

# A METHOD FOR PREDICTING THE ALKALINITY GENERATED BY ANOXIC LIMESTONE DRAINS

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## ABSTRACT

A method has been developed to predict the alkalinity generated by anoxic limestone drains (ALDs) using a specific mine water and a selected limestone material. Collapsible, 3.8-liter (1.0 gal) containers were loaded with limestone, filled with untreated mine water, and the generation of alkalinity was monitored by periodic extraction of water samples. In order to determine the predictive capabilities of this method, tests were conducted at two ALD sites where samples of untreated mine water were available. After two days of contact between untreated water and limestone, mean alkalinity concentrations within the experimental containers were within 6% of the actual alkalinity concentrations in the respective ALD effluents. This experimental method was used to compare alkalinity generation of seven carbonate rocks with differing compositions and two different mine waters. Generation of alkalinity within the experimental containers was similar for all of the limestones tested within each of the mine waters. Dolomite generated significantly less alkalinity than limestone. After two days of contact between mine water and carbonate rock, dolomite generated only 50 percent of the alkalinity that was generated by limestone. The two mine waters generated significantly different alkalinity concentrations in the experimental containers containing the similar limestones indicating that the chemistry of the untreated mine water plays an important role in alkalinity generation.

## INTRODUCTION

The treatment of acid mine drainage (AMD) can be an expensive long-term problem for the mining industry. Furthermore, AMD from abandoned mined lands often goes untreated, contaminating thousands of miles of streams and rivers. Recently, there has been much interest in passive forms of AMD treatment. Effective passive treatment can lower treatment costs and allow inexpensive, low maintenance treatment at many abandoned mine sites that otherwise would be left untreated.

In the past ten years, hundreds of wetland systems have been constructed to treat AMD. The performance of these constructed wetlands are generally most effective when the raw water contains alkalinity. The wetland then functions as an area for metal oxidation, hydrolysis, and settling. The acidity produced by metal hydrolysis reactions is neutralized by the influent alkalinity. The successful treatment of acidic mine waters requires the generation of alkalinity within the wetland. One way alkalinity is generated in a wetland is through the dissolution of limestone that placed in the bottom of the wetland. The majority of the water in existing wetlands does not actively flow through this limestone, therefore the addition of alkalinity to the acidic surface water is limited by diffusion processes. Alkalinity may also be generated in a wetland through bacterial sulfate reduction. Because the addition of alkalinity by diffusion and sulfate reduction in these systems is slow, the wetland area needed to treat contaminated acidic water is generally 5-7 times larger than for equally contaminated alkaline mine water (Hedin and Nairn, 1993).

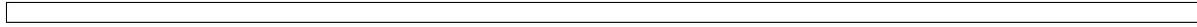
An alternative method for adding alkalinity to acidic water is through its direct contact with limestone. Limestone is readily available in coal mining areas and has considerable cost advantage over other alkaline materials. However, limestone is rarely used in conventional treatment systems because of its limited solubility and its tendency to armor with ferric hydroxide precipitates under atmospheric conditions. Recently, Turner and McCoy (1990) demonstrated the passive use of limestone in two systems where acidic water contacted limestone in a buried anoxic environment. The water discharging from these anoxic limestone drains (ALDs) was alkaline. The metal contaminants (Fe and Mn) rapidly precipitated in wetlands constructed immediately downflow of the ALD discharges.

Since Turner and McCoy reported their findings, dozens of ALDs have been constructed in Appalachia (Nairn et al., 1991; Brodie et al., 1991; Skousen and Faulkner, 1992). The performance of these systems has varied considerably. Some ALDs consistently discharge water with concentrations of alkalinity greater than 250 mg/L (Nairn et al., 1991; Nairn et al., 1992). However, many ALDs that appear to have been properly designed and sized, discharge water with concentrations of alkalinity less than 200 mg/L. This variation in alkalinity generation by ALDs adds considerable uncertainty to the design of passive treatment systems.

This paper describes a method for predicting the alkalinity that will be produced if an acidic mine water is treated with an ALD. Untreated mine water is placed in plastic containers that contain limestone or dolomite gravel. Water samples are periodically withdrawn from these containers and concentrations of alkalinity are measured. Anoxic conditions are maintained within the containers at all times. The results of three experiments are described. The first experiment was conducted at the Howe Bridge site to evaluate the suitability of the method by determining whether the generation of alkalinity within the containers simulated ALD performance. It also provided an estimate of the variability of alkalinity generation in three replicate containers. The second experiment utilized the containerized method to determine alkalinity generation by five different limestones in contact with water collected from the Howe Bridge site. The third experiment utilized the containerized method to determine alkalinity generation by six different limestones and one dolomite in contact with water collected from the Morrison site.

## METHODS

All experiments were conducted with 3.8-L (1.0 gal) capacity, cube-shaped, collapsible, low-density polyethylene containers which, hereafter, will be referred to as "cubitainers"\*. The caps of the cubitainers were modified to facilitate the filling of the containers with mine water and the anoxic sampling of water. Figure I is a schematic of this experimental apparatus.



\*Reference to specific products does not imply endorsement by the Bureau of Mines



All containers were filled with 4.0 kg of limestone or dolomite. The stone was sized to 1.3 cm x 3.5 cm (1/2 inch x 1-3/8 inch) and thoroughly rinsed with water to remove fines prior to being loaded in the cubitainers. This mass of limestone filled approximately 2/3 of the cubitainer volume.

All containers were tightly capped prior to filling with the untreated mine water in the field. Untreated mine water was pumped into the limestone-filled containers via the tubing that extended into the limestone until water overflowed the cubitainer through the other tubing for at least one minute. Care was taken to remove all air bubbles from the cubitainers. Immediately after filling, the cubitainers were placed in a plastic tub which was positioned under the effluent of the ALD. This placement ensured that the water temperature within the containers was similar to that within the ALD.

Water samples were collected from the cubitainers using a 60-ml plastic syringe. The syringe was affixed to the 3-way valve that was attached to gas-impermeable tubing that extended halfway into the cubitainer. Approximately 10 mL (about 3 tubing volumes) were collected and discarded. An additional 30 mL were collected, filtered (0.22 micron syringe filter), and immediately analyzed for alkalinity. The use of collapsible containers eliminated the need to replace the sampled volume.

Alkalinity determinations were made by titration with 0.10 N  $H_2SO_4$  to pH 4.5 (American Public Health Association, 1985) or by use of the Orion Total Alkalinity Kit (Orion Research Inc., Boston MA 02129). The alkalinity measured by the Orion method correlated closely to the alkalinity measured by the standard titration method (Orion Method = 0.97 x Titration Method - 1.66;  $r = 0.99$ ,  $n = 12$ ).

The first experiment was conducted at the Howe Bridge site in Jefferson County, PA. Mine water at the Howe Bridge site flows from an abandoned exploration well through a 15-meter (50 ft) long section of PVC pipe and into an anoxic limestone drain. A sampling port in the PVC pipe allows for the collection of raw mine water before it contacts the limestone. Three cubitainers, each containing the limestone that was used in the construction of the Howe Bridge ALD, were filled with raw mine water. Concentrations of alkalinity within the cubitainers were measured 11 times during the 72-hour period following their filling with mine water.

The second experiment also utilized the Howe Bridge mine water, but investigated the role of different limestone sources on alkalinity generation. Ten cubitainers containing five

different limestones were filled with untreated mine water (each limestone was tested in duplicate). Concentrations of alkalinity within the cubitainers were monitored for 11 days. The chemical composition of the untreated mine water used in this experiment are shown in table 1. The carbonate compositions of the five limestones used in this experiment are shown in table 2.

The third experiment was conducted at the Morrison ALD site in Clarion County. An ALD was constructed at this site to intercept seepage from the outslope of a reclaimed surface mine. A small volume of this seepage is not collected by the ALD and was used to represent the untreated mine water at this site. Fourteen cubitainers, containing the same five limestones that were tested in experiment #2 plus one additional limestone and one dolomite, were filled with untreated mine water (each stone was tested in duplicate). The carbonate compositions of the six limestones and single dolomite used in the experiment are shown in table 2. Concentrations of alkalinity within the cubitainers were monitored for 11 days. The chemical composition of the untreated mine water used in this experiment is shown in table 1.

## RESULTS

For experiment #1, concentrations of alkalinity increased with time in all three cubitainers (figure 2). There was little variation between the replicate containers. The coefficient of variation (standard deviation/mean) of alkalinity concentrations at each of the eleven sampled time intervals averaged 5.3% and ranged from 0.7% to 10.1%. In all cubitainers, changes in concentrations of alkalinity were greatest during the first 24 hours. After 48 hours, alkalinity values in each cubitainer plateaued **between 190 and 220 mg/L**. These values corresponded satisfactorily with the generation of alkalinity by the ALD. During our experiment, the Howe Bridge ALD discharged water that contained an average of 190 mg/L of alkalinity.

Results of experiments #2 and #3 are shown in figures 3 and 4, respectively. In all cases, variation in concentrations between duplicate containers was low. At both sites, concentrations of alkalinity increased rapidly during the first two days, and then increased at a much slower rate during the next nine days. At both sites, there was little difference in generation of alkalinity by different limestones. At the Howe Bridge site, where only limestones were tested, all containers generated similar concentrations of alkalinity. At the Morrison site, the six limestones displayed similar patterns of alkalinity generation. Containers containing dolomite, however, had consistently lower concentrations of alkalinity than the limestones (figure 4).

Cubitainers that contained mine water from the Morrison site produced higher concentrations of alkalinity than ones that contained mine water from the Howe Bridge site. The differences were apparent at all sampling time periods (table 3), and were independent of the type of limestone (table 2). At the cessation of the experiments (11 days), cubitainers containing limestone and Howe Bridge mine water had an average alkalinity of 206 mg/L, while containers containing limestone and the Morrison mine water averaged 333 mg/L of alkalinity. Variation between the concentrations of alkalinity produced by the two mine waters corresponds to the differences in performance by the anoxic limestone drains at the sites. During the second experiment, the effluent of the Howe Bridge ALD averaged 169

mg/L alkalinity, while the effluent of the Morrison ALD averaged 294 mg/L alkalinity (table 3).

## DISCUSSION

The cubitainer method described in this paper was found to generate concentrations of alkalinity that were similar to those observed in ALDs that received the same water and contained similar limestone. The correspondence between concentrations of alkalinity generated in cubitainers and those measured in ALD effluents was best after a 2-day contact period (table 3). In all of the experiments, the mean concentrations of alkalinity after 2 days were within 6% of the concentrations of alkalinity produced by the respective ALDs effluents during the testing period. The fact that alkalinity concentrations in the cubitainers after a 2-day period most closely corresponded to actual alkalinity concentrations in the ALD effluents is partly a result of the design of the ALD simulator: 3.8-L (1 gal) plastic containers containing 4 kg (8.8 lbs) of limestone gravel, sized to 1.3 cm x 3.5 cm (1/2 inch x 1-3/8 inch), and filled to capacity with untreated mine water. Different ratios of water:stone volume and different limestone sizes would likely result in different rates of alkalinity generation, although the concentration of alkalinity after long periods of time (at or near equilibrium) should be similar.

Turner and McCoy (1990) emphasized the use of high-calcium limestones. The results of the container experiments are in general agreement with these recommendations. The six limestones tested dissolved much faster than the single dolomite tested. Within the limestone category, however, we found no correlation between the calcium content of the rock and the generation of alkalinity (table 2). Note, however, that the limestone with the lowest calcium carbonate content (82%), generated the lowest levels of alkalinity at both of the sites.

The most significant factor that influenced the generation of alkalinity in these experiments was the mine water. All limestones, when exposed to the untreated mine water from the Morrison site, generated more alkalinity than when exposed to the untreated mine water from the Howe Bridge site (table 2). It is unclear at this time what aspects of the mine water chemistry are responsible for this difference in alkalinity generation. Both waters tested are contaminated with high concentrations of ferrous iron and manganese (table 1). The mine waters have similar ionic strengths and similar concentrations of sulfate. The Morrison water has CO<sub>2</sub> partial pressures that were estimated by WATEQ4F (Ball et al., 1987) to be 65% higher than the Howe Bridge water. Because both the equilibrium concentrations of bicarbonate alkalinity and the kinetics of limestone dissolution are directly related to CO<sub>2</sub> partial pressures (Hem, 1985; Berner and Morse, 1974), we suspect that this parameter may be very significant.

The cubitainer experiments described in this paper were not designed to simulate the *kinetics* of alkalinity generation in ALDs. The kinetics of limestone dissolution in the static cubitainers are controlled, in part, by the diffusion of ions between the carbonate surface and the bulk water solution. The experiments described here had a larger water:stone volume ratio than exists in ALDs (i.e. the cubitainers were not completely filled with limestone). The larger water:stone volume ratio of these cubitainer experiments was an intentional feature that allowed the repeated sampling of water without markedly

decreasing the volume of water contained in the containers. Recently, we have initiated experiments that utilize containers completely filled with limestone, thereby, simulating a water:stone volume ratio equal to that found in ALDs. The current experiments are expected to better simulate the kinetics of alkalinity generation in ALDs.

## SUMMARY

Prior to this research, there has been no method for predicting the alkalinity that will be generated in mine water flowing through a proposed anoxic limestone drain. The results of these experiments indicate that the method described in this paper has significant predictive capability for mine waters tested in this study. The contact of mine water with limestone in a plastic container under anoxic conditions results in concentrations of alkalinity that are similar to those produced by the ALDs that receive and treat the same raw mine water. Research is continuing to test this method on a wider range of mine water quality.

## LITERATURE CITED

American Public Health Association. 1985. Standard Methods for the Examination of Water and Wastewater. Washington, DC, 1985, 1268 pp.

Bal 1 , J. W. , D. K. Nordstrom and D. W. Zackmann. 1987. WATEQ4F - a personal computer translation of the geochemical model WATEQ2 with revised database. U.S. Geol. Survey Open File Report 87-50.

Berner, R. A. and J. W. Morse. 1974. Dissolution kinetics of calcium carbonate in sea water, part IV: theory of calcite dissolution. Amer. J. Sci., 274: 108134.

Brodie, G.A., C.R. Britt, T.M. Tomaszewski and H.N. Taylor. 1991. Use of passive anoxic limestone drains to enhance performance of acid drainage treatment wetlands. Paper in Proceedings Reclamation 2000: Technologies for Success, Durango, CO, ed. by W. Oaks and J. Bowden, ASSMR, Princeton, WV, pp. 211-222.

Hedin, R. S. and R. W. Nairn. 1993. Contaminant removal capabilities of wetlands constructed to treat coal mine drainage. Paper in Constructed Wetlands for Water Quality Improvement. ed. by G. A. Moshiri, Lewis Publishers, Chelsea, mi.

Hem, J. D. 1985. Study and Interpretation of the Chemical Characteristics of Natural Water, 3rd Edition. U.S. Geological Survey Water Supply Paper 2254, 263 PP.

Nairn, R. W., R. S. Hedin and G. R. Watzlaf. 1991. A Preliminary review of the use of anoxic limestone drains in the passive treatment of acid mine drainage. Paper in Proceedings of the 12th Annual West Virginia Surface Mine Drainage Task Force Symposium, Morgantown, WV.

Nairn, R. W., R. S. Hedin and G. R. Watzlaf. 1992. Generation of alkalinity in an anoxic limestone drain. Paper in Achieving Land Use Potential Through Reclamation, Proceedings of the 9th National American Society for Surface Mining and Reclamation Meeting, ASSMR, Princeton, WV, pp. 206-219.

Skousen, J. and B. Faulkner. 1992. Preliminary results of acid mine drainage treatment with anoxic limestone drains in West Virginia. Paper in Proceedings of the 13th Annual West Virginia Surface Mining Drainage Task Force Symposium, Morgantown, WV.

Turner, O. and D. McCoy. 1990. Anoxic alkaline drain treatment system, a low cost acid mine drainage treatment alternative. Paper in Proceedings of the 1990 National Symposium on Mining, Lexington, KY, ed. by D.H. Graves and R.W. De Vore, pp. 73-75.

Table 1. Water quality of untreated mine water used in cubitainer experiments.

Parameters	Howe Bridge	Morrison
pH, standard units	5.73	5.42
Alkalinity, mg/L as CaCO <sub>3</sub>	39	29
Acidity, mg/L as CaCO <sub>3</sub>	516	460
Ferrous Iron, mg/L	267	239
Total Iron, mg/L	267	239
Aluminum, mg/L	<1	<1
Manganese, mg/L	39	58
Calcium, mg/L	153	132
Magnesium, mg/L	102	143
Sodium, mg/L	11	54
Sulfate, mg/L	1290	1490
Temperature, °C	14	16
CO <sub>2</sub> Partial Pressure*, atm	10 <sup>-1.24</sup>	10 <sup>-1.05</sup>

\* calculated using WATEQ4F (Ball et al., 1987)

Table 2. Alkalinity concentrations (in mg/L as CaCO<sub>3</sub>) in cubitainers containing different stone types after a 2-day contact period.

Stone Information <sup>*</sup>				Alkalinity <sup>#</sup>	
Quarry Location (County, State)	Formation	MgCO <sub>3</sub> (%)	CaCO <sub>3</sub> (%)	Howe Bridge	Morrison
Butler, PA (a)	Vanport	1.4	91	187	320
Butler, PA (b)	Vanport	1.1	92	nt	315
Westmoreland, PA	Loyalhanna	na	94	172	283
Armstrong, PA	Vanport	1.4	94	183	300
Washington, MD	St. Paul	0.4	99	167	285
Centre, PA	Bellefonte	4.5	82	157	275
Blair, PA	Bellefonte (dolomite)	38	46	nt	149

\* Percentages of MgCO<sub>3</sub> and CaCO<sub>3</sub> provided by companies that supplied the stone. Letters in parentheses used for differentiation. "na" = not available.

# "nt" indicates that these stones were not tested at the Howe Bridge site.

Table 3. Comparison of alkalinity concentrations (in mg/L as CaCO<sub>3</sub>) in ALD effluents and in cubitainers after incubation for 1, 2, 3, 4, and 11 days.

Test	Site	Alkalinity concentration in ALD discharge	Mean alkalinity concentration after selected times (days) in cubitainers filled with limestone				
			1	2	3	4	11
#1	Howe Bridge	190	134	201	218	-	-
#2	Howe Bridge	169	130	173	-	201	206
#3	Morrison	294	247	296	-	323	333

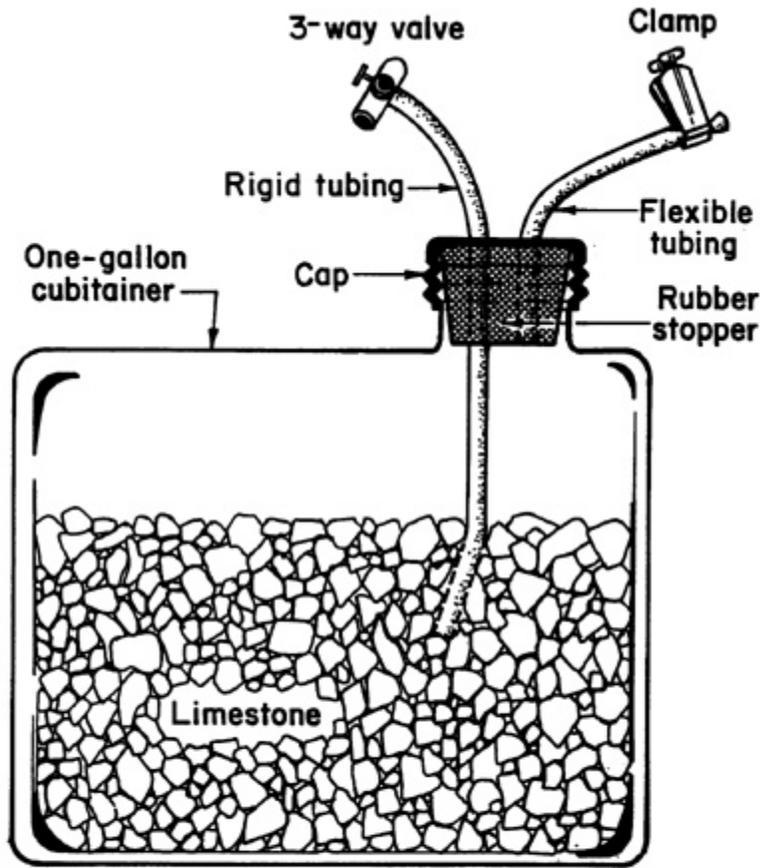


Figure 1. Schematic of cubitainer setup. Limestone sized to 1.3 cm x 3.5 cm (1/2 inch x 1-3/8 inch). All tubing is gas impermeable.

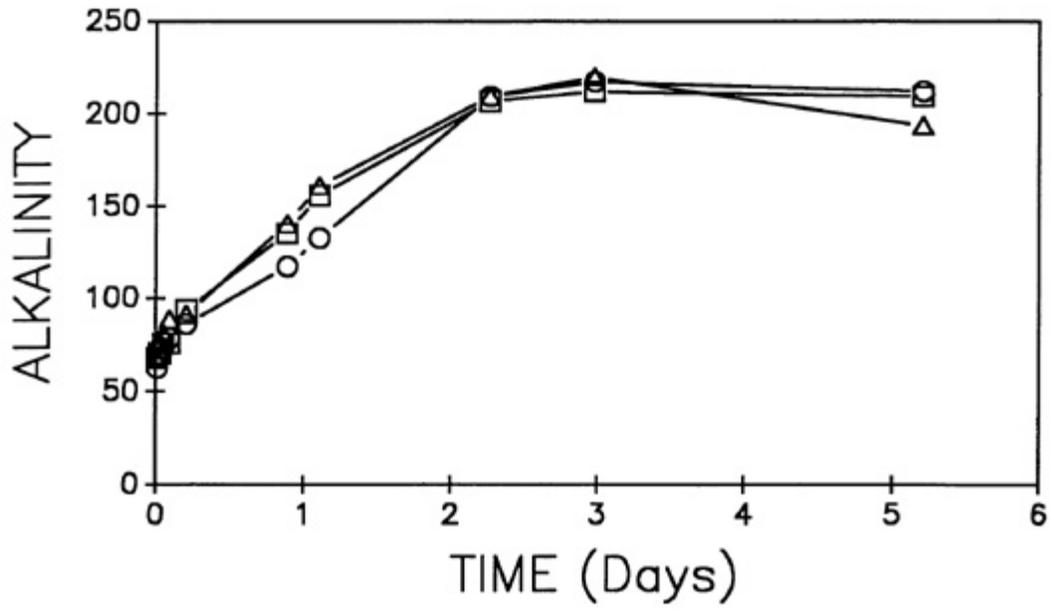


Figure 2. Alkalinity concentrations (mg/L as CaCO<sub>3</sub>) in three replicate cubitainers for experiment #1 at the Howe Bridge site.

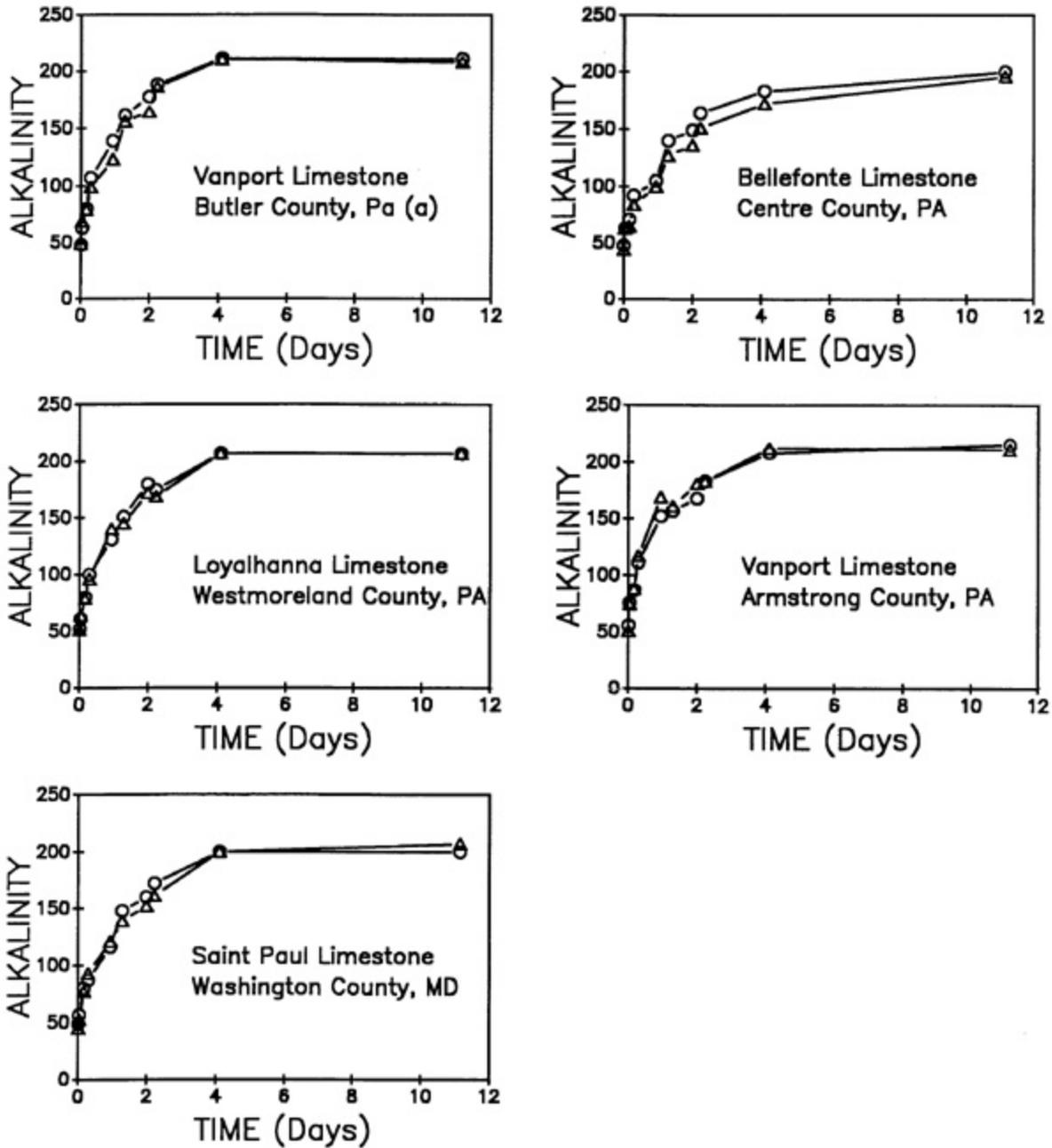


Figure 3. Alkalinity concentrations (mg/L as CaCO<sub>3</sub>) generated by five different limestone types for experiment #2 at the Howe Bridge site. Each graph plots the alkalinity concentrations in each of the duplicate cubitainers.

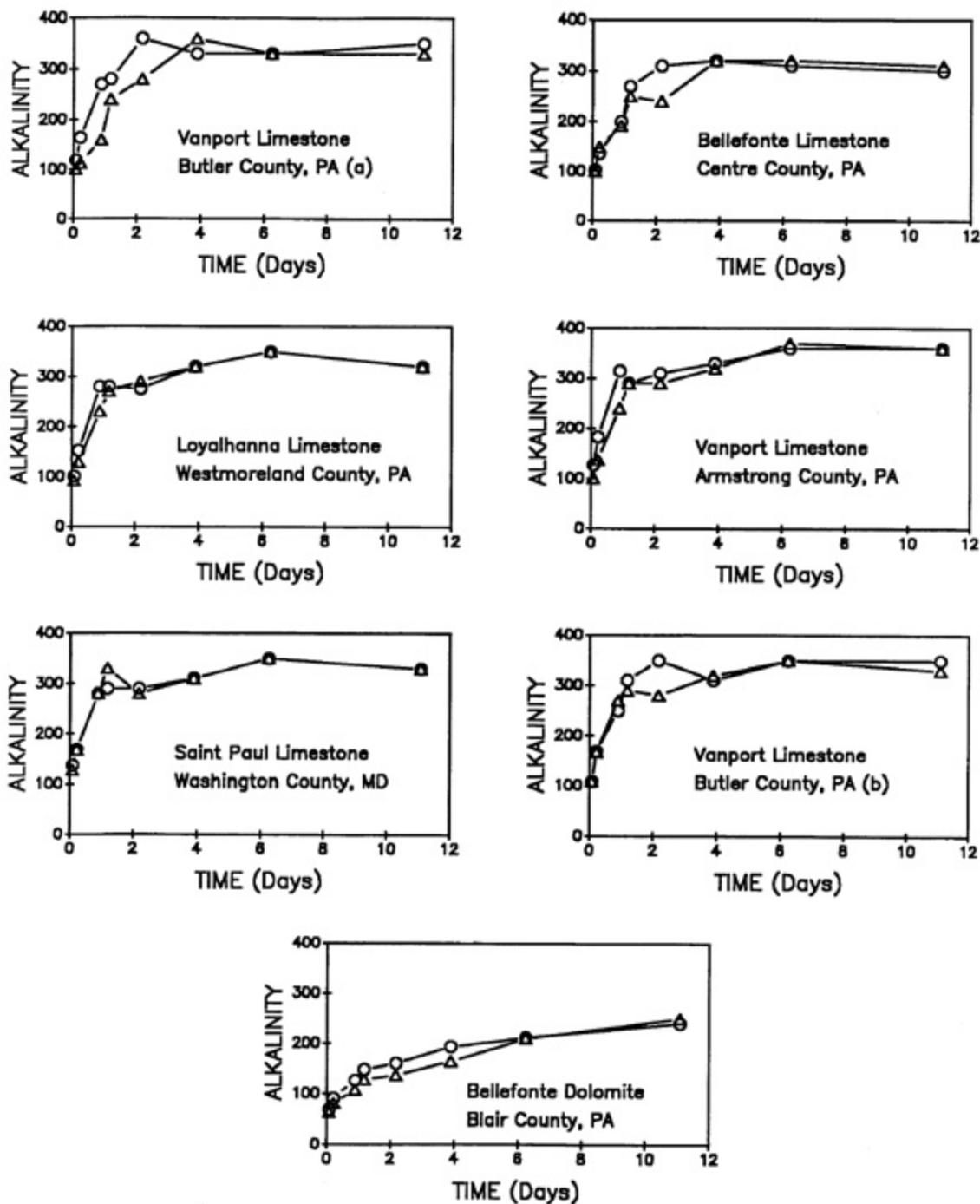


Figure 4. Alkalinity concentrations (mg/L as CaCO<sub>3</sub>) generated by six different limestone types and one dolomite for experiment #3 at the Morisson site. Each graph plots the alkalinity concentrations in each of the duplicate cubitainers.