Acid Mine Drainage Treatment with Armored Limestone in Open Limestone Channels

P. F. Ziemkiewicz, J. G. Skousen,* D. L. Brant, P. L. Sterner, and R. J. Lovett

ABSTRACT

Much attention has been devoted to developing inexpensive, limestone-based systems for treating acid mine drainage (AMD) with little or no maintenance. Treatment of AMD with limestone results in a surface coating of metal hydroxides, a process known as limestone armoring. Once armored, limestone is assumed to cease dissolution and acid neutralization. Laboratory and field experiments determined acidity changes in AMD when contacted by armored and unarmored limestone and investigated the implications of armoring on the construction of open limestone channels for treating AMD. Results of a laboratory titration study indicated armored limestone was only 2 to 45% less effective in neutralizing a hydrochloric acid solution as unarmored limestone. A laboratory container study showed that armored limestone was 90% as effective in neutralizing AMD as unarmored limestone. The field study surveyed 2- to 8-yr-old, rock-lined channels constructed of sandstone or limestone, and measured water quality changes down the length of the channel. Open limestone channels, though armored, reduced more acidity in AMD (4–62%) than the sandstone channel (2%). The results from open limestone channels were compared to an acid neutralization kinetics model that predicts the rate of acid neutralization for a specified channel size, and AMD flow and acidity concentration. The open limestone channels in the field neutralized more acidity than the model predicted. Open limestone channels show promise for neutralizing AMD in watershed restoration projects and abandoned mine land (AML) reclamation projects where one-time installation costs are incurred, little to no maintenance is required, and systems do not have to meet specific water quality standards.

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Acid mine drainage is one of the largest environmental problems facing the mining industry. Acid mine drainage originates from active and AML when pyrite (FeS_2) or other metal sulfides associated with mineral deposits are subjected to oxidizing conditions. Upon exposure to oxygen and water, the sulfide minerals progress through a combination of oxidation and microbial catalyzing reactions to produce large amounts of dissolved metals, sulfate, and acidity (Singer and Stumm, 1970). This acid also dissolves other minerals, releasing cations such as iron (Fe), manganese (Mn), and aluminum (Al). The resulting AMD is generally characterized by low pH (<3.5), high acidity (>500 mg/L as $CaCO_3$; all acidity values hereafter are in $CaCO_3$ equivalents), and high concentrations of total dissolved metals (>50 mg/L). Upon reaching a stream, AMD alters the stream's chemical balance by consuming alkalinity and introducing metal ions, resulting in a degradation of biological productivity. If sufficiently severe, AMD will also render the receiving water unfit for human, agricultural, industrial, or recreational uses (Atlas and Bartha, 1987).

In order to reduce the concentrations of dissolved metals and acidity, AMD is treated with alkaline chemicals by most mining operations and the precipitated metals are collected in settling ponds. Chemical treatment is expensive, however, and may be necessary long after mining has ceased. One alternative to chemical treatment is passive treatment, which refers to any zero to low maintenance AMD treatment method that does not require continual chemical addition and monitoring. Passive systems are of increasing interest as state, industry, and federal partnerships are formed to rehabilitate watersheds damaged by historic mining (Skousen et al.,

Abbreviations: ALD, anoxic limestone drain; AMD, acid mine drainage; AML, abandoned mine land; PADER, Pennsylvania Department of Environmental Resources.

1997; Titchenell and Skousen, 1996). Passive systems offer low maintenance and inexpensive 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 even fail under high-acid loading (Kleinmann et al., 1991; Wieder, 1989). Problems with ALDs occur when Fe(III) and Al are present in the water. These cations precipitate as hydroxides (e.g., $Fe(OH)_{3\,(s)}$) and coat the limestone surfaces (armoring) and can plug the limestone void space, thereby reducing limestone dissolution and acid neutralization.

Studies by Pearson and McDonnell (1974, 1975a,b) found that armored limestone was only 20% as effective in neutralizing AMD as unarmored limestone. Ziemkiewicz et al. (1994) conducted a preliminary study of open limestone channels on AML sites that had been reclaimed in West Virginia. Voids in limestone channels contained metal hydroxides where slopes were <10% and AMD simply flowed over the limestone with little water contact and treatment. Limestone in open limestone channels was also armored, presumably reducing the limestone dissolution rate and acid neutralization to 20% of unarmored limestone (Pearson and McDonnell, 1975a). Ziemkiewicz et al. (1994) concluded that limestone channels could effectively neutralize AMD if channels were constructed on steep slopes to reduce plugging of limestone pores by metal hydroxides, and if channels were built five times bigger to account for the armoring effect. A model was developed by Ziemkiewicz et al. (1994) to estimate limestone volumes and channel dimensions for achieving neutralization of AMD based on the following first-order kinetics:

$$\ln \frac{C_F}{C_O} = -kt \qquad [1]$$

where

C_F = final acidity (mg/L);
C_O = original acidity (mg/L);
k = rate constant (1/h);
t = time of reaction (h).

Based on data presented in Pearson and McDonnell (1975a), k was solved and equals −2.303/h, which represents the rate constant of acid neutralization by limestone. To account for armoring, the rate constant was multiplied by five (the 20% dissolution rate of armored limestone compared to unarmored limestone) to account for the increased contact time needed between armored limestone and AMD for treatment. Therefore, the residence time of AMD to achieve a target acidity level (C_F) from its initial acidity concentration (C_O) could be solved. The amount of limestone required for treatment was based on the flow rate and the measured acidity (in mg/L as $CaCO_3$) of the water. Wetted channel dimensions were computed to obtain sufficient residence time of the water in the limestone channel at specified water velocities and channel slopes.

This study determined acid neutralization by armored and unarmored limestone in laboratory titration and laboratory container studies. A field study evaluated existing open limestone channels and a sandstone channel to examine AMD treatment by armored limestone. The field study acid neutralization results were compared to acid neutralization predicted on these sites by the Ziemkiewicz et al. (1994) model.

MATERIALS AND METHODS

Laboratory Titration Study

Two samples of limestone were taken from each of two field sites. The field sites were open limestone channels at Robinson Run (RR) near Maidsville, WV, and near Dola, WV. One limestone sample from each site was armored by AMD (consistent metal hydroxide coating) and one sample was unarmored. The unarmored samples were along the upper bank of the channel and had not been contacted by flowing AMD. The four pieces of limestone were measured for weight, volume, and lengths to determine a shape and elongation factor after the methods presented in Pearson and McDonnell (1977). These values were used to determine surface area of each piece of limestone (Table 1). The samples were placed in six solutions (40 mL) acidified to a known pH by HCl: pH 5.0 = 2 mg/L acidity (these were measured acidity values), pH 4.5 = 4 mg/L acidity, pH 4.0 = 8.5 mg/L acidity, pH 3.5 = 22 mg/L acidity, pH 3.0 = 70 mg/L acidity, and pH 2.5 = 208 mg/L acidity. As limestone neutralized acid in the solution, pH was kept static by the addition of HCl by a Titralab VIT-90 automated titrator (Radiometer-America, Westlake, OH) for a period of 20 min. Since limestone dissolution rate is constant if pH remains constant, a period of 20 min was deemed adequate for determining limestone dissolution rate. This time period also minimized the amount of surface area change and dissolution of armoring on limestone pieces since the same pieces were used throughout the experiment. The amount of HCl added was determined in 5-min intervals (the HCl added during each 5-min period was very similar) and summed to give the total amount added during the 20-min experiment. At the end of 20 min, each limestone sample was removed from the solution, washed with distilled deionized water, and oven dried at 90°C for 1 h. After drying, the limestone sample was placed in a desiccator until room temperature (20°C) was reached, then the sample was used in the next lower pH solution experiment. Iron hydroxide armoring was reduced very gradually by placing the armored limestone in increasingly acidic solutions during the experiments and a

Table 1. Dimensions of limestone rocks used in the laboratory titration study. From these dimensions, shape, and elongation factors were calculated from equations in Pearson and McDonnell (1977) and surface area was calculated.

	Robinson Run		Dola	
Characteristic	Unarmored	Armored	Unarmored	Armored
Weight, g	8.24	7.81	7.97	7.36
Volume, cm^3	3.01	2.84	2.97	2.72
Unit wt., g/cm^3	2.74	2.75	2.68	2.71
Max. length, cm	2.80	3.31	2.83	2.70
Min. length, cm	1.02	0.83	1.18	1.01
Shape factor†	0.72	0.63	0.74	0.72
Elongation factor‡	1.73	2.08	1.63	1.71
% Armored§ (begin)	0	100.00	0	100.00
% Armored (end)	0	90.00	0	70.00
Surface area¶, cm^2	14.07	15.41	13.48	13.08

† Shape factor was calculated by Eq. [5] in Pearson and McDonnell (1977).
‡ Elongation factor was calculated by Eq. [4] in Pearson and McDonnell (1977).
§ % Armored was a visual estimate of the amount of surface area covered by iron hydroxide coating at the beginning of the experiment and after all titrations had been completed.
¶ Calculated by Eq. [1] in Pearson and McDonnell (1977).

Table 2. Solution/limestone combinations used in the laboratory container study. Each combination marked had three replications.

Water	Robinson Run armored limestone	Dola armored limestone	Unarmored limestone
Maidsville	X		X
Shaw mines		X	X
Synthetic AMD†		X	X
Deionized water	X	X	X

† AMD = acid mine drainage.

visual estimate of armoring at the beginning and ending of the experiments is given in Table 1. Each limestone sample and pH solution combination was replicated twice. The amount of HCl added to maintain static pH was used to calculate a reaction rate based on first-order kinetics. This data was used to compare the two limestones (RR and Dola) and the effect of armoring on acid neutralization.

Table 3. Total volume (mL) of acid used (0.01 *M* HCl) to maintain an initial pH and calculated reaction rates (μmol/cm² per s) of Robinson Run and Dola unarmored and armored limestone.

pH Solution	Unarmored Vol.	Unarmored Reaction rate	Armored Vol.	Armored Reaction rate	Reaction rate decrease due to armoring
	mL	μmol/cm^2 per s	mL	μmol/cm^2 per s	%†
Robinson Run					
5.0	0.57	0.94	0.48	0.74	21.3
4.5	1.15	2.02	0.94	1.60	20.8
4.0	2.66	5.12	1.81	3.12	39.1
3.5	7.60	14.83	4.81	8.62	41.9
3.0	17.55	34.12	11.10	19.47	42.9
2.5	34.65	67.43	18.20	36.95	45.2
Dola					
5.0	0.81	1.29	0.99	1.56	−17.3
4.5	1.39	2.53	1.29	2.47	2.4
4.0	2.86	5.79	2.74	5.50	5.0
3.5	8.10	16.89	6.43	13.05	22.7
3.0	22.55	44.52	16.40	36.69	17.6
2.5	40.70	84.47	28.60	58.01	31.3

† Calculated by 1 − (the armored reaction rate/the unarmored reaction rate).

Laboratory Container Study

This laboratory study was conducted using 2-L, high-density polyethylene containers filled with 2.3 kg of 5- to 10-cm sized, armored limestone or unarmored limestone. The two sources of armored limestone were from the same sites as those used in the titration study. The unarmored limestone was from the Deer Valley formation in Somerset Co., PA. One of four solutions was added to each of the containers (1.2 L). The four solutions were: AMD from the Maidsville Seep near Morgantown, WV (2080 mg/L acidity), AMD from Shaw Mines Run near Meyersdale, PA (518 mg/L acidity), a pH 3.0 HCl solution (171 mg/L acidity), and deionized water (control). Only 9 of the 12 possible limestone/solution combinations were used in this study (Table 2), and each of the selected combinations had three replications.

Two water samples of 40 mL each were collected with a plastic syringe from each container (one sample for general water chemistry and one for metal analysis) at the following time intervals after water introduction: 0, 1, 2, 4, 6, 12, 18, and 24 h. The water samples were filtered (0.45 μm) and metal analysis samples were acidified to pH < 2.0 with 1 mL of concentrated nitric acid (2.5% v/v) prior to analysis. The parameters tested were: pH (electrode), electrical conductivity (conductivity bridge), alkalinity, and acidity expressed as $CaCO_3$ (Brinkman auto-titrator), and concentrations of total Fe, Al, Mn, Ca, and Mg (Leaman Labs inductively coupled plasma spectrometry), and sulfate ($BaCl_2$ precipitation and measured on a Milton Roy Spectronic 20) (APHA, 1989). The water quality results were plotted to show acid neutralization with time and to provide a constrast between armored and unarmored limestone.

Field Study

In the field study, we selected eight existing rock-lined channels on reclaimed AML sites treating AMD. These channels were constructed for erosion control or to convey surface water off the site and were not designed to treat AMD. One channel was constructed of sandstone and seven were made of limestone. Two water samples of 250 mL each were col-

Table 4. Changes in acidity loss (mg/L) and the rate of acid loss (mg/L per min) resulting from adding three solutions to Robinson Run or Dola armored limestone and unarmored limestone.

Time	Armored limestone: Initial acidity	Armored: Acid loss	Armored: Acid loss	Unarmored limestone: Initial acidity	Unarmored: Acid loss	Unarmored: Acid loss
h	mg/L	mg/L	mg/L per min	mg/L	mg/L	mg/L per min
Maidsville-Robinson Run armored limestone						
0	2080	–†	–	2080	–	–
1	1740	376	6.27	1547	533	8.88
2	1692	12	0.20	1337	210	3.50
4	1513	179	1.49	1147	190	1.58
6	1374	139	1.16	1062	85	0.71
12	1210	164	0.46	998	64	0.18
18	1041	169	0.47	874	124	0.34
24	925	116	0.32	753	121	0.34
Shaw Mines-Dola armored limestone						
0	518	–	–	518	–	–
1	174	344	5.73	105	413	6.88
2	106	68	1.13	73	32	0.53
4	60	46	0.38	1	72	0.06
6	4	56	0.47	0	1	0.01
12	0	4	0.01	0	0	–
18	0	0	–	0	0	–
Synthetic AMD†-Dola armored limestone						
0	171	–	–	171	–	–
1	24	147	2.45	0	171	2.85
2	0	24	0.40	0	0	–

† Determination not performed.
‡ AMD = acid mine drainage.

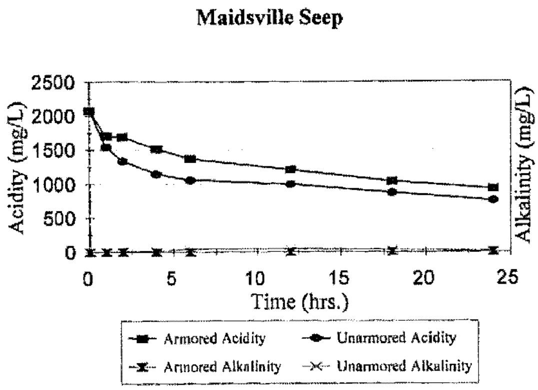

Fig. 1. Acidity reduction and alkalinity generation of Maidsville Seep acid mine drainage (AMD) with armored and unarmored limestone.

lected (one for general water chemistry and one for metals analysis) at identified distances along the channels and analyzed as described above at the same laboratory (APHA, 1989). One sample was filtered in the field (0.45 μm) and acidified to pH < 2.0 with 1 mL of nitric acid (0.4% v/v) for metals analysis. The other sample was not filtered and cooled to 4°C to determine pH, acidity, and alkalinity. Flows were measured with a Marsh-McBirney model 2000 Flo-Mate electromagnetic flow meter for larger flows (>95 L/min) or a calibrated bucket and a stopwatch for smaller flows (<95 L/min). Distances were measured with a 33-m surveying rope.

The results of water quality analyses from field channels were plotted against the kinetics model designed to predict the dimensions required to treat AMD with open limestone channels (Ziemkiewicz et al., 1994). The model estimates acid neutralization for an armored open limestone channel with specified dimensions and the AMD's flow and acidity concentration.

The Natural Resources Conservation Service's (NRCS) Coral/Graceton sandstone channel is located adjacent to U.S. Route 119 immediately northeast of the towns of Coral and Graceton, PA. The channel is 220 m long, 3 m wide and 0.1 m deep (720 by 9 by 0.5 ft) on a 10% slope. The flow of AMD through the channel was 1323 L/min (350 gpm) and the acidity was 550 mg/L.

The Morgantown Airport open limestone channels are located adjacent to U.S. Routes 119/857 east of Morgantown, WV, and consist of two armored limestone channels. The first channel (West) is 46 m long, 1.3 m wide, and 0.1 m deep (150 by 4 by 0.5 ft) on a 14% slope. The East channel 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 the 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.

Table 5. Alkalinity generation with Robinson Run and Dola armored limestones and unarmored limestone over a 24-h period when placed in deionized water.

Time	Unarmored limestone	Robinson Run armored limestone	Dola armored limestone
h		mg/L	
0	4	4	4
1	41	18	16
2	29	19	20
4	30	28	26
6	32	28	36
12	39	34	34
18	47	32	45
24	48	30	38

The NRCS Eichleberger no. 2 open limestone channel is located 6.5 km southeast of Coaldale, PA. The channel is 49 m long, 2 m wide, and 0.1 m deep (160 by 6 by 0.5 ft) on a 20% slope, and the limestone is 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. The Pennsylvania Department of Environmental Resources (PADER) open limestone channel is located 1.6 km west of Defiance, PA. This channel is 11 m long, 1 m wide, and 0.1 m deep (37 by 3 by 0.5 ft) on a 60% slope with a flow of 95 L/min (25 gpm). The acidity was 2600 mg/L at the source and the limestone is heavily armored. The Pennsylvania Game Commission open limestone channel is 11 m long, 1 m wide, and 0.1 m deep (35 by 3 by 0.5 ft) on a slope of 45%. It is located northeast of Vintondale, PA. The flow is 484 L/min (128 gpm) and the acidity is 330 mg/L at the source. This channel is limestone and heavily armored.

The Cottage Town open limestone channel is located 1.6 km west of Cairnbrook, PA. The channel is 137 m long, 1.3 m wide, and 0.1 m deep (450 by 4 by 0.5 ft) on a 9% slope with a flow of 302 L/min (80 gpm) throughout the entire length. The limestone was armored and the AMD had an acidity of 32 mg/L at the source. The Opawsky open limestone channel is located 1 km south of Mosgrove, PA. This channel is different from other open limestone channels because it had a wetland installed about a third of the way down the length of the channel that interrupted the flow. The top portion of the channel (46 m long, 2 m wide, and 0.3 m deep) is limestone and heavily armored on a 9% slope. The water after flowing through 46 m of limestone channel enters the wetland that

Table 6. Characteristics and performance (acid loss) of a sandstone open channel and seven open limestone channels at field sites in Pennsylvania and West Virginia.

Channel	Flow	Length	Rock type†	Slope	Contact time‡	Acidity Initial	Acidity Final	Acid loss	Acid loss
	L/min	m		%	min	mg/L	mg/L	%	mg/L
Coral/Graceton	1323	220	SS	10	37	550	540	2	10
Morg Airport W	113	46	LS	14	21	410	360	12	50
Morg Airport E	76	27	LS	20	6	355	330	7	25
Eichleberger no. 2	378	49	LS	20	29	510	325	36	185
PADER§	95	11	LS	60	4	2600	2500	4	100
PA Game Com.	484	11	LS	45	1	330	125	62	205
Cottage Town	302	137	LS	9	19	32	28	13	4
Opawsky	907	46	LS	9	86	30	15	50	15

† SS = sandstone, LS = limestone.
‡ Contact time was based on water flows, cross-sectional area of limestone (corrected for void space) and length of channel (Ziemkiewicz et al., 1994).
§ PADER = Pennsylvania Department of Environmental Resources.

Table 7. Rate of acid loss in a sandstone open channel and seven open limestone channels at field sites in Pennsylvania and West Virginia. The rate of acid loss (%/min and mg/L per min) in field channels is compared to the predicted rate of acid loss based on the kinetics model.

Channel	Acidity Initial	Acidity Final	Acid loss		Actual rate of acid loss		Predicted rate of acid loss	
	mg/L	mg/L	%	mg/L	%/min	mg/L per min	%/min	mg/L per min
Coral/Graceton	550	540	2	10	0.05	0.27	0.51	2.83
Morg Airport W	410	360	12	50	0.57	2.38	0.19	0.76
Morg Airport E	355	330	7	25	1.17	4.17	0.16	0.66
Eichleberger no. 2	510	325	36	185	1.24	6.38	0.55	2.86
PADER†	2600	2500	4	100	1.00	25.00	0.08	1.75
PA Game Com.	330	125	62	205	62.00	205.00	1.00	3.00
Cottage Town	32	28	13	4	0.68	0.21	0.66	0.21
Opawsky	30	15	50	15	0.58	0.17	0.70	0.21

† PADER = Pennsylvania Department of Environmental Resources.

covers an area of 350 m^2. Upon exiting the wetland, the water continues down the armored channel measuring 137 m long, 2 m wide, and 0.3 m deep (450 by 6 by 2 ft). The flow of AMD through the entire system was 907 L/min (240 gpm) and the acidity at the source was 30 mg/L.

RESULTS AND DISCUSSION

Laboratory Titration Study

Robinson Run (RR) armored limestone reaction rate was slower than unarmored limestone, and therefore less acid was needed to keep pH static throughout each experiment (Table 3). At a pH of 5.0, the unarmored limestone dissolution rate was 21% greater than the armored limestone rate. Between pH 3.0 and 4.0, the rate of limestone dissolution with armored limestone decreased to about 40% compared to unarmored limestone. At pH 2.5, there was a 45% decrease in acid neutralization due to armoring.

At a pH of 5.0, Dola armored limestone showed more acid neutralization than unarmored limestone, which was the only limestone/solution combination that showed armored limestone to dissolve faster than unarmored limestone (Table 3). We assumed that armoring could only reduce limestone dissolution. Both replicates gave the same result, so it is not clear why this happened. At pH 4.0 and 4.5, unarmored limestone from Dola was only 2 to 5% better at neutralizing acidity than armored limestone. However with lower pH solutions, armored limestone showed 17 to 31% reductions in the rate of acid neutralization vs. unarmored limestone.

These titration results show armored limestone to be 2 to 45% less effective in neutralizing hydrogen ion acidity compared to unarmored limestone. As solution pH decreased, the difference in acid neutralization became greater between armored and unarmored limestone. The data also indicate differences between the two limestone sources. The unarmored limestone at Dola neutralized more acid than unarmored RR limestone (Table 3). The RR armored limestone initially appeared to be more heavily armored than Dola armored limestone and the data show that the RR armored limestone dissolution rate was inhibited more than Dola armored limestone. Reintroducing the same armored limestone piece into increasingly acidic solutions certainly caused armoring to gradually dissolve, thereby increasing the effective surface area for reaction. Based on visual estimates, approximately 10% removal of armoring occurred from the RR limestone surface area during the experiment, while about 30% of the armoring on Dola limestone was removed by the end of the experiment. The greater unarmored surface area on the Dola armored limestone piece may account for the 30% decrease of limestone dissolution rate at pH 2.5 compared to 45% decrease for RR (Table 3).

Laboratory Container Study

The initial acidity of the Maidsville seep (2080 mg/L) was reduced to 925 mg/L (56% reduction) after 24 h with RR armored limestone (Table 4 and Fig. 1). The RR unarmored limestone neutralized 65% of the acidity (753 mg/L) after 24 h (a difference of only 9% between armored and unarmored limestone). The armored limestone from Dola completely eliminated the Shaw Mines' initial acidity of 518 mg/L in the containers after 6 h. Dola unarmored limestone achieved 100% treatment after 4 h.

The unarmored and Dola armored limestones were treated with a hydrochloric acid solution (0.02 *M* H_2SO_4, pH 3.0). The acidity was completely neutralized within 2 h with Dola armored limestone and within 1 h for unarmored limestone (Table 4). Alkalinity generation leveled off at 67 mg/L after 18 h for Dola armored limestone and 85 mg/L after 4 h for unarmored limestone (data not shown).

Deionized water was added to unarmored, Dola armored and RR armored limestone to determine alkalin-

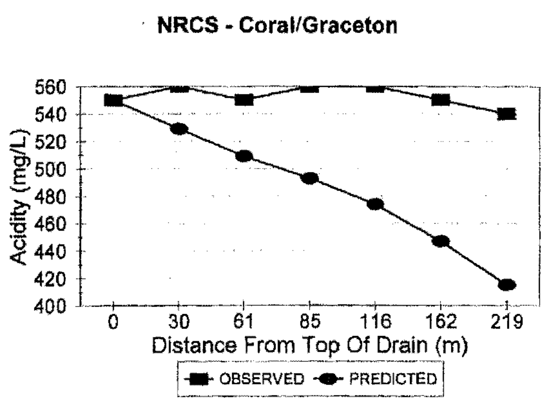

Fig. 2. Observed and predicted acidity reductions from a sandstone channel at the Coral/Graceton site.

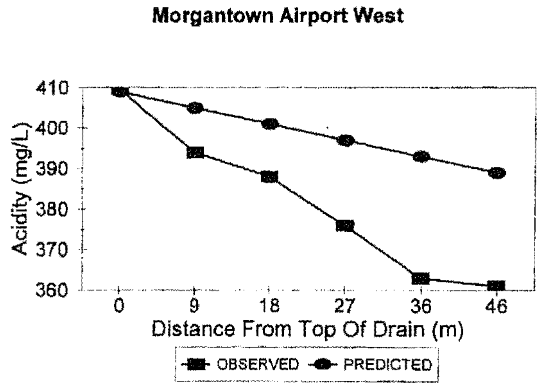

Fig. 3. Observed and predicted acidity reductions of an open limestone channel at Morgantown Airport West site.

ity generation with time among these three limestone samples in the absence of an acid solution. Data indicate that armored limestone required between 4 and 6 h to achieve maximum alkalinity, whereas unarmored limestone achieved maximum alkalinity during the first hour (Table 5). Unarmored limestone produced about 45 mg/L alkalinity, RR armored limestone gave 30 mg/L, and Dola armored limestone produced 38 mg/L. Both laboratory studies indicate that limestone dissolution was reduced between 2 and 50% due to armoring, much smaller than the 80% reduction values reported by Pearson and McDonnell (1975a).

Field Study

Flows, channel dimensions, slopes, contact time, and initial and final acidity concentrations for the field channels are summarized in Table 6. The NRCS Coral/Graceton sandstone channel served as a control to limestone channels. The resulting acidity reduction in this sandstone channel was 2% (Table 6) or 0.05% per min (Table 7). This is much less than the predicted 0.51% per min if it had been constructed with limestone (Fig. 2). The prediction line in Fig. 2 was based on the expected acid neutralization (with Pearson and McDonnell's data) by an open limestone channel from the model of Ziemkiewicz et al. (1994) using the initial acidity, water flow, length of channel, contact time, and the predicted limestone dissolution rate when armored.

The Morgantown Airport West open limestone channel performance was better than predicted (Fig. 3). The actual acidity reduction was 0.57% per min or 2.38 mg/L acidity decrease per min (Table 7) compared to the predicted reduction of 0.19% per min from the model. The Morgantown Airport East channels also performed better than predicted with an acidity reduction of 1.17% per min compared to a predicted reduction of 0.16% per min (Fig. 4).

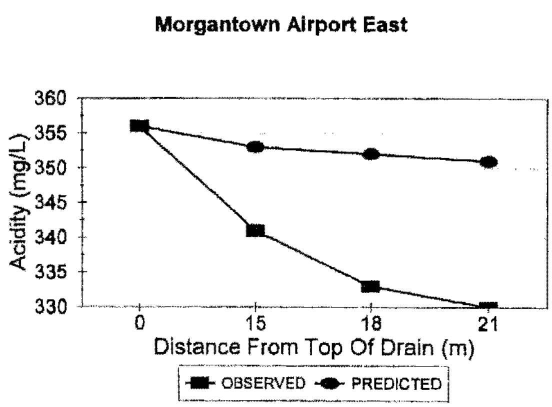

Fig. 4. Observed and predicted acidity reductions of an open limestone channel at Morgantown Airport East site.

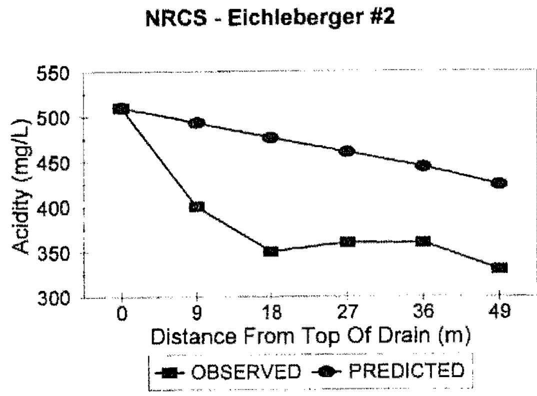

Fig. 5. Observed and predicted acidity reductions of an open limestone channel at the Natural Resources Conservation Service (NRCS) Eichleberger no. 2 site.

The NRCS Eichleberger no. 2 open limestone channel performed better than expected with an actual acidity reduction of 1.24% per min (or 6.38 mg/L acid reduction per min) compared to a predicted reduction of 0.55% per min (Fig. 5). The PADER open limestone channel is a very short channel with high acidity (Table 6), but removes 1% of the acidity per min or 25 mg/L acidity per min (Table 7). This was an order of magnitude better than the predicted acidity reduction of about 0.1% per min with such a short channel (Fig. 6). The PA Game Commission open limestone channel is a very short channel (Table 6), but it shows an impressive performance with 62% acidity removal per min (or 205 mg/L acid removed per min) compared to a predicted performance of 1% per min acidity removal (Table 7 and Fig. 7). The steep grades of these last two channels increased water velocities and splashing, which must have enhanced limestone dissolution and acidity reductions.

The Cottage Town open limestone channel has a

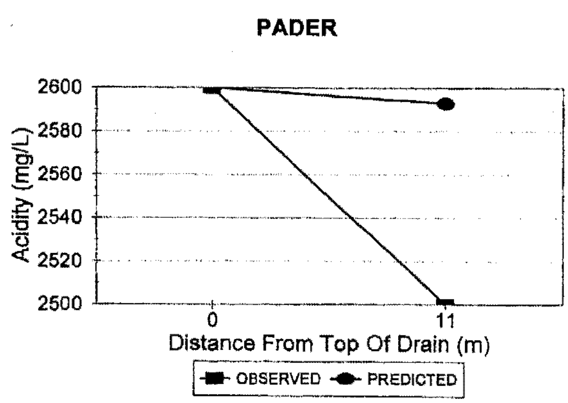

Fig. 6. Observed and predicted acidity reductions of an open limestone channel at the Pennsylvania Department of Environment Resources (PADER) site.

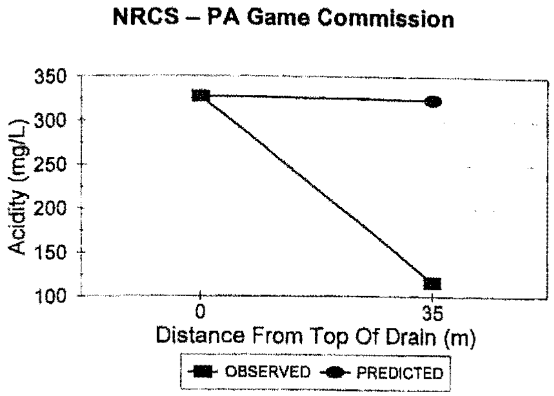

Fig. 7. Observed and predicted acidity reductions of an open limestone channel at the Natural Resources Conservation Service (NRCS) PA Game Commission site.

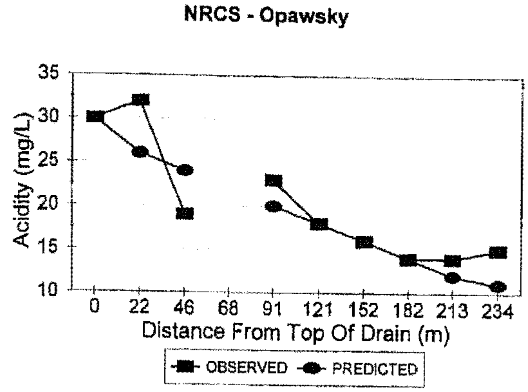

Fig. 9. Observed and prediced acidity reductions of an open limestone channel at the Natural Resources Conservation Service (NRCS) Opawsky site.

small amount of acidity (32 mg/L) entering the channel (Fig. 8) and exhibits an acidity removal better than that predicted over the first 110 m of the channel (1.83% per min compared to 0.47% per min predicted). Acidity concentration increases over the last 27 m of the channel because a small source of AMD enters the base of the channel. This brings the overall acidity removal closer to the predicted value (0.68% compared to 0.66% per min). The NRCS Opawsky open limestone channel's performance was slightly worse than predicted (0.58% acidity removal per min or 0.17 mg/L acid removal per min compared to a predicted removal of 0.70% per min) but the channel still removed 50% of the acidity (Fig. 9 and Table 7).

In the field study, acidity reductions in AMD after flowing through open limestone channels varied from 4 to 62%, and acid reductions per min of contact time with armored limestone were between 0.5 and 62% per min or 0.2 to 205 mg/L per min. The steeper channels (PADER and PA Game Commission) performed better (25 and 205 mg/L acid removed per min, respectively) than the two channels on flatter (9%) slopes (Cottage Town and Opawsky with 0.21 and 0.17 mg/L per min, respectively). In the sandstone channel, acidity decreased by only 2% and by a factor of 0.05% per min of contact time with sandstone.

Limestone dissolution increases with more acidic solutions. Acidity removal by limestone (armored or unarmored) is proportional to its contact time with AMD, but characteristics of the channel like slope and water velocity can increase acidity reductions. Open limestone channels work best on steep slopes. The key factor in designing open limestone channels is preventing iron and aluminum precipitates from settling in voids in the limestone channel. One limestone channel not reported here was found on a nearly flat slope (1–3%). It was filled with metal hydroxides and sediment, and it was ineffective in neutralizing acidity. The most successful channels had slopes above 40% and used coarse limestone (15- to 30-cm sized material). Both slope of channel and size of limestone can minimize the settling of precipitates in suspension, and thereby reduce plugging of the limestone channel. Evidence of the effect of slope on armored limestone dissolution is seen on the PADER and PA Game Commission open limestone channels that were constructed on slopes >40%. The age of the channels we studied varied from 2 to 8 yr and none of these channels had required maintenance. If constructed correctly, open limestone channels should be nearly maintenance free and less expensive to construct than other AMD treatment systems.

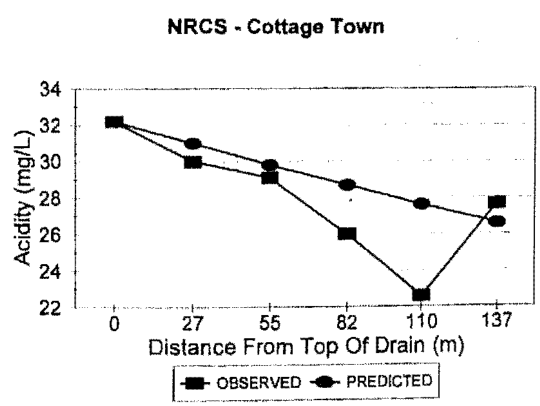

Fig. 8. Observed and predicted acidity reductions of an open limestone channel at the Natural Resources Conservation Service (NRCS) Cottage Town site.

Each of the passive treatment systems (aerobic wetlands, anaerobic wetlands, ALDs, successive alkalinity producing systems, and open limestone channels) have an area of application (see Faulkner and Skousen, 1995). It is difficult to achieve water quality standards (as required by NPDES permits on active mining operations) by passive AMD treatment with any one method alone. However, coupling these systems could allow some acidity reduction and metal precipitation in one system, then introducing the partially treated AMD into another system for additional acidity and metal removal. The primary application of most passive treatment systems is on watershed restoration and AML reclamation projects, and perhaps for pretreatment of AMD before chemical treatment. Open limestone channels are particularly useful in steep terrain where long (300–1000 m) channels are possible, and they offer a unique AMD treatment opportunity where no other passive system is appropriate. Open limestone channels will produce metal hydroxide precipitates like any effective AMD treatment system, so settlement basins should be incorporated into the design. Larger open limestone channels should have settling ponds or wetlands placed at intermediate points (flat channel segments) to remove the precipitates and help prevent plugging in limestone channels.

SUMMARY AND CONCLUSIONS

Treatment of AMD by armored limestone has been assumed to be minimal. Results of two laboratory studies indicate that armored limestone was only 2 to 45% less effective in neutralizing acid than unarmored limestone depending on the pH of the solution. Seven armored open limestone channels reduced acid concentrations in AMD between 4 and 62%, while a sandstone channel reduced acid concentration by only 2%. Open limestone channels work best where the channel is constructed on steep slopes (>20%) and where flow velocities keep metal hydroxides in suspension, thereby limiting their precipitation and plugging of limestone pores in the channel. Open limestone channels should be designed and constructed on watershed restoration and AML projects to reduce acid concentrations in AMD before reaching receiving streams, and in conjunction with other passive treatment systems to maximize water treatment and metal removal. Open limestone channels, if constructed correctly, should be maintenance free and provide AMD treatment for decades.

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REFERENCES

American Public Health Association. 1989. Standard methods for the examination of water and wastewater. 17th ed. APHA, Washington, DC.

Atlas, R.M., and R. Bartha. 1987. Microbial ecology. 2nd ed. The Benjamin/Cummings Publ. Co., Menlo Park, CA.

Brodie, G.A. 1990. Treatment of acid drainage using constructed wetlands—Experiences of the Tennessee Valley Authority. p. 77–83. *In* D. Graves (ed.) Proc. 1990 National Symposium on Mining. 14–18 May 1990. Univ. of Kentucky, Lexington.

Faulkner, B., and J. Skousen. 1994. Treatment of acid mine drainage by passive treatment systems. p. 250–257. *In* Proc. Int. Land Reclamation and Mine Drainage Conf. Vol. 2. 24–29 Apr. 1994. Bureau of Mines SP 06B-94. USDI, Pittsburgh, PA.

Faulkner, B., and J. Skousen. 1995. Effects of land reclamation and passive treatment systems on improving water quality. Green Lands 25:34–40. West Virginia Mining Reclamation Assoc., Charleston.

Hedin, R.S. 1989. Treatment of coal mine drainage with constructed wetlands. p. 349–362. *In* Wetlands ecology and conservation: Emphasis in Pennsylvania. The Pennsylvania Academy of Science, Easton.

Kleinmann, R.L.P., H. Edenborn, and R.S. Hedin. 1991. Biological treatment of mine water—An overview. p. 27–42. *In* Proc. 2nd Int. Conf. on Abatement of Acidic Drainage. 16–18 Sept. 1991. Mine Environment Neutral Drainage Program, Montreal, Canada.

Pearson, F.H., and A.J. McDonnell. 1974. Chemical kinetics of neutralization of acidic water by crushed limestone. p. 85–98. *In* Proc. No. 18, Water Resources Problems Related to Mining. Am. Water Resources Assoc., Columbus, OH.

Pearson, F.H., and A.J. McDonnell. 1975a. Use of crushed limestone to neutralize acid wastes. No. EE1, Proc. Paper 11131. J. Environ. Eng. Div., Am. Soc. Civil Eng. 101:139–158.

Pearson, F.H., and A.J. McDonnell. 1975b. Limestone barriers to neutralize acidic streams. No. EE3, Proc. Paper 11382. J. Environ. Eng. Div., Am. Soc. Civil Eng. 101:425–440.

Pearson, F.H., and A.J. McDonnell. 1977. Characterization of coarse porous media. No. EE4, Proc. Paper 13125. J. Environ. Eng. Div., Am. Soc. of Civil Eng. 103:615–624.

Singer, P.C., and W. Stumm. 1970. Acid mine drainage: The rate determining step. Science (Washington, DC) 167:1121–1123.

Skousen, J., M. Burnett, D. Bassage, C. Black, P. Ziemkiewicz, and D. Zucker. 1997. The watershed approach to acid mine drainage abatement: Sovern Run. Green Lands 27:43–49. West Virginia Mining Reclamation Assoc., Charleston.

Titchenell, T., and J. Skousen. 1996. Acid mine drainage treatment in Greens Run by an anoxic limestone drain. p. I1–I11. *In* Proc. 17th West Virginia Surface Mine Drainage Task Force Symp., 2–3 Apr. 1996. West Virginia Univ., Morgantown.

Wieder, R.K. 1989. A survey of constructed wetlands for acid coal mine drainage treatment in the eastern United States. Wetlands 9:299–315.

Ziemkiewicz, P., J. Skousen, and R. Lovett. 1994. Open limestone channels for treating acid mine drainage: A new look at an old idea. Green Lands 24:36–41. West Virginia Mining Reclamation Assoc., Charleston.