

GENERATION OF ALKALINITY IN AN ANOXIC LIMESTONE DRAIN¹

by

Robert W. Nairn, Robert S. Hedin
and George R. Watzlaf²

Abstract. The rate of limestone dissolution and alkalinity generation in an anoxic limestone drain is determined by many factors, including the quality of the limestone used and the partial pressure of carbon dioxide within the system. Carbon dioxide concentrations greater than 600 times atmospheric levels have been found within an anoxic limestone drain located in northwestern Pennsylvania. This situation greatly increases the solubility of limestone, making elevated alkalinity concentrations possible. Before construction of the drain, the mine drainage contained over 400 mg/L acidity as CaCO₃ equivalent but alkalinity concentrations of more than 300 mg/L have been found at the exit of the drain. Alkalinity generation rates of approximately 117 grams of alkalinity (as CaCO₃ eq.) meter⁻³ of drain (bulk volume) day⁻¹ have been determined for this system. The anoxic limestone drain discharges the mine water into a settling pond-constructed wetland system where metal oxidation, hydrolysis and precipitation occurs in a strongly buffered, alkaline solution. The use of the anoxic limestone drain resulted in substantial cost savings compared to conventional chemical treatment of this drainage.

Additional Key Words: calcium carbonate, carbon dioxide, solubility, dissolution.

¹Paper presented at the 1992 National Meeting of the American Society for Surface Mining and Reclamation, Duluth, Minnesota, June 14-18, 1992. Publication in this proceedings does not preclude authors from publishing their manuscripts, whole or in part, in other publication outlets.

²Robert W. Nairn and Robert S. Hedin are Research Biologists and George R. Watzlaf is an Environmental Engineer, U.S. Department of the Interior, Bureau of Mines, Pittsburgh, PA 15236.

Proceedings America Society of Mining and Reclamation, 1992 pp 206-219
DOI: 10.21000/JASMR92010206

Introduction

Conventional treatment of acid mine drainage (AMD) involves the addition of costly alkaline chemicals, which neutralize acidity and raise pH, causing the metals to precipitate in settling ponds (Skousen et al. 1990). The chemicals typically used in the treatment of AMD are calcium hydroxide ($\text{Ca}(\text{OH})_2$), calcium oxide (CaO), sodium carbonate (Na_2CO_3), sodium hydroxide (NaOH) and ammonia (NH_3). The operation of a chemical treatment system may require the expenditure of hundreds of thousands of dollars per year. In addition, improper use of the treatment chemicals can be hazardous to the user, and accidental overtreatment can be environmentally devastating to the receiving stream. Due to these prohibitive costs and long-term operation and maintenance commitments, discharges from abandoned mines often flow unabated into receiving streams.

In addition to these chemical options, limestone (calcium carbonate, CaCO_3) has been used in AMD treatment with variable success. When limestone contacts acidic water, it dissolves and produces dissolved calcium and bicarbonate alkalinity. The alkalinity neutralizes mineral acidity and buffers against decreases in pH. The advantages of limestone treatment include: an increase in sludge density, with a corresponding decrease in sludge volume; lower potential for overtreatment, few safety problems and low costs per unit weight of reagent necessary to treat a given acidity (US EPA 1971). However, armoring reactions that inhibit limestone dissolution rates prevent its widespread use in the treatment of AMD (Wentzler and Aplan 1972, US EPA 1983). When mine waters containing appreciable amounts of iron contact limestone in an oxidizing environment, the limestone is coated rapidly with ferric hydroxide precipitates. The rate of dissolution is inhibited and the production of alkalinity virtually ceases. Despite

this problem, attempts have been made to utilize limestone in AMD treatment. Glover (1967) and Hill and Wilmoth (1971) examined the use of stationary beds, fluidized beds, and tumblers. Mihok et al. (1968) investigated the use of a rotating vessel to produce a limestone slurry that was injected into AMD. Despite these studies, limestone is rarely used in active treatment systems due to the prohibitively high maintenance and operation costs required to ensure that armoring does not occur.

The dissolution of limestone under anoxic conditions (in the absence of oxygen), however, may provide a means for its use in AMD treatment. If AMD contacts limestone in an anoxic environment, the dissolution and subsequent production of alkalinity can proceed without inhibitory armoring. Recently, the idea of generating alkalinity in anoxic limestone drains has gained attention in the mining community (Turner and McCoy 1990, Brodie et al. 1991, Nairn et al. 1991, Skousen 1991). The basic design and construction principles for anoxic limestone drains are relatively simple. An excavation is made to intercept acid seep waters within a surface mine spoil or at an underground mine adit. The excavation is filled with high quality limestone ($> 90\% \text{CaCO}_3$) which is covered with plastic and clay to inhibit oxygen penetration and the loss of carbon dioxide. The anoxic environment allows the limestone to dissolve, but inhibits the oxidation of iron and thereby eliminates armoring. The water exiting a drain is charged with alkalinity but still contains elevated levels of dissolved iron and manganese. After exiting, the water is aerated and metal oxidation, hydrolysis and precipitation occurs in a strongly-buffered, alkaline solution in a settling pond or constructed wetland.

In this paper, the operation of an anoxic limestone drain for the first year after construction is evaluated by the Bureau of Mines. Water quality data

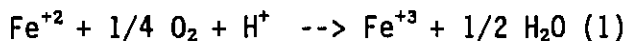
were obtained from within the drain and at its exit. Gas composition within the drain was determined. Factors affecting the generation of alkalinity in the drain are discussed. Calculated alkalinity generation rates allow a preliminary evaluation of the performance of the drain. The effect of the drain upon both the raw water quality and the performance of the downflow passive treatment system is summarized.

Background

The following discussion presents the various chemical processes important to the function of anoxic limestone drains. Fundamental features of both AMD chemistry and carbonate chemistry are discussed.

Relevant AMD Chemistry

Soluble iron is found in two forms in AMD: reduced ferrous iron (Fe^{+2}) or oxidized ferric iron (Fe^{+3}). Ferrous iron is soluble in the pH range encountered in most mine drainage (pH 2-8). In the presence of oxygen, however, ferrous iron quickly oxidizes to ferric iron (1). The oxidation reaction is bacterially catalyzed at pH < 4 but is primarily abiotic at higher pH. At pH > 3.5, ferric iron quickly hydrolyzes and produces a ferric hydroxide ($\text{Fe}(\text{OH})_3$) precipitate (commonly known as "yellowboy") and proton acidity (2). Proton acidity will lower pH unless sufficiently buffered by alkalinity. Note that the iron hydrolysis reaction (2) requires only water and not oxygen.



If limestone is introduced to AMD in an oxidizing environment, its dissolution will initially raise the pH to circumneutral levels (pH 6-8). Ferrous iron will rapidly oxidize (1) and ferric iron will then hydrolyze (2). The limestone quickly armors with

$\text{Fe}(\text{OH})_3$ and is rendered useless. This also occurs if the AMD already contains dissolved ferric iron (Fe^{+3}). Thus, as the limestone dissolves, it is creating the perfect environment to prevent its further dissolution. However, if AMD can be intercepted by an anoxic limestone drain before iron oxidation occurs, the limestone can dissolve and alkalinity can be introduced without armoring.

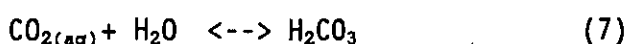
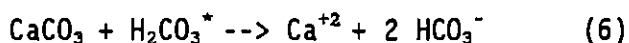
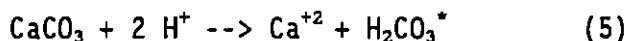
It is important to note that the precipitation of compounds other than iron hydroxides may also prove important in the long-term operation of anoxic limestone drains. For example, aluminum occurs as soluble Al^{+3} in AMD, and can hydrolyze and precipitate without an oxidation step (3). Aluminum will precipitate at pH > 4. Therefore, the neutral pH environment within a drain, although anoxic, will cause aluminum hydroxide precipitation. Also, for AMD with sufficiently high sulfate concentrations, calcium sulfate ($\text{CaSO}_4 + 2\text{H}_2\text{O}$, gypsum) precipitation could occur in an anoxic limestone drain (4).



Carbonate Dissolution

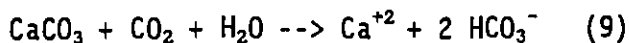
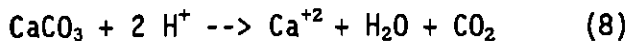
The carbonate system is the most important buffering system in natural waters, as well as one of the most complex (Snoeyink and Jenkins 1980). The chemical species that make up the carbonate system include gaseous carbon dioxide (CO_2), dissolved or aqueous carbon dioxide ($\text{CO}_{2(\text{aq})}$), carbonic acid (H_2CO_3), bicarbonate (HCO_3^-), carbonate (CO_3^-), and carbonate-containing solids such as CaCO_3 . The dissolution of limestone is known to be a surface process (Plummer et al. 1979, Sverdrup and Warfvinge 1985). The reaction sequence for carbonate dissolution in acid waters, as described by Cravotta et al. (1990), will be the basis for the following discussion.

When acid waters contact limestone, the limestone dissolves and produces dissolved calcium and dissolved carbon dioxide (5). Dissolved CO₂ is a weak acid and continues to react with limestone, producing dissolved calcium and bicarbonate alkalinity (6). The conventional notation for dissolved CO₂ is "H₂CO₃^{*}", and includes both CO_{2(aq)} and carbonic acid (Stumm and Morgan 1981). This relationship is shown in reaction (7).



The bicarbonate alkalinity produced in reaction (6) is available for acid neutralization reactions. When reactions (1) and (2) occur after the water discharges from the drain, the alkalinity introduced in the anoxic limestone drain buffers the proton acidity produced and maintains circumneutral pH levels.

When evaluating the use of anoxic limestone drains, it is important to note that limestone dissolution is dependent upon the open or closed nature of the system (Snoeyink and Jenkins 1980). If an anoxic limestone drain is assumed to be a closed system, the partial pressure of carbon dioxide (pCO₂) becomes quite important in the potential rate of limestone dissolution and thus, alkalinity generation. The equilibrium constant for reaction (7) is near 10^{-2.8} and the great majority of dissolved CO₂ is present as CO_{2(aq)} (Manahan 1991). Therefore, reactions (5) and (6) can be viewed as:



As limestone dissolves, CO₂ is produced and, in a closed system, pCO₂ increases (8). The CO₂ produced continues to react with the limestone,

producing bicarbonate alkalinity (9). The solubility of limestone and limestone dissolution rates are dependent on the availability of CO₂ (Jacobson and Langmuir 1970). Under atmospheric pCO₂ (0.0003 atm), the dissolution of CaCO₃ in pure water will result in about 60 mg/L alkalinity as CaCO₃ eq. (Snoeyink and Jenkins 1980). As pCO₂ increases, the alkalinity able to be dissolved in water will increase (Lovell 1973). For example, water contacting limestone at a pCO₂ of 0.05 atm (common for the groundwater environment in carbonate terrain), will have an alkalinity of approximately 360 mg/L (Lovell 1973, Hem 1985). Theoretically, in a 100% CO₂ atmosphere (pCO₂ = 1.0 atm), water in contact with limestone can attain an alkalinity greater than 1,000 mg/L (Lovell 1973).

By excluding oxygen, anoxic limestone drains provide an environment for continued limestone dissolution without some of the armoring problems encountered when oxygen is present. Also, their buried and closed nature allows the generation of much greater alkalinity concentrations than possible in an open system, due to the presence of elevated pCO₂.

Methods

Site Description

The site monitored in this study is located in Paint Township, Clarion County, Pennsylvania. The site was surface mined and reclaimed in the late 1970's. Prior to construction of the anoxic limestone drain, acid mine drainage seeping from a toe-of-the-spoil discharge was chemically treated and directed into a settling pond and a constructed wetland.

The anoxic limestone drain was constructed by the responsible mining company in October 1990. The drain is approximately 50 m long, 0.6 m wide and contains #4 limestone (approximately 2.5 - 15 cm in size) to a depth of 1 m

(figure 1). The limestone is covered with two layers of 5 mil plastic. The plastic is overlain by 0.3 to 3 m of on-site clay in order to restore the original surface topography. The drain contains roughly 64,000 kg (70 short tons) of limestone. The limestone was obtained from two local quarries which mine the Vanport limestone of the Clarion Formation, Allegheny Group. The chemical composition of the limestone (% dry weight) was determined by wet chemical methods to be approximately 93 % CaCO_3 , 1.2 % MgCO_3 and 6.0 % other constituents.

During construction of the drain, three sampling wells were installed along its length. A number of 0.6 cm holes were drilled in the bottom one meter of three lengths of 5 cm inside diameter schedule 40 polyvinyl chloride pipe. The perforated end was placed on

the bottom of the excavation before the trench was backfilled with limestone. This end of the pipe was then surrounded by limestone. The top of the pipe extends above the surface of the ground to allow access. The three sampling wells (labelled 1, 2, and 3, from source to exit) allow the collection of both water and gas samples within the drain (figure 1). The outflow of the drain is directed through a 30 cm diameter pipe and flows through the remainder of the passive treatment system. The system consists of an 80 m long aerobic channel, a settling pond (surface area = 500 m^2) and a two-cell constructed wetland (combined surface area = 600 m^2). Figure 2 shows a layout of the entire passive treatment system.

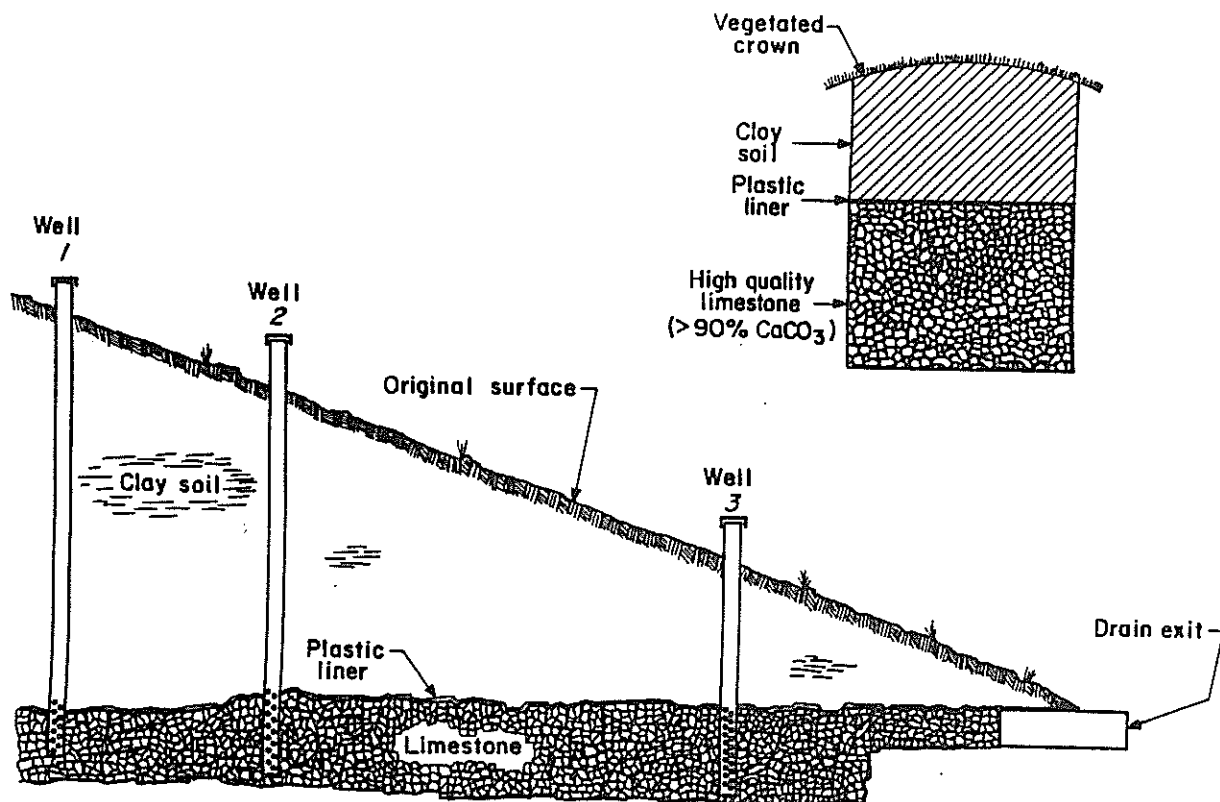
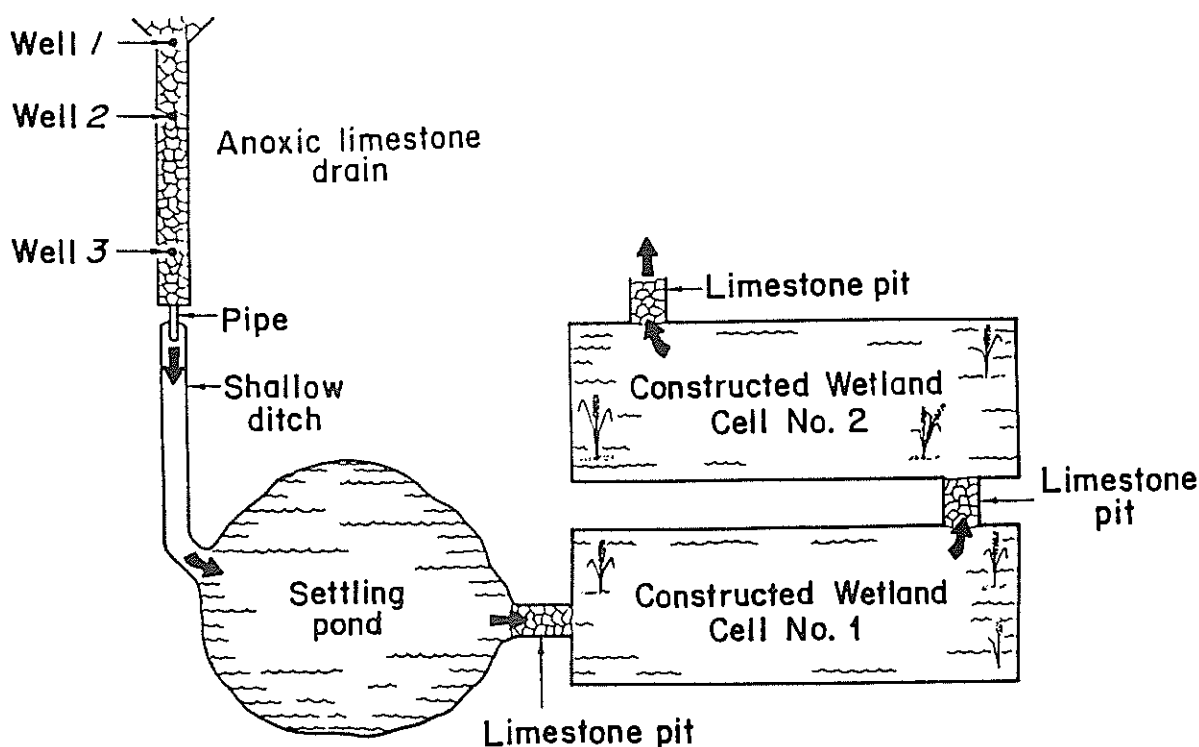


Figure 1. Longitudinal-section and cross-section of the anoxic limestone drain. The figure is not to scale.

Figure 2. Schematic of the entire passive treatment system. The figure is not to scale.



Water Collection and Analysis

The site was visited and sampled at least once a month between October 1990 and October 1991. Flow rates were determined at the exit of the drain by the container and stopwatch method. For each sampling date, a mean was calculated for three to five flow measurements. Water samples were collected in 250 mL plastic bottles from the three sampling wells, the drain discharge and at various locations in the downflow passive treatment system. Both raw and acidified (2 mL HCl) samples were collected. An additional sample for dissolved metal analysis was filtered through a 0.2 micron filter and was then acidified with 2 mL HCl. All samples were immediately placed on ice in an insulated cooler and returned to the laboratory. Samples were refrigerated at 4° C until analyzed.

Concentrations of six total cations (Fe, Mn, Al, Ca, Mg and Na) were determined for the acidified samples using Inductively Coupled Argon Plasma Spectroscopy (Instrumentation Laboratory Plasma 100 Model³). Ferrous iron concentrations were determined by potassium dichromate titration. Sulfate concentrations were measured by barium chloride titration, using thorin as an endpoint indicator. Acidity was determined by boiling a 50 mL sample with 1 mL of 30 % H₂O₂ and titrating to pH 8.3 with 0.1 N NaOH.

Measurements of pH, temperature, dissolved oxygen (DO) and alkalinity were made in the field. Determinations of pH and temperature were made after electrode and meter calibration in pH 2,

³Reference to specific products does not imply endorsement by the Bureau of Mines.

4, and 7 buffers with a temperature-compensated Orion SA270 or 290A pH/ISE meter. In situ DO measurements were made with a Yellow Springs Instruments Model 57 portable meter, after adjusting for temperature and elevation. Field alkalinity determinations were made with the Orion Total Alkalinity Test Kit reagent and the pH meter. A Na_2CO_3 alkalinity standard (1000 mg/L alkalinity as CaCO_3 eq.) was tested once every ten samples. Water depths within the sampling wells were determined with a YSI Model 3000 temperature-level-conductivity meter.

All metals and sulfate concentrations are reported as mg/L. Acidity and alkalinity are reported as mg/L CaCO_3 equivalent.

Gas Collection and Analysis

Triplicate gas samples were collected from each of the three sampling wells in 20 mL evacuated Vacutainers (Becton Dickinson Vacutainer Systems) fitted with a rubber septum. Samples were collected with a modified syringe sampler, consisting of a 60 mL plastic syringe fitted with a three-way valve. The valve was attached to a length of gas-impermeable amber latex tubing and to an inverted needle located inside another syringe. After placing the tubing to the desired depth in the sampling well, the 60 mL syringe and tubing were purged 2-5 times. Gas samples were then obtained by placing the Vacutainer inside the other syringe and piercing the septum with the needle. Gas samples were analyzed by gas chromatography with a Hewlett Packard 5880/5890 Gas Chromatograph, using helium as the carrier. Standard air components (CO_2 , O_2 , N_2 , Ar, CO, and CH_4) were determined on a % by volume basis.

Results

Pre-drain water quality (the baseline water quality unaffected by flow through the anoxic limestone drain) was estimated from two sources. The AMD

seep for which the drain was constructed was sampled only occasionally prior to drain construction. After construction, collection of a sample unaffected by the drain was impossible. However, another AMD seep located nearby was sampled and water quality data for this seep are similar to the limited data for the original seep. Two-tailed t-tests performed at the 0.05 significance level found no significant differences between the means of all measured water quality parameters (pH, alkalinity, acidity, total Fe, Mn and SO_4) for the two seeps. In both cases, the AMD had a pH < 5.5 and contained < 25 mg/L alkalinity and elevated concentrations of dissolved iron and manganese. Therefore, the data from the two seeps are combined as pre-drain water quality (table 1).

The quality of the water exiting the drain (post-drain) differed from the pre-drain water quality in several important respects (table 1). The pH of the waters exiting the drain was greater than or equal to 6.0 on all sampling dates. The mean alkalinity for samples collected at the drain exit was 255 mg/L as CaCO_3 eq. Alkalinity concentrations greater than 300 mg/L were measured on several occasions (figure 3). Mean calcium concentrations increased from 117 mg/L to 229 mg/L. With the exception of iron concentrations on one sampling date, the concentrations of all other parameters (Fe^{+2} , total Fe, Mn, Al, Mg, Na, and SO_4) were within the range of concentrations for the pre-drain water samples (table 1).

Flow rates at the drain exit ranged from 1 to 12 L/min. The low flows were due to a protracted drought throughout the region during the latter half of the study period. The mean and median flow rates were 7.5 and 6.9 L/min, respectively.

Alkalinity concentrations increased linearly in the sampling wells along the length of the drain. Mean alkalinity concentrations in wells 1, 2, and 3 were 190, 202 and 251 mg/L,

Table 1. Water quality before and after construction of the anoxic limestone drain. See the text for an interpretation of the pre-drain data. All post-drain samples were collected at the exit of the drain. Concentrations are mg/L, except alkalinity and acidity as mg/L CaCO₃ eq. Mineral acidity was calculated from the mean concentrations of Fe, Mn and Al and pH. se is the standard error of the mean and n is the sample size.

	Pre-drain				Post-drain			
	Mean	Range	se	n	Mean	Range	se	n
pH	4.7	3.0-5.3	0.2	11	6.2	6.0-6.5	0.1	15
Acid.	438	298-611	30	11	83	0-143	19	8
Min. Acid.	456	-	-	-	385	-	-	-
Alk.	15	0-24	5	8	255	204-335	12	15
Fe _{tot}	208	102-411	26	11	168	97-213	8	15
Fe ⁺²	208	124-261	19	6	167	97-206	8	15
Mn	44	5-61	5	11	46	33-54	2	15
Al	0.6	<0.2-1	0.1	6	0.2	<0.2-1	0.1	15
Ca	117	74-128	9	6	229	205-245	3	15
Mg	116	66-139	11	6	109	84-133	4	15
Na	46	25-59	5	6	37	28-45	1	15
SO ₄	1332	830-1757	85	11	1168	875-1350	36	15

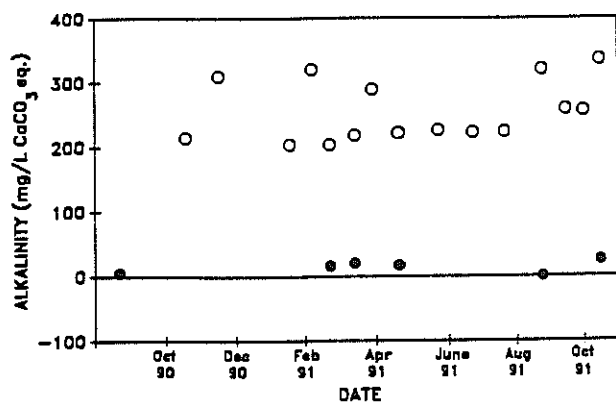


Figure 3. Alkalinity concentrations as a function of time. The open circles represent alkalinity concentrations at the drain exit. The first closed circle (nearest the left axis) represents the mean alkalinity concentration before drain construction (n=6). The remaining closed circles represent the alkalinity of samples collected at a nearby seep.

respectively. However, mean alkalinity concentrations from sampling well 3 to the drain exit were quite similar (251 and 255 mg/L).

Dissolved oxygen concentrations in each of the sampling wells and at the drain exit were consistently < 1.0 mg/L.

The gas composition in each of the sampling wells demonstrated an overall enrichment in CO₂ compared to atmospheric concentrations. Individual samples contained CO₂ concentrations 13 to 617 times atmospheric concentrations. Mean gas concentrations in each of the sampling wells are shown in table 2.

Discussion

The amount of alkalinity that can be generated in an anoxic limestone drain is a function of both solubility and kinetic considerations. The solubility of limestone defines the maximum potential concentration of

Table 2. Mean gas composition (% by volume) within each of the three sampling wells in the anoxic limestone drain and for atmospheric air. Partial pressures (in atm) can be determined by dividing by 100.

Gas	Atmospheric air	Well 1	Well 2	Well 3
CO ₂	0.03	14.2	5.1	12.7
O ₂	20.9	5.6	15.6	8.8
N ₂	78.0	79.2	78.4	77.4
Other	0.9	0.9	0.9	0.9

alkalinity under the particular conditions within a drain. The most important factor affecting limestone solubility in a drain is most likely the partial pressure of carbon dioxide. Additional factors affecting limestone solubility include water temperature, ionic strength of the mine drainage, complex formation, common ion effects, water velocity, turbulence, and limestone quality (% CaCO₃). Kinetic factors, such as the surface area of the limestone, determine the time it takes to reach saturation. The retention time of water within a drain determines whether the discharge water is saturated or undersaturated with alkalinity.

In this study, the retention time of the water within the drain was long enough so that saturation was attained. Alkalinity concentrations in the water exiting the drain appear to be limited by solubility factors, not kinetic factors. Alkalinity concentrations increased linearly for the first half of the drain, in sampling wells 1, 2 and 3. However, little increase in alkalinity concentrations occurred in the second half, as water flowed from sampling well 3 to the drain exit (figure 4). Mean alkalinity concentrations at these two sampling stations were not statistically different (t-test, $t = 0.22$, $P > 0.05$). Assuming that there are no inflows of acidic water between well 3 and the drain exit, the lack of an increase in alkalinity between the last two sampling stations suggests that the water was

saturated with alkalinity, at the given pCO₂, by the time it reached well 3.

If kinetic factors were dominant, a positive relationship would exist between the retention time of the water and the alkalinity of the drain discharge. The relationship between these parameters was weak ($r=0.5$, figure 5). The apparent maximum alkalinity concentration was attained at theoretical retention times differing by a factor of seven. Jacobson and Langmuir (1970) found that subsurface flow in carbonate aquifers permits the

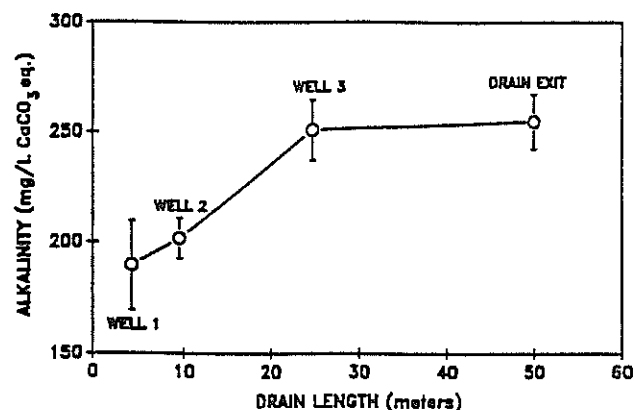


Figure 4. Alkalinity concentrations for the sampling wells and the anoxic limestone drain exit. The symbol represents the mean concentration and the error bars are +/- one standard error. Well 1 was located approximately 4.3 m from the source, well 2 at 9.5 m, well 3 at 25 m, and the exit was 50 m from the source.

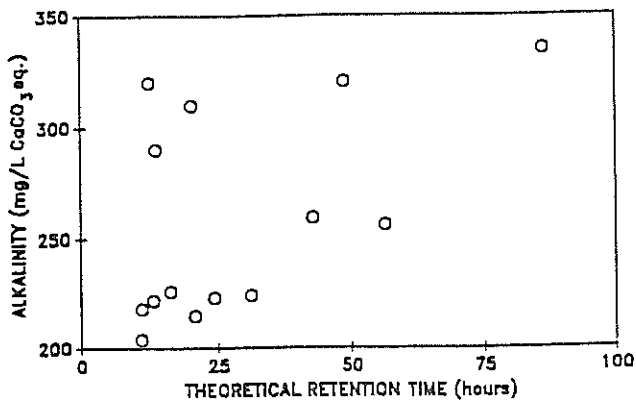


Figure 5. Alkalinity concentrations at the exit of the anoxic limestone drain as a function of the theoretical retention time. The statistical relationship is weak ($r = 0.5$).

rapid generation and maintenance of dissolved CO_2 concentrations. In a closed system such as a drain, the solubility of limestone and, thus, alkalinity concentrations are controlled by CO_2 concentrations.

The elevated concentrations of alkalinity found in the drain are indicative of high partial pressures of carbon dioxide. The dissolution of limestone in water under open conditions at atmospheric pCO_2 (0.0003 atm) results in an alkalinity of about 60 mg/L (Snoeyink and Jenkins 1980). Partial pressures of CO_2 greater than atmospheric levels increase the amount of alkalinity that can be dissolved in water in a closed system. Plummer et al. (1979) and Berner and Morse (1974) found that below $\text{pCO}_2 = 0.03$ atm, CaCO_3 dissolution was independent of the partial pressure of CO_2 . In the drain, the CO_2 released by limestone dissolution is retained and promotes further dissolution of the limestone and greater alkalinity concentrations. Assuming equilibrium with the gas phase, the percent composition of the gases in the sampling wells can be converted to partial pressures for the water in the drain. The partial pressure of CO_2 within the drain ranged from 0.004 to 0.185 atm. This range of CO_2 partial

pressures straddles the pCO_2 that has been found to influence CaCO_3 dissolution. Calculations using the mean equilibrium pCO_2 result in alkalinity concentrations approximately 1.4 times the observed concentrations. This difference is likely due to the fact the system is not completely closed and a certain amount of CO_2 is lost, or that equilibrium has not been achieved.

Alkalinity concentrations in the water exiting the drain appear to be limited by solubility factors, rather than kinetic factors. If the drain had been built 50 m longer (twice its actual length), the mean alkalinity concentrations at the exit would most likely not be 500 mg/L (twice the actual mean), but approximately 250 mg/L, or at best, near 300 mg/L (the maximum alkalinity concentration measured at the drain exit). These data agree well with field alkalinity measurements collected at a number of other similarly constructed anoxic limestone drains in Pennsylvania, Tennessee, Alabama and Ohio (U.S. Bureau of Mines, unpublished data). These drains were built in a similar manner but contain various quantities of limestone and were constructed in assorted shapes and sizes. In all cases, the limit for effluent alkalinity concentrations appears to be 300 - 400 mg/L.

Alkalinity Generation Rates

Rates of alkalinity generation were estimated from measured alkalinity concentrations, flow rates and the volume of limestone contacted by the water. Based on water levels measured in the wells, the drain appears to be nearly full of water along its entire length. Due to the level of the exit pipe, however, 0.7 m is the depth used in the alkalinity generation calculations. If the calculation is based on the entire length of the drain, an alkalinity generation rate of 117 grams of alkalinity (as CaCO_3 eq.) meter⁻³ (bulk volume) day⁻¹ results. It is important to note that this rate is

calculated for the bulk volume of the drain (the total volume of both limestone and water). On a limestone mass basis, the alkalinity generation rate is approximately 35 grams ton⁻¹ of limestone day⁻¹.

Because the function of an anoxic limestone drain depends on the dissolution of a solid, drains have a theoretical maximum lifetime. From the alkalinity generation data, the potential longevity of the drain can be estimated. Taking into account the CaCO₃ content of the limestone and assuming complete dissolution, the mean alkalinity generation rate of 117 g m⁻³ day⁻¹ results in a maximum drain longevity of about 65 years. Presumably, structural failure of the drain due to dissolution of the limestone will occur before this time.

Function of the Downflow Passive Treatment System

The alkalinity generated in the drain had a dramatic effect on the performance of the entire passive treatment system (table 3). After exiting from the drain, the iron in the mine water underwent oxidation and hydrolysis and precipitated as an iron hydroxide in the aerobic channel and adjacent settling pond. The water then entered a two-cell constructed wetland where final iron removal and manganese removal occurred. On all sampling dates, the effluent of the second wetland cell contained iron concentrations within regulatory compliance (< 3 mg/L) and, on some days, below the detectable limits (< 0.2 mg/L). Manganese concentrations decreased in the wetland on all sampling dates, sometimes to within regulatory compliance (< 4 mg/L). However, the mean manganese concentration for samples collected at effluent exceeded compliance. Because effluent limits for manganese do not apply at this site, active chemical treatment has been discontinued.

Table 3. Mean water quality before drain construction (pre-drain) and at the final effluent (discharge of the second wetland cell). Concentrations are mg/L, except alkalinity and acidity as mg/L CaCO₃ eq. Mineral acidity was calculated from the mean concentrations of Fe, Mn and Al and pH.

	Pre-drain	Final effluent
pH	4.7	6.5
Acid.	438	58
Min. Acid.	456	35
Alk.	15	64
Fe _{tot}	208	1
Fe ⁺²	208	1
Mn	44	17
Al	0.6	0.4
Ca	117	179
Mg	116	82
Na	46	43
SO ₄	1332	832

Cost Savings

The estimated total cost of construction of the anoxic limestone drain was about \$1300 (table 4). This estimate includes a hypothetical equipment rental (\$350) which, in fact, was available at this site. Therefore, the actual cost was probably less than \$1000. Prior to construction of the anoxic limestone drain, the AMD was chemically treated with solid NaOH beads. The cost of the chemicals alone was approximately \$4.50 per day, not including labor. This amounts to yearly costs of about \$1640 in chemical purchases. Therefore, the cost of

Table 4. Estimated cost of construction of the anoxic limestone drain.

Limestone (70 tons @ \$10/ton)	\$700
Plastic liner (600 ft ² @ 5¢/ft ²)	30
Labor (approximate)	180
Equipment (backhoe, if rented @ \$35/hour for 10 hours)	350
Seed and fertilizer (approximate)	40
Estimated total cost	\$1300

construction of the drain was recovered within the first nine and one-half months of operation in savings in chemical costs alone. If costs of operation and maintenance, sludge handling and disposal, and associated labor are included, the estimated average cost of chemical treatment at this site is about \$20 per day (over \$7000 per year). Based on an estimated longevity of 30 years and no maintenance costs, the long-term cost of the drain is about 12¢ per day.

Summary

An anoxic limestone drain dramatically improved the quality of the water discharging from a reclaimed surface mine for a period of one year. The water exiting the drain contained substantial amounts of alkalinity and had a pH > 6.0. Considerable metal removal occurred in a channel, pond and constructed wetland following the drain.

Anoxic limestone drains, in conjunction with settling ponds and constructed wetlands, may represent an alternative

to conventional active chemical treatment of AMD at many mine sites. In other cases, anoxic limestone drains (or above-ground anoxic limestone reactors) may be able to be used as beneficial, cost-saving components of active treatment systems. In either case, anoxic limestone drains must be viewed as partial treatment systems that generate alkalinity and facilitate subsequent metal removal.

While promising, the technology is nevertheless preliminary. Potential concerns regarding certain mine drainage constituents and the longevity of the drains have yet to be resolved. Currently, the most important factors influencing the function of drains appear to be the concentration of acidity in the raw drainage, the limestone quality, and the partial pressure of CO₂ within the drain. At the present time, the maximum effluent alkalinity concentration for anoxic limestone drains appears to be about 300 mg/L as CaCO₃ eq. The continued development and refinement of the anoxic limestone drain technology should help to further reduce the costs associated with the treatment of AMD.

Literature Cited

- Berner, R. A. and J. W. Morse. 1974. Dissolution kinetics of calcium carbonate in sea water, Part IV. Theory of calcite dissolution. *Amer. Jour. Sci.*, v. 274. pp. 108-134. <http://dx.doi.org/10.2475/ajs.274.2.108>
- 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. In: W. Oaks and J. Bowden (eds.) *Proceedings Reclamation 2000: Technologies for Success, Durango, CO*, pp. 211-222. <http://dx.doi.org/10.21000/JASMR91010211>

- Cravotta III, C. A., K. B. C. Brady, M. W. Smith and R. L. Beam. 1990. Effectiveness of the addition of alkaline materials at surface coal mines in preventing or abating acid mine drainage: Part 1. Geochemical considerations. *In*: J. Skousen, J. Sencindiver and D. Samuel (eds.) Proceedings of the 1990 Mining and Reclamation Conference and Exhibition: Volume 1, Charleston, WV, pp. 221-225.
<http://dx.doi.org/10.21000/JASMR90010221>
- Glover, H. G. 1967. The control of acid mine drainage by biochemical oxidation and limestone neutralization treatment. *In*: Proceedings of the 22nd Industrial Waste Conference, West Lafayette, IN, pp. 823-847.
- Hem, J. D. 1985. Study and interpretation of the chemical characteristics of natural water (3rd ed.) United States Geological Survey Water Supply Paper 2254, pp. 61-146.
- Hill, R. D. and R. C. Wilmoth. 1971. Limestone treatment of acid mine drainage. *Trans. SME AIME*, v. 250, pp. 162-166.
- Jacobson, R. L. and D. Langmuir. 1970. The chemical history of some spring waters in carbonate rocks. *Groundwater*, v. 8. pp. 5-8.
<http://dx.doi.org/10.1111/i.1745-6584.1970.tb01302.x>
- Lovell, H. L. 1973. An appraisal of neutralization processes to treat coal mine drainage. U.S. EPA report EPA-670/2-73-093. pp. 72-98.
- Manahan, S. E. 1991. *Environmental Chemistry* (4th ed.). Lewis Publishers, Boca Raton, FL, 612 pp.
- Mihok, E. A., M. Deul, C. E. Chamberla, and J. G. Selmeczi. 1968. The Limestone Neutralization Process. Bureau of Mines Report of Investigation 7191, 20 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. *In*: Proceedings of the 12th Annual West Virginia Surface Mine Drainage Task Force Symposium, Morgantown, WV, pp. 23-38.
- Plummer, L. N., D. L. Parkhurst and T. M. L. Wigley. 1979. Critical review of the kinetics of calcite dissolution and precipitation. *In*: E.A. Jenne (ed.) Chemical Modelling in Aqueous Systems, ACS Symposium Series 93, Washington, D.C., pp. 537-573.
- Skousen J., K. Politan, T. Hilton, and A. Meek. 1990. Acid mine drainage treatment systems: chemicals and costs. *Green Lands*, v. 20, no. 4, pp. 31-37.
- Skousen, J. 1991. Anoxic limestone drains for acid mine drainage treatment. *Green Lands*, v.21, no. 4, pp. 30-35.
- Snoeyink, V. L. and D. Jenkins, 1980. *Water Chemistry*. John Wiley and Sons, New York, NY, 463 pp.
- Stumm, W. and J. J. Morgan, 1981. *Aquatic Chemistry: An Introduction Emphasizing Chemical Equilibria in Natural Waters* (2nd ed.). John Wiley and Sons, New York, NY, 780 pp.
- Sverdrup, H. and P. Warfvinge. 1985. A reacidification model for acidified lakes neutralized with calcite. *Water Res. Res.*, v. 21, no. 9, pp. 1374-1380.
<http://dx.doi.org/10.1029/WR021i009p01374>

Turner, D. and D. McCoy. 1990. Anoxic alkaline drain treatment system, a low cost acid mine drainage treatment alternative. In: D. H. Graves and R. W. De Vore (eds.) Proceedings of the 1990 National Symposium on Mining, Lexington, KY, pp. 73-75.

Wentzler, T. H. and F. F. Aplan. 1972. Kinetics of limestone dissolution by acid waste waters. In: C. Rampacek (ed.) Environmental Control, San Francisco, CA. pp. 513-523.

United States Environmental Protection Agency. 1983. Design Manual: Neutralization of Acid Mine Drainage. Office of Research and Development, Industrial Environmental Research Laboratory, 231 pp.

United States Environmental Protection Agency. 1971. Studies of limestone treatment of acid mine drainage, Part II., Water Pollution Control Research Series W72-06849, 135 pp.