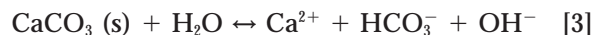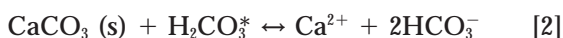# Ecosystem Restoration

Size and Performance of Anoxic Limestone Drains to Neutralize Acidic Mine Drainage

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ABSTRACT

Acidic mine drainage (AMD) can be neutralized effectively in underground, anoxic limestone drains (ALDs). Owing to reaction between the AMD and limestone ($CaCO_3$), the pH and concentrations of alkalinity and calcium increase asymptotically with detention time in the ALD, while concentrations of sulfate, ferrous iron, and manganese typically are unaffected. This paper introduces a method to predict the alkalinity produced within an ALD and to estimate the mass of limestone required for its construction on the basis of data from short-term, closed-container (cubitainer) tests. The cubitainer tests, which used an initial mass of 4 kg crushed limestone completely inundated with 2.8 L AMD, were conducted for 11 to 16 d and provided estimates for the initial and maximum alkalinities and corresponding rates of alkalinity production and limestone dissolution. Long-term (5–11 yr) data for alkalinity and $CaCO_3$ flux at the Howe Bridge, Morrison, and Buck Mountain ALDs in Pennsylvania, USA, indicate that rates of alkalinity production and limestone dissolution under field conditions were comparable with those in cubitainers filled with limestone and AMD from each site. The alkalinity of effluent and intermediate samples along the flow path through the ALDs and long-term trends in the residual mass of limestone and the effluent alkalinity were estimated as a function of the computed detention time within the ALD and second-order dissolution rate models for cubitainer tests. Thus, cubitainer tests can be a useful tool for designing ALDs and predicting their performance.

ACIDIC OR ABANDONED MINE DRAINAGE degrades aquatic ecosystems and water supplies in coal- and metal-mining districts worldwide (Nordstrom, 2000). Acidic mine drainage can contain elevated concentrations of dissolved sulfate (SO_4^{2-}), ferrous iron (Fe^{2+}), and ferric iron (Fe^{3+}) produced by the oxidation of pyrite (FeS_2) and can range in quality from strongly acidic to near-neutral (Rose and Cravotta, 1998; Cravotta et al., 1999; Nordstrom and Alpers, 1999). Concentrations of calcium (Ca^{2+}), magnesium (Mg^{2+}), manganese (Mn^{2+}), aluminum (Al^{3+}), and other solutes can be elevated because of the dissolution of carbonate, oxide, and aluminosilicate minerals by acidic water. Near-neutral AMD can result from the reaction of acidic water with calcareous minerals. For example, dissolution of calcite ($CaCO_3$), which is the principal component of limestone, can increase pH, alkalinity (CO_3^{2-} + HCO_3^- + OH^-), and Ca^{2+} by the following reactions or some combination thereof:

$$CaCO_3 \text{ (s)} + 2H^+ \leftrightarrow Ca^{2+} + H_2CO_3^* \quad [1]$$

$$CaCO_3 \text{ (s)} + H_2CO_3^* \leftrightarrow Ca^{2+} + 2HCO_3^- \quad [2]$$

$$CaCO_3 \text{ (s)} + H_2O \leftrightarrow Ca^{2+} + HCO_3^- + OH^- \quad [3]$$

where $[H_2CO_3^*] = [CO_2 \text{ (aq)}] + [H_2CO_3^0]$ (Plummer et al., 1979). Hence, the stoichiometric dissolution of 1 mol $CaCO_3$ will produce 1 mol Ca^{2+} and up to 2 mol alkalinity as HCO_3^-. On the basis of Eq. [2], an alkalinity concentration of 122 mg L^{-1} as HCO_3^- equals 100 mg L^{-1} as $CaCO_3$, and a Ca^{2+} concentration of 40 mg L^{-1} equals 100 mg L^{-1} as $CaCO_3$ (hardness).

Acidity and metals can be removed from AMD through various passive treatment systems that increase pH and alkalinity and, ultimately, facilitate Fe^{2+} oxidation (Hedin et al., 1994a; Skousen et al., 1998). Many systems use crushed limestone in a packed bed that is flooded continuously with AMD to neutralize the acidity, thereby generating alkalinity. As the pH increases to near-neutral values, concentrations of Fe^{3+}, Al^{3+}, and other metals in AMD can decline owing to their precipitation or adsorption; however, concentrations of SO_4^{2-}, Fe^{2+}, and Mn^{2+} generally will not be affected (Blowes and Ptacek, 1994; Cravotta and Trahan, 1999). For example, anoxic limestone drains (ALDs) are particularly effective for generating alkalinity (Turner and McCoy, 1990; Brodie et al., 1991; Hedin and Watzlaf, 1994; Hedin et al., 1994b; Watzlaf et al., 2000). A typical ALD consists of crushed limestone of uniform size that is placed in a buried bed to intercept net-acidic AMD before its exposure to atmospheric O_2. Excluding O_2 from contact with the water in an ALD minimizes the potential for oxidation of Fe^{2+} to Fe^{3+} and the consequent precipitation of $Fe(OH)_3$ and related solids (e.g., Bigham et al., 1996; Cravotta and Trahan, 1999).

The precipitation of $Fe(OH)_3$ and various compounds of Al^{3+} and, possibly, Ca^{2+} and SO_4^{2-}, within a bed of limestone can "armor" the limestone surfaces, potentially decreasing the rate and extent of limestone dissolution and alkalinity production (Hedin and Watzlaf, 1994; Robbins et al., 1999). Furthermore, the accumulation of precipitated compounds can decrease the porosity and permeability of the bed (Robbins et al., 1996; Watzlaf et al., 2000). Owing to its solubility, gypsum ($CaSO_4·2H_2O$) usually is undersaturated in the effluent from ALDs evaluated in Pennsylvania and West Virginia (Hedin and Watzlaf, 1994; Cravotta and Trahan, 1999; Robbins et al., 1999). Hence, design criteria for ALDs as proposed by Hedin et al. (1994a) and Hedin and Watzlaf (1994) generally are conservative with respect to the permissible concentrations of dissolved O_2, Fe^{3+}, and Al^{3+} in influent (<1 mg L^{-1} O_2, Fe^{3+}, or

Abbreviations: ALD, anoxic limestone drain; AMD, acidic mine drainage.

Al^{3+}) to minimize potential for clogging or armoring by Fe(III) or Al solids.

Continuous inundation with AMD and retention of carbon dioxide (CO_2) within an ALD can enhance limestone dissolution and alkalinity production because the rate and extent of limestone dissolution tend to increase with increased partial pressure of carbon dioxide (P_{CO_2}) and/or decreased pH (e.g., Plummer et al., 1979; Morse, 1983; Langmuir, 1997). By the mechanism indicated by Eq. [1] and [2], a greater quantity of alkalinity can be generated in an enclosed ALD compared with alternative treatment systems such as limestone channels (Ziemkiewicz et al., 1997; Cravotta and Weitzel, 2001) or diversion wells (Arnold, 1991; Cram, 1996; Cravotta and Weitzel, 2001) that are open to the atmosphere. After treatment by an ALD, effluent typically is routed through ponds and/or wetlands where exposure to the atmosphere facilitates Fe^{2+} oxidation and the precipitation and settling of solid $Fe(OH)_3$.

Hedin and Watzlaf (1994) evaluated construction characteristics, detention times, and chemistry of influent and effluent of more than 20 anoxic and oxic limestone drains to determine the optimum size for maximum alkalinity production. They derived a sizing equation to estimate the initial mass of limestone (M_0) required for an optimal ALD. This ALD sizing equation included a term for longevity and a term for detention time:

$$M_0 = Q[(t_L\ C_M/X_{CaCO_3}) + (t_d\ \rho_B/\phi)] \qquad [4]$$

where Q is the volumetric flow rate, t_L is the longevity or duration of treatment, C_M is the maximum alkalinity concentration, X_{CaCO_3} is the limestone weight fraction as $CaCO_3$, t_d is the detention time, ρ_B is the bulk density, and ϕ is the porosity. Hedin and Watzlaf (1994) and Hedin et al. (1994a,b) solved Eq. [4] for the limestone mass using longevity of 20 yr, detention time of 15 h, and porosity of 0.49. A design life of 20 yr provides reasonable limits on the size and cost of the treatment system and considers the possibility for water quality to slowly improve without treatment. Closed-container tests by Watzlaf and Hedin (1993) indicated the alkalinity concentration after 15 h of contact with limestone typically was about 80% of the maximum concentration attained after 48 h; only marginal increases in alkalinity could be expected with increased detention time. The porosity of 0.49 is an average for limestone fragments packed in a 20-L bucket, representative of the limestone used at the Morrison and Howe Bridge ALDs (G.R. Watzlaf, personal communication, 2001). Equation [4] assumes constant alkalinity concentration and $CaCO_3$ flux for the specified duration of treatment. However, alkalinity tends to decrease with decreased detention time. For a given flow rate and porosity, the detention time will decrease with decreased limestone mass. The limestone mass will decrease with age of the ALD. For large flows that have relatively low net acidity but still require treatment, the specification of a 15-h detention time would indicate excessively large quantities of limestone and associated costs for installation.

This paper describes methods for estimating alkalinity production in ALDs and the mass of a limestone bed needed for anoxic treatment of AMD. Long-term (5–11 yr) data for influent and effluent and corresponding short-term (2 wk) data for cubitainer tests of the Howe Bridge, Morrison, and Buck Mountain ALDs in Pennsylvania are used to test the hypotheses that (i) alkalinity produced by reaction of AMD with limestone in cubitainers indicates the alkalinity as a function of detention time within the ALDs and (ii) the AMD reaction with limestone in cubitainers reflects the dissolution rate under field conditions. The AMD at these sites initially contained some alkalinity (pH > 4.5) and met criteria for construction of an ALD (<1 mg L^{-1} O_2, Fe^{3+}, or Al^{3+}). Alkalinity data for influent, effluent, and intermediate samples along the flow path through the ALDs are compared with those for cubitainer tests. Estimates of $CaCO_3$ flux at the ALDs based on annual averages of flow rates and concentrations of alkalinity and calcium in influent and effluent are compared with estimates using alkalinity data, dissolution rate equations, and rate constants derived from cubitainer tests. Last, the rate equations are rearranged to provide an alternative to Eq. [4] for estimating the initial mass of limestone required to produce effluent of a specified alkalinity, while accounting for continuous declines in limestone mass, detention time, and alkalinity with age of the ALD.

MATERIALS AND METHODS

Description of Limestone Drains

Howe Bridge

The Howe Bridge ALD is located in Jefferson County, PA (41°13′39″ N, 79°11′09″ W), and was constructed in 1991 of 455 Mg of limestone fragments ranging in size from 5.1 to 7.6 cm (Hedin et al., 1994b; Watzlaf et al., 2000). The limestone was reported to have a purity of 82% (w/w) as $CaCO_3$. Influent for this ALD was captured from an abandoned gas drill hole and piped to the limestone drain. This influent water can be sampled via a well before contact with limestone. Four sampling wells were installed at evenly spaced locations along the length of the ALD.

Morrison

The Morrison ALD is located in Clarion County, PA (41°12′11″ N, 79°25′58″ W), and was constructed in 1990 of 65 Mg of limestone fragments ranging in size from 5.1 to 7.6 cm (Hedin et al., 1994b; Watzlaf et al., 2000). The limestone was reported to have a purity of 92% (w/w) $CaCO_3$. The AMD seepage from multiple points is intercepted within a limestone-filled trench at the toe of the spoil of a reclaimed surface mine. An adjacent seep, of similar water quality to the pre-construction water, is used to represent influent water quality. Three sampling wells were installed along the length of the ALD.

Buck Mountain

The Buck Mountain ALD is located in Schuylkill County, PA (40°40′32″ N, 76°22′29″ W), and was constructed in 1997 of 320 Mg of limestone fragments ranging in size from 6 to 10 cm (Cravotta and Weitzel, 2001; Cravotta, 2002; Cravotta and Watzlaf, 2002). The limestone was reported to have a

purity of 92% (w/w) $CaCO_3$. Seepage of AMD from a collapsed drainage tunnel is collected at various points where water wells up along the length of the drain. Because the ALD construction involved placement of limestone within the collapsed drainage tunnel, influent water quality is based on preconstruction data and an adjacent seep of similar water quality to the preconstruction water. Seven access wells were installed at evenly spaced locations along the length of the drain. Perforated piping was installed along the length of the drain to flush accumulated solids.

Methods of Sampling and Analysis

Effluent from each of the ALDs was accessible for volumetric flow measurement and water quality monitoring. Additional samples were collected from capped access wells at intermediate points between the inflow and outflow to indicate progressive changes in water quality along the length of the ALDs. Samples were retrieved from access wells by use of pumps or bailers. The actual influent was not accessible at the Morrison and Buck Mountain drains, so adjacent untreated seeps with similar chemical characteristics as the untreated, preconstruction AMD were sampled to represent the influent.

Standard methods were used for sampling and analysis of water samples (e.g., Wood, 1976; Fishman and Friedman, 1989; Wilde et al., 1998; Greenberg et al., 1992). Water temperature, pH, and dissolved O_2 were measured using instruments calibrated in the field at the time of sample collection. Water samples were split into subsamples in the field and stored on ice in sample-rinsed polyethylene bottles until laboratory analysis. Two unfiltered subsamples were collected and capped with no headspace for analysis of (i) alkalinity and acidity and (ii) anions. Alkalinity and acidity were titrated within 24 h after sample collection with sulfuric acid (1.6 N H_2SO_4) to pH 4.5, then with sodium hydroxide (0.1 M NaOH) to pH 8.3. A third subsample was filtered through a 0.45-μm nitrocellulose filter, transferred to an acid-rinsed bottle, and preserved with nitric acid at pH < 2 for analysis of "dissolved" cations, including calcium, iron, and aluminum. Dissolved cation concentrations were determined by inductively coupled plasma atomic emission spectroscopy (ICP–AES). Concentrations of Fe^{2+} were determined by colorimetry (Greenberg et al., 1992), or by calculation of the Fe^{2+} to Fe^{3+} ratio on the basis of redox potential measured with a combination Pt and Ag/AgCl electrode, checked with Zobell's solution, and corrected to 25°C according to methods of Nordstrom (1977).

The flow rate and water quality were monitored monthly during the first year and less frequently thereafter for 11 yr at the Morrison ALD, 10 yr at the Howe Bridge ALD, and 5 yr at the Buck Mountain ALD. The water quality data for the Morrison and Howe Bridge ALDs were compiled by the U.S. Department of Energy (USDOE) (G.R. Watzlaf, personal communication, 2001), and those for the Buck Mountain ALD were compiled by the U.S. Geological Survey (USGS) (Durlin and Schaffstall, 1997, 1998, 1999, 2000, 2001, 2002). These data were collected independently by USDOE and USGS and exchanged as part of an informal collaboration (Cravotta and Watzlaf, 2002). The annual and long-term averages for flow rate, pH, and concentrations of net acidity (acidity − alkalinity), alkalinity, calcium, and other selected solutes in influent and effluent of the three ALDs were computed to evaluate the extent of contaminant attenuation and the $CaCO_3$ fluxes and rates of limestone dissolution within the ALDs at each site.

In addition to the evaluation of field data, cubitainer test data for the Howe Bridge and Morrison sites that had been
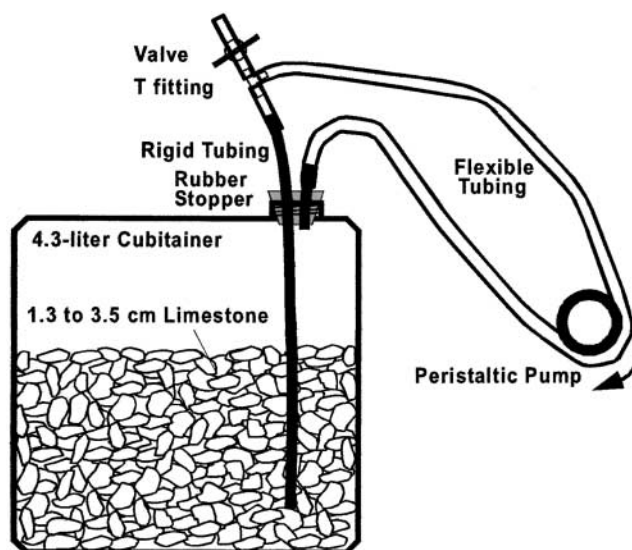

Fig. 1. Schematic of nominal 3.78-L (1-gallon) cubitainer containing 4 kg limestone and filled with mine discharge water to evaluate alkalinity production rates (after Watzlaf and Hedin, 1993). Limestone sized to 1.3 × 3.5 cm.

reported by Watzlaf and Hedin (1993) and new data for the Buck Mountain site were used to indicate qualitative and quantitative effects of variable influent compositions, detention times, and limestone purity on limestone drain performance. Collapsible polyethylene cubitainers (3.78-L [1-gallon] nominal volume) were filled to two-thirds capacity with 4 kg of 1.3- by 3.5-cm limestone fragments of the same composition used for a given ALD, then untreated mine water was added to exclude any air and maintained at field water temperature (Fig. 1). Before loading in cubitainers, the crushed limestone was sieved and rinsed thoroughly with tap water and then dried. Multiple cubitainers were prepared to replicate these tests. Over 11 to 16 d, samples were withdrawn through a valve by 60-mL syringe. After discarding approximately 10 mL fluid from the sample tubing, a 50-mL sample was collected and forced from the syringe through a 0.45-μm nylon filter, then immediately analyzed for alkalinity (pH 4.5 endpoint). Because the alkalinity changed little with prolonged contact time, samples were withdrawn at 0.5-h intervals during the first 3 to 4 h, then hourly until 6 to 8 h had elapsed; samples were withdrawn at 24-h intervals or less frequently after the first day.

Closed cubitainer tests at the Howe Bridge and Morrison ALDs were conducted in the field only under static (uncirculated) conditions. Equipment and protocols similar to those used for the Howe Bridge and Morrison cubitainer tests were used for the Buck Mountain tests. However, the Buck Mountain tests were conducted in the laboratory under static and circulated conditions. Untreated seepage from the Buck Mountain site was collected into empty cubitainers leaving no headspace and immediately transported to the laboratory. Within an hour of collection, the influent was used to fill other cubitainers containing 4 kg limestone. Circulation without the introduction of air (closed conditions) was facilitated by use of a peristaltic pump (Fig. 1). The pumping rate was maintained between 0.1 and 0.5 L min^{-1} to simulate mixed flow through the ALD and minimize stratification within the cubitainers. Tests were conducted in duplicate (concurrently in November or December 2001) or repeated. The approximate field temperature of 9°C was maintained using an ice bath during the first day. After the first 8 h of the tests, the cubitainers and

pump were placed in a refrigerator and maintained at 5°C. To determine the volume of influent, each cubitainer was weighed after loading the limestone, after adding the influent, and at the completion of testing.

RESULTS

Over the 5- to 11-yr monitoring period at the Howe Bridge, Morrison, and Buck Mountain ALDs, the average flow rates were 117, 7, and 460 L min^{-1}, respectively (Table 1). The annual average flow rate and detention time (void volume divided by flow rate) varied by a factor of two or three at each site (Table 2).

Effluent from each ALD had higher pH, alkalinity, and calcium, and lower acidity and aluminum concentrations than influent (Table 1). The pH and alkalinity increased asymptotically with increased detention time or downflow distance within each ALD (Fig. 2). Because influent to each ALD had pH greater than 4.5 and initially contained alkalinity, the rates of increase in alkalinity and calcium were equivalent and proportional to the rate of limestone dissolution. The influent and effluent at the Howe Bridge and Morrison ALDs contained greater concentrations of alkalinity, acidity, sulfate, iron, and calcium than those at the Buck Mountain site (Tables 1 and 2). Despite having attained near-neutral pH, effluent from both the Howe Bridge and Morrison ALDs was net acidic because of elevated concentrations of Fe^{2+} and Mn^{2+} (Table 1). Despite significant production of alkalinity in all three ALDs, the effluent from each was undersaturated with respect to calcite (Table 1).

As reported by Watzlaf and Hedin (1993), alkalinity for cubitainer tests approached a steady state, maximum concentration after about 4 d and was about 80% of the maximum at 15 h (Fig. 3). The maximum alkalinity for the Morrison cubitainer tests was approximately 340 mg L^{-1}, that for the Howe Bridge tests was approximately 210 mg L^{-1} (Fig. 3A), and that for the Buck Mountain tests was 174 mg L^{-1} (Fig. 3B). These maxima were comparable with those of effluent associated with low flow rates from the respective ALDs (Table 2). The greater maximum concentration of alkalinity for the Morrison tests compared with the Howe Bridge tests can be attributed to lower pH and higher P_{CO_2} for the Morrison influent (Table 1). The Buck Mountain influent had lower pH and P_{CO_2} and was more undersaturated with respect to calcite than the other sites (Table 1).

DISCUSSION

Alkalinity Production Rate

The alkalinity produced in a limestone bed, and its effectiveness in buffering the pH of AMD, depend on the pH and P_{CO_2} of influent and the detention time of water within the bed. Typically, alkalinity, calcium, and pH increase asymptotically with increased detention time or downflow distance within an ALD owing to rapid dissolution of limestone near the inflow and declining dissolution rates as the solution approaches equilibrium with calcite (Cravotta and Trahan, 1999; Watzlaf

Table 1. Average water quality of influent (I) and effluent (E) at Howe Bridge, Morrison, and Buck Mountain anoxic limestone drains (ALDs) in Pennsylvania.

ALD†	Year built	Mass of limestone	Flow rate	pH		Net acidity		Calcite saturation‡		P_{CO_2}‡		Alkalinity		Calcium§		Sulfate		Iron		Manganese		Aluminum	
				I	E	I	E	I	E	I	E	I	E	I	E	I	E	I	E	I	E	I	E
		Mg	L min^{-1}			mg L^{-1} as CaCO$_3$		log(IAP/K)		log(atm)¶		mg L^{-1} as CaCO$_3$				mg L^{-1}							
Howe Bridge	1991	455	117	5.8	6.3	495	369	−2.1	−0.7	−1.2	−1.1	36	158	371	493	1240	1230	255	254	40	40	<0.2	<0.2
Morrison	1990	65	7	5.3	6.4	434	76	−2.9	−0.4	−0.8	−1.0	30	291	275	543	1200	1010	209	165	47	39	0.5	0.5
Buck Mountain	1997	320	460	4.9	6.4	19	−61	−5.9	−1.7	−1.6	−1.5	2	82	8	94	61	56	10	10	1	1	0.5	<0.2

† Grand average of annual averages for period of record. Data for influent and effluent quality at Howe Bridge and Morrison ALDs from U.S. Department of Energy (G.R. Watzlaf, personal communication, 2001) and at Buck Mountain from U.S. Geological Survey (Durlin and Schaffstall, 1997, 1998, 1999, 2000, 2001, 2002). Influent quality at Morrison and Buck Mountain for nearby seep.
‡ Partial pressure of carbon dioxide (P_{CO_2}) and calcite saturation index [SI = log(IAP/K)] computed using thermodynamic data from Ball and Nordstrom (1991), where K is the solubility product constant and IAP is the corresponding ion activity product.
§ Calcium concentration as CaCO$_3$ computed as 2.5 times the concentration of Ca. Differences between influent and effluent alkalinity or Ca indicate approximate quantity of limestone dissolved in the ALD each year since construction.
¶ 1 atm = 0.101 MPa.

Table 2. Annual average flow rate and concentrations of alkalinity and calcium, and corresponding estimates of limestone mass dissolved, mass remaining, and detention time at Howe Bridge, Morrison, and Buck Mountain anoxic limestone drains (ALDs) in Pennsylvania.

Age	Flow rate	Alkalinity		Limestone mass		Detention time	Calcium		Limestone mass†		Detention time‡
		Influent	Effluent	Dissolved	Remaining		Influent	Effluent	Dissolved	Remaining	
yr	L min⁻¹	— mg L⁻¹ as CaCO₃ —		Mg yr⁻¹	Mg	h	— mg L⁻¹ as CaCO₃ —		Mg yr⁻¹	Mg	h
				Howe Bridge							
0	117	36	36	0.00	455	23.6	371	371	0.00	455	23.6
1	92	31	167	8.00	447	29.4	379	514	7.95	447	29.4
2	95	33	162	7.89	439	27.8	418	551	8.12	439	27.8
3	101	32	152	7.79	431	25.7	404	528	8.03	431	25.7
4	87	25	151	7.01	424	29.4	393	525	7.43	423	29.3
5	114	38	160	8.88	415	22.0	366	482	8.45	415	22.0
6	108	45	170	8.68	407	22.7	370	479	7.55	407	22.7
7	112	43	167	8.88	398	21.5	355	463	7.70	400	21.6
8	117	40	150	8.23	390	20.2	345	473	9.54	390	20.2
9	176	37	158	13.62	376	12.9	342	473	14.79	375	12.9
10	164	39	149	11.60	364	13.4	343	443	10.54	365	13.4
Average§	117	36	158	9.06	NA¶	22.6	371	493	9.01	NA	22.6
				Morrison							
0	6.8	30	30	0.00	65	57.7	275	275	0.00	65	57.7
1	8.0	13	247	1.07	64	48.2	289	572	1.30	64	48.0
2	4.4	24	270	0.61	63	87.7	294	565	0.68	63	87.3
3	7.7	26	281	1.13	62	48.7	291	556	1.17	62	48.4
4	8.6	34	287	1.24	61	42.9	286	541	1.25	61	42.6
5	6.2	32	263	0.82	60	58.3	273	517	0.87	60	58.0
6	9.4	29	288	1.38	59	38.0	268	531	1.41	58	37.7
7	8.6	39	305	1.30	57	40.6	253	514	1.28	57	40.3
8	8.1	42	310	1.23	56	42.2	291	516	1.04	56	42.1
9	5.4	32	315	0.88	55	61.6	271	590	0.99	55	61.2
10	3.8	31	329	0.64	55	87.4	262	576	0.68	54	86.9
11	4.8	29	304	0.76	54	67.3	247	493	0.68	54	67.0
Average	6.8	30	291	1.01	NA	56.6	275	543	1.03	NA	56.4
				Buck Mountain							
0	460	2	2	0.00	320	4.2	8	8	0.00	320	4.2
1	429	2	69	16.54	303	4.3	8	75	16.48	304	4.3
2	537	2	82	24.55	279	3.1	8	98	27.80	276	3.1
3	579	2	117	38.19	241	2.5	8	104	31.93	244	2.5
4	553	2	85	26.42	214	2.3	8	108	31.51	212	2.3
5	198	2	56	6.17	208	6.3	8	84	8.65	204	6.2
Average	460	2	82	22.37	NA	3.7	8	94	23.28	NA	3.7

† Mass dissolved computed as the product of flow rate and the difference between effluent and influent concentration of alkalinity or calcium divided by limestone purity. Mass remaining is difference between that dissolved in the year and that remaining for prior year.
‡ Detention time for annual average flow rate and limestone mass remaining computed using Eq. [12] and assuming porosity of 0.49.
§ Grand average of annual averages for period of record. Flow rate at time of construction (age = 0) assumed equal to the grand average.
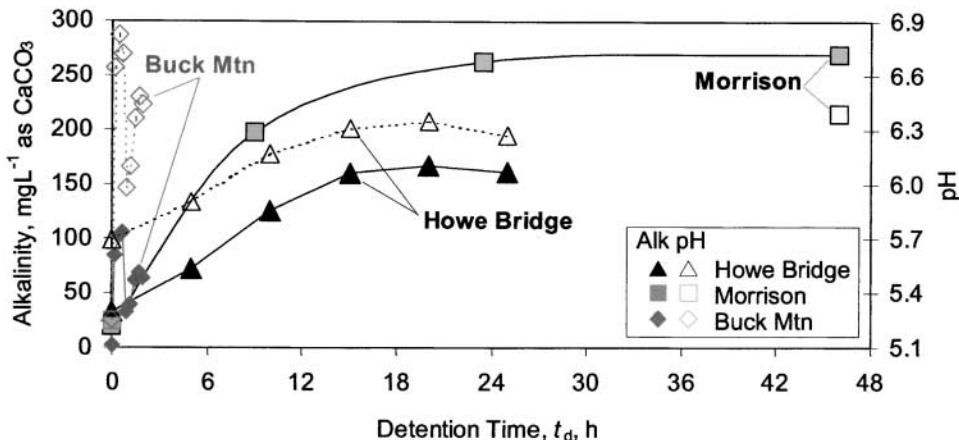¶ Not applicable.

Fig. 2. Changes in alkalinity with detention time of mine drainage within limestone drains at Howe Bridge, Morrison, and Buck Mountain sites. Detention time (t_d) computed as product of porosity (ϕ), downflow distance (L), and cross-sectional area (A) divided by flow rate (Q): $t_d = \phi LA/Q$, assuming $\phi = 0.49$.

et al., 2000; Cravotta and Watzlaf, 2002). More complex trends, such as that exhibited at the Buck Mountain site (Fig. 2), can arise because of multiple inflows of untreated AMD along the length of the ALD.

An asymptotic approach to the "maximum" alkalinity for long detention times in the ALDs (Fig. 2) and cubitainer tests (Fig. 3) indicates that the overall rate of limestone dissolution decreases exponentially as the solution approaches equilibrium with calcite. According to Lasaga (1981), the kinetics relation for an approach to a steady state concentration can be written as:

$$d\,C/d\,t = k(C_M - C)^n \qquad [5]$$

where C is the concentration of alkalinity or calcium, C_M is the maximum concentration, k is the rate constant, and n is the order of reaction. Although calcite dissolution is complex and the exponent, n, can be any positive number, two forms of Eq. [5] generally are considered, where $n = 1$ (first order) and $n = 2$ (second order).

Calcite dissolution has been described as a first-order reaction by a number of investigators, primarily for highly undersaturated conditions (Morse, 1983). Integration of Eq. [5] for a first-order reaction yields:

$$\ln[(C_M - C_t)/(C_M - C_0)] = -k'\,t_d \qquad [6]$$

where C_0 is the initial concentration and C_t is the concentration at any detention time (t_d). Linear regression of $\ln[(C_M - C_t)/(C_M - C_0)]$ versus detention time for the averages of replicate cubitainer tests yielded estimates for k' of 0.051 and 0.053 h^{-1} for Howe Bridge and Morrison, respectively (Fig. 4A). Two different slopes for the Buck Mountain tests indicate k' of 0.070 h^{-1} for static conditions and 0.193 h^{-1} for circulated conditions (Fig. 4B). Taking the antilogarithm and rearranging Eq. [6]:

$$C_t = C_M - [(C_M - C_0)\exp(-k'\,t_d)] \qquad [7]$$

alkalinity at any detention time can be computed as a function of the first-order rate constants and the initial and maximum alkalinities. Rearranging Eq. [7] and taking the logarithm, the minimum required detention time

can be determined where C_t is equal to the acidity, but less than C_M:

$$t_d = \ln[(C_M - C_0)/(C_M - C_t)]/k' \qquad [8]$$

For complete neutralization, the effluent alkalinity must exceed the acidity.

Alternatively, integration of Eq. [5] for values of n other than 1 yields:

$$(C_M - C_t)^{1-n} - (C_M - C_0)^{1-n} = (n-1)k''\,t_d \qquad [9]$$

The value of n that yields a straight line for a plot of $(C_M - C_t)^{1-n}$ versus detention time is the order of the reaction in Eq. [9]. Dietz and Dempsey (2002) recently evaluated calcite dissolution in accordance with a second-order model based on the stoichiometry indicated by Eq. [2], where 1 mol CaCO$_3$ produces 2 mol HCO$_3^-$. For a second-order reaction, the exponent term ($1 - n$) becomes -1, and the rate constant, k'', can be determined by linear regression of $[1/(C_M - C_t) - 1/(C_M - C_0)]$ versus detention time (Fig. 5). The slopes indicate values of k'' of 0.00057 and 0.00036 L mg^{-1} h^{-1} for Howe Bridge and Morrison, respectively (Fig. 5A), and 0.00048 and 0.00171 L mg^{-1} h^{-1} for the static and circulated tests, respectively, for Buck Mountain (Fig. 5B). Given these values of k'' and the initial and maximum alkalinities, Eq. [9] can be rearranged and solved for alkalinity as a function of detention time for a second-order model:

$$C_t = C_M - \{1/[k''\,t_d + 1/(C_M - C_0)]\} \qquad [10]$$

Rearranging Eq. [10], the detention time can be computed for any C_t that is less than C_M:

$$t_d = 1/[k''(C_M - C_t)] - 1/[k''(C_M - C_0)] \qquad [11]$$

The measured alkalinity and that computed for first-order and second-order models for continuous variation in alkalinity with detention time are shown in Fig. 3. The second-order rate expression (Eq. [10]) provides a better estimate of the alkalinity at short detention times than the first-order rate expression (Eq. [7]). At long detention times, both methods reflect the asymptotic approach to maximum alkalinity. Despite faster dissolu-
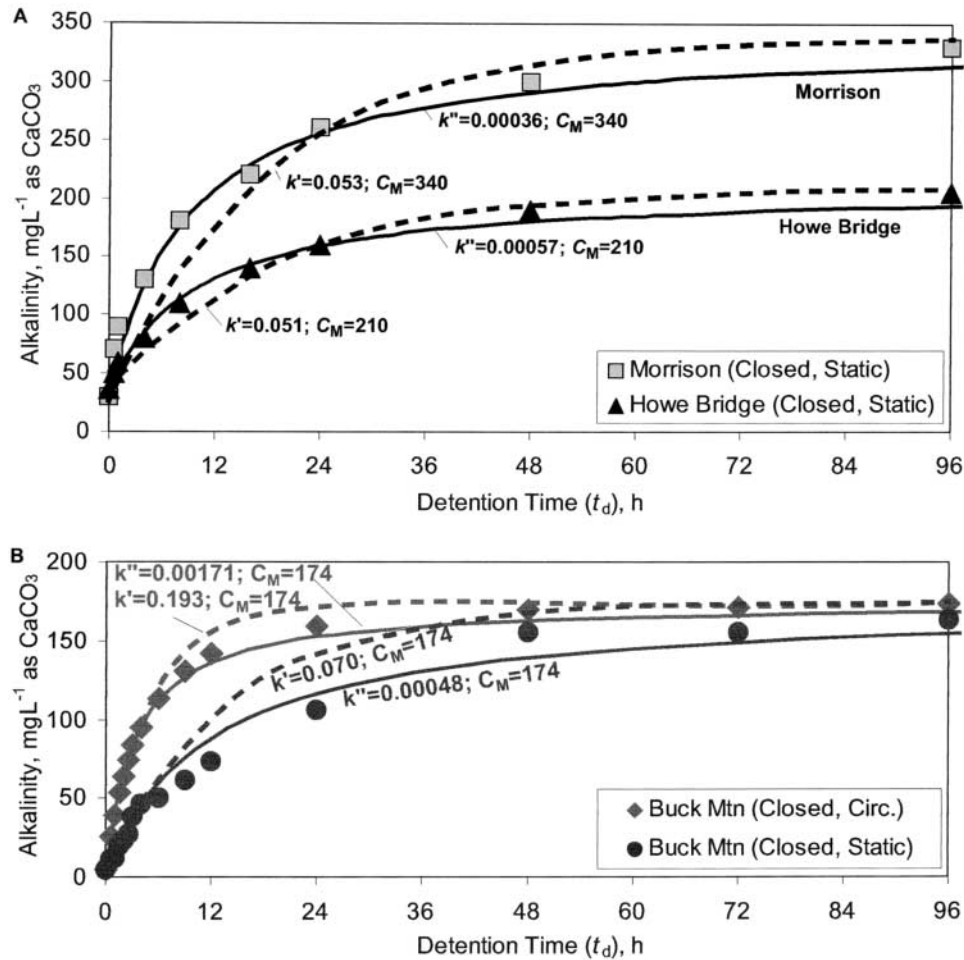
Fig. 3. Generalized alkalinity data (points) for cubitainer tests of the influent to Howe Bridge, Morrison, and Buck Mountain anoxic limestone drains (ALDs) and corresponding estimates of alkalinity concentration (C_i) computed on the basis of first-order (Eq. [7], dashed curves) and second-order (Eq. [10], solid curves) rate models and corresponding rate constants derived from cubitainer data (Fig. 4 and 5). (*A*) Howe Bridge and Morrison tests conducted under static–closed conditions (after Watzlaf and Hedin, 1993). (*B*) Buck Mountain tests conducted under static–closed and circulated–closed conditions.

tion under circulated conditions compared with static conditions for the Buck Mountain tests (Fig. 3B, 4B, and 5B), the maximum alkalinity of 174 mg L^{-1} for both was attained at about 11 d. Faster dissolution under circulated conditions can arise because of thinning of the stagnant boundary layer at the calcite surface and implies rate control by diffusional transport processes (Morse, 1983).

Application of Eq. [7] or [10] using rate constants derived from the cubitainer tests may be useful to indicate alkalinity variations within an ALD (Fig. 2) or with temporal changes in flow rate or mass of limestone (Table 2), because each of these situations implies changes in detention time. Detention time and, hence, rates of alkalinity production within a limestone bed can be estimated on the basis of the volumetric flow rate (Q), the limestone mass (M) and density (ρ_S), and the porosity (ϕ) of the packed bed (Cravotta and Trahan, 1999; Cravotta and Watzlaf, 2002). Knowing the porosity and flow rate and assuming particle density = 2.65 g cm^{-3} considered typical for limestone (Freeze and Cherry, 1979; Cravotta and Trahan, 1999), the detention

time for water flowing through a limestone bed with a given mass can be estimated:

$$t_d = M/[Q\,\rho_S(1 - \phi)/\phi] \qquad [12]$$

or the mass of limestone required to achieve a given detention time can be determined:

$$M = t_d[Q\,\rho_S(1 - \phi)/\phi] \qquad [13]$$

The porosity of packed limestone beds ranges from 0.38 to 0.52 for well-sorted limestone fragments, with larger values associated with larger particles of 5.1 to 7.6 cm (Rice et al., 1970). On the basis of Eq. [12] and assuming an average porosity of 0.49, initial detention times at average flow were estimated to be 24, 58, and 4.2 h at the Howe Bridge, Morrison, and Buck Mountain ALDs, respectively (Table 2). Detention times would be less for smaller porosity values or smaller limestone mass.

Alkalinity versus detention time in the Howe Bridge, Morrison, and Buck Mountain ALDs is shown in Fig. 6. Data for longitudinal samples from monitoring wells within the ALDs, shown previously in Fig. 2, are plotted as individual points at detention times estimated for
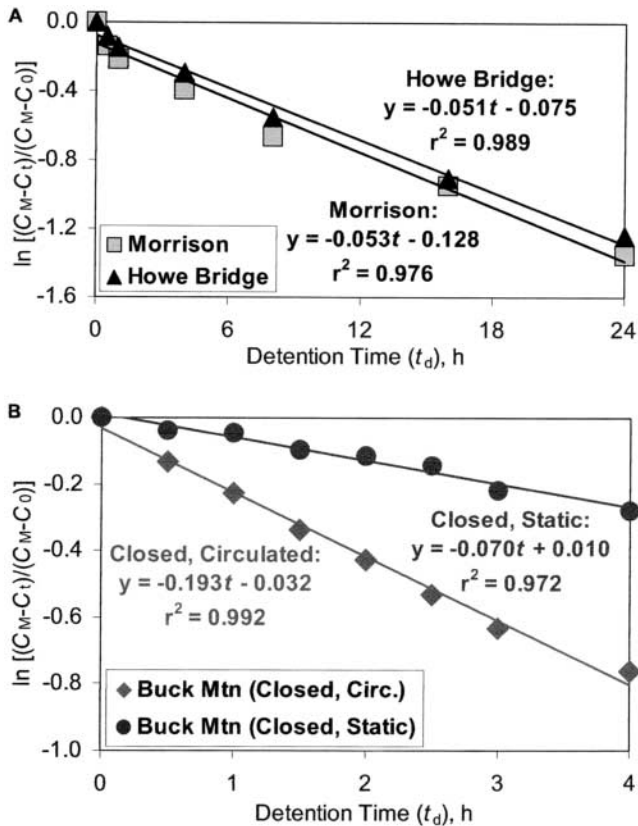
Fig. 4. First-order rate constant for cubitainer tests: (*A*) Howe Bridge and Morrison; (*B*) Buck Mountain negative value of slope indicates rate constant (k') for computation of alkalinity as a function of detention time (C_t) on the basis of Eq. [7].

Fig. 5. Second-order rate constant for cubitainer tests: (*A*) Howe Bridge and Morrison; (*B*) Buck Mountain value of slope indicates rate constant (k'') for computation of alkalinity as a function of detention time (C_t) on the basis of Eq. [10].

porosity of 0.49. The first-order (Eq. [7]) and second-order (Eq. [10]) simulations assume a continuous reduction in detention time. For the simulations, the greatest detention time for each of the ALDs is associated with the initial mass of limestone; shorter detention times are associated with decreased mass, while maintaining constant porosity of 0.49, particle density of 2.65 g cm^{-3}, and average flow rate in accordance with Eq. [12]. Other factors being constant, the decrease in detention time is consistent with shortened flow paths through the ALDs, increased flow rate, decreased porosity, or decreased mass. Generally, the trend simulated using the second-order rate model with rate constants derived from the cubitainer tests (Eq. [10]) matches the observed data for the intermediate and downflow reaches of the ALDs. For the Buck Mountain ALD, the closed, circulated cubitainer tests provided a much better match with field conditions than the static tests. Nevertheless, the observed values near the inflow deviate from simulated alkalinity for the Buck Mountain ALD that intercepts AMD at several points along its length.

Estimation of Limestone Drain Size and Performance

The required mass of limestone for construction of an ALD can be estimated on the basis of the limestone dissolution rate. The decline in limestone mass and cor-
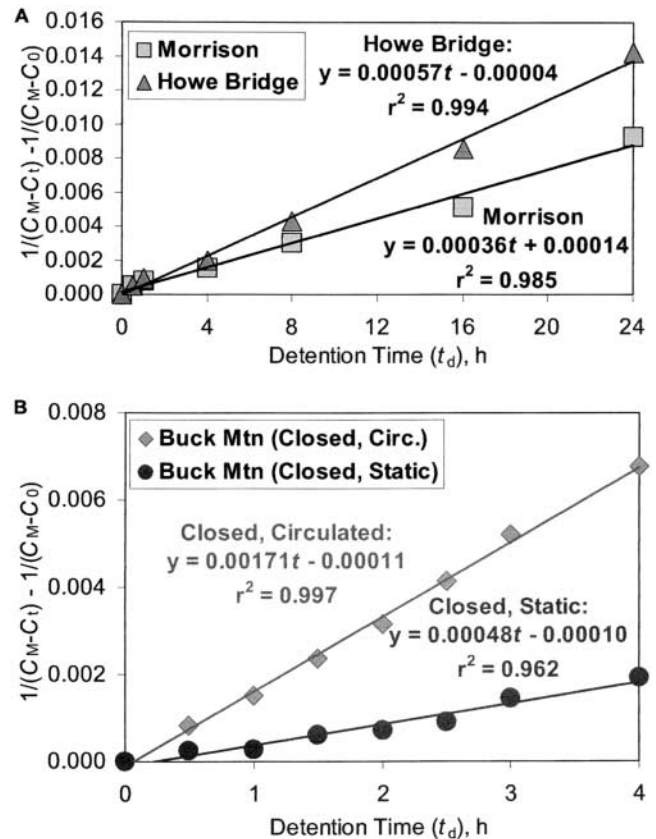
responding rate of limestone dissolution for an existing ALD can be computed from the calcium flux and, possibly, the alkalinity flux. Data for the Howe Bridge, Morrison, and Buck Mountain ALDs indicate equivalent, proportional increases in the concentrations or fluxes of calcium and alkalinity resulting from limestone dissolution (Tables 1 and 2). At the Howe Bridge ALD, the average alkalinity and calcium concentrations increased by 122 and 121 mg L^{-1}, respectively, in effluent compared with influent. At the Morrison ALD, the alkalinity and calcium concentrations increased by 261 and 268 mg L^{-1}, respectively, and at the Buck Mountain ALD, the alkalinity and calcium concentrations increased by 80 and 86 mg L^{-1}, respectively. Equality between the concentrations of alkalinity and calcium, expressed as $CaCO_3$, indicates that (i) the stoichiometry of Eq. [2] is applicable and (ii) the rate of limestone dissolution can be estimated using alkalinity or calcium flux data. The quantitative relation between the mass of limestone dissolved and measured alkalinity flux applies specifically to anoxic influent that initially contains alkalinity and that meets criteria for construction of an ALD. Influent that has pH < 4.5 or that contains Fe^{3+} or Al^{3+} has potential to consume alkalinity; reaction between limestone and such influent may not result in the quantitative accumulation of alkalinity. For this situation, calcium could be measured as the reaction progress variable instead of, or in addition to, alkalinity.
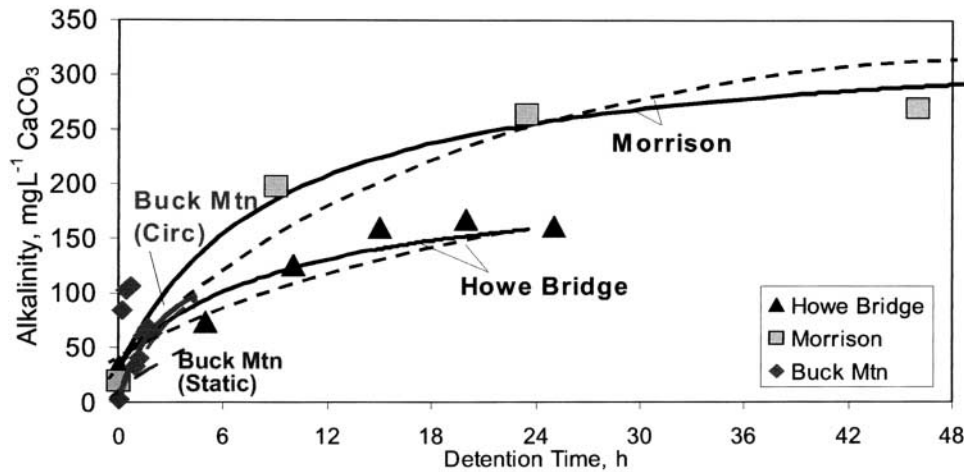
Fig. 6. Simulated (curves) and measured (points) changes in alkalinity with detention time in Howe Bridge, Morrison, and Buck Mountain anoxic limestone drains (ALDs) including exponential decay and the rate constants, k' and k'', derived from cubitainer tests. Dashed curves were computed for the first-order rate model (Eq. [7]) and solid curves for the second-order rate model (Eq. [10]). Measured data are typical values along the profile as shown in Fig. 2.

If field data are lacking or an ALD has not yet been constructed, the limestone dissolution rate may be estimated using the alkalinity rate constant, k' or k'', from cubitainer tests. Using Eq. [12], detention time can be estimated for water flowing through a limestone bed with a given initial mass, and using Eq. [7] or [10], the alkalinity concentration can be computed. The remaining mass of limestone at different times can be estimated by the difference between initial mass and the cumulative $CaCO_3$ mass dissolved as indicated by the alkalinity flux. The limestone mass dissolved during the time interval ($\Delta M = M_0 - M_t$) is the product of alkalinity produced during the time interval ($\Delta C_{CaCO_3} = C_t - C_0$ or $\Delta C_{CaCO_3} = C_{EF} - C_{IN}$) and the volume of solution ($V_L = Q\Delta t$), divided by limestone purity:

$$M_t = M_0 - (\Delta C_{CaCO_3} \ V_L / X_{CaCO_3}) \qquad [14]$$

To project the decrease in limestone mass and the corresponding detention time and alkalinity with elapsed time or age of an ALD, computations using Eq. [14], [12], and [10] or [7] must be repeated for successive time increments. This finite-difference application of Eq. [14] to compute the remaining limestone mass depends on the results for preceding time steps. Alternatively, the mass of limestone dissolved over elapsed time since construction of an ALD can be assumed to follow exponential or first-order decay, and then is approximated by an analytical equation (Cravotta, 2002; Cravotta and Watzlaf, 2002).

Given the empirically derived constants for alkalinity production rate, the initial alkalinity (C_0), and the maximum alkalinity (C_M), the decrease in limestone mass with time (age) and any associated decrease in alkalinity concentration with decreased mass of a limestone drain can be estimated. Figure 7 shows the results of computations of mass decay and associated alkalinity for the Howe Bridge, Morrison, and Buck Mountain ALDs using the first-order and second-order decay rates, k' and k'', respectively, derived from cubitainer data (Fig. 3, 4, and 5). In Fig. 7A, 7B, and 7C, the predicted

trends shown as dashed curves were computed assuming continuous alkalinity production in accordance with the first-order model (Eq. [7]), and those as solid curves assume alkalinity production in accordance with the second-order model (Eq. [10]).

The predicted change in mass of limestone with age of the Howe Bridge, Morrison, and Buck Mountain ALDs is shown as Fig. 7A. The predicted trends are similar to computed estimates on the basis of annual average alkalinity or calcium flux at the ALDs. The predicted decrease in limestone mass was estimated on the basis of the alkalinity flux for average flow rate and predicted concentration (Eq. [14]). The predicted alkalinity was computed as a function of detention time for a given mass of limestone, assuming constant porosity of 0.49, particle density of 2.65 g cm^{-3}, and average flow rate (Eq. [12]). The second-order model is presumed to be more realistic than the first-order model because the former closely matched the alkalinity production in cubitainers (Fig. 3) and along the length of the ALDs (Fig. 6). Nevertheless, both models indicate similar trends to about 20 yr of age, which is the typical design life for an ALD (e.g., Hedin and Watzlaf, 1994; Hedin et al., 1994a,b).

The detention time changes as the mass of limestone decreases exponentially with age, assuming a constant flow rate and porosity, in accordance with Eq. [12] (Fig. 7B). The first-order and second-order models indicate similar trends to about 20 yr of age. Although porosity was assumed constant for computation of the "observed" detention time, data points are scattered about the estimated trend line because the annual average flow rates were not constant, but varied by as much as a factor of two from year to year at each site (Table 2).

Long-term trends for computed and observed alkalinity of effluent from the Howe Bridge, Morrison, and Buck Mountain ALDs are shown in Fig. 7C. The simulated alkalinity was computed for corresponding decreases in limestone mass and detention times and used the site-specific cubitainer data for C_0, C_M, and k' or k''
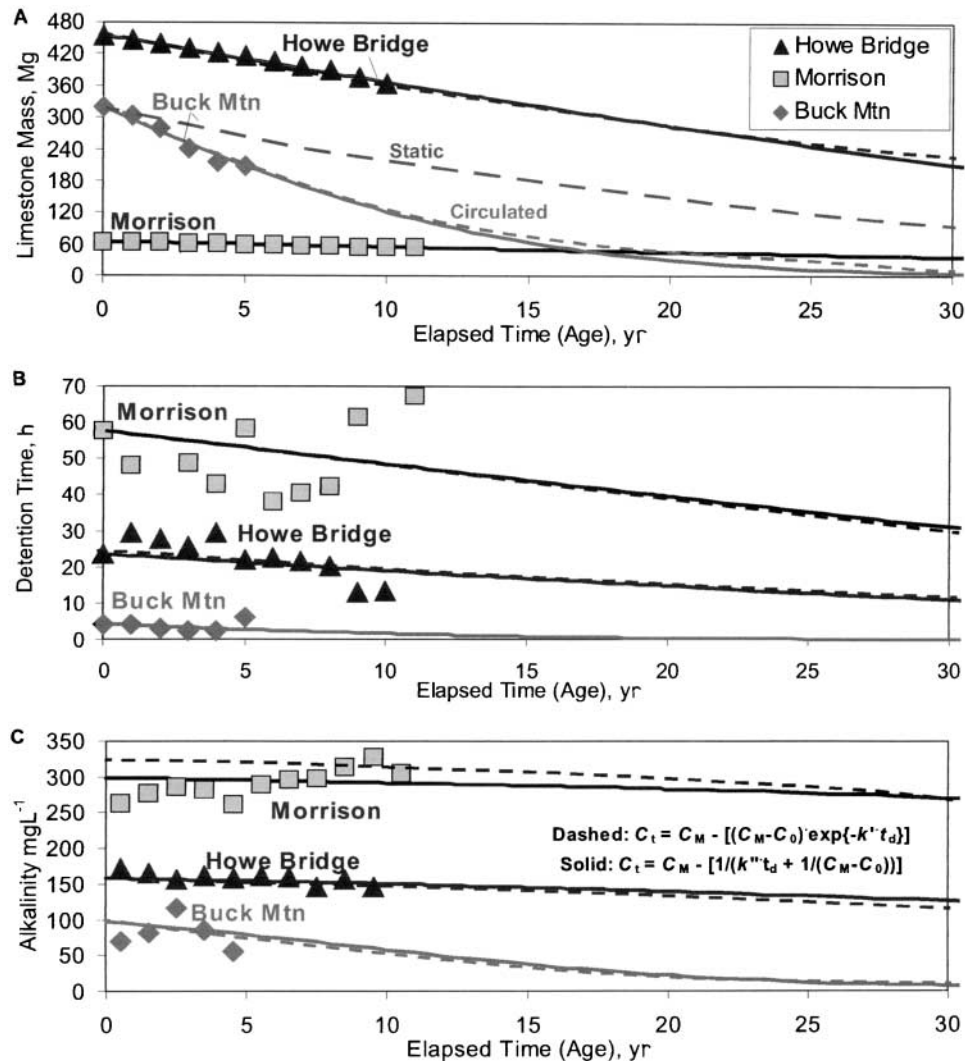
Fig. 7. Simulated (curves) and measured (points) changes in limestone mass, detention time, and alkalinity with age of Howe Bridge, Morrison, and Buck Mountain anoxic limestone drains (ALDs). Plots include exponential decay and the rate constants, k' and k'', derived from cubitainer tests and assuming constant flow rate (Q), particle density ($\rho_s = 2650$ kg m^{-3}), and porosity ($\phi = 0.49$). (A) Limestone mass versus age. (B) Detention time versus age. (C) Alkalinity versus age. Dashed curves estimated using k' (Eq. [7]); solid curves use k'' (Eq. [10]). Measured data in A, B, and C are based on annual averages for effluent (Table 2).

(Fig. 3, 4, and 7). Data for the annual average alkalinity of effluent from each of the drains generally follow the simulated trends. To provide the same baseline influent alkalinity to compare simulated and observed data, the observed values were normalized as the difference between the annual averages for effluent and influent added to the grand average influent concentration. A close match between simulated and observed values of alkalinity is obtained assuming a porosity of 0.49 at the Howe Bridge site. Although the simulated concentrations are consistent with the range of observed alkalinities for the Morrison and Buck Mountain ALDs, the simulated and observed trends are not closely matched. The Howe Bridge ALD functions as a piston or plug-flow system, with untreated water piped into the limestone drain and detention time of treated water increasing along the length of the drain. In contrast, the Morrison and Buck Mountain drains intercept several seeps along their length and hence the effluent is a mixture of water

having various detention times. Furthermore, the influent samples for the Morrison and Buck Mountain drains are collected from adjacent seeps. The sampled seep may not be representative of all the various seeps into the drain.

Dissolution causes a decrease in the mass of a limestone bed with time; however, the porosity may or may not change. Mixing or shrinking of limestone particle sizes, settling and compaction of the particles, and/or precipitation of secondary solids within voids can decrease porosity and detention times. In contrast, some voids could become enlarged, as may be the case for karst development, where dissolution takes place preferentially at surfaces bounding voids that transmit fluid. For example, if the total void volume increases through time, detention time within an ALD could increase for a given flow rate. The observed long-term trend of increasing alkalinity for the Morrison ALD (Fig. 7C) could result from increases in detention time.

Management and Design Implications

The limestone dissolution rate for the Buck Mountain ALD is substantially greater than that for the Howe Bridge and Morrison ALDs. The greater rate may result from the lower pH of influent and the relatively short detention time or faster flow rate at the Buck Mountain site compared with the other sites. Circulation of effluent in cubitainers produced greater initial rates of limestone dissolution than obtained under static conditions. After slightly less than 5 yr of operation, only two-thirds of the initial 320 Mg of limestone was estimated to remain at the Buck Mountain ALD (Fig. 7A). In contrast, after 10 yr, approximately three-quarters of the initial mass of limestone was estimated to remain at the Howe Bridge and Morrison sites (Fig. 7A). Despite decreased flow rates and increased detention time over the past 3 yr at the Buck Mountain site, the annual average alkalinity has declined, indicating its future efficacy was doubtful. According to Fig. 7C, the initial mass of 320 Mg limestone was projected to have a longevity of about 20 yr after which the alkalinity of the Buck Mountain ALD effluent would be less than the current average acidity of 21 mg L^{-1}. However, the Buck Mountain ALD is the primary source of alkalinity in the headwaters area of Swatara Creek, and net alkaline effluent would be necessary to buffer additional sources of acidity to the stream (Cravotta and Weitzel, 2001). On the basis of these observations and the data analysis for this paper, the Buck Mountain ALD was expanded in January 2002 by adding 90 Mg of limestone at its original outflow.

The general agreement between field observations and simulated trends based on data from cubitainer tests and assuming exponential decay (Fig. 6 and 7) indicates that (i) extrapolation from the current conditions at the existing ALDs may be warranted and (ii) the size of future limestone drains may be estimated using the data and analysis presented in this paper. The design goal is to determine the optimum size of an ALD with an appropriate longevity to ensure future neutralization of AMD. The required initial limestone mass to satisfy the design longevity can be determined for a specified age and alkalinity, for example $t = 20$ yr and C_t = acidity ($C_t < C_M$). For a second-order dissolution reaction, the "future" limestone mass can be computed by substituting Eq. [11] into Eq. [13]:

$$M_t = \{1/[k''[(C_M-C_t)]] - 1/[k''(C_M - C_0)][Q \rho_S(1 - \phi)/\phi] \quad [15]$$

For example, assume 21 mg L^{-1} alkalinity will be needed to neutralize the acidity at the Buck Mountain ALD. This corresponds with a detention time of about 0.37 h for a limestone mass of about 28 Mg, solving Eq. [15] for $k'' = 0.00171$ L mg^{-1} h^{-1}; $C_t = 21$, $C_M = 174$, and $C_0 = 4.5$ mg L^{-1}; $Q = 460$ L min^{-1}; $\rho_S = 2.65$ g cm^{-3}; and $\phi = 0.49$. Additional calculations using Eq. [14] indicate an initial limestone mass of 320 Mg would be required to have 28 Mg remaining at an elapsed time of 20 yr (Fig. 7A). Cravotta (2002) presented an alternative, direct method of computation of the mass of limestone using first-order equations, only.

The estimation of the limestone mass for construction of an ALD and a priori evaluation of its expected performance by the procedure outlined above requires knowledge of the same variables as Eq. [4] plus the rate constant, and the initial concentration of alkalinity of the influent. Although particle density, ρ_S, and porosity, ϕ, can be assumed constant, site-specific data should be obtained for the flow rate, Q, the rate constants, k' and k'', and the initial and maximum concentration of alkalinity, C_0 and C_M, respectively. If the computations indicate an ALD size that would be too large for site conditions, smaller systems with shorter longevity may be considered with the understanding that the ALD may require reconstruction near the end of its design life. Furthermore, because of variability or uncertainty in critical parameters, computations could be performed over the range of expected values for flow rate and porosity.

The field data for ALD effluent represent effects of variable influent composition and flow rate, but relatively narrow ranges of detention times and the corresponding effluent composition and $CaCO_3$ flux at each site (Table 2). In contrast, the cubitainer data reveal the effluent composition (alkalinity) and corresponding $CaCO_3$ flux varied widely as a function of detention time while the total mass of limestone in the cubitainers was essentially constant (decreased by less than 0.02% from beginning to end of tests). Hence, the cubitainer tests not only encompassed the range of detention times for field conditions, but they indicated conditions for shorter and longer detention times that may result with changes in the mass of limestone, porosity, or flow rate.

Actual performance will vary as a function of the influent composition, detention time, and flow paths. Hence, multiple tests could be considered to evaluate variable influent compositions, limestone diameters, mineral coatings, and/or system conditions (open/closed; circulation rates). Because the composition of the influent AMD is a critical factor affecting the alkalinity produced by limestone of a given composition, cubitainer tests could be conducted repeatedly through time to determine the range of expected conditions within a limestone drain, or the "influent" composition for concurrent cubitainer tests could be altered to evaluate effects from changes in concentration of specific dissolved constituents. For an evaluation of mineral coatings on rate constants, tests could be conducted with uncoated limestone and that coated with hydrous Fe(III), Mn, and/or Al oxides. Potential for clogging and/or flushing also could be evaluated considering measurements of porosity, permeability, and solids transport through a packed bed.

CONCLUSIONS

Although numerous case studies have been reported, published criteria for the construction of limestone drains are imprecise and inadequate owing to (i) the wide ranges in flow rates and compositions of mine drainage and (ii) variable dissolution rates of limestone and production of alkalinity as functions of water chem-

istry, detention time, and limestone characteristics. Generally, chemical processes within limestone drains can be characterized as functions of distance and time as water flows downgradient through the limestone bed. Immediately near the inflow, the pH of the treated water begins to increase as limestone dissolves, ultimately approaching neutrality and calcite saturation, provided that detention time within the drain is sufficient. The alkalinity and $CaCO_3$ flux generally will vary as a function of influent flow rate and chemistry, detention time, and/or mass of limestone remaining.

Trends within the Howe Bridge, Morrison, and Buck Mountain ALDs generally indicated a decline in the rate of alkalinity production with increased distance, or detention time. Similar trends were obtained for alkalinity as a function of detention time for empirical cubitainer tests using influent and limestone from each site. These trends indicate the limestone dissolution rate decreases as the alkalinity increases and calcite equilibrium is approached.

Time-series data for the cubitainer tests were used to derive first-order and second-order models to estimate the concentration of alkalinity at the outflow or intermediate points within a limestone bed as a function of the detention time, influent alkalinity (C_0), maximum or steady state alkalinity (C_M), and the rate constant. Linear regression of $\ln[(C_M - C_t)/(C_M - C_0)]$ versus detention time for the tests yielded estimates of the first-order rate constant, k' for Eq. [7]; regression of $[1/(C_M - C_t) - 1/(C_M - C_0)]$ versus detention time yielded estimates of the second-order rate constant, k'' for Eq. [10]. The initial and maximum alkalinities were determined for the first sample and after 96 h of the tests.

Estimates of the decrease in limestone mass within the ALDs under field conditions were computed on the basis of annual calcium and alkalinity flux at the Howe Bridge, Morrison, and Buck Mountain ALDs, which are 10, 11, and 5 yr old, respectively. The alkalinity production rates derived on the basis of the short-term cubitainer tests for each site resulted in comparable predictions of the annual $CaCO_3$ mass flux from each ALD. Only data for the first 4 to 24 h of the cubitainer tests were necessary and useful for the computation of the limestone dissolution rate.

On the basis of the first-order or second-order rate equations for alkalinity production and limestone dissolution based on data derived from the cubitainer tests, trends were projected from initial conditions, through the current monitoring record, and into the future to simulate the performance of the Howe Bridge, Morrison, and Buck Mountain ALDs. The computed trends for the exponential decline in limestone mass and corresponding concentrations of alkalinity at the outflow and intermediate points within each of the ALDs generally reflected observed conditions, assuming constant flow rate and porosity. The second-order model provided a better estimate of the observed alkalinity variations than the first-order model. Thus, the exponential decay expressions and data for maximum alkalinity and the rate constant, k'', obtained from cubitainer tests, may be applicable to estimate the initial mass of limestone required for construction of a new ALD or another AMD treatment system incorporating a submerged limestone bed(s). The application of these equations to evaluate new construction also would require site-specific information for the flow rate(s) and available land area.

This paper demonstrated that cubitainer testing of untreated AMD and limestone can provide estimates of maximum alkalinity and the rate of limestone dissolution in ALDs under field conditions. The tests can be adapted to simulate specific field conditions using different sizes or purity of limestone fragments, uncoated or coated limestone, variable circulation rates, varying degrees of aeration, and/or variable influent composition. For the Buck Mountain cubitainer tests, circulated and static conditions produced different outcomes, with faster rates of dissolution associated with circulated conditions. This implies rate control by diffusional transport, and secondary minerals that accumulate on limestone could affect the dissolution rate. Data used in this paper for the extraction of rate constants were consistent with field detention times.

The "as-built" dimensions and mass of limestone for an ALD need to be documented accurately to estimate porosity and field detention time. Accurate, periodic measurements of flow rate and influent and effluent chemistry are needed to evaluate the effectiveness of treatment. Additional data for intermediate sampling locations can be useful to evaluate spatial and temporal variations in water chemistry and limestone dissolution. Documentation of hydraulic head at sampling locations could be useful to characterize changes in porosity and permeability distributions within the drain. Variations in porosity within the drain due to dissolution of limestone or precipitation of secondary minerals could be evaluated to refine estimates of detention time and longevity using the above equations.

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