

# THE EFFECTS OF ANOXIC LIMESTONE DRAINS ON MINE WATER CHEMISTRY<sup>1</sup>

Robert S. Hedin and George R. Watzlaf<sup>2</sup>

**Abstract:** Construction and water quality characteristics of 21 anoxic limestone drains (ALDs) were studied in order to identify and evaluate factors responsible for the variable performance of these passive treatment systems. Nineteen of these ALDs discharged water that contained bicarbonate alkalinity ranging from 69 to 469 mg/L as CaCO<sub>3</sub>. In addition to adding alkalinity to the mine water, some ALDs decreased the mineral acidity of the mine water. Acidity removal ranged from 0 to 5,901 mg/L. Large changes in acidity were primarily associated with retention of ferric iron and aluminum. Equilibrium calculations indicated that all of the ALD effluents were undersaturated with respect to calcite and oversaturated with siderite. Retention of ferrous iron, however, was only indicated at two sites when retention times were longer than 25 days. Half of the ALD effluents were in equilibrium with rhodochrosite, however, retention of manganese was not indicated at any sites. Two of the ALD effluents were saturated with gypsum. One of these sites retained 4,500 mg/L sulfate. At two sites, where mine water could be sampled at points along the flow path within the ALDs, concentrations of alkalinity were found to plateau at maximum values well before the end of the ALD. These maximum values of alkalinity were developed after 14 to 23 hours of retention time. An ALD sizing technique is suggested that incorporates the minimum retention time findings.

**Additional Key Words:** acid mine drainage, passive treatment, carbonate chemistry, calcite.

## Introduction

Since Turner and McCoy (1990) first described the use of buried beds of limestone to treat acid mine drainage (AMD), dozens of similar passive treatment systems have been constructed in Appalachia. Commonly called "anoxic limestone drains" or "ALDs," the systems function by promoting the contact of acid mine drainage with limestone gravel under anoxic conditions. The anoxic conditions limit the oxidation of ferrous iron, thereby minimizing the armoring of limestone with ferric hydroxide.

Anoxic limestone drains are generally used to treat acid mine drainage (AMD) before it flows into a constructed wetland. The ALD raises the pH of the water to circumneutral levels (pH 6 to 7) and introduces bicarbonate alkalinity. Upon exiting the ALD, the circumneutral pH level promotes metal precipitation and the bicarbonate alkalinity neutralizes the acidity produced by metal hydrolysis (Hedin and Nairn 1993).

ALDs can be a tremendously cost-effective water treatment technique. The Tennessee Valley Authority (TVA) has used ALDs to enhance the performance of existing constructed wetlands and avoid hundreds of thousands of dollars of chemical treatment costs (Brodie 1991). In western Pennsylvania, chemical treatment has been eliminated at several sites where the mine waters are treated with ALDs before flowing into constructed wetlands (Nairn et al. 1992, Hedin and Nairn 1993).

The concentration of alkalinity contained in the ALD effluents varies considerably (Faulkner and Skousen 1993, Nairn et al. 1991). This variation has important repercussions for the design and sizing of the total passive treatment system. When an ALD does not generate enough alkalinity to totally neutralize the acidity contained in the mine drainage, additional alternative alkalinity-generating treatments are necessary.

In this paper we report the chemical characteristics of the effluents of 21 ALDs located in Appalachia. We evaluated the alkalinity-generating and acidity-neutralizing processes to better understand the chemical changes occurring in these systems.

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<sup>2</sup>Robert S. Hedin, Research Biologist, and George R. Watzlaf, Environmental Engineer, U.S. Department of the Interior, Bureau of Mines, Pittsburgh, PA, USA.

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## Methods

Water samples of the final effluent were collected from all ALDs. Alkalinity and pH were measured in the field. The pH was measured with a calibrated Orion SA270 or 290A pH/ISE meter. Alkalinity determinations were made with the Orion Total Alkalinity Test Kit and a pH meter. The results of this method agree well with results obtained by the standard titration procedure (Watzlaf and Hedin 1993). Concentrations of Fe, Mn, Al, Ca, and Mg were determined for samples acidified in the field (2 mL of 12.1N HCl per 250 mL of sample) using inductively coupled argon plasma spectroscopy (ICP). Ferrous iron concentrations were determined for acidified samples by titration with  $K_2Cr_2O_7$  (Fales and Kenny 1940). Ferric iron was calculated from the difference of total iron and ferrous iron measurements. Sulfate concentrations were determined by either ion chromatography or ICP. The net acidity or alkalinity of each sample was determined in the laboratory by boiling 50 mL of raw sample with 1 mL of 30%  $H_2O_2$  and titrating acidic solutions to pH 8.3 with 0.1N NaOH and alkaline solutions to pH 4.8 with 0.1N  $H_2SO_4$  (American Public Health Association 1985). All concentrations of alkalinity and acidity are reported as mg/L as  $CaCO_3$ . Analyses of duplicate and spiked samples indicated an analytical error of less than 3% for all parameters.

Partial pressures of  $CO_2$  and mineral saturation indices were calculated from the results of water analyses using the U.S. Geological Survey WATEQ, version 4F, computer model (Ball et al. 1987). A bicarbonate input to the model was estimated by assuming that field alkalinity resulted entirely from  $HCO_3^-$ . This assumption is reasonable for the pH range of alkalinity-containing water samples collected in this study (pH 5.5 to 6.7). Flow rates were determined at the effluents of ALDs by measuring the time necessary to collect a known volume of water. The theoretical retention or detention time ( $t_d$ ) of mine water within each ALD was estimated using the equation:

$$t_d = \frac{M V_v}{\rho_b Q}$$

where M is the mass of limestone,  $V_v$  is the bulk void volume expressed in decimal form,  $\rho_b$  is bulk density of the limestone, and Q is the volume flow of the mine water. For the ALDs studied in this paper, the bulk density for limestone was assumed to be 1,600  $kg/m^3$  (2,700  $lb/yd^3$ ) and a void volume of 45 to 50% (based on measurements of limestone used at three sites) was used.

## Results and Discussion

The chemical compositions of the effluents of 21 ALDs are shown in table 1. Pre-ALD water quality is also shown. Two types of pre-ALD water quality were collected. At 10 sites, the mine water was able to be sampled before it flowed into the ALD at the same time that ALD effluent samples were collected. At eight sites, sampling of the raw water was not possible, therefore, the existing water quality data for the acidic discharges before the ALDs were constructed are reported. For most sites, the pre-ALD samples predate the ALD effluent samples by several years. Comparisons of the chemical compositions of the current ALD effluents and the historic raw water quality at these eight sites may be partly compromised by recent changes in the raw water chemistry unrelated to the construction and performance of the ALDs. We were unable to chemically characterize pre-ALD water at three ALD sites. The original water at the Ohio site was reportedly highly acidic with pH values less than 3. The original water at the REM-L ALD was reportedly similar to the REM-R discharge (which was sampled previous to ALD construction). No information exists on the water quality at the Maud site prior to construction of the ALD.

Concentrations of alkalinity in the effluents of the ALDs ranged from 0 to 469 mg/L. Of the 21 ALDs sampled, 19 discharged water that contained alkalinity. These effluent alkalinity concentrations, the amount of limestone used, the average effluent flow rate, and calculated theoretical retention times ( $t_d$ ) for each ALD are presented in table 2. We were unable to obtain construction information for six of the 21 ALDs.

### Changes in Water Quality at the ALD Sites

For all of the ALDs that produced alkalinity, the chemistry of the effluent water samples differed from that of the raw water (table 1). Differences in the water quality between the raw water and ALD effluent could arise from three general reasons. First, at sites where the raw water was characterized by samples collected several years ago, differences between these old analyses and analyses of recently collected ALD effluents samples may arise from recent changes in the chemistry of the raw mine water.

Table 1. Influent (In) and effluent (Out) water chemistry of 21 anoxic limestone drains in Appalachia. Values of pH in standard units. All concentrations in mg/L; alkalinity concentrations expressed in mg/L of calcium carbonate. "NA" indicates data is not available.

Site	Alkalinity		pH		Ca		Fe		Al		Mn		Sulfate	
	In	Out	In	Out	In	Out	In	Out	In	Out	In	Out	In	Out
Rid-2L <sup>1</sup>	0	469	2.3	6.2	97	855	1416	202	486	<1	23	11	6,719	2,227
Ohio	NA	400	NA	6.1	NA	592	NA	625	NA	<1	NA	80	NA	4,250
Hathaway <sup>2</sup>	0	385	3.3	6.5	NA	445	195	54	23	<1	44	14	2,237	1,303
TVA-AROAD <sup>1</sup>	0	350	2.8	6.6	57	87	16	38	19	<1	4	2	430	55
Rid-2R <sup>1</sup>	0	306	3.7	6.3	92	316	217	164	31	<1	7	7	979	957
Rid-1 <sup>1</sup>	3	290	4.7	6.5	215	400	5	27	2	<1	23	27	711	992
TVA-2 <sup>3</sup>	0	280	3.5	6.7	NA	111	40	24	<2	<1	13	7	NA	210
Morrison <sup>1</sup>	23	271	5.3	6.3	119	230	216	151	1	<1	51	42	1,340	1,081
Schnep <sup>2</sup>	0	191	3.3	6.3	NA	240	92	61	7	<1	28	39	980	908
Willi <sup>4</sup>	0	187	2.7	6.3	145	360	48	<1	62	<1	45	34	1,538	1,185
Empire <sup>5</sup>	0	180	4.0	6.2	NA	176	37	67	NA	<1	22	29	1,155	1,025
Jennings <sup>1</sup>	0	177	3.3	6.3	86	215	81	62	21	<1	9	9	691	680
Howe-2 <sup>1</sup>	24	174	5.9	6.5	162	229	276	271	<1	<1	39	39	1,298	1,309
Howe-1 <sup>1</sup>	33	161	5.6	6.2	159	211	279	277	<1	<1	41	40	1,323	1,329
Maud	NA	155	NA	6.5	NA	153	NA	<1	NA	<1	NA	2	NA	333
REM-L	NA	138	NA	6.0	NA	223	NA	184	NA	<1	NA	45	NA	1,247
Shade <sup>4</sup>	0	123	3.5	6.6	132	254	3	1	22	<1	32	36	1,042	1,300
TVA-4 <sup>3</sup>	NA	120	4.9	6.7	NA	85	135	<1	NA	<1	24	3	NA	155
REM-R <sup>4</sup>	0	69	4.3	5.5	258	257	589	507	5	3	136	132	2,825	2,655
Fawn <sup>1</sup>	0	0	3.5	3.7	346	379	417	445	103	152	25	29	5,000	5,432
Ohiopyle <sup>1</sup>	0	0	3.3	3.6	209	178	10	3	112	87	79	63	2,345	2,043

<sup>1</sup>"In" samples collected at the same time that "Out" samples were collected.

<sup>2</sup>"In" samples describe discharge before construction of ALD; data supplied by PA Dept. of Environmental Resources.

<sup>3</sup>"In" samples describe discharge before construction of ALD; data from Brodie (1991).

<sup>4</sup>"In" samples describe discharge before construction of ALD; data collected by U.S. Bureau of Mines.

<sup>5</sup>"In" samples describe discharge before construction of ALD; data from Turner and McCoy (1990).

Table 2. Selected parameters of the 21 ALD sites. Alkalinity concentrations in mg/L as calcium carbonate as measured at each field site. "NA" indicates data is not available.

Site	Limestone mass, mt	Flow, L/min	Mass per flow, mt/(L/min)	t <sub>d</sub> <sup>1</sup> , h	Alkalinity, mg/L
Rid-2L	114	0.8	142.5	698	469
Ohio	NA	NA	NA	NA	400
Hathaway	945	NA	NA	NA	385
TVA-AROAD	NA	265	NA	NA	350
Rid-2R	162	0.5	324.0	1,588	306
Rid-1	108	5	24.0	118	290
TVA-2	NA	NA	NA	NA	280
Morrison	64	7	9.4	46	271
Schnepp	132	57	2.3	11	191
Willi	182	5	36.4	178	187
Empire	NA	NA	NA	NA	180
Jennings	364	92	4.0	19	177
Howe-2	132	53	2.5	12	174
Howe-1	455	92	4.9	24	161
Maud	NA	NA	NA	NA	155
REM-L	125	82	1.5	7	138
Shade	35	15	2.3	11	123
TVA-4	364	131	2.8	14	120
REM-R	124	115	1.1	5	69
Fawn	NA	NA	NA	NA	0
Ohiopyle	225	218	1.0	5	0

<sup>1</sup>Theoretical detention time.

Second, the ALD may collect water that was not originally intended to be collected by the ALD prior to construction. When ALDs are intended to collect contaminated seepage (as well as treat it), the ALD likely collects nontarget water as well. If these nontarget waters are uncontaminated, dilution of contaminant concentrations in the ALD will occur. If these nontarget inputs are more contaminated than the sampled raw water, it is possible that contaminant concentrations will increase with flow through the ALD.

We evaluated the significance of nontarget inputs of mine water at four ALD sites by comparing influent and effluent concentrations of conservative ions (table 3). The conservative ions compared were magnesium (Mg), manganese (Mn), and sulfate. Magnesium does not form any solids under the chemical conditions that exist in ALDs. Because all of the limestones used at the ALD sites were high-calcium/low magnesium, and because the solubility of dolomite is low, magnesium levels do not change appreciably as water flow an ALD. Manganese and sulfate

concentrations were also compared because we have found these ions to behave conservatively in ALDs where the solubility product of gypsum is not exceeded. At the Jennings, Howe-1, and Howe-2 ALDs the raw water is piped to the ALD from a discrete source and thus these ALDs were not intended to collect any other water. At these sites, there is little or no change in Mg, Mn, or sulfate concentrations. At the Morrison site, which is designed to collect mine drainage along the toe of the spoil, the raw water was diluted by an average 18%. When the site was sampled in conjunction with rainstorms, changes in Mg and Mn were as high as 50%. Clearly, this ALD collects uncontaminated water as well as the targeted acid mine drainage. We suspect that

when ALDs are constructed for both collection and treatment of AMD, the collection of uncontaminated water may often occur. At these sites, improvements in water quality may be partly attributable to dilution of contaminants and the true performance of the ALD can only be assessed when dilution is quantified and taken into account.

Faulkner and Skousen (1993) report that some ALDs in West Virginia have unintentionally collected nontarget acid mine drainage. Two of the ALDs sampled in our study collected nontarget waters that were more contaminated than the original target waters. The Rid-1 site discharged water that contained 440% more Fe and 40% more sulfate than the influent water (table 1). The Fawn site discharged water with contaminant concentrations that were 7% to 48% higher than those of the influent water. These unexpected inflows have most likely contributed to the failure of this ALD. The interception of nontarget contaminated water may also be a common feature of ALDs that are constructed to collect mine water. During construction of the Schnepf ALD, excavations intercepted and collected acid mine drainage that was not originally targeted.

The third reason that the chemistry of the raw mine drainage and the ALD effluent differ is due to chemical reactions within the ALD. These reactions will determine the performance and ultimate longevity of the ALD system. The chemical reactions that occur in an ALD fall into two types: reactions that increase the concentrations of alkalinity in the water and reactions that decrease the acidity of the water (table 4). Alkalinity is increased primarily by reactions that increase concentrations of bicarbonate ion,  $\text{HCO}_3^-$ . In natural systems, the principal reaction that generates bicarbonate alkalinity is the reaction of carbonic acid ( $\text{H}_2\text{CO}_3$ ) with calcite. The acidity of mine water is decreased in ALDs through the neutralization of proton acidity ( $\text{H}^+$ ) and the precipitation of iron, manganese, and aluminum. Ferric iron and aluminum potentially precipitate as hydroxides, while ferrous iron and manganese potentially precipitate as carbonates.

Alkalinity-generating and acidity-removing reactions are linked by several reactions. The neutralization of proton acidity associated with free  $\text{H}^+$  and metal hydrolysis reactions generates carbon dioxide which, through the formation of carbonic acid, increases the generation of alkalinity. Bicarbonate produced by calcite dissolution potentially reacts with  $\text{Fe}^{2+}$  and  $\text{Mn}^{2+}$  to form siderite ( $\text{FeCO}_3$ ) and rhodochrosite ( $\text{MnCO}_3$ ).

Alkalinity-generating and acidity-removing reactions occur in a predictable order that is consistent with the solubility products of the solids. When highly acidic, metal contaminated water contacts limestone, the first reaction that occurs is the neutralization of proton acidity. This reaction raises the pH, which decreases the solubility of metal hydroxides. Between pH 3 and 4, ferric iron precipitates as ferric hydroxide. Between pH 4 and 5, aluminum precipitates as aluminum hydroxide. As the pH rises above pH 4.5, bicarbonate begins to accumulate in appreciable amounts. As bicarbonate concentration increases, the solubility of metal carbonates may be exceeded, causing the precipitation of siderite and then rhodochrosite. With each of these reactions, calcium is released into solution. As the concentration of calcium increases, the potential for gypsum ( $\text{CaSO}_4$ ) precipitation increases.

Table 5 shows the concentrations of alkalinity generated and calculations of the decrease in acidity for the ALDs. Variation of the alkalinity generated was less than the variation in the decrease in acidity. The generation of alkalinity in an ALD is limited to a maximum value by the solubility of calcite. High partial pressures of carbon dioxide increase the equilibrium concentrations of bicarbonate; however, even under very high  $\text{CO}_2$  partial pressures,

Table 3. Percentage change in magnesium, manganese, and sulfate concentrations at sites where water can be sampled before it enters the ALD and from the effluent.

Site	Mg	Mn	SO <sub>4</sub>
Morrison	-18%	-18%	-19%
Jennings	0%	-1%	-2%
Howe-2	+1%	0%	+1%
Howe-1	0%	-1%	0%

Table 4. Chemical reactions involving calcite that can occur in anoxic limestone drains.

Alkalinity-generating reactions:
$\text{CaCO}_3 + \text{H}^+ \rightarrow \text{Ca}^{2+} + \text{HCO}_3^-$
$\text{CaCO}_3 + \text{H}_2\text{CO}_3 \rightarrow \text{Ca}^{2+} + 2\text{HCO}_3^-$
$\text{CaCO}_3 + \text{SO}_4^{2-} + \text{H}_2\text{O} \rightarrow \text{CaSO}_4 + \text{OH}^- + \text{HCO}_3^-$
Acidity-lowering reactions:
$\text{CaCO}_3 + 2\text{H}^+ \rightarrow \text{Ca}^{2+} + \text{H}_2\text{O} + \text{CO}_2$
$3\text{CaCO}_3 + 2\text{Fe}^{3+} + 6\text{H}_2\text{O} \rightarrow 3\text{Ca}^{2+} + 2\text{Fe}(\text{OH})_3 + 3\text{H}_2\text{CO}_3$
$3\text{CaCO}_3 + 2\text{Al}^{3+} + 6\text{H}_2\text{O} \rightarrow 3\text{Ca}^{2+} + 2\text{Al}(\text{OH})_3 + 3\text{H}_2\text{CO}_3$
$\text{CaCO}_3 + \text{Fe}^{2+} \rightarrow \text{Ca}^{2+} + \text{FeCO}_3$
$\text{CaCO}_3 + \text{Mn}^{2+} \rightarrow \text{Ca}^{2+} + \text{MnCO}_3$

the concentrations of alkalinity that develop in ALDs rarely exceed 500 mg/L (table 6). Changes in acidity at the ALD sites, however, ranged as high as 5,900 mg/L. Large changes in acidity values were generally a result of retention of ferric iron and aluminum. ALDs have a high potential to retain  $\text{Fe}^{3+}$  and  $\text{Al}^{3+}$  because at circumneutral pH, the metal hydroxide of ferric iron and aluminum rapidly precipitate. Precipitation of these metal solids within the ALD may armor limestone and/or decrease the permeability of the system - both of which could decrease the performance and theoretical longevity of the ALD (Nairn et al. 1991).

All but one of the ALD effluents that contained iron were supersaturated with siderite (table 6); however, little removal of ferrous iron ( $\text{Fe}^{2+}$ ) was observed (table 5). This is likely due to the kinetics of siderite formation and that equilibrium has not been reached. WATEQ is used only to identify those solids that are supersaturated and therefore have the potential for forming. Changes in  $\text{Fe}^{2+}$  concentrations at the Morrison ALD were largely consistent with a dilution effect. Changes in  $\text{Fe}^{2+}$  concentrations at the REM-R ALD are subject to uncertainties associated with comparing pre-ALD water quality (collected 3 years ago) with the current ALD effluent. Retention of  $\text{Fe}^{2+}$  definitely occurred at the Rid-2L and Rid-2R sites. At both sites, samples of the raw water were collected in conjunction with samples of the ALD effluent. Both of these ALDs were characterized, at the time of sampling, by very long retention times (table 2). While most ALDs had retention times of less than two days, retention times at the Rid-2 sites were more than a month. If siderite forms in ALDs, the reaction appears to be slow and only becomes important when the systems are constructed to have extremely long retention times. Half of the ALD effluents were saturated with rhodochrosite (table 6). No strong evidence was found to suggest that Mn was being retained in any of the ALD systems. The absence of retention of Mn may be due to kinetic limitations, like those proposed for siderite; also rhodochrosite is more soluble than siderite and is unlikely to form until ferrous iron concentrations decrease.

Only two of the ALD effluents were saturated with gypsum (table 6). Both of the mine waters at these sites contained concentrations of sulfate > 4,000 mg/L. At the Ohio site, influent sulfate concentrations are not available. At the Rid-2L ALD, sulfate concentrations of the mine water as it flowed through the ALD decreased from 6,719 to 2,227 mg/L. Several hundred milligrams per liter of the sulfate removal may be attributed to adsorption of sulfate to ferric hydroxide solids (Winland et al. 1991), but most of the loss in sulfate is likely due to gypsum formation. Formation of gypsum in ALDs appears to be limited to sites with very high concentrations of sulfate. For alkalinity-generating ALDs, gypsum saturation was not indicated when sulfate concentrations were less than 2,000 mg/L.

### Retention Time and Alkalinity Generation

Calcite dissolution is not an instantaneous chemical process. For uncontaminated ground water to become saturated with calcite, months of contact time between the water and limestone is necessary (Deines and Langmuir 1974). Most ALDs have retention times that are less than 2 days (table 2) and discharge waters that are

Table 5. Change in concentrations (mg/L) of alkaline and acidic water quality parameters as the mine drainage flows through the ALDs. Alkalinity and acidity concentrations in mg/L as calcium carbonate. Sites with unknown influent water quality are not included in this table. "NA" indicates data is not available.

Site	Alkalinity <sup>1</sup>	Acidity <sup>2</sup>	Fe <sup>1</sup>	Fe <sup>3+</sup>	Fe <sup>2+</sup>	Al	Mn
Rid-2L	+469	-5,901	-1,214	-680	-534	-486	-12
Hathaway	+385	-595	-141	NA	NA	-23	-30
AROAD	+350	-78	+23	-10	+33	-19	-2
Rid-2R	+306	-236	-53	-1	-52	-31	0
Rid-1	+287	+60	+22	-1	+23	-2	+4
TVA-2	+280	-32	-16	NA	NA	0	-6
Morrison	+248	-102	-65	0	-65	-1	-9
Schnepf	+191	-190	-35	NA	NA	-7	+11
Willi	+187	-639	-48	-48	0	-62	-11
Jennings	+177	-146	-11	-10	-1	-21	0
Howe-2	+134	-16	-5	0	-5	0	0
Howe-1	+128	+19	-2	0	-2	0	-1
Shade	+123	-193	-2	0	-2	-22	+4
TVA-4	+120	-278	-135	NA	NA	0	-21
REM-R	+69	-148	-82	-32	-50	-2	-4
Fawn	0	+370	+28	0	+28	+49	+5
Ohiopyle	0	-143	-7	-6	-1	-25	-16

<sup>1</sup>Calculated by (field alkalinity out) - (field alkalinity in).

<sup>2</sup>Calculated to represent change in acidity only (increases in alkalinity were removed from this value): [(net acid out) + (field alk out)] - [(net acid in) + (field alk in)].

undersaturated with calcite (table 6). The kinetics of calcite dissolution are strongly influenced by degree of undersaturation (Berner and Morse 1974). Calcite dissolution is fast for highly undersaturated waters (pH < 4), but decreases dramatically as the waters approach saturation.

At the Howe-1 and Morrison ALDs, the presence of sampling wells within the ALDs allowed an evaluation of alkalinity generation. At both ALDs, concentrations of alkalinity plateau at maximum values within the limestone bed, significantly before the ALD discharge (fig. 1A). While the concentration of alkalinity at which the two sites plateau differs, the waters have similar calcite saturation indices;  $10^{-1.1}$  at Howe-1 and  $10^{-0.9}$  at Morrison (fig. 1B). Interestingly, at both sites the alkalinity plateau occurs when rhodochrosite has reached saturation levels (fig. 1B). The decrease in the rate of alkalinity generation at both ALDs may result from inhibition of calcite dissolution by manganese carbonate complexes (Terjesen et al. 1960). If this hypothesis is correct, then the concentration of alkalinity that an ALD is capable of producing may be controlled, in part, by the concentrations of Mn in the raw water. The retention time necessary for the mine water to reach an alkalinity plateau was 14 hours for Howe-1 and 23 hours for Morrison (fig. 1A). These patterns indicate that retention time will primarily affect the generation of alkalinity in ALDs at low retention times. If retention times are less than 14 hours, concentrations of alkalinity in

Table 6. CO<sub>2</sub> partial pressures and mineral saturation indices for the ALD effluent water samples. "NA" indicates data is not available.

Site	pCO <sub>2</sub> , %	Saturation index (log)				Alkalinity, mg/L
		CaCO <sub>3</sub>	CaSO <sub>4</sub>	FeCO <sub>3</sub>	MnCO <sub>3</sub>	
Rid-2L	26.8	0.246	+0.153	+0.930	-0.378	469
Peabody	22.9	-0.830	+0.119	+1.061	+0.121	400
Hathaway	11.1	-0.155	-0.192	+0.722	NA	385
AROAD	8.3	-0.472	-1.796	+0.907	-0.365	350
Rid-2R	7.9	-0.364	-0.328	+1.161	-0.287	306
Rid-1	8.3	-0.263	-0.280	+0.375	+0.327	290
TVA-2	5.4	-0.531	-1.176	+0.586	+0.029	280
Morrison	11.2	-0.819	-0.477	+0.834	+0.231	271
Schnepp	9.6	-0.905	-0.495	+0.305	+0.093	191
Willi	8.1	-0.790	-0.255	NA	-0.001	187
Empire	11.1	-1.173	-0.604	+0.247	-0.158	180
Jennings	8.2	-0.870	-0.610	+0.392	-0.472	177
Howe-2	4.7	-0.770	-0.434	+1.141	+0.251	174
Howe-1	7.2	-1.239	-0.466	+0.748	-0.141	161
Maud	5.2	-0.900	-0.880	NA	NA	155
REM-L	10.8	-1.482	-0.441	+0.315	-0.345	138
Shade	2.2	-0.914	-0.372	NA	+0.073	123
TVA-4	2.2	-0.899	-1.318	NA	-0.574	120
REM-R	14.2	-2.418	-0.271	-0.215	-0.850	69
Fawn	NA	NA	NA	NA	NA	0
Smith	NA	NA	NA	NA	NA	0

in the effluent water may be limited by insufficient contact time between the water and limestone. For example, the two ALDs with the shortest known theoretical retention times, Ohioyle and REM-R, with retention times of 5 hours each, produced the lowest alkalinity values - 0 and 69 mg/L, respectively. In these cases where retention time is a limiting factor, the addition of more limestone (and more retention time) will likely increase the effluent concentrations of alkalinity. If retention times are greater than 23 hours, the concentration of alkalinity in the ALD effluent will be primarily affected by chemical factors such as dissolved CO<sub>2</sub>, metal, and sulfate concentrations. The addition of more limestone to these systems to increase retention time will have little effect on effluent concentrations of alkalinity.

#### Implications for Sizing ALDs

Previously proposed ALD sizing methods have been based on the drainage flow rate, the anticipated calcite

dissolution rate, and the desired lifetime of the ALD (Nairn et al. 1991, Brodie et al. 1991). An improved sizing technique should also incorporate the concept of minimum retention time. Data presented in this paper indicate that, in order to produce a maximum concentration of alkalinity, retention time of mine water in the ALD must be ~15 hours. To achieve this 15-hour retention time, the requirement for the mass of limestone (M) can be expressed as:

$$M = \frac{Q \rho_b t_d}{V_v}$$

where Q is the volume flow of the mine water,  $\rho_b$  is bulk density of the limestone,  $t_d$  is the detention time and is set equal to 15 hours, and  $V_v$  is the bulk void volume expressed in decimal form. In addition to the mass of limestone required for a 15-hours retention time, enough limestone must be added to satisfy the dissolution losses expected over the proposed treatment period. This can be expressed as:

$$M = \frac{Q C T}{x}$$

where Q is the volume flow of the mine water, C is the predicted concentration of alkalinity in the ALD effluent, T is the design life of the ALD (i.e. proposed treatment period), and x is the calcium carbonate content of the limestone in decimal form. The summation of these two equations represents the total requirement of limestone. For example, an ALD is to contain limestone that has a bulk density of 1600 kg/m<sup>3</sup>, contains 90% calcium carbonate, and has a bulk void volume of 50%. The ALD is expected to deliver 300 mg/L of alkalinity to a flow of 25 L/min of AMD for 20 years. The mass of limestone (M) required is calculated by:

$$M = \frac{Q \rho_b t_d}{V_v} + \frac{Q C T}{x} = \frac{(25 \text{ L/min} \times 60 \text{ min/hr}) (1600 \text{ kg/m}^3 \times \text{m}^3/1000 \text{ L} \times \text{mt}/1000 \text{ kg}) (15 \text{ hr})}{0.50} + \frac{(25 \text{ L/min} \times 60 \text{ min/hr}) (300 \text{ mg/L} \times \text{mt}/10^9 \text{ mg}) (20 \text{ yr} \times 8766 \text{ hr/yr})}{0.90} = 72.0 \text{ mt} + 87.7 \text{ mt} = 159.7 \text{ mt}$$

As the limestone dissolves, the hydraulic integrity of the system should decrease. Since these systems have only recently been used in the treatment of AMD, no data exists describing how this dissolution may affect the performance of the ALD. If the ALD is expected to remove acidity as well as generate alkalinity (through retention of Fe<sup>3+</sup> or Al<sup>3+</sup>), the demands of these reactions on calcite dissolution should be added into the sizing calculation. However, the effects on the generation of alkalinity and longevity of the ALD by ferric and aluminum hydroxide precipitation and retention can not be confidently predicted. Any ferric iron and aluminum in the raw mine water has the potential to significantly and adversely affect the performance of ALDs.

### Conclusions

- 1) The variation in alkalinity generation was less than the variation in acidity removal.
- 2) Large changes in acidity resulted from retention of ferric iron and aluminum.

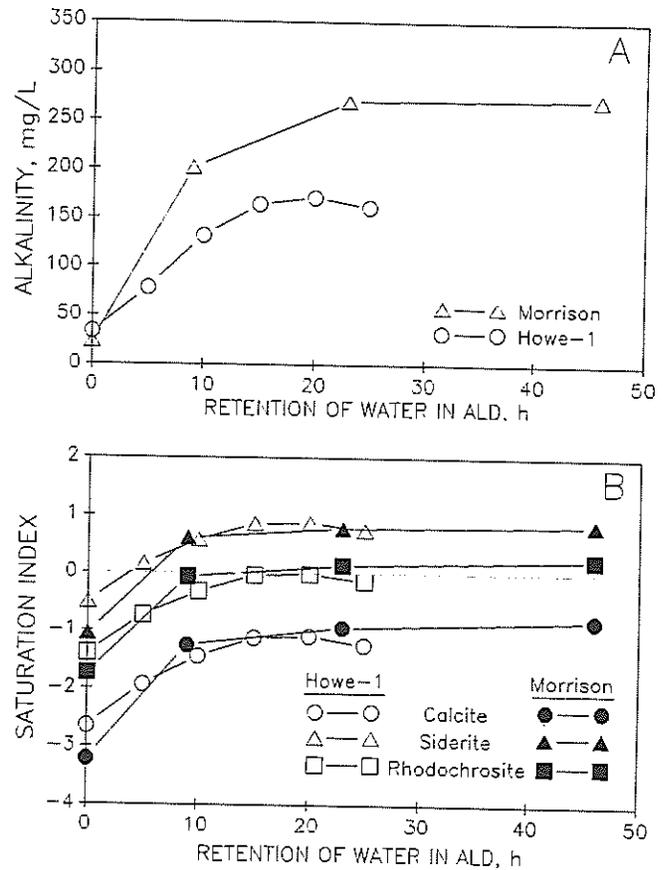


Figure 1. Changes in alkalinity (A) and calcite, siderite, and rhodochrosite (B) saturation indices as the water flows through the Howe-1 and Morrison ALDs. Retention of water in ALD is based on the average mine water flow rate at each site and the position of sampling wells within the ALD.

- 3) Ferrous iron was not significantly retained unless retention times were greater than 650 hours.
- 4) Manganese was not retained in any ALD.
- 5) Sulfate was not retained and gypsum was not supersaturated (based on WATEQ) at any drain which received water with less than 2000 mg/L of sulfate.
- 6) Concentration of alkalinity reached maximum levels after 14-23 hours of contact.
- 7) Retention times over 23 hours will not markedly increase alkalinity concentrations.
- 8) The mass of limestone required for treatment can be calculated by:

$$M = \frac{Q \rho_b t_d}{V_v} + \frac{Q C T}{x}$$

where Q is the volume flow of water,  $\rho_b$  is bulk density of the limestone,  $t_d$  is the detention time and is set equal to 15 hours,  $V_v$  is the bulk void volume expressed in decimal form, C is the predicted concentration of alkalinity in the ALD effluent, T is the design life of the ALD, and x is the CaCO<sub>3</sub> content of the limestone in decimal form.

Some of the links to the original papers Literature Cited are somewhat obscure.

- American Public Health Association. 1985. Standard methods for the examination of water and wastewater. Washington, DC. 1,268 p.
- Ball, J. W., D. K. Nordstrom, and D. W. Zachmann. 1987. WATEQ4F - a personal computer translation of the geochemical model WATEQ2 with revised database. USGS Open File Report 87-50.
- Berner, R. A. and J. W. Morse. 1974. Dissolution kinetics of calcium carbonate in sea water, 4, theory of calcite dissolution. *Am. J. Sci.* 274:108-134. <http://dx.doi.org/10.2475/ajs.274.2.108>
- Brodie, G. A. 1991. Achieving compliance with staged, aerobic, constructed wetlands to treat acid drainage. p. 151-174. In Proceedings of the American Society for Surface Mining Reclamation Meeting, Princeton, WV. <http://dx.doi.org/10.21000/JASMR91010151>
- Brodie, G. A., C. R. Britt, T. M. Tomaszewski, and H. N. Taylor. 1991. Use of passive anoxic limestone drains to enhance performance of acid drainage treatment wetlands. p. 211-222. In Proceedings of the Annual Meeting of the American Society for Surface Mining Reclamation, Princeton, WV. <http://dx.doi.org/10.21000/JASMR91010151>
- Deines, P. and D. Langmuir. 1974. Stable carbon isotope ratios and the existence of a gas phase in the evolution of carbonate ground waters. *Geochim. et Cosmochim. Acta* 38:1147-1164. [http://dx.doi.org/10.1016/0016-7037\(74\)90010-6](http://dx.doi.org/10.1016/0016-7037(74)90010-6)
- Fales, H. A. and F. Kenny. 1940. Inorganic quantitative analysis. D. Appleton Century Co, New York.
- Faulkner, B. B. and J. G. Skousen. 1993. Monitoring of passive treatment systems: an update. In Proceedings of the 14th Annual West Virginia Surface Mine Drainage Task Force Symposium. WV Univ., Morgantown, WV.
- Hedin, R. S. and R. W. Naim. 1993. Contaminant removal capabilities of wetlands constructed to treat coal mine drainage. p. 187-195. In G. A. Moshiri (ed.), *Constructed wetlands for water quality improvement*. Lewis Publishers, Boca Raton, FL.
- Naim, R. W., R. S. Hedin, and G. R. Watzlaf. 1991. A preliminary review of the use of anoxic limestone drains in the passive treatment of acid mine drainage. In Proceedings of the 12th West Virginia Surface Mine Drainage Task Force Symposium. WV Univ., Morgantown, WV.
- Naim, R. W., R. S. Hedin, and G. R. Watzlaf. 1992. Generation of alkalinity in an anoxic limestone drain. p. 206-219. In Proceedings of the American Society for Surface Mining and Reclamation Meeting. (Duluth, MN, June 14-18, 1992). <http://dx.doi.org/10.21000/JASMR92010206>
- Terjesen, S. G., O. Erga, G. Thorsen, and A. Ve. 1960. Phase boundary process as rate determining steps in reactions between solids and liquids: the inhibitory action of metal ions on the formation of calcium bicarbonate by the reaction of calcite with aqueous carbon dioxide. *Chem. Eng. Sci.* 14:277-289. [http://dx.doi.org/10.1016/0009-2509\(61\)80010-6](http://dx.doi.org/10.1016/0009-2509(61)80010-6)
- Turner, D. and D. McCoy. 1990. Anoxic alkaline drain treatment system, a low cost acid mine drainage treatment alternative. p. 73-75. In D. H. Graves and R. W. DeVore (eds.), *Proceedings 1990 National Symposium on Mining*. (Lexington, KY, May 14-18, 1990).
- Watzlaf, G. R. and R. S. Hedin. 1993. A method for predicting the alkalinity generated by anoxic limestone drains. In Proceedings of the 14th Annual West Virginia Surface Mine Drainage Task Force Symposium. WV Univ., Morgantown, WV.
- Winland, R. L., S. J. Traina, and J. M. Bigham. 1991. Chemical composition of ochreous precipitates from Ohio coal mine drainage. *J. Environ. Qual.* 20:452-460. <http://dx.doi.org/10.2134/jeq1991.00472425002000020019x>