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ACID MINE DRAINAGE TREATMENT WITH OPEN LIMESTONE CHANNELS[1]

by

Paul F. Ziemkiewicz[2], David L. Brant[2], and Jeffrey G. Skousen[3]

Abstract. Acid mine drainage (AMD) is often associated with mining of pyritic coal and metal deposits. Typical AMD associated with coal mines in the eastern U.S. can have acidity and iron concentrations ranging from the teens to the thousands of mg/l. Aluminum and manganese can be present in concentrations ranging from zero to the low hundreds of mg/l. Much attention has been devoted to developing inexpensive, limestone (LS)-based systems for treating AMD with little or no maintenance. However, LS tends to coat with metal hydroxides when exposed to AMD in an oxidized state, a process known as "armoring". It is generally assumed that once armored, LS ceases to neutralize acid. Another problem is that the hydroxides tend to settle into plug the pore spaces in LS beds forcing water to move around rather than through the LS. While both are caused by the precipitation of metal hydroxides, armoring and plugging are two different problems. Plugging of LS pores can be avoided by maintaining a high flushing rate through the LS bed. Armoring, however, occurs regardless of water velocity. This study investigated the influence of armoring on LS solubility and the implications of armoring and plugging on the construction of open (oxidizing) LS channels for treating AMD. We evaluated the AMD treatment performance of armored and unarmored LS in oxidizing environments both in laboratory and field studies. The results showed ferric and aluminum hydroxide floc remained suspended in solution until the LS was allowed to dry. As the floc dried, the LS became armored. The laboratory study treated AMD with armored LS (ALS) from two field sites and unarmored LS (ULS). ALS dissolved 25 to 33% more slowly than ULS. The field study surveyed 2- to 8-year-old rock-lined waterways constructed for erosion control. One waterway was constructed of sandstone rip-rap and seven others were constructed with LS. The results indicated that OLC's, though armored, continued to reduce acidity at rates similar to those of the laboratory study. The results were used to verify a dissolution kinetics model which predicts the required dimensions of an OLC for treatment of given flows and acidities.

Additional Key Words: Abandoned mine lands, chemical water treatment, passive treatment, reclamation

Introduction

Acid mine drainage (AMD) continues to be one of the largest problems facing the mining industry. AMD originates from active and abandoned mines as pyrite (FeS_2) or other metal sulfides associated with the mineral deposit are exposed to oxidizing conditions. Upon exposure, the sulfide minerals progress through a combination of auto-oxidation and microbial oxidation reactions to produce large amounts of acid, iron and sulfate. This acidity then dissolves other minerals, releasing ions such as manganese and aluminum. The resulting solution is AMD. Upon reaching a stream, AMD alters the chemical balance: it consumes alkalinity, introduces metal ions and generally degrades its biological productivity. If sufficiently severe, AMD will also render the receiving waters unfit for human, agricultural, industrial or recreational use (Atlas and Bartha 1987).

AMD can be treated with alkali chemicals and this is the method of choice for most active mines. This is expensive and must continue long after mining has ceased. An alternative is passive treatment. Passive treatment refers to any zero to low maintenance AMD treatment scheme. These systems are of increasing interest as state, industry and federal partnerships are formed to rehabilitate watersheds damaged by historic mining. Passive systems offer low maintenance, inexpensive, and long-term solutions to AMD remediation (Brodie 1990, Hedin 1989). Anoxic limestone drains (ALDs), wetlands, or a combination of both are the most often used passive systems (Faulkner and Skousen 1994). Wetlands are effective in handling low acid loadings but often encounter difficulties or fail under high loading. Problems with ALDs occur when ferric iron, aluminum,

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or ferrous iron and dissolved oxygen are present. Under these conditions, metals will precipitate and armor the LS reducing its dissolution efficiency compared to unarmored LS. Precipitates may occlude all of the pore volume within the drain preventing water from contacting the LS.

Studies by Pearson and McDonnell (1974, 1975a, 1975b) found that armored LS (ALS) dissolved at about 20% the rate of unarmored LS (ULS). Ziemkiewicz et al. (1994) conducted a preliminary study of OLCs on field sites and developed a spreadsheet to estimate LS volumes and channel dimensions for treating AMD. Open limestone channels will become armored, presumably reducing the limestone dissolution rate to 20% of ULS. But unlike ALDs, plugging of LS pores can be controlled by maintaining high flows and the armoring effect can be accounted for by adding a design factor of five (Ziemkiewicz et al. 1994).

This study compares the AMD treatment efficiency of armored and unarmored LS in the laboratory. In addition, a field study was conducted to survey existing open LS-lined waterways to evaluate the effects of armored LS on AMD treatment.

Experimental Design

Laboratory Study

The lab study was conducted using containers (2 liter, high-density polyethylene) filled with 2.3 kg (5 lbs) of 5 - 10 cm (2 - 4 in) ALS or ULS (Figure 1). One of five sources of AMD or deionized water (blank) (1.2 liters) was added to each of the containers. The two sources of ALS were from Robinson Run (RR) and Dola, WV. The ULS was from the Deer Valley formation provided by Action Mining in Somerset County, PA. The five AMD sources (all Pittsburgh coal bed) were: Maidsville Seep near Morgantown, WV; Shaw Mines Run and Weir-11, near Meyersdale, PA; Coal Run, near Salisbury, PA; and a synthetic AMD containing only sulfuric acid and deionized water. Only 13 of the 18 possible LS/water combinations were used in the study (Table 1), and each of the selected combinations had 3 replications.

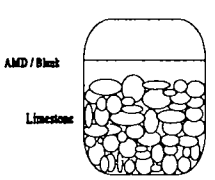

Figure 1. Containers used for the laboratory study filled with limestone and AMD or deionized water.

The method for estimating the solubility of ALS vs. ULS was adapted from Watzlaf and Hedin (1993). Water samples (60 mls) were collected with 60-ml plastic syringes from containers in duplicate (one sample for general water chemistry and one for metals analysis) at the following time intervals after water introduction: 0 hr, 1 hr, 2 hrs, 4 hrs, 6 hrs, 12 hrs, 18 hrs, and 24 hrs. The samples were filtered (0.45 micron) and metal analyses samples were acidified with 1 ml of concentrated nitric acid prior to submission to the NRCCE Analytical Laboratory for analysis. The parameters tested were: pH (electrode), electrical conductivity (conductivity bridge), alkalinity and acidity (Brinkman auto-titrator), and concentrations of iron, aluminum, manganese, calcium, magnesium (Leaman Labs inductively coupled plasma spectrometry), and sulfate (Milton Roy Spectronic 20) (Clesceri et al. 1989).

Field Study

The field study surveyed existing rock-lined waterways on abandoned mine lands (AML) sites containing AMD (Table 2). These waterways were constructed for erosion control or stream bank stabilization only. One waterway was constructed with sandstone and the other seven waterways were made with LS. Two water samples (250 mls each) were collected at identified distances along the channels (one for general water chemistry and one for metals analysis) and analyzed as described above (Clesceri et al. 1989). The samples were field filtered (0.45 micron) and acidified with 1 ml of nitric acid for metals analysis or cooled to 4°C for general chemistry. Flows were measured with a Marsh - McBirney model 2000 Flo-Mate electromagnetic flow meter for larger flows (> 95 l/min or 25 gpm) or a calibrated bucket and a stopwatch for smaller flows (< 95 l/min or 25 gpm). Distances were measured with a 100-foot surveying rope.

The results of water quality analyses from field channels were plotted against our kinetics spreadsheet (RBOLD) designed to predict the dimensions required to treat AMD with OLCs (Ziemkiewicz et al. 1994). RBOLD translates ALS dissolution kinetics into spreadsheet which estimates the reduction in acid load for a given LS channel, or estimates the size of a channel required to achieve desired acid load reductions.

Description of Field Sites

NRCS Coral/Graceton Site

The Coral/Graceton site is located adjacent to U.S. Route 119 immediately northeast of the towns of Coral and Graceton in Indiana County, PA. The channel is 220 m long, 3 m wide and 0.1 m deep (720 x

Table 1. Water and limestone combinations used in the laboratory study. Each combination checked had three replications.

Water	Robinson Run ALS	Dola ALS	ULS
Maidsville	X		X
Shaw Mines		X	X
Weir-11		X	X
Coal Run		X	X
Synthetic AMD		X	X
Deionized Water	X	X	X

9 x 0.5 ft) on a 10% slope, and was constructed with sandstone. The flow of AMD through the channel, measured at the source and mouth of the rock lined waterway, was 1323 l/min (350 gpm) and the acidity at the source was 550 mg/l.

Morgantown Airport Site

The Morgantown Airport site is located adjacent to U.S. Routes 119/857 east of Morgantown, WV. There are two channels (both LS and heavily armored) at this location. The first channel (West) is 46 m long, 1.3 m wide and 0.1 m deep (150 x 4 x 0.5 ft) on a 14% slope. The second channel (East) is branched, with the first branch being 21 m long (70 ft) and the second branch being 27 m (90 ft) long (same widths and depth as West channel) both on 20% slopes. The flow of AMD in the West channel was 113 l/min (30 gpm) and the acidity was 410 mg/l. The total combined flow in the East channel was 76 l/min (20 gpm) and the acidities were 355 mg/l for the first branch and 335 mg/l in the second. The flow rates were equal at the sources and the mouths of each channel.

NRCS Eichleberger #2 Site

The Eichleberger #2 site is located in Bedford County, PA, 6.5 km southeast of the village of Coaldale. The channel is 49 m long, 2 m wide and 0.1 m deep (160 x 6 x 0.5 ft) on a 20% slope, and was constructed with LS that became heavily armored. The flow through the channel was consistent at 378 l/min (100 gpm) and the acidity at the source was 510 mg/l.

Pa DER Site

The Pennsylvania Dept. of Environmental Resources site is located in Bedford County, PA, 1.6 km west of the village of Defiance. This channel is 11 m long, 1 m wide, and 0.1 m deep (37 x 3 x 0.5 ft) on a slope of 60% with a flow of 95 l/min (25 gpm). The acidity was 2600 mg/l at the source. This channel is also constructed of LS that became heavily armored.

PA Game Commission Site

The Pennsylvania Game Commission site is also a small channel of 11 m long, 1 m wide, and 0.1 m deep (35 x 3 x 0.5 ft) on a slope of 45%. It is located on the northeast side of Vintondale in Cambria County, PA. The flow is 484 l/min (128 gpm) and the acidity is 330 mg/l at the source. This channel was constructed of LS and became armored after construction.

Cottage Town Site

The Cottage Town site is located 1.6 km west of Cairnbrook in Somerset County, PA. The channel is 137 m long, 1.3 m wide and 0.1 m deep (450 x 4 x 0.5 ft) on a 9% slope with a flow of 302 l/min (80 gpm) throughout the entire length. LS was used for the construction of the channel. The LS was heavily armored and the AMD had an acidity of 32 mg/l at the source.

NRCS - Opawsky Site

The Opawsky site is located in Armstrong County, PA, 1 km south of Mosgrove. This site was different from the other sites due to the construction of a wetland 46 m (150 ft) that was installed at the bottom of the upper section of OLC. The top portion of the channel was constructed of LS for 46 m long, 2 m wide and 0.3 m deep (150 x 6 x 2 ft) on a slope of 9%. The LS was armored and the flow of AMD throughout the entire system was 907 l/min (240 gpm). This portion of the channel entered a wetland that covered an area of 350 m^2 (7.6 m by 46 m). The lower 137 m (450 ft) of the channel was also constructed of LS that was armored. The acidity at the source was 30 mg/l.

Results

Laboratory Study

The initial acidity of the Maidsville seep (2080 mg/l) was reduced to 925 mg/l (56% reduction) after 24 hours with RR ALS (Figure 2). This compares to ULS that eliminated 65% of the acidity after 24 hours. The ALS from Dola completely eliminated the Shaw Mines'

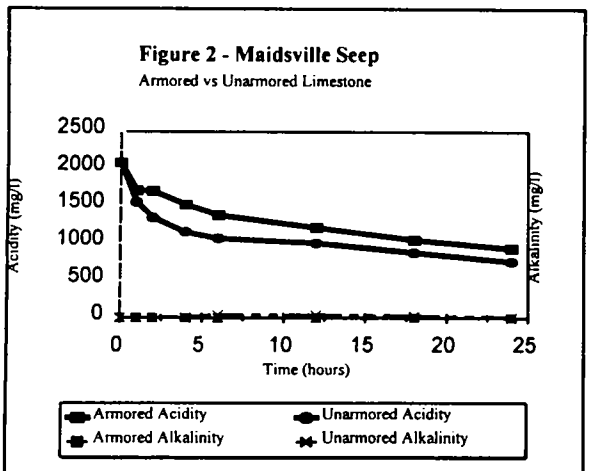

Figure 2. Acidity reduction and alkalinity generation of Maidsville Seep AMD with armored and unarmored limestone.

initial acidity of 518 mg/l in the containers after 6 hrs (Figure 3). Unarmored LS achieved 100% treatment after 4 hrs. Alkalinity production leveled off after 12 hours for both armored (75 mg/l) and unarmored (120 mg/l) LS.

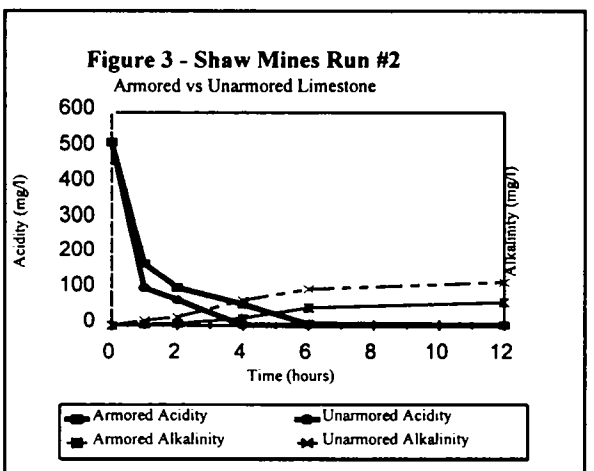

Figure 3. Acidity reduction and alkalinity generation of Shaw Mines AMD with armored and unarmored limestone.

The initial acidity of Weir-11 (1370 mg/l) was reduced to 20 mg/l (99% reduction) after 21 hours using Dola ALS (Figure 4). Unarmored LS treated all the acidity and produced 50 mg/l alkalinity during the same time period. Coal Run, a stream contaminated by a turn of the century deep mine, had an initial acidity of 905 mg/l (Figure 5). The Dola ALS and ULS both completely neutralized the acidity of the water after 21 hrs. Both types of LS produced net alkaline water during the same time period, producing 61 mg/l for the Dola ALS and 84 mg/l for ULS.

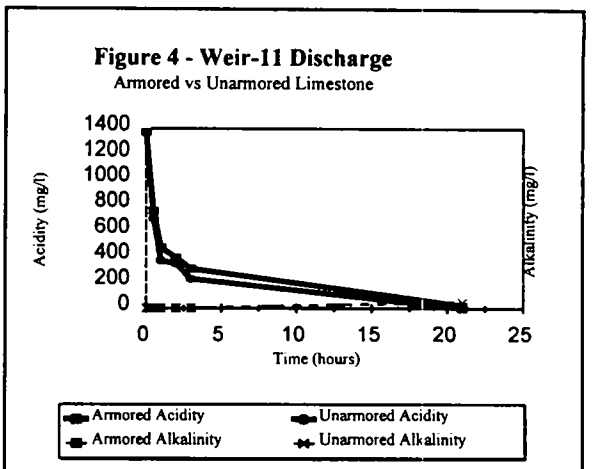

Figure 4. Acidity reduction and alkalinity generation of Weir - 11 AMD with armored and unarmored limestone.

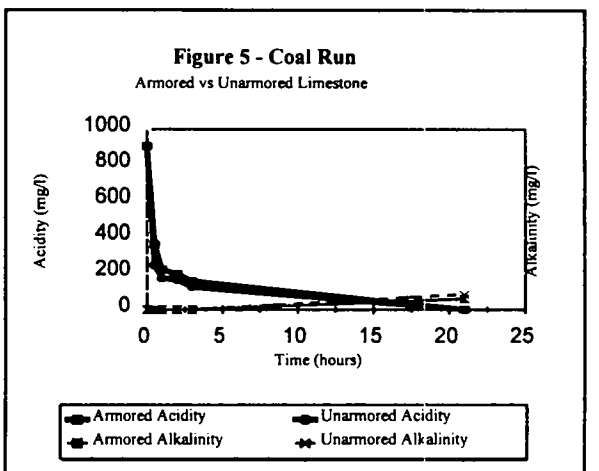

Figure 5. Acidity reduction and alkalinity generation of Coal Run AMD by armored and unarmored limestone.

Deionized water was added to the three LS types used in the study to isolate the effect of armoring in the absence of acid leachate. The results indicate that the ALS initially produced some acidity but that the solutions became alkaline within the first hour. The ULS produced the highest alkalinities at 50 mg/l while Dola ALS produced 30 mg/l and RR ALS gave 40 mg/l (Figure 6).

The three LS types were treated with a synthetic AMD (0.02M H_2SO_4). The acidity was completely neutralized within 2 hrs with ALS and within 1 hr for ULS. Alkalinity generation leveled off at 67 mg/l after 18 hrs for ALS and 85 mg/l after 4 hrs for ULS (Figure 7).

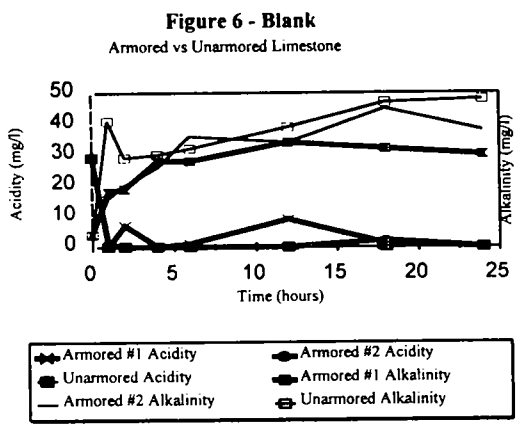

Figure 6. Acidity and alkalinity generation with deionized water on armored and unarmored limestone.

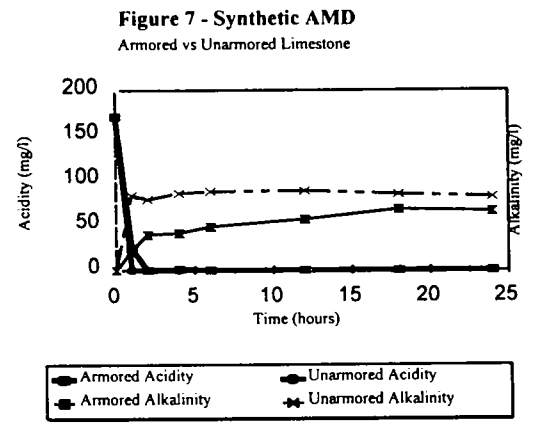

Figure 7. Acidity and alkalinity generation of Synthetic AMD with armored and unarmored limestone.

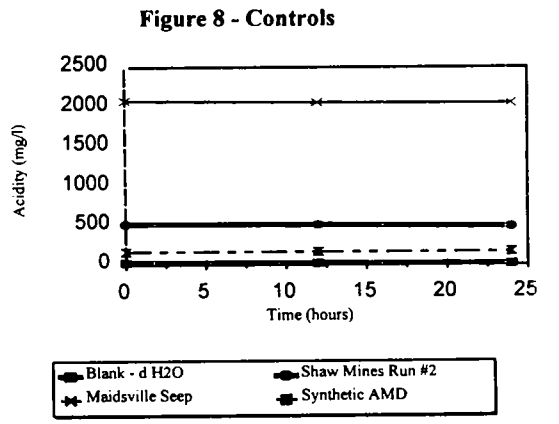

Figure 8. Acidity changes over time with three AMD sources without limestone.

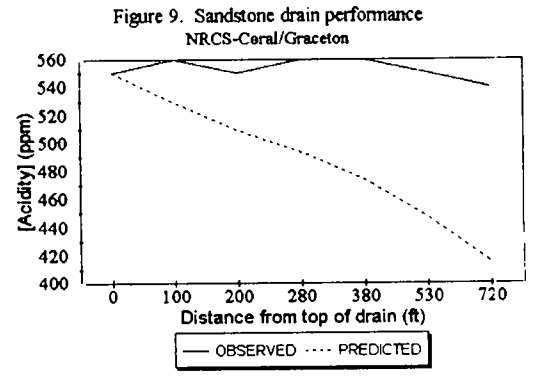

Figure 9. Observed and predicted acidity reductions from a sandstone drain at the Coral/Graceton site in Indiana County, PA.

Four water types used in the study were placed in cells and monitored over a 14 hr period to confirm whether any changes occurred in acidity levels on exposure to air. Figure 8 indicates that no changes occurred.

Field Study

The NRCS Coral/Graceton waterway was constructed with sandstone to serve as a control to LS channels. The prediction line was based on the use of LS. The resulting acidity reduction on the site was 0.0028% per ft (Table 2), much less than the predicted 0.034% per ft if it would have been constructed with LS (Figure 9).

The Morgantown Airport West channel performance was better than predicted (Figure 10). The actual acidity reduction was 0.0800% per ft (Table 2) compared to the predicted reduction of 0.032% per ft. The Morgantown Airport East channels also performed better than predicted with an acidity reduction of 0.0780% per ft compared to a predicted reduction of 0.020% per ft (Figure 11).

The NRCS Eichleberger #2 channel also performed better than expected with an actual acidity reduction of 0.2250% per ft compared to a predicted reduction of 0.104% per ft (Figure 12). The PA DER site is a very short channel with high acidity, but removes 0.1080% of the acidity per ft. This was an order of magnitude better than the predicted acidity reduction of 0.010% per ft (Figure 13).

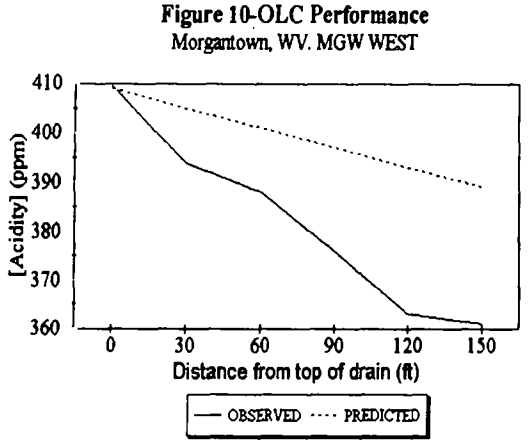

Figure 10. Observed and predicted acidity reductions of an open limestone channel at the Morgantown Airport west drain.

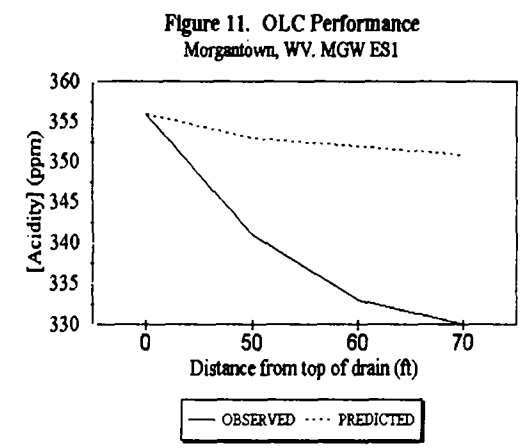

Figure 11. Observed and predicted acidity reductions of an open limestone channel at the Morgantown Airport east drain.

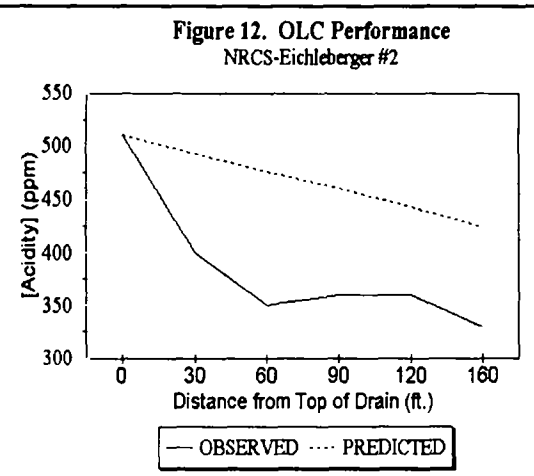

Figure 12. Observed and predicted acidity reductions of an open limestone channel at the NRCS Eichleberger #2 site in Bedford County, PA.

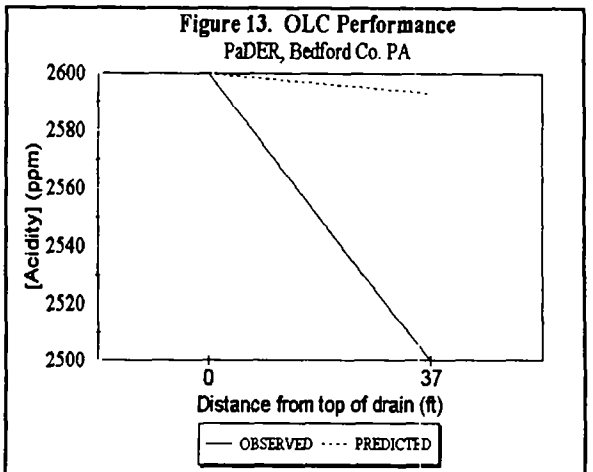

Figure 13. Observed and predicted acidity reductions of an open limestone channel at the Pa DER site in Bedford County, PA.

The PA Game Commission OLC is also a very short channel (Figure 14), but it shows an impressive performance (1.7710% acidity removal per ft compared to a predicted performance of 0.044% per ft acidity removal). The steep grades of these two channels really increased water velocities and enhanced LS dissolution.

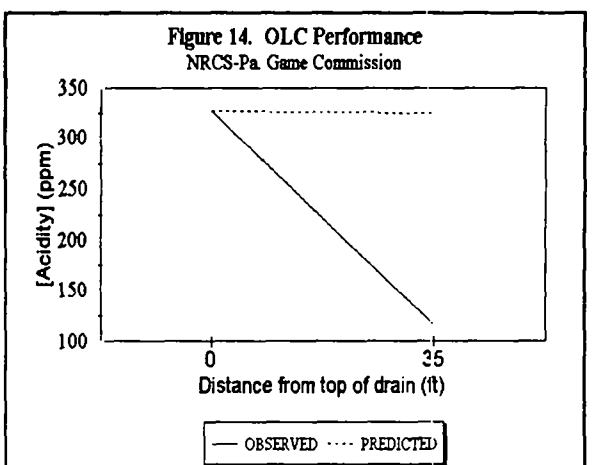

Figure 14. Observed and predicted acidity reduction of an open limestone channel at the PA Game Commission site in Cambria County, PA.

The Cottage Town site has a small amount of acidity entering the channel (Figure 15) and exhibits an acidity removal better than that predicted over the first 110 m (360 ft) of the channel (0.0870% per ft compared to 0.035% per ft predicted). Acidity increases over the last 27 m (90 ft) of the channel probably due to a small source of AMD entering at the base of the channel. But

this brings the overall acidity removal closer to the predicted value (.0290% compared to .0350% per ft of channel).

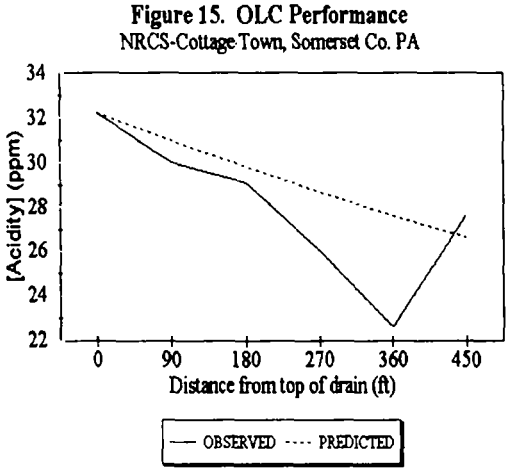

Figure 15. Observed and predicted acidity reductions of an open limestone channel at the NRCS Cottage Town site in Somerset County, PA.

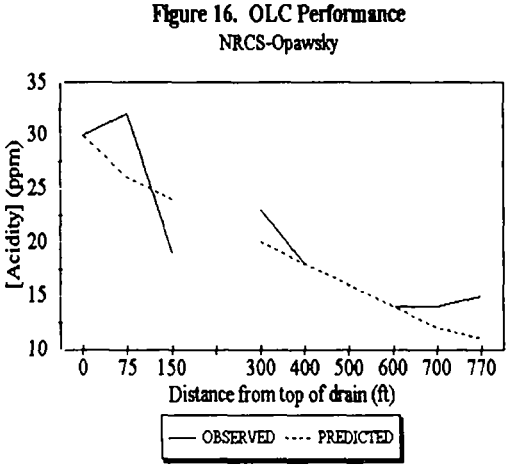

Figure 16. Observed and predicted acidity reduction of an open limestone channel at the NRCS Opawsky site in Armstrong County, PA.

The NRCS Opawsky site's performance was slightly worse than predicted (0.33% acidity removal per ft compared to a predicted removal of 0.42% per ft) but still removed 50% of the acidity (Figure 16).

Discussion and Conclusions

In the laboratory study, ALS treated acidity one-third to one-fourth as fast as ULS. This factor also applies to alkalinity production from these two types of LS. These values are close to the one-fifth factor reported by Pearson and McDonnell (1974). Acidity reduction of OLCs in the field varied between 4% and 62%, and acid reductions per ft of channel were between .029 and 1.77% (Table 2). The steeper channels performed better than the two channels with shallower (9%) slopes. In the sandstone channel, acidity decreased by only 2% and by a factor of .0028% per ft of channel.

The results confirmed the logarithmic acidity decay curve with ALS reported by Pearson and McDonnell (1974). Thus acidity removal by ALS is proportional to the increment of channel length and cross sectional area, regardless of initial acidity. In other words, a fixed proportion of acidity is removed by ALS per ft of channel (width and depth included). Acidity loss is rapid at first then gradually slows down.

OLC's work best on steep slopes. The key factor in designing OLCs is to prevent iron and aluminum flocs from settling out and plugging the LS pores in the channel. One LS channel not reported here was found on a nearly flat slope (1 to 3%). It was filled with floc and was ineffective in treating acidity. The successful channels generally had slopes above 10% and used coarse LS (15-to 30-cm sized material or 6- to 12- in sized material). Both slope and size of LS can maximize void space and water velocity thereby inhibiting floc settling. Evidence of the effect of slope on ALS dissolution is seen on the PA Game Commission and PaDER sites that had LS channels constructed on slopes > 40%.

Each of the passive treatment systems (aerobic wetlands, anaerobic wetlands, ALDs, APS, and OLCs) have an area of application (see Faulkner and Skousen 1995 for descriptions and applications of each). It will be difficult to achieve effluent limits by passive water treatment in most cases by using any one method alone. However, coupling these systems could allow some acidity reduction and metal precipitation with one system, then routing the water into another system for additional acidity and metal removal. The primary application of most passive treatment systems will be on watershed restoration projects, AML sites, and perhaps for pre-treatments for active treatment systems using chemicals. OLCs are particularly useful in steep terrain where long (300 to 1000 m) channels are possible, and they offer a unique treatment where no other passive system is likely to be appropriate. OLCs will produce metal flocs, so settlement basins should be incorporated in the design. Larger OLCs should have settling ponds or wetlands placed at intermediate points (flat channel segments) to remove the precipitates and help prevent plugging.

Table 2. Characteristics and performance of a sandstone open channel and eight OLCs at field sites in Pennsylvania and West Virginia (SS=sandstone, LS=limestone).

Site	Flow	Length	Rock type	Slope	Acidity Initial	Acidity Final	Acid Loss	Rate of Acid loss
	(gpm)	(ft)		(%)	(---- mg/l----	)	(%)	(%/ft)
Coral/Graceton	350	720	SS	10	550	540	2	.0028
Morg Airport E	20	90	LS	20	355	330	7	.0780
Morg Airport W	30	150	LS	14	410	360	12	.0800
Eichleberger #2	100	160	LS	20	510	325	36	.2250
Pa-DER	25	37	LS	60	2600	2500	4	.1080
PA Game Com.	128	35	LS	45	330	125	62	1.7710
Cottage Town	80	450	LS	9	32	28	13	.0290
Opawsky	240	150	LS	9	30	15	50	.3333

The age of the channels we studied varied from 2 to 8 yrs and none of these channels had required maintenance. If constructed correctly, OLCs should be nearly maintenance free and less expensive to construct than other AMD treatment systems.

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AN APATITE DRAIN: NEW METHOD FOR IRON AND ALUMINUM REMOVAL FROM FROM HIGHLY CONTAMINATED ACID MINE DRAINAGE[1]

by

Jung-Chan Choi and Terry R. West[2]

Abstract. The apatite drain system is a new method for acid mine drainage (AMD) treatment. Laboratory tests and the field experiment showed that this technique can be used for removal of high concentrations of iron and aluminum in the AMD with pH less than 4.0. In addition, this system removes both ferric and ferrous irons whereas constructed wetlands system remove only ferric iron when it is converted from ferrous iron in the wetlands. The geochemical model was then used to simulate the changes in concentration of aqueous constituents and in pH, and the potential mineral phase. The results of MINTEQ2 supports the conclusion of experiments. Apatite removed iron, sulfate, and aluminum from AMD and pH was inversely proportional to apatite added until it had reached the equilibrium point (pH=4.09 at 25°C). Nevertheless, the role of apatite as a precipitant and a pH buffer was restricted by the solubility of it.

INTRODUCTION

AMD forms when certain sulfide minerals are exposed to the atmosphere and oxidized in the absence of calcareous material. Although commonly associated with coal mines, the problem also occurs in areas where pyrite or marcasite becomes exposed during land disturbance such as in metallic sulfide mines, highway road cut, subway tunnels, etc.

In the process of AMD forming, sulfide minerals oxidized to form a series of soluble hydrous iron sulfates. Usually, these compound appear as white and yellow crusts on the weathered rocks or sediment surfaces. Natural waters readily dissolve the salts and hydrolyze to form acidic drainage with high concentration of sulfate and ferrous iron. Subsequently, the ferrous iron is oxidized to the ferric state, complexing with water to form a ferric hydroxides (yellow boy) that impart the red and yellow color characteristic of acid mine drainage.

Conventional AMD treatment is a simple process: the water is neutralized, typically to a pH of 8 to 9, and then aerated to oxidize the iron to the ferric state if ferrous iron exists in AMD, causing precipitation of $Fe(OH)_3$ (yellow

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boy sludge). The water is then separated from the sludge in a series of settling basins or ponds and is discharged.

Alkaline reagents used in conventional AMD treatment are lime (CaO), limestone ($CaCO_3$), sodium hydroxide (NaOH), and sodium carbonate (Na_2CO_3). However, these reagents are expensive, potentially dangerous, and when misused can results in the discharge of excessive alkaline water. It is obvious that conventional treatment of run-off and seepage is not a long-term solution, because formation of AMD can persists for many decades.

Staged aerobic constructed wetlands offer a potential low-cost, natural, low maintenance, and long-term alternative to conventional treatment of AMD. In an aerobic wetlands system, oxidation reactions occur and the metals precipitate as oxides and hydroxides. Constructed wetlands contain cattails growing in a clay or spoil substrate. However, plantless systems have also been constructed and function in a similar way to systems containing plants. However, aerobic ponds are not recommended when the water entering the wetlands system has a pH less than 4. At such a low pH, iron oxidation and precipitation reactions are quite slow, and significant removal of iron in the aerobic pond would not be expected (Hedin et al., 1994).

The Anoxic Limestone Drain (ALD), which consists of a shallow, limestone-filled trench excavated into the source material and sealed from the atmosphere, passively introduces buffering capacity, as alkalinity, into the AMD and may comprise the initial component of a staged wetlands system. Changes in pH due to acid production from Fe hydrolysis in the wetlands are buffered due to the high alkalinity in the influent (Brodie, 1991). Dissolution of limestone added 100-200 mg/l of alkalinity as $CaCO_3$ to the water (Kleinmann et al., 1990).

However, not all water is suitable for pretreatment with the ALD. The primary chemical factors believed to limits the utility of the ALD are the presence of ferric iron, aluminum and dissolved oxygen (DO). When acidic water containing any ferric iron or aluminum contact limestone, metal hydroxides will form. No oxygen is necessary. Ferric hydroxide can armor the limestone, limiting its further dissolution. Whether aluminum hydroxides armor the limestone has not been determined. The buildup of both precipitates within the ALD can eventually decrease the drain permeability and cause plugging. The presence of dissolved oxygen in mine water will promote the oxidation of ferrous iron within the ALD, and thus potentially cause amoring and plugging.

APATITE DRAIN SYSTEM

Seeps of some Indiana Abandoned Coal Mine sites show high concentration of ferric iron and aluminum and very low pH because refuse piles have weathered for several decades. Therefore, constructed wetlands system with ALD is not appropriate.

Laboratory tests by the authors showed a high potential for apatite where limestone has failed. Apatite removed iron and aluminum as an metal phosphate at low pH. According to the laboratory test using pebble to sand-sized apatite (50 mm to 0.6 mm) with aerobic condition, apatite removed iron from 100 to 1,200 mg/l and aluminum from 0 to 800 mg/l, and removal was inversely proportional to flow rates. Flow rate ranged between 1.17×10^{-4} to 1.43×10^{-3} cm/sec. In addition, pH increased to values as high as 3.2 in the effluent water from pH of influent water ranging from 2.1 to 2.2 (Choi and West, 1995a).

According to this result, an apatite drain was constructed on September 30, 1994 at the Green Valley Abandoned Mine site near Terre Haute in west central Indiana. The primary objective of this experiment is to evaluate the long-term ability of the apatite drain to mitigate AMD under field conditions. The drain was 9 m long, 3.3 m wide, and 0.75 m deep, and receives AMD seepage from reclaimed gob

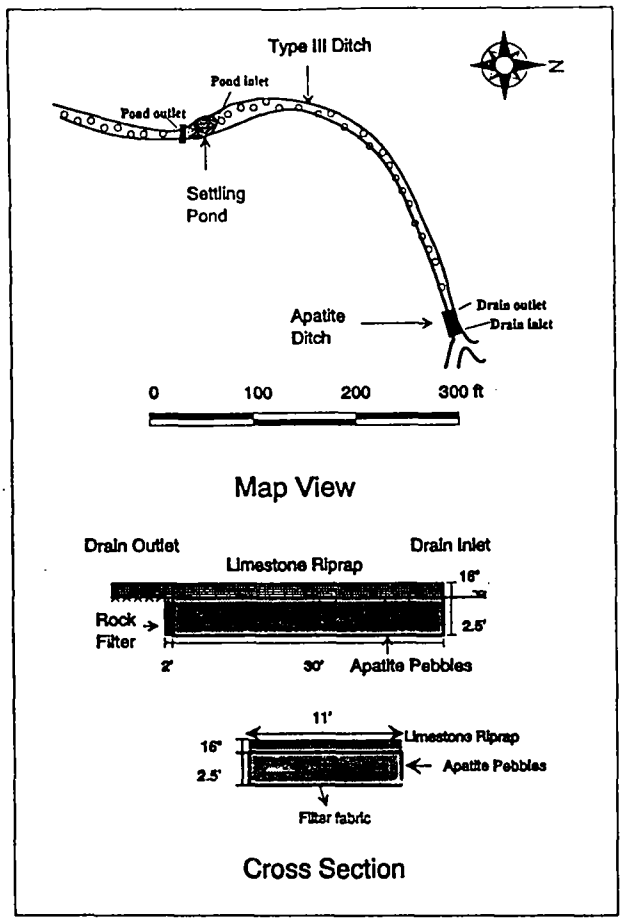

Figure 1. Schematic of an apatite drain design

piles (See Figure 1). The apatite drain was covered with limestone riprap (D_{50}=36 cm) and filter fabric (coefficient of permeability>10^{-3} cm/sec) to protect the drain system from stormwater and siltation. Limestone riprap was also used as a rock filter at the end of the apatite drain. The drain consists of about 50 metric tones of 50 mm to 0.6 mm sized marine apatite (francolite) which came from Payne Creek Phosphate Mine in central Florida. A gabion structure was constructed downstream of the drain to create a settling pond to collect precipitates.

Apatite removed iron from 800 to 4,200 mg/l, aluminum from 120 to 830 mg/l and sulfate from 2,090 to 13,430 mg/l between the section of drain inlet and pond outlet during the nine month monitoring period (See Figure 2).

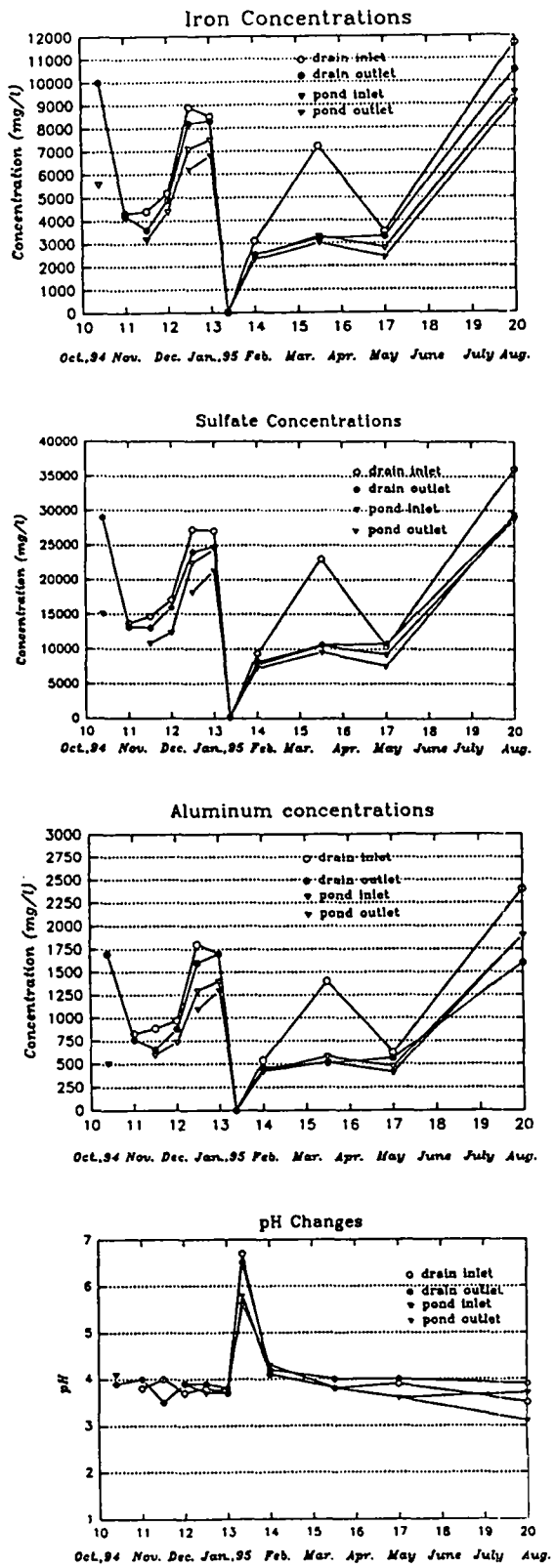

Figure 2. Iron, aluminum and sulfate removals, and pH changes

The pH is nearly constant for the influent and effluent, ranging between 3.1 and 4.3. Flow rate measured at the gabion structure ranged from 0.8 to 1.2 gpm except January 11, 1995 when a stormwater event was occurred (flow rate>100 gpm). Precipitates of iron and aluminum phosphate (yellow and white suspended solids) continued to accumulate in the settling pond (Choi and West, 1995b).

OBJECTIVE OF STUDY

A preliminary question to consider is under what conditions an apatite drain system is effective. The effectiveness of an apatite drain seems to depend on pH, flow rate, and grain size.

According to the X-ray diffraction analysis, only gypsum was detected in the precipitates collected from the water in the settling pond. It seems that remaining precipitates consist of amorphous phosphates. Therefore, it is necessary to define the composition of the precipitates resulted from reactions between AMD and apatite.

To solve these problems, the MINTEQA2 computer program was used to simulate the experimental changes in concentration of aqueous constituent in the acid mine water. MINTEQA2 is a geochemical equilibrium speciation model capable of computing equilibrium among the dissolved, adsorbed, solid, and gas phases in an environmental setting (Allison et al., 1991). The model can be used to calculate the equilibrium composition of dilute aqueous solutions in the laboratory or in natural aqueous systems. It can be used to calculate the mass distribution between the dissolved, adsorbed, and multiple solid phases under a variety of conditions including a gas phase with constant partial pressure.

The objectives of this study is to apply MINTEQA2 to the attenuation problem of AMD, to predict the outcome solution chemistry, to compare it with the experimental data, and to find out chemical processes responsible for the chemical composition of actual experiments.

GEOCHEMICAL MODELING

The apatite added to treat AMD was assumed to have homogeneous, ideal chemical composition, which can be represented by hydrapatite ($Ca_5(PO_4)_3OH$). The elements of interest in this simulation were iron, aluminum, manganese and sulfate, which react mostly with three constituents, that is, calcium, phosphate and H_2O. Francolite was not considered because it has four more elements added to the system (See Table 1) and the iteration number to reach convergence may exceed the 200 maximum allowed by MINTEQA2 which could cause error of the iteration number. The chemical characteristics for the untreated water

Table 1. Chemical analyses of phosphate pebble (+1 mm) in weight percent (from Cathcart, 1989).

$Ca_{10-X-Y}Na_XMg_Y(PO_4)_{6-Z}(CO_3)_ZF_{0.4Z}F_2$	
P_2O_5	30.7-36.1
CaO	40.8-49.0
F	3.63-4.01
SiO_2	6.33-10.4
Al_2O_3	0.57-3.77
Fe_2O_3	0.55-1.38
MgO	0.14-0.35
Na_2O	0.11-0.57
K_2O	0.11-0.57
Ti_2O_8	0.04-0.06
MnO	0.01-0.03
S	0.10-0.52
CO_2	1.83-3.80
Ratios	
CaO/P_2O_5	1.40
F/P_2O_5	0.133

Table 2. Chemical data from laboratory testing to evaluate the effectiveness of apatite for AMD control using the seepage water collected from Seep 108 located at the toe of the southwestern edge of the Southeast Gob Pile at the Friar Tuck Abandoned Mine site near Dugger, Indiana (from Choi and West, 1995a).

Water Sample	pH	Eh	Alk. (eq.	Acid. $CaCO_3$)	SO_4^{2-} (	Ca^{2+}	Mg^{2+} mg/l	K^+	Na^+	Zn^{2+})
August 29, 1991 - September 4, 1991										
Seep 108A	2.1	386	0	31200	36200	510	1300	28	50	100
Bottle A	2.4	333	0	29500	34100	620	1300	27	65	100
Bottle B	2.9	250	0	27400	33900	650	1300	27	90	100
Bottle C	3.0	237	0	25700	31300	610	1300	29	93	100
Bottle D	3.2	222	0	23900	29100	560	1500	31	96	100

Water Sample	Fe^{2+} (	Fe^{3+}	Al^{3+} mg/l	Mn_{tot}	Si	TDS)	Charge Balance	Flow rate (l/min/kg)
August 29, 1991 - September 4, 1991								
Seep 108A	4600	800	3600	250	72	47600	0.2	
Bottle A	4500	300	3400	240	69	44700	-0.1	9.52×10^{-4}
Bottle B	4500	400	3500	250	73	44800	1.5	5.35×10^{-4}
Bottle C	4400	300	3200	250	75	41800	3.1	2.39×10^{-4}
Bottle D	4300	400	3000	250	77	39500	5.4	1.21×10^{-4}

were obtained from Choi and West (1995a) and are shown in Table 2. Precipitation was allowed but no oxidation/reduction reaction was permitted. The pH was allowed to change in response to the dissolution of hydraptite and precipitation of other constituents, whereas the Eh was ignored in the program runs. The hydraptite was considered as an infinite solid for the first run to calculate the maximum amount of hydrapatite soluble in the solution with different water temperatures. Adsorption was not allowed in these runs because the data for the adsorption model such as a particular metal oxide and its surface area and sorption site concentration, could not be obtained from the experimental data. The trace elements which have a strong tendency to adsorb on ferric hydroxide were not considered in this geochemical modeling, either.

In order to simulate the pH variation with respect to the amount of apatite added and to find the reduction of metals and sulfate in the system, another run was executed with stepwise increasing apatite amount added at initial pH. Additionally, an excution was performed to trace the sequence of mineral precipitation.

RESULTS AND DISCUSSION

Speciation calculations using MINTEQA2 show that the dominant free ions and complexes for Al, Fe, and Mn include $AlSO_4^+$ and $Al(SO_4)^{2-}$, Fe^{2+}, $FeSO_4$, $FeSO_4^+$ and $Fe(SO_4)_2^-$, and Mn^{2+}, and $MnSO_4$, respectively.

When the water temperature was set at 25°C, most of the dissociation of apatite occurred at pH below 3.8. When 0.04 mol of apatite was added to the solution, the pH of equilibrium solution was 3.8. Beyond this point, the increasing rate of pH was conspicuously reduced, which may be closely related to the solubility of apatite. The maximum dissolvable amount of apatite with Seep 108A was 0.082 mol/l at pH 4.09, beyond which pH was constant and surplus of hydrapatite was not dissolved.

When the water temperature was set as 4°C, The maximum amount of apatite dissolvable in the solution was 0.046 mol/l at pH 4.62. The

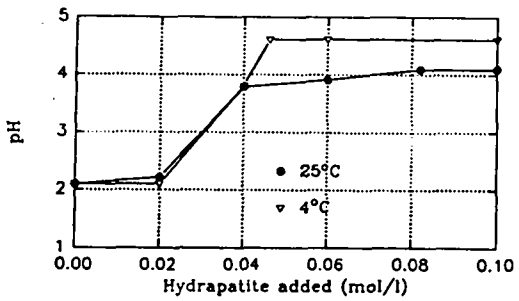

Figure 3. Simulation of MINTEQA2 on variation of pH as a function of amount of apatite added into solution and temperature

pH as a function of the added amount of apatite and temperature is shown in Figure 3.

When precipitation was allowed to occur, the possible minerals precipitated are listed in Table 3. Precipitation of manganese phosphate consumed H^+. The dissolution of hydraptite at low pH also removed H^+ from solution, which is supported by dissolved species of phosphate such as $FeH_2PO_4^+$, $H_2PO_4^-$, and $MgH_2PO_4^+$.

The solubility of apatite was closely related with the characteristics of its own chemical composition and chemistry of the solution. Especially, the solubility of hydrapatite is a function of Ca^{2+} activity in the solution (Wilson and Ellis, 1984). The Ca^{2+} is a more reactive ion component than PO_4^{3-} so that the solubility of hydraptite is controlled by the activity of Ca^{2+} ion.

Fe^{3+} and Mn^{2+} were quickly removed as soon as hydrapatite was added. Once apatite was added, the first minerals possibly precipitated were strengite and $MnHPO_4$, which are iron phosphate and manganese phosphate, respectively. Strengite ($FePO_{4(s)}$) and variscite ($AlPO_{4(s)}$) are the stable solid phase when the phosphate is precipitated in the low pH range. However, the pH of minimum variscite solubility occurs at about 1 pH unit higher than that of strengite, so that the precipitation of variscite did not occur.

The modeled concentration of dissolved manganese as a function of PO_4^{3-} does not correlate very well with the actual analysis data (See Table 2). According to the data of simulation, manganese ion was completely precipitated as a mineral of manganese phosphate. However, the actual concentration of manganese apparently did not decrease and no precipitation was observed. Thise behavior of manganese an be explained in several ways. Differences between the two results can be accounted for by the assumption that the total concentration of Mn in the experimental data would consists of Mn^{2+} only. Secondly, microcrystalline manganese phosphate might be analyzed as a dissolved phase. This kind of error can be eliminated by filtering and centrifuging the solution before analysis.

Table 3. Potential minerals precipitated at equilibrium

PHOSPHATE	
Hydrapatite	$Ca_5(PO_4)_3OH$
Strengite	$FePO_4\ 2H_2O$
Vivianate	$Fe_3(PO_4)_2\ 8H_2O$
MnHPO4	
OXIDE	
Hematite	Fe_2O_3
Ca-Nontronite	$Ca_{0.167}Fe_2(Si_{3.67}Al_{0.33})O_{10}(OH)_2$
Diaspore	AlO(OH)
SULFATE	
Gypsum	$CaSO_4\ 2H_2O$
Alunite	$K\ Al_3(SO_4)_2(OH)_6$
$AlOHSO_4$	

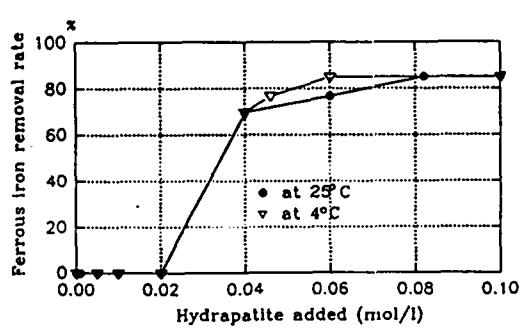

Figure 4. Ferrous iron removal rate as a function of amount of apatite added into solution.

Additionally, manganese ion can be formed in oxyhydroxides at low temperature. Therefore, it might exist in a state of flocculation in the solution and could be analyzed along with dissolved phase. Ferrous iron is a dominant cation in the acid mine drainage. Its chemical reactions have a significant effect on themobility of other solutes. Exposure to atmospheric O_2 results in oxidation of much of ferrous state to ferric state. However, the rate of conversion of ferrous to ferric iron in the aerated solutions is very slow below pH 4.0. The precipitation of ferrous iron depends on the concentration of phosphate in the solution and on the solubility of hydrapatite at low pH (See Figure 4). Therefore, the solubility of apatite is the key factor as a reagent for the treatment of AMD.

The aluminum concentration of the simulation data were clearly related to the pH control imposed on the system by the apatite solution. Nordstorm (1982) suggested that an aluminum sulfate ($(Al_2SO_4)_3$) solid may control aluminum solubility in some acid sulfate-rich waters. The minerals $AlOHSO_4$, Diaspore (AlOOH), and alunite ($KAl_3(SO_4)_2(OH)_6$) are all predicted to be supersaturated by MINTEQA2.

Lindsay (1979) mentioned that the solubility of SO_4^{2-} in soil is limited by the solubility of gypsum. The Ca^{2+}, together with high SO_4^{2-} concentrations from pyrite oxidation, yields in a saturated condition with respect to gypsum. The simulation results show that gypsum and alunite as well as $AlOHSO_4$ were precipitated out of solution.

Another run of MINTEQA2 has been performed to trace the sequence of mineral precipitation (See Table 4). On the basis of the output of this run, the sequence of mineral precipitation and dissolution could be traced step by step. In case of ferric iron, first mineral speciated was strengite During this excution. However, when pH was increased, the phosphate from strengite combined with ferrous iron and vivianite was precipitated. On the other hand ferric iron was precipitated as hematite and/or Ca-nontronite. The sequence

Table4. Variation of specific elements and mineral assemblages (0.06 mol/l hydrapatite added)

STEP	ELEMENT (% precipitated)					(not dissolved, mmol/kg)
	Fe^{3+}	Fe^{2+}	Al^{3+}	Mn^{2+}	$SO4^{2-}$	Hydrapatite
1	0.0	0.0	0.0	0.0	0.0	0.0549
2	100.0	0.0	0.0	0.0	0.0	0.0533
3	100.0	0.0	0.0	0.0	0.0	0.0533
4	100.0	0.0	94.0	0.0	0.0	0.0524
5	100.0	0.0	90.1	100.0	0.0	-
6	100.0	0.0	90.3	100.0	0.0	-
7	100.0	0.0	99.9	100.0	77.1	-
8	100.0	0.0	99.8	100.0	82.4	-
9	100.0	79.3	99.8	100.0	92.1	-
10	100.0	79.0	99.8	100.0	92.2	-
11	100.0	78.9	99.8	100.0	92.2	-
12	100.0	64.5	99.6	100.0	95.3	-
13	100.0	76.7	99.7	100.0	93.0	-

STEP	MINERAL PRECIPITATED (mmol/kg)								
	Strengite	Ca-nontronite	Hematite	Vivianite	Alunite	Diaspore	$AlOHSO_4$	$MnHPO_4$	Gypsum
1	0.0000	-	-	-	-	-	-	-	-
2	0.0150	-	-	-	-	-	-	-	-
3	0.0150	-	-	-	-	-	-	0.0048	-
4	0.0150	-	-	-	-	-	-	0.0048	-
5	0.0150	-	-	-	-	0.1317	-	0.0048	-
6	0.0150	-	-	-	-	0.1262	-	0.0048	-
7	0.0150	-	-	-	-	0.1265	-	0.0048	0.3149
8	0.0150	-	-	-	-	0.1265	0.0214	0.0048	0.3045
9	0.0150	-	-	0.0229	-	0.1185	0.0666	0.0048	0.2987
10	0.0136	0.0007	-	0.0228	-	0.0723	0.0673	0.0478	0.2974
11	0.0136	0.0007	-	0.0228	-	0.0712	0.0661	0.0478	0.2974
12	-	0.0007	0.0385	0.0186	0.0007	0.0416	0.0953	0.0478	0.2804
13	-	0.0007	0.0068	0.0221	0.0007	0.0658	0.0714	0.0478	0.2950

of aluminum precipitation started with diaspore and ended up with $AlHSO_4$ and alunite. The run of MINTEQA2 shows the precipitation sequence with time, which can be used to predict the mineral assemblage that is a product of the reaction of hydrapatite with AMD.

CONCLUSION

The apatite drain system is a new method for AMD treatment. A naturally occurred material was thought which will remove metals from AMD, produce insoluble and powdery precipitates, have buffering capacity or at the least maintain the pH after reaction, and dissolve slowly so that it lasts several years or several decades. Apatite from Florida satisfied these conditions.

Laboratory tests and the field experiment showed that this technique can be used for removal of high concentrations of iron and aluminum in AMD. In addition, this system removes both ferric and ferrous irons whereas constructed wetlands systems remove only ferric iron when it is converted from ferrous state in the wetlands. However, only gypsum was detected in the precipitates collected from the settling pond according to the X-ray diffraction analysis. Therefore, it seems that precipitates consist of amorphous phosphate.

A geochemical speciation model (MINTEQA2) was applied to simulate the precipitation of mineral phase, the solubility of apatite, pH variance with the apatite dissolution and the sequence of mineral precipitations. Hydrápatite, which is one of simple form of apatite and also has buffering capacity similar to francolite, was used for this simulation. The main conclusions are as follows:

- H^+ was neutralized primarily with phosphate mineral. These reactions were relatively rapid and resulted in a steep pH gradient over a narrow range of phosphate addition.
- The maximum amount of hydrapatite dissolvable in the solution was 0.082 mol/l at pH 4.09 and 25°C, whereas it was 0.046 mol/l at pH 4.62 and 4°C.
- Ferric iron was quickly removed as strengite at low pH and was transformed into hematite and Ca-nontronite as pH rose.
- The concentration of ferrous iron in the treated AMD was controlled by precipitation of vivianite (iron phosphate). The oxidation of ferrous to ferric iron was apparently limited by low pH.
- It is likely that concentration of Al was controlled by the solubility of $AlOHSO_4$ at low pH. Diaspore and alunite were other potential solid phases at low pH.
- Manganese might be formed by the precipitation of manganese phosphate (MnHPO4), which is the most stable Mn solid phases.
- Calcium and sulfate concentrations were controlled by the precipitation of gypsum.

The results of MINTEQA2 runs appeared to support the conclusion of the experimental works. Apatite is effective in removing iron, sulfate, and aluminum from AMD and pH was inversely proportional to flow rates until it had reached the equilibrium point (pH = 4.09 at 25°C).

However, further research on the apatite drain system is necessary to define the actual mechanism of the precipitation process and the constituents of those precipitates in order to optimize design of the apatite drain system.

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ASSESSMENT OF THE APPLICABILITY OF AN ANOXIC LIMESTONE DRAIN FOR A SURFACE MINE IN EAST CENTRAL TENNESSEE[1]

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Abstract: Anoxic limestone drains (ALDs) are a cost-effective technique for adding alkalinity to acid mine drainage. However, the applicability of an ALD is limited to a rather narrow range of mine drainage chemical conditions due to concerns about the armoring of limestone with ferric hydroxide, the plugging of flow paths with aluminum hydroxide, and the limited solubility of calcite. While the armoring and plugging potentials can be assessed with careful water quality analyses, the solubility of limestone in a particular mine water cannot, at this time, be predicted from mine water chemistry. Thus, the danger always exists that the ALD will generate insufficient alkalinity to completely neutralize the acidic water, resulting in either insufficiently treated discharge or a need for additional treatment. In order to remove uncertainty from the design of a 4,000-ton ALD, we conducted limestone incubation tests and pilot-scale ALD tests. Incubation tests were done using a modified version of the "cubitainer" procedure developed by the United States Bureau of Mines. The pilot ALD consisted of 65 tons of limestone. Hydrologic loading experiments were conducted that provided an assessment of the ALD performance under design flow conditions and flow rates four times higher than the design flow. Under design flow conditions, the pilot ALD discharged water with alkalinity concentrations similar to that predicted by the cubitainer tests (360 parts per million). With increased flow, concentrations of alkalinity in the pilot ALD effluent decreased, with the water becoming net acidic at a flow rate of 15 gallons per minute. The results of the pilot ALD were used to size a full-scale ALD and model ALD performance under a variety of flow conditions.

Additional Key Words: cubitainer, passive alkaline addition.

Introduction

Anoxic limestone Drains (ALDs) have made the passive treatment of acid mine drainage possible on hundreds of mine sites in the Appalachian coal region. The theory of ALDs is quite simple. Acidic water is directed through a buried bed of limestone gravel (Turner and McCoy, 1990). Limestone dissolution raises pH and adds bicarbonate alkalinity to the water, which promotes metals precipitation in subsequent ponds or wetlands. Anoxic conditions within the limestone bed prevent iron oxidation and limestone armoring. In some cases, it is economically feasible to construct ALDs which

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may last decades due to the low cost and limited solubility of limestone.

However, ALD technology is not without shortcomings. The use of ALDs is not suitable under certain water chemistry conditions. Ferric iron and aluminum both precipitate within an ALD, decreasing performance by armoring limestone and plugging flow paths (Hedin, et.al.). It is also possible that a properly designed and constructed ALD will not generate sufficient alkalinity to completely neutralize acidic water due to limited limestone solubility. Water chemistry which appears similar based on evaluation of standard acid mine drainage analytes may generate dissimilar alkalinity concentrations.

This paper describes the design process of a large ALD system (4,000 tons of limestone). Because of the financial commitment involved in the construction of a 4,000-ton ALD system, it was considered prudent to thoroughly evaluate the ALD concept prior to construction. This paper describes our use of cubitainer tests and a small "test" ALD to provide data.

The research was conducted at Sequatchie Valley Coal Corporation (SVC). SVC operated area surface coal mines located in east central Tennessee. One surface mine, locally referred to as Area 1, was mined from 1978 to 1982. Backfilling, regrading, revegetation, and related reclamation activities were largely completed by 1983. However, acidic seeps began to develop at topographic lows after 1983. In the period that followed, SVC collected acidic water and used standard chemical treatment and precipitation methods. Realizing that chemical treatment may not be in the best interest of SVC or the environment, SVC considered the applicability of constructed wetlands and related passive technologies (Hedin and Massey, 1995). SVC implemented an approach consisting of short term management and development of long term solutions to water quality problems.

Evaluation of groundwater quality data at Area 1 revealed good news, but also raised some questions. Positive results included the absence of aluminum and a pH of 5.5 standard units. At a pH of approximately 5.5 standard units, no ferric iron should exist (Stumm and Morgan, 1970). Therefore, armoring of limestone with iron hydroxides and flow path clogging by aluminum precipitates would not be anticipated in an ALD constructed at Area 1. However, acidity concentrations were measured above 300 ppm. ALDs have been properly sized and constructed which generate less than 200 ppm alkalinity (Hedin, et.al., 1994), which would be insufficient to completely neutralize acidity at Area 1. Therefore, as part of the evaluation of ALD applicability at Area 1, SVC desired a knowledge of the amount of alkalinity likely to be produced by an ALD. Cubitainer testing (Watzlaf and Hedin, 1993) was subsequently conducted to estimate alkalinity likely to be generation by an ALD.

Cubitainer Testing

The United States Bureau of Mines (USBM) presented an ALD alkalinity prediction method in April 1993 at the *Thirteenth Annual West Virginia Surface Mine Drainage Task Force Symposium*. The method involves placing limestone and untreated mine water in collapsible containers (cubitainers) and monitoring the alkalinity generation by periodic extraction of water. The method was developed by the USBM during studies of two ALDs with significantly different alkalinity generation characteristics. The USBM studies determined that mine water chemistry, not limestone quality, determined the alkalinity generation characteristics of an ALD. In addition, the researchers noted that the 48 hour alkalinity concentrations predicted by the cubitainer testing method were within six percent of the actual alkalinity generated by the ALDs (Watzlaf and Hedin, 1993). Prior to this research, a method for predicting ALD alkalinity generation did not exist.

In 1993, SVC engaged Skelly and Loy to assist in the evaluation of passive alternatives to chemical water treatment at Area 1. As part of the assignment, the USBM cubitainer procedure was utilized to estimate the alkalinity which may be generated by an ALD at Area 1. Specifics of the cubitainer method follow.

Collapsible, one-cubic foot cubitainers and smaller one-gallon cubitainers were used for the testing procedure. One-cubic foot containers provided adequate water to conduct a series of analytical and biological tests after the cubitainer test was

completed. The cubitainers were equipped with two-holed rubber stoppers and lids. Gas impermeable "Nalgene" tubing was then placed through each stopper hole. To form an airtight seal, silicon sealant was placed around the stopper holes and tubing. Two pieces of tubing were used. One was cut to sufficient length to extend to the bottom of the cubitainer while the other was inserted flush with the bottom of the stopper. Clamps were then attached to the tubing. An on/off clamp was attached to the longer tube (used for filling) and an adjustable clamp was attached to the shorter tube (used for expelling oxygen, nitrogen, and liquid samples). By utilizing the adjustable clamp, flow rates into and out of the cubitainers were controlled to avoid introducing oxygen into the container.

Each cubitainer was filled approximately ⅔ full (20 Kg) of 1½"x¾" limestone. The limestone was obtained locally from the Monteagle Formation. Prior to being placed into the cubitainer, the limestone was thoroughly rinsed to remove all fine particles of calcium carbonate. Rinsing was completed in a two-step process. The first rinse was completed using water from the SVC office facility well. Once the limestone was rinsed of fine particles of calcium carbonate on all surfaces, the sample was rinsed with deionized water. This second rinse was employed to completely remove residue (if present) from the well water. Limestone was then placed on a clean tarp and left to dry completely. Once dry, the limestone was introduced into the cubitainers preparing them to be filled with the water sample.

Utilizing the dewatering well field in-place at Area 1, the wells were purged with a minimum of three well volumes prior to the collection of any water samples. Background water quality parameters for pH, dissolved oxygen, and temperature were taken initially before any well purging began. Once wells were purged, readings were again taken to ensure that dissolved oxygen levels remained low, generally less than one part per million (ppm).

The cubitainer filling process then proceeded following the prescribed methods used by the USBM. In addition to using larger cubitainers, one procedural enhancement was employed. Prior to filling each cubitainer with water, each cube was filled with nitrogen. The nitrogen was pumped into each cube to remove oxygen. Through the use of an adjustable clamp, the cube was then collapsed, forcing the nitrogen and remaining oxygen out of the cube. The clamp was fully closed and the cube was refilled with nitrogen. This process was conducted three times, encouraging the replacement of oxygen with nitrogen. Once completed, the cubitainer was filled with sample water.

As another means to minimize oxygen introduction to the cubitainers, water obtained from the sample well was collected using an ISCO Model No. 3710 portable sampler equipped with a peristaltic type pump. Multiple water samples were collected from the well at a ten-foot depth. Continuous dissolved oxygen readings were monitored at this depth. Water flow rates and nitrogen release from the cubitainer were then controlled using the clamps. Each of the cubitainers was filled through the tubing which extended to the bottom of the cube. Water was introduced while forcing the nitrogen from the cubitainer. The filling procedure continued until no visible air space remained within the cubitainer.

Once each cubitainer was filled, the tubes were clamped shut. The cubitainers were then placed into a trough filled with continuously circulating water originating from the well field. The purpose of the filled trough water bath was to keep the filled cubitainers at a constant temperature (approximately equivalent to the groundwater temperature). This procedure also served to keep the cubitainers in an anoxic state. Water was pumped from the dewatering wells into the trough for the duration of the 48-hour test period.

Cubitainers remained in the water bath for a period of 48 hours. After a period of 48 hours, the one-cubic foot cubitainers were taken out of the water bath and retained for subsequent aeration and settling, analytical testing, and biological testing. The one-gallon cubitainers were kept in temperature controlled coolers for a period of one week. Samples of cubitainer water were collected after 4, 8, 24, 48, 72, 96, and 120 hours. Alkalinity and pH readings were made on each of these samples.

Cubitainer Results

Evaluation of the alkalinity results revealed that the alkalinity increased from approximately 140 mg/l to 340 mg/l in the first 48 hours of the cubitainer test performed on the larger containers. Figure 1 depicts time versus alkalinity for the first five days of the smaller scale, longer duration, one-gallon cubitainer test which confirmed results from the larger cubitainers. This figure indicates that near maximum alkalinity was achieved in the first 48 hours of the test period. Therefore, if past research conducted by the USBM is validated by this cubitainer testing, it would be expected that a properly sized and constructed ALD at Area 1 would generate alkalinity of a similar magnitude. These results indicated favorable conditions existed for utilization of an ALD at Area 1.

Pilot-Scale ALD Testing

The cubitainer test provided confidence on the applicability of an ALD solution for Area 1. As plans for the full scale ALD evolved, questions regarding ALD performance under variable flow conditions were raised. To address this concern, a small ALD was designed that would allow testing of alkalinity generated under variable flow regimes.

The 65-ton test ALD was constructed in January 1995. A rectangular pit 60 feet long, six feet wide, and four feet deep was developed to contain the gravel sized limestone. The ALD limestone was wrapped in filter fabric and plastic and buried under two feet of spoil. The plastic may inhibit water losses or gains while the spoil is intended to ensure anoxic conditions existed within the ALD. The source water was obtained from a nearby groundwater pumping system. In order to test the ALD under a variety of flow conditions, a control valve was placed in the test ALD influent line to allow for flow rate adjustment. The exit pipe was placed above the top elevation of the ALD to ensure that the limestone would remain completely under water.

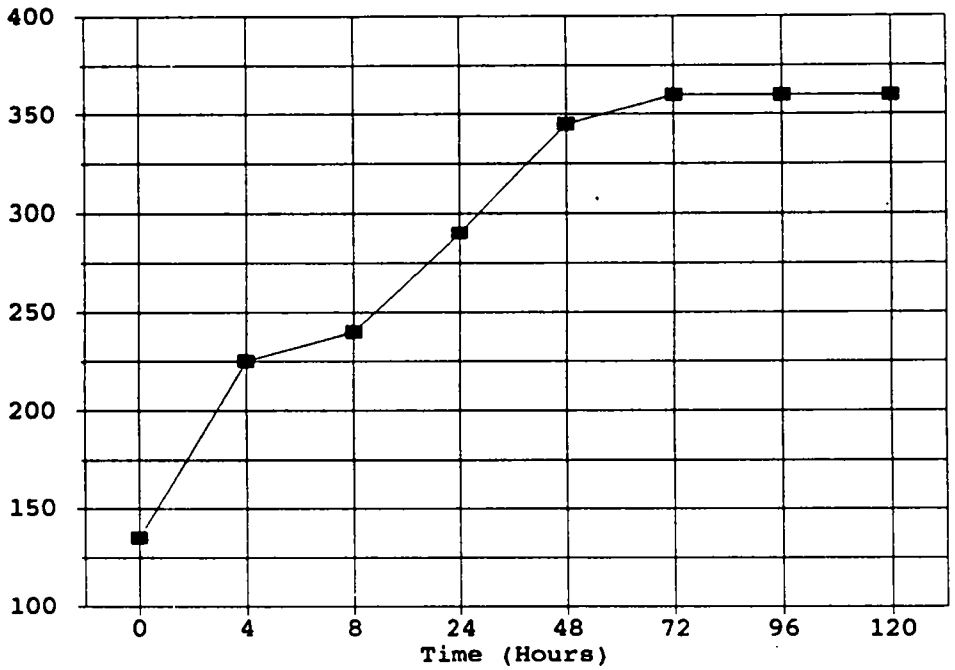

Figure 1. Cubitainer Test Contact Time Versus Alkalinity

The ALD was operated between February and May 1995. The test ALD was used to determine alkalinity generation over a range of flow conditions. In order to obtain the maximum alkalinity concentration, an ALD should contain at least 12 tons of limestone for each gallon per minute (gpm) of flow (Hedin et. al., 1994). Thus, the base flow rate used for the test ALD was approximately five gpm.

Figure 2 graphically depicts flow rate versus alkalinity concentrations for flow rates which approximate the base flow rate (three to eight gpm). These data exclude flow rate adjustment tests described later in this paper. After initial system flushing, water exiting the test ALD contained alkalinity concentrations of approximately 360 ppm. After a few months of operation, the alkalinity stabilized at approximately 320 ppm.

Figure 3 depicts flow rate versus alkalinity concentrations during flow rate adjustment tests in the ALD. As expected, alkalinity generation decreased as flow increased. The flow was increased up to 20 gpm (approximately 3 tons of limestone per gpm of flow). This flow is equivalent in tons of limestone per gpm to a flow much greater than the maximum expected flow to the ALD. Therefore, the pilot-scale test covered the full range of conditions anticipated in the proposed full scale ALD. At a flow rate of 15 gpm, alkalinity concentrations had been reduced to approximately 265 ppm and the water exiting the test ALD became net acidic.

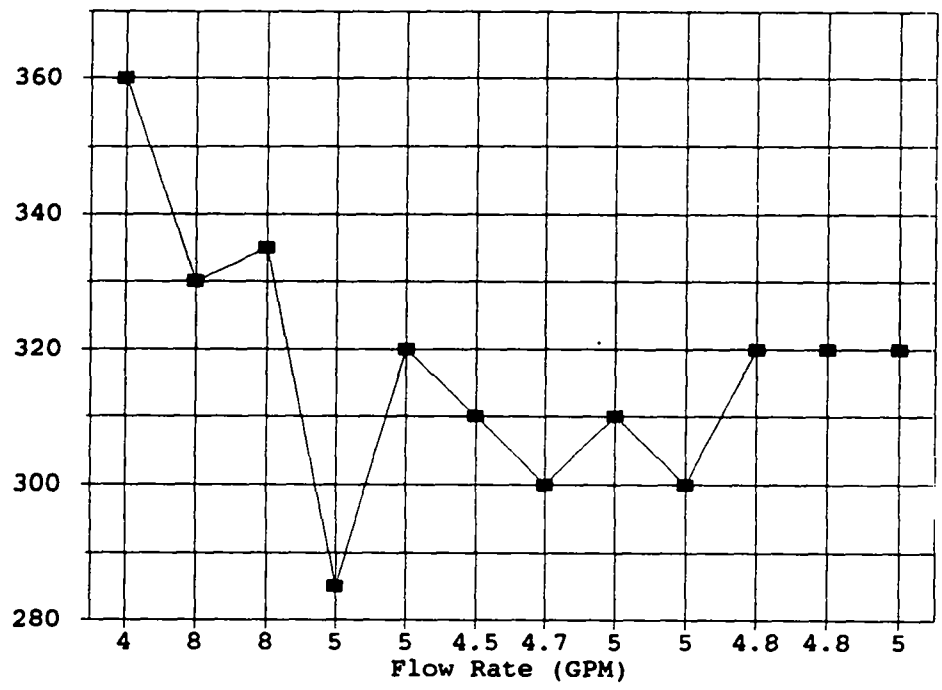

Figure 2. Pilot ALD Flow Rate Versus Alkalinity

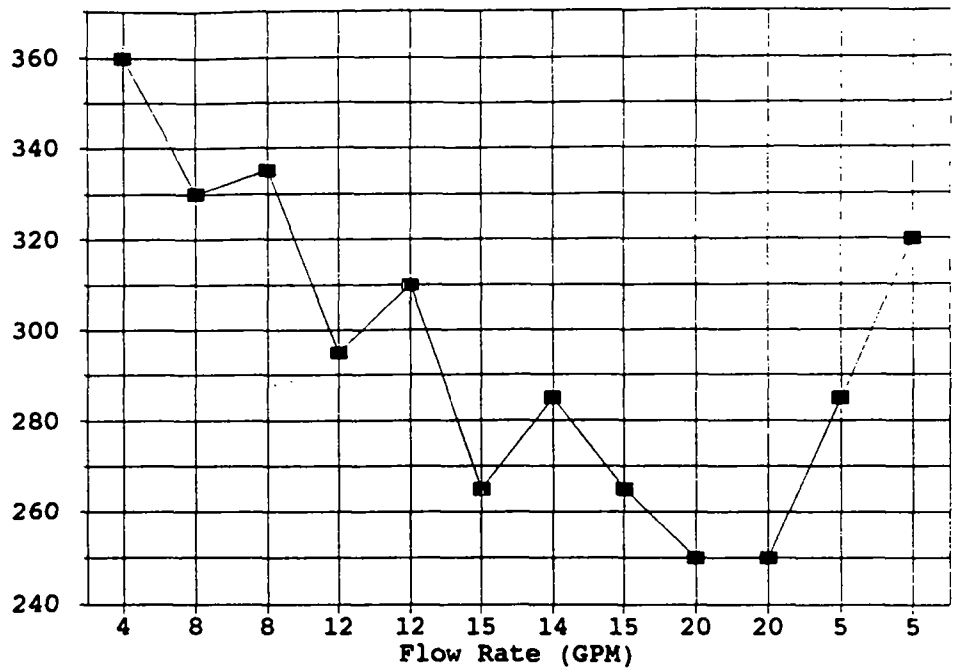

Figure 3. Pilot ALD Flow Rate Versus Alkalinity Flow Rate Adjustment Test

During maximum flow conditions expected in the full scale system, the limestone to flow ratio is anticipated to be eight. At a comparable flow rate in the test ALD (eight gpm), alkalinity concentrations exceeded 300 ppm. Using this result as a prediction tool, net alkalinity would be expected even during maximum flow conditions.

The last two months of test ALD data collection was evaluated to determine potential variation of alkalinity generation when flow remained relatively constant. The alkalinity generation was remarkably constant in the range of 310 to 320 ppm. These data are depicted by the last eight readings of Figure 2.

Conclusions

Due to the inability to determine alkalinity generation in an ALD based on water chemistry alone, other techniques must be employed. Two available methods are cubitainer testing and pilot-scale ALD testing. As documented here, both methods provided similar results under recommended ALD sizing criteria. In addition, a pilot-scale system can be used to simulate extreme flow conditions which may be anticipated. The pilot-scale test can also be used to estimate the flow rate at which the ALD effluent would become net acidic. At that point, the ALD alone would generate insufficient alkalinity to completely neutralize the acidic water.

The methods presented in this paper formed the design basis for a 4,000-ton full scale ALD which has been installed at SVC's Area 1 near the end of 1995. Initial results from the full scale ALD are remarkably similar to both the cubitainer test and pilot-scale ALD test. The first discharges from the full-scale ALD to the receiving streams have alkalinity concentrations of approximately 340 ppm. This result validates the usefulness of the techniques described in this paper.

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