPS in this study have been constructed and put into operation only within the past 2.5 to 5 years. One system has been in operation and monitored for more than nine years. Alkalinity due to sulfate reduction was highest during the first two summers of operation. Alkalinity due to a limestone dissolution has been consistent throughout the life of the system. For the six RAPS in this study, sulfate reduction contributed an average of 28% of the total alkalinity. Rate of total alkalinity generation range from 15.6 $gd^{-1}m^{-2}$ to 62.4 $gd^{-1}m^{-2}$ and were dependent on influent water quality and contact time.

Additional Key Words: passive treatment, anoxic limestone drains, wetlands, sulfate reduction, successive alkalinity-producing systems, acid mine drainage, ALD, SAPS.

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 have 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 meters) unvegetated pond, and a shallow (~0.15 meters) wetland that usually contains cattails (typically *Typha latifolia*) that are either planted or volunteer. 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 grams 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 dependant 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 of 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

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[2] George R. Watzlaf, Environmental Engineer; Karl T. Schroeder, Chemist; and Candace Kairies, Environmental Scientist, National Energy Technology Laboratory, U. S. Department of Energy, Pittsburgh, PA 15236-0940.

the area and funding limitations for the project.

Net acidic drainage requires the addition of alkalinity prior to the aerobic wetland. Although a number of passive and semi-passive treatment technologies have been used to add alkalinity to net acidic waters; only two for which we have long-term data will be considered here. The anoxic limestone drain (ALD) uses only the dissolution of calcite (calcium carbonate) in limestone as the alkalinity addition technique, while reducing and alkalinity-producing systems (RAPS) incorporate an additional microbial mechanism. ALDs are used for the sole purpose of generating alkalinity and must be followed by ponds and aerobic wetlands to oxidize and remove the dissolved iron and manganese.

An ALD is a buried bed of limestone engineered to intercept mine water while it is in an anoxic state (Turner and McCoy 1990). Dimensions are typically on the order of 1 meter deep, 1-7 meters wide, and 25-100 meters 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, the calcium carbonate content of the limestone, and the initial calcium concentration in the drainage. The first two factors have been shown to significantly effect the final concentration of alkalinity in the effluent (Hedin et al. 1994b). Field tests have shown that the rate of limestone dissolution slows considerably after about 15 hours of contact with mine drainage. 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 dissolves 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 will reduce the effective lifetime by lowering permeability and/or coating the stone (armoring). ALDs are not appropriate for waters high in aluminum because it 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 plastic sheeting and/or clay. Additionally, capping may increase the extent of calcite dissolution and alkaline addition by trapping evolved CO_2, which promotes further calcite dissolution via equation 2. ALDs are self-buffering, providing a pH of about 6.5, so that it is essentially impossible to overtreat the water. With a controlled pH and anoxic conditions, ferrous iron and manganese should not be retained in the drain.

$$2\,H^+ + CaCO_3 \longrightarrow Ca^{2+} + CO_2 + H_2O \qquad (1)$$

$$CO_2 + H_2O + CaCO_3 \longrightarrow 2\,HCO_3^- + Ca^{2+} \qquad (2)$$

Reducing and Alkalinity-Producing System (RAPS) is a generic term that describes the chemistry within a certain type of passive treatment. In addition to producing alkalinity via the dissolution of limestone, these systems promote reducing conditions by the incorporation of organic matter. The RAPS design directs water to flow down through the organic matter and limestone. The reducing conditions facilitate sulfate reduction, which generates alkalinity (equation 3), and may also precipitate some metals as sulfides. Ferric iron can be reduced to ferrous iron, eliminating the precipitation of ferric hydroxide and subsequent clogging and armoring of the limestone.

$$2\,CH_2O + SO_4^{2-} \longrightarrow H_2S + 2\,HCO_3^- \qquad (3)$$

This type of system was first implemented by Doug Kepler (currently with Damariscotta, an environmental consulting firm in Clarion, PA) at the Howe Bridge site. These systems were termed Successive Alkalinity-Producing Systems (SAPS), indicating that more than one of these units could be used in series to treat very highly acidic water (Kepler and McCleary 1994). Similar systems are also referred to as Vertical Flow Systems, Vertical Flow Ponds, or Vertical Flow Wetlands. These systems, which rely on similar chemistry will be referred to as RAPS in this paper. A layer of limestone (0.6 -1.2 meters thick) is placed on the bottom of an excavated area. A network of perforated pipes is placed in the lower portion of this limestone layer. Over the limestone, organic material (0.15 - 0.61 meters thick) is placed and serves as the nutrient source for the sulfate reducing bacteria. In Pennsylvania, spent mushroom compost has been the organic material of choice. It consists of horse manure (56% by weight), hay (22%), straw (10%), chicken manure (10%), and gypsum (2%). Mine water flows down through the system, encountering the reducing zone of the compost before contacting the limestone. In the reducing environment, dissolved oxygen (DO) is removed, which prevents ferrous iron oxidation, and any ferric iron already present is reduced to the ferrous state. Thus, RAPS are appropriate for water containing ferric iron, which could armor the limestone in an ALD.

It is thought that RAPS may also be more resistant to plugging by aluminum than ALDs because of their larger cross sectional area and higher available head pressures (Watzlaf and Hyman 1995). However, RAPS still need to be monitored further in order to demonstrate aluminum tolerance in the field. While the oldest RAPS at Howe Bridge continues to perform well, it does not receive any aluminum (<0.2 mg/L) . Other possible causes of reduced permeability include precipitation of ferric (oxy) hydroxides, storm mobilized silt and other solids, and precipitation of metal sulfides within the organic layer. Thus, continued monitoring of the actual performance of these systems is warranted.

In practice, RAPS, ALDs, settling ponds, and aerobic wetlands are used as unit operations in a total remediation system. For example, RAPS are usually preceded by a settling pond/wetland to settle iron and other solids, which could reduce permeability of the system. RAPS and ALDs are followed by settling ponds and aerobic wetlands for oxidation, precipitation and settling of metals. After these ponds and wetlands, additional RAPS may be used, each separated by a settling pond and wetland, to sequentially improve the water quality when sufficient alkalinity cannot be introduced in the initial ALD or RAPS.

Although much is known about the alkalinity-producing capability of ALDs and RAPS, relatively little is known about the long-term performance of systems in actual use. The oldest alkalinity-producing system (the Morrison ALD) is only now approaching 10 years of operation. In this report, we describe the results obtained from long-term monitoring of a number of ALDs and RAPS. It is our purpose to describe the results obtained to date and to 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

Representative influent and effluent water quality samples were collected periodically. For selected 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. At each sampling location, an unacidified and acidified sample (150 mL each) were collected. If the sample contained any visible particulate matter, it was 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 and RAPS. For all of the ALDs and the Howe Bridge and Jennings RAPS, flows were determined from the time necessary to collect a known volume of water. For the Oven Run site D RAPS, flows were measured using permanent calibrated flumes installed at the site. For the Oven Run site E RAPS, portable pipe weirs were used to measure flow.

Site Descriptions

Anoxic Limestone Drains (ALDs)

Howe Bridge 1 Discharge from 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. Discharge from another 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 (Right and Left). 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 (Right and Left) 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. The ALD treats an abandoned underground mine discharge which is collected in an inert river gravel bed and piped to the system. Influent water is sampled prior to contact with limestone via a sampling well. The ALD consists of a series 6 buried limestone cells. Water flows into the bottom of each cell and exits through the top before being piped to the next cell.

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

Reducing and Alkalinity Producing Systems (RAPS)

Howe Bridge. Water flows through a compost wetland (0.14 ha) prior to entering a RAPS (0.14 ha). The RAPS contains a 0.4-m layer of limestone gravel covered by a 0.2-m layer of spent mushroom compost and about 1.5 m depth of water. Perforated drainage pipes (black plastic corrugated sewer pipe) are placed in a serpentine pattern in the bottom of the limestone layer. These pipes only cover about one-half of the total surface area of the system (~0.07 ha). Influent water is collected prior to the compost wetland.

Oven Run D (#1 and #2). This system treats discharges from reclaimed surface and daylighted deep mines. Two RAPS are in series, each with a surface area of about 0.15 ha. Both contain a 0.91-m thick layer of limestone and a 0.15-m thick layer of compost covered by 1.5 m of water. Each RAPS is preceded by a wetland with a surface area of 0.11 ha and a depth of 0.076 to 0.152 m of water. Influent water for each RAPS is sampled prior to the wetlands

Oven Run E (#1 and #2). Abandoned deep mine drainage is piped to two RAPS in series. Each RAPS has a surface area of 0.26 ha and the same thickness of limestone, compost and water as the RAPS at Over Run D outlined above. RAPS #1 is preceded by a 1.8-m deep pond (0.10 ha) and a wetland (0.12 ha). RAPS #2 is preceded by a pond (0.11 ha) and a wetland (0.11 ha).

Jennings. A system of perforated pipes was placed within a 0.31-m thick bed of inert river gravel, which was wrapped with a geotextile fabric. Above the gravel layer is a mixture of limestone and spent mushroom compost that is 0.8 m thick. This mixture consists of 270 tonnes of compost and 345 tonnes of limestone aggregate (9.5 mm x 1 mm; i.e., 3/8 in x 16 mesh). Influent water is sampled prior to entering the RAPS (Jennings Water Quality Improvement Coalition 1999).

Results

Anoxic Limestone Drains

Data describing the 10 ALDs in this report are listed in Tables 1 and 2. Morrison, the oldest of the ALDs, is only now reaching its 10th anniversary. 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 Figure 1 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 Figure 1, 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. Thus, a minimum contact time of 15 hours ensures that at least 90% of the maximum achievable alkalinity is realized in the ALD.

All detention times were calculated using effluent flows and a limestone void volume of 49%. Tracer tests have shown that this calculated detention time agrees well with the time it takes for 50 % of the mass of the tracer to pass through the ALD (within 10%).

It should be noted that effluent alkalinity could be used as the dependent variable in Figure 1 because all of these ALDs received circumneutral mine waters that

Table 1. Dimensions, stone size, and source of influent water quality data for anoxic limestone drains.

ALD Site	ALD Dimensions: Length x Width x Depth, meters			Stone Size, cm	Source of Influent Water Quality Data
Howe Bridge 1	36.6	6.1	1.2	5.1 - 7.6	Well
Howe Bridge 2	13.7	4.6	0.9	5.1 - 7.6	Well
Morrison	45.7	0.9	0.9	5.1 - 7.6	Adjacent Seep
Filson - Right	54.9	6.1	0.9	5.1 - 7.6	Adjacent Seep
Filson - Left	54.9	6.1	0.9	5.1 - 7.6	Adjacent Seep
Elklick	36.6	3.1	0.9	5.1 - 20.3	Well
REM - Right	13.7	7.6	0.9	7.6	Historical
REM - Left	61	16.8	0.9	7.6	Historical
Schnepp	12.2	6.1	0.9	1.9 - 2.5	Historical
Jennings[1]	228	1	1	15.2	Well

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

Table 2. Initial and current conditions of anoxic limestone drains.

ALD Site	Year Built	Initial Conditions			Avg. Flow	Current Conditions		Year when
		Limestone		t_d[1]		Limestone	t_d[1]	
		tonnes	% $CaCO_3$	hrs	L/min	tonnes	hrs	$t_d = 15$ hrs
Morrison	1990	65	92	47	8.0	52	32	2019
Howe Bridge 1	1991	455	82	25	96.8	405	22	2021
REM-R	1992	125	82	6.8	112	88	4.8	NA
REM-L	1992	125	82	8.1	96.2	80	5.2	NA
Jennings	1993	365	90	27	73.4	356	NA	NA
Howe Bridge 2	1993	132	82	15	48.4	109	12	1993
Schnepp	1993	130	90	30	19.8	116	27	2023
Filson-R	1994	590	88	72	44.0	559	68	2078
Filson-L	1994	635	88	109	31.2	611	105	2114
Elklick	1994	165	85	22	37.1	153	20	2017

[1] t_d based on quantity of limestone and average flow rates using $t_d = V/Q$ and assuming 49% void volume within the limestone

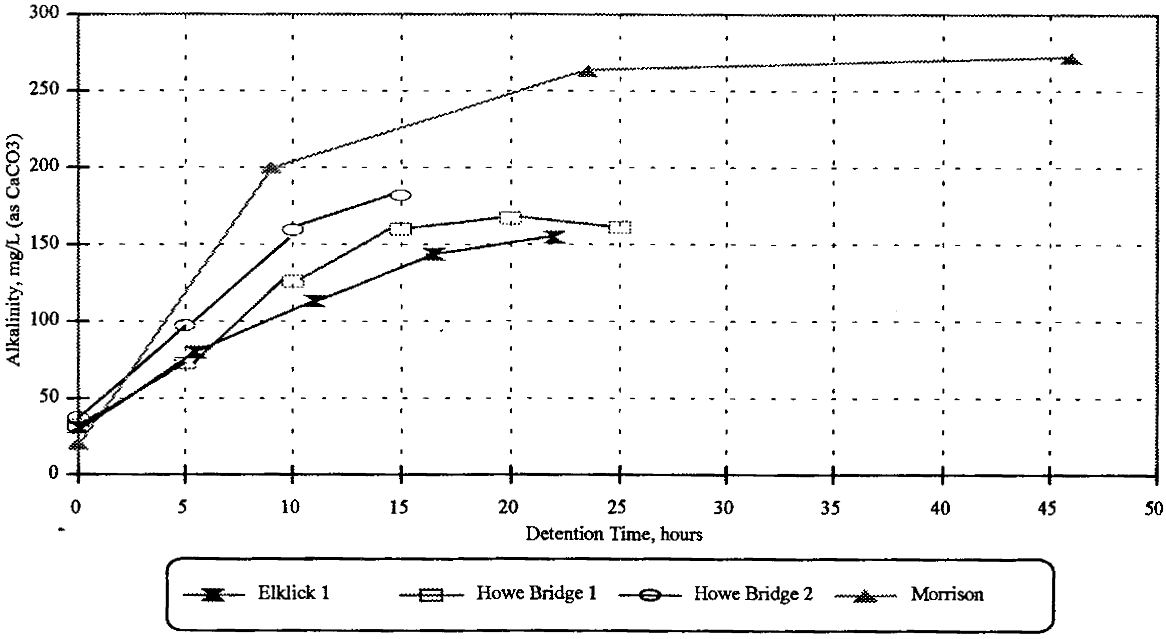

Figure 1. Alkalinity concentrations as water flows through selected ALDs.

had ferrous iron as the only major contributor to the net acidity. The behavior of mine waters with a low initial pH or appreciable aluminum concentrations would be better described using net acidity as the dependent variable.

The final concentration of alkalinity that is produced in an ALD depends upon the nature of the mine drainage. An empirical test has been developed that estimates the alkalinity concentration that will be produced in an ALD treating a specific mine water using limestone in collapsible containers (cubitainers) (Watzlaf and Hedin 1993). This test enables the determination of limestone consumption rates, the quantity of limestone needed for a desired design life, and whether the ALD will make the mine water net alkaline.

The amount of calcium carbonate remaining in these ALDs was calculated using the difference between the influent and effluent net acidity loadings over the life of the system. 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, although most ALDs are still operating at near maximum efficiency, as judged from detention times in excess of 15 hours. As an estimate of expected longevity, the year in which the ALD detention time was 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 2). 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.

Inlet and outlet water quality analyses for these ALDs are presented in Table 3. All of the ALDs successfully add alkalinity, increasing the effluent levels by 50 to 270 mg/L. 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 is mirrored by an 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, compared to an expected ratio of 1.00.

Manganese balances across the ALDs indicated that little or no retention was occurring, as would be expected for water having a pH of less than 7 under anoxic conditions. Only three of the sites had water containing aluminum in excess of 1 mg/L. The highest aluminum concentration was observed at the Jennings

Table 3. 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		Iron, mg/L		Manganese mg/L		Aluminum, mg/L	
	In	Out	In	Out	In	Out	In	Out	In	Out	In	Out
Morrison[2]	387	51.4	28.7	278	115	223	207	156	48.7	40.9	0.5	<0.2
Howe Bridge 1	472	352	32.6	155	157	209	276	275	41.5	41.5	<0.2	<0.2
REM-R[3]	NA	835	0	54	258	232	589	447	136	126	5	3.2
REM-L	NA	259	NA	113	NA	201	NA	185	NA	50.8	NA	<0.2
Jennings	280	-33.5	0	139	82.9	208	75.6	59.3	8.39	8.33	20.9	1.1
Howe Bridge 2	411	274	35.3	163	154	206	250	248	36.6	35.9	<0.2	<0.2
Schnepp[3]	225	-42.5	0	168	NA	198	92	61.5	28	26.3	7	<0.2
Filson-R[2]	100	-139	47.9	299	69.2	189	59.3	55.5	19.9	19.8	0.4	<0.2
Filson-L[2]	104	-175	47.9	317	69.2	180	59.3	68.6	19.9	15.9	0.4	<0.2
Elklick	52.0	-63.0	33.8	159	77.1	129	59.2	53.3	4.77	4.89	<0.2	<0.2

[1] Negative net acidity values indicate net alkalinity.

[2] "In" concentrations based on water quality of a nearby seep which was similar in quality to the untreated mine drainage prior to construction of the ALD.

[3] "In" concentrations based on historical water quality data of the untreated mine drainage prior to construction of the ALD.

site (21 mg/L) and is thought to be responsible for the premature failure of this ALD. 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. In those cases where matched inlet and outlet samples were obtainable, the iron balances (with the exception of Jennings) indicated iron was not retained within the ALD (all of the iron was in the ferrous form). At sites where inlet concentrations were estimated from historical data, the listed "in" value probably overestimated the contamination actually entering these ALDs because the water quality in this area has shown a general improvement over the past ten years. Using historical data for the influent water quality biases the data with the more contaminated water samples which were collected and analyzed 7 or more years ago.

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 (Figure 2). It is also of interest to note that no seasonal variation was observed for these ALDs, probably due to the fairly narrow range of influent water temperature, which is typical of groundwater.

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, 1993. 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 3. In September of 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, Figure 3 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. These two species were retained nearly quantitatively and with no loss in efficiency even as the flow deceased towards the end of 1993. Both of these

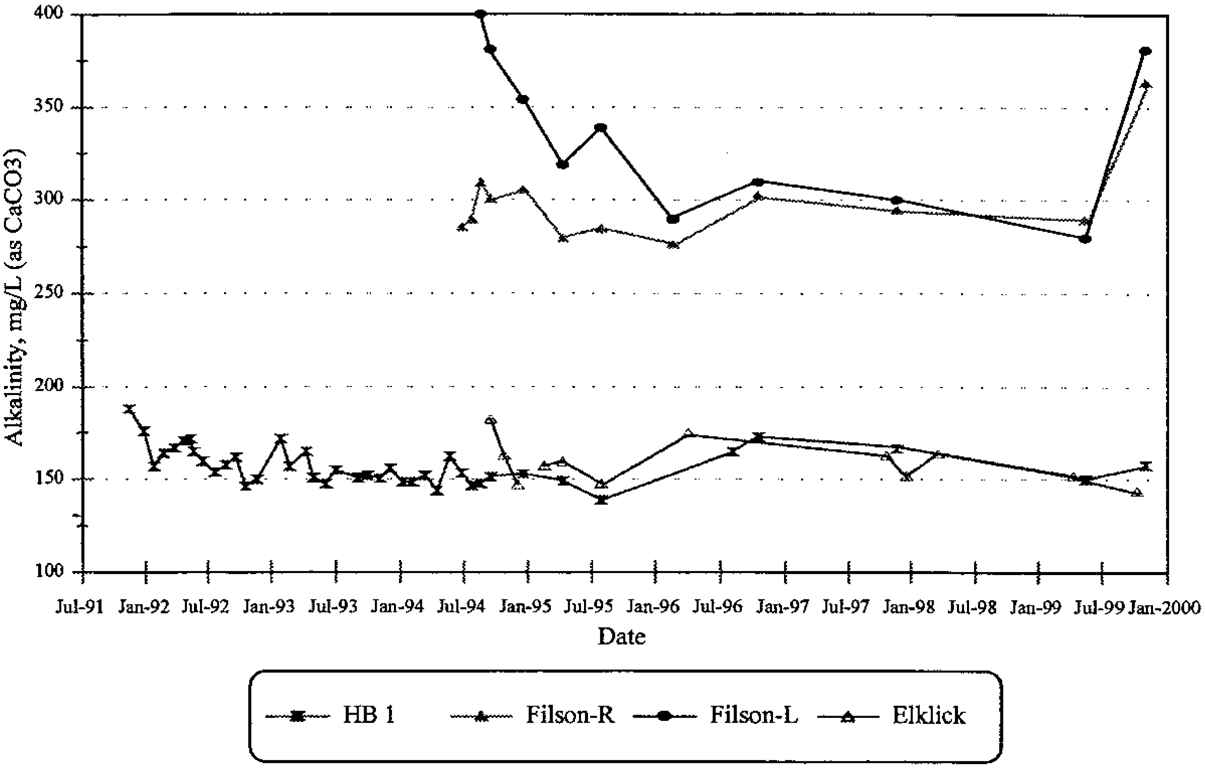

Figure 2. Effluent alkalinity concentrations of selected ALDs.

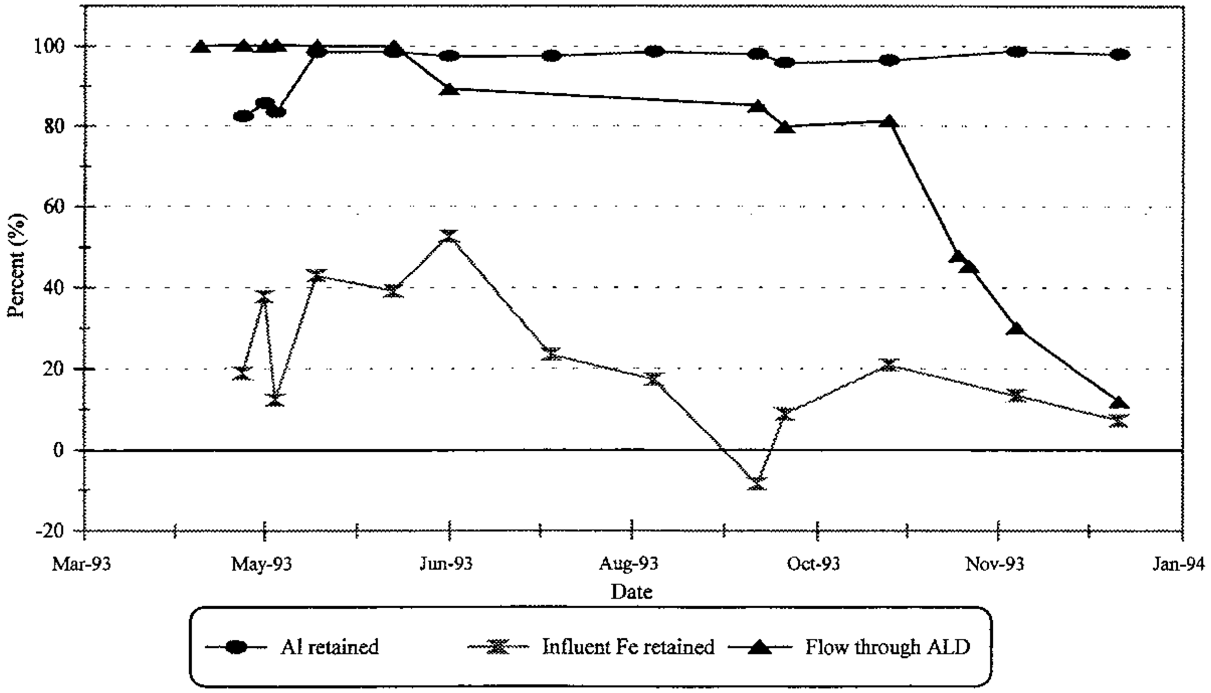

Figure 3. Flow of water through ALD and percent of aluminum and iron retained in the ALD at Jennings.

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, because about 40% of the iron precipitate was due to the oxidation or adsorption processes discussed above, 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, reminiscent of aluminum precipitates seen in the field. Although aluminum is thought to be the major problem at this site, iron may have also contributed. In the absence of reducing conditions, such as are generated in RAPS, ferric iron in the influent can precipitate and may eventually decrease the permeability of the system. It is not clear that this actually occurred in the Jennings ALD.

Reducing and Alkalinity Producing Systems

While alkalinity is produced solely by limestone dissolution in ALDs, in RAPS it is produced by both limestone dissolution and sulfate reduction. Table 4 presents the data obtained for 6 RAPS that have been monitored for up to 9 years. Shown in the Table are (1) the alkalinity produced by limestone dissolution (based on increases in calcium, where a 1 mg/L increase stoichiometrically yields 2.497 mg/L of alkalinity as $CaCO_3$); (2) the alkalinity produced by sulfate reduction (based on decreases in sulfate, where a 1 mg/L decrease stoichiometrically yields 1.042 mg/L of alkalinity as $CaCO_3$); (3) the measured total alkalinity generated by the RAPS; and (4) the specific rate of generation of alkalinity calculated as grams per day per square meter of surface area measured at the top of the compost layer.

The Howe Bridge RAPS produced approximately equal amounts of alkalinity from sulfate reduction and limestone dissolution over the past 9 years. Much of the alkalinity from sulfate reduction occurred in the first 2-3 summers of operation (Figure 4). Sulfate reduction exhibited very seasonal trends in the first few years of operation. Although it is more difficult to see seasonal trends in more recent years due to lower sampling frequency, it is apparent that the alkalinity production is not reaching the high levels achieved in the first few years. Alkalinity generation rates were calculated as 19.6 $gd^{-1}m^{-2}$ using the total surface area of the top of the compost. However, the perforated piping in the limestone layer extended only about half way into the system, potentially causing it to perform as if water actively flowed through only half of the RAPS. Taking this into account, actual alkalinity generation rates are probably on the order of 39 $gd^{-1}m^{-2}$.

Both Oven Run sites D and E consist of two RAPS in series. The rationale for this was two-fold: (1) one system could be put offline for maintenance and (2) it was envisioned that the first system would contribute more alkalinity during the first half of the system's design life and the second system would contribute more alkalinity in the last half of the design life. At site D, the first RAPS produced alkalinity at a rate of 57.4 $gd^{-1}m^{-2}$ and the second at a rate of 20.6 $gd^{1}m^{2}$ over its five years of operation. Similarly, at site E, the first RAPS produced alkalinity at a rate of 42.7 $gd^{-1}m^{-2}$ and the second at a rate of 15.6 $gd^{-1}m^{-2}$ over its three years of operation. It was difficult to determine any seasonal trends in the alkalinity production at either site due to the low sampling density and extremely variable flow rates at each site (a very wet period followed by an extended drought period produced a greater than 10-fold difference between high and low flows).

For the Jennings RAPS, the compost and limestone were mixed together instead of maintaining two distinct layers. This design was chosen because laboratory tests indicated that the water at Jennings was capable of depleting the calcium carbonate within a 0.7-meter thick layer of spent mushroom compost in about two years (Watzlaf 1997). After the calcium carbonate was depleted in the laboratory tests, sulfate reduction virtually ceased because the pH of the compost fell below levels conducive to sulfate reduction by the sulfate reducing bacteria (pH<4). The rapid depletion of calcium carbonate was caused by the production of acidity during aluminum precipitation (an aluminum concentration of 23 mg/L will produce 128 mg/L of acidity upon hydrolysis). The Jennings RAPS produced the greatest change in net acidity of any of the systems with over 90% of the alkalinity production attributable

Table 4. Construction specifications and quantification of alkalinity generation within RAPS.

RAPS Site	Year Constructed	Avg. Flow, L/min	Compost			Limestone			Total Alk. Gen.[3], mg/L as $CaCO_3$	Alkalinity Generation Rate, $gd^{-1}m^{-2}$
			Quantity, tonnes or m^3	t_d[1], hr	Alk due to SO_4 reduction, mg/L as $CaCO_3$	Quantity, tonnes	t_d[1], hr	Alk due to limestone dissolution, mg/L as $CaCO_3$		
Howe Bridge	1991	74.1	272 tonnes	8.4	123	454	33	118	219	19.6-39.2
Oven Run D #1	1995	367	140 m^3	1.6	15	1349	20	66	104	57.4
Oven Run D #2	1995	395	140 m^3	1.5	18	1349	18	19	35	20.6
Oven Run E #1	1997	314	248 m^3	3.3	71	2425	41	125	158	42.7
Oven Run E #2	1997	328	248 m^3	3.2	3	2425	40	53	56	15.6
Jennings[2]	1997	66.6	270 tonnes	22	45	345	22	421	438	62.4

[1] t_d based on quantity of limestone or compost at construction and average flow rates using $t_d = V/Q$ and assuming void volumes of 49% for limestone and specific yields of 25% and 20% for compost and compost/limestone mixture, respectively.

[2] Jennings contained a compost and limestone mixture, the 25-hr t_d is for the mixed layer.

[3] Total alkalinity generated based on changes in net acidity between influent and effluent of RAPS

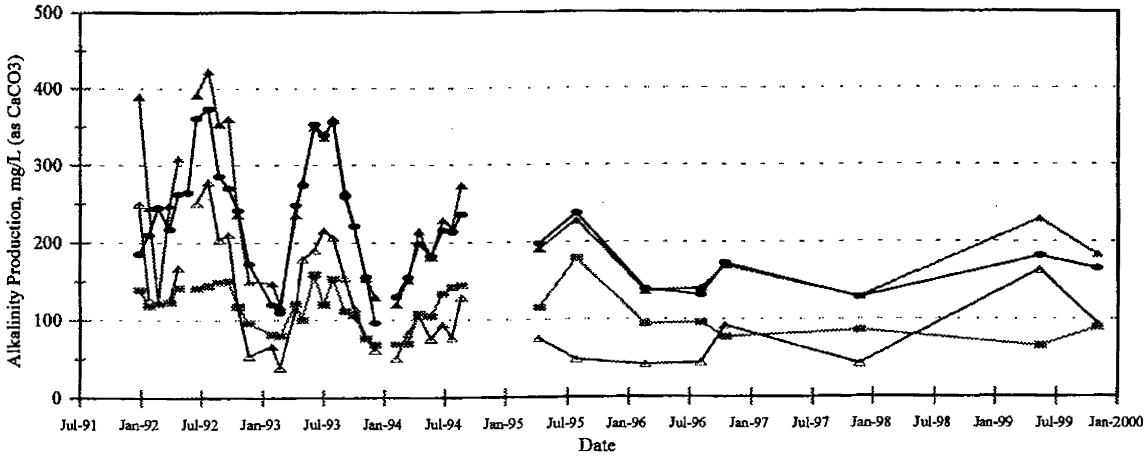

Figure 4. Alkalinity generation in the Howe Bridge RAPS. Alkalinity from "sulfate reduction" and "limestone dissolution" were calculated by differences in sulfate and calcium, respectively. The "sum" of these calculated alkalinities is also plotted along with "actual" measured changes in net acidity.

to limestone dissolution. As discussed above, some (128 mg/L) of this change can be attributed to aluminum precipitation. The Jennings RAPS displayed no clear seasonal trends.

Table 5 shows changes in the major water quality parameters. The change in calcium and sulfate concentrations were used to estimate the contributions of limestone dissolution and sulfate reduction, respectively, as described above. Net acidity was determined using the peroxide oxidation method and the change in net acidity between the inlet and outlet is listed as the total alkalinity generated in the second to last column in Table 4. Manganese, which is expected to be conserved in these systems, is present in the influent and effluent at about the same levels. Iron, and aluminum when present, are retained by the systems.

The majority of these metals are presumably retained in the wetlands that precede the RAPS, though significant levels of iron may be removed on top of the compost in the RAPS. However, the Jennings site has no such wetland and still retains 85% of the iron and all of the aluminum. In some cases, such as the Oven Run E sites, preventative maintenance is performed by periodic high-flow flushing, during which the RAPS pond level is lowered. The effect of such preventative maintenance on the lifetime of the RAPS has not been quantified.

Conclusions

ALDs offer an effective means of introducing alkalinity into net acidic waters containing neither ferric iron nor aluminum. The presence of either of these ions will reduce permeability of the ALD by precipitation, which will cause premature failure by clogging. In the absence of these ions, ALDs have continued to perform well with no obvious seasonal variation nor long-term degradation. Near maximum levels of alkalinity (usually between 150 and 300 mg/L) are achieved with 15 hours or more of contact time. ALDs are tolerant of both ferrous iron and manganese. ALDs must be viewed as an unit operation, not a stand-alone remediation technique and must be followed by a pond and wetland for iron oxidation, precipitation, and settling.

Alkaline addition in RAPS is often dominated by the limestone dissolution pathway. The amount of acid neutralization potential afforded by a RAPS ranges from 35 to over 400 mg/L $CaCO_3$. The acid neutralization potential afforded by a RAPS ranges from 35 to over 400 mg/L $CaCO_3$. Sulfate reduction contributed an average of 28 % (with a range of 5-51 %)

Table 5. Water quality before and after contact with the reducing and alkalinity producing system.

RAPS	Net Acidity,[1] mg/L as $CaCO_3$		Alkalinity, mg/L as $CaCO_3$		Calcium, mg/L		Iron, mg/L		Manganese mg/L		Aluminum, mg/L		Sulfate mg/L	
	In	Out	In[2]	Out	In	Out	In[2]	Out	In	Out	In	Out	In	Out
Howe Bridge	323	106	31.3	56.8	193	240	193	73.7	37.7	36.0	<0.2	<0.2	1214	1102
Oven Run D #1	114	9.94	0	28.0	297	323	37.6	3.01	29.0	28.2	1.75	0.94	1372	1358
Oven Run D #2	16.1	-18.6	NA	41.9	320	327	1.42	0.44	27.9	24.4	1.56	0.41	1340	1323
Oven Run E #1	207	49.4	0	16.7	155	205	18.7	11.4	13.3	12.5	17.5	8.7	971	902
Oven Run E #2	49.4	-6.5	16.7	35.0	205	226	11.4	6.28	12.5	11.9	8.7	1.85	902	899
Jennings	272	-166	0	212	105	274	69.1	10.3	17.6	15.9	22.7	<0.2	772	729

[1] Negative net acidity values indicate net alkalinity.

[2] "In" concentrations (for all RAPS except Jennings) flow through wetland prior to entering RAPS, therefore alkalinity and iron concentrations into RAPS typically lower than listed in table.

of the total alkalinity produced in the system. The rate of alkaline addition for a single RAPS is about 40 - 60 $gd^{-1}m^{-2}$. Rates for the second RAPS in a series fall off to about ½ to 1/3 of the rate of the first system. Much of the variability in performance can be attributed to influent water quality and detention time. As with ALDs, RAPS should be viewed as unit operations, not stand alone technologies. They need to be preceded by a pond/wetland to precipitate iron and other settleable solids. As with ALDs, RAPS also need to be followed by a pond and wetland for iron oxidation, precipitation, and settling.

Care should be taken to obtain sufficient water quality data of the target drainage, including seasonal variation, before developing 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. Site and funding constraints may limit the applicability of passive techniques for some mine drainages. However, for those drainages with appropriate water quality and land availability, ALDs and RAPS continue to perform well.

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