EVALUATION OF TWO OPEN LIMESTONE CHANNELS FOR TREATING ACID MINE DRAINAGE[1]

By

Arthur W. Rose and Fara J. Lourenso[2]

Abstract. Ziemkiewicz et al. (1994, 1997) proposed open limestone channels for treating acid mine drainage (AMD) and showed the usefulness of several channels, but questions remain on the effect of Fe-oxide coatings, possible within-channel inflows and long-term behavior. Two gently sloping channels, 108 to 127 m long, with coatings 0.5 to 1.0 cm thick, at the Cooney Pot Ridge Mine, Cambria Co., PA, cause acidity decreases of 10-50 mg/L $CaCO_3$ and Ca increases of 2-7 mg/L from AMD with 800-1000 mg/L acidity, 200-500 mg/L Fe and pH 3-3.5, after 1 to 1.5 years of operation. Lab experiments show rates of Ca release through the coatings of about 6 x 10^{-7} mg Ca/cm^2-s, compared with values of 7 and 20 x 10^{-7} mg/cm^2-s estimated for the channels. A diffusion coefficient of 9 x 10^{-7} cm^2/s is estimated for the coatings. The rate of neutralization is clearly dependent on coating thickness, pH, Fe, Ca and other solution parameters. The channel was much more effective in the first 4 to 6 months of operation before coatings built up.

A major part of the acidity decrease along the channels is apparently due to precipitation of Fe-hydroxysulfates such as schwertmannite. The channels also serve as an efficient means of aerating the AMD and precipitating Fe minerals, so that considerable dissolved Fe is removed from solution. These two effects are not dependent on the limestone.

The coatings are fragile and easily separated from the limestone, so for these gently sloping channels, occasional agitation of the limestone fragments to remove coatings may greatly increase their effectiveness.

Additional key words: Passive treatment, calcite reactivity, diffusion.

Introduction

An open limestone channel (OLC) is a channel lined with fragments of limestone used to neutralize and add alkalinity to acid mine drainage (AMD). Ziemkiewicz et al. (1994, 1996, 1997) investigated several field sites and conducted lab experiments on open limestone channels. They concluded that OLC's had the potential for neutralizing AMD in selected situations, despite armoring of limestone fragments by precipitates of ferric hydroxide and related materials. Based on experiments by Pearson and McDonnell (1975ab), Ziemkiewicz et al. (1997) estimated that coated limestone was about 20% as effective as non-coated limestone. However, the Pearson and McDonnell (1975b, p. 428) value of 20% was apparently based on only a single field site with coated limestone. Also, the coating thickness was not reported, and the AMD had relatively low Fe and Al concentrations (5-10 ppm). Nevertheless, Ziemkiewicz et al. (1997) observed decreases in acidity in several limestone channels that exceeded model predictions using 20% effectiveness. Ziemkiewicz et al. (1997) recommended slopes greater than 20% to scour off precipitates and remove silt, but studied channels with slopes from 9 to 60%.

Other workers have been skeptical of the benefits of OLC's, because the armoring was thought to prevent significant reaction and because of possible unrecognized inflows of diluting or

---

[1] Paper presented at the 2000 National Annual Meeting of the American Society for Surface Mining and Reclamation, Tampa, FL, June 11-15, 2000.

[2] Arthur W. Rose is Professor Emeritus of Geochemistry, Department of Geosciences, Penn State University, University Park, PA 16802. Fara J. Lourenso, formerly a student at Penn State University, is currently at the University of Arizona.

Proceedings America Society of Mining and Reclamation, 2000 pp 236-247
DOI: 10.21000/JASMR00010236

https://doi.org/10.21000/JASMR00010236

neutralizing water along the channels studied by Ziemkiewicz et al. (1997). The purpose of this paper is to investigate two channels carefully and to evaluate processes occurring in OLC's. In addition to the field study, a lab experiment was conducted to measure reaction rate of AMD with coated limestone in order to provide additional quantitative information for modeling (Lourenso, 1999).

Chemical Processes

Acid mine drainage is a complex solution derived by accelerated oxidation of pyrite and other sulfides exposed to weathering by mining. The AMD solution may further evolve by reactions with a variety of rock and soil along its flow path. AMD characteristically has high dissolved SO_4 and Fe, accompanied in many cases by elevated contents of Mn, Al, Ca and other cations. The pH is variable, ranging from about 7 down to 2.5 and occasionally lower, with a tendency for bimodal peaks near 3.0 and 6.5 (Rose and Cravotta, 1998). Most commonly, acidity exceeds alkalinity but many instances of the reverse are documented. Based on this wide variability, it is expected that the effectiveness of OLC's will depend on the composition of the AMD being treated.

The major processes occurring in OLC's are (1) increase of pH and decrease of acidity by reaction of AMD with calcite, (2) oxidation of Fe^{2+} to Fe^{3+} by exposure to air, (3) precipitation of $Fe(OH)_3$, $Al(OH)_3$, and MnO_2 and other substances to form coatings on limestone plus suspended particulates, and (4) plugging of interstices between fragments by precipitates, silt and leaves.

The reaction of acid with calcite can be expressed by the following reactions:

$$CaCO_3 + 2H^+ = Ca^{2+} + CO_2 + H_2O \quad (1)$$

$$CaCO_3 + H^+ = Ca^{2+} + HCO_3^- \quad (2)$$

Reaction (1) predominates for solutions with final pH less than 6.4, and reaction (2) for solutions above pH 6.4. The result of reaction between AMD and calcite is to increase pH, decrease acidity and increase alkalinity. Analogous reactions occur with dolomite ($CaMg(CO_3)_2$), though at a slower rate.

If pH increases above about 3.5, Fe^{3+} tends to precipitate and H^+ is released:

$$Fe^{3+} + 3\,H_2O = Fe(OH)_3 + 3\,H^+ \quad (3)$$

The precipitates may also consist of jarosite ($(K,Na,H)Fe_3(SO_4)_2(OH)_6$) or schwertmannite (approximately $Fe_8O_8(OH)_6SO_4$) with production of slightly less H^+ per Fe^{3+}, or goethite (FeOOH). If pH increases above about 4, $Al(OH)_3$ or similar compounds will precipitate with a similar release of H^+. Oxidation and precipitation of Mn oxides or hydroxides can have similar effects, though Mn precipitates do not form in quantity until near-neutral solutions are reached. These precipitates, especially the Fe^{3+} compounds, typically form coatings on the limestone. Another possible precipitate is gypsum, $CaSO_4 \cdot 2H_2O$, by reaction of Ca from limestone with SO_4 in the AMD.

As a result of the formation of coatings of Fe and Al compounds on the limestone, the solution can no longer react directly with the calcite. However, further reaction can occur by diffusion through the relatively porous coating. Hydrogen ions diffuse inward to react with $CaCO_3$, and Ca and carbonate species diffuse outward. Iron, SO_4 and other ions may also diffuse inward and precipitate within the coating under appropriate conditions.

The rate of reaction of uncoated calcite with acid is rapid (Plummer et al., 1978) though field and laboratory evidence indicates that reaction rates with SO_4-bearing solutions are slower than for the HCl used in lab studies (Rose, 1999). On formation of a coating, the reaction rate slows markedly, and is limited by the rate of diffusion through the coating. The rate of dissolution, at least at low pH values, is probably determined by the flux of Ca or carbonate through the coating, because of the very rapid diffusion of H^+. The flux (J) is given by

$$J = D\, dC/dx \cong D\, \Delta C/\Delta x \quad (4)$$

where D is the diffusion coefficient, C is the concentration of the diffusing species, and x is the distance within the diffusion gradient (Figure 1). In a simple model with a planar surface, as the coating increases in thickness (x increases), and the values of D and the concentration difference remain essentially constant, then J is inversely proportional to x, and is expected to decrease as the coating grows in thickness. However, values of D for the coating were not previously available to make quantitative estimates.

Field Study of Limestone Channels

Two OLC's were studied at the Pot Ridge surface mine of Cooney Bros. Coal Co. in southern Cambria Co., PA (approx. 40°16'N, 78°45'W) along the south side of Paint Creek. In this area, numerous seeps of AMD are being collected and passed through passive treatment facilities, mainly vertical flow systems (SAPS, Kepler and McCleary, 1994). At several locations, OLC's have been constructed to contribute treatment of the AMD during transfer to the SAPS units. One OLC constitutes a major inflow to the A-series system and the other to the C-series system.

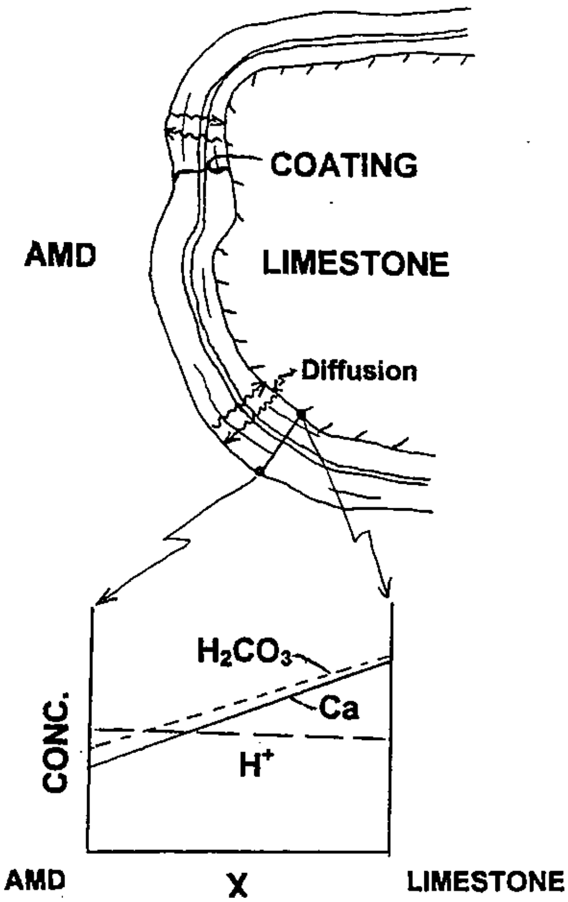

Figure 1. Sketch of coated limestone in contact with acid mine drainage, showing diffusive transfer across the coating, and schematic gradients in reactants and products across the coating.

Characteristics of the two channels are provided in Table 1 and Figure 2. The channels were constructed of coarse limestone (5-15 cm largest dimension) about 0.3 m deep with a flat central cross-section about 1 m wide and channel sides sloped upward from this at about 30°. Longitudinal slopes were 1-3° (2-3%), so these are not the steeply sloped channels preferred by Ziemkiewicz et al. (1997).

At the time of the field study, the channels had been in operation for 1 to 1.5 years. Limestone was completely coated with Fe-oxide to thicknesses of 0.5 to 0.8 cm; Channel A was slightly less coated than Channel C. Some AMD was flowing through the spaces within the limestone fragments. Several intermediate inflows occur along Channel C (Figure 2). At the time of writing (Jan. 2000), precipitates in Channel C have largely filled the spaces between fragments, and most flow is along the surface of the channel. Channel A has now been destroyed during construction of additional systems. Tests with dilute acid indicate that about 25% of the "limestone" in Channel C is actually dolomite. This difference has not caused obvious differences in effectiveness or coating thickness.

In order to evaluate the neutralization effect of the channels on acidity, water samples were collected at the beginning and end of the channels on several occasions. The pH, temperature, specific conductance and Eh of the AMD were determined in the field, and two bottles of filtered water (0.4 μm filter) were collected, one acidified with 2 ml of concentrated HCl. On return to the lab, hot acidity was promptly determined on the non-acidified sample using method 305.1 (U.S. EPA, 1983), and Fe, Al, Mn, SO_4, Na, K, Ca, Mg, and Si were determined by inductively coupled plasma spectrometry by the Materials Characterization Laboratory, Penn State University. A 90° V-notch weir was emplaced near the lower end of Channel A, and similar weirs at the upper and lower ends of Channel C to

Table 1. Characteristics of the Open Limestone Channels

	Channel A	Channel C
Length	108 m	127 m
Wetted width	0.9-1.1 m	1.0-1.5 m
Typical water depth	5-8 cm	5-8 cm
Typical flow rate (9/15/98)	35 l/min	100 l/min
Slope	2°	2.5°(4%)
Construction date	Aug. 1997	May 1997
Intermediate inflows	None	Yes, small
Limestone size	5-12 cm	5-15 cm
Limestone purity	No data	25% dolomite

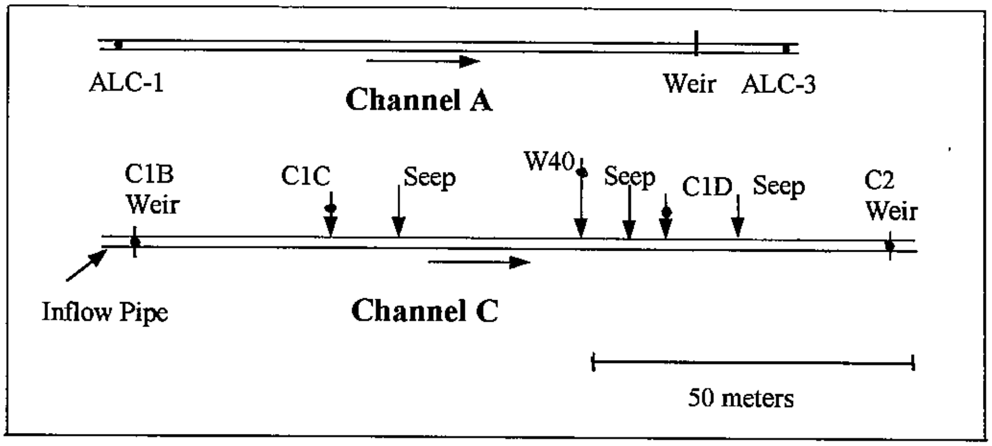

Figure 2. Sketch of Channel A and C, showing sampling points.

measure flows. Data from these measurements are shown in Table 2.

Results of Field Study

The most meaningful parameters for evaluating neutralization are decreased acidity and increased calcium, but complications prevent a simple interpretation. As indicated in Table 2, for Channel A, the acidity decreased by 54 and 40 mg/L $CaCO_3$ on 9/1/98 and 9/15/98, respectively (3.6 to 4.8%). These acidity decreases are considered to be real, based on replications of these determinations and earlier tests showing that acidities could be reproduced within 10 mg/L if done carefully. Calcium showed a distinct increase of 6 mg/L (3.4%) on 9/1/98, but near constancy for 9/15. For 9/1, the acidity decrease of 54 mg/L CaCO3 implies dissolution of 22 mg/L Ca, much larger than the observed Ca increase. The 9/15 data is even more discrepant. These discrepancies suggest that more complicated reactions are involved.

The near constancy of Mn and Mg suggests that dilution has not been significant, as also indicated by lack of observed inflows. The decrease in Fe is expected due to oxidation of Fe^{2+} to Fe^{3+} and precipitation of ferric minerals, with release of H^+ (reaction 3). Precipitation of $Fe(OH)_3$, goethite (FeOOH) or hematite (Fe_2O_3) would cause no change in acidity. However, the distinct decrease of SO_4 suggests the precipitation of a hydroxysulfate such as schwertmannite or a solid solution involving hydronium jarosite by a reaction like the following:

$$8Fe^{2+} + 2O_2 + SO_4^{2-} + 10H_2O = Fe_8O_8(OH)_6SO_4 + 14H^+ \quad (5)$$

$$3Fe^{2+} + 0.75O_2 + 2SO_4^{2-} + 5.5H_2O = H_3OFe_3(SO_4)_2(OH)_6 + 2H^+ \quad (6)$$

In addition to removing SO_4 from solution, these reactions decrease the dissolved acidity, in contrast to equation (3), in which the effects of oxidation and precipitation of Fe are balanced by increases in H^+. The precipitation of

Table 2. Field and chemical data for samples from channels

	Data in mg/L except pH, Spec. Cond. (uS/cm), T (oC), Eh (mv), Flow (L/min)															
Site	Date	SO4	Al	Ca	Fe	K	Mg	Mn	Na	Si	Acid	pH	SpCon	T	Eh	Flow
	Channel A															
ALC1	9/1/98	2316	56	176	402	4.5	181	137	3.8	15	1128	3.39	2590	20.5	556	
ALC3	9/1/98	2262	57	182	386	4.5	188	137	4	16	1074	3.32	2490	25	573	
Difference		-46	1	6	-16	0	7	0	0.2	1	-54	-0.07	-100	4.5	17	
ALC1	9/15/98	2316	56	176	402	4.5	178	132	3.9	16	1120	3.39	2740	20.9	590	
ALC3	9/15/98	2235	53	175	380	4.3	178	132	3.8	16	1080	3.25	2950	23.5	593	35
Difference		-81	-3	-1	-22	-2	0	0	-1	0	-40	-0.14	-220	2.6	3	
	Channel C (See Table 3 for corrected differences)															
C1B	9/15/98	1452	31	104	313	5.2	108	74	2.8	14	830	3.79	1820	13	568	76
C2	9/15/98	1527	33	107	280	5.3	108	76	3.1	13	799	3.22	1950	19	646	125
	Intermediate inflows															
C1C	9/15/98	855	29	56	37	3.1	63	43	2.1	10	409	2.83	1500	21	739	
C1D	9/15/98	894	20	89	22	3.9	73	53	2	6	362	2.68	2000	25	750	
W40	9/15/98	1056	29	65	75	3	69	26	1.9	13	585	2.61	2200	17	753	41.8
C1B	11/4/98	1455	24	102	318	4.6	122	38	2.1	13	772	3.94	860	10		91
C2	11/4/98	1467	25	105	268	4.3	108	36	2	12	722	3.20	770	8		114
C1B	6/23/99	1707	60	122	304	4.2	135	46	2.9	19	944	3.47	2400	15		61
C2	6/23/99	1515	46	117	210	3.8	118	40	2.5	15	723	3.06	2650	20		68

hydroxysulfates is expected, based on the observations of Bigham et al. (1996) that schwertmannite was the dominant precipitate from acid mine drainage beween pH 2.8 and 4.5, and that a jarosite phase was observed below pH 2.8. An additional possibility is that gypsum ($CaSO_4{\cdot}2H_2O$) is precipitating, depleting the solution in SO_4 and Ca. X-ray diffraction patterns of coating material show a combination of goethite and schwertmannite, and possible gypsum.

Because of the complex stoichiometry of schwertmannite and jarosite, plus possible gypsum precipitation, a unique chemical reaction explaining the combination of changes in acidity, Fe, Ca and SO_4 is not justified, but it is concluded that part of the decrease in acidity arises from hydroxysulfate precipitation. The increase in Ca is viewed as the best indicator of the neutralizing effects of the channel, but the value is a minimum because of the possibility of gypsum precipitation.

Data for Channel C are listed in Table 2. Again, consistent distinct decreases in acidity are found but increases in Ca are small to non-existent. However, for this site there are additional small inflows between sample points C1B and C2. Measurements of flow indicate that inflows amount to about 10-20% of the flow at station 1B. Small decreases in Mn and Mg suggest dilution along the channel. Samples of the observed inflow (C1C, C1D, W40) have distinctly lower acidity and Ca than the main flow at C1B, and would be expected to cause dilution of the concentrations.

The effects of intermediate inflows can be estimated by the relation

$$C_dV_d = C_0V_0 + C_iV_1 \qquad (7)$$

where C is concentration, V is volume (or flow rate), and subscripts 0, i and d refer to the beginning point, intermediate inflows, and endpoint of the channel. Using the values for site W40 for the concentration of the intermediate inflows, and an estimated 10% for the volume of intermediate inflows relative to V_0, Table 3 lists the corrected changes for acidity and Ca. Acidity decreases through the channel for all three dates,

Table 3. Changes in concentration along Channel C, corrected for intermediate inflows. Concentration at intermediate inflows is taken as value for site W40, making up 10% of flow at C1B.

	9/15	11/4	6/23
Acidity (mg/L CaCO3)			
Upstream	830	771	944
Calc. Downst. Dilution	809	755	912
Observed Downstream	798	722	723
Difference	11	33	189
Calcium (mg/L)			
Upstream	104	102	122
Calc. downst. dilution	100	99	117
Observed downstream	107	105	117
Difference	7	6	0

and Ca increases for 2 of the 3 dates. Sulfate actually increases slightly along the channel, so hydroxysulfate precipitation seems to be minimal or lacking here at the time of sampling, or some of the hydroxysulfate may be converting to goethite, releasing SO_4.

Based on the data from these two sites, the channels are accomplishing a small but distinct amount of neutralization, even with relatively thick (0.5-0.8 cm) coatings of Fe-oxides.

Laboratory Study

To evaluate the reaction rate of coated limestone, two samples of coated limestone from Channel C were reacted in the laboratory for about 2 months. Each sample was placed on a plastic collar in a glass bowl and 450 to 658 ml of AMD added to immerse the coated part of the sample. The AMD was collected from Channel C on September 24, 1998 and stored in a glass bottle throughout the experiment. Some precipitation of Fe-hydroxides from the stock was noted over the period of the experiment.

The wetted surface of Sample 1 was estimated at the end of the experiment to be 150 cm^2. The solution was stirred with a magnetic stirrer. Reaction of sample 1 began on Nov. 10, 1998, in 658 ml of AMD. After 1 week the water level had markedly declined by evaporation, so for all further work, the bowls were covered by plastic sheets sealed to the bowl with stopcock grease.

Reaction of sample 3 was initiated November 17, 1998, using 450 ml of AMD. The wetted surface of Sample 3 was estimated to be 109 cm^2.

Water samples, usually of 300 ml, were collected every week from each bowl. The water samples were filtered through 0.4 µm, one portion was acidified with HCl and another not. The samples were analyzed as for the field samples. The water removed by sampling and any evaporation was replaced by refilling with the AMD stock solution up to a mark on each bowl. A sample of the AMD stock solution was also analyzed each week. Data on the samples are listed in Table 4.

The reaction rate of the samples is estimated by the flux of Ca (mg/day) into the solution. To calculate the flux of Ca (F_{Ca}), the following equation was used:

$$F_{Ca} = (Ca_f - Ca_i)/t = (C_{nf}V_f - C_{of}(V_{of} - V_s) - C_{st}V_a)/t \quad (8)$$

where Ca_f is the mass of Ca in solution at the end of the period, Ca_i is the mass of Ca in solution at the beginning of the period, C_{nf} is the concentration of Ca in solution at the end of the period, C_{of} is the concentration at the end of the previous period, C_{st} is the concentration in the stock AMD, V_f is the total volume in the bowl at the end of the period ($=V_t - V_a + V_s$), V_{of} is the corresponding volume at the end of the previous period, V_t is the total volume in the bowl up to the fill line, V_s is the volume of the previous sample, V_a is the volume of stock solution added after the

Table 4. Chemical data from lab experiments.

Data in mg/L, except pH, Volume added (L), Volume sample (L)

Date	Acidity	pH	SO4	Al	Ca	Fe	K	Mg	Mn	Na	Si	V added	V sample
	Sample 1 (start date 11/10/98)												
11/10/98	709		1320	22	101	194	4.1	105	34	1.8	11		
11/17/98	601		1497	17	211	66	4.7	110	31	2.9	12	0.3	0.3
11/24/98	663	2.5	1920	19	286	106	6.3	111	31	2.9	14	0.37	0.3
12/1/98	858	2.35	2007	23	266	161	6.8	117	33	3.8	15	0.388	0.305
12/8/98	1031	2.4	2259	26	273	197	6.5	112	32	3.5	16	0.287	0.287
12/21/98	1086	2.52	2472	40	335	142	9.7	124	31	2.9	17	0.085	0.05
1/5/99	1334	2.3	3216	48	452	168	5.9	148	30	2.9	21		
	Sample 3 (start date 11/17/98)												
11/17/98	704	2.5	1359	21	102	152	4.3	104	33	1.7	11		
11/24/98	446	2.59	1491	18	233	44	5	100	29	2.2	11	0.36	0.313
12/1/98	657	2.5	1773	22	250	115	6.7	118	34	3	13	0.37	0.305
12/8/98	893	2.35	1995	22	229	185	6.2	110	32	2.8	13	0.295	0.275
12/21/98	694	2.52	2235	28	378	76	6.4	132	33	2.5	15	0.085	0.05
1/5/99	542	2.4	2286	27	323	33	6.3	148	31	2.7	18		
	Stock Solution												
11/10/98	709		1320	22	101	194	4.1	105	34	1.8	11		
11/17/98	704		1359	21	102	152	4.3	104	33	1.7	11		
11/24/98	689	2.55	1434	26	104	119	5	108	33	2.6	12		
12/1/98	723	2.5	1395	26	107	111	4.9	109	34	3	12		
12/8/98	686	2.4	1389	26	104	96	4.9	106	33	2.7	12		
12/21/98	700	2.45	1374	24	107	74	4.7	98	32	2.2	12		

previous period to bring the volume back to the fill line and t is the length of the period.

The value for the flux can then be converted to a rate (R, mg/cm^2-s):

$$R = F_{Ca}/A \qquad (9)$$

where A is the wetted area of the sample.

Results of Laboratory Study and Comparison with Field Results

The data from the above experiments is listed in Table 4, and calculations of the flux and rate in Table 5. As can be seen in the latter tables, the rate of Ca liberation ranges from 4.6 to 10.3 mg/d for the two experiments. When adjusted for area, the rates are 0.051 and 0.057 mg/cm^2-d, or an average of 6.3 x 10^{-7} mg/cm^2-s.

An analogous set of rates can be estimated from the field, where AMD flows along and through the limestone and reacts with it. Table 6 summarizes calculation of the reaction rate from field data for Channel C, giving 2.3 x 10^{-6} mg/cm^2-s. A rate of 0.7 x 10^{-7} mg/cm^2-s can be similarly derived from data for Channel 1. The rate for Channel C is about 3 times the rate for the lab and Channel A. Possibly the field rate is over-estimated because of under-estimation of the reacting area in the limestone bed of Channel C. However, given the accuracy and variability of the field data, the three rates seem to agree within expected errors at about 1 x 10^{-6} mg/cm^2-s for these relatively thick coatings developed in 1 to 1.5 years on the limestones.

Evaluation of Diffusion

Examination of the coatings indicates that they are layered, with most of the coating being composed of very porous Fe hydroxides through

Table 5. Calculation of flux from lab experiments*

Date	Ca mg/L	Vs L	Va L	Vf L	Cai mg	Caf mg	Cst mg/L	D Ca mg	t days	D/t mg/d	F mg/cm^2-d
Sample 1											
10-Nov	101			0.658			101				
17-Nov	211	0.3	0.3	0.658	66.458	138.838	102	72.38	7	10.34	
24-Nov	286	0.3	0.37	0.588	106.138	168.168	104	62.03	7	8.86	
1-Dec	266	0.305	0.388	0.575	120.848	152.95	107	32.102	7	4.59	
8-Dec	273	0.287	0.287	0.658	113.336	179.634	104	66.298	7	9.47	
21-Dec	335	0.05	0.085	0.623	131.131	208.705	107	77.574	13	5.97	
5-Jan	452	0.3	0.3	0.658	201.05	297.416		96.366	15	6.42	
									Av.	7.61	0.051
Sample 3											
17-Nov	102			0.45			102				
24-Nov	233	0.313	0.36	0.403	45.9	93.899	104	47.999	7	6.86	
1-Dec	250	0.305	0.37	0.385	58.41	96.25	107	37.84	7	5.41	
8-Dec	229	0.275	0.295	0.43	59.59	98.47	104	38.88	7	5.55	
21-Dec	378	0.05	0.085	0.415	66.175	156.87	107	90.695	13	6.98	
5-Jan	323	0.3	0.3	0.45	147.065	145.35		-1.715	15	-0.11	
									Av.	6.20	0.057

*Ca=mg/L Ca in solution; Vs=volume of sample; Va= volume added to restore level
Vf=Calculated final volume at end of period; Cai=Mass of Ca in solution, beginning of period
Caf=Mass of Ca in solution at end of period; Cst=concentration of stock solution;
D Ca=Caf-Cai; t=length of period; F=flux for period.

Table 6. Estimation of dissolution rate from field data for Channel 3

$R = \Delta Ca \cdot V/(T \cdot A)$

V = volume of water in channel

Assume half of water flows on surface and half within stones. Water depth is taken as 5 cm; length and width from Table 1.

V = length x width x depth x 2 = $1.27 \times 10^4 \times 120 \times 5 \times 2 = 1.52 \times 10^7$ cm^3 = 1.52×10^4 L

T = contact time of water in channel = V/flow rate

Flow rate = 100 L/min = 1.6 L/s = 1.6×10^3 cm^3/s

T = 1.52×10^7 cm^3/1.6×10^3 cm^3/s = 9500 s = 2.6 hr

Assume reactive area is twice the plan area of channel

A = $2 \times 1.27 \times 10^4 \times 120 = 3.05 \times 10^6$ cm^2

ΔCa = observed gain in Ca = (7 + 6 + 0)/3 = 4.3 mg/L

R = 4.3 mg/L x 1.52×10^7 cm^3 /(9500 s x 3.05×10^6 cm^2)

R = 2.3×10^{-6} mg/cm^2-s

the pores of which relatively rapid diffusion might occur. The density of 4 small specimens is 1.29, 1.42, 1.55 and 2.06 g/cm^3. Given a density for goethite of 3.3 to 4.3 g/cm^3, these densities imply porosities of 40 to 70%. However, most coatings (including several measured for density) contain a thin (1 mm) intermediate zone of denser Fe hydroxides that may be seasonally precipitated. This zone probably limits the diffusion rate. X-ray diffraction patterns indicate that the coatings are composed of a mixture of goethite with lesser schwertmannite. No gypsum was detected in the X-ray patterns, but transparent needles that are inferred to be gypsum are observed coating calcite beneath the coatings. Gypsum is slightly undersaturated in the AMD (saturation index for 9/15/98 is -0.76) but would be expected in the higher Ca environment adjacent to the limestone.

Using eq. (4) and some simplifying assumptions, the Ca flux values can be converted to diffusion coefficients. The average thickness of coating (Δx) on sample 1 was estimated to be 0.5 cm, and on sample 3 was 1.0 cm. The major diffusing constituents are Ca, H_2CO_3 (CO_2), and H^+. The rate of calcite dissolution is assumed to be limited by the most slowly diffusing constituent. Because of its very small size, H^+ is expected to diffuse very rapidly, so that the concentration of H^+ at the calcite surface would be only slightly lower than the concentration in the AMD. The molecular weights of Ca and CO_2 are similar, and considering that the Ca^{2+} cation is probably hydrated by 6 water molecules, it is probably the largest and most slowly diffusing species. Therefore Ca diffusion is assumed to be the dominant control on the diffusion-controlled reaction. Minor inward diffusion of SO_4 may occur if $CaSO_4$ is precipitated adjacent to calcite, as it appears to be. However, the thickness of the $CaSO_4$ zone is probably constant after a short time, so little SO_4 flux is expected. Minor inward diffusion of Fe may occur if any Fe minerals are precipitating within the coating, but the porous nature of the coatings indicates this does not normally occur. Based on this reasoning, the gradient in Ca is assumed to control the reaction rate.

At the calcite interface, Ca concentration is limited by precipitation of gypsum ($CaSO_4 \cdot 2H_2O$). If the rate of gypsum precipitation is low, then the SO_4 concentration at the calcite interface will be approximately equal to the concentration in the AMD. On 9/15/98, the SO_4 concentration in the AMD was 1527 mg/L, with 107 mg/L Ca. Based on speciation calculations using WATEQ4F (Ball and Nordstrom, 1991), the concentration of Ca can increase to about 420 mg/L at gypsum saturation, giving a difference in Ca concentration of about 8.4×10^{-3} moles/L (8.4×10^{-6} M/cm^3) across the coating. For a flux of 0.05 mg/cm^2-d (1.25×10^{-6} M/cm^2-d), and a coating thickness of 0.5 cm, D is estimated to be 8.6×10^{-7} cm^2-s. This value is reasonable for diffusion through a relatively porous medium.

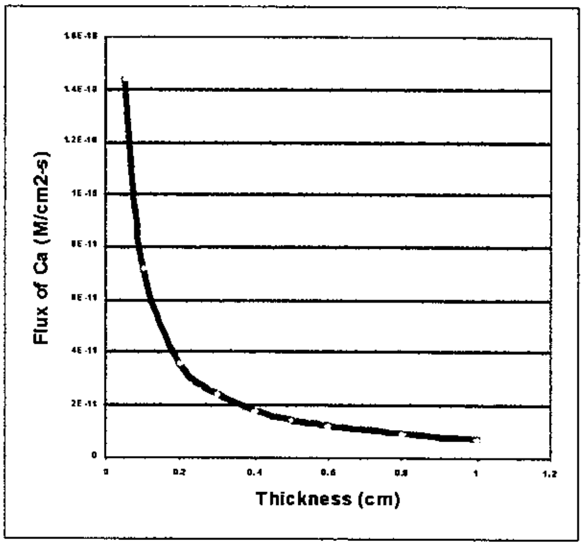

Figure 3. Calculated flux of Ca through the coating, as a function of coating thickness, showing rapid decrease in flux with increasing thickness.

Time Variation of the Effectiveness of Open Limestone Channels

From the value of the diffusion coefficient one can model the growth of the coating over time. Figure 3 shows the decrease in flux with increasing coating thickness, based on eq. (4). The flux of Ca slows markedly as the coating increases in thickness. The rate is slow after the coating reaches a few millimeters in thickness.

With some simplifying assumptions, the thickness of the coating may be calculated as a function of time. The overall reaction relating calcite dissolution and Fe-hydroxide precipitation is

$$2Fe^{3+} + 3CaCO_3 + 4H_2O = 2FeOOH + 3Ca^{2+} + 3H_2CO_3 \quad (10)$$

From this can be calculated a ratio of 59 g of FeOOH precipitated per mole of Ca^{2+} released. If the density of the Fe-hydroxide layer is 2.5 g/cm^3, then 24 cm^3 of Fe hydroxide coating is formed per mole of Ca^{2+} released.

If the thickness of the coating is taken as x, then from eq. (4),

$$x = \int J\, dt = \int D\, dc/dx\, dt \quad (11)$$

This can be integrated to

$$x = \sqrt{(2D\, \Delta C\, t)} \quad (12)$$

The coating thickness as a function of time is illustrated in Figure 4. Growth is rapid at first and then slows markedly over a few months. However, note that the coating thickness reached after 1 to 2 years is less than 1 mm, compared to 5 to 10 mm actually observed. This comparison suggests that most of the coating results from Fe precipitated by oxidation reactions (eq. 3) rather than from neutralization by limestone dissolution.

A dominance of oxidation over neutralization in causing Fe-hydroxide precipitation is also indicated by the ratio of Fe loss to Ca gain along the channels. According to the molecular weights in eq. (5), the Fe/Ca ratio should be 112/120=0.93, but the observed ratios along the channels are 3, 22, 11 and 17 (Table 3).

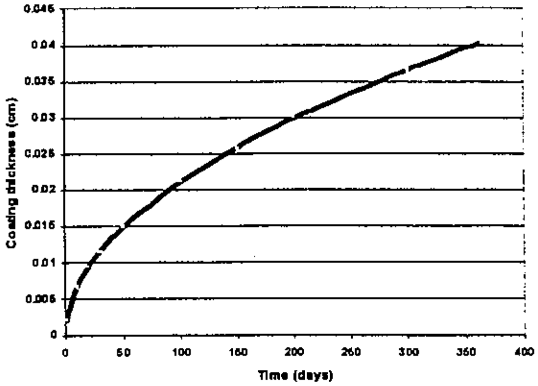

Figure 4. Calculated thickness of coating as a function of time, using value of D estimated from experiments. Note that after 1 year, coating is only calculated to be 0.4 mm thick, indicating that the observed coatings grow mainly from oxidation and precipitation of Fe.

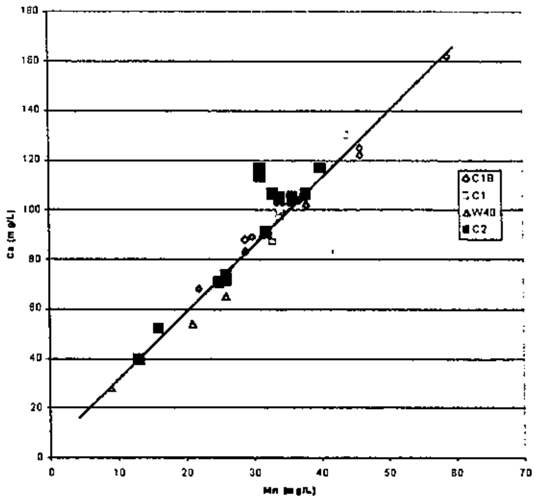

Figure 5. Ca vs. Mn of AMD at various sites in Channel C for period August 1997 to October 1999. Site C1 is the pipe furnishing the main inflow to the channel, and C1B is the total inflow at the head of the channel. C2 is the lower end of the channel, and W40 represents the main intermediate inflow. The C2 points above the line at Ca=110, Mn=30 are the first 4 months of channel operation, and show clear addition of Ca from limestone reaction.

The effectiveness of Channel C appears to have varied appreciably with time. Unfortunately, no data exist on the size of the intermediate inflows until 9/15/98, so some interpretation of the earlier data is necessary to allow for dilution. Manganese is not expected to be changed by neutralization or other reactions along the channel. Therefore, decreases in Mn from C1B to C2 are indicative of dilution of the inflow by AMD of lower concentration, and a plot of Ca/Mn can distinguish real loss or gain of Ca from effects of dilution.

Figure 5 shows the Ca vs. Mn values for the main inflow (C1, C1B) to the channel and some intermediate inflows (W40). These concentrations fall close to a line, indicating that outflow from the channel should fall along this line unless chemical gains or losses have occurred along the channel. Four outflow samples show markedly higher Ca. These are samples from 8/25/97, 9/10/97, 9/27/97 and 10/31/97, during the first 4-6 months of channel operation after construction in May or June of 1997. On 12/16/97, the Ca/Mn ratio falls along the inflow line. This data indicate that the channel was much more effective during the initial 4-6 months than during the 1998 investigation. Ca-Mn relations for 11/4/98 and 6/23/99 also fall above the line, indicating significant neutralization. Comparison with flow data for these dates suggests that more neutralization may occur during periods of low flow.

Discussion and Conclusions

The data presented above indicate that neutralization of highly acid, Fe-rich AMD by open limestone channels does occur, but that by the time coatings reach a few millimeters in thickness, the rate is slow. In high-Fe AMD, the channels are relatively effective for at least a few months, after which the neutralization effect decreases to a low level.

The data also indicates several beneficial effects of the channels in addition to neutralization. A major effect is oxidation and precipitation of Fe. Iron-rich AMD with pH above about 3.2 will precipitate Fe hydroxides and hydroxysulfates on aeration. At Channel C, where inflow contains 250 to 500 mg/L Fe, about 100 mg/L of Fe is commonly lost along the channel as it flows in a shallow stream. The loss of Fe along the channel relieves some pressure on later segments of the treatment system. A second effect is that the Fe precipitate is evidently a hydroxysulfate in part, and this precipitate removes some acidity from the AMD. Although the hydroxysulfate represents stored acidity and can later be released, it probably is released at a slow rate that is less harmful. However, note that both these beneficial effects would work about as well in a channel without limestone.

Ziemkiewicz et al. (1997) recommend that limestone channels have a slope of 20% or greater in order that the water flow will scour off coatings and maintain the limestone reactivity. This is undoubtedly a desirable design feature. An alternative that could be implemented on gently sloping channels like those at Pot Ridge is to periodically disturb the channel material. The coatings are observed to be easily dislodged from the limestone; we had difficulty obtaining intact specimens for the lab studies. The required disturbance might be accomplished by driving a small tractor with a cultivator attachment along the channel so as to stir up the limestone fragments and dislodge the coatings. Although this procedure would depart from a completely "passive" system, the cost/benefit appears to be large.

References

Ball, J.W. and D.K. Nordstrom, 1991. User's manual for WATEQ4F, with revised thermodynamic data base and test cases for calculating speciation of major, trace and redox elements in natural waters. U.S. Geological Survey Open File Report 91-183, 22 p.

Bigham, J.M., U. Schwertmann, S.J. Traina, R.L. Winland and M. Wolf, 1996. Schwertmannite and the geochemical modeling of iron in acid sulfate waters. Geochimica et Cosmochimica Acta 60:2111-2121. https://doi.org/10.1016/0016-7037(96)00091-9

Kepler, D.A. and E.C. McCleary, 1994. Successive alkalinity producing systems (SAPS) for the treatment of acid mine drainage. Proc. International Land Reclamation and Mine Drainage Conference (Pittsburgh, PA, April 24-29, 1994), U.S. Bur. Mines Publ. SP06A-94, p. 195-204. https://doi.org/10.21000/JASMR94010195

Lourenso, F.J., 1999. Open limestone channels: A strategy to remediate acid mine drainage in southwestern Pennsylvania. Senior thesis in Geosciences, Penn State Univ., 47 p.

Pearson, F.H. and A.J. McDonnell, 1975a. Use of crushed limestone to neutralize acid wastes. Jour. of the Environmental Engineering Div., Am. Soc. of Civil Engineers 101:139-158.

Pearson, F.H. and A.J. McDonnell, 1975b. Limestone barriers to neutralize acidic streams. Jour. of the Environmental Engineering Div., Am. Soc. of Civil Engineers 101:425-440.

Plummer, L.N., T.M.I. Wigley and D.L. Parkhurst, 1978. The kinetics of calcite dissolution in

CO_2-water systems at 5° to 60°C and 0 to 1.0 atm CO_2. American Journal of Science 278:179-216.
https://doi.org/10.2475/ajs.278.2.179

Rose, A.W., 1999. Chemistry and kinetics of calcite dissolution in passive treatment systems. Proc.16th Ann. Meeting, Amer. Soc. for Surface Mining and Reclamation (Scottsdale, AZ, Aug. 13-19, 1999), p. 599-608.
https://doi.org/10.21000/JASMR99010599

Rose, A.W and C.A. Cravotta, 1998. Geochemistry of coal mine drainage. In Coal mine drainage prediction and pollution prevention in Pennsylvania, ed. by K.B.C. Brady, M.W. Smith and J. Schueck, PA Dept. of Environmental Prot., Harrisburg, p. 1-1 to 1-21.

U.S. EPA, 1983. Methods for chemical analysis of water and wastes. U.S. Environmental Protection Agency, Report PB84-128677, Method 305.1

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(4), 36-41.

Ziemkiewicz, P.F., D.L. Brant and J.G. Skousen, 1996. Acid mine drainage treatment with open limestone channels. Proc. 17th annual West Virginia Surface Mine Drainage Task Force Symposium (Morgantown, W.V., April 2-3, 1996), p. M1-M15.

Ziemkiewicz, P.F., J.G. Skousen, D.L. Brant, P.L. Sterner and R.J. Lovett, 1997. Acid mine drainage treatment with armored limestone in open limestone channels. Journal of Environmental Quality 26:1017-1024.
https://doi.org/10.2134/jeq1997.00472425002600040013x