

# LIMESTONE DISSOLUTION IN PASSIVE SYSTEMS FOR NEUTRALIZATION OF ACIDIC MINE DRAINAGE

C. A. Cravotta III  
U.S. Geological Survey  
New Cumberland, Pennsylvania

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This presentation describes the use of short-term closed-container (cubitainer) tests to indicate limestone dissolution rates and the corresponding alkalinity of effluent as a function of detention time in a limestone bed for passive neutralization of acidic mine drainage (AMD). Various test configurations can simulate conditions closed to the atmosphere (underground system) or open to the atmosphere (above-ground system) and the effects of limestone purity, secondary coatings, and particle size on dissolution rate. Coupled with data on the average flow rate and acidity concentration of the tested AMD, the cubitainer rate data can be used to estimate the long-term performance and minimum effective size of a limestone bed in an anoxic limestone drain (ALD) or comparable system.

Construction characteristics and data on influent and effluent composition were collected for 5 to 11 years at five limestone drains in Pennsylvania. Influent at the Morrison and Howe Bridge discharges in the Bituminous Coalfield had average pH of 5.3 and 5.8 and net acidity (= computed acidity – alkalinity) of 434 and 495 mg/L as CaCO<sub>3</sub>, respectively. Influent at the Orchard, Buck Mtn., and Hegins discharges in the Southern Anthracite Coalfield were characterized by lower pH and acidity, with average pH of 3.5, 4.6, and 3.5 and net acidity of 30, 28, and 47 mg/L as CaCO<sub>3</sub>, respectively. Effluent from each drain had higher pH, alkalinity, and Ca, and lower acidity, Fe, and Al concentrations than the influent. Although estimated detention time averaged 56 hours at Morrison, 22 hours at Howe Bridge, and less than 5 hours at the Orchard, Buck Mtn., and Hegins ALDs, net-alkaline effluent was produced from only the Orchard and Buck Mtn. ALDs. The long-term average flow multiplied by the difference between average concentrations of Ca for influent and effluent indicated average annual limestone dissolution rates of 1.0, 9.0, 1.5, 22.9, and 5.0 tonne/yr at the Morrison, Howe Bridge, Orchard, Buck Mtn., and Hegins drains, respectively. These annual dissolution rates have progressively declined with age of the systems as the limestone has been consumed.

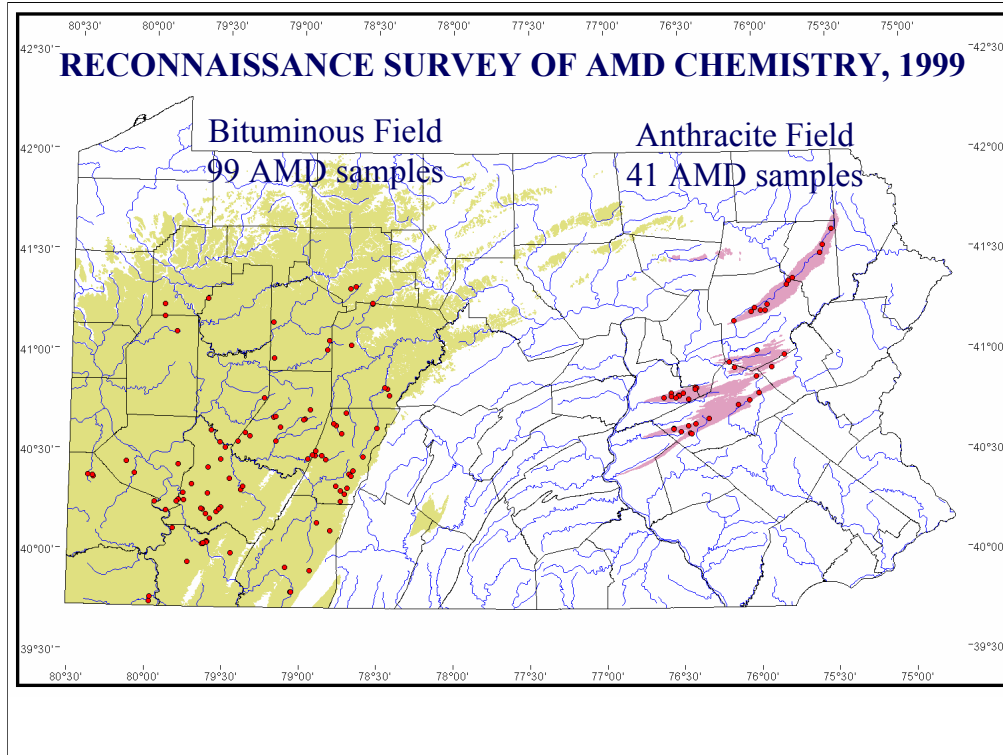
For the five limestone drains in Pennsylvania, cubitainer tests with AMD influent from each of the sites indicated limestone dissolution rates were larger for high-purity limestone than for dolomite and for conditions closed to the atmosphere than open conditions, but the rates for fresh, uncoated versus environmentally exposed, metal-hydroxide-coated limestone were comparable for a given condition. The dissolution rates as measured by cubitainer tests, after corrections for surface area and fluid volume, were in agreement with field data for alkalinity and dissolved Ca production rate. Models developed on the basis of the cubitainer tests accurately revealed decadal-scale declines in limestone mass and corresponding alkalinity concentrations with increased age of a limestone treatment bed. Thus, cubitainer tests can be a useful tool for designing ALDs or similar systems and predicting their performance. Because a limestone bed could become plugged long before the limestone substrate has been consumed, engineering designs that are larger than the minimum size indicated by cubitainer tests and/or that incorporate provisions for flushing or replacement of the limestone bed could be warranted.



## OVERVIEW

- Water-quality and construction data used to evaluate performance of limestone drains in bituminous and anthracite coalfields of Pennsylvania.
- Cubitainer tests used to evaluate effects of detention time, limestone purity, system enclosure, and “armoring” on limestone dissolution rates.
- Data for flow rate, limestone mass, and cubitainer dissolution rates used to simulate performance of limestone drains (current and future).

OVERVIEW: 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) in the bituminous and anthracite coalfields of Pennsylvania. Data for influent and effluent from the Morrison, Howe Bridge, Orchard, Buck Mtn., and Hegins discharges are evaluated to indicate the performance of the limestone drains and possible trends. Then, 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.

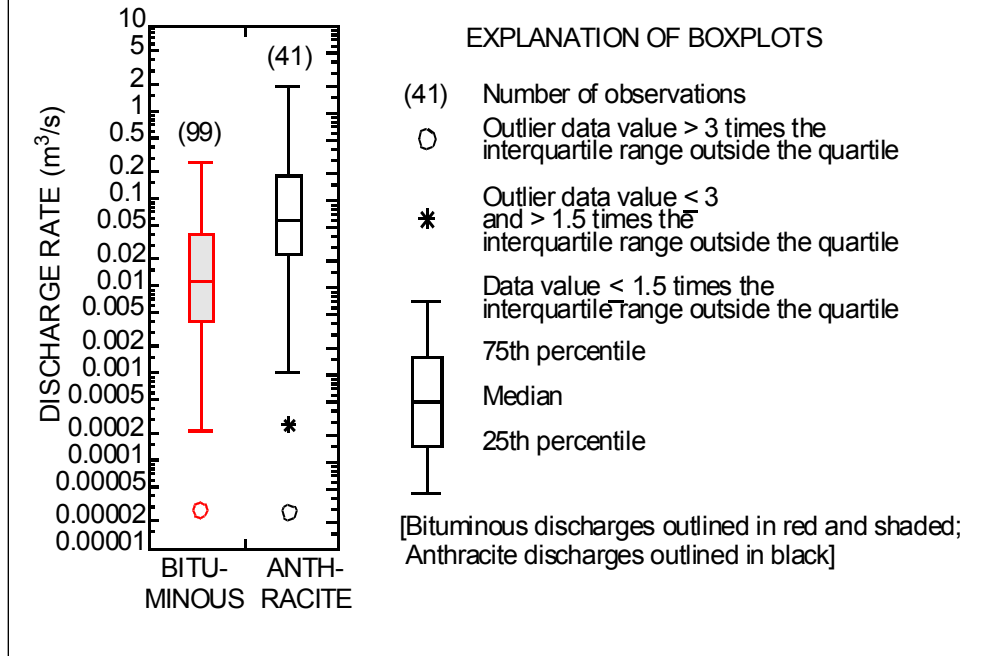


COAL MAP: A total of 140 AMD sources from abandoned underground mines in Pennsylvania were sampled by the U.S. Geological Survey (USGS) during low-flow conditions in 1999. The 99 bituminous discharges had previously been studied by the Southern Alleghenies Conservancy (1998). The 41 anthracite discharges had previously been studied by the USGS (Growitz and others, 1985; Wood, 1996).

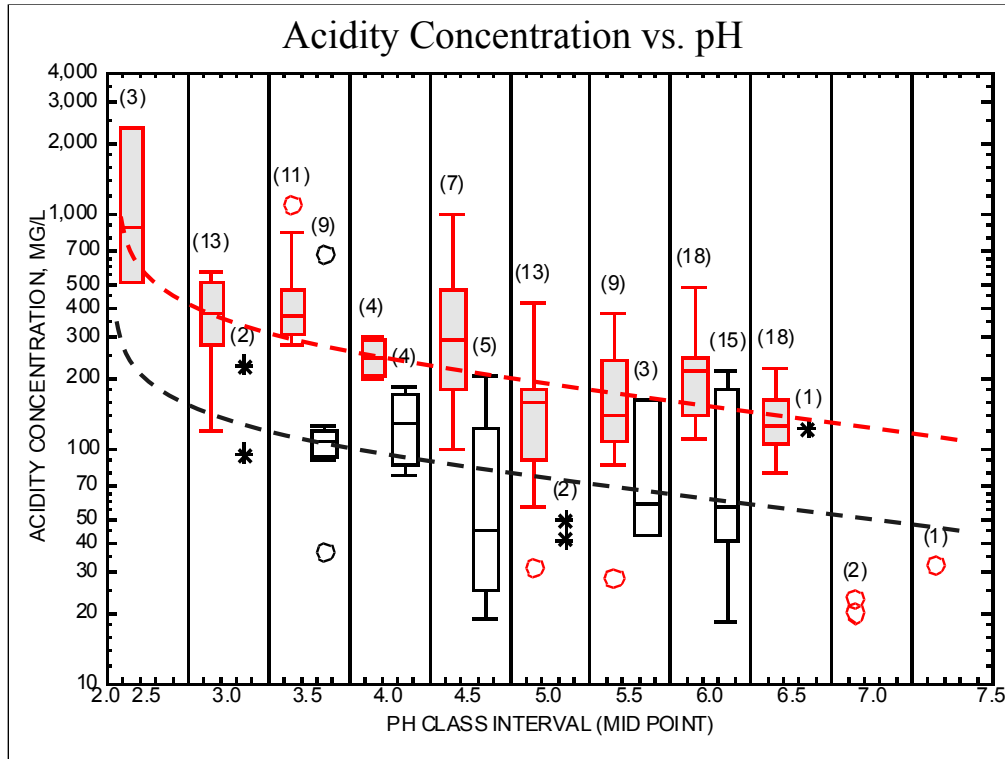
Data on flow rate, pH, redox potential (Eh), specific conductance, dissolved oxygen, and temperature were measured in the field when samples were collected. Samples for analysis of dissolved inorganic constituents were filtered using 0.45-um capsule filters inside a an enclosed glove box. Concentrations of major anions, major cations, and trace elements were determined using inductively coupled plasma emission mass spectrometry (ICP-MS), inductively coupled plasma atomic emission spectroscopy (ICP-AES), and ion chromatography (IC) (Fishman and Friedman, 1989; Faires, 1993; Crock and others, 1999). Gold was concentrated on charcoal sachets added to unfiltered samples and then analyzed by independent neutron activation analysis (INAA) (Crock and others, 1999).

Alkalinity and cold acidity on unfiltered samples were determined in the laboratory within 48 hours of sampling. After 4 years of storage at ambient temperature, the samples were reanalyzed for “aged” pH, alkalinity, and hot acidity.

## BITUMINOUS & ANTHRACITE “AMD”



FLOW RATE: Despite similar pH frequency distribution for discharges from bituminous and anthracite coal mines, the flow rates from bituminous discharges typically are much smaller than those from anthracite discharges. The median flow rate of bituminous discharges is about 1/5 of that for anthracite discharges. The larger flow rates from anthracite discharges reflects the larger size of the recharge areas to the interconnected mine workings in synclinal basins compared with smaller size recharge areas for more isolated bituminous mines.



ACIDITY vs. pH : In addition to smaller flow rates, bituminous discharges typically have greater concentrations acidity, sulfate, iron, and other contaminants. The anthracite discharges tend to be more dilute, reflecting their higher flows and inundation of mine workings. The median acidity for bituminous discharges is approximately 300 mg/L compared with acidity <100 mg/L for the large-volume anthracite discharges.

## NEUTRALIZATION OF ACIDITY

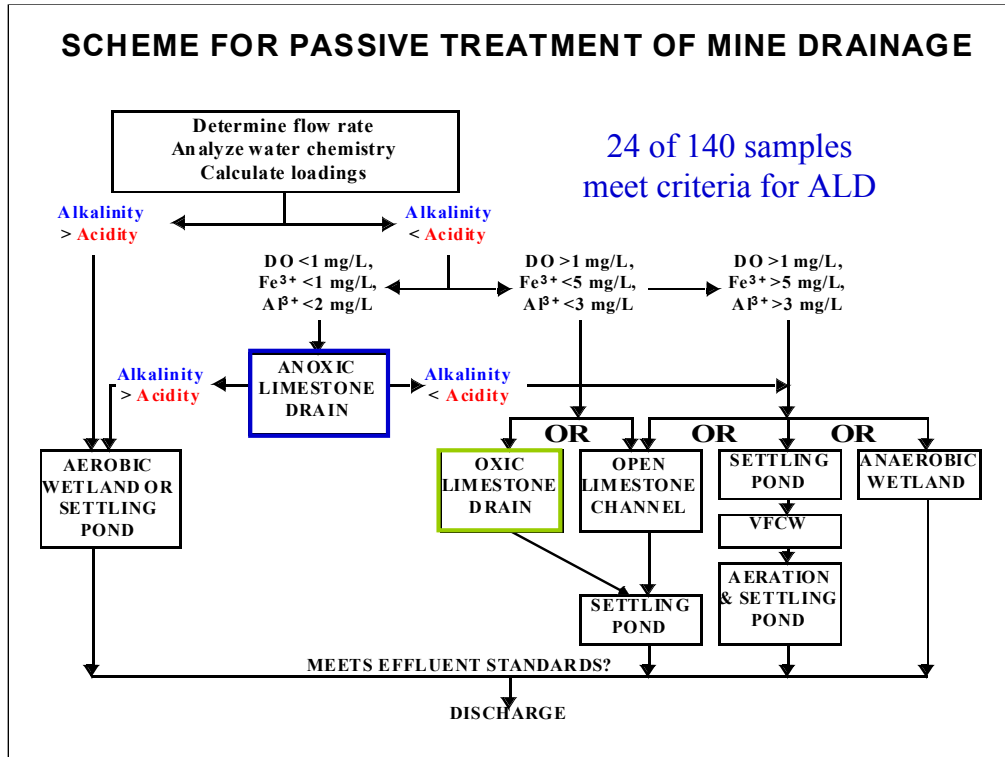


- 1)  $\text{CaCO}_3 (\text{s}) + 2 \text{H}^+ \leftrightarrow \text{Ca}^{2+} + \text{H}_2\text{CO}_3^*$
- 2)  $\text{CaCO}_3 (\text{s}) + \text{H}_2\text{CO}_3^* \leftrightarrow \text{Ca}^{2+} + 2 \text{HCO}_3^-$
- 3)  $\text{CaCO}_3 (\text{s}) + \text{H}_2\text{O} \leftrightarrow \text{Ca}^{2+} + \text{HCO}_3^- + \text{OH}^-$

$$\begin{aligned} \text{Calcite Dissolution Rate} = & \\ & k_1 \cdot \{\text{H}^+\} + k_2 \cdot \{\text{H}_2\text{CO}_3^*\} + k_3 \cdot \{\text{H}_2\text{O}\} \\ & - k_4 \cdot \{\text{Ca}^{2+}\} \cdot \{\text{HCO}_3^-\} \end{aligned}$$

NEUTRALIZATION: The acid produced by sulfide oxidation can be neutralized by reaction with calcite ( $\text{CaCO}_3$ ) which is the dominant component of limestone and cementing agents in calcareous sandstone, siltstone, and shale. Alkalinity and dissolved calcium ( $\text{Ca}^{2+}$ ) are products of neutralization by limestone. Where limestone or other calcareous rocks are absent or deficient at a mine site, their addition to mine spoil or mine drainage can be effective for prevention or neutralization of AMD. In equations 1 and 2,  $[\text{H}_2\text{CO}_3^*] = [\text{CO}_2 (\text{aq})] + [\text{H}_2\text{CO}_3^0]$ . In equations 2 and 3, alkalinity is represented by bicarbonate ( $\text{HCO}_3^-$ ) and hydroxyl ( $\text{OH}^-$ ).

The overall rate of calcite dissolution depends on the pH, the partial pressure of carbon dioxide ( $P_{\text{CO}_2}$ ), and the activities of  $\text{H}_2\text{O}$ ,  $\text{Ca}^{2+}$ , and  $\text{HCO}_3^-$  near the calcite surface (Plummer *et al.*, 1979). Plummer *et al.* (1979) described the dissolution rate as a combination of forward reactions (dissolution) represented by  $k_1$ ,  $k_2$ , and  $k_3$  and the reverse reaction (precipitation) represented by  $k_4$ . Generally, dissolution is faster at conditions far from equilibrium with calcite, typically characterized by low pH and high  $P_{\text{CO}_2}$ . The overall rate of calcite dissolution will decrease as the pH and activities of  $\text{Ca}^{2+}$  and  $\text{HCO}_3^-$  increase and the  $P_{\text{CO}_2}$  decreases.



DECISION TREE: Flow rate and water chemistry data for a mine discharge are needed to evaluate treatment alternatives. Different alternatives are appropriate depending on the “net acidity” or “net alkalinity” of the AMD. If the alkalinity exceeds the acidity, the pH will remain near neutral with oxidation. Aerobic wetlands or oxidation ponds would be indicated. If the acidity exceeds alkalinity, systems that add alkalinity and maintain or increase pH are indicated. Alkalinity can be generated by dissolution of limestone ( $\text{CaCO}_3$ ) and/or sulfate reduction in various passive treatment systems.

Many systems utilize crushed limestone “aggregate” 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 oxygen ( $\text{O}_2$ ). Stringent requirements for low concentrations of dissolved  $\text{O}_2$ , ferric iron ( $\text{Fe}^{3+}$ ), and aluminum (Al) in the influent AMD make ALDs inappropriate for treatment of oxic or highly mineralized water, which commonly occurs in mined areas. Of 140 AMD samples collected in 1999 from bituminous and anthracite coal mines in Pennsylvania, only 17 percent were net acidic *and* had  $<1$  mg/L of dissolved  $\text{O}_2$ ,  $\text{Fe}^{3+}$ , and Al. For these conditions, systems such as an “oxic limestone drain” (OLD), vertical flow compost wetland (VFCW), or anaerobic wetland may be appropriate.

Furthermore, because anthracite discharges generally have greater flow rate and lower acidity concentration than bituminous discharges with equivalent pH, sizing criteria for developed for bituminous AMD passive-treatment systems (Hedin et al., 1994; Hedin and Watzlaf, 1994) that specify minimum detention time (e.g. 15 hours for ALD) or tonnage (25 tons per gallon per minute) could result in size estimates that are substantially larger than needed to overcome the influent acidity.

## SIZE OF ALD/OLD

- Hedin and Watzlaf (1994) derived “linear” sizing method for ALD to ensure maximum production of alkalinity for specified life of the drain.
- Cravotta (2003) derived “exponential” sizing method for ALD/OLD to ensure net alkalinity over the specified life of the drain.



### OPTIMUM SIZE OF LIMESTONE DRAIN:

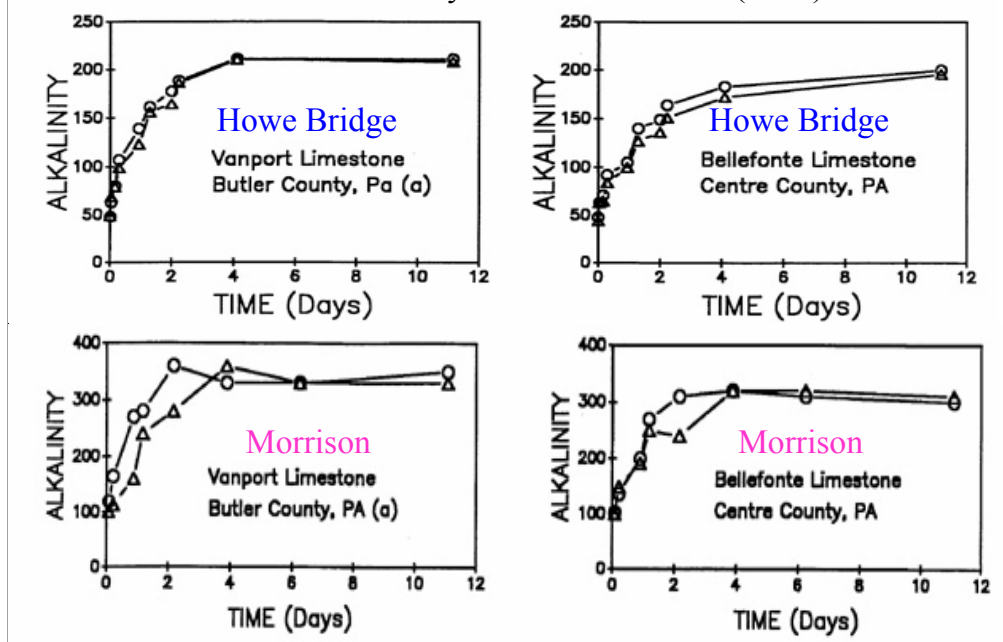
Hedin and Watzlaf (1994) derived “linear” sizing method for ALD to ensure maximum production of alkalinity for specified life of the drain.

Cravotta (2003) derived “exponential” sizing method for ALD/OLD to ensure net alkalinity over the specified life of the drain.



# ALKALINITY vs. DETENTION TIME

Cubitainer Tests by Watzlaf and Hedin (1993)



CUBITAINER DATA RELATE ALKALINITY AND DETENTION TIME: Details will be discussed in more detail later.

Limestone dissolution tests under closed, uncirculated conditions for mine water from the Howe Bridge and Morrison discharges (Watzlaf and Hedin, 1993) show initially rapid increase in alkalinity and asymptotic approach to steady-state or maximum alkalinity concentration after about 4 days detention time. The maximum alkalinity concentration was approximately 200 mg/L for Howe Bridge and 350 mg/L for Morrison. At 15 hrs detention time, the alkalinity concentration was approximately 80% of the maximum concentration.

## LIMESTONE DRAIN SIZE (LINEAR):

Limestone mass (M) to yield maximum alkalinity ( $C_M$ ):

$$M = Q \cdot [(t_L \cdot C_M / X_{\text{CaCO}_3}) + (t_d \cdot \rho_S \cdot (1 - \phi) / \phi)]$$

where  $t_d$  is detention time ( $\geq 15$  hr),  $Q$  is average flow rate,  $t_L$  is longevity in years,  $X_{\text{CaCO}_3}$  is purity of limestone as  $\text{CaCO}_3$  weight fraction,  $\rho_S$  is limestone density ( $2.65 \text{ g/cm}^3$ ), and  $\phi$  is porosity (0.49).

Hedin & Watzlaf (1994) “*The effects of anoxic limestone drains on mine water chemistry.*” U.S. Bureau of Mines Special Pub. SP 06A.

Hedin, Nairn, and Kleinmann (1994) “*Passive treatment of coal mine drainage.*” U.S. Bureau of Mines Information Circular IC 9389.

LIMESTONE DRAIN SIZING EQUATION: Hedin and Watzlaf (1994) evaluated construction characteristics, detention times, and chemistry of influent and effluent of more than 20 limestone drains to determine the optimum size for maximum alkalinity production. They derived the above limestone drain sizing equation that included a term for longevity and a term for detention time. Hedin and Watzlaf (1994) wanted to ensure that the initial limestone mass was sufficient to produce a constant, maximum alkalinity until the specified longevity had elapsed; thereafter, alkalinity would decline. However, the above method has several limitations. The first term assumes linear decay (constant mass flux), which is inconsistent with expected exponential decay, and the second term assumes alkalinity is constant (maximum) until mass is less than that required for  $t_d = 15$  hr. The assumption of constant, maximum alkalinity for long detention times ( $>48$  hr) is supported by data obtained using cubitainer tests and to some extent field data. However, at shorter detention times, the alkalinity can vary as a function of influent chemistry, detention time, and/or mass of limestone remaining. For large flows that have relatively low net acidity, but still require treatment, the above approach would indicate excessively large quantities of limestone and large space required for installation.

## LIMESTONE DRAIN SIZE (EXP.):

“Optimum” size where detention time ( $t_d$ ) after aging yields alkalinity ( $C_t$ ) equal to acidity based on rate constants,  $k'$  or  $k''$ , and initial ( $C_0$ ) and maximum ( $C_M$ ) alkalinities:

$$1^{\text{st}}: C_t = C_M - [(C_M - C_0) \cdot \exp\{-k' \cdot t_d\}]$$

$$2^{\text{nd}}: C_t = C_M - \{1/[k'' \cdot t_d + 1/(C_M - C_0)]\}$$

Cravotta (2003) “*Size and performance of anoxic limestone drains to neutralize acidic mine drainage.*” *Journal of Environmental Quality*, vol. 32, p. 1277-1289.

LIMESTONE DRAIN SIZE (EXPONENTIAL): The sizing method of Hedin and Watzlaf (1994) is intended to produce a constant alkalinity, approaching the maximum concentration in equilibrium with  $\text{CaCO}_3$ , and is warranted for AMD with high acidity ( $>300$  mg/L). However, shorter detention times may be warranted for an 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.

Cravotta (2003) demonstrated that time-series data for cubitainer tests could be used to derive first-order and second-order rate 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 ( $C_0$ ), maximum or steady-state concentration ( $C_M$ ), and the rate constant,  $k'$  or  $k''$ . 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.

## DETENTION TIME & LIMESTONE MASS:

Detention time in limestone bed was estimated from flow rate (Q) and water-filled void volume ( $V_V$ ) or porosity ( $\phi$ ):

$$t_d = V_V/Q = \phi \cdot V_B/Q$$

Substitute  $V_B = M/\rho_B$ ,  $\rho_B = \rho_S \cdot (1-\phi)$ , and rearrange to solve for limestone mass to achieve a given detention time...

$$M = Q \cdot (t_d \cdot \rho_S \cdot (1-\phi) / \phi)$$

Cravotta & Watzlaf (2002) "*Design and performance of limestone drains to increase pH and remove dissolved metals from acidic mine drainage.*" Handbook of Groundwater Remediation Using Permeable Reactive Barriers, Academic Press, p. 19-66.

LIMESTONE DRAIN SIZE: Cravotta and Watzlaf (2002) reviewed variables affecting detention time in limestone drains. Detention time ( $t_d$ ) and, hence, rates of alkalinity production or other effects of limestone dissolution within limestone beds can be estimated on the basis of volumetric flow rate (Q) and estimated void volume ( $V_V$ ) within the bed,

$$t_d = V_V/Q = \phi \cdot V_B/Q$$

where  $V_B$  is the bulk volume and  $\phi$  is the porosity ( $\phi = V_V/V_B$ ). If the total mass of limestone (M) and bulk volume ( $V_B$ ) of the drain are known, the porosity can be computed. Bulk density ( $\rho_B$ ) is defined as

$$\rho_B = M/V_B$$

and is proportionally related to porosity ( $\phi$ ) by the stone density ( $\rho_S$ ) where

$$\rho_B = \rho_S \cdot (1-\phi).$$

Hence, assuming  $\rho_S = 2.65 \text{ g/cm}^3$  considered typical for limestone, porosity can be determined for various bulk densities and vice versa:

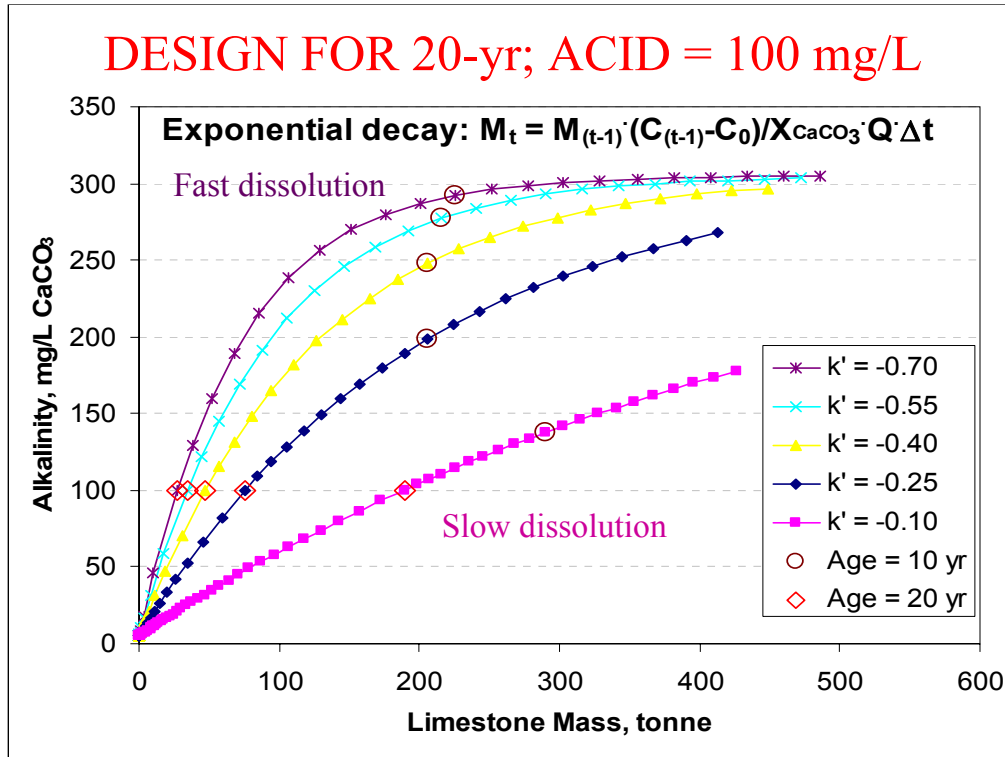
$$\phi = 1 - (\rho_B/\rho_S).$$

Knowing  $\rho_S$ ,  $\phi$ , and Q, and substituting  $V_B = M/(\rho_S \cdot (1-\phi))$ , detention time for water flowing through a limestone drain with a given mass can be computed as:

$$t_d = M/[Q \cdot \rho_S \cdot (1-\phi) / \phi]$$

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

$$M = t_d \cdot [Q \cdot \rho_S \cdot (1-\phi) / \phi].$$



LIMESTONE MASS vs. TIME vs. ALKALINITY: Using the 1<sup>st</sup>-order rate equation of Cravotta (2003) and empirical rate constant,  $k'$ , for the reaction between a given limestone and raw water from a mine discharge, the initial mass of limestone to yield alkalinity greater than or equal to the acidity can be estimated for the specified life span of the limestone drain. In this example, the goal is to produce effluent with alkalinity greater than or equal to the acidity of 100 mg/L for a specified life span of 20 years. The initial and maximum alkalinity concentrations are assumed to be 5 and 305 mg/L, respectively; the flow rate is assumed to be a constant 300 L/min, limestone purity 90% CaCO<sub>3</sub>, and porosity 0.49. To achieve an alkalinity of 100 mg/L at an age of 20 years, different initial quantities of limestone, ranging from 413 to 486 tonnes, would be needed depending on the alkalinity production rate (ranging from -0.10 to -0.70 hr<sup>-1</sup>). A larger initial quantity of limestone is required for the fast dissolution rate compared to slower rates. The detention time is assumed to decrease proportionally with limestone mass as the system ages and limestone mass declines. The alkalinity concentration and flux are initially greatest when the quantity of limestone (detention time) is largest. At an age of 20 years, the alkalinity concentration and flux are the same for the range of rates and remaining mass of limestone.

## FIELD DATA

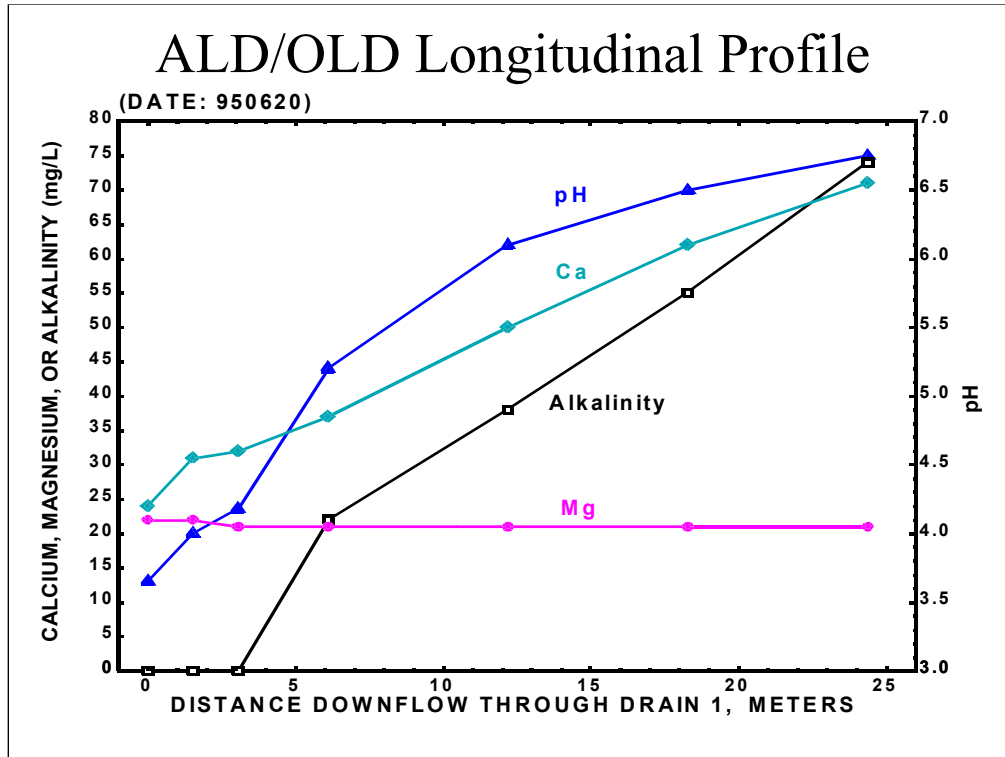
- Anoxic or oxic limestone drains (ALDs/OLDs) effectively increase pH and alkalinity of AMD.
- Effluent pH, alkalinity, and Ca concentrations increase asymptotically with detention time (marginal increase with prolonged detention time; 3 - 50 hr).
- Alkalinity *loading* from ALDs/OLDs increased with increased flow rate (decreased detention time).

### FIELD DATA:

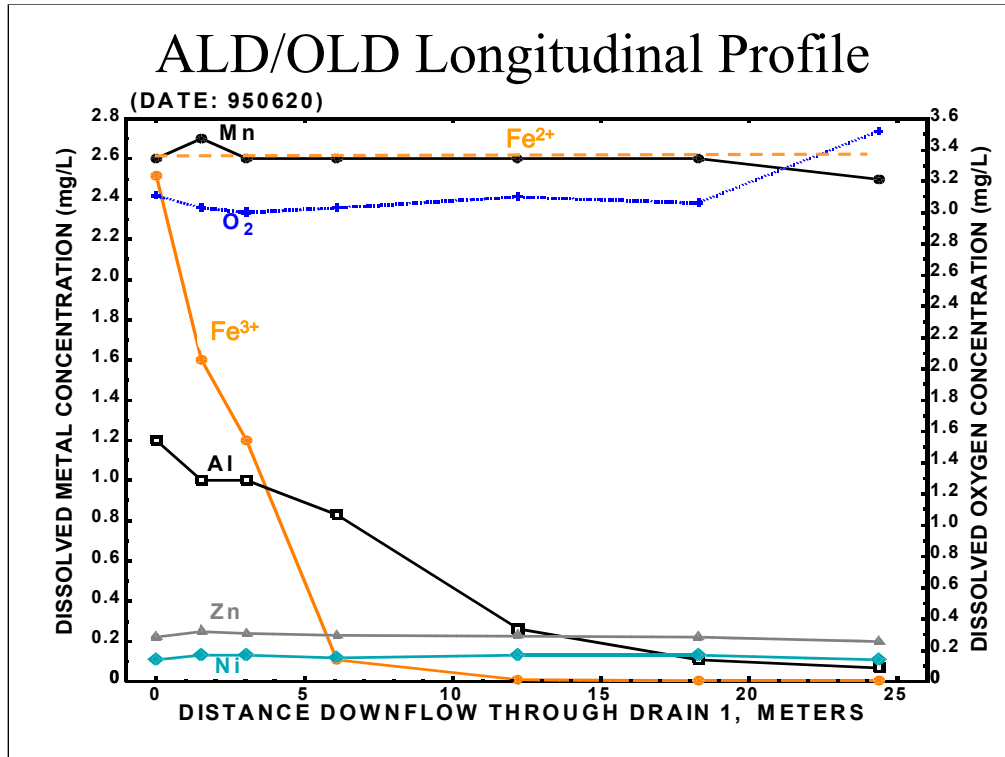
Anoxic or oxic limestone drains (ALDs/OLDs) can be effective to increase pH and alkalinity of AMD.

Effluent pH, alkalinity, and Ca concentrations increase asymptotically with detention time; marginal increases with prolonged detention times (3 hr vs. 15 hr).

Alkalinity *loading* from ALDs/OLDs increased with increased flow rate (decreased detention time).

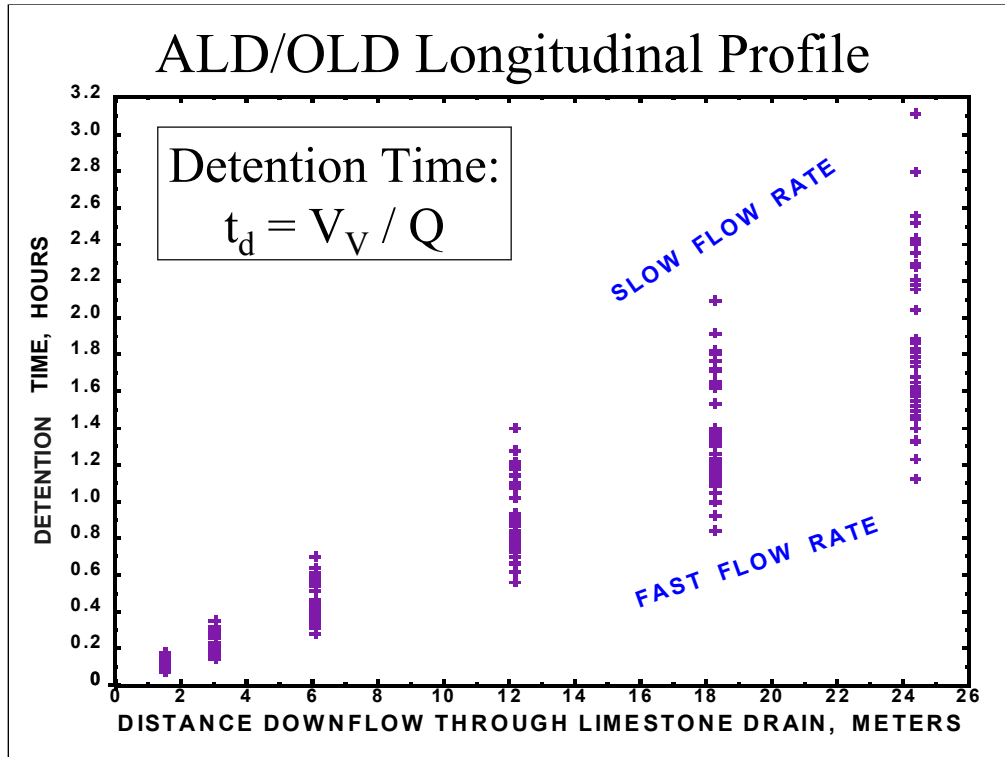


LONGITUDINAL TRENDS (A): Typical effect of limestone drain treatment is illustrated by rapid increase in pH near inflow to near neutral pH near outflow. Alkalinity and calcium concentrations also increase progressively downflow as limestone dissolution progresses. Typically, magnesium, sulfate, and other major ions do not change significantly as a result of limestone treatment. Data are for Orchard OLD (Cravotta and Trahan, 1999).

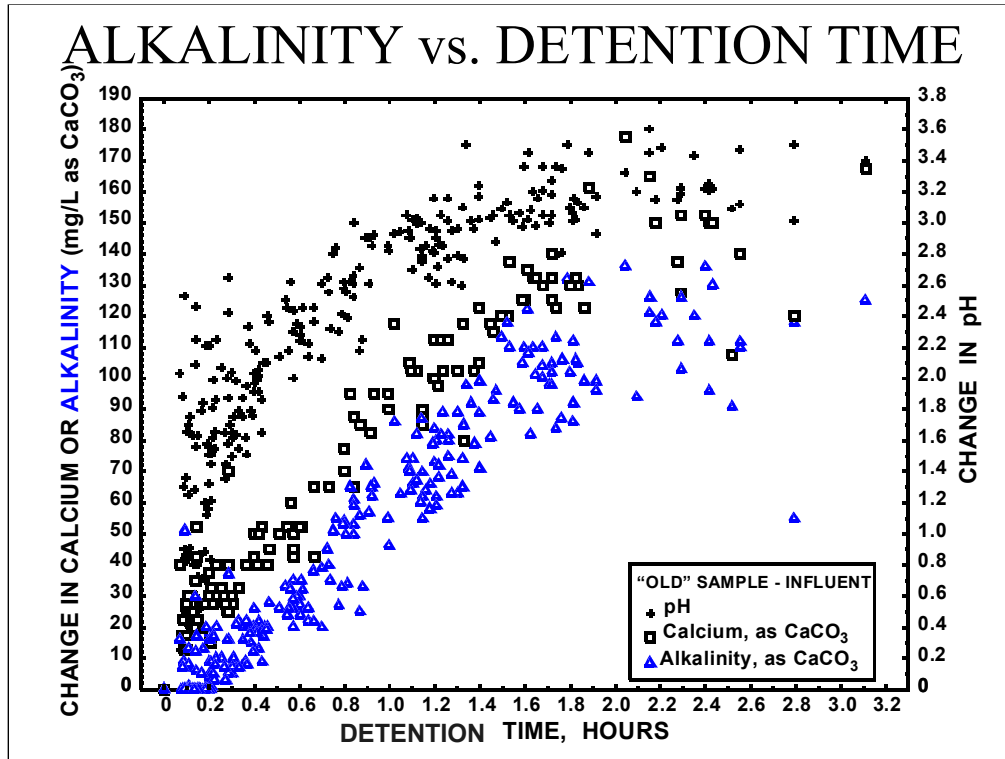


LONGITUDINAL TRENDS (B): Because of increased pH and alkalinity, hydrolysis of Fe(III) and Al is facilitated. Other metals tend to be transported conservatively through an OLD or ALD. Some decreases in trace metals could result from adsorption to Fe(III) oxides. Data are for Orchard OLD (Cravotta and Trahan, 1999).

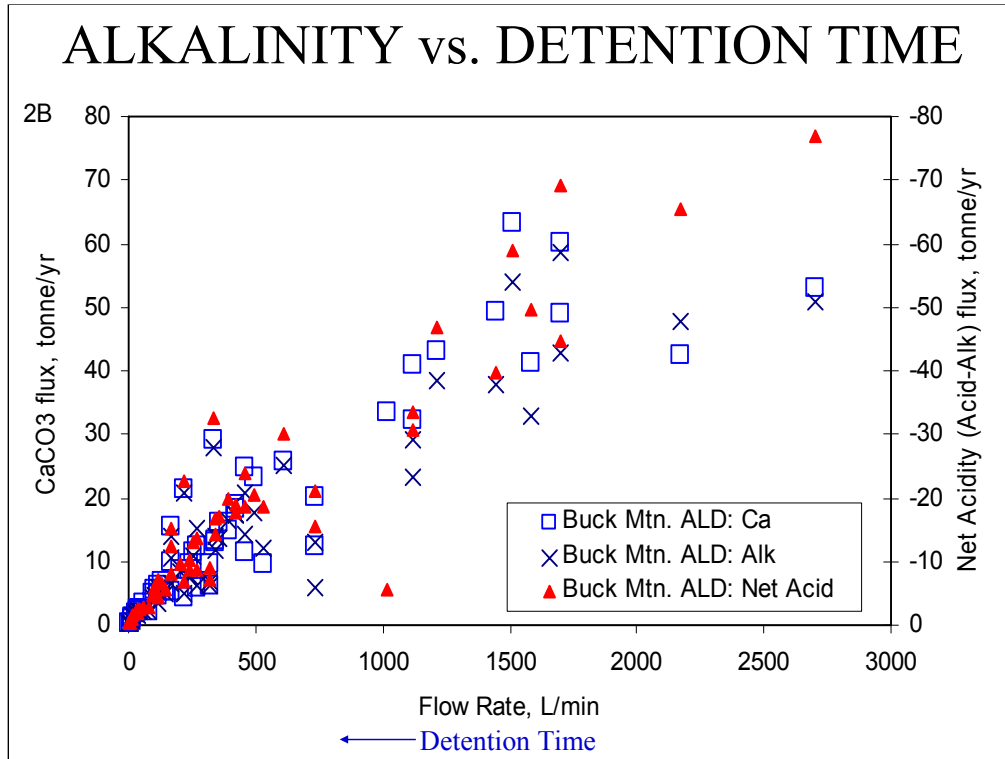




**DOWNFLOW DISTANCE AND DETENTION TIME:** Because of variations in flow rate at different sampling events, the detention times within the limestone drain varied for samples collected at the outflow and intermediate locations along the flow path. Knowing the void volume of the drain at the sampled location and the flow rate, water-quality data can be “normalized” by the flow rate for evaluation relative to detention time. Data are for Orchard OLD (Cravotta and Trahan, 1999).

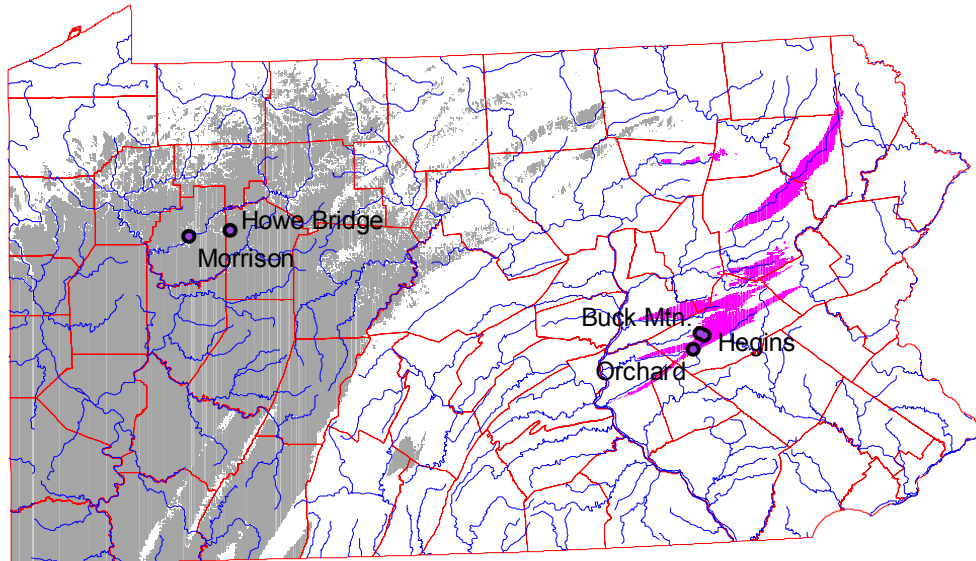


WATER QUALITY CHANGE (Outflow-Inflow) as function of detention time. Data are for Orchard OLD (Cravotta and Trahan, 1999).



WATER QUALITY CHANGE (Outflow-Inflow) as function of detention time. Data are for Buck Mtn. ALD (Cravotta and others, 2004). Increased loading of alkalinity and calcium with increased flow rate result from decreased detention time with flow and nonlinear, asymptotic relation between concentration and detention time. If flow is doubled and detention time halved, alkalinity concentration is greater than half that at start.

## ALD/OLD “PERFORMANCE”



**BITUMINOUS**

**ANTHRACITE**

### ALD/OLD PERFORMANCE:

Morrison ALD and Howe Bridge ALD in bituminous coalfield; construction characteristics and water-quality data from U.S. Department of Energy (Cravotta and Watzlaf, 2002).

Orchard OLD, Buck Mtn. ALD, and Hegins OLD in anthracite coalfield; construction characteristics and water-quality data from U.S. Geological Survey (Cravotta, 2004).

Limestone Drain Site	Year Built	Limestone Fragments			Drain Dimensions			Flow Rate, L.min <sup>-1</sup>	Detention Time, <sup>a</sup> hr
		Mass, tonne	Purity, X <sub>CaCO<sub>3</sub></sub> , wt%	Size Range, cm	Length, m	Width, m	Depth, m		
Morrison	1990	65	92	5.1-7.6	45.7	.9	.9	7	44.5
Howe Bridge 1	1991	455	82	5.1-7.6	36.6	6.1	1.2	117	18.7
Orchard	1995	30	97	6.0-10	73.2	2.4	.8	39	3.5
Buck Mtn	1997	320	92	6.0-10	50.0	2.4	2.0	534	3.7
Hegins	2000	730	92	24-36	50.0	6.0	1.8	351	12.6

a. Detention time ( $t_d = \phi V_B / Q$ ) for average flow rate (Q) and bulk volume ( $V_B$ ) assuming porosity ( $\phi$ ) of 0.49.

Bituminous Anthracite

PHYSICAL CHARACTERISTICS:

Large limestone particles used at Hegins compared to Morrison, Howe Bridge, Orchard, and Buck Mtn.

Flow rates ranged widely, from 7 L/min at Morrison to 534 L/min at Buck Mtn.

Considering flow rate, mass of limestone, and assumed porosity of 0.49, detention times ranged from more than 40 hours at Morrison to less than 4 hours at Orchard and Buck Mtn.

Table 2. Average<sup>a</sup> quality of influent and effluent at limestone drains in Pennsylvania

Limestone Drain Site	Dissolved Oxygen		pH		Net Acidity		Alkalinity		Calcium <sup>b</sup>		Sulfate		Iron		Man- gane- se		Aluminum	
	mg.L <sup>-1</sup>		units		mg.L <sup>-1</sup> as CaCO <sub>3</sub>		mg.L <sup>-1</sup>		mg.L <sup>-1</sup>		mg.L <sup>-1</sup>		mg.L <sup>-1</sup>		mg.L <sup>-1</sup>		mg.L <sup>-1</sup>	
	In	Eff	In	Eff	In	Eff	In	Eff	In	Eff	In	Eff	In	Eff	In	Eff	In	Eff
Morrison	<0.5	<0.5	5.3	6.4	434	76	30	291	275	543	1200	1010	209	165	47	39	0.5	<0.2
Howe Bridge	<0.5	<0.5	5.8	6.3	495	369	36	158	371	493	1240	1230	255	254	40	40	<0.2	<0.2
Orchard	3.4	4.3	3.5	5.9	30	-49	0	56	54	128	176	172	2.1	0.5	2.4	1.6	1.2	0.3
Buck Mtn.	1.3	2.7	4.6	6.3	28	-55	2	77	10	92	72	62	13	10	1.2	1.2	0.6	<0.2
Hegins	10.1	10.8	3.5	4.5	47	28	0	<1	23	41	232	223	0.2	0.1	1.7	1.6	5.1	4.3

a. Grand average of annual averages for period of record. Data for influent and effluent quality at Howe Bridge and Morrison ALDs from U.S. Department of Energy (G. R. Watzlaf, 2001, personal commun.) and at Orchard, Buck Mtn., and Hegins from U.S. Geological Survey (Durlin and Schaffstall, 1997-2004). Influent quality at Morrison and Buck Mtn. for nearby seep.

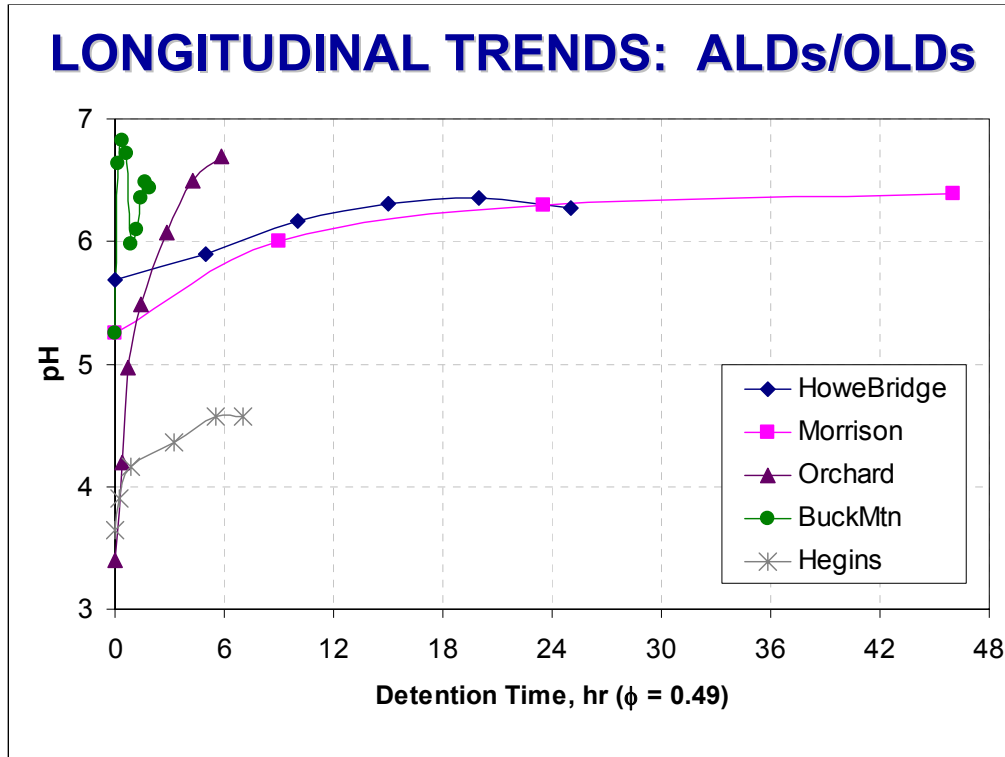
b. Calcium concentration as CaCO<sub>3</sub> computed as 2.5 times the concentration of Ca. Differences between influent and effluent alkalinity or Ca indicate approximate quantity of limestone dissolved in the ALD each year since construction.

**AVERAGE INFLUENT AND EFFLUENT QUALITY:**

Influent and effluent are “anoxic” at Morrison, Howe Bridge, and Buck Mtn. and “oxic” at Orchard and Hegins.

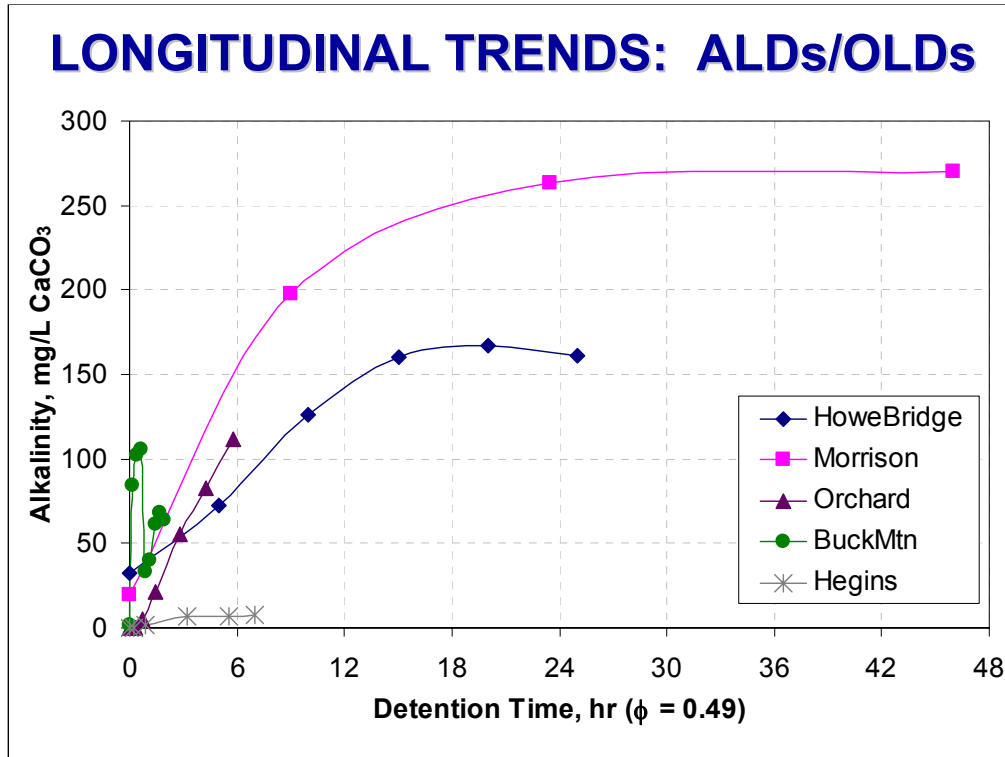
Net acidic influent ranging from more than 400 mg/L at Morrison and Howe Bridge to less than 50 mg/L at Orchard, Buck Mtn., and Hegins.

Only Orchard and Buck Mtn. produced net alkaline effluent.



LONGITUDINAL TRENDS: pH vs. detention time (assuming porosity of 0.49).

The pH of effluent increases asymptotically with detention time along the flow path through ALD/OLD. The non-uniform shape of curve for Buck Mtn. ALD results from multiple inflows of AMD along the flow path within the ALD.



LONGITUDINAL TRENDS: Alkalinity vs. detention time (assuming porosity of 0.49).

Alkalinity increases asymptotically with detention time. Maximum alkalinities are achieved for Morrison and Howe Bridge ALDs that have highest detention times. The non-uniform shape of curve for Buck Mtn. ALD results from multiple inflows of AMD along the flow path within the ALD.



## CUBITAINER TESTS -- 1

- Alkalinity generation rate and maximum concentration in closed “cubitainers” is consistent with ALDs.
- Untreated mine water of the same composition in cubitainers yielded similar alkalinities for different limestones containing 82 to 99% CaCO<sub>3</sub>.
- Two different mine waters in cubitainers containing similar limestones yielded different alkalinities.

Watzlaf & Hedin (1993) “A method for predicting the alkalinity generated by anoxic limestone drains.” *Proceedings 14th Annual Meeting West Virginia Surface Mine Drainage Task Force.*

### CUBITAINER TESTS 1:

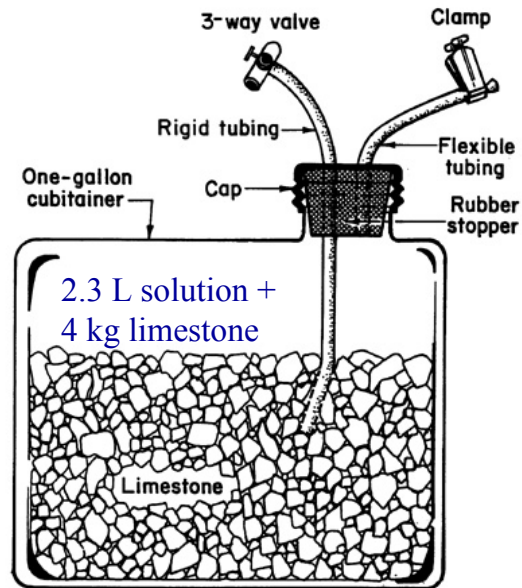
Alkalinity generation rate and maximum concentration in closed “cubitainers” is consistent with ALDs.

Untreated mine water of the same composition in cubitainers yielded similar alkalinities for different limestones containing 82 to 99% CaCO<sub>3</sub>.

Two different mine waters in cubitainers containing similar limestones yielded different alkalinities.

## “CUBITAINER TESTS -- 1”

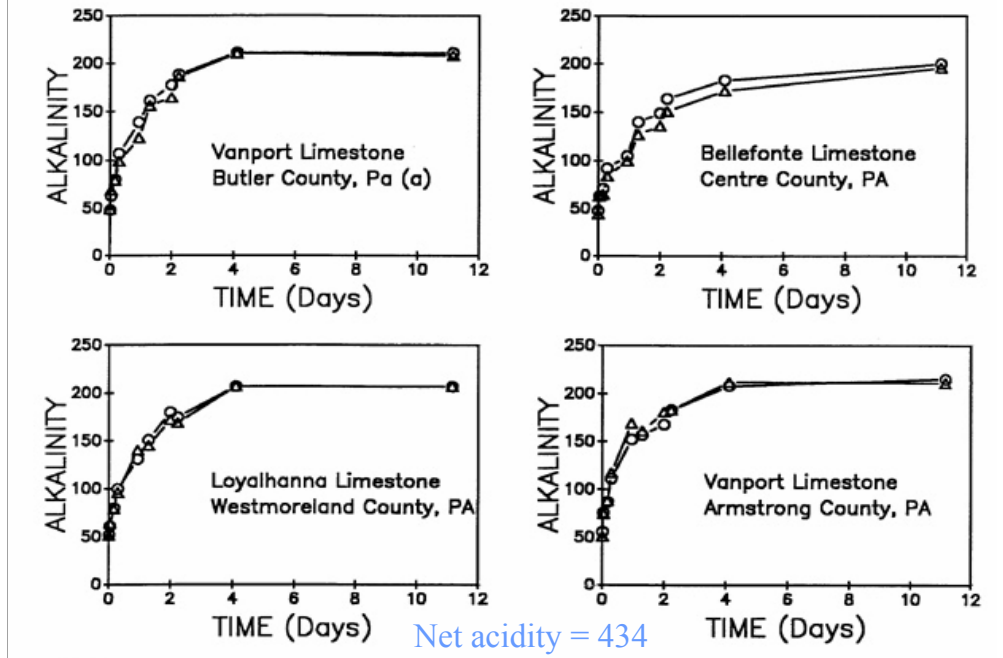
Watzlaf & Hedin (1993)  
“A method for predicting  
the alkalinity generated  
by anoxic limestone  
drains.” *Proceedings  
14th Annual Meeting  
West Virginia Surface  
Mine Drainage Task  
Force.*



Static, closed

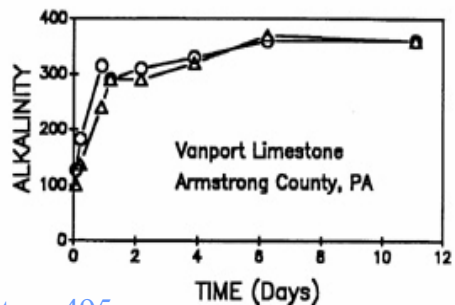
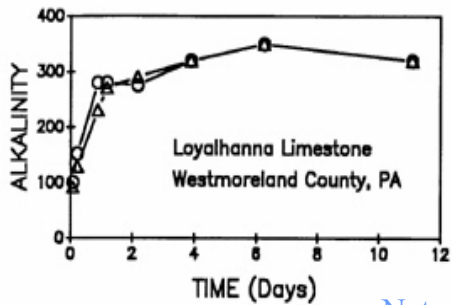
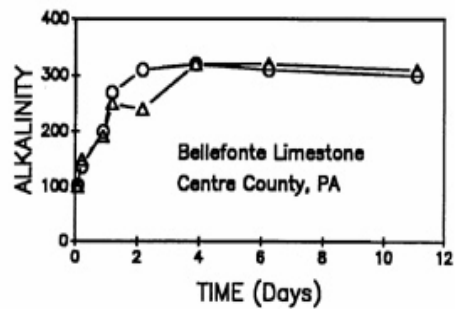
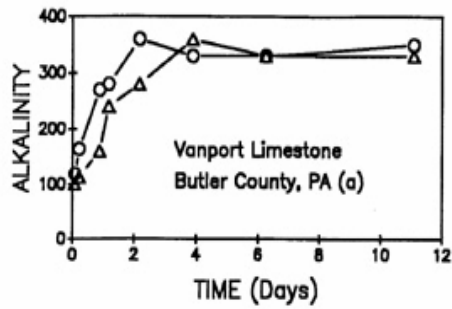
CUBITAINER SETUP: Watzlaf and Hedin (1993) used 1-gallon collapsible polyethylene containers filled with 4 kg washed limestone (2/3 full) and remainder with raw mine water. System was kept closed in water bath at temperature of AMD source. Filtered samples were withdrawn to determine changes in alkalinity concentration with detention time.

## CUBITAINER DATA: HOWE BRIDGE



CUBITAINER DATA: Howe Bridge 1 data for limestone dissolution tests under closed, uncirculated conditions show initially rapid increase in alkalinity and asymptotic approach to steady-state or maximum alkalinity concentration after about 4 days detention time. The maximum alkalinity concentration was approximately 200 mg/L. At 15 hrs detention time, the alkalinity concentration was approximately 80% of the maximum concentration.

## CUBITAINER DATA: MORRISON



Net acidity = 495

CUBITAINER DATA: Morrison data for limestone dissolution tests under closed, uncirculated conditions show initially rapid increase in alkalinity and asymptotic approach to steady-state or maximum alkalinity concentration after about 4 days detention time. The maximum alkalinity concentration was approximately 350 mg/L. At 15 hrs detention time, the alkalinity concentration was approximately 80% of the maximum concentration.

## SIMULATIONS -- 1

- Data for cubitainer tests of Hedin and Watzlaf (1993) and ALD monitoring used to simulate performance of ALDs:
  - ✓ cubitainer data for 1<sup>st</sup>- and 2<sup>nd</sup>-order equations predict alkalinity as a function of detention time;
  - ✓ ALD initial limestone mass, average flow rate, and assumed constant porosity (0.49).

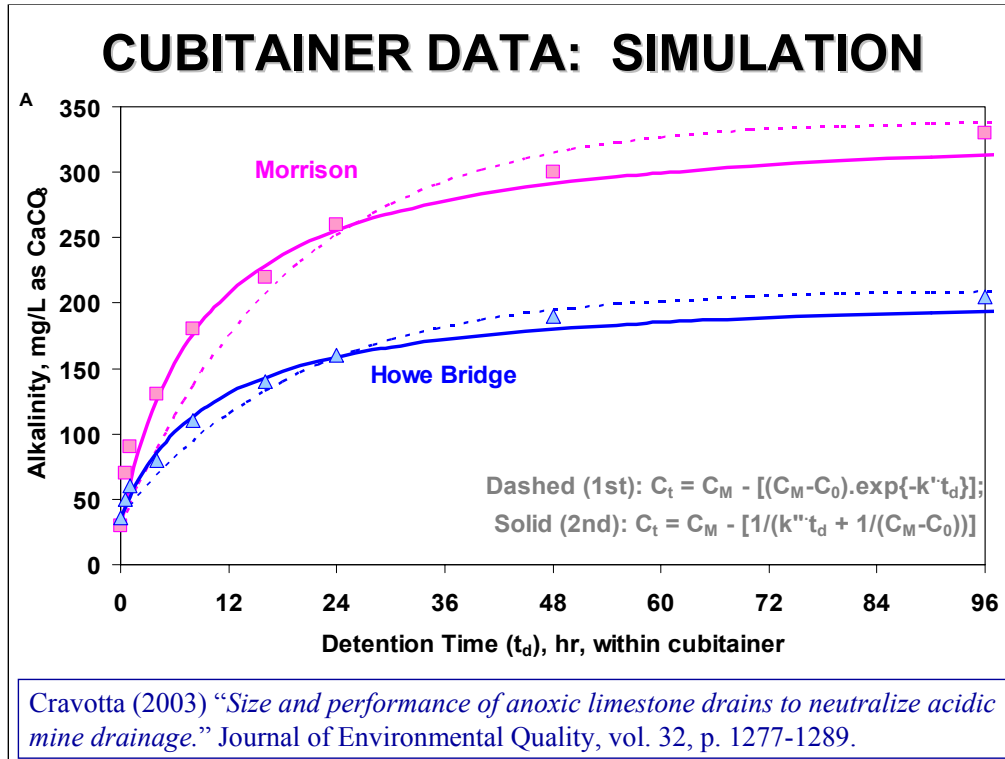
Cravotta (2003) "*Size and performance of anoxic limestone drains to neutralize acidic mine drainage.*" *Journal of Environmental Quality*, vol. 32, p. 1277-1289.

### SIMULATIONS 1:

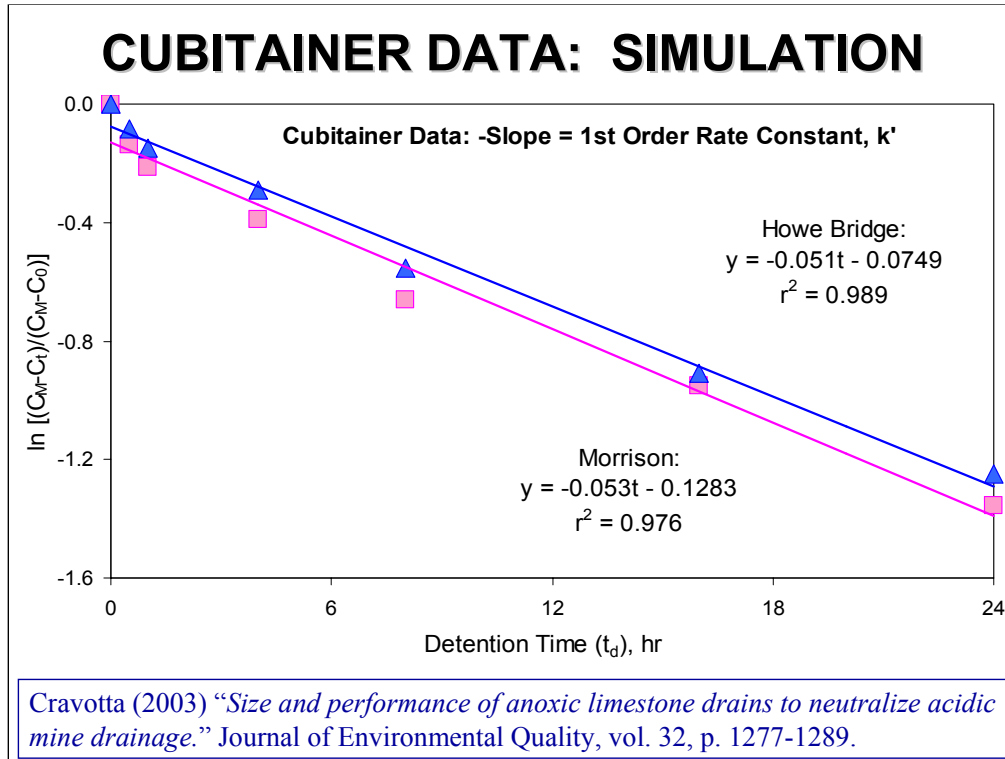
Cravotta(2003) used field data for cubitainer tests and ALD monitoring to simulate performance of limestone drains (current and future):

cubitainer results for maximum alkalinity and first- and second-order dissolution rates;

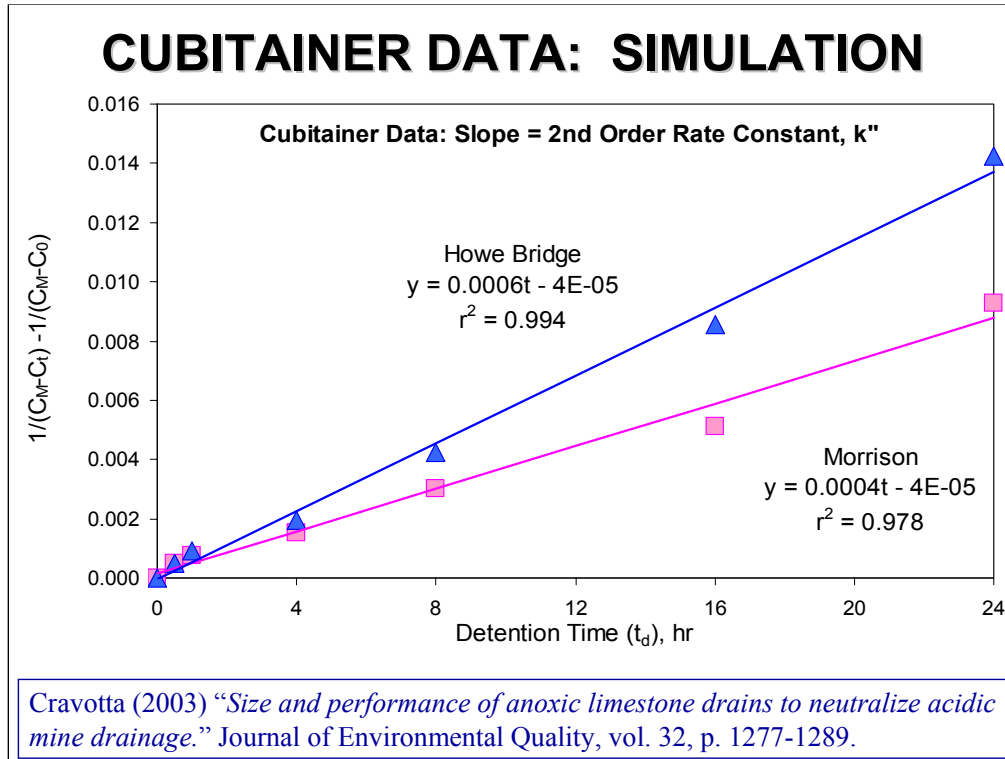
ALD flow rate (average), initial limestone mass, and assumed porosity of 0.49.



CUBITAINER DATA SIMULATION: Cravotta (2003) used generalized data points from Hedin and Watzlaf (1993) to compute 1<sup>st</sup> and 2<sup>nd</sup> order rate equations that described change in alkalinity with detention time. The generalized time-series data for the cubitainer tests were used to derive first-order and second-order equations to estimate the concentration of alkalinity ( $C_t$ ) of effluent as a function of the detention time ( $t_d$ ) within a limestone bed, influent concentration ( $C_0$ ), maximum or steady-state concentration ( $C_M$ ), and the rate constant as shown in the next slides.

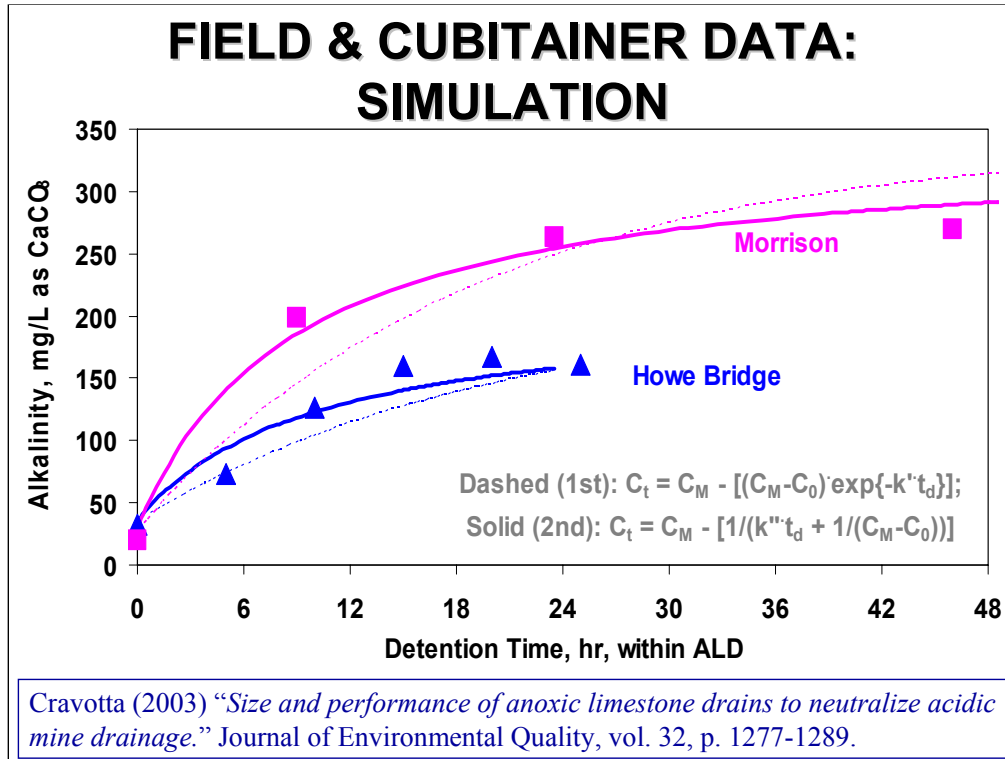


CUBITAINER DATA SIMULATION: Linear regression of  $\ln[(C_M - C_t)/(C_M - C_0)]$  versus detention time for the cubitainer tests yielded estimates of the first-order rate constant,  $k'$ , in the expression:  $C_t = C_M - [(C_M - C_0) \cdot \exp\{-k' \cdot t_d\}]$ .



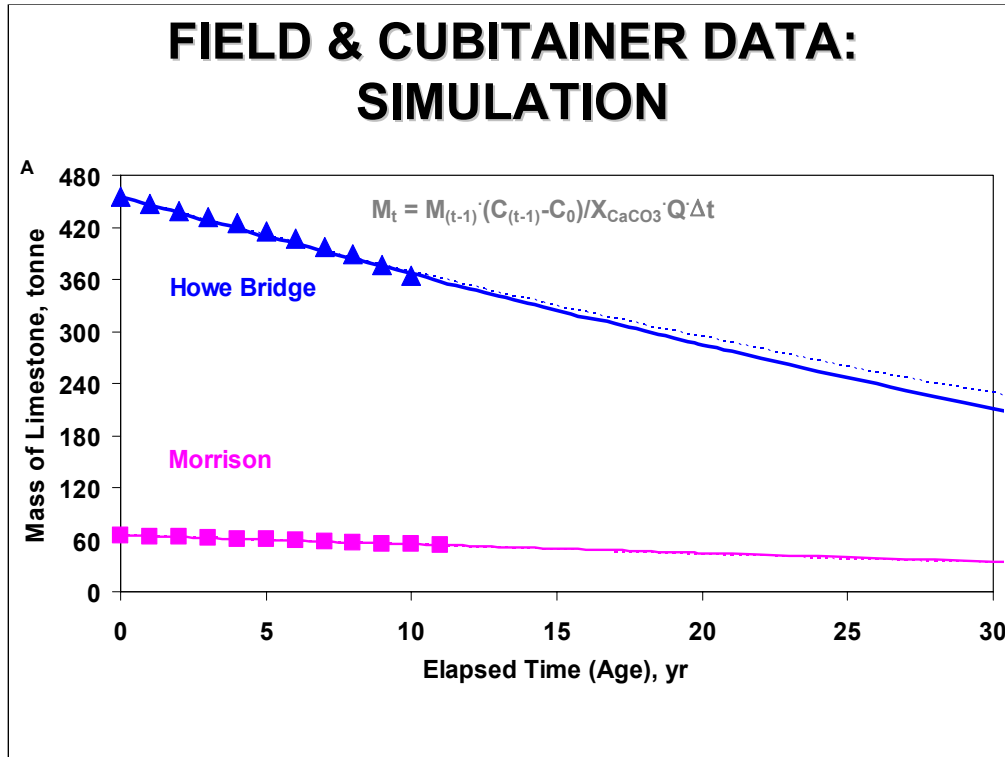
CUBITAINER DATA SIMULATION: Linear regression of  $[1/(C_M - C_t) - 1/(C_M - C_0)]$  versus detention time yielded estimates of the second-order rate constant,  $k''$ , in the expression:  $C_t = C_M - \{1/[k'' \cdot t_d + 1/(C_M - C_0)]\}$ .



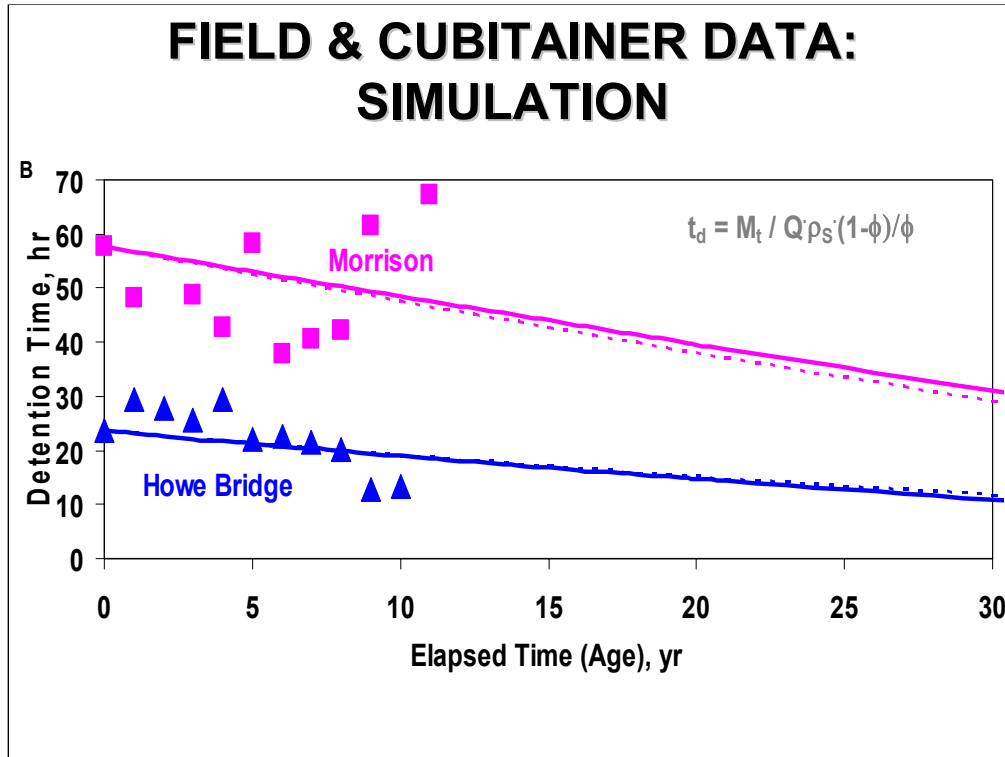


FIELD DATA SIMULATION: Cravotta (2003) showed the 1<sup>st</sup> and 2<sup>nd</sup> order rate equations from cubitainer tests described change in alkalinity with detention time within the ALDs under field conditions. The simulated curves assume average flow rate, constant porosity (0.49), and represents the change in detention time as mass approaches zero over a decadal time scale.

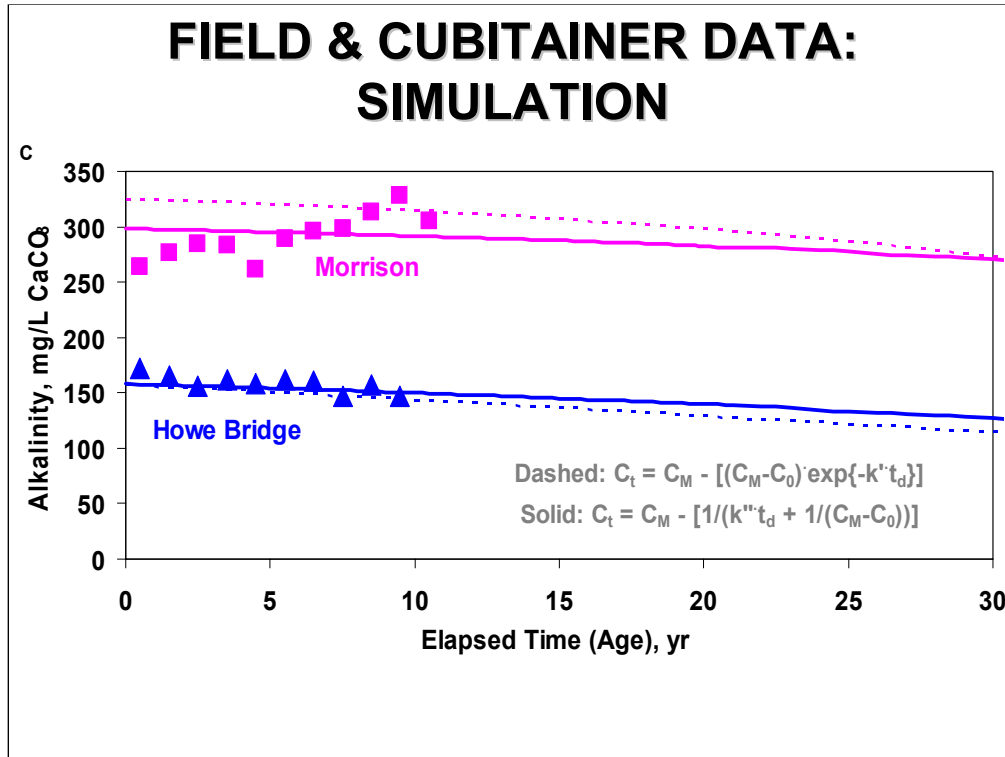
The CaCO<sub>3</sub> concentration and flux at the average flow rate of effluent were estimated using the 1<sup>st</sup> and 2<sup>nd</sup> order rate constants and the mass-specified detention time. As the limestone mass declined with age, its total volume was assumed to decline proportionally, while the porosity and particle density of 2.65 g/cm<sup>3</sup> 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<sub>3</sub> 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<sub>3</sub> 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.



SIMULATIONS: Simulated decline in limestone mass, detention time, and alkalinity with age of Howe Bridge and Morrison limestone drains on the basis of cubitainer tests (curves: 1<sup>st</sup> order dashed; 2<sup>nd</sup> order solid): *A*, Mass versus age considering rate constants,  $k^c$  and  $k^r$ , for dissolved alkalinity in cubitainers. *B*, Detention time versus age for average flow ( $Q$ ) and specified porosity (0.49). *C*, Alkalinity versus age for declining mass and detention time, assuming constant flow and porosity, and rate constants,  $k^c$  and  $k^r$ , for alkalinity in cubitainers. Symbols based on observed annual average flow and concentration.



SIMULATIONS: Simulated decline in limestone mass, detention time, and alkalinity with age of Howe Bridge and Morrison limestone drains on the basis of cubitainer tests (curves: 1<sup>st</sup> order dashed; 2<sup>nd</sup> order solid): *A*, Mass versus age considering rate constants,  $k^c$  and  $k'^c$ , for dissolved alkalinity in cubitainers. *B*, Detention time versus age for average flow ( $Q$ ) and specified porosity (0.49). *C*, Alkalinity versus age for declining mass and detention time, assuming constant flow and porosity, and rate constants,  $k^c$  and  $k'^c$ , for alkalinity in cubitainers. Symbols based on observed annual average flow and concentration.



SIMULATIONS: Simulated decline in limestone mass, detention time, and alkalinity with age of Howe Bridge and Morrison limestone drains on the basis of cubitainer tests (curves: 1<sup>st</sup> order dashed; 2<sup>nd</sup> order solid): *A*, Mass versus age considering rate constants,  $k^c$  and  $k^v$ , for dissolved alkalinity in cubitainers. *B*, Detention time versus age for average flow ( $Q$ ) and specified porosity (0.49). *C*, Alkalinity versus age for declining mass and detention time, assuming constant flow and porosity, and rate constants,  $k^c$  and  $k^v$ , for alkalinity in cubitainers. Symbols based on observed annual average flow and concentration.

## CUBITAINER TESTS -- 2

- Exponential rate of limestone dissolution in closed or open “cubitainers” is consistent with ALDs/OLDs.
- Dissolution rate and maximum alkalinity are greater for closed conditions than open conditions.
- Uncoated and coated limestone have similar dissolution rates for the same mine water under closed conditions.

*Cravotta and others (2004) “Optimization of limestone drains for long-term treatment of acidic mine drainage, Swatara Creek Basin, Schuylkill County, PA.” 2004 National Meeting of the American Society of Mine Reclamation, p. 366-411.*

### CUBITAINER TESTS 2:

Exponential rate of limestone dissolution in closed or open “cubitainers” is consistent with ALDs/OLDs.

Dissolution rate and maximum alkalinity are greater for closed conditions than open conditions.

Uncoated and coated limestone have similar dissolution rates for the same mine water under closed conditions.

**CIRCULATED:**

**UNCOATED**

**vs.**

**COATED**

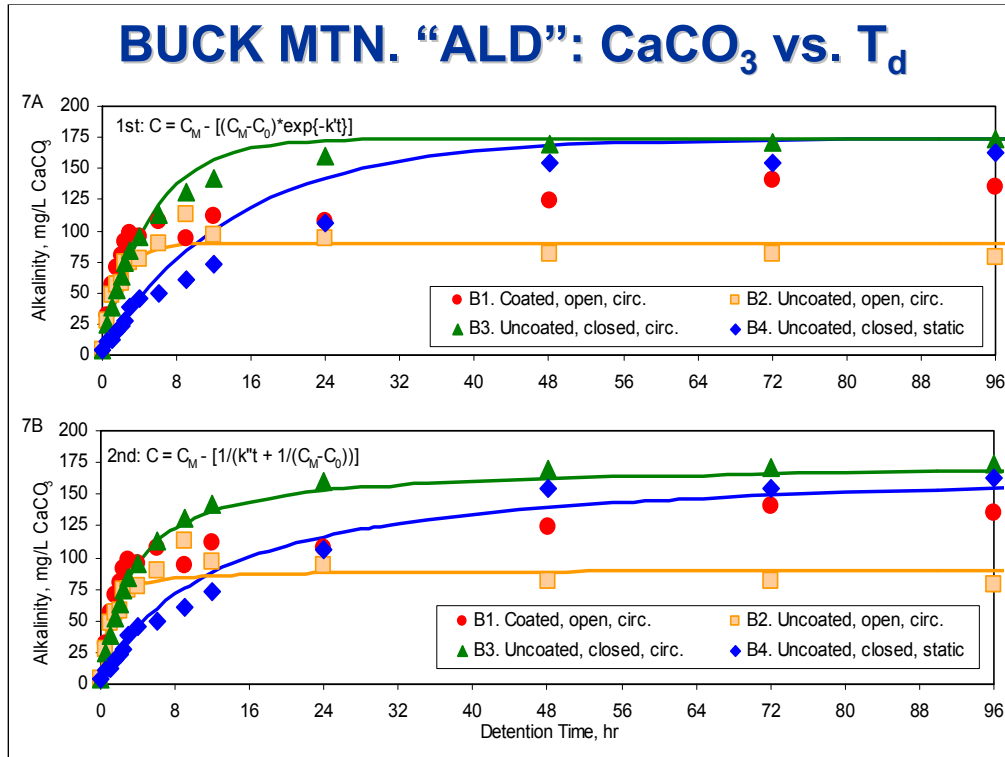


**CLOSED**

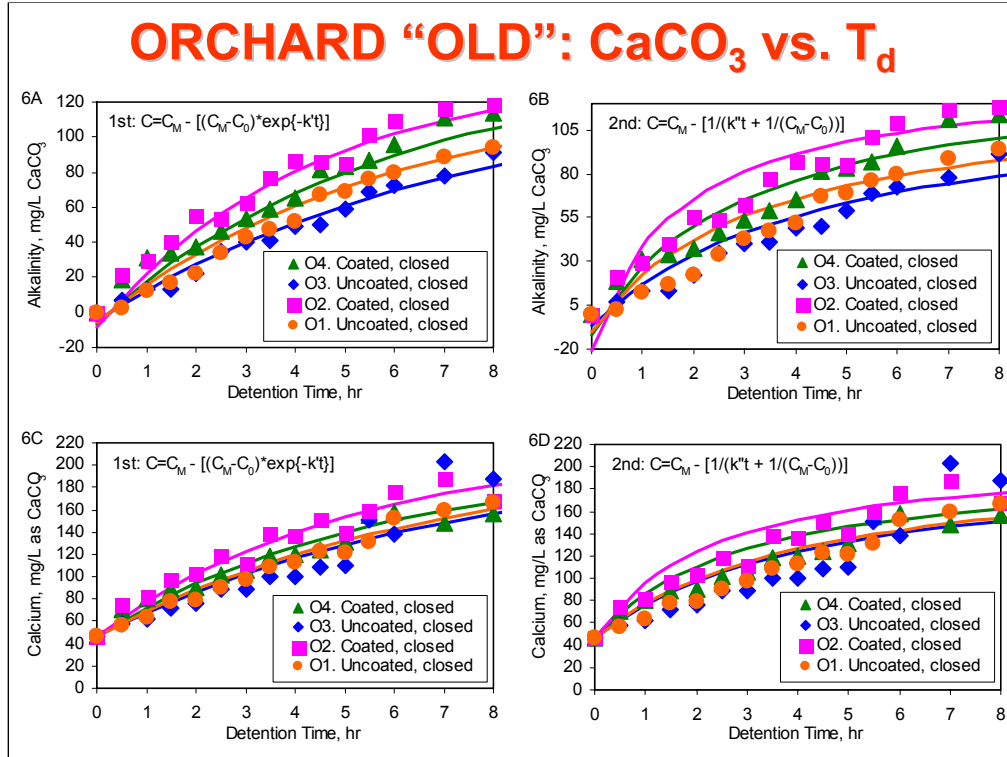
**vs.**

**OPEN**

CUBITAINER TEST VARIABLES: Tests were conducted for uncoated and coated limestone under closed and open conditions. Mine water for the tests was from the Buck Mtn., Orchard, and Hegins Mine discharges in the Swatara Creek Basin.



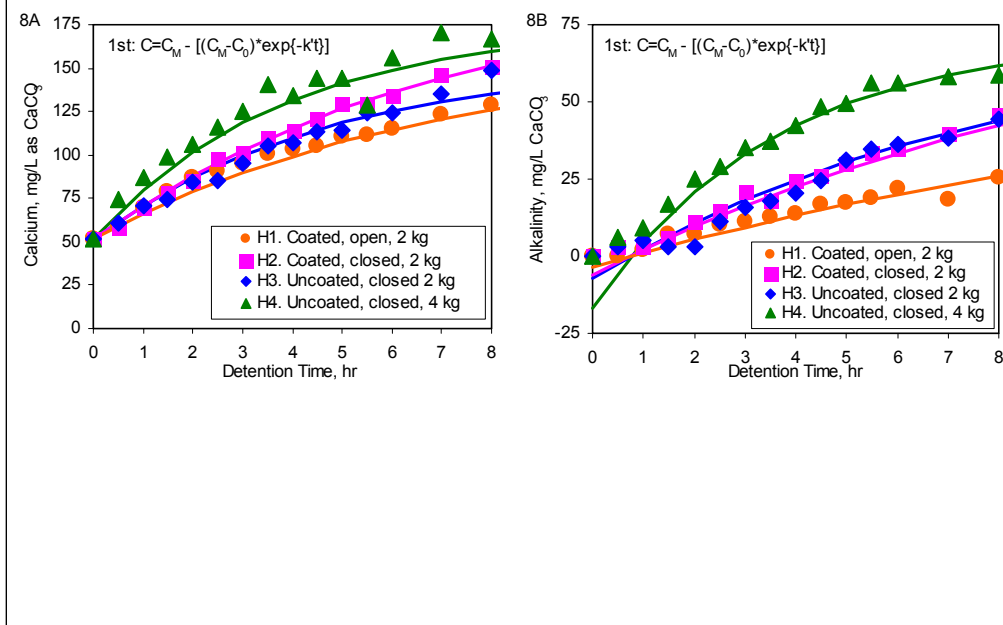
CUBITAINER TESTS BUCK MTN: Concentration of alkalinity versus detention time for cubitainer tests of effects of mineral coating, circulation, and system closure on limestone dissolution and alkalinity production rates for Buck Mtn. ALD: *A*, curve fitted by 1<sup>st</sup> order rate equation; *B*, curved fitted by 2<sup>nd</sup> order rate equation. 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.



CUBITAINER TESTS ORCHARD: Concentration of alkalinity and calcium as CaCO<sub>3</sub> versus detention time for cubitainer tests of effects of mineral coating on limestone dissolution and alkalinity production rates for Orchard OLD: *A*, alkalinity, 1<sup>st</sup> order curve; *B*, alkalinity, 2<sup>nd</sup> order curve; *C*, Ca, 1<sup>st</sup> order curve; *D*, Ca, 2<sup>nd</sup> 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.



## HEGINS "OLD": CaCO<sub>3</sub> vs. T<sub>d</sub>



CUBITAINER TESTS HEGINS: Concentrations as CaCO<sub>3</sub> versus detention time for cubitainer tests of effects of mineral coating on limestone dissolution and alkalinity production rates for Hegers OLD: *A*, calcium; *B*, alkalinity. Limestone left at Hegers 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.

## SIMULATIONS -- 2

- Laboratory and field data used to simulate performance of limestone drains (current and future):
  - ✓ cubitainer data for maximum Ca or alkalinity and 1<sup>st</sup>-order rate equations for Ca or alkalinity;
  - ✓ ALD/OLD initial limestone mass, average flow rate, and assumed constant porosity (0.49).

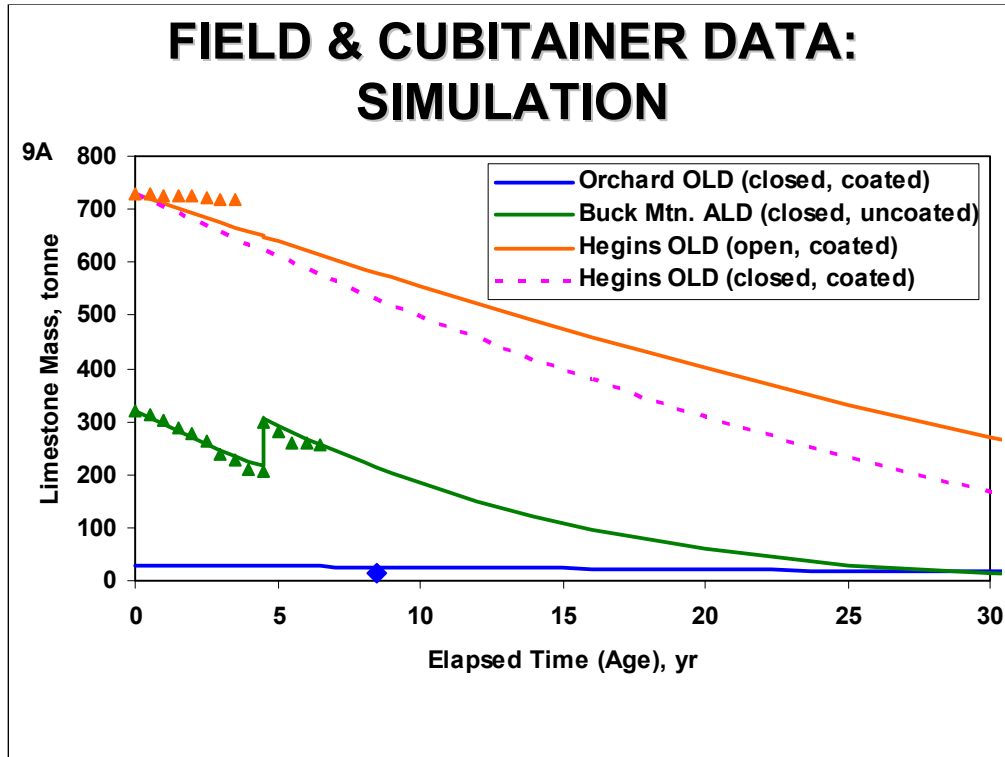
*Cravotta and others (2004) "Optimization of limestone drains for long-term treatment of acidic mine drainage, Swatara Creek Basin, Schuylkill County, PA ." 2004 National Meeting of the American Society of Mine Reclamation, p. 366-411.*

### SIMULATIONS 1:

Laboratory and field data were used to simulate performance of limestone drains (current and future):

cubitainer results for maximum alkalinity and first- and second-order dissolution rates;

ALD flow rate (average), initial limestone mass, and assumed porosity of 0.49.

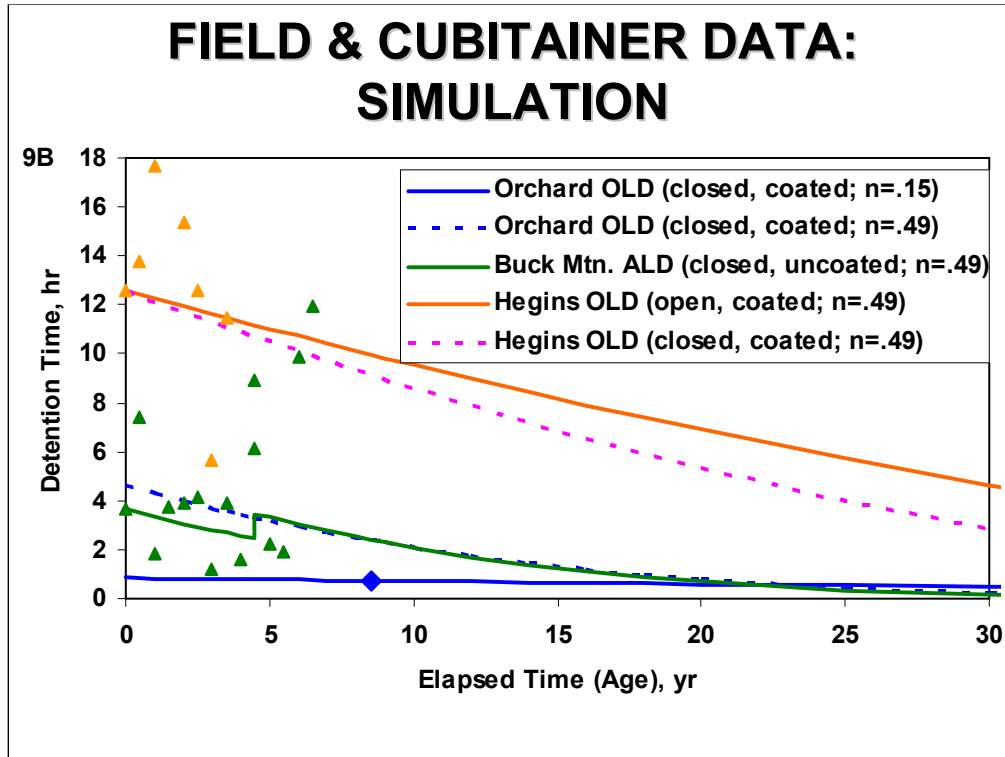


SIMULATIONS: Simulated decline in limestone mass, detention time, and alkalinity with age of Orchard, Buck Mtn., and Hegins limestone drains on the basis of cubitainer tests (first-order curves): *A*, Mass versus age considering rate constant,  $k'$ , for dissolved Ca in cubitainers. *B*, Detention time 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.

Generally, estimates of limestone mass remaining over time for Hegins based on field flux data are in poor agreement with simulations based on cubitainer rate estimates. The rate of limestone dissolution in the field appears to be slower than that indicated by the cubitainer tests.

In contrast, the field flux rates for the for Buck Mtn ALD are in agreement with trends indicated by simulations based on cubitainer data. The sharp peak at 4.5 years reflects the addition of 90 tonnes of limestone in January 2001.

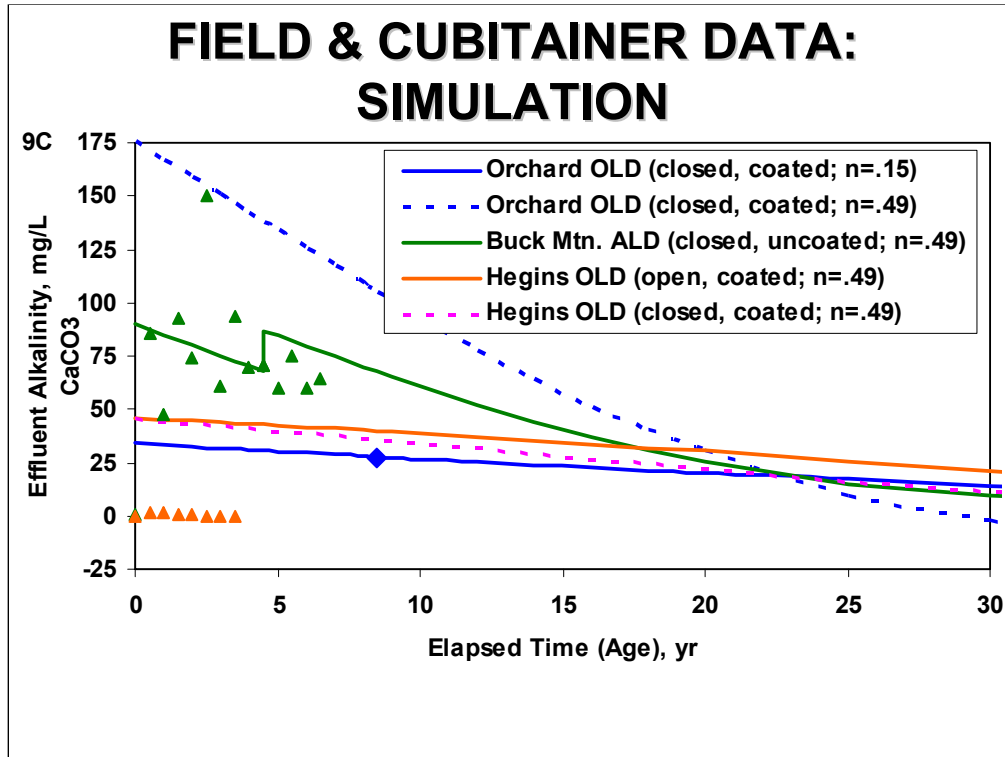
Because the Orchard OLD became clogged with debris, field data are insufficient to compare with simulations based on cubitainer data.



SIMULATIONS: 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.

Although the estimated detention times on the basis of semi-annual average flow rate are scattered widely, they bracket the simulated detention time for the same porosity. The scatter in observed data results from variability in actual flow rates over time. The simulations assume a constant flow rate based on the long-term average.

Note the effect of porosity on detention times as indicated by simulations for the Orchard OLD. Although initial porosity could be as large as 0.49, with clogging of the limestone bed, the porosity will decline. The alkalinity production rate will decrease with decreased porosity and detention time.



SIMULATIONS: 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.

Observed alkalinities for the Buck Mtn. ALD bracket the trends indicated by simulations based on cubitainer data. The scattering of observed values results from actual variations in flow rate and detention time.

For Hegins, the differences in observed alkalinities and the simulations based on cubitainer data indicate greater dissolution rates for cubitainer tests compared to actual field conditions. Large fragments of limestone were used to construct the Hegins OLD. However, a given mass of small particles will have more surface area than the same mass of large particles. Hence, the surface area of limestone relative to the solution volume is needed to compare rate data for different particle sizes in the cubitainers and field OLD.

## SIMULATIONS -- 3

- Refine simulations by adjusting for different surface area to volume ratio between cubitainer and field:
  - ✓ Normalized rate constant computed from overall rate constant, cubitainer solution volume, and substrate surface area in cubitainer ( $K = k \cdot (V/A)$ );
  - ✓ Surface area for ellipsoid particle used with porosity to estimate  $V/A$  for cubitainer and ALD/OLD.



SIMULATIONS 3: Refine simulations by adjusting for different surface area to volume ratio between cubitainer and field. Because a given mass of small particles will have more surface area than the same mass of large particles, the surface area of limestone relative to the solution volume is needed to compare rate data for different particle sizes. The rate data for a given mass of limestone can be adjusted for the surface area exposed:

Normalized rate constant computed from overall rate constant, cubitainer solution volume, and substrate surface area in cubitainer ( $K = k \cdot (V/A)$ );

Surface area for ellipsoid particle used with porosity (volume of voids) to estimate  $V/A$  for cubitainer and the corresponding (actual or proposed) ALD/OLD.



**GEOMETRIC SURFACE AREA OF CUBITAINER SUBSTRATE:** This slide shows subsets of 50 each of sieved, cleaned limestone samples from the Anville, Burkholder, and Ashcom Quarries in central Pennsylvania plus steel slag from stockpiles near Johnstown, Pennsylvania, that had been prepared for use in various cubitainer tests. The particle size used in the cubitainer tests is limited by the nominal 1-inch diameter of the cubitainer opening. Each particle was numbered, weighed, and marked for long, intermediate, and short axis, and the axis lengths were measured with calipers. The data were recorded in a spreadsheet for subsequent computations of surface area.

Additionally, to determine the substrate volume and density and the bulk volume and porosity, the particles were placed in a plastic beaker filled with a known volume of water. The volume of water displaced by the particles indicated the total volume of solids. Then, water was withdrawn to the minimum level sufficient to cover the particles completely. At this point, the bulk volume was indicated by that for the particles plus water, and the pore volume was indicated by the volume of water, only. The particle density was computed by the total mass of the particles divided by the total volume of solids. Now, the volume of individual particles could be computed by dividing the particle mass by the unit particle density.

Sample Identification		Weight (g)	Dimensions (cm)				Surface Area (cm <sup>2</sup> )			Unit Surface Area (cm <sup>2</sup> /g)		
Quarry Name	Sample #	Each Piece	Long Axis	Inter-mediate	Short Axis	Average Axis	Rectan-gular Prism	Sphere	Ellipsoid	Rectan-gular Prism	Sphere	Ellipsoid
Annvile	1	18.24	2.96	2.90	1.49	2.45	34.63	18.86	20.91	1.90	1.03	1.15
Annvile	2	17.77	3.16	2.08	1.70	2.31	30.96	16.81	21.15	1.74	0.95	1.19
Annvile	3	10.01	2.40	1.80	1.31	1.84	19.64	10.60	13.96	1.96	1.06	1.39
Annvile	48	9.93	3.03	2.14	1.19	2.12	25.27	14.12	15.40	2.55	1.42	1.55
Annvile	49	8.46	3.33	2.49	0.87	2.23	26.71	15.62	15.10	3.16	1.85	1.78
Annvile	50	11.09	3.27	2.80	0.80	2.29	28.02	16.47	16.93	2.53	1.49	1.53
<b>Average</b>		<b>13.42</b>	<b>3.23</b>	<b>2.13</b>	<b>1.31</b>	<b>2.23</b>	<b>27.82</b>	<b>15.73</b>	<b>18.46</b>	<b>2.18</b>	<b>1.24</b>	<b>1.44</b>
Sample Identification		Weight (g)	Dimensions (cm)				Surface Area (cm <sup>2</sup> )			Unit Surface Area (cm <sup>2</sup> /g)		
Quarry Name	Sample #	Each Piece	Long Axis	Inter-mediate	Short Axis	Average Axis	Rectan-gular Prism	Sphere	Ellipsoid	Rectan-gular Prism	Sphere	Ellipsoid
Burkolder	1	12.89	2.53	2.20	1.47	2.07	25.04	13.42	15.44	1.94	1.04	1.20
Burkolder	2	12.88	2.28	2.10	1.56	1.98	23.24	12.32	14.89	1.80	0.96	1.16
Burkolder	3	12.00	2.42	1.80	1.49	1.90	21.29	11.38	14.61	1.77	0.95	1.22
Burkolder	48	9.04	3.10	2.10	1.33	2.18	26.85	14.88	14.19	2.97	1.65	1.57
Burkolder	49	11.88	3.03	2.30	1.36	2.23	28.44	15.62	16.00	2.39	1.31	1.35
Burkolder	50	7.37	2.55	2.39	0.99	1.98	21.97	12.27	11.56	2.98	1.66	1.57
<b>Average</b>		<b>8.36</b>	<b>2.53</b>	<b>1.84</b>	<b>1.12</b>	<b>1.83</b>	<b>19.20</b>	<b>10.67</b>	<b>12.22</b>	<b>2.40</b>	<b>1.34</b>	<b>1.54</b>
Sample Identification		Weight (g)	Dimensions (cm)				Surface Area (cm <sup>2</sup> )			Unit Surface Area (cm <sup>2</sup> /g)		
Quarry Name	Sample #	Each Piece	Long Axis	Inter-mediate	Short Axis	Average Axis	Rectan-gular Prism	Sphere	Ellipsoid	Rectan-gular Prism	Sphere	Ellipsoid
Ashcom	1	8.22	3.00	1.76	1.08	1.95	20.84	11.91	14.09	2.53	1.45	1.71
Ashcom	2	11.06	3.50	2.08	1.01	2.20	25.83	15.16	17.73	2.34	1.37	1.60
Ashcom	3	16.15	3.15	2.04	1.40	2.20	27.38	15.16	20.27	1.70	0.94	1.26
Ashcom	48	6.32	2.86	1.80	0.90	1.85	18.68	10.79	12.10	2.96	1.71	1.91
Ashcom	49	9.08	2.76	1.89	1.00	1.88	19.73	11.14	14.18	2.17	1.23	1.56
Ashcom	50	8.05	2.20	1.91	1.18	1.76	18.10	9.77	12.12	2.25	1.21	1.51
<b>Average</b>		<b>12.37</b>	<b>2.46</b>	<b>2.17</b>	<b>1.17</b>	<b>2.17</b>	<b>26.28</b>	<b>15.06</b>	<b>17.66</b>	<b>2.28</b>	<b>1.33</b>	<b>1.63</b>

GEOMETRIC SURFACE AREA OF CUBITAINER SUBSTRATE: The measured dimensions, weight, and volume of 50 samples of the limestone substrates used in the cubitainer tests were used to estimate the unit surface area of each substrate. Three different geometries were considered: rectangular prism, sphere, and ellipsoidal sphere. An ellipsoidal sphere was assumed to best represent the particles shape because the particles were intermediate between rectangular and round. For a given total length of three axes (x+y+z), the unit surface area of an ellipsoidal sphere is intermediate between that for a rectangular prism and a sphere.

Assuming an ellipsoidal sphere as the geometry, the average unit surface area of Annville limestone used in tests for Orchard, Buck Mtn., and Hegin was 1.44 cm<sup>2</sup>/g.

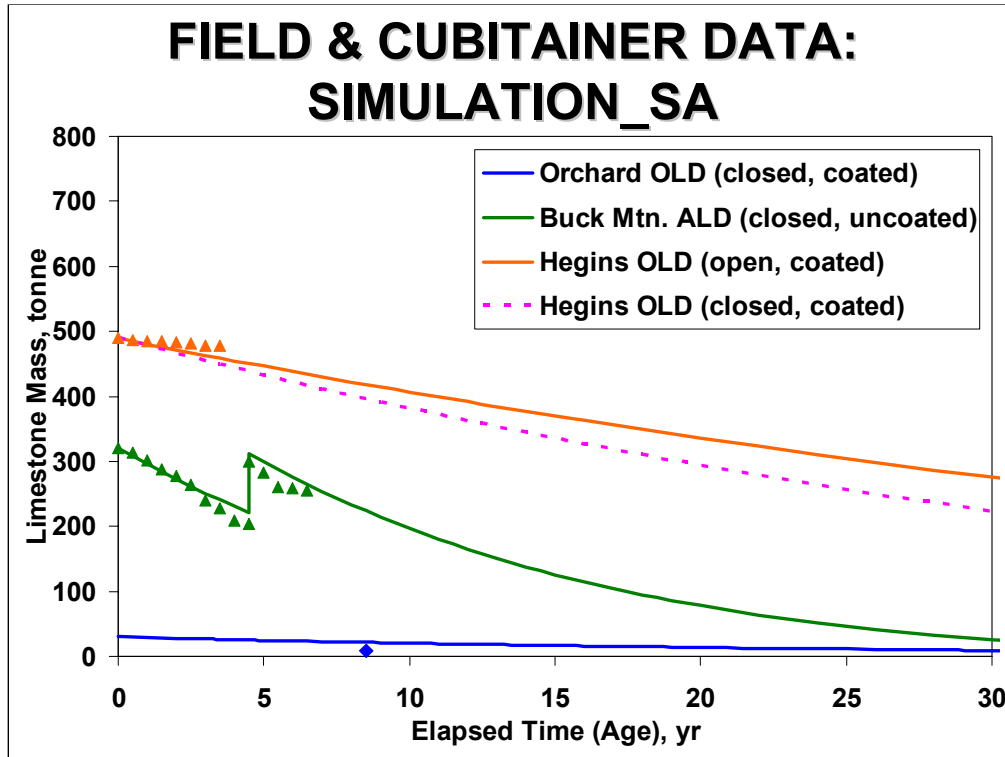


## SURFACE AREA OF AGGREGATE

Gradation Number		Weight (g)	Particle Dimensions (cm)				Particle Surface Area (cm <sup>2</sup> )			Unit Surface Area (cm <sup>2</sup> /g)			Ellipsoid Computations			
AASHTO	PA		Average Particle	Long Axis	Inter-mediate	Short Axis	Average Axis	Rectan-gular Prism	Sphere	Ellipsoid	Rectan-gular Prism	Sphere	Ellipsoid	Particle Volume	D	E
R-5		22160.145	45.72	22.86	13.34	27.31	3919.35	2342.26	2862.08	0.18	0.11	0.13	8362.32	25.18	1.82	0.70
R-4		7113.133	30.48	16.51	8.89	18.63	1841.93	1089.98	1319.11	0.26	0.15	0.19	2684.20	17.24	1.77	0.71
R-3		1185.522	16.51	8.89	5.08	10.16	551.61	324.29	395.61	0.47	0.27	0.33	447.37	9.49	1.74	0.72
1	4	341.978	8.89	6.35	3.81	6.35	229.03	126.68	155.24	0.67	0.37	0.45	129.05	6.27	1.42	0.80
3	3A	78.166	5.08	3.81	2.54	3.81	83.87	45.60	56.39	1.07	0.58	0.72	29.50	3.83	1.33	0.82
5		9.771	2.54	1.91	1.27	1.91	20.97	11.40	14.10	2.15	1.17	1.44	3.69	1.92	1.33	0.82
57	2B	3.257	2.54	1.27	0.635	1.48	11.29	6.90	8.25	3.47	2.12	2.53	1.23	1.33	1.91	0.67
	2 NS	9.771	2.54	1.91	1.27	1.91	20.97	11.40	14.10	2.15	1.17	1.44	3.69	1.92	1.33	0.82
67	2	1.832	1.91	0.95	0.635	1.16	7.26	4.26	5.28	3.96	2.32	2.88	0.69	1.10	1.74	0.72
Intermediate axis length was estimated to be the same as #50 stone size or where range overlapped value for 50 percent passing (e.g. 40-60).																
Short axis length was estimated to be the same or greater than the 0 percent passing size.																
Long axis length was estimated to be the size smaller than the 100 percent passing size.																
Weight and volume of average particle assumes particle density is 2.65 g/cm <sup>3</sup> and particle volume for ellipsoid is 60 percent of volume of rectangular prism (per Table2_CubitainerSamples).																
Surface area computed for various geometric forms:																
Sphere: $4\pi \times \text{Average of Axes}^2$																
Rectangular Prism: $2 \times (\text{Long Axis} \times \text{Short Axis}) + 2 \times (\text{Long Axis} \times \text{Intermediate Axis}) + 2 \times (\text{Short Axis} \times \text{Intermediate Axis})$																
Ellipsoid: $(\pi \times D^2) / S$ $D = 2 \times (\text{vol} / (4/3\pi))^{1/3}$ $S = 1.15 - 0.25E$ $E = \text{Long Axis} / D$																

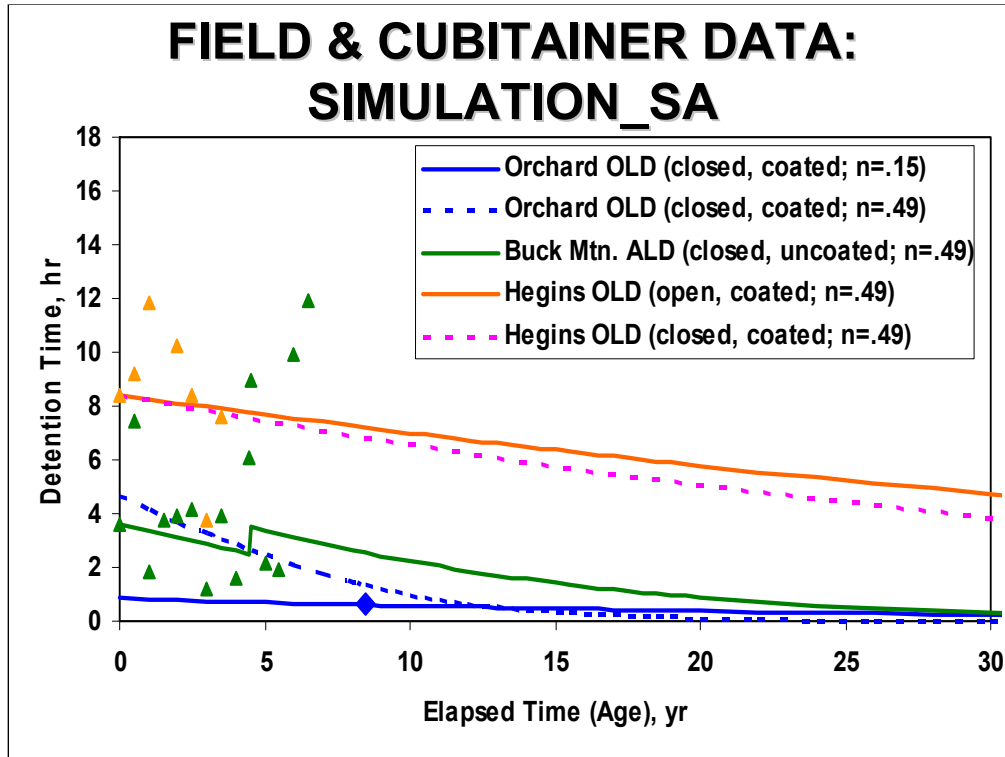
**SURFACE AREA OF AGGREGATE:** Particle size data for standard grades of aggregate as reported in the erosion and sedimentation manual of the Pennsylvania Department of Environmental Protection Agency (2000) were used to compile this table. The particle size of the sieved materials used in cubitainer tests corresponds with PA# 2NS aggregate highlighted in yellow. For PA# 2NS material, 100 percent of the particles will pass through a 1.5-inch screen, and none will pass through a 0.5-inch screen.

Based on reported on the basis of the short, intermediate, and long axis lengths above, the surface area for common gradations of aggregate used in limestone beds for AMD treatment is estimated assuming a specific shape. Generally, because the aggregate shapes are intermediate between a rectangular prism and a sphere, the ellipsoidal particle shape can be assumed applicable.



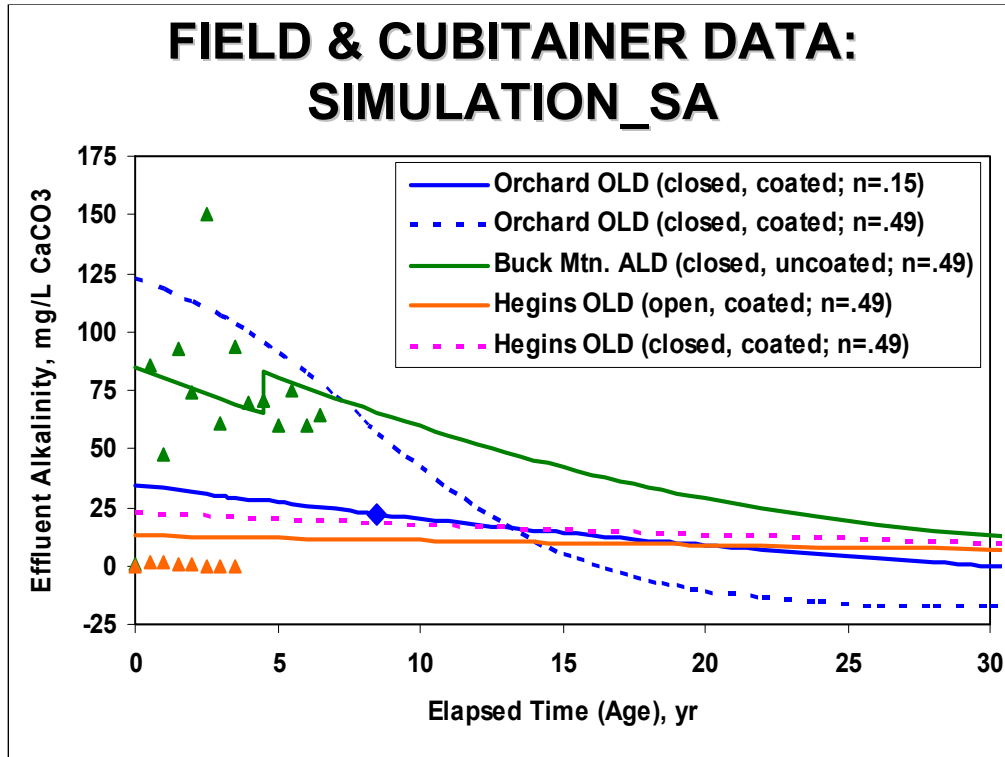
SIMULATIONS\_SA: Simulated decline in limestone mass, detention time, and alkalinity with age of Orchard, Buck Mtn., and Hegins limestone drains on the basis of cubitainer tests (first-order curves): *A*, Mass versus age considering normalized rate constant,  $K'$ , for dissolved Ca in cubitainers. *B*, 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 normalized 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.

Surface area of OLD/ALD estimated for AASHTO 3 for Orchard OLD and Buck Mtn. ALD and R-5 for Hegins OLD. Fluid volume computed assuming porosity of 0.49. Assuming only 2/3 inundated, exposed mass and surface area of Hegins OLD estimated as 2/3 total.



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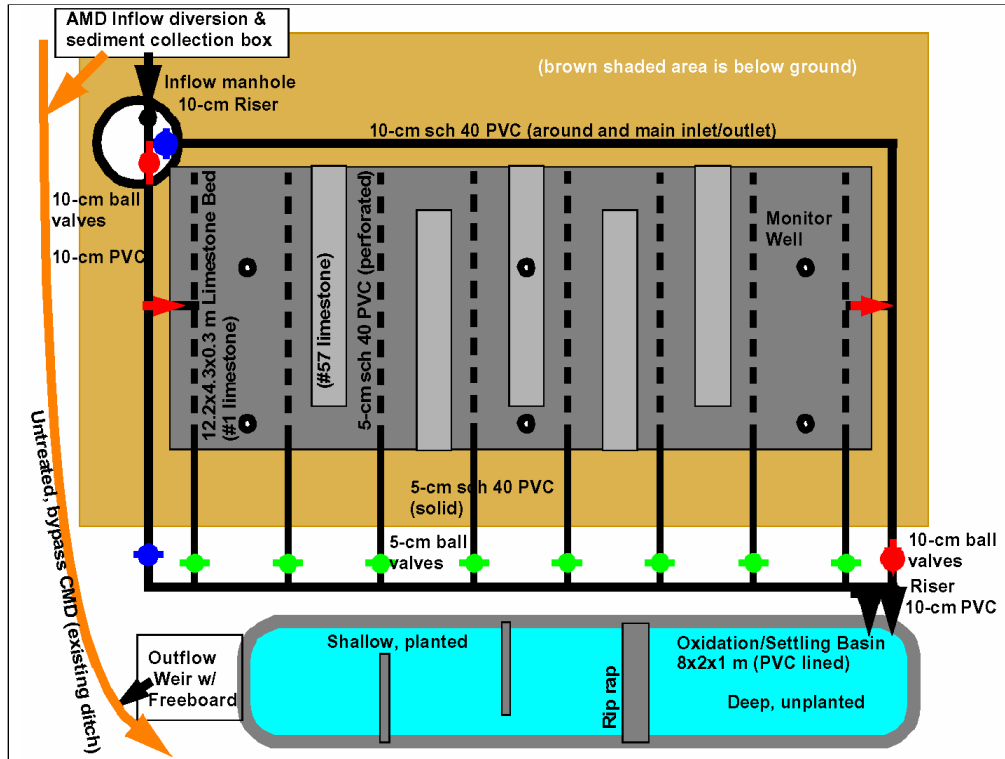


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Surface area of OLD/ALD estimated for AASHTO #3 for Orchard OLD and Buck Mtn. ALD and R-5 for Hegins OLD. Fluid volume computed assuming porosity of 0.49 or 0.15 as noted. Assuming only 2/3 inundated, exposed mass and surface area of Hegins OLD estimated as 2/3 total.



HEGINS TRACER TEST: Actual detention times were less than half of the estimated detention times based on flow rate and estimated fluid-filled void volume. 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.



FLUSHABLE OLD: 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).

## CONCLUSIONS

- Anoxic/oxic limestone drains can be effective for neutralizing acid *and* attenuating metals.
- In limestone drains and cubitainers:
  - ✓ Ca and alkalinity flux estimates indicate dissolution rate.
  - ✓ Limestone dissolution rate was greater under closed conditions than open conditions.
  - ✓ Limestone dissolution rate was not affected by Fe-coating; however, Al-coating may slow rate(?).

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## CONCLUSIONS

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- Performance of Swatara ALDs/OLDs can be improved:
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  - ✓ Burial of Hegins OLD with compost/soil.

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First-order rate models based on “short-term” cubitainer tests can be used to determine size and future performance of limestone drain.

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