NEW METHOD TO ESTIMATE SIZE AND LONGEVITY OF ANOXIC LIMESTONE DRAINS

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Extended Abstract

A new method is proposed using first-order decay equations with data from short-term closed-container (cubitainer) tests previously described by Watzlaf and Hedin (1993) to estimate the mass of a limestone bed for anoxic treatment of acidic mine drainage (AMD) and the expected alkalinity concentration at the outflow or intermediate points within the limestone bed. The longevity of an anoxic limestone drain (ALD) or the remaining mass of limestone (M_t) at any time (t) is determined as a function of the initial mass of limestone (M_0) and decay constant (k), with units of 1/year:

$$M_t = M_0 \cdot \exp\{-k \cdot t\}. \tag{1}$$

Detention time (t_d) within the limestone bed is estimated as a function of the estimated mass of limestone and associated estimates of flow rate (Q), porosity (ϕ), and limestone density (ρ_S):

$$t_d = M_t / [\rho_S \cdot Q \cdot (1-\phi)/\phi]. \tag{2}$$

The concentration of alkalinity at the outflow or intermediate points within the limestone bed is determined as a function of the detention time, the influent alkalinity (C_0), the maximum or steady-state alkalinity (C_M), and the rate constant (k'), with units of 1/hour:

$$C_t = C_M - [(C_M - C_0) \cdot \exp\{-k' \cdot t_d\}]. \tag{3}$$

The cubitainer tests, which used an initial mass of 4 kg crushed limestone and solution volume of 2.8 liter, provided estimates for the rate constants, k' and k, and the initial and maximum alkalinities, C_0 and C_M (Cravotta and Watzlaf, in press). Application of the above equations using these estimates, and assuming limestone density of 2.65 g/cm^3 and porosity of 0.49, provided accurate estimates for the long-term (5- to 11-yr) trends of declining alkalinity in effluent at the Howe Bridge, Morrison, and Buck Mtn. limestone drains, which effectively treat AMD in Pennsylvania (e.g. Hedin et al., 1994; Cravotta and Weitzel, 2001). The equations and rate constants also can be used to estimate the initial mass of limestone required to achieve a future mass, detention time, and associated alkalinity. This application avoids the assumptions of Hedin and Watzlaf (1994) of constant alkalinity and $CaCO_3$ mass flux over the lifetime of the drain.

Selected References

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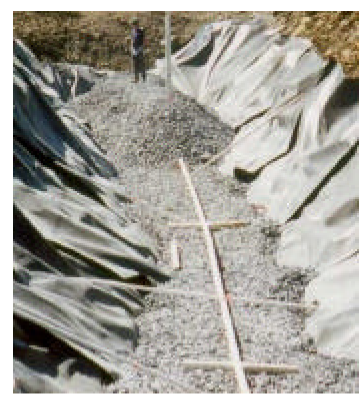
Acidic Mine Drainage (AMD) commonly has elevated concentrations of sulfate (SO_4^{2-}), iron (Fe^{2+}, Fe^{3+}), manganese (Mn^{2+}), aluminum (Al^{3+}), and other metals that result from the oxidation of pyrite (FeS_2) and the dissolution of oxide, carbonate, and aluminosilicate minerals by acidic water. Dissolution of calcite ($CaCO_3$), the principal component of limestone, can neutralize acidity, increase pH, alkalinity, and Ca^{2+}, and promote the precipitation and adsorption of metals.



Anoxic Limestone Drains (ALDs) can generate alkalinity and neutralize AMD. Typically, crushed limestone of uniform size is placed in a buried bed(s) that intercepts net acidic (acidity > alkalinity) AMD before its exposure to atmospheric oxygen (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 within the limestone bed.

Cubitainer Tests can be used to indicate qualitative and quantitative effects of variable influent compositions, detention times, and limestone purity on limestone drain performance. The collapsible, “1-gallon” polyethylene containers, were loaded with 4 kg of 1.3-by-3.5-cm limestone fragments (2/3 total volume), filled with the untreated mine water and then maintained at field water temperature to evaluate the generation of alkalinity.

FIELD OBSERVATIONS AT HOWE BRIDGE, MORRISON, AND BUCK MTN. ALDs INDICATED ASYMPTOTIC INCREASE IN ALKALINITY WITH DETENTION TIME

Table 1. Average[1] quality of influent and effluent at Howe Bridge, Morrison, and Buck Mtn. ALDs in Pennsylvania

Limestone Drain Site[2]	Year Built	Mass Limestone, tonne	Flow Rate, l/min	pH		Pco_2		Calcite Saturation		Net Acidity[3]		Alkalinity		Calcium[4]		Sulfate		Iron		Manganese		Aluminum	
				units		log(atm)		log(IAP/K)		mg/l as $CaCO_3$						mg/l							
				In	Eff	In	Eff	In	Eff	In	Eff	In	Eff	In	Eff	In	Eff	In	Eff	In	Eff	In	Eff
Howe Bridge	1991	455	117	5.8	6.3	-1.2	-1.1	-2.1	-0.7	495	369	36	158	371	493	1240	1230	255	254	40	40	<0.2	<0.2
Morrison	1990	65	50	5.3	6.4	-0.8	-1.0	-2.9	-0.4	434	76	30	291	275	543	1200	1010	209	165	47	39	.5	<.2
Buck Mtn	1997	320	460	4.9	6.4	-1.6	-1.5	-5.9	-1.7	19	-61	2	82	8	94	51	56	10	10	1	1	.5	<.2

1 Grand average of annual averages for period of record.
2 Data for influent and effluent quality at Howe Bridge and Morrison ALDs from U.S. Department of Energy and at Buck Mtn. from U.S. Geological Survey. Influent quality at Morrison and Buck Mtn. for nearby seep.
3 Net acidity = acidity - alkalinity; negative values indicate net alkaline conditions.
4 Calcium concentration as $CaCO_3$ computed as 2.5 times the concentration as Ca.

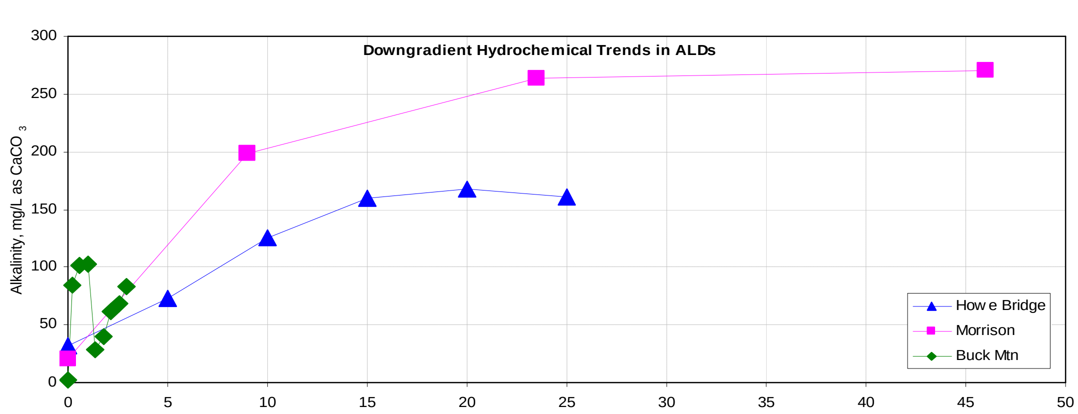


Figure 1. Changes in alkalinity concentration with detention time (downflow distance) of mine drainage within limestone drains at Howe Bridge, Morrison, and Buck Mtn. sites. Detention time computed as product of porosity (ϕ), downflow distance (L), and cross-sectional area (A) divided by flow rate (Q): $t_d = \phi \cdot L \cdot A/Q$, assuming $\phi = 0.49$.

Although numerous case studies have been reported, published criteria for the construction of anoxic limestone drains (ALDs) generally are imprecise and inadequate owing to (1) the wide ranges in flow rates and compositions of mine drainage and (2) nonlinear and variable dissolution of limestone and production of alkalinity as functions of water chemistry, detention time, and limestone characteristics. This paper introduces a new method using first-order decay equations and data from short-term closed-container (cubitainer) tests to evaluate long-term performance (longevity, alkalinity production) or to estimate the mass of limestone needed for anoxic limestone treatment. Data for previously published and recently completed cubitainer tests and for the chemical compositions of influent and effluent of the Howe Bridge, Morrison, and Buck Mtn. ALDs that were constructed to treat discharges from abandoned coal mines in Pennsylvania, U.S.A., are introduced to demonstrate this method.

Over the 5- to 11-yr monitoring period, the average flow rates were 117, 50, and 460 l/min through the Howe Bridge, Morrison, and Buck Mtn. ALDs, respectively (Table 1). The annual average flow rate and computed detention time (void volume divided by flow rate) varied by about a factor of two over the monitoring period at each site (Table 2). The influent and effluent at the Howe Bridge and Morrison ALDs contained greater concentrations of alkalinity, acidity, SO_4, Fe, and Ca than those at the Buck Mtn. site (Table 1). Effluent from each ALD had higher pH, alkalinity, and Ca, and lower acidity and Al concentrations than influent. In contrast, concentrations of SO_4, Fe^{2+}, and Mn^{2+} were largely unaffected by dissolution of the limestone bed. Despite substantial alkalinity production, effluent from the Howe Bridge and Morrison ALDs was net acidic owing to elevated Fe^{2+} and Mn^{2+} concentrations.

Generally, chemical processes within a limestone drain can be characterized as functions of distance and time as water flows downgradient through the limestone bed. Typically, the pH, alkalinity, and Ca 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 water approaches calcite equilibrium (Fig. 1, Table 1). More complex trends, such as that exhibited at the Buck Mtn. site (Fig. 1), can arise because of multiple inflows of untreated AMD along the length of the ALD. At pH greater than 4.5, the rate of increase in alkalinity or Ca is directly proportional to the rate of limestone dissolution. Generally, the rate of limestone dissolution decreases as pH increases, Pco_2 decreases, and calcite equilibrium is approached. Despite significant production of alkalinity in all three ALDs and prolonged detention within the Morrison ALD, the effluent from each was undersaturated with respect to calcite (Table 2).

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FIELD OBSERVATIONS AT HOWE BRIDGE, MORRISON, AND BUCK MTN. ALDs INDICATED EXPONENTIAL DECLINE IN LIMESTONE MASS

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 Mtn. ALDs in Pennsylvania

Age	Flow Rate	Alkalinity mg/L as $CaCO_3$		Limestone Mass[1]		Detention Time[2]	Calcium mg/L as $CaCO_3$		Limestone Mass[1]		Detention Time[2]
				Dissolved	Remaining				Dissolved	Remaining	
yr	l/min	Influent	Effluent	tonne/yr	tonne	hr	Influent	Effluent	tonne/yr	tonne	hr
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
Avg:[3]	*117*	*36*	*158*	*9.06*	*n.a.*	*22.6*	*371*	*493*	*9.01*	*n.a.*	*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
Avg:	*6.8*	*30*	*291*	*1.01*	*n.a.*	*56.6*	*275*	*543*	*1.03*	*n.a.*	*56.4*
Buck Mtn											
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
Avg:	*460*	*2*	*82*	*22.37*	*n.a.*	*3.7*	*8*	*94*	*23.28*	*n.a.*	*3.7*

1 Mass dissolved is product of flow rate and difference between effluent and influent concentration of alkalinity or calcium divided by limestone purity ($\Delta M = Q(C_E - C_I)/X_{CaCO3}$). Mass remaining is difference between that dissolved in the year and that remaining for prior year ($M_t = M_{t-1} - \Delta M$).

2 Detention time for annual average flow rate and limestone mass computed as $t_d = M_t/[\rho_S \cdot Q \cdot (1-\phi)/\phi]$, assuming porosity ($\phi$) of 0.49 and limestone density (ρ_S) of 2,650 kg/m^3.

3 Grand average of annual averages for period of record. Flow rate at time of construction (age = 0) assumed equal to the grand average.

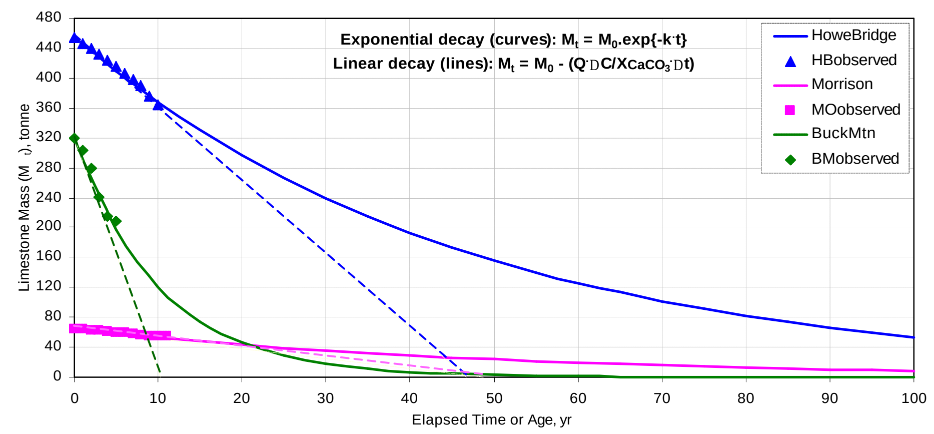
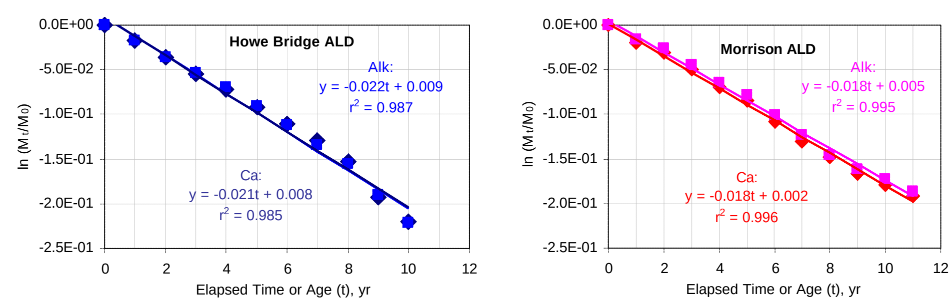


Figure 2. Decline in mass of limestone with age of limestone drain. Solid curves indicate continuous dissolution on the basis of Eq. (1) and rate constants (k) derived from field data (Table 2, Fig. 3). Dashed lines indicate decay trends for constant alkalinity flux. Measured data points from Table 2.



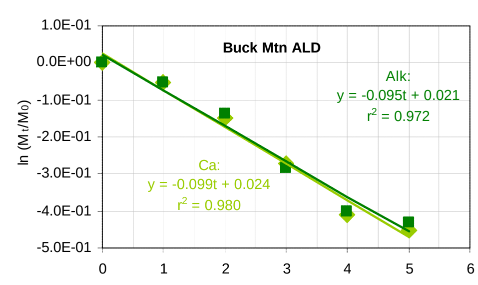


Figure 3. Natural logarithm of remaining limestone mass (M_t) divided by initial mass (M_0) versus elapsed time since installation of Howe Bridge, Morrison, and Buck Mtn. ALDs. Data from Table 2. Negative value of slope indicates limestone dissolution rate constant (k) for exponential decline in limestone mass with age of the ALD in accordance with Eq. (1): $M_t = M_0 \cdot exp\{-k \cdot t\}$.

CUBITAINER TESTS INDICATED RATES OF ALKALINITY PRODUCTION AND LIMESTONE DISSOLUTION THAT WERE CONSISTENT WITH FIELD OBSERVATIONS

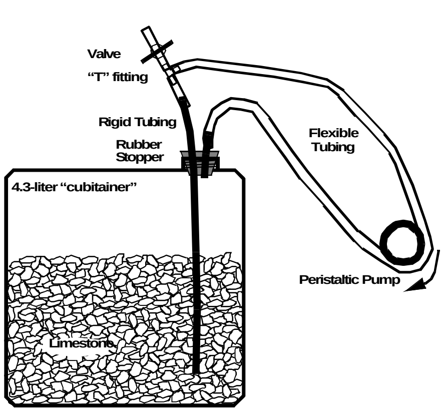


Figure 4. Schematic of polyethylene "cubitainer" containing 4 kg limestone and filled with mine discharge water to evaluate alkalinity production rates (after Watzlaf and Hedin, 1993).

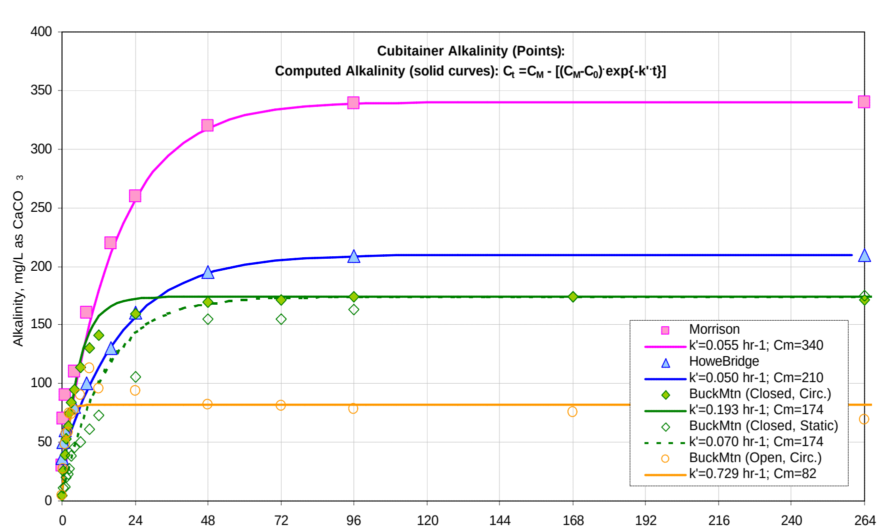


Figure 5. Alkalinity data for Howe Bridge, Morrison, and Buck Mtn. Cubitainer tests. Generalized alkalinity points for Howe Bridge and Morrison tests (after Watzlaf and Hedin, 1993) and curve for alkalinity concentration (C_t) as a function of detention time computed on the basis of Eq. (3) using the rate constant (k'), maximum alkalinity (C_M), and initial alkalinity (C_0) derived from cubitainer tests (Fig. 6). Alkalinity points and computed curves for C_t for Buck Mtn. cubitainer tests conducted under static, closed; circulated, closed; and circulated open conditions.

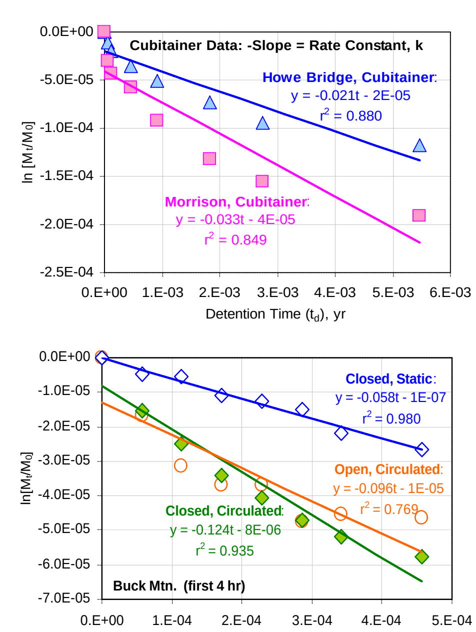


Figure 7. Natural logarithm of remaining limestone mass (M_t) divided by initial mass (M_0) versus initial elapsed time of cubitainer tests for Howe Bridge, Morrison, and Buck Mtn. ALDs. Remaining mass computed by subtracting cumulative flux of $CaCO_3$ from the initial limestone mass and dividing by limestone purity. Negative value of slope indicates first-order rate constant (k) for exponential decline in limestone mass with age of the ALD on the basis of Eq. (1).

Cubitainer Test Methods

Crushed limestone was sieved and rinsed thoroughly with tap water, and for the Buck Mtn. tests, was rinsed with 5% hydrochloric acid and deionized water, and then dried prior to loading it into the empty cubitainers (Fig. 4). For the Howe Bridge and Morrison tests, duplicates were conducted under static closed (uncirculated) conditions at ambient water temperature in the field using several varieties of limestone with reported purity ranging from 82 to 99% by weight $CaCO_3$. The Buck Mtn. cubitainer tests were conducted in the laboratory using a single variety of limestone (92% $CaCO_3$) under static closed, circulated closed, and circulated open conditions, but otherwise following similar procedures as those for the Howe Bridge and Morrison tests.

Periodically over 11 to 16 days, samples were withdrawn through a valve to fill a 60-ml syringe after purging approximately 10-ml fluid from the sample tubing. Samples were withdrawn at 0.5-hr intervals during the first 4 hr and then hourly until 6 to 8 hr had elapsed; samples were withdrawn at 24-hr intervals or less frequently after the first day. Immediately after its withdrawal from the cubitainer, the sample was forced through a 0.45-µm pore-size nylon filter and then analyzed for alkalinity (pH 4.5 endpoint). Alkalinity data were then used to determine the alkalinity rate constant, k', and the limestone dissolution rate constant, k, following methods of Cravotta and Watzlaf (in press).

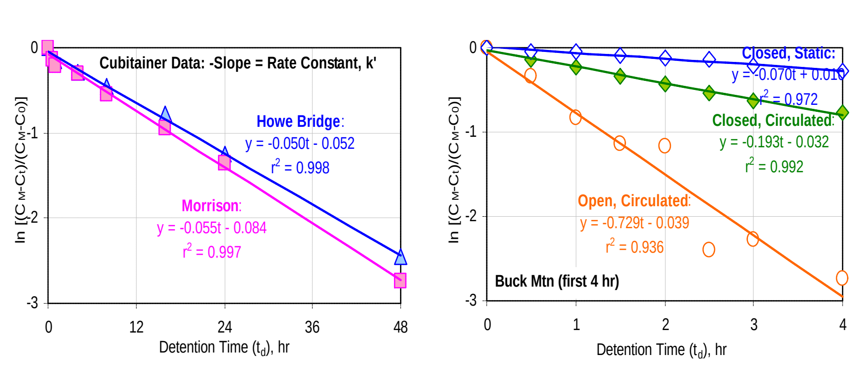


Figure 6. Natural logarithm of difference between steady-state maximum alkalinity (C_M) and measured alkalinity (C_t) divided by difference between C_M and initial alkalinity (C_0) versus time for cubitainer tests for Howe Bridge, Morrison, and Buck Mtn. Sites. Negative value of slope indicates rate constant (k') for computation of alkalinity as a function of detention time (C_t) on the basis of Eq. (3): $C_t = C_M - [(C_M - C_0) \cdot exp\{-k' \cdot t_d\}]$.

Exponential, first-order decay of the mass of limestone (Eq. (1)) in an ALD under field conditions is indicated by linear slopes for logarithmic plots of the computed annual remaining mass relative to the initial mass (M_t/M_0) versus age for the Howe Bridge, Morrison, and Buck Mtn. ALDs, which are 10, 11, and 5 yr old, respectively. Values for the limestone dissolution rate constant, k, that were derived on the basis of the annual $CaCO_3$ mass flux from each ALD were equivalent to those derived on the basis of short-term cubitainer tests for each site. Only data for the first 4 to 48 hr of the cubitainer tests were necessary for computation of the rate constants, k and k'.

In cooperation with **Pennsylvania Department of Environmental Protection**
Schuylkill County Conservation District
U.S. Department of Energy

EXPONENTIAL DECAY EQUATIONS ENABLE EVALUATION OF SIZE AND PERFORMANCE OF ANOXIC LIMESTONE DRAINS

Estimation of Limestone Drain Size and Performance

Given the empirically derived constants for limestone dissolution rate, k, and/or alkalinity production rate, k', and the initial alkalinity (C_0), and the maximum alkalinity (C_M), which can be determined with cubitainer tests, the decline in limestone mass through time (age) and the associated decline in alkalinity concentration with decreased mass (detention time) of a limestone drain can be estimated. Figure 8 shows the results of computations of mass decay and associated alkalinity for the Howe Bridge, Morrison, and Buck Mtn. ALDs using k and k' derived from cubitainer data (Figs. 5, 6, and 7). Observed data for the actual drains are indicated by individual points (Table 2).

The projected change in mass of limestone with age of the Howe Bridge, Morrison, and Buck Mtn. ALDs is shown as Figure 8A. The solid projection assumes continuous, exponential decay in accordance with Eq. (1) and utilizes the initial mass when constructed and the mass-flux decay constant, k, derived from cubitainer data (Fig. 7). The dashed projection assumes that flow rate and porosity are constant and that alkalinity concentration is a function of the detention time for a given mass of limestone per Eqs. (2) and (3). Changes in limestone mass were computed on the basis of the computed alkalinity flux for short time intervals (finite difference). The dashed and solid curves indicate similar trends to about 20 years of age, which is the typical design life for an ALD (Hedin and Watzlaf, 1994). The estimated decay trends (curves) are similar to actual trends on the basis of annual average alkalinity flux (points; Fig. 2).

Figure 8B shows the corresponding change in detention time as the mass of limestone declines exponentially with age, assuming a constant flow rate and porosity, in accordance with Eq. (2) (solid curves). The dashed projection is based on estimates of remaining mass computed on the basis of alkalinity flux computed per Eq. (3). The dashed and solid curves indicate similar trends to about 20 years 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).

Figure 8C shows long-term trends for computed and observed alkalinity of effluent from the Howe Bridge, Morrison, and Buck Mtn. limestone drains. The simulated alkalinity was computed using Eq. (3) for progressively declining detention times and used the site-specific cubitainer data for C_0, C_M, k, and k' (Figs. 5, 6, and 7). Solid curves estimated mass decline on the basis of Eq. (1) using the limestone dissolution rate constant, k. Dashed curves estimated mass decline on the basis of alkalinity flux per Eq. (3) using only the alkalinity rate constant, k'. Data points for the annual average alkalinity of effluent from each of the drains (Table 2) 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 for 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 Mtn. 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 Mtn. 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 Mtn. drains are collected from adjacent seeps. The sampled seep may not be representative of all the various seeps into the drain.

Figure 8D shows simulated and observed trends for alkalinity with detention time computed in accordance with Eq. (3). For the simulations, the greatest detention time for each of the limestone drains is associated with the initial condition (age = 0); detention time and corresponding alkalinity values decrease with increased age and associated decreased limestone mass (Eq. (1)). To extend the simulated curves to small detention times at the outflow, the remaining mass and corresponding values for detention time and alkalinity were computed over an elapsed time of 200 yr. The resultant estimates for effluent alkalinity after 200 yr of continuous dissolution correspond with current conditions near the inflow to the drains. Field data for longitudinal samples from monitoring wells within the drains, shown previously in Figure 1, are plotted as individual points in Figure 8D for comparison with the simulated curves. Assuming a porosity of 0.49, the simulated trend on the basis of the cubitainer tests for the Howe Bridge site matches the observed data for this site. The simulated and observed trends for the Morrison and Buck Mtn. sites are comparable near the outflow of the ALDs; however, for reasons already given, observed values deviate from simulated alkalinity as a function of detention time.

Management and Design Implications

The general agreement between field observations and simulated trends based on data from cubitainer tests and first-order, exponential decay equations indicates that (1) extrapolation from the current conditions at the existing ALDs may be warranted and (2) the size of future limestone drains may be estimated using the previously described equations and test methods. The goal is to determine the optimum size of an ALD with an appropriate longevity to ensure future neutralization of AMD.

For complete neutralization, the effluent alkalinity must exceed the acidity. Rearranging Eq. (3) and taking the logarithm, the minimum detention time can be determined where C_t is equal to the acidity ($C_t < C_M$):

$$t_d = \ln[(C_M - C_0)/(C_M - C_t)] / k'. \qquad (4)$$

Rearranging Eq. (2), the mass of limestone necessary to achieve the minimum detention time can be estimated:

$$M_t = Q \cdot (t_d \cdot \rho_S \cdot (1-\phi)/\phi). \qquad (5)$$

Substituting Eq. (5) into Eq. (1) and rearranging, the initial mass of limestone required to achieve the minimum detention time at a future time, or age (t), can be determined:

$$M_0 = (Q \cdot t_d \cdot \rho_S \cdot (1-\phi)/\phi) \cdot \exp\{k \cdot t\}, \qquad (6)$$

Substituting Eq. (4) into Eq, (6),

$$M_0 = (Q \cdot \rho_S \cdot (1-\phi)/\phi) \cdot (\ln[(C_M - C_0)/(C_M - C_t)] / k') \cdot \exp\{k \cdot t\}. \qquad (7)$$

Equation (7) can be solved for a specified age and minimum alkalinity, for example t = 20 yr and C_t = acidity, to indicate the required initial limestone mass to satisfy the design longevity. 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 concentrations of alkalinity or Ca, 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. Because actual performance will vary as a function of the influent composition, detention time, and flow paths, multiple tests should be considered to evaluate variable influent compositions or system conditions (open/closed) and associated rate constants. Furthermore, because of variability or uncertainty in critical parameters, computations should be performed for a range of values for porosity, flow rate, and acidity.

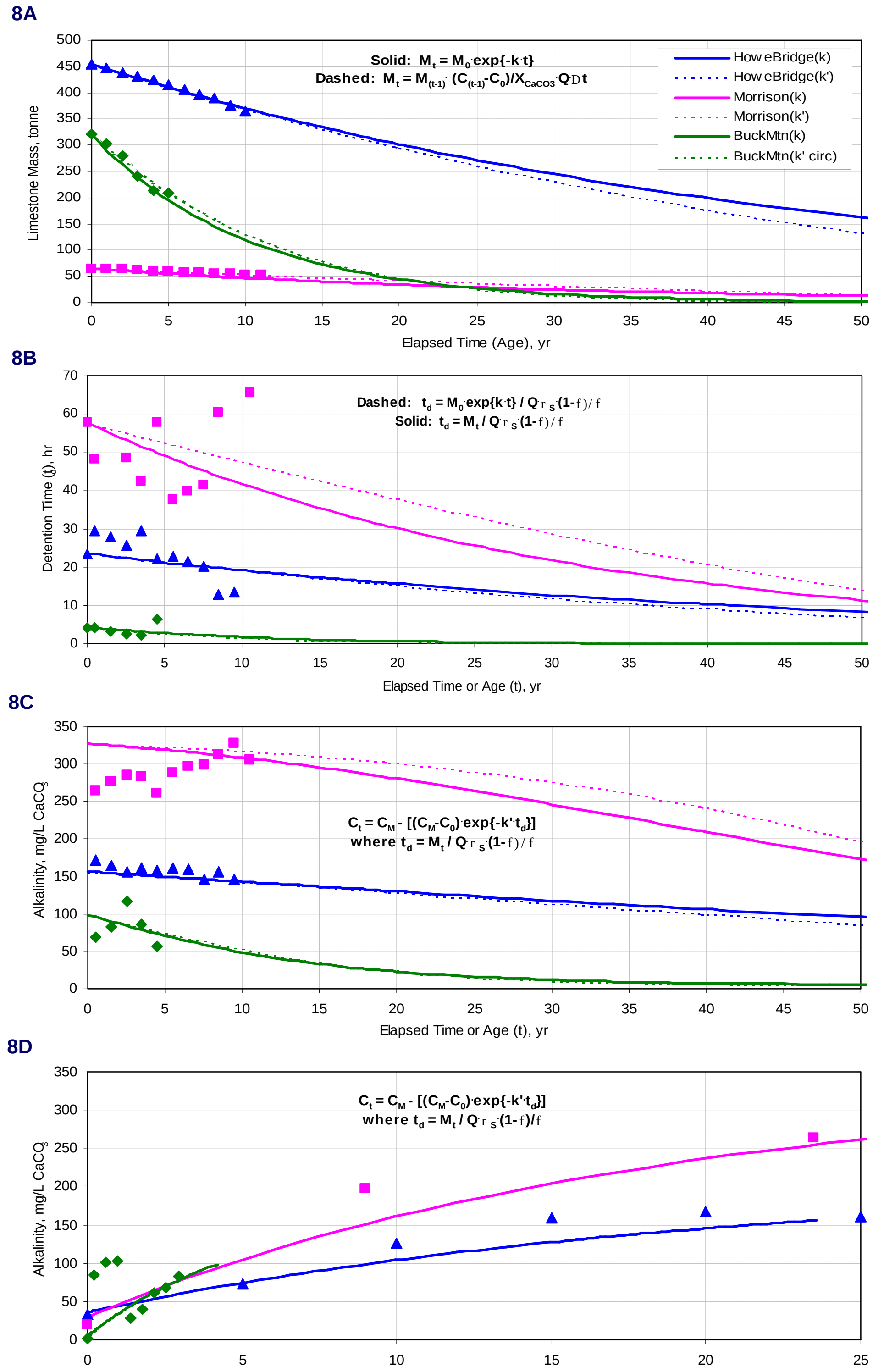


Figure 8. Simulated (curves) and measured (points) change in limestone mass, detention time, and alkalinity concentration with age of Howe Bridge, Morrison, and Buck Mtn. limestone drains considering exponential decay and the rate constants, k and k', derived from cubitainer tests. Computations assumed constant flow rate (Q), porosity (ϕ= 0.49), and particle density (ρ_S = 2,650 kg/m³). *A*, Limestone mass versus age; *B*, Detention time versus age; *C*, Alkalinity versus age; *D*, Alkalinity versus detention time. Dashed curves estimated using only k'; solid curves use only k for *A* and *B*, and k and k' for *C* and *D* (solid and dashed curves in *D* overlap). Measured data in *C* are annual averages for effluent and in *D* are typical values along longitudinal profile.

CONCLUSIONS

Longitudinal trends within the Howe Bridge, Morrison, and Buck Mtn. 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. Linear slopes for logarithmic plots of $[(C_M - C_t)/(C_M - C_0)]$ versus detention time for the cubitainer tests yielded estimates of the alkalinity rate constant, k', and for logarithmic plots of $[M_t/M_0]$ versus detention time yielded estimates of the limestone dissolution rate constant, k. The initial and maximum alkalinities were determined for the first sample and after 48 hr of the tests.

On the basis of first-order, exponential decay expressions introduced in this paper using 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 Mtn. ALDs. For the period of monitoring, assuming constant flow rate and porosity, 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. Thus, the exponential decay expressions and data for maximum alkalinity and the rate constants, k' and k, obtained from cubitainer tests may be applicable to estimate the initial mass of limestone required for construction of an ALD. The application of these equations to evaluate new construction requires site-specific information for flow rate(s) and available land area.

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