CASE STUDY OF POT RIDGE PASSIVE TREATMENT SYSTEMS, CAMBRIA COUNTY, PENNSYLVANIA[1]

by

Arthur W. Rose, Gregory S. Alcorn, L. Barry Phelps and Phillip R. Bower[2]

Abstract. Several combinations of anoxic limestone drains (ALD), vertical flow systems (VFS or SAPS), and open limestone channels with associated ponds were constructed at the Pot Ridge reclaimed surface coal mine in 1995 and 1997, and have been monitored and investigated since then. Acid mine drainage flowing into the systems is strongly acid (pH 2.5-3.5, acidity 500-1000 mg/L, Fe 100-300 mg/L, Al 20-70 mg/L).

The TEST system, constructed in 1995, consists of two collection ALD's, a pond, a VFS and a final pond. Flows from the ALD have decreased over time, apparently because of partial plugging by Al concentrations of 20-30 mg/L. Acidity decreases markedly in the following oxidation-settling pond, probably by precipitation of ferric hydroxysulfates. The TEST VFS reduces acidity by about 400 mg/L, to a pH of 4.5-5, but effluent generally has <50 mg/L alkalinity. During summer and fall, SO_4 decreases through the VFS due to SO_4 reduction, but in winter and spring, SO_4 is released from the VFS, indicating that the 20 cm of compost is unable to maintain reducing conditions, and that precipitated Fe sulfides are being oxidized. This unit has a retention time averaging 10 days.

The C system, constructed in 1997, treats AMD by two VFS plus an open limestone channel and several ponds at a flow of 100-300 L/min. Inflow has acidity of 600-900 mg/L at pH 3.5-4, Fe of 200-300 mg/L and Al 20-40 mg/L. About 300 mg/L acidity is removed by hydroxysulfate precipitation in ponds. Effluent from the first VFS, with an average retention time of about 3 days, has acidity of 200-350 mg/L, pH 3.2-3.7, Fe 20-60 mg/L and Al 10-20 mg/L. The outflow during the first two years contained appreciable ferric iron, indicating incomplete reduction in 30 cm of compost, but recently, at somewhat lower flow, the Fe is all ferrous. The second VFS produces water with acidity 5-150 mg/L (mostly as Mn), alkalinity 30-80 mg/L, pH 4.0-6.3, Fe<30 mg/L, Al<10 mg/L and Mn 20-30 mg/L. In the A system, two VFS remove about 340 mg/L acidity each from highly acid water (influent acidity 1050 mg/L).

The five VFS remove acidity (=increase net alkalinity) at rates of 35-50 $g/m^2/d$, or 16-26 g/d per tonne of limestone, in the range of other VFS reported in the literature. Problems encountered have included plugging of pipes with Fe hydroxide, overflow at high flow rates, accumulation of Fe hydroxide precipitate on top of the compost, incomplete reduction in compost layers, and the partial plugging of the ALD with Al hydroxides. Although design improvements are possible, the units greatly improve these highly acid, Fe-rich waters.

Additional key words: acid mine drainage, vertical flow systems, SAPS, anoxic limestone drains, sulfate reduction.

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[2]Arthur W. Rose and L. Barry Phelps are retired faculty at Penn State University, Departments of Geosciences and Mineral Engineering, University Park, PA 16802; Gregory Alcorn is an M.S. graduate in Mining Engineering, and Philip Bower is a B.S. graduate from Penn State University

Introduction

In the past 10 years, many acid mine drainage (AMD) outflows have been treated by passive systems (Hedin et al., 1994). Examples are aerobic and anaerobic wetlands, anoxic limestone drains (ALDs), and vertical flow systems (VFS, also termed sequential alkalinity producing systems, SAPS, vertical flow wetlands, or reducing and alkalinity-producing systems). As a new technology applied to widely varied sites and water quality, the design of these systems is still evolving. Many of these systems are successful, but some fallen short of expectation or shown design flaws.

This paper presents monitoring and design information on an extensive set of passive systems at the Pot Ridge surface mine of Cooney Bros. Coal Co. in southern Cambria Co., Pennsylvania. The first system was constructed in 1995, and has been monitored for 5 years. A second series of passive systems was constructed in 1996. Four additional systems have since been constructed at the site, and furnish additional information on design. Successful passive remediation at the site is challenging because of very high acidity.

Site and Design Information

The Pot Ridge mine is in the headwaters of Paint Creek along the border between Cambria and Somerset Counties in central Pennsylvania (Figure 1). Coal seams mined in the area include the Mercer, Brookville, Clarion and Lower Kittanning (B) seams. The coal seams dip a few degrees WNW, sub-parallel to the topography. The B seam was present beneath several small hills at the site, and was mined out underground prior to 1970. Local thick portions of the Clarion seam were mined underground in several small mines, and several small areas were surface mined along the outcrop. Starting in the mid-1980's, the Mercer, Brookville and Clarion seams plus remnants of the B coal were mined by Cooney Bros. Coal Co. in about 250 acres along the south side of Paint Creek. Additional large areas of these coals were mined in updip areas, and about 10 acres were mined in the Campanera tract on the north side of Paint Creek.

In 1992, numerous AMD seeps along the down-dip edge of the Brookville-Clarion seams generated several large areas of Fe-oxide precipitation and tree kill. In 1994, Penn State University agreed to conduct a hydrologic and water quality study of the seeps and to recommend remediation methods. More than 40 seepages were located, and weirs were established at 13 of the larger flows (Alcorn, 1996). Filtered water from these weirs was sampled at approximately a two-week intervals for over 1 year and analyzed for pH, acidity, alkalinity, Fe, Al, Mn, SO_4. Some of the seeps emanate from small long-abandoned underground workings, but water balance studies indicate that most of the flow represents infiltration into the large up-dip surface-mined areas. Water from several wells in the spoil of the recent strip mines is highly acid. In 1994, Cooney Bros. Coal Co. agreed to treat the water and build a series of passive treatment units over the period 1996 to 2002. Most of these facilities have now been built.

TEST System

The first set of facilities, the TEST system, treats AMD from an older, poorly reclaimed strip mine on the Clarion or Brookville seam. A detailed description of the design and construction of this system is provided by Alcorn (1996). The system consists of two collection ALD's, a short limestone channel, an oxidation and settling pond, a VFS, a short channel and a second pond (Figure 2). The combined flow of weirs #40 and 41 at this location averaged 235 L/min with a weighted average composition of 460 mg/L acidity, 70
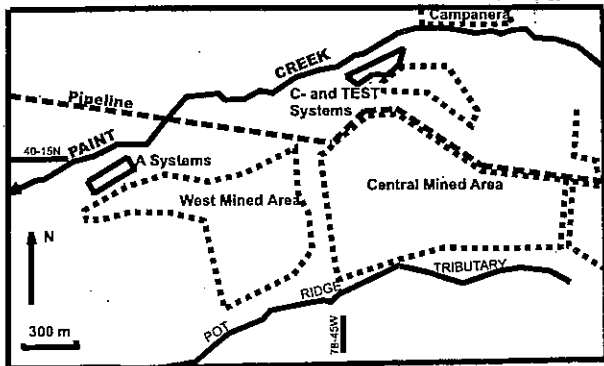
Table 1. Data on test facilities

A. Anoxic limestone drains and vertical flow units

Unit	Length	Width	Depth	Limest.	Ls. size
	m	m	m	T	cm
ALD 1	62(+28*)	1.5	1.8	330	7.6-10
ALD 2	98(+29*)	1.5	1.8	465	7.6-10
VFS	30	30	1.8	2515	7.6-10

*Sloping section from main ALD to outlet

B. Ponds

Unit	Area	Depth	Retention
	m²	m	days
Pond 1	1560	3	5
Pond 2	1560	3	3

C. Other parameters

Design life	25 yrs.
Slopes	2:1 (except downslope on VFS)
Limestone	>90%CaCO₃
Porosity of ls. Layer	50% (approx.)
Density Fe precipitate	1.5 g/cm³ (assumed).
Mushroom compost	300 m³
Piping	15 cm Schedule 40 PVC
	2 holes/ 15 cm in perf. section

Figure 1. Map of Pot Ridge mine area, showing locations of passive systems and mined areas.
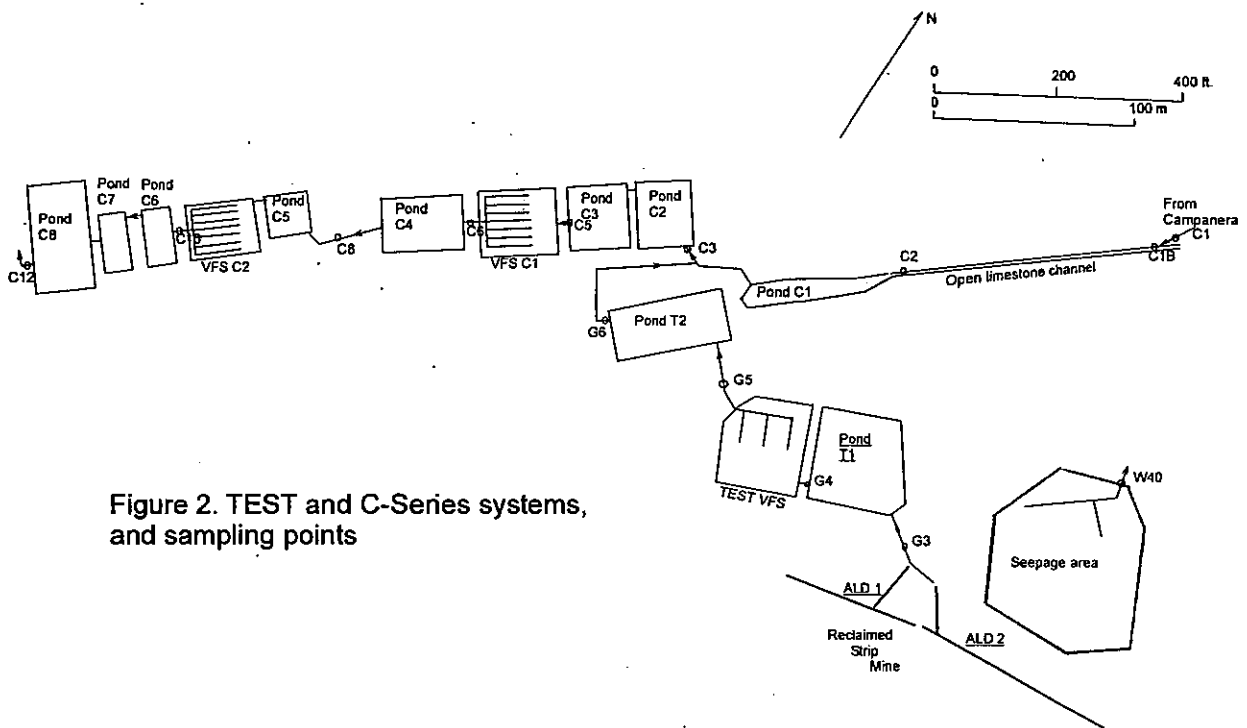
Figure 2. TEST and C-Series systems, and sampling points

mg/L Fe, 19 mg/L Mn, 18 mg/L Al and pH 2.93. To allow for temporarily increased flow rates, the facility was sized for a flow of 325 L/min, which was adequate for all flows except a 2-week period of exceptional spring runoff in 1994.

The ALD's were intended mainly to capture the flow and add some alkalinity prior to emergence at the surface (Table 1). A trench 1.2 m wide and 3.1 to 5 m deep was filled with about 1.5 m of coarse limestone. It was hoped that the coarse size would inhibit plugging by Al hydroxide. The limestone was covered by a layer of hay and then by 8-mil plastic and 0.3 m of clay, followed by soil up to the surface. The more steeply sloping connectors from the upper part of the ALD's to the outflows were covered on sides, bottom and top by plastic. A 6 meter length of 15 cm perforated PVC pipe terminating in a riser to the surface was placed in the bottom of each connecting segment as the outlet for the drains. A short channel lined with coarse limestone connected the ALD outlet to Pond T1.

The ponds were sized to provide a 24-hour retention time (Hellier et al., 1994), after allowance for 25 years of Fe-oxide precipitate with a density of 1.5 g/cm³ (Alcorn, 1996). The dam around the lower side of the pond was constructed with shale from active mining about 1 mile away, to 2:1 inner slopes and 3:1 slopes on parts of the downhill side, with a 3.7 to 4.6 m top width. The fill was compacted by the haulage trucks. A

freeboard of 0.6 m was allowed above a 0.45 m overflow culvert. Clay encountered in the base of the pond was partly left in place and partly used to line the sides of the pond as a 0.3 m layer.

The walls of the VFS were constructed of compacted clay and rock hauled from the active mine site, and the inner walls lined with 0.6 m of compacted clay. The top was built up to the same level as Pond T1. A 17 m length of 15 cm PVC pipe was placed in 0.6 m of clay under the downslope side of the dam, and a riser was later added at the outflow end, with a plug in a T at the base for draining the VFS (Figure 3). Three perforated collection pipes, each 9.2 m long and spaced 8 m apart, were placed on a 0.15 m layer of limestone, and connected at one end to a non-perforated pipe leading to the outflow pipe (Figure 2). Coarse limestone was then added to a total thickness of 1.8 m. The limestone was covered by a layer of Tyvek polypropylene filter fabric with 70-100 mesh equivalent openings. About 30 cm of spent mushroom compost was raked into place on top of the filter fabric. A strip of 1.5 m wide chicken wire was buried around the upper edge of the dam to inhibit muskrat burrowing and dam failure. The completed VFS was connected to pond T1 by a short channel. The water depth over the compost is about 0.7 m, with about 0.6 m of freeboard.

The final pond, T2, with dimensions of 25 x 50 m was constructed below the outfall of the VFS. The
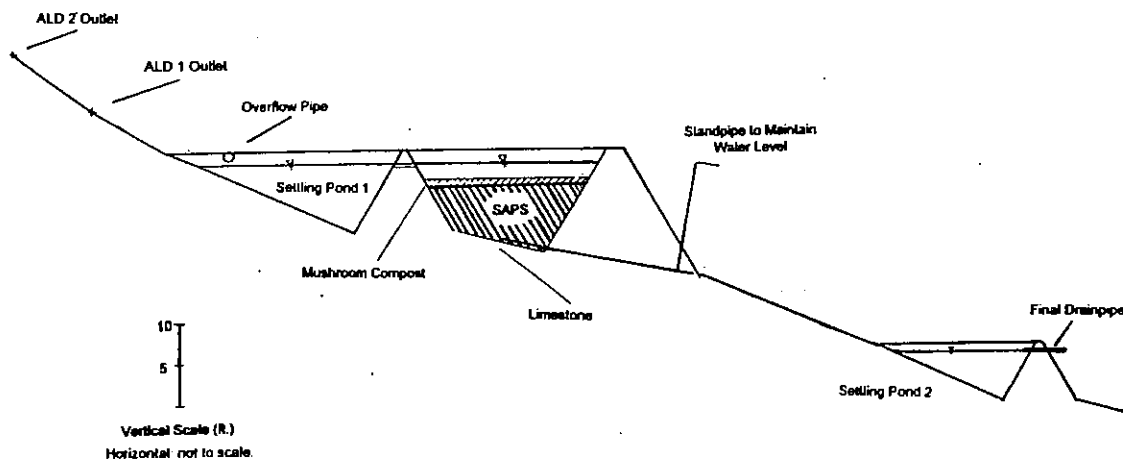
Figure 3. Schematic cross section of the TEST system (after Alcorn, 1996).

walls were constructed of clay from the site, to a maximum height of 2.2 m and a top width of 3.1 m. Outflow is via a 15 cm pipe placed 0.3 m below the top of the dam.

All construction was done by Cooney Bros. personnel and equipment. Alcorn (1996) estimated the total construction costs of $132,800 based on standard hourly costs for equipment, and $15/hr for labor. These costs do not include design and minor engineering at the site by Penn State personnel. Cost components include site clearing $25,690, VFS $71,172, ALD's $19,753, and ponds $16,476. Material costs amounted to $45,682, mainly $36,077 for limestone and $7044 for compost.

C-Series System

This system, constructed by Cooney Bros. Coal Co in summer 1997, is downslope from the TEST system (Figure 2). It is based a general layout by the authors and the design features of the TEST system. Major units are a collection system next to Paint Creek at the Campanera tract, a 300 m pipeline to a 130 m open limestone channel (which also gathers water from seeps upslope), a small holding pond (Pond C1), two oxidation and precipitation ponds (Ponds C2 and C3), Vertical Flow System C-1, Pond C4, a pipe and open limestone channel leading to Pond C5, VFS C-2, and Ponds C6, C7 and C8 (Figure 2).

Limited pre-construction information indicated that discharge from the Campanara seep averaged 60 L/min with acidity 773 mg/L, Fe 333 mg/L, Mn 31 mg/L and appreciable Al. This water was captured in a small reservoir, piped across Paint Creek and through a buried pipeline to intersect the open limestone channel. Additional seepage upslope of the open limestone channel was estimated to add 170 L/min of somewhat

less acid water. The open limestone channel was described by Rose and Lourenso (2000).

Pond C1 is elongate (60 x 9 m) and serves to settle out some Fe formed along the OLC and as a surge pond. Outflow from this pond is through a vertical perforated pipe, originally extending above water level but later broken off. A spillway allows flows exceeding about 350 L/min to overflow down a rock-lined channel. Normal outflow from pond C1 flows down a short limestone-lined channel to Pond C2. The flow from the TEST system joins the C1 outflow along this channel. Ponds C2 and C3 are each about 30 m square and about 1.5 m deep and are intended for thorough oxidation and precipitation of Fe. Outflow from Pond C3 to Vertical Flow System C1 is through a 15 cm pipe opening upward into a funnel-shaped inlet.

Vertical Flow System C1 is about 30 x 37 m in surface dimensions. Construction is similar to the TEST VFS, with 1.5 m of limestone (7.6-10 cm, about 80% $CaCO_3$) overlain by a filter fabric, about 30 cm compost, and about 1.2 m of water. Seven perforated collection pipes, each 18 m long, connect at one end to an 18 m non-perforated pipe. A "T" at the center of this pipe leads through the lower dam to a fixed outflow midway down the bank of Pond C4 which is similar to Ponds C2 and C3. A small drainage and line of trees separates Pond C4 from Pond C5. This drainage is spanned by a 15 cm pipe leading to a 20 m open limestone channel. Pond C5 is smaller, about 20 m square, and flows out through a 15 cm pipe.

Vertical Flow System C2 is similar to VFS C1. It flows out to two small ponds for oxidation and settling. Removal of Mn was required by PA DEP, so NaOH is added into Pond C-6. Pond C8, much larger than other ponds, was added to provide a long retention time for Mn precipitation.

A-Series System

This system was constructed in late summer 1997 to treat part of the flow from the western end of the property. Seeps in this area averaged pH 2.97, 1200 mg/L acidity, 190 mg/L Fe, 68 mg/L Mn, 75 mg/L Al and 2020 mg/L SO_4 at a flow rate of 730 L/min. The A-series units treat a part of this flow, which is the most acid on the property. The system consists of three collection and oxidation ponds (A1, A2 and A3), VFS A1, followed by two oxidation and settling ponds (Ponds A4 and A5), VFS A2, and Pond A6. Ponds A1 to A3 were constructed at the location of major seepages. During excavation of Pond A-1, difficulty was encountered from a "hole" (apparently a buried adit) and considerable flows into the bottom of the pond. Small seeps along the slope above Pond A1 were diverted into this facility, but much of the flow enters the bottom of the pond. Design and construction of these facilities is similar to the C-Series ponds and VFS.

Monitoring

Initially, waters from the TEST and C-system were sampled approximately monthly, and starting in 1999, at approximately quarterly intervals. At the TEST site, stations G3 (ALD outflow), G4 (VFS inflow), G5 (VFS outflow) and G6 (Pond 2 outflow) have been sampled on this schedule. V-notch weirs were emplaced at G3 and just below G5. For the C-series, sites C1, C2, C5, C6, C8, C10 and C12 have been sampled at most visits. At C1, initial sampling was from the pipe outflow from the Campanera site, prior to mixing with a smaller flow from the upstream part of the OLC. Starting 12/97, the combined flow along the OLC just below this pipe was sampled (Site C1B). Weirs were emplaced at C8, and in 7/98 at C1B and C2.

At the A-system, sampling has been occasional starting in 10/97. Sites are A1i (inflow to VFS-1), A1o (outflow of VFS-1) and A2o (outflow of VFS-2). Only one flow measurement of 57 L/min is available for this site, but typical flow is estimated at 55-120 L/min.

Most samples were collected by the authors and analyzed at Penn State Univ. The pH, temperature and specific conductivity were measured at the sample site. Flows were estimated from the water height in the V-notch weirs. If pH exceeded 4.5, alkalinity was estimated in the field using a Hach titration kit. On some occasions, Eh was measured using a Pt electrode, standardized with Zobell solution. Ferric iron was estimated from the sum of ferric species calculated using PHREEQC (Parkhurst, 1995). Samples were

filtered through 0.45 µm, and one portion was acidified with 2 ml of concentrated HCl. The acidified sample was analyzed at the Materials Characterization Laboratory at Penn State University by inductively coupled plasma atomic emisssion specrometry (ICP-AES) for Al, Ca, Fe, Mg, Mn, K, Na, Si and total S (calculated as SO_4). The non acidified sample was used to determine acidity, using EPA method 305.1 (EPA, 1983). During 1995-96, samples were also collected monthly by Mahaffey Laboratories (Grampian, PA) and analyzed by standard procedures approved by PA DEP.

On December 10, 1998, several water samples were collected from within the compost using a sampling probe consisting of a 10 µm filter tip (Upchurch Scientific A-427 ultMWPE filter body) mounted on the end of a 2 cm PVC pipe (Bower, 1999). Thin tubing attached to the filter enabled a sample to be drawn from within the compost using a hand vacuum pump with an intervening small flask to capture the sample. Water was collected from the compost surface, and at depths of 5.6, 10.2 and 20.3 cm in the compost, and analyzed like the other water samples (Table 2). Also, a 23-cm long core of the compost was collected using a 6.4-cm-diam. soft sediment corer pushed into the compost with a twisting motion. The corer had a valve at the top to vent water during coring and close to retain water and core during retrieval. The core was refrigerated until examined and analyzed about a month later, to minimize oxidation.

Core was analyzed for forms of S using a coulometric method for H_2S described by Wilkin and

Table 2. Data on water from compost layer of TEST system

Sample	G4	1	2	3	4	G5
Depth (cm)		0	5.6	10.2	20.3	
Al (mg/L)	33	53	36	41	31	1
Ca	155	156	152	120	147	228
Fe	224	177	43	63	36	87
K	21	5.1	7.6	5	15	5.3
Mg	131	116	127	121	96	84
Mn	42	38	41	38	31	26
Na	2.2	1.9	2.6	2.2	2.3	1.5
Si	12	11	12	12	12	4.5
SO_4	1800	1730	1530	1480	1150	1040
pH	2.87	2.99	2.5	2.4	3.23	5.58
Acidity	950	830	680	710	610	137
Eh (v.)	0.678	0.711	0.660	0.664	0.440	0.268
Temp. (C)	6	5	6	6	10	6

Samples collected 12/10/99 using a filter-tipped probe. G4 is inflow to VFS; G5 is outflow of VFS.

Barnes (1997). The compost was divided into 5 approximately equal layers (Figure 4). A 0.8 g sample of each compost layer was placed in the coulometer with a few milliters of water, N_2 was bubbled through to release H_2S from pore water, and the H_2S measured in the coulometer. Then 15 ml of 0.5 M HCl was injected and stirred, to release acid volatile sulfide (FeS and similar compounds). Finally, 10 ml of 1 M $CrCl_2$ solution was added and stirred to release H_2S from pyrite. Results are provided in Figure 4.

Results and Discussion

TEST System

Table 3 summarizes the average chemistry and flow for the TEST system. Acidity and alkalinity, combined as net alkalinity (alkalinity minus acidity) are considered the best single indicator of system effectiveness. Influent acidity averaging 509 mg/L $CaCO_3$ is changed to average net alkalinity of 22 mg/L at Pond T2 outflow.

Most of this acidity decrease occurs in the VFS, but a significant decrease occurs in Pond T1. Similar decreases in acidity are noted in other oxidation ponds at the property and along the open limestone channel (Rose and Lourenso, 2000), so the acidity loss in the pond is considered to be real. Simple oxidation and precipitation of $Fe(OH)_3$, FeOOH, Fe_2O_3 or other simple Fe oxides and hydroxides should not change acidity or alkalinity, because initial Fe^{2+} acidity is only changed to H^+.

$$Fe^{2+} + 0.25\,O_2 + 2.5\,H_2O = Fe(OH)_3 + 2\,H^+ \quad (1)$$
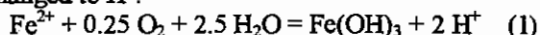
However, precipitation of schwertmannite ($Fe_8O_8(OH)_6SO_4$) or jarosite ($KFe_3(SO4)_2(OH)_6$) is expected at acid pH and can decrease dissolved acidity (Bigham et al., 1996; Rose and Lourenso, 2000):

$$8Fe^{2+} + 2O_2 + SO_4^{2-} + 10H_2O =$$
$$Fe_8O_8(OH)_6SO_4 + 14H^+ \quad (2)$$
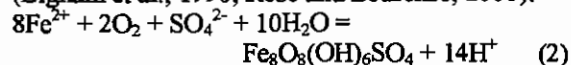
This reaction is believed to be the cause of the decrease. The influent water is supersaturated in jarosite and schwertmannite. The SO_4-bearing precipitate represents "stored acidity" and could dissolve to regenerate acidity, but if the precipitate is buried by later precipitate, any dissolution is limited.

Figure 5 illustrates the net alkalinity of inflow and outflow vs. time. During the first few months after construction, the outflow was strongly alkaline, probably due to exchange of Fe^{3+}, Al^{3+} and H^+ onto the compost, plus possible dissolution of fine limestone particles. Sulfate values in the effluent are also high for the first 2 months, perhaps due to dissolution of gypsum from the compost. These short-term effects have been noted at all new VFS units in the area. After this initial period of a few months, the effluent net alkalinity of the TEST system is generally within 100 mg/L of zero except in periods of very high influent acidity. The average increase in net alkalinity is 430 mg/L.

Table 3. Average composition of filtered waters from TEST system

| | | Site | | |
	Units	G3	G4	G5	G6
Al	mg/L	21.3(45)	19.0(37)	1.62 (40)	1.52 (33)
Ca	mg/L	107 (36)	85.8(34)	201 (40)	182 (33)
Fe total	mg/L	164 (46)	71.5 (37)	28.1 (49)	4.6 (37)
Fe^{3+}	mg/L		43(6)	<1(6)	
K	mg/L	3.5 (22)	4.1 (26)	4.2 (28)	5.6 (23)
Mg	mg/L	92 (24)	67.4 (26)	72 (29)	65 (23)
Mn	mg/L	27.7 (46)	23.3 (37)	20.4 (49)	18.6 (43)
Na	mg/L	4.4 (24)	1.9 (26)	2.0 (28)	1.8 (23)
Si	mg/L	11 (24)	8.3 (25)	7.9 (29)	5.9 (22)
SO_4	mg/L	1004(45	811(37)	898 49)	710 43)
Acid.	mg/L	509(45)	396(35)	34 (48)	22 (42)
Alkal.	mg/L	1.2 (45)	0 (36)	67 (46)	45 (42)
Net Alk.	mg/L	-508(36)	-396 (36)	33 (46)	23 (42)
pH		3.74(48)	3.05(36)	6.39(50)	6.1 (43)
Temp.	C	13 (25)	13.7 (25)	13.1 (27)	15 (25)
Eh	mv	513 (3)	656 (6)	232 (9)	331 (3)
Tot.Org C	mg/L	ND	ND	279 (4)	10.7 (7)
Flow	l/min	59.7(31)		78 (18)	

( ) Number of samples
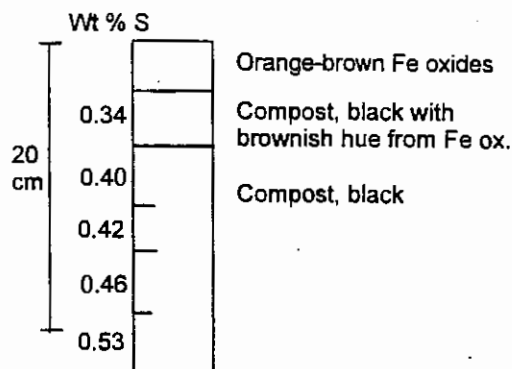
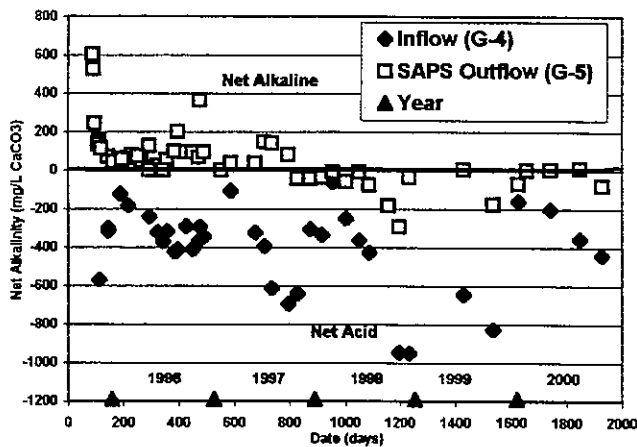Figure 4. Log of core through compost in TEST VFS, and % total sulfur.

Figure 5. Net alkalinity of inflow(solid symbols) and outflow (open symbols) for TEST VFS.

The average Ca increase of 115 mg/L in the VFS corresponds to dissolution of 287 mg/L $CaCO_3$. Thus, about 66% of the 430 mg/L increase in net alkalinity is due to dissolution of limestone.

At least some of the remaining increase in alkalinity is presumably due to sulfate reduction, but the details of this are complex. The analyses of S in the core through the compost (Figure 4) indicate only traces of dissolved H_2S and acid volatile H_2S (=FeS), but 0.2 to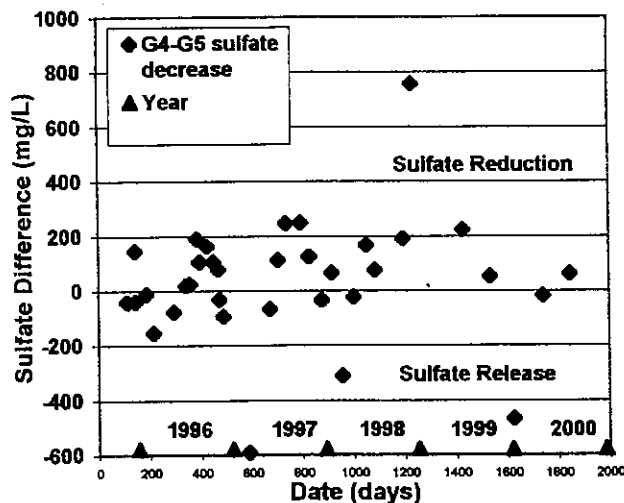 0.3 wt% S as pyrite as tiny grains were observed by binocular microscopic observation of the core. In addition, an H_2S smell is consistently observed at the G5 outflow. Therefore, Fe is being sulfidized in the compost, even in the near-surface horizon at the core location.

The extent of sulfate reduction can be estimated from the decrease in SO_4 through the VFS, assuming that sulfide dissolution and sulfate precipitation in the VFS are negligible. Figure 6 illustrates the changes in SO_4 through the VFS. Sulfate reduction is clearly seasonal, with SO_4 consumption during summer and fall, and SO_4 release in some winter and spring periods, as indicated by a "sine-curve" pattern on a plot of SO_4 difference vs. day of year (Figure 7). The average decrease in SO4 is 31 mg/L, giving an average alkalinity production from SO_4 reduction of only about 32 mg/L (1.042 mg/L alkalinity from SO_4-reduction per 1 mg/L decrease in SO_4). However, a few samples show a large SO_4 release from the VFS, and obscure the more general pattern.

Release of SO_4 from the VFS suggests that previously precipitated sulfides are being oxidized and dissolved. Samples from 3/97, 3/98 and 1/00 show SO_4 release in excess of 300 mg/L, and most other winter and early spring samples show some SO_4 release (Figure 7). The net alkalinity generation at these times is lower than average. Capture of Fe by the VFS is also low at these times of SO_4 release, suggesting that FeS is not being precipitated, but rather that Fe^{2+} is passing through the VFS. Effluent temperatures are commonly 3 to 5°C during the periods of SO_4 release. All these features indicate that the ability of the compost to
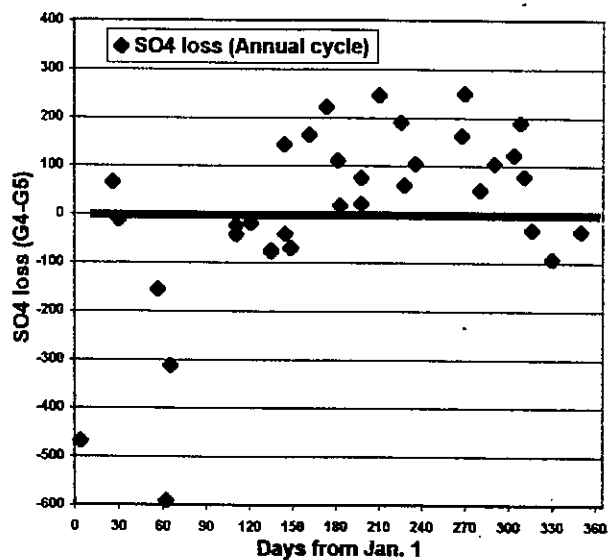

Figure 6. Sulfate removed during passage through TEST VFS (inflow minus outflow concentrations).

Figure 7. Sulfate loss in TEST VFS vs. days from Jan. 1 each year, showing seasonal cycle. Negative values indicate release of sulfate.

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reduce ferric iron, O_2, and SO_4 decreases or ceases when temperatures are below about 6-8°C at the existing flow rates. As a result, the FeS and FeS_2 in at least the upper part of the compost is oxidized and SO_4 is released. The lack of an accompanying pulse of Fe suggests that some Fe is oxidized and precipitated as Fe hydroxides in the VFS at this time. Presumably this ferric hydroxide is re-sulfidized in late spring at warmer temperatures when the compost recovers its sulfate reduction capability.

The rate of net alkalinity generation by the VFS (in g/day) shows a correlation with flow rate (Figure 8). Evaluation of data on Figure 8 indicates 2 groups of samples. A main group shows an increasing rate of net alkalinity generation with increasing flow. For these dates, essentially all influent acidity is neutralized, and with increased flow, net alkalinity is generated more rapidly. The figure suggests that the VFS is capable of producing at least 60,000 g/day of net alkalinity during warm weather. A second group of samples plots at lower rates of alkalinity generation than the first samples. All of these samples represent dates in winter and spring when SO_4 was being released from the VFS. Based on the previous discussion, these are times when FeS and FeS_2 were being oxidized owing to low temperatures (and relatively high flow rates). The oxidation of FeS and FeS_2 generates H^+ and consumes some net alkalinity that would otherwise be released.
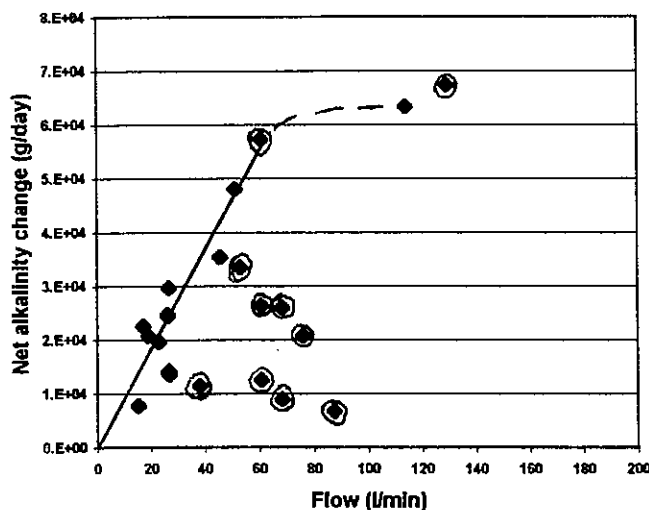
More than half the Fe in the flow from the ALD

Figure 8. Change in net alkalinity in TEST VFS as a function of flow rate. Circled points show sulfate release in winter-spring. Line indicates estimated fit for summer-fall conditions.

precipitates in Pond T1, as a result of oxidation. This process is accompanied by a decrease in pH, as shown in eq. (1). At G4, where water flows from Pond T1 into the VFS, 10 to 50% of the Fe is commonly ferric, but the pH is low enough that $Fe(OH)_3$ is slightly undersaturated according to calculations by PHREEQC. Jarosite and schwertmannite are slightly supersaturated.

Appreciable Fe disappears in the VFS. Part of this loss precipitates as Fe hydroxides in the surface water of the VFS and has accumulated as a layer about 3.7 cm thick on top of the compost. Only a small amount of Fe is present as suspended particulates in the outflow at G5. Of five dates on which non-filtered acidified samples from G5 were analyzed for comparison with filtered samples, only two indicated suspended particulate Fe, with a maximum of 2 mg/L, indicating negligible flux of particulate Fe from the VFS. A significant amount of Fe, probably most of the decrease between G4 and G5, is precipitating as Fe sulfide in the compost layer, or during cold periods, as ferric hydroxide. The core, collected in early December, contained Fe hydroxides in the top 3.5 cm of compost and Fe sulfides throughout, and SO_4 was being retained in the system at that date, indicating active SO_4 reduction. However, the bottom of the compost was still at 10°C, and it is possible that in more rapidly flowing channels through the compost, sulfide reduction had slowed. Most of the remaining dissolved Fe oxidizes and precipitates in Pond T2, leaving an average of less than 5 mg/L in the effluent at G-6.

The Al content decreases from 19 to 1.6 mg/L in the VFS. Comparison of five filtered vs. unfiltered samples from G5 shows an average 4.6 mg/L of particulate Al (range 0.2 to 8.6 mg/L). The remaining decrease in Al is apparently retained within the VFS. Precipitation of Al within ALD's is known to plug them in times as short as a few months. However, for the TEST VFS, the annual decrease in Al flux of about 500,000 g between G4 and G5 would occupy only about 0.05% of the pore volume of the limestone layer of the VFS (assuming a density of 1.2 g/cm^3 for gelatinous precipitate). Based on this estimate, general plugging of the limestone layer does not seem likely, though portions of it could become plugged.

C-Series System

The average chemistry of 7 sites in the C-series system is listed in Table 4. Flow through this system averages about 200 L/min, with a range from 99 to 350 L/min. Most flows in '97-'98 were markedly higher than flows since 9/98, undoubtedly related to drought conditions in 1998-99, plus decreases in inflow related

Table 4. Data for average water quality, C-Series System

	Units	C1B	C2	C5	C6	C8	C10	C12
Al	mg/L	33(9)	22(17)	16(15)	12(14)	12(16)	5.0(12)	0.5(11)
Ca	mg/L	105(9)	86(17)	100(15)	128(14)	138(16)	152(12)	136(11)
Fe	mg/L	302(9)	165(17)	88(15)	35(14)	24(16)	9.8(12)	0.3(11)
Fe(3+)	mg/L			77(5)	12(5)			
K	mg/L	4.6(9)	3.9(17)	3.9(15)	3.9(14)	6.5(16)	6.0(12)	4.3(11)
Mg	mg/L	109(9)	77(17)	73(15)	82(14)	85(16)	73(12)	46(11)
Mn	mg/L	37(9)	27(17)	25(15)	23(14)	25(16)	20(12)	4.9(11)
Na	mg/L	2.2(9)	1.96(17)	1.77(15)	1.71(14)	2.01(16)	1.86(12)	116(11)
Si	mg/L	13.3(9)	10.6(17)	8.77(15)	8.6(14)	9.2(16)	6.5(12)	2.01(11)
SO4	mg/L	1402(9)	1114(17)	944(15)	875(14)	904(16)	778(12)	769(11)
Acidity	mg/L*	739(9)	530(17)	408(15)	223(14)	205(16)	89(12)	10(11)
Alkalinity	mg/L*	0(9)	0(17)	0(15)	0(14)	0(16)	14(12)	44(10)
Net Alk.	mg/L*	-739	-530	-408	-223	-116	-75	34
pH		3.69(9)	3.21(18)	3.07(16)	3.41(15)	3.40(17)	5.13(13)	7.85(12)
Temp.	C	11.1(9)	12.2(15)	13.5(15)	12.1(14)	14.7(15)	13.1(13)	14.8(12)
Eh	mv	568(1)	646(1)	710(5)	640(5)	750(1)	453(5)	439(1)
Flow	L/min	76(3)	114(8)			216(14)		

*mg/L CaCO3

( ) Number of samples

to plugging of the pipeline from the Campanera site in 1999.

The acidity decreases by about 200 mg/L along the open limestone channel (see Rose and Lourenso, 2000), and from 530 mg/L at site C2 (end of the open limestone channel) to 408 mg/L at site C5, the inflow of the SAPS. This decrease appears to result from precipitation of schwertmannite or jarosite in the intervening 3 ponds, perhaps slightly supplemented by inflow of water from the TEST system. In VFS C1, net alkalinity increases by 185 mg/L CaCO₃, a relatively small increase compared with the TEST and other systems. Possible reasons are discussed below. After a small increase in Pond C4, the net alkalinity increases by 130 mg/L in VFS C2, and the outflow is still distinctly acid. Addition of NaOH after site C10 provides a net alkaline effluent at site C12.

Only about 40% of the 185 mg/L increase in net alkalinity from C5 to C6 is attributable to dissolution of limestone, as estimated from increase in Ca. Similarly, through VFS C2 between C8 and C10, only about 55% of the 127 mg/L increase in net alkalinity is attributable to limestone dissolution. Thus, these two VFS are less effective than the TEST system both in alkalinity generation and in the component due to limestone dissolution.

Of the initial 300 mg/L Fe at C1B (the start of open limestone channel), nearly half is precipitated in the open limestone channel, and nearly half of the remainder is precipitated in oxidation-settling ponds C1, C2 and C3, with an accompanying pH decrease from 3.7 to 3.1. Note that up to about 60% of the decrease in Fe between C1B and C2 may be by dilution from small less concentrated flows, as indicated by the decrease in Mn. Much of the remaining 88 mg/L Fe is removed in VFS C1 and C2. The water flowing into VFS C1 at site C5 has most of its 88 mg/L Fe as ferric. In the outflow (site C6), about 30% of the Fe is ferric on average, but the proportion of ferric decreased from nearly 100% in 1/98 to <1% in 6/99. The significant amount of ferric Fe in the C6 effluent prior to 6/99 suggests that the compost layer was not effective in the first year, and that appreciable Fe probably precipitated in the VFS. An H₂S smell was first recorded at C6 in 7/98, but it is typically weaker than at G5 at the TEST VFS.

A clear seasonal trend in SO₄ reduction is not evident in VFS C1 or C2, though SO₄ loss and alkalinity generation do appear to average higher in summer than in winter-spring.

A possible reason for high ferric in the C6 effluent from VFS C1 in the first year is that the compost layer was thin over part of the limestone layer, or that the flux of ferric iron exceeded the reducing capacity of the compost layer, so that considerable ferric iron entered the limestone without being reduced. More recently, with a reduced flow rate, perhaps ferric-reducing

bacteria have colonized the thin compost, or an accumulation of Fe-oxides on top of the compost or within limestone below the high-flow zone has modified the flow pattern and caused more flow through zones of thicker compost.

A-Series System

The results of sampling inflow and outflow of the two VFS in this system are summarized in Table 5. The influent water has very high acidity and Fe concentration, with a flow estimated at 100 L/min. In the first VFS, acidity decreases by about 340 mg/L, and by another 340 mg/L in the second VFS. Most of the Fe is removed by the two VFS and the intervening ponds. However, the water is still strongly net acid after passage through the two units.

Rates of Alkalinity Generation and Iron Precipitation

The rates of alkalinity generation vary considerably among the five VFS, but tend to be on the high side of values reported by other workers (Table 6).

The best parameter to use for evaluation and design of VFS is not clear because of multiple processes creating alkalinity. In previous studies, the rate of

Table 5. Average concentrations of samples from the A-Series System

	VFS A1 inflow	VFS A1 outflow	VFS A2 outflow
Al	70.00	45.00	29.00
Ca	148.00	238.00	358.00
Fe	231.00	149.00	26.00
K	4.60	5.20	5.30
Mg	172.00	217.00	242.00
Mn	59.00	59.00	62.00
Na	3.90	3.30	3.00
Si	21.00	17.00	14.00
SO4	2270.00	2280.00	2149.00
Acidity	1046.00	702.00	367.00
Alkalinity	0.00	0.00	3.00
Net Alk.	-1046.00	-702.00	-364.00
pH	3.03	3.62	4.18
Temp.	16.00	13.00	14.00
Eh	698.00	555.00	430.00
Flow		57.	

Averages based on 6 samples taken 12/97 to 8/00
Only 1 value of Eh measured at each site. Only 1 flow measured.

alkalinity generation has commonly been expressed per unit surface area ($g/m^2/d$, Watzlaf et al., 2000), or as a simple increase in net alkalinity concentration (150-300 mg/L, Kepler and McCleary, 1994). Jage et al. (2000) find that alkalinity generation is related to retention time, Fe concentration and non-Mn acidity. Hedin and Watzlaf (1994) indicate that retention times exceeding 23 hours add little or no alkalinity, but Jage et al (2000, Figure 2). show that retention times up to about 200 hours (8 days) can have significant effects for highly acid sites.

Most alkalinity generation occurs in the limestone layer of VFS, and generation in the limestone layer is much less variable seasonally than in the compost layer. Watzlaf et al. (2000) show an average of 72% generated in the limestone, range 54-95%. The Pot Ridge results show a similar relation.. In the limestone layer, rate of net alkalinity generation is expected to depend mainly on the surface area of limestone fragments (a function of limestone mass and fragment size) and the retention time in the limestone layer. Thus, units of g/tonne/day of limestone seem relevant. The pH of influent water and perhaps SO_4, Fe or other concentrations may also have effects. Alkalinity generation in the compost layer would be added to the effects of the limestone layer, but for treatment of strongly acid water in cold weather, should not be counted on in design of facilities. The TEST, C1, C2, A1 and A2 VFS systems produce alkalinity in the range 16-26 g/T/d, or 35-50 $g/m^2/d$. The latter value is within the range of 16-62 $g/m^2/d$ reported by Watzlaf et al. (2000).

Design and Maintenance Considerations

An obvious problem has been the decrease in flow from the ALD's feeding the TEST system. This problem is undoubtedly caused by plugging with Al hydroxides, as described by previous workers (Watzlaf et al., 2000). However, ALD-2 has not completely plugged, perhaps because of the coarse limestone size. Although ALD's are not recommended for Al-bearing AMD, a possible remedy for plugging is furnished by pumping on the outlet to dislodge and flush out the precipitate. This procedure was tried by Cooney personnel on a nearby ALD and succeeded in restoring the flow.

A second problem is plugging of pipes by precipitation of Fe hydroxides. The pipeline from the Campanera area to site C1 plugged after about 2 years (fall 1999) and was dug up and replaced by a deep trench. The water entering the pipe was probably supersaturated with Fe-hydroxides and contained dissolved O_2 that allowed Fe-oxidizing bacteria attached to the pipe walls to multiply and encrust the

Table 6. Rates of alkalinity generation in Vertical Flow Systems

System	TEST	C1	C2	A1-A2	Watzlaf(2000)
Sample points	G4-G5	C5-C6	C8-C10	A1i-A1o	
Flow (L/min)	69	216	216	(60-120*)	
Area (m²)	1020	1150	950	1140	
Volume of limestone (m³)	2040	1770	1460	1750	
Mass of limestone (T)	2250	2210	1825	2400	
Retention time (d)	10	3.3	2.3	(6*)	
Net alk. change (mg/L)	363	185	126	344	
Net alk. ch. in limestone (mg/L)	310	70	93	225	
Rate, g/m²/d	35	50	41	(40*)	16-62
Rate, g/m²/d (limestone only)	30	19	30	(28*)	
Rate, g/T/d	16	26	21	(20*)	
Rate, g/T/d (limestone only)	14	10	16	(14*)	

*based on estimated flow

pipe with precipitate. At approximately the same date the outlet pipe from Pond C3 into VFS C1 became partly plugged. It is not clear whether this plugging resulted from Fe precipitates or floating debris, or a combination. Pond C3 then overflowed and has partly eroded the dike between the pond and the VFS. In addition, the pipe from Pond C4 to the channel at site C8 plugged in Fall 2000 because of Fe precipitation. Previous temporary plugging of the outlet pipe from Pond T2 by floating debris was observed. Use of channels rather than pipes, provision of cleanouts for pipes, and designs that minimize Fe^{3+} and O_2 in pipes are recommended.

High flow rates can cause problems with the systems. The open limestone channel from site C1 to C2 captures appreciable surface runoff during storms. A spillway on Pond C1 allows this overflow to escape down a channel to Paint Creek, but at times the flow is so rapid that large rip-rap is moved and the pond wall is eroded.

The head required to accomodate a given flow through the TEST VFS has evidently increased, and the Pond T1-TEST VFS system overflows at lower flows than originally. This change is probably due to the accumulation of Fe-oxide precipitate on top of the compost in the VFS. To partially solve this problem, the level of the outflow pipe was decreased by cutting off 0.3 m in about 1998, but moderate flows are again causing overflow. Periodic removal of the precipitate from the surface of the compost may be required in high-iron systems.

Outflow from VFS C1 (site C6) was not strongly reducing for the first 2 years of operation, suggesting that the compost was not thick enough to reduce Fe^{3+}

and O_2 at the existing flow rates. This problem has since been observed more clearly in a flushable VFS recently built near the A area. At this VFS, which treats AMD with very high Fe concentration, opening of the flushing valve releases water rich in suspended Fe oxides from the limestone layer. The compost at both these sites is about 0.3 m thick. Either this is not thick enough, or the compost was not spread evenly over the surface, so that flow is concentrated in thin zones in the compost layer. Because permeability of the compost layer is much lower than the limestone layer, the flow rate through the system depends mainly on thickness of the compost layer, and care should be taken to spread compost evenly over the limestone layer.

Several ponds have overflowed owing to inadequate freeboard in the VFS dams, requiring addition of fill to these dams. Adequate freeboard should be designed into these systems so that they will have at least 0.3 m of freeboard under high flow conditions.

Conclusions

AMD of the Pot Ridge area is high-Fe, -Al, -Mn water with high acidity, higher than at other sites where passive treatment has been attempted. At the TEST and A-Series VFS, the acidity decreases by 300 to 400 mg/L by passage through a single VFS unit. The effects of the C-Series VFS units are about half this value. Rates of net alkalinity generation for all 5 systems are 35 to 50 g/m²/d, in the middle to upper part of the range reported by Watzlaf et al. (2000). The TEST VFS removes about 90% of the 366 mg/L influent acidity in a single unit, with a retention time of 10 days. The C1 and C2 VFS remove about 40% of 410 mg/L acidity in passage through each of two units,

with a retention time of 2 to 3 days. These data, in combination with those of Jage et al. (2000), suggest that retention times much longer than the conventional 12 to 24 hours are desirable.

Limestone dissolution is responsible for 50 to 85% of the alkalinity added. Sulfate reduction, the other main alkalinity-producing process, is effective in summer and fall. However, in the TEST VFS during winter and early spring, SO_4 is consistently released, apparently due to oxidation of FeS. A compost layer thicker than the 30 cm used in these units may be desirable for more effective treatment of high-Fe, low-pH AMD.

Considerable acidity is removed during oxidation and precipitation of Fe in ponds before and after the VFS. The acidity is removed by precipitation of the Fe hydroxysulfates schwertmannite or jarosite.

These VFS and ALD's were constructed using coarse limestone (8-10 cm). Although up to 17 ppm Al is retained within the TEST VFS, calculations indicate that Al precipitate will fill less than 1% of the pore space in 10 years, so that plugging of the VFS will probably not be a problem. The ALD's have largely but not completely plugged, probably because influx of Al-bearing water is concentrated in a more limited volume and cross-sectional area.

Acknowledgements

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