

OPTIMIZATION OF LIMESTONE DRAINS FOR LONG-TERM TREATMENT OF MINE DRAINAGE, SWATARA CREEK BASIN, SCHUYLKILL COUNTY, PA¹

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Abstract. Limestone drains were constructed in 1995, 1997, and 2000 to treat acidic mine drainage (AMD) from the Orchard, Buck Mtn., and Hegins discharges, respectively, in the Swatara Creek Basin, Southern Anthracite Coalfield, east-central Pennsylvania. This report summarizes the construction characteristics and performance of each of the limestone drains on the basis of influent and effluent quality and laboratory tests of variables affecting limestone dissolution rates. Data for influent and effluent indicate substantial alkalinity production by the Orchard and Buck Mtn. limestone drains and only marginal benefits from the Hegins drain. Nevertheless, the annual alkalinity loading rates have progressively declined with age of all three systems. Collapsible-container (cubitainer) testing was conducted to evaluate current scenarios and possible options for reconstruction and maintenance of the limestone drains to optimize their long-term performance. The cubitainer tests indicated dissolution rates for the current configurations that were in agreement with field flux data (net loading) for alkalinity and dissolved calcium. The dissolution rates in cubitainers were larger for closed conditions than open conditions, but the rates were comparable for coated and uncoated limestone for a given condition. Models developed on the basis of the cubitainer testing indicate (1) exponential declines in limestone mass and corresponding alkalinity loading rates with increased age of limestone drains and (2) potential for improved performance with enlargement, complete burial, and/or regular flushing of the systems.

Additional Key Words: limestone dissolution rate, cubitainer tests, armoring.

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Introduction

Acidic, abandoned mine drainage (AMD) from the Orchard, Buck Mountain (Mtn.), and Hegins discharges was a major source of metals and acidity loading to the headwaters of Swatara Creek, which drains a 112-km² area in the Southern Anthracite Field of east-central Pennsylvania (Fig. 1) (Wood *et al.*, 1986; Eggleston *et al.*, 1999), until limestone drains were constructed in 1995, 1997, and 2000, respectively. Previously reported data collected by the U.S. Geological Survey (USGS) before and after the construction of these limestone drains and other treatment systems in the watershed indicate that coincident downstream buffering in Swatara Creek has mitigated acidic base flow and stormflow and decreased metals concentrations (Cravotta, 2000; Cravotta and Weitzel, 2001). As a consequence of the improved water quality, the aquatic ecological community in Swatara Creek has rebounded (Cravotta and Bilger, 2001; Cravotta *et al.*, 2002). During ecological surveys prior to 1991, no fish were found at Ravine (Fig. 1). Increasing numbers of fish species have been found annually since 1996. In 2002, 25 species of fish were documented. A concurrent increase in the abundance of benthic macroinvertebrate taxa that are considered intolerant of pollution also indicates water-quality improvements (Cravotta and Bilger, 2001; Cravotta *et al.*, 2002). Nevertheless, limestone drains are designed with a finite lifetime (e.g. Cravotta and Watzlaf, 2002; Cravotta, 2003). Alkalinity concentrations of the treated effluent and, possibly, the downstream base flow are expected to decline as the systems age and the limestone is consumed.

Purpose and Scope

This paper describes the physical characteristics and results of field monitoring and laboratory testing of acid neutralization and alkalinity production in limestone drains for treatment of AMD (acidity and metals) from the Orchard, Buck Mtn., and Hegins discharges in the Swatara Creek Basin, Pa. First, background on the geochemistry and limestone treatment of AMD is presented. Second, data for influent and effluent at the Orchard, Buck Mtn., and Hegins discharges are evaluated to indicate the performance of the limestone drains and possible trends. Third, short-term (2-wk) data for collapsible-cubitainer (cubitainer) laboratory tests of each AMD source are used (1) to quantify the effects of detention time, armoring, and system enclosure on limestone-drain performance; (2) to develop models of long-term trends for

performance on the basis of these variables; and (3) to identify possible methods, configurations, and/or mechanisms that may be implemented to optimize performance of the limestone drains.

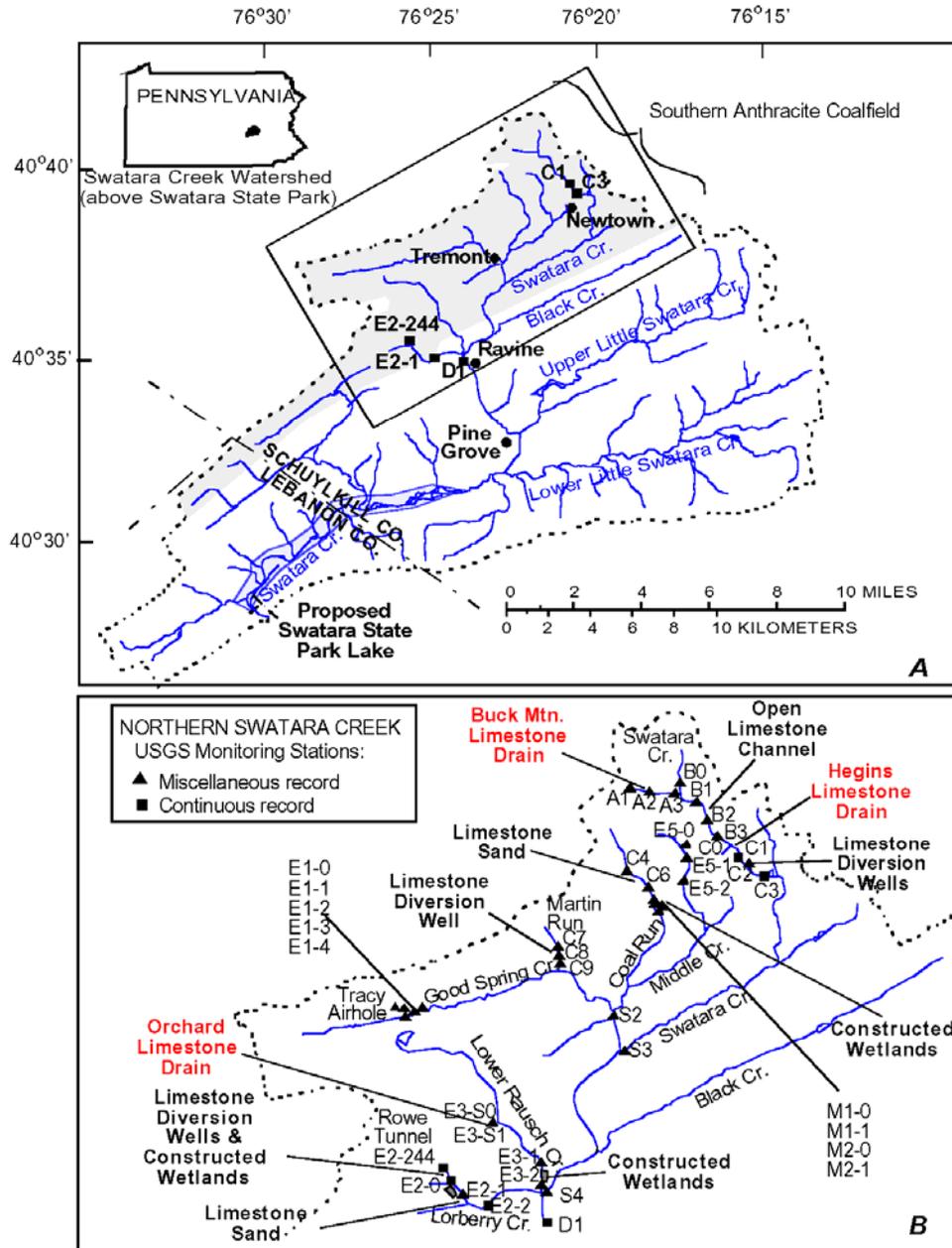


Figure 1. Locations of the Orchard, Buck Mtn., and Hegins limestone drains and associated water-quality monitoring sites in the Swatara Creek Basin, Schuylkill County, Pa: *A*, Continuous monitoring sites on Swatara Creek above Swatara State Park; *B*, monitoring sites within the Southern Anthracite Coalfield, upstream from Ravine (area denoted in *A*).

Background

AMD can contain elevated concentrations of dissolved sulfate (SO_4), ferrous iron (Fe^{II}), and ferric iron (Fe^{III}) produced by the oxidation of pyrite (FeS_2) and can range in quality from strongly acidic to moderately alkaline (Rose and Cravotta, 1998; Cravotta *et al.*, 1999; Nordstrom and Alpers, 1999; Cravotta and Kirby, this volume). Concentrations of calcium (Ca), magnesium (Mg), manganese (Mn), aluminum (Al), and other solutes can be elevated because of the dissolution of carbonate, oxide, and aluminosilicate minerals by acidic water. Near-neutral, net-alkaline AMD can result from the reaction of acidic water with minerals containing Ca, Mg, and other base cations. For example, dissolution of calcite (CaCO_3), which is the principal component of limestone, can increase pH, alkalinity ($\text{HCO}_3^- + \text{OH}^-$), and Ca concentration by the following reactions or some combination thereof:



where $[\text{H}_2\text{CO}_3^*] = [\text{CO}_2 (\text{aq})] + [\text{H}_2\text{CO}_3^0]$ (Plummer *et al.*, 1979; Stumm and Morgan, 1996; Drever, 1997). 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 equation (2), an alkalinity concentration of 122 mg/L as HCO_3^- equals 100 mg/L as CaCO_3 , and a Ca^{2+} concentration of 40 mg/L equals 100 mg/L as CaCO_3 (hardness). (To avoid confusion between the identity of the aqueous ions and complexes shown in reactions and the analytical concentrations of chemical constituents, symbols for the total analytical concentration of chemical constituents are indicated without regard to valence, such as Ca, Fe, HCO_3 , and SO_4 ; symbols with superscripted roman numerals are used to indicate the sum of aqueous species with a specific redox state, for example Fe^{II} and Fe^{III} .)

Acidity and metals can be removed from AMD through various passive treatment systems that increase pH and alkalinity and, ultimately, facilitate Fe^{II} oxidation (Hedin *et al.*, 1994; Skousen *et al.*, 1998; Kirby *et al.*, 1999). Many systems utilize crushed limestone in a packed bed that is flooded continuously with AMD to neutralize the acidity, thereby generating alkalinity. For example, an “anoxic limestone drain” (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 (Turner and McCoy, 1990; Brodie *et al.*, 1991; Hedin and Watzlaf, 1994; Hedin

et al., 1994; Watzlaf *et al.*, 2000). Excluding O₂ from contact with the water in an ALD minimizes the potential for oxidation of Fe^{II} to Fe^{III} and the consequent precipitation of Fe(OH)₃ and related solids (e.g., Cravotta and Trahan, 1999; Bigham and Nordstrom, 2000). As the pH increases to near-neutral values in an ALD, concentrations of Fe^{III}, Al, and other metals in AMD can decline owing to their precipitation or adsorption; however, concentrations of SO₄, Fe^{II}, and Mn^{II} generally will not be affected (Cravotta and Watzlaf, 2002).

Criteria for sizing an ALD consider the flow rate and the imbalance between alkalinity and acidity of the influent. Hedin and Watzlaf (1994) and Hedin *et al.* (1994) recommended a method to estimate the quantity of limestone to achieve a detention time of 15 h or more at average flow for a 20-yr life span. This sizing method is intended to produce a constant alkalinity, approaching the maximum concentration in equilibrium with CaCO₃, and is warranted for AMD with high acidity (>300 mg/L). However, shorter detention times may be warranted for a AMD source that has a low acidity and/or a large flow rate and where space for construction is limited. In such cases, an appropriate size can be determined by evaluating the rate of reaction between the limestone and the AMD and the corresponding alkalinity concentrations for a range of detention times (Cravotta, 2003). Using this method, an initial quantity of limestone may be estimated that accounts for long-term dissolution of the ALD and that yields a residual mass of limestone over the ALD lifespan that gives the necessary detention time at average flow to produce an alkalinity concentration greater than or equal to the influent acidity.

The precipitation of Fe(OH)₃, Al(OH)₃, and various other compounds 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 limestone bed (Robbins *et al.*, 1996; Watzlaf *et al.*, 2000). 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 O₂, Fe^{III}, and Al in influent (<1 mg/L O₂, Fe^{III}, or Al) to minimize potential for clogging or armoring by Fe^{III} or Al solids.

Continuous inundation with AMD and retention of carbon dioxide (CO₂) 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 equations (1) and (2), a greater quantity of alkalinity can be generated in an enclosed ALD compared to 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 the exsolution of CO_2 , Fe^{II} oxidation, and the precipitation and settling of solid $Fe(OH)_3$.

Stringent requirements for low concentrations of O_2 , Fe^{III} , and Al in the influent AMD make ALDs inappropriate for treatment of oxic or highly mineralized water, which commonly occurs in mined areas. For example, of 140 AMD samples collected in 1999 from bituminous and anthracite coal mines in Pennsylvania (Cravotta and Kirby, this volume), only 17 percent were net acidic *and* had <1 mg/L of dissolved O_2 , Fe^{III} , and Al. Thus, ALDs could be appropriate for AMD treatment at some of the 140 sites, provided the dissolved O_2 , Fe^{III} , and Al concentrations remain at low levels *and* resources and space are available for construction of the treatment system. However, the majority of these discharges do not meet criteria for an ALD.

Alternative treatment systems, including a “reducing and alkalinity producing system” (RAPS) or an “oxic limestone drain” (OLD), can be used for the neutralization and removal of metals from acidic effluent that does not meet criteria for an ALD. In a RAPS, pretreatment through a compost bed is used to decrease concentrations of dissolved O_2 , Fe^{III} , and Al in the mine water to acceptable levels before routing the water through an underlying limestone bed (Kepler and McCleary, 1994; Skousen *et al.*, 1998; Watzlaf *et al.*, 2000; Demchak *et al.*, 2001; Rose, this volume). The RAPS can be particularly effective for treatment of AMD containing a high concentration of Al (Rose, this volume). Nevertheless, the reactivity of the compost in a RAPS may be short lived (Demchak *et al.*, 2001), and short-term laboratory studies (<2 yr) indicate that limestone alone can be as effective as this layered system for neutralization of mine water containing dissolved O_2 and low to moderate concentrations of Fe^{III} and Al (<10 mg/L) (Watzlaf, 1997; Sterner *et al.*, 1998). For example, in an OLD, compost is not used for pretreatment of effluent containing low to moderate concentrations of Fe^{III} and Al; Fe oxidation

and hydrolysis reactions will not be prevented but must be managed (Cravotta and Trahan, 1999; Cravotta and Watzlaf, 2002).

Despite potential for armoring and clogging of the compost and/or limestone bed in a RAPS or OLD system, the hydrous Fe^{III} oxides can be effective for the sorption of dissolved Mn^{II} and trace metals (e.g. Kooner, 1993; Webster *et al.*, 1998; Cravotta and Trahan, 1999). Precipitation of Mn oxides is possible after most dissolved Fe has been precipitated (Watzlaf, 1997; Cravotta and Trahan, 1999). If sufficiently rapid flow rates can be attained, some precipitates can be transported as suspended particles through the limestone bed. Perforated piping typically is installed within the limestone bed of RAPS and OLD systems to facilitate the flushing of accumulated precipitates. However, consensus on scientifically based design criteria for a RAPS, an OLD, and most other passive treatment systems has not been reached.

Site Descriptions and Methods of Sampling and Analysis

Description of Limestone Drains

As described by Cravotta and Weitzel (2001), Cravotta and Watzlaf (2002), and, in more detail in this report, the untreated effluent at the Buck Mtn. site initially met criteria for an ALD; however, the untreated effluent at the other two sites contained elevated dissolved O₂, Fe^{III}, and/or Al. Hence the Orchard and Hegins systems are classified as OLDs (even though the Hegins drain was not buried). The physical characteristics of the Orchard, Buck Mtn., and Hegins ALDs/OLDs are summarized in Table 1. The values given for limestone mass, bulk volume, and porosity are approximate; precise measurements of these properties were not made. The site locations are shown in Fig. 1.

Table 1. Physical characteristics of Orchard, Buck Mtn., and Hegins limestone drains, Swatara Creek Basin, Schuylkill County, Pa.

Site	Date Built	Flow Rate (L/min)	Limestone		Approximate Dimensions of Limestone Bed				Bulk Volume (m ³)	Bulk Density (kg/m ³)	Porosity ^a (m ³ /m ³)	Detention Time ^b (hr)
			Mass (tonne)	CaCO ₃ (wt%)	Size Range (cm)	Length (m)	Width (m)	Depth (m)				
Orchard	Mar-95	39	30 ^c	97	6-10	73.2	2.4	0.8	16.7	1,797	0.32	1.2
Buck Mtn.	May-97	534	320	92	6-10	50.0	2.4	2.0	240	1,333	0.49	3.7
Hegins	Jun-00	526	730	92	20-30	50.0	6.0	1.8	540	1,352	0.49	8.4

a. Limestone mass and dimensions approximate. Bulk density, $\rho_B = M_0 / V_B$, computed as initial limestone mass (M_0) divided by bulk volume (V_B). Porosity, $n = (\rho_S - \rho_B) / \rho_S$, computed assuming constant particle density, $\rho_S = 2,650 \text{ kg/m}^3$ (Cravotta and Watzlaf, 2002).

b. Detention time estimated as the product of the porosity and bulk volume (void volume) divided by average flow rate.

c. This report assumes 30 tonne limestone used to construct Orchard O.L.D. Although 38 tonne limestone reportedly was placed at the site, porosity estimated for this mass and the known bulk volume is only 0.14. An unknown quantity of limestone delivered to each site was spread on the surface.

Table 2. Average influent and effluent quality at Orchard, Buck Mtn., and Hegins limestone drains from date of construction to September 2003, Swatara Creek Basin, Schuylkill County, Pa.^a

Site	Dissolved Oxygen (mg/L)		pH, field (units)		Net Acidity ^b (mg/L as CaCO ₃)		Alkalinity (mg/L as CaCO ₃)		Calcium ^c (mg/L as CaCO ₃)		Magnesium ^c (mg/L)		Sulfate (mg/L)		Iron (mg/L)		Manganese (mg/L)		Aluminum (mg/L)		
	In	Out	In	Out	In	Out	In	Out	In	Out	In	Out	In	Out	In	Out	In	Out	In	Out	
	Orchard	3.4	4.3	3.5	3.5	5.9	30.3	-49.2	0.0	55.7	53.9	128.0	86.3	78.1	176	172	2.09	0.50	2.40	1.59	1.16
Buck Mtn.	1.3	2.7	4.6	4.6	6.3	28.1	-55.2	2.3	77.0	10.3	92.0	30.0	28.2	72	62	13.25	10.44	1.17	1.18	0.63	<0.20
Hegins	10.1	10.8	3.5	3.5	4.5	47.4	28.1	0.0	0.5	22.9	40.8	145.2	140.1	232	223	0.19	0.13	1.74	1.56	5.06	4.26

a. Values are grand averages of semi-annual averages from date of construction. Data for Orchard extend only through May 2002.

Influent data for Buck Mtn. are the average for untreated AMD prior to construction and untreated seepage below ALD after construction.

b. Acidity and net acidity computed on the basis of equations (3) and (4), assuming equivalents of 2 per mole of Fe and Mn and 3 per mole of Al.

c. Calcium and magnesium concentration as CaCO₃ computed as 2.5 and 4.1 times the concentration of Ca and Mg, respectively. Flow times difference between influent and effluent Ca as CaCO₃ indicates approximate quantity of limestone dissolved each year since construction.

Orchard OLD. The Orchard OLD was constructed in 1995 reportedly using 38 tonnes limestone fragments ranging in size from 6 to 10 cm (Cravotta and Trahan, 1999; Cravotta and Watzlaf, 2002). Owing to an unusually low estimate for porosity on the basis of this mass of limestone and the bulk volume of the drain (Table 1), this report assumes that only 30 tonnes limestone were placed in the drains. An unknown fraction of the delivered limestone was spread on the surface around the site. The limestone composition, as reported by the source quarry, was 97 weight percent CaCO_3 . Equal quantities of the limestone were placed in three semi-circular troughs in a horizontal trench, shrouded with a vinyl liner, and subsequently buried. Seepage from the collapsed drift was collected behind a wooden dam and then piped to the three parallel limestone drains. Valving at the inflow to each drain was used to control inflow rates. No piping was installed within the drain for flushing. Access wells were installed at five locations along the length of each drain. Influent is accessible before contacting limestone (station 403626076253001). Effluent is accessible at the pipe outlet from each drain (stations 403626076253016, 403626076253026, 403626076253036). (The USGS station number, given here and below, is used by Durlin and Schaffstall (1998-2004) to identify water-quality monitoring sites and is needed to access the data on the World Wide Web at <http://waterdata.usgs.gov/pa/nwis>.)

Buck Mtn. ALD. The Buck Mtn. ALD was constructed in 1997 as a narrow trench filled with 320 tonnes limestone fragments ranging in size from 6 to 10 cm (Cravotta and Weitzel, 2001; Cravotta and Watzlaf, 2002; Cravotta, 2003). The limestone composition, as reported by the source quarry, was 92 weight percent CaCO_3 . Seepage of AMD from a collapsed drainage tunnel was collected at the upflow end of the trench and several additional points downflow within the trench. To intercept seepage that welled up along the length of the trench, a continuous geotextile liner had to be cut into pieces that were installed overlapping like shingles, with the top shingle at the upflow end. Although this arrangement worked to direct influent into and down the drain, it complicated the monitoring and interpretation of water-quality variations with increased distance or detention time along the drain. The pH and alkalinity typically increased from the upper end of the drain to intermediate sampling points, then decreased sharply where additional fresh influent entered at intermediate points, and ultimately increased toward the outflow (Cravotta, 2003). Perforated piping was installed near the base of the limestone bed along the length of the drain to flush accumulated solids. Seven access wells were

installed at evenly spaced locations along the length of the drain. Influent water quality is based on pre-construction data and an adjacent seep of similar water quality to the pre-construction water (station 404032076222901). Effluent is accessible at the pipe outlet (station 0157154970).

Hegins OLD. The Hegins OLD was constructed in 2000 of 730 tonnes limestone fragments ranging in size from 20 to 30 cm (Cravotta and Watzlaf, 2002; Forney, 2003). The limestone composition, as reported by the source quarry, was 92 weight percent CaCO₃. Discharge from the collapsed Falls Coal Company mine drift was piped approximately 35 m down a steep gradient into the drain, consisting of four clay-lined cells in series within the original channel. A clay berm and plastic liner were used to separate cells 1 and 2; the other cells were separated with berms of finely crushed siltstone (2 to 4 cm). Outflow spills from the top of each cell or leaks through the berms into the next cell. Perforated piping with valves for each cell was installed along the length of the drain for flushing of accumulated solids. A steel, rectangular notch weir at the outflow of the drain facilitates discharge measurements and helps dam water near the base of the treatment system. Access wells were installed at four locations in each of the cells. Influent is accessible before contacting limestone (station 403955076211801). Effluent is accessible at the weir (station 403955076211802). At the time of this report, the Hegins drain had not been buried nor continuously flooded. The bulk of the limestone is inundated only at high flow rates.

Water-Quality Sampling and Analysis

Standard methods were used for sampling and analysis of water samples (Wood, 1976; U.S. Geological Survey, 1997 to present; Rantz *et al.*, 1982a, b; Fishman and Friedman, 1989; Ficklin and Mosier, 1999). Flow rate was measured by use of a flow meter, a weir, or volumetrically. Water temperature, dissolved O₂, specific conductance (SC), pH, and Eh were measured using an immersible sonde equipped with multiple electrodes that had been calibrated at the time of sample collection. Field Eh and pH were determined using a gel-filled combination Pt and Ag/AgCl electrode with pH sensor. The Eh/pH electrode was calibrated in Zobell's solution and in pH 2.0, 4.0, and 7.0 buffer solutions. Values for Eh were corrected to 25° C relative to the standard hydrogen electrode in accordance with methods of Nordstrom (1977). The dissolved O₂ was calibrated in air saturated with water. The SC was calibrated in a standardized potassium

chloride (KCl) solution with conductance value greater than that expected of samples and checked in lower concentration KCl solutions.

Water samples were collected into sample-rinsed polyethylene bottles and stored on ice until analyzed. One unfiltered subsample was capped with no head space, and then titrated for alkalinity with sulfuric acid (1.6 N H₂SO₄) to the endpoint pH of 4.5 in the field or in the laboratory within 48 h (fresh alkalinity) after sample collection (Fishman and Friedman, 1989; American Society for Testing and Materials, 2000). Some of the unfiltered samples also were titrated with sodium hydroxide (1.6 N NaOH) for “hot” acidity to the endpoint pH of 8.3 (American Society for Testing and Materials, 2000). The pH before and during titrations was measured using a liquid-filled combination Ag/AgCl electrode calibrated in pH 4.0, 7.0, and 10.0 buffer solution. Alkalinity was reported as zero for samples with laboratory pH <4.5; acidity was reported as zero for samples with laboratory pH >6.4. The assignment of zero acidity for these high-pH samples is not necessarily correct; such samples could contain acidity in the form of Fe^{II} and Mn^{II} and, if analyzed according to standard methods, may have positive or negative acidity (American Society for Testing and Materials, 2000; Cravotta and Kirby, this volume).

Major cations, anions, and metals were measured on filtered samples (0.45- μ m) at one of four different laboratories at different times during the course of study: USGS National Water Quality Laboratory, Denver, Colo.; Pennsylvania Department of Environmental Protection (PaDEP) Laboratory, Harrisburg, Pa.; U.S. Department of Energy NIOSH Laboratory, Pittsburgh, Pa.; and Activation Laboratories, Ontario, Canada. Analytical methods generally were consistent among the laboratories; however, detection limits varied for some constituents, such as Al. The concentrations of SO₄ and Cl in an unpreserved subsample were analyzed by ion chromatography (IC) (Fishman and Friedman, 1989; Crock *et al.*, 1999). Another subsample preserved with nitric acid at pH <2 was analyzed for “dissolved” cations by inductively coupled plasma atomic emission spectroscopy (ICP-AES) (Fishman and Friedman, 1989; Crock *et al.*, 1999). Concentrations of Fe^{II} were determined by calculation of the Fe²⁺/Fe³⁺ ratio on the basis of the half reaction, Fe²⁺ = Fe³⁺ + e⁻, and data for Eh and temperature of the sample (e.g. Nordstrom *et al.*, 1979). Charge imbalances routinely were less than 10 percent relative to the mean of cation and anion equivalents.

The flow rate and water quality were monitored monthly during the first year and less frequently thereafter for 7 yr at the Orchard OLD (through 2002), 7 yr at the Buck Mtn. ALD

(through present), and 4 yr at the Hegins OLD (through present). The water-quality data were compiled in the USGS National Water Information System data base (<http://waterdata.usgs.gov/pa/nwis>) and published annually (Durlin and Schaffstall, 1998-2004). The semi-annual and long-term averages for flow rate, pH, and concentrations of alkalinity, acidity, net acidity, Ca, and other selected solutes in influent and effluent of the three limestone drains were computed to evaluate the extent of contaminant attenuation and the rates of limestone dissolution within the limestone drains at each site. Time-weighted averages were used because of the irregular sampling frequency.

Computation of Acidity and Net Acidity

The acidity due to metals was computed from pH and dissolved metals concentrations (C_{Fe} , C_{Mn} , C_{Al}) in milligrams per liter:

$$\text{Acidity}_{\text{computed}} \text{ (mg/L CaCO}_3\text{)} = 50 \cdot (10^{(3-\text{pH})}) + 2 \cdot C_{Fe}/55.8 + 2 \cdot C_{Mn}/54.9 + 3 \cdot C_{Al}/27.0 \quad (3)$$

The “net acidity” was computed by subtracting the measured, fresh alkalinity from the computed acidity:

$$\text{Net acidity (mg/L CaCO}_3\text{)} = \text{Acidity}_{\text{computed}} - \text{Alkalinity}_{\text{measured}} \quad (4)$$

According to Cravotta and Kirby (this volume), the computed net acidity closely approximates the measured “hot” acidity where the H_2SO_4 added to the sample is subtracted from the NaOH added (American Society of Testing and Materials, 2000). Hot-acidity data were not collected on a consistent basis and thus are not used for this report.

Tracer Tests

On July 16, 2002, a tracer test was conducted by rapidly injecting a 1 liter solution containing 120 g sodium bromide (NaBr) at the inflow to the Hegins OLD. Water samples were withdrawn from access pipes near the downflow end of each cell and at the outflow weir at 15-min intervals for an elapsed time of 7 h after the injection. An ion-specific electrode was used to measure the concentration of Br in the samples. Although SC and Br electrode readings were recorded during the tracer test to note passage of peak concentrations, the field Br readings were not stable because sample temperatures were variable through the day. One day after the tests

were completed, the samples were remeasured in the laboratory at a constant temperature of 25° C. The samples were buffered with sodium nitrate (NaNO₃) and electrode readings were recorded in millivolts. The Br concentrations were computed on the basis of repeated electrode readings on standard solutions containing 0.1 to 1,000 mg/L Br. A linear regression fit of the log- linear plot of Br concentration and the associated electrode readings was used to express sample results as the Br concentration. The data for the Br concentrations in samples were evaluated to estimate actual detention time within each cell and for the entire system. The tracer detention-time data were compared with computed detention times on the basis of volume estimates and flow rate through each cell. Cravotta and Watzlaf (2002) provide details on the methods for computation of detention times in limestone beds.

Cubitainer Tests

In addition to the collection of field performance data, short-term testing of the reaction between limestone and untreated effluent in cubitainers (collapsible polyethylene containers of 1-gallon nominal volume) was conducted in the laboratory over elapsed times of approximately 2 weeks by methods of Cravotta (2003), which were modified after Watzlaf and Hedin (1993). The cubitainer tests were conducted *after* the ALD/OLD systems were constructed in an effort to evaluate the effects of detention times, system closure to the atmosphere, and “armoring” by secondary mineral encrustations on reactions within the limestone drains. Before loading in cubitainers, crushed limestone of the same composition used for a given ALD was sieved to retain fragments approximately 1.3-by-3.5-cm, washed with 5 percent (by volume) hydrochloric acid (HCl), rinsed thoroughly with tap water and deionized water, and then dried. A 4-kg subsample of the limestone fragments was left in contact with the AMD at each site for 3 to 6 weeks to become “armored.” Generally, this mineral-coated limestone sample was retrieved from the field when the fresh influent was collected for the cubitainer tests. The untreated AMD from each site was collected into empty cubitainers, capped with no head space, and immediately transported to the laboratory. Within an hour of collection, the influent was used to fill other cubitainers containing 2 or 4 kg of uncoated or coated limestone.

A peristaltic pump with four heads on a single shaft was connected to four cubitainers for simultaneous circulation of solutions without the introduction of air (closed conditions) or with the introduction of air (open conditions). The pumping rate was maintained between 0.1 and 0.5

L/min to simulate mixed flow through the ALD/OLD and minimize stratification within the cubitainers. Tests were conducted concurrently with uncoated or coated limestone and/or closed or open conditions. The approximate field temperature of 9° to 11° 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. Effluent samples from the cubitainers were withdrawn through a valve using a 120-mL syringe. After discarding approximately 10-mL fluid from the sample tubing, two 50-mL subsamples were forced from the syringe through a 0.45- μ m nylon filter, and immediately analyzed for alkalinity (pH 4.5 endpoint). Samples for Ca were acidified with HNO₃ and analyzed by ICP-AES. Samples were collected at 0.5-h intervals during the first 4 to 6 h, hourly until 6 to 8 h had elapsed, and at 24-h and less frequent intervals after the first day. Calcite saturation index (SI) and Pco₂ were computed using measured values for temperature, SC, pH, alkalinity, and Ca; van't Hoff temperature-corrected equilibrium constants from Ball and Nordstrom (1991); and Debye-Huckel activity coefficients based on estimated ionic strength (Langmuir, 1997).

Following the methods of Cravotta (2003), time-series data for the cubitainer tests were used to derive first-order and second-order equations to estimate the concentration of alkalinity or Ca (C_t) of effluent as a function of the detention time (t_d) within a limestone bed, influent concentration (C₀), maximum or steady-state concentration (C_S), and the rate constant. As explained by Lasaga (1981), linear regression of ln[(C_S-C_t)/(C_S-C₀)] versus detention time for the tests yields estimates of the first-order rate constant, k', in the expression:

$$C_t = C_S - [(C_S - C_0) \cdot \exp\{-k' \cdot t_d\}], \quad (5)$$

Linear regression of [1/(C_S-C_t) - 1/(C_S-C₀)] versus detention time yields estimates of the second-order rate constant, k'', in the expression:

$$C_t = C_S - \{1/[k'' \cdot t_d + 1/(C_S - C_0)]\}. \quad (6)$$

Continuous curves for concentration at any detention time that were obtained on the basis of equations (5) and (6) with data from cubitainers were compared with field data for concentrations at points within the limestone drains. By combining the cubitainer rate estimates with information on the initial mass of limestone, porosity, and the long-term average flow rate through the OLD/ALD, exponential decay models were obtained indicating possible long-term

trends, on a decadal scale, for changes in mass of limestone, detention time, and alkalinity of effluent with age of the OLD/ALD at each site.

Results and Discussion

Limestone Drain Influent and Effluent Quality

Over the 3- to 7-yr monitoring period, the average flow rates for the Orchard, Buck Mtn., and Hegins drains were 39, 534, and 526 L/min, respectively (Table 1). For a given pore volume for the limestone bed, the detention time will decrease with increased flow rate (Freeze and Cherry, 1979; Cravotta and Watzlaf, 2002). At the average flow rate and given the reported bulk volume and porosity values in Table 1, detention times within the Orchard, Buck Mtn., and Hegins drains would be approximately 2.3, 3.7, and 8.4 h, respectively. As shown in Fig. 2 and discussed below, the instantaneous flows at each site ranged by more than a factor of 10 with corresponding effects on the effluent composition. Hence, data for each of the drains show the pH, alkalinity, and Ca concentrations of the effluent increased with decreased flow velocity or increased detention time, as generally expected for systems that are undersaturated with respect to calcite (Figs. 2 and 3). (Note that flow and effluent data shown in Fig. 2 for the Orchard OLD are for each of the three parallel drains that together had a cumulative average flow of 39 L/min shown in Table 1.)

The influent at the Orchard, Buck Mtn., and Hegins OLDs/ALDs had average pH of 3.5, 4.6, and 3.5 and average net acidity of 30.3, 28.1, and 47.4 mg/L as CaCO₃, respectively (Table 2). The Hegins discharge had greater concentrations of SO₄, Mg, and Al (~5 mg/L) but smaller concentrations of Fe (<0.5 mg/L) than the Orchard or Buck Mtn. discharges. The Orchard and Buck Mtn. discharges had relatively low concentration of Al (<1.2 mg/L). The Buck Mtn. discharge had Fe >10 mg/L compared to Fe ~2 mg/L at the Orchard discharge. Nevertheless, the Buck Mtn. discharge generally was more dilute than the other discharges on the basis of its SO₄, Ca, and Mg concentrations (Table 2).

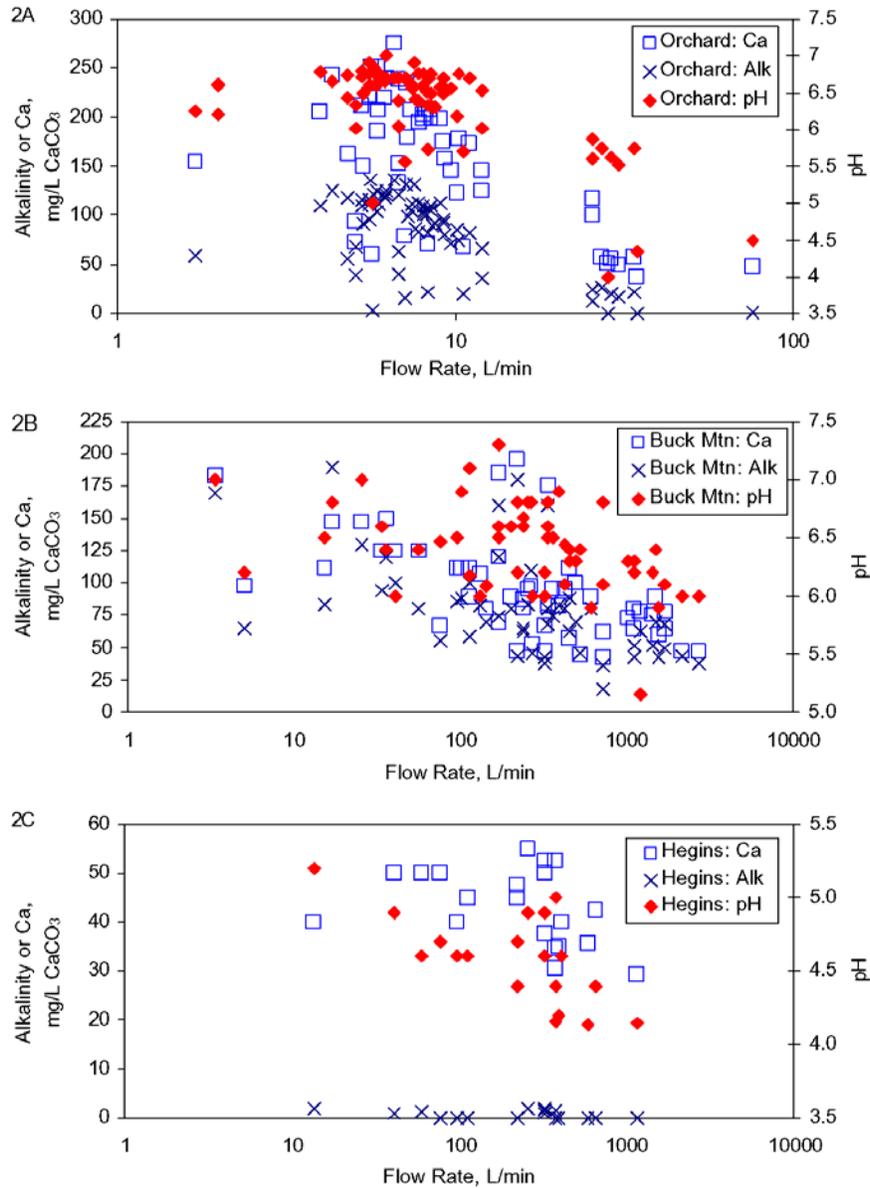


Figure 2. Relations between the flow rate and effluent pH or CaCO₃ concentration: *A*, Orchard OLD; *B*, Buck Mtn. ALD; *C*, Hegins OLD. Data are plotted for period since construction to September 2003.

Effluent from each OLD/ALD had higher average pH, alkalinity, and Ca, and lower average acidity, Fe, and Al concentrations than the influent (Table 2). Generally, Mg, Mn, and SO₄ concentrations were not affected or declined slightly within each OLD/ALD (Table 2). The effluents were undersaturated with respect to calcite (Cravotta and Trahan, 1999; Cravotta and Watzlaf, 2002). The increased Ca concentration as CaCO₃ was comparable to the decreased net-acidity concentration (Table 2). The Orchard OLD and Buck Mtn. ALD effectively neutralized

the AMD, yielding near-neutral pH values and net acidities that were negative (alkalinity > computed acidity). Furthermore, although the Hegins OLD has not completely neutralized the AMD, it has provided partial treatment, increasing effluent pH by 1 unit on average and reducing acidity by approximately 20 mg/L. The partially neutralized effluent introduces less acidity, Al, and other metals than the untreated AMD to Swatara Creek with expected benefits to aquatic organisms.

The long-term average flow multiplied by the difference between average concentrations of Ca for influent and effluent (Table 2) indicates average CaCO₃ fluxes of 1.5, 22.9, and 5.0 tonne/yr at the Orchard, Buck Mtn., and Hegins OLDs/ALDs, respectively. Simple linear extrapolation of the average annual fluxes indicates a 19-yr supply to complete exhaustion for the 30 tonnes limestone originally placed in the Orchard OLD, a 15-yr supply for the 320 tonnes limestone in the Buck Mtn. ALD, and 158-yr supply for the 730 tonnes limestone in the Hegins OLD. The mass of limestone dissolved annually could have been slightly greater than these estimates because it was not pure CaCO₃ (divide the flux by the fraction of CaCO₃ in the limestone). However, the long-term averages for the composition of influent and effluent reported in Table 2 and linear extrapolation of the flux estimates could give a misleading impression of the current and future performance of the limestone drains. For example, Cravotta and Watzlaf (2002) argued that the limestone mass consumption rate is not linear, but is exponential. Instead of an abrupt end to treatment, exponential decay would result in sustained but progressively smaller yields of alkalinity as the limestone mass decreases over time, as shown later in this report.

An evaluation of the water-quality data over time indicates declines in performance of all three systems with age (Figs. 3, 4, and 5), with site-specific problems as follows:

Orchard OLD. The pH, alkalinity, and Ca in the treated effluent have declined with age of the Orchard OLD (Fig. 3). Based on the annual flux of Ca, more than half of the original 30 tonnes of limestone should remain. However, the current distribution of limestone and the pore volume within the drain is uneven. Because of greater dissolution rates associated with low-pH influent, the limestone has been preferentially consumed near the inflow, and the remaining limestone bed in the downflow section has gradually accumulated Fe^{III} precipitate (Cravotta and Trahan, 1999). Several different tests have indicated potential for rapid dissolution of the coated limestone, as

discussed below. Nevertheless, the accumulation of precipitate has caused a decrease in the effective porosity of the limestone bed with a corresponding reduction in the detention time at average flow rate. Moreover, the inflow piping system has failed. In fall 2001 and, again, in fall 2002, the inflow pipe was buried and clogged by loose rock and soil that had collapsed from the slope above. At the time of this report, the Orchard OLD had stopped transmitting water. A flushing system is needed to prevent the accumulation of solids in the drain, and the inflow pipes need to be replaced to avoid future sediment deposition and clogging.

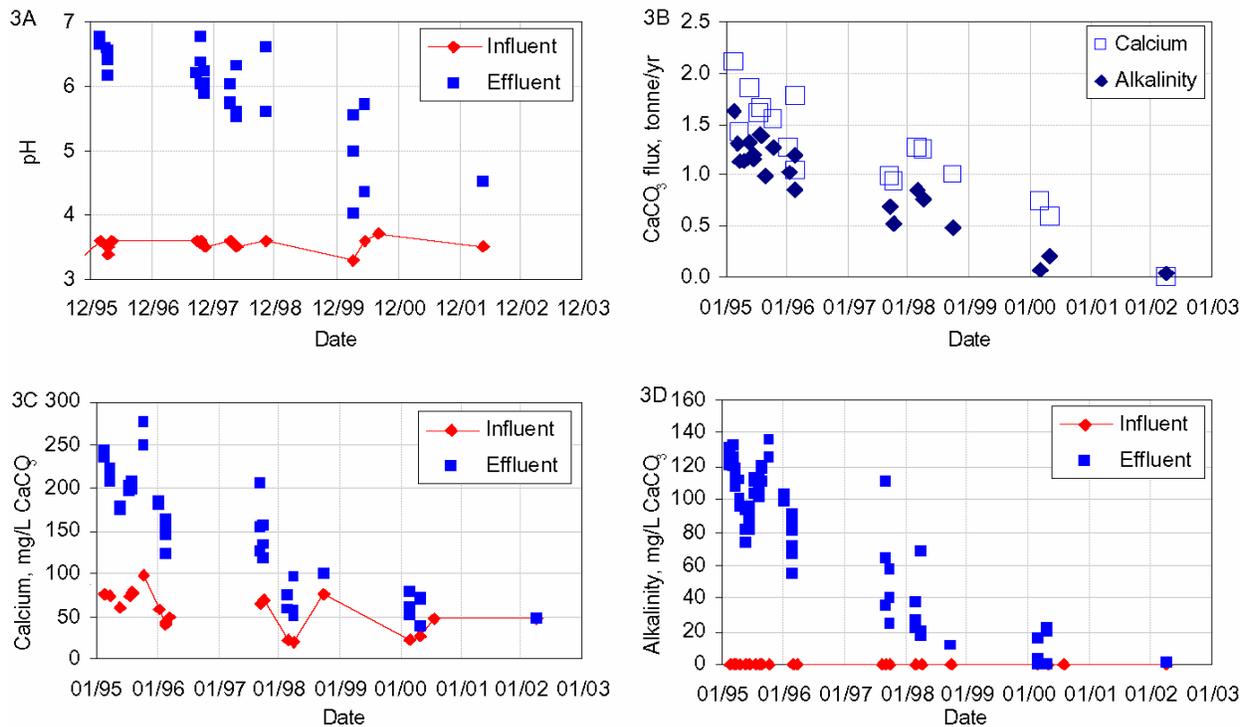


Figure 3. Time series plots of water-quality data for Orchard OLD, January 1995 to May 2002: A, pH; B, flux of dissolved calcium and alkalinity as CaCO₃; C, calcium concentration; D, alkalinity concentration.

Buck Mtn. ALD. The Buck Mtn. ALD contributes more alkalinity to Swatara Creek than the other two systems combined, with fluxes of alkalinity and Ca as CaCO₃ averaging 20.9 and 22.9 tonne/yr, respectively (Fig. 4). Given these fluxes, and without additions described below, approximately half of the original 320 tonnes of limestone currently would remain. Note that the observed limestone dissolution rate for the Orchard OLD (Cravotta and Trahan, 1996, 1999) was used for the conceptual design of the Buck Mtn. ALD. On this basis, 640 tonnes of limestone were delivered to construct the Buck Mtn. ALD with a conceptual design life of at least 10 years

and initial detention time of 5 to 6 h at average flow (C. A. Cravotta III, 1997, written commun.). However, only 320 tonnes of the limestone were used in the ALD; the other half was distributed downstream below several additional AMD seeps within the channel (D. J. Koury, 1997, written commun.).

Despite variable flow rates, ranging to nearly 3,000 L/min, the Buck Mtn. ALD has consistently produced net-alkaline effluent with near-neutral pH (Fig. 4). Although the pH, alkalinity, and Ca concentrations of effluent decreased to their lowest levels with highest flow rates (Fig. 2), the largest alkalinity and CaCO₃ fluxes were associated with high-flow conditions. This implies that increased detention time yields only marginal increases in concentration and is consistent with reported asymptotic increases in pH, alkalinity, and Ca concentrations along longitudinal profiles through ALDs (Watzlaf *et al.*, 2000; Cravotta and Watzlaf, 2002) and with increased detention time in cubitainers (Cravotta, 2003). It also implies that the Buck Mtn. ALD is an important source of alkalinity during base-flow and stormflow conditions. Nevertheless, the large alkalinity fluxes from the Buck Mtn. ALD indicate a rapid consumption of its limestone and potential for its performance to decline in the near future.

Storm runoff had partly exposed the Buck Mtn. limestone drain in September 2001. Water-quality data available at that time indicated larger than expected declines in the alkalinity and Ca fluxes (Fig. 4). Hence, the Buck Mtn. limestone drain was repaired and enlarged in January 2002 with the addition of 90 tonnes limestone at its outflow. The effect of this addition on pH and alkalinity of effluent has been marginal (Fig. 4). Current data indicate the continued rapid dissolution of the limestone mass and the potential need for future additions or reconstruction.

Hegins OLD. The Hegins limestone drain has not performed adequately since it was installed, and its performance has declined rapidly with age (Fig. 5). Despite having nearly twice the mass of limestone and a flow rate comparable to that at the Buck Mtn. ALD, the flux of Ca as CaCO₃ averaged only 5.0 tonne/yr from the Hegins drain (Fig. 5). Hence, only about 20 tonnes of the original 730 tonnes had dissolved over its 3.5 yrs of operation. Although an underground (closed) system was planned, the drain was not buried because of cost overruns. Furthermore, the limestone has not been continuously flooded. Large fragments of limestone (>20 cm) were used anticipating the need to flush solids from the system. However, large fragments have a small surface area compared to smaller fragments. Moreover, instead of lining the cells with a

thin bed of finely crushed limestone as planned, a clay liner was used to reduce leakage and dam water within limestone filled cells. Equilibrium computations indicate the low-pH influent is undersaturated with kaolinite; the clay may dissolve providing an additional source of Al.

The primary goal of treatment of the Hargins discharge was to increase pH, optimally to 6.5, to remove dissolved Al, which was elevated in influent at this site (Fig. 5). Although the pH could approach equilibrium values near pH of 8.3 at the limestone surface, the Hargins OLD effluent had an average pH of 4.5 (Table 2). The effluent pH declined with age of the system from initial values near 5.0 to current values below 4.5 (Fig. 5). On average, the effluent had about 15 percent lower concentration of Al than influent (Table 2). The limestone immersed at the inflow was corroded and free of precipitate; that immersed within the subsequent treatment cells and near the outflow was encrusted with Al-hydroxysulfate and associated precipitate (Loop, 2003). The accumulation of Al precipitates within the limestone bed was anticipated. A flushing system was installed; however, the system has not been flushed routinely.

Data collected during flushing in July 2002 indicated the removal of only a small fraction of accumulated metals from the Hargins drain (Forney, 2003). Nevertheless, during high-flow conditions in 2002 and 2003, concentrations of total and dissolved Al in the effluent were larger than those of the influent (Fig. 5). Some of the Al-rich solids that had accumulated in lower sections of the drain during lower flow conditions may have redissolved at higher flows as the low-pH AMD extended further down into the system. The clay used for the liner also could be an additional source of Al.

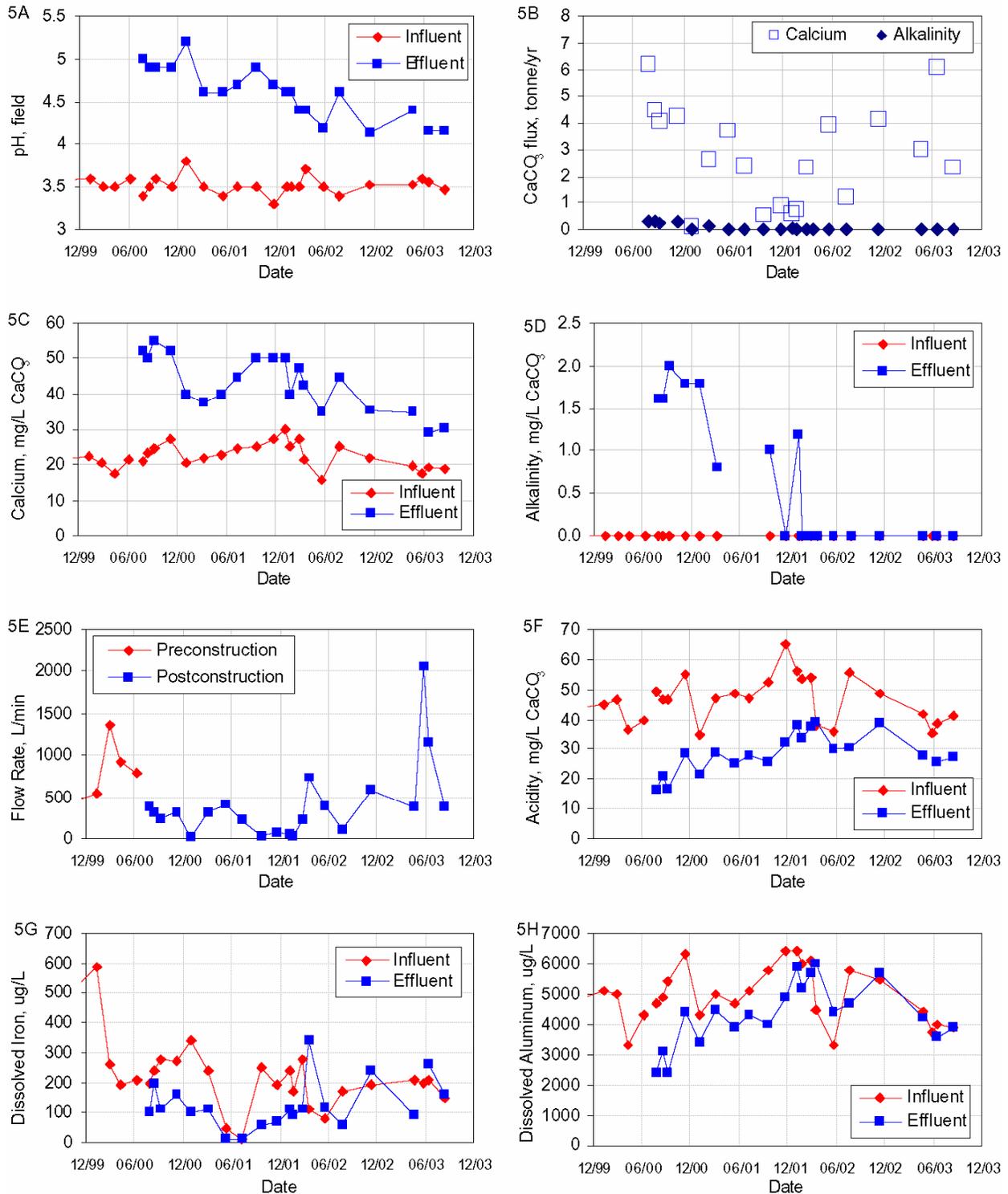


Figure 4. Water-quality data for Buck Mtn. ALD, March 1996 to September 2003: *A*, pH; *B*, flux of dissolved calcium and alkalinity as CaCO₃; *C*, calcium concentration; *D*, alkalinity concentration; *E*, flow rate; *F*, computed acidity, *G*, dissolved iron; *H*, dissolved aluminum (values <0 below detection). Data from Durlin and Schaffstall (1998-2004). Yellow triangle on date axis at January 10, 2002, indicates when additional 90 tonnes of limestone were added.

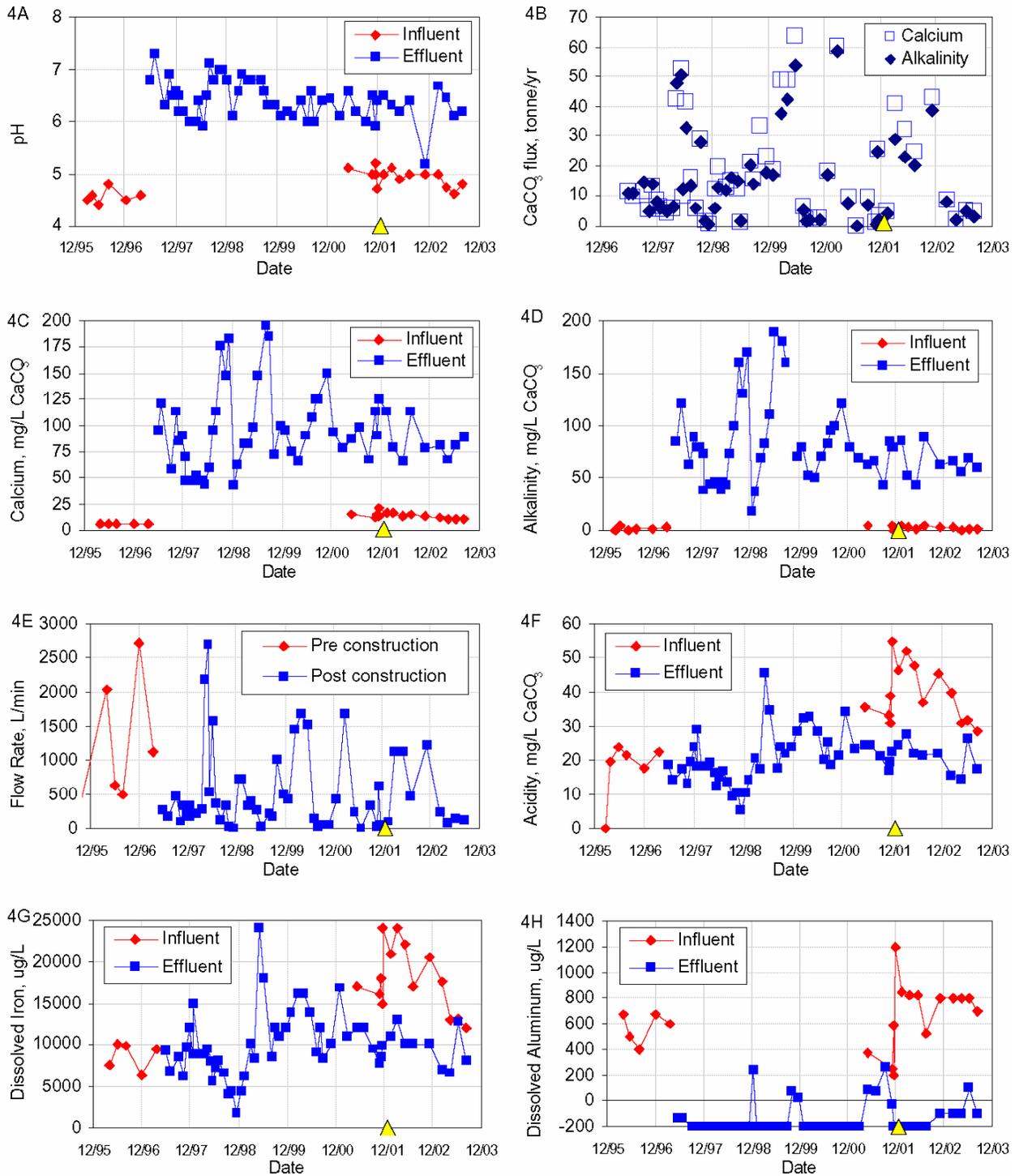


Figure 5. Time-series plots of water-quality data for Hegins OLD, December 1999 to September 2003: *A*, pH; *B*, flux of dissolved calcium and alkalinity as CaCO_3 ; *C*, calcium concentration; *D*, alkalinity concentration; *E*, flow rate; *F*, computed acidity, *G*, dissolved iron; *H*, dissolved aluminum. Data from Durlin and Schaffstall (2000-2004).

Table 3. Summary of cubitainer test conditions^a and results for Orchard, Buck Mtn., and Heginns discharges, Swatara Creek Basin, Schuylkill County, Pa.

Site/Test	Circulated	Coated	Lime-stone Mass Closed (kg)	Alkalinity ^b				Calcium				Spec. Cond. (µS/cm)	pH (units)	Calcite SI ^{c,d} (log IAP/Kt)	Pco ₂ ^{c,d} (log atm)							
				(mg/L as CaCO ₃)		(1/h)		(L/mg/h)		(mg/L as CaCO ₃)						(1/h)		(L/mg/h)				
				C ₀	C _S	k'	k	C ₀	C _S	k'	k					C ₀	C _S	k'	k	0 h	4 h	336 h
Orchard																						
O1 Uncoated	Y	N	Y	2.0	0.0	127.0	-0.174	0.0022	46.3	212.0	-0.146	0.0014	306	3.5	6.3	7.3	<5.1	-1.8	-0.3	>1.4	-1.6	-2.3
O3 Uncoated	Y	N	Y	2.0	0.0	128.0	-0.136	0.0016	46.3	209.0	-0.142	0.0014	306	3.5	6.8	7.5	<4.2	-1.1	-0.1	>1.3	-1.8	-2.5
O2 Coated	Y	Y	Y	2.0	0.0	138.0	-0.233	0.0038	46.3	215.8	-0.201	0.0025	306	3.5	6.4	7.5	<3.0	-1.8	-0.1	>1.4	-1.7	-2.4
O4 Coated	Y	Y	Y	2.0	0.0	143.0	-0.171	0.0021	46.3	204.8	-0.179	0.0021	306	3.5	6.6	7.5	<3.0	-1.4	-0.1	>1.5	-1.8	-2.4
Buck Mtn																						
B1 Open Coated	Y	Y	N	4.0	4.5	108.0	-0.603	0.0221	8.0	147.8	-	-	186	4.8	7.0	7.6	-5.5	-0.6	-0.3	-1.1	-2.2	-2.8
B2 Open Uncoated	Y	N	N	4.0	4.5	90.0	-0.498	0.0179	8.0	233.0	-	-	186	4.8	7.0	7.8	-5.5	-0.7	0.0	-1.1	-2.1	-3.0
B3 Closed Uncoated	Y	N	Y	4.0	4.5	174.0	-0.193	0.0017	8.0	298.8	-	-	186	4.8	6.7	7.6	-5.5	-0.9	0.3	-1.1	-1.6	-2.4
B4 Closed Uncoated	N	N	Y	4.0	4.5	174.0	-0.070	0.0005	8.0	262.5	-	-	186	4.8	6.1	7.4	-5.5	-2.2	0.0	-1.1	-1.4	-2.2
Heginns																						
H1 Open Coated	Y	Y	N	2.0	0.0	67.0	-0.067	0.0012	51.3	160.3	-0.145	0.0022	600	3.5	6.7	7.7	<5.2	-2.2	-0.3	>1.4	-2.5	-2.9
H2 Closed Coated	Y	Y	Y	2.0	0.0	83.0	-0.098	0.0016	51.3	198.3	-0.144	0.0015	600	3.5	6.4	7.4	<5.2	-2.2	-0.3	>1.4	-2.0	-2.5
H3 Closed Uncoated	Y	N	Y	2.0	0.0	72.0	-0.129	0.0026	51.3	154.0	-0.213	0.0041	600	3.5	6.3	7.6	<5.2	-2.4	-0.3	>1.4	-2.0	-2.8
H4 Closed Uncoated	Y	N	Y	4.0	0.0	71.0	-0.281	0.0095	51.3	175.3	-0.260	0.0055	600	3.5	6.8	7.8	<5.2	-1.4	-0.1	>1.4	-2.2	-2.9

a. All tests conducted in laboratory using collapsible 1-gallon nominal polyethylene containers filled with fresh influent from the discharge and 2- or 4-kg high-purity (CaCO₃ = 97%) limestone fragments (1.3-by-3.5-cm). Data collected at 0.5-h intervals for first 6 h and less frequently to 336 h.
b. Initial and steady-state concentration (C₀ and C_S), rate constant (k' or k''), and equation (5) or (6) give concentration as function of detention time.
c. Calcite saturation index (SI) and partial pressure of CO₂ (Pco₂) computed using measured values for temperature, specific conductance (SC), pH, alkalinity, and Ca; van't Hoff temperature-corrected equilibrium constants from Ball and Nordstrom (1991); and Debye-Huckel activity coefficients on the basis of estimated ionic strength, I = 1.88(10⁻⁵)^{SC} (Langmuir, 1997).
d. Alkalinity needed to compute SI and Pco₂. For Orchard and Heginns tests, computed SI and Pco₂ at 0 h are given for first sample (at 0.5 or 1.0 h) with positive value for alkalinity. For Buck Mtn. tests, Ca was measured for initial and final samples, only; at 4 h, Ca estimated from alkalinity.

Limestone Dissolution in Cubitainers

Cubitainer testing was performed to evaluate the effect of detention time and other variables affecting limestone dissolution and alkalinity production in the limestone drains, such as mineral coatings and enclosure of the systems (Table 3, Figs. 6, 7, and 8). Tests were conducted using the same limestone source material in all tests with fresh influent from each of the three discharges. Generally, only pH and alkalinity were monitored for the Buck Mtn. tests; however, because of their low initial pH, Ca also was measured as a reaction progress variable for the Orchard and Hegins tests. In the case of Buck Mtn., alkalinity data were used to estimate Ca concentration assuming the stoichiometry of equation (2). The Ca data were interpreted to indicate the limestone dissolution rate and the calcite saturation index. The effluents for all tests at 4 h detention time were undersaturated with calcite; however, the final effluents after 336 h, or 2 wks, detention time were saturated with calcite ($SI = \pm 0.3$) (Table 3).

Orchard OLD. The cubitainer tests for the Orchard discharge were conducted in May 2002 with duplicate pairs of cubitainers, containing 2 kg coated or 2 kg uncoated limestone, under closed, circulated conditions (Table 3, Fig. 6). The Fe^{III} -coated limestone and fresh influent with pH of 3.5 and dissolved O_2 of 5.2 mg/L were collected from the inflow to the Orchard OLD on the first day of the tests. The Orchard cubitainer tests showed that dissolution of Fe^{III} -coated limestone under closed, circulated conditions was slightly faster but ultimately yielded comparable maximum alkalinity compared to the uncoated limestone under closed-circulated conditions. The trends for alkalinity and Ca concentration for a given test condition were closely parallel. The maximum alkalinity for the coated limestone was approximately 140 mg/L, and that for the uncoated limestone was approximately 130 mg/L. The final effluent for the different tests had comparable values of pH from 7.3 to 7.5 and dissolved Ca from 82 to 86 mg/L. The last paragraph of this paper hypothesizes why coated limestone dissolved as rapidly as uncoated limestone for a given condition, and why dissolution rates under closed conditions exceeded those for open conditions.

The computed P_{CO_2} for Orchard cubitainer influent was $>10^{-1.4}$ atm; the P_{CO_2} for the final effluent was $10^{-2.4}$ atm in closed cubitainers (Table 3). Actual P_{CO_2} within cubitainers could have been higher than computed values because samples analyzed for alkalinity and pH were withdrawn under vacuum, promoting the exsolution of CO_2 and other gases as indicated by

bubbles inside the syringe. Because the influent initially contained dissolved O_2 , oxidation of Fe^{II} was likely in the closed cubitainers, consistent with an underground, continuously flooded OLD system. The rapid dissolution of coated limestone during cubitainer testing was consistent with field observations reported by Cravotta and Trahan (1999). Generally, a first-order model fits the dissolution-rate data for alkalinity and Ca better than a second-order model (Fig. 6).

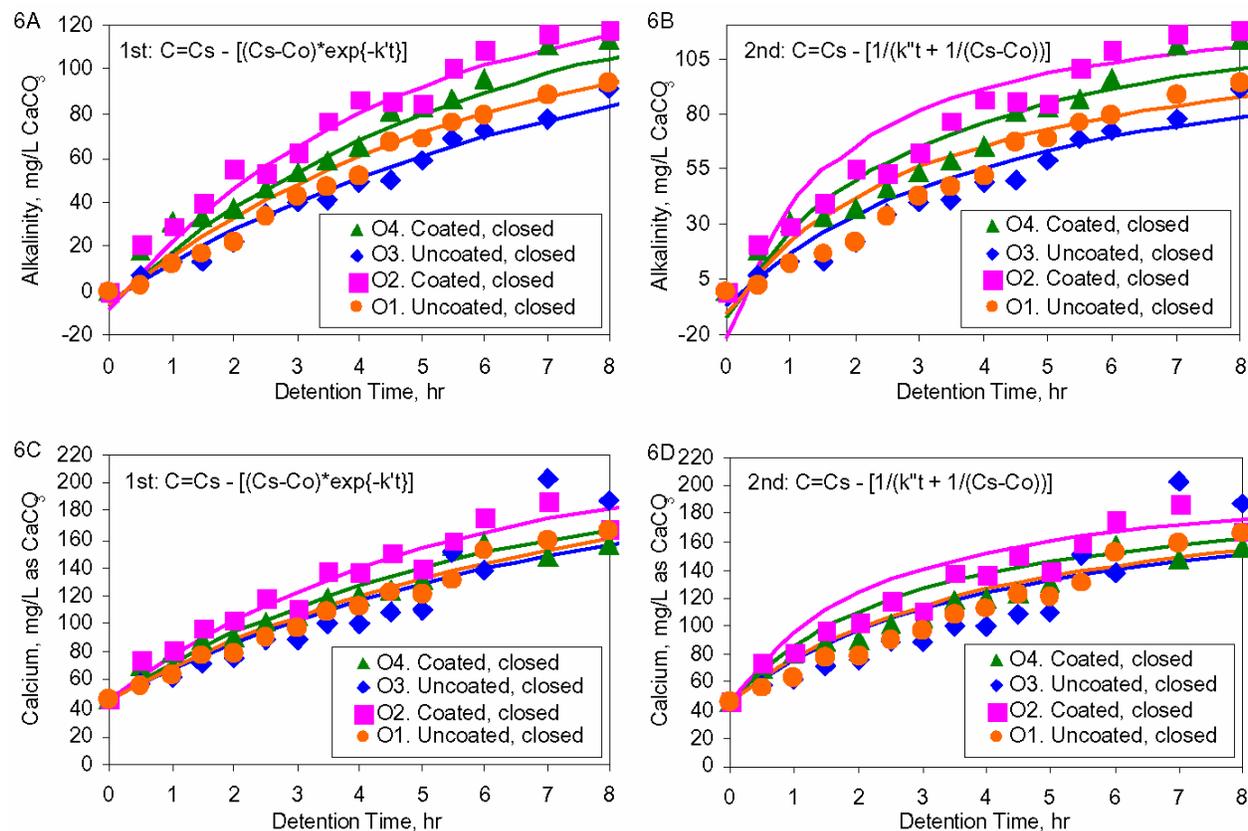


Figure 6. Concentration of alkalinity and calcium as $CaCO_3$ versus detention time for cubitainer tests of effects of mineral coating on limestone dissolution and alkalinity production rates for Orchard OLD: *A*, alkalinity, first-order curve; *B*, alkalinity, second-order curve; *C*, Ca, first-order curve; *D*, Ca, second-order curve. Limestone left at Orchard site for 6 wks prior to testing became coated with Fe-hydroxide. Tests were conducted in May 2002 with 2 kg coated or uncoated limestone under closed, circulated conditions. Summary data are in Table 3.

Buck Mtn. ALD. The cubitainer tests for the Buck Mtn. discharge were conducted in November 2001 and repeated in December 2001 (Table 3, Fig. 7). In both sets of tests, 4 kg of limestone was reacted with fresh influent from a nearby untreated seep having quality similar to that of the original untreated discharge prior to construction of the ALD (Fig. 4). The fresh influent had pH of 4.7 to 5.0 and was anoxic (<0.5 mg/L dissolved O_2). Similar results were obtained for

replicate tests; averages are shown in Fig. 7. The Buck Mtn. cubitainer tests showed that dissolution under closed, circulated conditions was faster and ultimately yielded greater maximum alkalinity than dissolution of the same material under open, circulated conditions. Although the dissolution rate was slower under static conditions than circulated conditions, the same maximum alkalinities of about 170 mg/L ultimately were achieved for uncoated limestone under both static and circulated conditions (Fig. 7).

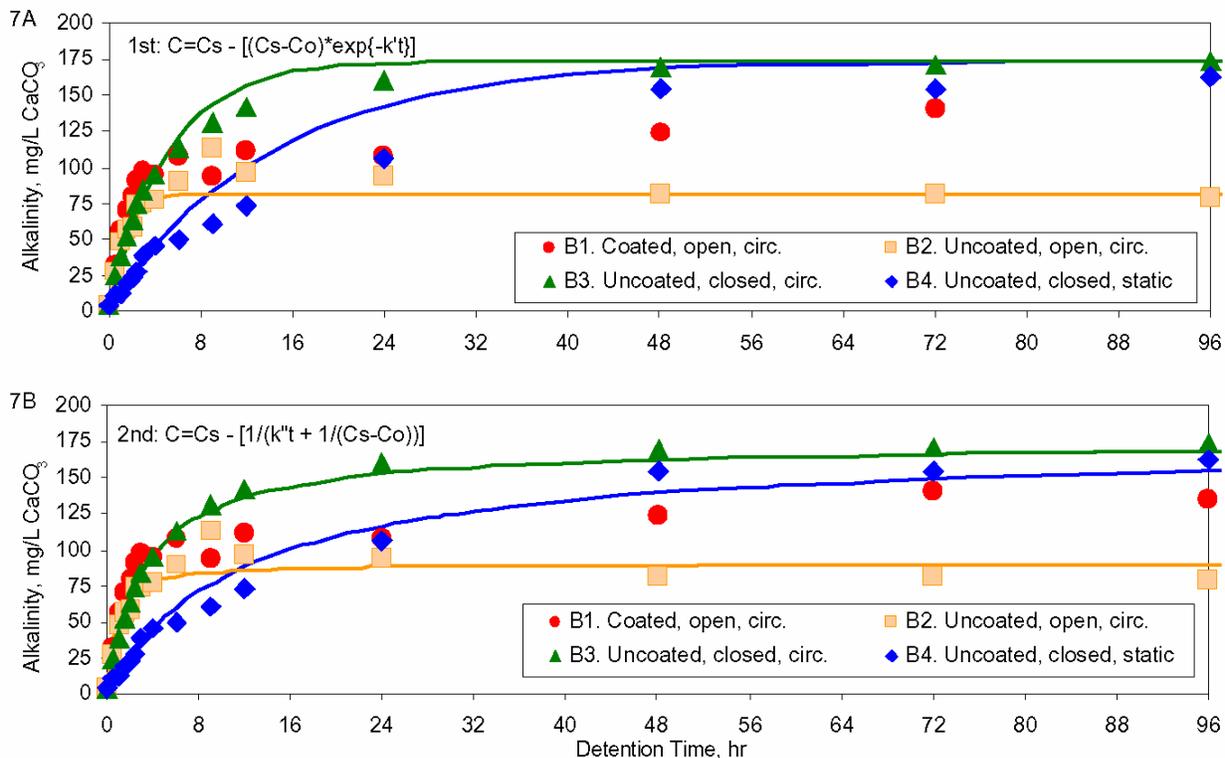


Figure 7. Concentration of alkalinity versus detention time for cubitainer tests of effects of mineral coating, circulation, and system closure on limestone dissolution and alkalinity production rates for Buck Mtn. ALD: *A*, curve fitted by first-order rate equation (5); *B*, curved fitted by second-order rate equation (6). Limestone left at Buck Mtn. site for 6 wks prior to testing became coated with Fe-hydroxide. Tests were conducted in November 2001 with 4 kg coated or uncoated limestone and then repeated in December 2001. Plotted values are averages; summary data in Table 3.

The Buck Mtn. cubitainer tests also showed that under open, circulated conditions, Fe^{III}-coated limestone could yield initially greater alkalinity than uncoated limestone, with alkalinity values for both the coated and uncoated samples peaking during the first 96 h and then eventually leveling off after 4 days to steady-state values near 80 mg/L. The consumption of initial alkalinity produced under open conditions resulted from the oxidation of Fe^{II}. In contrast,

oxidation of Fe^{II} was negligible in the closed cubitainers, consistent with an underground, continuously flooded ALD.

Despite lower alkalinities, the pH after the first 4 h was always greater for the effluents from the open cubitainers than the closed cubitainers (Table 3). The higher pH resulted from exsolution of CO_2 . For the Buck Mtn. cubitainer tests, the computed P_{CO_2} of influent was $10^{-1.1}$ atm; the P_{CO_2} of the final effluent in open cubitainers was $\leq 10^{-2.8}$ atm compared to $\geq 10^{-2.4}$ atm in closed cubitainers (Table 3). Although a second-order model best approximated the alkalinity changes with prolonged detention time in the closed containers, the first-order model was equally representative of the data for the first 6 h (Fig. 7).

Hegins OLD. The cubitainer tests for the Hegins discharge were repeated in January and March 2002 using 2 kg coated limestone under open, circulated conditions and 2 kg coated limestone, 2 kg uncoated limestone, or 4 kg uncoated limestone under closed, circulated conditions (Table 3, Fig. 8). Fresh influent with pH of 3.5 and dissolved $\text{O}_2 > 9$ mg/L and Al-coated limestone were collected from the inflow to the Hegins OLD on the first day of each series of the tests. The open, circulated test conditions represented the current “unburied, unflooded” OLD. Similar results were obtained for replicate tests; averages are shown in Figure 8. The maximum alkalinities in January and March for the coated limestone were 67 to 47 mg/L under open conditions compared to 83 and 81 mg/L under closed conditions. The Ca concentration data paralleled the alkalinity data, with maxima of 87 and 64 mg/L under open conditions compared to 110 and 79 mg/L under closed conditions in January and March, respectively. The trends for alkalinity and Ca concentration for a given test condition followed a first-order model (Fig. 8).

The cubitainer test data for the Hegins discharge indicate the 2-kg Al-coated limestone dissolved more slowly under open conditions than closed conditions. Furthermore, under the closed conditions, the dissolution rate and maximum alkalinity and Ca concentrations for the 2-kg samples of the coated and uncoated limestone were comparable (Fig. 8). This implies that despite the previous accumulation of Al-coatings on limestone in the existing treatment system, burial and complete flooding to “close” the system and retain CO_2 could improve its performance. The final effluent for the different tests had comparable P_{CO_2} of $10^{-2.4}$ atm to $10^{-2.9}$

atm and pH values of 7.4 to 7.8 (Table 3). The final effluents for the 2-kg samples were slightly less saturated with calcite than the effluent for the 4-kg sample (Table 3).

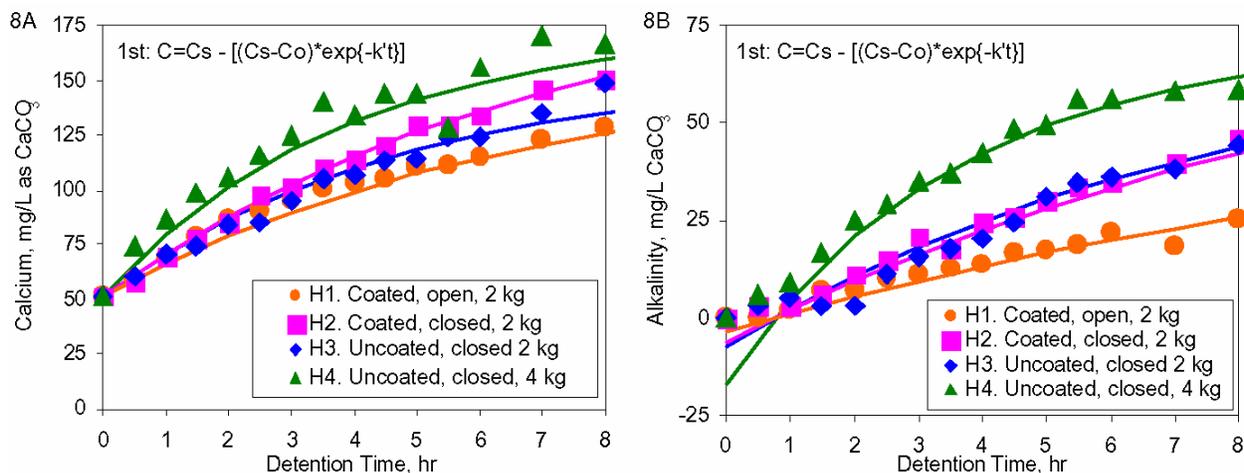


Figure 8. Concentrations as CaCO₃ versus detention time for cubitainer tests of effects of mineral coating on limestone dissolution and alkalinity production rates for Hegins OLD: *A*, calcium; *B*, alkalinity. Limestone left at Hegins site for 6 wks prior to testing became coated with Al-hydroxide. Tests were conducted in January and March 2002 with 2 or 4 kg coated or uncoated limestone under closed or open conditions. Summary data are in Table 3.

The Hegins cubitainer tests also showed that dissolution of 4 kg uncoated limestone yielded initially greater alkalinity and Ca concentrations than dissolution of 2 kg uncoated limestone under the closed, circulated conditions (Fig. 8). The 4-kg sample had twice the surface area of the 2-kg sample with the same particle size. By corollary, a 2 kg-sample of larger particles would have smaller surface area and slower dissolution rates than the material tested. This implies that the alkalinity production rate can be decreased by decreasing the exposed surface area for a given mass of limestone. Apparently, the accumulation of Al-coatings did not affect the reactive surface area. However, the large particle size used for the Hegins OLD treatment system may have had a limiting effect on alkalinity production (Tables 1 and 2). The cubitainer tests for the Hegins discharge indicate dissolution rates that are significantly greater than those computed on the basis of the field flux of Ca (Fig. 9). The implication is that the conditions for cubitainer testing do not reflect field conditions, or data used to compute field dissolution rates have been misinterpreted, as explained below.

Combining Field and Laboratory Data to Explain Limestone Drain Performance

Using the Ca fluxes based on the influent and effluent data at each site, the limestone dissolution rates relative to the initial mass were estimated to be approximately 7.8, 5.3, and 0.7 percent per year at the Buck Mtn., Orchard, and Hegins limestone drains, respectively. The dissolution rate for the Buck Mtn. ALD was among the fastest, that for the Orchard OLD was near the median, and that for Hegins OLD among the slowest of 13 sites evaluated in Pennsylvania and Maryland (Cravotta and Watzlaf, 2002). The decay rates based on the field flux data are comparable to the first-order decay rates derived from cubitainer data (Table 3, Figs. 6, 7, and 8). Given the results from cubitainer tests, the decrease in limestone mass with time (age) and any associated decreases in detention time and the corresponding alkalinity concentration can be estimated as demonstrated by Cravotta (2003).

Fig. 9 shows the results of computations of mass decay and associated alkalinity for the Orchard, Buck Mtn., and Hegins OLDs/ALDs using the first-order decay rate, k' , initial alkalinity (C_0), and maximum steady-state alkalinity (C_S) derived from cubitainer data (Table 3, Figs. 6, 7, and 8). The CaCO_3 concentration and flux at the average flow rate of effluent (Table 1) were estimated using the first-order decay constant and the mass-specified detention time. As the limestone mass declined with age, its total volume was assumed to decline proportionally; the porosity and particle density of 2.65 g/cm^3 were assumed to be constant. Hence, for a constant flow rate, the detention time was assumed to decline with the decreased mass (increased age). The predicted decrease in limestone mass at each time step was estimated by subtracting the CaCO_3 flux from the mass to indicate that remaining for the next time step. Given the remaining mass at each time step, calculations of detention time and corresponding concentrations and fluxes of CaCO_3 were repeated. The projected long-term trends on the basis of cubitainer test results are shown as solid and dashed curves. The solid curves represent current conditions, and dashed curves represent conditions after proposed reconstruction. The point symbols indicate field observations.

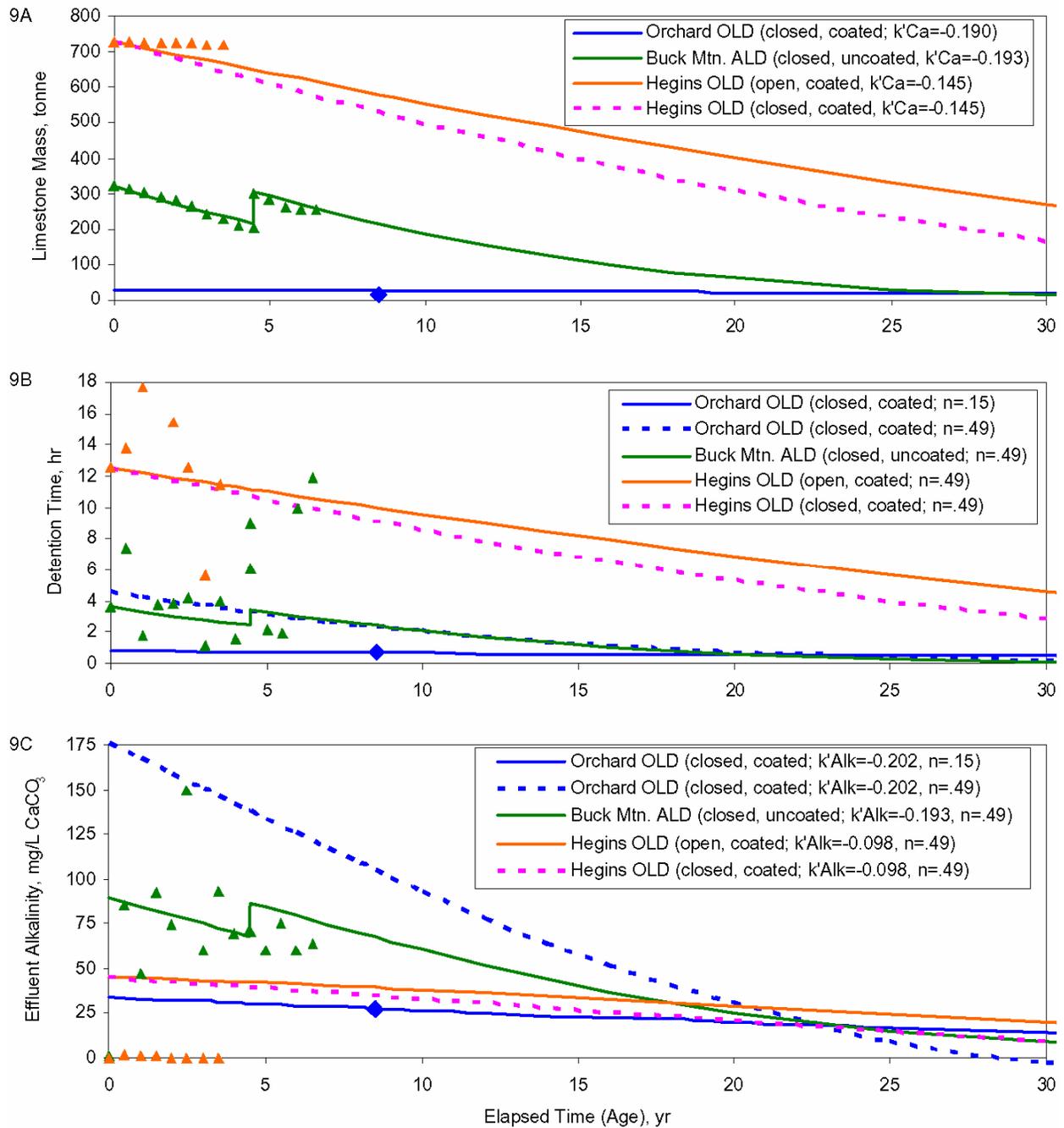


Figure 9. Simulated decline in limestone mass, detention time, and alkalinity with age of Orchard, Buck Mtn., and Hegins limestone drains on the basis of cubitainer tests (first-order curves): *A*, Mass versus age considering rate constant, k' , for dissolved Ca in cubitainers. *B*, Detention time versus age for average flow (Q) and specified porosity (n). *C*, Alkalinity versus age for declining mass and detention time, assuming constant flow and porosity, and rate constant, k' , for alkalinity in cubitainers. Symbols based on observed semi-annual average flow and concentration at the Buck Mtn. and Hegins drains and grand averages for the Orchard drain. Solid curves represent current conditions; dashed curves represent conditions after proposed reconstruction.

The predicted trends for the Buck Mtn. ALD are similar to computed changes in mass based on the initial mass and corresponding reductions based on the semi-annual average alkalinity or calcium flux at the ALD. The addition of 90 tonnes limestone to the Buck Mtn. ALD in January 2002 clearly shows as a break in the slope (Fig. 9). The semi-annual averages for alkalinity of effluent generally were in the range of the cubitainer-based estimates for the Buck Mtn. ALD, but the observed data varied considerably because of large variations in the flow rate. In contrast, the computed estimates for limestone dissolution rates on the basis of Ca flux and corresponding Ca or alkalinity concentration for the computed detention time for the Hegins OLD are far from the observed values, indicating slower rates of limestone dissolution in the field or shorter detention times compared to the laboratory. If the mass of limestone is simulated as 110 tonnes (15 percent of 730 tonnes), the field data more closely match the simulations (not shown). Alternatively, adjustments could be made to compensate for the ratio of limestone surface area to fluid volume in order to obtain a match between the field data and the simulations based on cubitainer data. The model used to project trends in Figure 9 accounted only for detention time and limestone mass, not surface area.

In accordance with methods of Cravotta (2003), the longevity of each of the limestone drains may be determined by comparing the projected trends in residual limestone mass and corresponding alkalinity or Ca on the basis of the cubitainer tests (Fig. 9C) with the long-term average net acidity of the AMD influent. For example, the net acidity, alkalinity, and Ca of the Buck Mtn. influent are 28.1, 2.3, and 10.3 mg/L as CaCO₃, respectively (Table 2). Hence, the addition of 28.1 mg/L as CaCO₃ to the effluent to achieve alkalinity of 30.4 and Ca of 38.4 mg/L as CaCO₃, respectively, is required to attain net acidity = 0. The projected trends shown in Figure 9 indicate a longevity of 15 to 20 yrs for the Buck Mtn. ALD, after which the alkalinity of effluent would be less than 30.4 mg/L as CaCO₃. Note that this longevity estimate is comparable to the estimate based on linear extrapolation of field flux data. In contrast, the determination of longevity for the Orchard and Hegins OLDs on the basis of trends indicated in Figure 9 is not valid, because the Orchard OLD has clogged and the performance of the Hegins OLD is not consistent with the model indicated in Fig. 9.

The average net acidity, alkalinity, and Ca of the influent to the Hegins OLD were 47.4, 0, and 22.9 mg/L as CaCO₃ (Table 2). Although the estimated detention time was approximately 8 h for the Hegins OLD on the basis of its average flow rate, estimated bulk volume, and assumed

porosity of 0.49 (Table 1, Fig. 9), the effluent data for the Hegins OLD indicated an average increase of only 17 mg/L Ca as CaCO₃ and a maximum alkalinity of <2 mg/L (Fig. 5, Table 2). The Hegins cubitainer tests indicated effluent alkalinities of 20 to 60 mg/L and corresponding increases in Ca of 75 to 100 mg/L as CaCO₃ after 8 h of contact with coated or uncoated limestone (Figs. 8 and 9). Hence, on the basis of the cubitainer tests, an 8-hr detention time would have been sufficient for complete neutralization of the acidity. The cubitainer tests clearly demonstrate that the Al-coated and uncoated limestone will dissolve under open or closed conditions, with more rapid dissolution under closed conditions, but the results were not consistent with those observed in the field. Hence, the tracer test at the Hegins OLD was conducted to investigate the relation between effluent quality and field detention time and to determine if the field detention time estimates based on flow data were reasonable.

At the Hegins OLD, a NaBr tracer injection test was conducted during low base-flow conditions in July 2002 when the flow rate at the outflow weir was only 112 L/min (Fig. 10), compared to the long-term average of 351 L/min (Table 1). Approximately two-thirds of the limestone in all cells was inundated. Assuming a porosity of 0.49, the total fluid-filled volume was estimated to be 37.18 m³. The detention time within the system would be approximately 5.5 h. The peak Br concentrations were apparent at each cell, with an elapsed time for the tracer to completely pass through the fourth cell in about 2.5 h, which was only half the expected detention time. Given a detention time of 2.5 h, the alkalinity estimate would be 7.4 mg/L based on cubitainer tests for the coated limestone under open conditions (Fig. 8); the actual effluent alkalinity was <1 mg/L.

The discrepancy between the observed and estimated detention times and the observed and estimated alkalinities indicates the saturated volumes for the cells could be smaller than assumed, the inflow rate could exceed that measured at the outflow (leakage), and/or flow could bypass or short-circuit some zones within the cells. Furthermore, the differences in alkalinity observed for cubitainers and field conditions also indicates greater dissolution rates for smaller fragments with corresponding larger surface area in cubitainer tests compared to actual conditions and indicates a need to consider the exposed surface area as well as the detention time. This study considered only the detention time and mass of limestone, not the surface area.

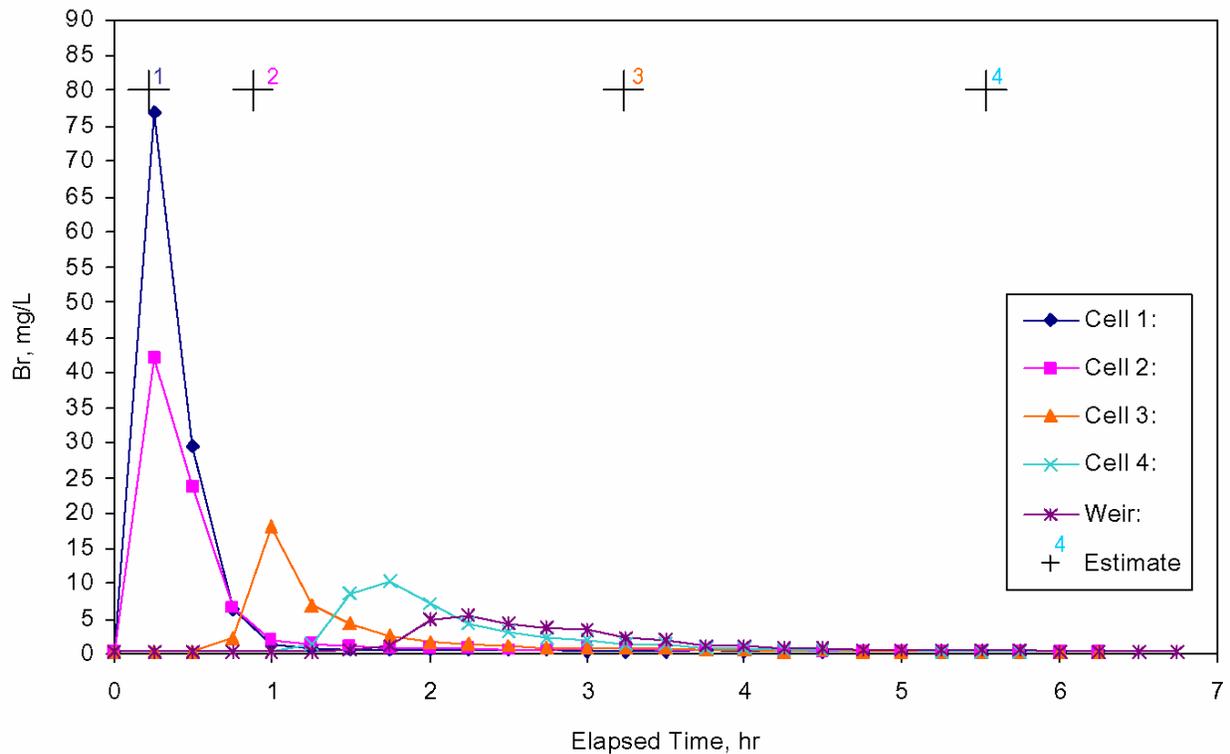


Figure 10. Bromide concentrations after NaBr tracer injection to the inflow of Hegins OLD on July 16, 2002. Estimated detention time for progression through cells 1, 2, 3, and 4, shown as cross symbols, is the cumulative detention time based on the flow rate of 112 L/min and estimated saturated volumes for cells 1, 2, 3, and 4 of 1.43, 4.51, 15.85, and 15.40 m³, respectively, during time of tracer test.

Concepts for Optimization of Limestone Drain Performance

The cubitainer tests and field results for the Buck Mtn., Orchard, and Hegins OLDs/ALDs consistently indicated that limestone dissolution was greater under closed conditions than under open conditions. Thin coatings of secondary Fe^{III} and/or Al oxides on the limestone surfaces were a subordinate factor, having little if any negative effect on dissolution rate. Observations of slow dissolution rates of limestone in the Hegins OLD and, elsewhere, in open channels largely can be explained because these systems are open and generally well aerated, facilitating the exsolution of CO₂. The results of cubitainer tests indicate the same coated limestone fragments will dissolve more rapidly in an underground “closed” system where subjected to continuous inundation, without aeration.

The results of this study are consistent with some previous reports and have helped illustrate possible outcomes for different types of underground or open limestone systems. Cravotta and

Weitzel (2001) found that “(1) open limestone channels and limestone-sand dosing generally had negligible effects on water quality [of Swatara Creek], whereas (2) limestone diversion wells and limestone drains generally were effective at producing near-neutral pH and attenuating dissolved metals during base flow but were less effective during stormflow conditions.” They concluded, “to maintain stream pH during storms, additional or larger limestone diversion wells could be constructed to begin or increase alkalinity production as the stream stage rises and/or additional or larger limestone drains could be constructed to produce greater amounts of alkalinity and enhance the buffering capacity of base flow. Increasing the buffering capacity of base flow also will mitigate acidification effects during drought conditions.” Diversion wells require frequent refilling with limestone and regular maintenance to prevent clogging, making these systems generally useful for supplemental treatment capacity during high-flow conditions. In contrast, limestone drains provide a more reliable, sustained source of alkalinity than diversion wells. By design, limestone drains contain a large mass of limestone that could feasibly last decades with little or no maintenance. As indicated with the cubitainer-test data (Figs. 6, 7, and 8), the concentration of alkalinity in effluent from a limestone drain will increase with increased detention time. The detention time will vary with flow rate, mass of limestone, and/or porosity. Furthermore, as indicated with the Buck Mtn. ALD, the alkalinity fluxes from limestone drains may be greater for high-flow conditions than for base flow, because most of the alkalinity generated by contact with limestone results after relatively short detention time.

At the Orchard OLD, limestone dissolution rates remain high; however, porosity and alkalinity have decreased because of Fe-hydroxide sludge accumulation in voids and corresponding shortened detention times within the limestone bed (Cravotta and Trahan, 1999). In Figures 9b and 9c, two trends are shown to illustrate the effect of porosity reduction, where the porosity of the Orchard OLD is simulated as 0.49 (dashed curve) and 0.15 (solid curve). To maintain a high porosity and prevent future clogging, the Orchard OLD could be completely reconstructed with a flushing system using medium size (6 to 10 cm), high-purity limestone fragments.

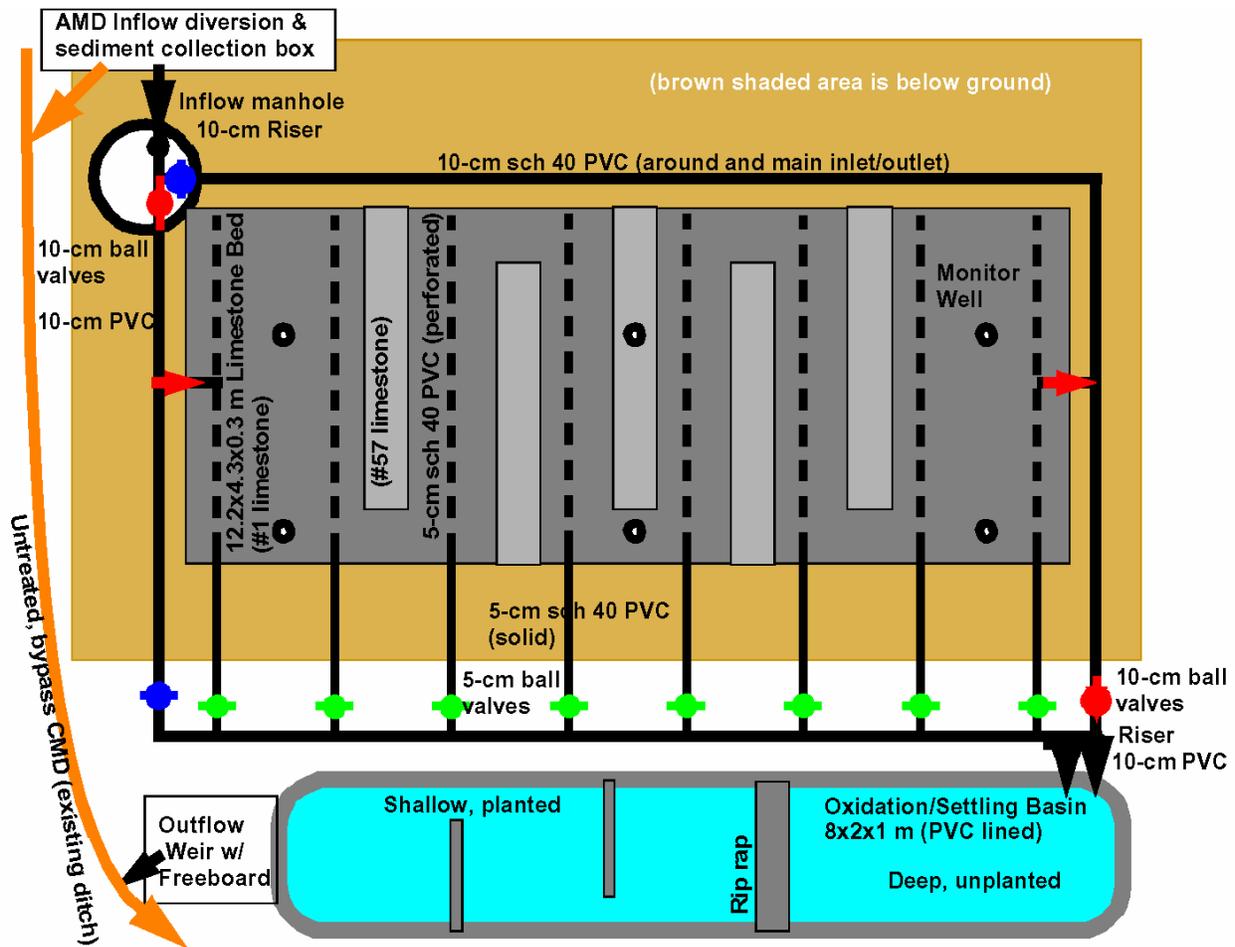


Figure 11. Conceptual plan for flushable oxic limestone drain and subsequent oxidation settling basin at the Orchard discharge site. Flow through drain is left-to-right if red valves open and blue valves closed; flow is right-to-left if red valves closed and blue valves open. Flushing of solids possible simply by reversing flow direction and/or by opening green valves to drain fluid and solids from base of limestone bed. Primary limestone bed consists of coarse limestone fragments (ASHTO #1); optional deflector berms consist of finer limestone fragments (ASHTO #57).

One concept for reconstruction of the Orchard OLD features reversible flow through a horizontal limestone bed (Fig. 11). The hydraulic gradient is maintained by having an intake elevation greater than the outflow; standpipes for both inflow and outflow extend above the top of the limestone bed to maintain its continuous inundation. A horizontal, inflow/outflow pipe surrounds the base of the drain, with valves to control flow direction (blue, red). The regular reversal of flow direction will reduce potential for limestone to be preferentially dissolved at one end of the drain and will facilitate the attenuation of Mn and trace metals by adsorption to residual Fe^{III} solids that tend to form upon initial contact between low-pH influent and the limestone bed and that can be effective sorbents under near-neutral pH conditions (Cravotta and

Trahan, 1999). Some solids accumulated within the limestone bed near the inflow can be flushed out of the system simply by reversing the flow direction. Additional solids accumulated near the base of the limestone bed can be flushed by temporarily opening valves (green) on perforated laterals extended through the base of the limestone bed to the surface; the flush valves would remain closed during normal operation. To prevent accidental short-circuiting, the perforated laterals are perpendicular to the primary flow direction. To facilitate access, the lateral pipes and valves could be extended to the surface along one side of the drain and the inflow pipe and valves could be exposed within a trench or pit (Fig. 11).

At the Hegins OLD, to increase alkalinity production rate and possibly improve the yield of solids when flushed, the drain could be enlarged with the addition of smaller particles of limestone, and the entire limestone drain could be buried. Cubitainer-test results for the Hegins limestone drain evaluated alkalinity production by uncoated and coated limestone under open and closed conditions (Fig. 8). Greater alkalinity concentrations and limestone-dissolution rates were obtained for closed conditions compared to open conditions. However, the dissolution rates for uncoated and coated limestone were comparable under closed conditions. Hence, despite the accumulated Al-hydroxysulfate precipitate on limestone surfaces, burial of the Hegins drain could increase its alkalinity production rate. Burial would aid in the retention of CO₂ generated by the initial reaction between limestone and acid. A greater quantity of the CO₂ could dissolve and react with limestone in a “closed” system generating greater quantities of alkalinity than produced in an “open” system from which the CO₂ escapes. To promote the accumulation of CO₂, the drain could be covered with a layer of organic compost as an additional source of CO₂ and then capped with a layer of compacted backfill. Before burial, a permeable geotextile liner could be placed over the currently exposed limestone drain to prevent debris from clogging voids between the limestone fragments. After burying the drain, which occupies a former discharge channel, a rip-rap lined channel could be installed along the length of the drain to divert surface runoff and avoid the unintended flushing of solids from the system.

Summary and Conclusions

Data for the quality of influent and effluent at three limestone drains in the Swatara Creek Basin indicate acid neutralization takes place within each of the systems. The Hegins OLD does not completely neutralize the AMD influent whereas the Orchard OLD and Buck Mtn. ALD have effectively neutralized the AMD influent. Nevertheless, the Orchard OLD has clogged, and the effectiveness of each limestone drain is projected to decline as the systems age and their limestone is consumed. Declines in alkalinity production by the limestone drains ultimately could have negative consequences for stream-water quality and ecology of Swatara Creek.

The effluent composition at each of the sites was variable, largely resulting from variations in flow rates and corresponding variations in detention time. Generally, the pH and concentrations of alkalinity and Ca in effluent from the limestone drains were greater at low flow rates compared to high flow rates, reflecting the inverse relation between flow rate and detention time. Typically, the pH, alkalinity, and Ca increased asymptotically with increased detention time in the cubitainers owing to rapid dissolution of limestone by the low-pH and high- P_{CO_2} influent and declining dissolution rates as the solution pH increased and approached equilibrium with calcite. Because influent to the Orchard and Hegins OLDs had pH <4.5 and was far from equilibrium with calcite, it aggressively dissolved limestone despite mineral coatings on the limestone fragments.

Generally, quantitative dissolution of limestone after contact with AMD influent is indicated by the change in concentration of Ca, which is directly proportional to the amount of limestone dissolved regardless of the pH (equations 1 and 2). In contrast with Ca, alkalinity can not be measured at pH <4.5 and, hence, is not useful to indicate the initial quantity of limestone dissolved by low-pH influent such as that at the Orchard and Hegins sites. Ultimately, for pH >4.5, the ratio of Ca and alkalinity produced within the cubitainers and the limestone drains was a constant value reflecting the stoichiometry of equation (2). Only alkalinity data were previously compiled and interpreted by Cravotta (2003) for cubitainer tests of three AMD sources initially containing alkalinity. As shown in this report, data for the pH, alkalinity, plus Ca can be interpreted to indicate neutralization of low-pH AMD and the extent of, or potential for, reaction with limestone. Although not used for this report, the authors currently use a colorimetric method to measure Ca concentration in the same sample analyzed for alkalinity

(American Public Health Association, 1976). Alternatively, the “hot” acidity can be measured on samples titrated for alkalinity as another measure of treatment effectiveness (American Society for Testing and Materials, 2000).

Cubitainer tests of reaction between the untreated AMD and limestone indicated that the limestone dissolution rate was faster and ultimate alkalinity was larger for closed conditions compared to conditions open to the atmosphere. Furthermore, the tests revealed that mineral coatings on the limestone had little if any effect on the dissolution rates under closed conditions. The exponential equations used to project the long-term trends for field conditions, on the basis of cubitainer test data, enable (1) the evaluation of effects of flow rate, mineral coatings, and system closure on limestone drain performance; (2) the estimation of the effluent alkalinity as a function of detention time; (3) the evaluation of possible effects due to changes in limestone mass or detention time; and/or (4) the computation of the required mass of limestone for repair or new construction. To improve the match between the field data and the simulations based on cubitainer data, adjustments in the rate constants could be made to compensate for the ratio of limestone surface area to fluid volume.

Ideally, each of the limestone drains can be enlarged, including the installation of a weir where lacking for flow monitoring and a detention basin for the oxidation and precipitation of iron-hydroxide sludge that can be flushed from the drain. A grant was awarded recently to the Schuylkill Conservation District (SCD) for the installation of these features (Ryan Koch, 2003, written commun.): (1) the complete reconstruction of the limestone drain at the Orchard site to enlarge its capacity, install a flushing system, and add a detention basin; (2) the completion of repairs at the Buck Mtn. site to fix damage caused by stormflow erosion, enlarge its capacity, and add a detention basin; and (3) the completion of construction at the Hegins site to reduce leakage, enlarge the capacity, and bury the limestone drain with compost and soil. Information gained from the continued monitoring and evaluation of the current and future configurations of the limestone drains in the Swatara Creek Basin will be useful to refine criteria for the optimization of limestone drains for long-term treatment of contaminated mine drainage. Site-specific design criteria may be developed considering the optimum detention time to achieve a balance between the influent acidity and effluent alkalinity and possible effects from the accumulation or removal of precipitates on limestone dissolution rate, porosity, and surface area.

Several observations in this report warrant additional investigation. Greater alkalinities and greater rates of limestone dissolution for closed conditions than open conditions were expected; however, comparable results for coated and uncoated limestone for a given condition were unexpected. One hypothesis is that protons can diffuse readily from the bulk solution (high H^+ concentration) through a thin film on the limestone surface (low H^+ concentration) where they react with $CaCO_3$ producing CO_2 (equation 1). However, the diffusion of much larger CO_2 molecules away from the limestone surface to the bulk solution is impeded by this film resulting in locally elevated P_{CO_2} adjacent to the limestone and more extensive reaction (equation 2). Under closed conditions, elevated P_{CO_2} and corresponding lower pH for the bulk solution would result in a steeper proton gradient between the solution and limestone surfaces compared to an open system. Generally, for open conditions, the P_{CO_2} is smaller and the pH tends to be greater than corresponding values for closed conditions. Consequently, the driving forces for limestone dissolution (low pH and/or high P_{CO_2}) are enhanced in a closed system and diminished in an open system. The effects of film thickness and composition, limestone purity and surface properties, and solution characteristics should be considered for future evaluation of the above hypothesis. The properties and effects of Al minerals compared to Fe^{III} minerals warrants special consideration given the relatively poor short-term performance of the Hegins OLD compared to that of the Orchard OLD. For example, the Al-hydroxysulfate coatings formed from relatively low-pH solutions at the Hegins OLD (Loop, 2003) may be more adhesive and less permeable to protons than Al-hydroxide or Fe^{III} coatings (e.g. Bigham and Nordstrom, 2000; Hammarstrom *et al.*, 2003). Data on the conditions of formation of specific minerals and their potential to foul treatment systems are needed to determine if burial, the addition of compost, and/or regular flushing will be effective measures to maintain system performance.

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Literature Cited

- American Public Health Association, 1976, EDTA titrimetric method, In Greenberg, A. E., Rand, M. C., and Paris, M. J. (eds.), *Standard methods for the examination of water and wastewater* (14th): Washington, D.C., American Public Health Association, p. 202-206.
- American Society for Testing and Materials, 2000, Standard test methods for acidity and alkalinity of water: D 1067-92, In *Annual Book of ASTM Standards*, Water and Environmental Technology: West Conshocken, Pa., ASTM, Sect. 11.01, p. 65-71.
- Arnold, D. E., 1991, Diversion wells--a low-cost approach to treatment of acid mine drainage, In Proceedings 12th Annual West Virginia Surface Mine Drainage Task Force Symposium: West Virginia Mining and Reclamation Association, p. 39-50.
- Ball, J. W., and Nordstrom, D. K., 1991, User's manual for WATEQ4F with revised data base: U.S. Geological Survey Open-File Report 91-183, 189 p.
- Bigham, J. M., and Nordstrom, D. K., 2000, Iron and aluminum hydroxysulfate minerals from acid sulfate waters, In Jambor, J. L., Alpers, C. N., and Nordstrom, D. K., (eds.), *Sulfate minerals, crystallography, geochemistry and environmental significance*: Mineralogical Society of America Reviews in Mineralogy and Geochemistry, vol. 40, p. 351-403.
- Brodie, G. A., Britt, C. R., Tomaszewski, T. M., and Taylor, H. N., 1991, Use of passive anoxic limestone drains to enhance performance of acid drainage treatment wetlands, In Proceedings 1991 National Meeting of the American Society for Surface Mining and Reclamation. American Society for Surface Mining and Reclamation, p. 211-228.
- Cram, J. C., 1996, Diversion well treatment of acid water, Lick Creek, Tioga County, Pennsylvania: Pennsylvania State University, University Park, Pa., M.S. thesis, 99 p.

- Cravotta, C. A., III, 2000, Relations among sulfate, metals, sediment, and streamflow data for a stream draining a coal-mined watershed in east-central Pennsylvania, In Fifth International Conference on Acid Rock Drainage: Society for Mining, Metallurgy, and Exploration, Inc., vol. 1, p. 401-410.
- , 2003, Size and performance of anoxic limestone drains to neutralize acidic mine drainage: *Journal of Environmental Quality*, vol. 32, p. 1277-1289.
- , and Bilger, M. D., 2001, Water-quality trends for a stream draining the Southern Anthracite Field, Pennsylvania: *Geochemistry-Exploration, Environment, Analysis*, vol. 1, p. 33-50.
- , and Kirby, C. S., this volume, Acidity and alkalinity in mine drainage--practical considerations, In 2004 National Meeting of the American Society of Mining and Reclamation and the 25th West Virginia Surface Mine Drainage Task Force, April 18-24, 2004: American Society of Mine Reclamation.
- , and Trahan, M. K., 1996, Limestone drains to increase pH and remove dissolved metals from an acidic coal-mine discharge in Pennsylvania, In Proceedings of the 13th Annual Meeting of the American Society for Surface Mining and Reclamation: American Society for Surface Mining and Reclamation, p. 836-840.
- , and Trahan, M. K., 1999, Limestone drains to increase pH and remove dissolved metals from acidic mine drainage: *Applied Geochemistry*, vol. 14, p. 581-606.
- , and Watzlaf, G. R., 2002, Design and performance of limestone drains to increase pH and remove metals from acidic mine drainage, In Naftz, D. L., Morrison, S. J., Fuller, C. C., and Davis, J. A. (eds.), Handbook of groundwater remediation using permeable reactive barriers--Application to radionuclides, trace metals, and nutrients: San Diego, Ca., Academic Press, p. 19-66.
- , and Weitzel, J. B., 2001, Detecting change in water quality from implementation of limestone treatment systems in a coal-mined watershed, Pennsylvania, In Proceedings 8th National Nonpoint Source Monitoring Program Workshop: U.S. Environmental Protection Agency Seminar Series EPA/905-R-01-008.

- , Bilger, M. D., Brightbill, R. A., and Bogar, D., 2002, Restoration and monitoring of aquatic quality in a coal-mined watershed, Swatara Creek at Ravine, Pennsylvania (poster), In Proceedings of the 19th Annual Meeting of American Society of Mining & Reclamation, Lexington, Kentucky, June 9-13, 2002: American Society of Mining & Reclamation, p. 1061.
- , Brady, K. B. C., Rose, A. W., and Douds, J. B., 1999, Frequency distribution of the pH of coal-mine drainage in Pennsylvania, In Morganwalp, D. W., and Buxton, H. (eds.), U.S. Geological Survey Toxic Substances Hydrology Program--Proceedings of the Technical Meeting, Charleston, South Carolina, March 8-12, 1999: U.S. Geological Survey Water Resources Investigations Report 99-4018A, p. 313-324.
- Crock, J. G., Arbogast, B. F., and Lamothe, P. J., 1999, Laboratory methods for the analysis of environmental samples, In Plumlee G. S., and Logsdon, M. J. (eds.), *The Environmental Geochemistry of Mineral Deposits--Part A. Processes, techniques, and health issues*: Society of Economic Geologists, Reviews in Economic Geology, vol. 6A, p. 265-287.
- Demchak, J., Morrow, T., and Skousen, J., 2001, Treatment of acid mine drainage by four vertical flow wetlands in Pennsylvania: *Geochemistry-Exploration, Environment, Analysis*, vol. 1, p. 71-80.
- Durlin, R. R., and Schaffstall, W. P., 1998, Water resources data, Pennsylvania, water year 1997, volume 2, Susquehanna and Potomac River Basins: U.S. Geological Survey Water-Data Rep. PA-97-2, p. 342-392.
- , 1999, Water resources data, Pennsylvania, water year 1998, volume 2, Susquehanna and Potomac River Basins: U.S. Geological Survey Water-Data Rep. PA-98-2, p. 346-400.
- , 2000, Water resources data, Pennsylvania, water year 1999, volume 2, Susquehanna and Potomac River Basins: U.S. Geological Survey Water-Data Rep. PA-99-2, p. 342-386.
- , 2001, Water resources data, Pennsylvania, water year 2000, volume 2, Susquehanna and Potomac River Basins: U.S. Geological Survey Water-Data Rep. PA-00-2, p. 350-392.
- , 2002, Water resources data, Pennsylvania, water year 2001, volume 2, Susquehanna and Potomac River Basins: U.S. Geological Survey Water-Data Rep. PA-01-2, p. 316-370.
- , 2003, Water resources data, Pennsylvania, water year 2002, volume 2, Susquehanna and Potomac River Basins: U.S. Geological Survey Water-Data Rep. PA-02-2, p. 350-412.

- , 2004, Water resources data, Pennsylvania, water year 2003, volume 2, Susquehanna and Potomac River Basins: U.S. Geological Survey Water-Data Rep. PA-03-2, in press.
- Drever, J. I., 1997, *The geochemistry of natural waters--Surface and groundwater environments* (3rd): Englewood Cliffs, N.J., Prentice-Hall, Inc., 436 p.
- Eggleston, J. R., Kehn, T. M., and Wood, G. H., Jr., 1999, Anthracite, *In* Schultz, C. H. (ed.), *The geology of Pennsylvania*: Pennsylvania Geological Survey, 4th series, Special Publication 1, p. 458-469.
- Ficklin, W. H., and Mosier, E. L., 1999, Field methods for sampling and analysis of environmental samples for unstable and selected stable constituents, *In* Plumlee G. S., and Logsdon, M. J. (eds.), *The Environmental Geochemistry of Mineral Deposits--Part A. Processes, techniques, and health issues*: Society of Economic Geologists, Reviews in Economic Geology, vol. 6A, p. 249-264.
- Fishman, M. J. and Friedman, L. C. (eds.), 1989, Methods for determination of inorganic substances in water and fluvial sediments: U.S. Geological Survey Techniques of Water-Resources Investigations, Book 5, Chapter A1, 545 p.
- Forney, L. A., 2003, Improving an existing acid mine drainage treatment system to assist in improving the water quality of a Pennsylvania stream: Middletown, Pa., Pennsylvania State University, Unpublished Masters Paper, 86 p.
- Freeze, R. A., and Cherry, 1979, *Groundwater*: Englewood Cliffs, N. J., Prentice-Hall, Inc., 604 p.
- Hammarstrom, J. M., Sibrell, P. L., and Belkin, H. E., 2003, Characterization of limestone reacted with acid-mine drainage in a pulsed limestone bed treatment system at the Friendship Hill National Historic Site, Pennsylvania, USA: *Applied Geochemistry*, vol. 18, p. 1705-1721.
- Hedin, R. S., and Watzlaf, G. R., 1994, The effects of anoxic limestone drains on mine water chemistry: U.S. Bureau of Mines Special Publication SP 06A, p. 185-194.
- , Nairn, R. W., and Kleinmann, R. L. P., 1994, Passive treatment of coal mine drainage: U.S. Bureau of Mines Information Circular IC 9389, 35 p.
- Kepler, D. A. and McCleary, E. C., 1994, Successive alkalinity producing systems (SAP's) for the treatment of acidic mine drainage: U.S. Bureau of Mines Special Publication SP 06A, p. 195-204.

- Kirby, C. S., Thomas, H. M., Southam, G., and Donald, R., 1999, Relative contributions of abiotic and biological factors in Fe(II) oxidation in mine drainage: *Applied Geochemistry*, vol. 14, p. 511-530.
- Kooner, Z. S., 1993, Comparative study of adsorption behavior of copper, lead, and zinc onto goethite in aqueous systems: *Environmental Geology*, vol. 21, p. 342-250.
- Langmuir, Donald, 1997, *Aqueous environmental geochemistry*: New Jersey, Prentice-Hall, 600 p.
- Lasaga, A. C., 1981, Rate laws of chemical reactions, In Lasaga, A. C., and Kirkpatrick, R. J. (eds.), *Kinetics of geochemical processes*: Mineralogical Society of America Reviews in Mineralogy, vol. 8, p. 1-68.
- Loop, C. M., 2003, Aqueous and precipitate chemistry of coal mine drainage water in alkaline environments: University Park, Pa., Pennsylvania State University, Unpublished Ph.D. dissertation, 200 p.
- Morse, J. W., 1983, The kinetics of calcium carbonate dissolution and precipitation, In Reeder, R. J. (ed.), *Carbonates--mineralogy and chemistry*: Mineralogical Society of America Reviews in Mineralogy, vol. 11, p. 227-264.
- Nordstrom, D. K., 1977, Thermochemical redox equilibria of Zobell's solution: *Geochimica et Cosmochimica Acta*, vol. 41, p. 1835-1841.
- , and Alpers, C. N., 1999, Geochemistry of acid mine waters, In Plumlee, G. S., and Logsdon, M. J. (eds.), *The Environmental Geochemistry of Mineral Deposits--Part A. Processes, methods, and health issues*: Reviews in Economic Geology, vol. 6A, p. 133-160.
- , Jenne, E. A., and Ball, J. W., 1979, Redox equilibria of iron in acid mine waters, In Jenne, E. A. (ed.), *Chemical modeling in aqueous systems--Speciation, sorption, solubility, and kinetics*: American Chemical Society Symposium Series 93, p. 51-79.
- Plummer, L. N., Parkhurst, D. L., and Wigley, M. L., 1979, Critical review of the kinetics of calcite dissolution and precipitation, In Jenne, E. A. (ed.), *Chemical modeling in aqueous systems--Speciation, sorption, solubility, and kinetics*: American Chemical Society Symposium Series 93, p. 537-573.
- Rantz, S. E., and others, 1982a, Measurement and computation of streamflow--1. Measurement of stage and discharge: U.S. Geological Survey Water-Supply Paper 2175, 284 p.

- , 1982b, Measurement and computation of streamflow--2. Computation of discharge: U.S. Geological Survey Water-Supply Paper 2175, 631 p.
- Robbins, E. I., Nord, G. L., Savela, C. E., Eddy, J. I., Livi, K. J. T., Gullett, C. D., Nordstrom, D. K., Chou, I. -M., and Briggs, K. M., 1996, Microbial and mineralogical analysis of aluminum- rich precipitates that occlude porosity in a failed anoxic limestone drain, Monongalia County, West Virginia, In Chiang, Shiao-Hung (ed.), *Coal-energy and the environment*: Pittsburgh, Pa., Reed & Witting Company, Proceedings Thirteenth Annual International Pittsburgh Coal Conference, vol. 2, p. 761-767.
- , Cravotta, C. A., III, Savela, C. E., and Nord, G. L., Jr., 1999, Hydrobiogeochemical interactions in “anoxic” limestone drains for neutralization of acidic mine drainage: *Fuel*, vol. 78, p. 259-270.
- Rose, A. W., this volume, Vertical flow systems--Effects of time and definition of acidity, In 2004 National Meeting of the American Society of Mining and Reclamation and the 25th West Virginia Surface Mine Drainage Task Force, April 18-24, 2004: American Society of Mine Reclamation.
- , and Cravotta, C. A., III, 1998, Geochemistry of coal-mine drainage, In Brady, K. B. C., Smith, M. W., and Schueck., J. (eds.), *Coal Mine Drainage Prediction and Pollution Prevention in Pennsylvania*: Harrisburg, Pa., Pennsylvania Department of Environmental Protection, 5600-BK-DEP2256, p. 1.1-1.22.
- Skousen, J. G., Rose, A. W., Geidel, G., Foreman, J., Evans, R., Hellier, W., and others, 1998, *Handbook of technologies for avoidance and remediation of acid mine drainage*: Morgantown, W.Va., National Mine Land Reclamation Center, 131 p.
- Sterner, P. L., Skousen, J. J., and Donovan, J. J., 1998, Geochemistry of laboratory anoxic limestone drains, In Proceedings of the 1998 National Meeting of the American Society for Surface Mining and Reclamation: American Society for Surface Mining and Reclamation, p. 214-234.
- Stumm, Werner, and Morgan, J. J., 1996, *Aquatic chemistry--Chemical equilibria and rates in natural waters* (3rd): New York, John Wiley and Sons, 1022 p.
- Turner, D., and McCoy, D., 1990, Anoxic alkaline drain treatment system, a low cost acid mine drainage treatment alternative, In 1990 Symposium on Surface Mining Hydrology, Sedimentology and Reclamation: University of Kentucky, Lexington, Ky., p. 73-75.

- U.S. Geological Survey, 1997 to present, National field manual for the collection of water-quality data: U.S. Geological Survey Techniques of Water-Resources Investigations, book 9, chaps. A1-A9, 2 vols., variously paged (<http://pubs.water.usgs.gov/twri9A>).
- Watzlaf, G. R., 1997, Passive treatment of acid mine drainage in down-flow limestone systems, *In* Proceedings of the 1997 National Meeting of the American Society for Surface Mining and Reclamation, May 10-15, 1997, Austin, Texas: American Society for Surface Mining and Reclamation, p. 611-622.
- , and Hedin, R. S., 1993, A method for predicting the alkalinity generated by anoxic limestone drains, *In* Proceedings 14th Annual Meeting West Virginia Surface Mine Drainage Task Force: West Virginia University, Morgantown, W.Va., 12 p.
- , Schroeder, K. T., and Kairies, C., 2000, Long-term performance of alkalinity-producing passive systems for the treatment of mine drainage, *In* Proceedings of the 2000 National Meeting of the American Society for Surface Mining and Reclamation: American Society for Surface Mining and Reclamation, p. 262-274.
- Webster, J. G., Swedlund, P. J. and Webster, K. S., 1998, Trace metal adsorption onto an acid mine drainage iron(III) oxy hydroxy sulfate: *Environmental Science & Technology*, vol. 32, p. 1361- 1368.
- Wood, G. H., Jr., Kehn, T. M., and Eggleston, J. R., 1986, Deposition and structural history of the Pennsylvania Anthracite region, *In* Lyons P. C. and Rice C. L. (eds.), *Paleoenvironmental and tectonic controls in coal-forming basins of the United States*: Geological Society of America Special Paper 210, p. 31-47.
- Wood, W. W., 1976, Guidelines for the collection and field analysis of ground-water samples for selected unstable constituents: U.S. Geological Survey Techniques of Water Resources Investigations, Book 1, Chapter D2, 24 p.
- Ziemkiewicz, P. F., Skousen, J. G., Brant, D. L., Sterner, P. L., and Lovett, R. J., 1997, Acid mine drainage treatment with armored limestone in open limestone channels: *Journal of Environmental Quality*, vol. 26, p. 1017-1024.