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:

\[
M_t = M_0 \cdot \exp\{-k \cdot t\}.
\]

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 \( \phi \), and limestone density \( \rho_S \):

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

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:

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

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 alkalinitities, \( C_0 \) 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 ALD.

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Selected References


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

Although numerous case studies have been reported, published criteria for the construction of limestone drains 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 the 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 Mt. 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 Mt. 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\(_4^{2-}\), Fe, and Ca than those at the Buck Mt. 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\(_4^{2-}\), Fe\(^{3+}\), and Mn\(^{2+}\) were largely unaffected by the dissolution of the limestone bed. Despite substantial alkalinity production, effluent from the Howe Bridge ALD was not acidic owing to the elevated concentrations of Fe\(^{3+}\) and Mn\(^{2+}\).

Generally, chemical processes within a limestone drain can be characterized as functions of distance and time as water flows downward 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. 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 2). More complex trends, such as those exhibited at the Buck Mt. 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, PO\(_4^{3-}\) 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).
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 in Howe Bridge, Morrison, and Buck Mt ALDs in Pennsylvania

<table>
<thead>
<tr>
<th>Age (yr)</th>
<th>Flow Rate (l/min)</th>
<th>Concentration of Alkalinity (mg/L as CaCO(_3))</th>
<th>Concentration of Calcium (mg/L)</th>
<th>Limestone Mass Remaining (tonne/yr)</th>
<th>Detention Time (yr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>117</td>
<td>958</td>
<td>57</td>
<td>53</td>
<td>0.00</td>
</tr>
<tr>
<td>1</td>
<td>118</td>
<td>958</td>
<td>57</td>
<td>53</td>
<td>0.00</td>
</tr>
</tbody>
</table>

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.

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

Cubitainer Tests
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, circulated closed, and circulated open conditions. The Buck Mtn. cubitainer tests conducted under static, closed; and circulated open conditions.

Periodically over 11 to 16 days, samples were withdrawn through a valve to fill a 60-ml vialage after purging approximately 10 ml fluid from the sample tubing. Samples were withdrawn at 5-h intervals during the first 4 hr and then hourly until 8 or 8.5 hr had elapsed. Samples were withdrawn at 24-h intervals or less frequently after the first day. Immediately after its withdrawal from the cubitainer, the sample was filtered 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 Watzka (in press).

Figure 4. Schematic of polyethylene “cubitainer” containing 4 kg limestone and filled with mine discharge water to evaluate alkalinity production rates (after Watzka and Helms, 1993).

Figure 5. Alkalinity data for Howe Bridge, Morrison, and Buck Mtn. Cubitainer tests. Generalized alkalinity points for Howe Bridge and Morrison tests (after Watzka and Helms, 1993) and curve for alkalinity concentration (CA) as a function of detention time computed on the basis of Eq. (3) using the rate constant (k), maximum alkalinity (CM), and initial alkalinity (C0) derived from cubitainer tests (Fig. 6). Alkalinity points and computed curves for CA for Buck Mtn. cubitainer tests conducted under static, circulated; closed, and circulated open conditions.

Figure 6. Natural logarithm of the limestone mass (M) divided by initial mass (M0) versus initial elapsed time of cubitainer tests for Howe Bridge, Morrison, and Buck Mtn. ALDs. Remaining mass was 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 in accordance with Eq. (1) (M0 = M0 exp(-kt)).

Figure 7. Natural logarithm of remaining limestone mass (M) divided by initial mass (M0) versus initial elapsed time of cubitainer tests for Howe Bridge, Morrison, and Buck Mtn. ALDs. Remaining mass was 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 in accordance with Eq. (1) (M0 = M0 exp(-kt)).
EXPERIMENTAL 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', the initial alkalinity (C0), and the maximum alkalinity (Cmax), which can be determined with cubitainer tests, the decline in limestone mass through time and any 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-decay constant, k, derived from the cubitainer data (Fig. 7). The dashed projection assumes a constant flow rate and porosity and that alkalinity concentration is a function of the detention time for a given mass of limestone per Eq. (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, 1996). 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 C0, Cmax, 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) follow the simulated trends. To provide the same basis for the sites, 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 (t = 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 of 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 is equal to the acidity:

\[ t = \frac{(Q/C_\text{max})(k')}{k'} \ln \left( \frac{C_\text{max}}{C_\text{sat}} \right) \]  

(4)

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

\[ M = \frac{Q}{r \cdot (1-exp(-kt))} \]  

(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, and age t, can be determined:

\[ M = \frac{Q}{r \cdot (1-exp(-kt))} / \exp(kt) \]  

(6)

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

\[ M = \frac{Q}{r \cdot (1-exp(-kt))} / \left[ (Q/C_\text{max})(k')/(k') \exp(kt) \right] \]  

(7)

Equation (7) can be solved for a specified age and minimum alkalinity, for example t = 20 yr and C = Csat, to indicate the required initial limestone mass to satisfy the design longevity. Although particle density, ρp, 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, C0, and Cmax 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 patterns, multiple tests should be considered to evaluate variable influent concentrations or system conditions (open/closed). Furthermore, because of variability or uncertainty in critical parameters, computations should be performed over the range of expected values for flow rate and porosity.

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(CO3)/C(HCO3)] versus detention time for the cubitainer tests yielded estimates of the alkalinity rate constant, k', and for logarithmic plots of [M(Mg)] versus detention time yielded estimates of the limestone dissolution rate constant, k. The initial and maximum alkalinity 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 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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