Renovation of a failed constructed wetland treating acid mine drainage

C.D. Barton · A.D. Karathanasis

Abstract Acid mine drainage (AMD) from abandoned underground mines significantly impairs water quality in the Jones Branch watershed in McCreary Co., Kentucky, USA. A 1022-m^2 surface-flow wetland was constructed in 1989 to reduce the AMD effects, however, the system failed after six months due to insufficient utilization of the treatment area, inadequate alkalinity production and metal overloading. In an attempt to improve treatment efficiencies, a renovation project was designed incorporating two anoxic limestone drains (ALDs) and a series of anaerobic subsurface drains that promote vertical flow of mine water through a successive alkalinity producing system (SAPS) of limestone beds overlain by organic compost. Analytical results from the 19-month post-renovation period are very encouraging. Mean iron concentrations have decreased from 787 to 39 mg l^{-1}, pH increased from 3.38 to 6.46 and acidity has been reduced from 2244 to 199 mg l^{-1} ($CaCO_3$ equivalent). Mass removal rates averaged 98% for Al, 95% for Fe, 94% for acidity, 55% for sulfate and 49% for Mn during the study period. The results indicate that increased alkalinity production from limestone dissolution and longer residence time have contributed to sufficient buffering and metal retention. The combination of ALDs and SAPS technologies used in the renovation and the sequence in which they were implemented within the wetland system proved to be an adequate and very promising design for the treatment of this and other sources of high metal load AMD.

Key Words Constructed wetlands · Acid mine drainage · Anoxic limestone drains

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Introduction

The exposure and oxidation of iron sulfide materials from coal mining activities have resulted in acid mine drainage (AMD), a serious water pollution problem for the Appalachian region of the United States. The U.S. Bureau of Mines has estimated that approximately 20000 km of streams and rivers are impacted by AMD in the United States (Kleinmann 1989). In recent years, several low-cost passive treatment technologies have been developed that utilize natural chemical and biological processes to clean contaminated mine waters without the expense or potential hazards associated with chemical additions. Constructed wetlands, anoxic limestone drains (ALDs), and successive alkalinity producing systems (SAPS) are examples of such technologies that offer a potential solution to the AMD problem.

Two types of constructed wetlands have been used for AMD treatment: (1) surface flow or “aerobic wetlands”, in which water flows through emergent vegetation and above the surface of a relatively shallow substrate composed of organic material or in situ soil, and (2) subsurface flow or “anaerobic wetlands”, in which water flows through a relatively deep permeable organic substrate that promotes the contact of drainage with plant roots and substrate materials. In general, surface flow wetlands treat AMD by promoting metal precipitation through oxidation/hydrolysis reactions and retention of the precipitate by physical entrapment. Most surface flow wetlands do not produce adequate alkalinity to buffer the acidity produced from hydrolysis, thus, treatment of net acidic and moderate (20–75 mg/l Fe) to high (>75 mg/l Fe) metal content AMD by these systems alone has not been very successful (Wieder 1989; Brodie and others 1993). Subsurface flow wetlands also rely on oxidation/hydrolysis reactions near the surface, but primarily depend on chemical and microbial reduction processes within the substrate. Anoxic conditions, generated in the organic substrate, are favorable for the formation of metal sulfides and alkalinity from bacterially mediated sulfate reduction (McIntire and Edenborn 1990). Bicarbonate production from limestone dissolution also acts as a buffer to neutralize proton acidity released from metal hydrolysis (McIntire and Edenborn 1990; Hedin and others 1994).

Although limestone is the most inexpensive alkaline source in coal mining regions, it has been utilized infrequently for AMD treatment because of its low solubility and tendency to become armored with ferric hydroxides in oxidized environments (USEnvironmental Protection Agency 1983; Nairn and others 1992; Faulkner and Skousen 1994; Hedin and others 1994). Turner and McCoy (1990) proposed that buried beds of limestone, now referred to as ALDs, can be useful in AMD treatment. In an anaerobic environment, ALDs can raise pH to circumneutral levels and produce bicarbonate alkalinity without inducing precipitation of metal hydroxides and associated armoring. The alkaline water produced in the ALDs generates sufficient buffering to withstand hydrolysis and precipitation processes, when exposed to aerobic conditions, without dropping the pH level significantly (Brodie and others 1993).

Recently, several systems have been developed which utilize both ALDs and anaerobic wetland processes. Kepler and McCleary (1994) proposed a SAPS design which promotes vertical flow of AMD through organic substrates and limestone beds. High biological oxygen demand in the organic substrate promotes sulfate reduction and reduces Fe^{3+} to Fe^{2+} before entry into a limestone layer, which functions as a submerged ALD. The limestone layer approximates a closed system in which CO_2 levels increase under waterlogged conditions and facilitate dissolution processes. This system has the potential to neutralize large amounts of acidity and decrease treatment area requirements (Kepler and McCleary 1994).

There is a critical need to improve wetland design parameters and use more efficient approaches that could adequately suppress acidity and Fe levels in high-metal-load acid mine effluents to the extent that they meet acceptable discharge parameters. In addition, improvements that could be used to restore failing or low efficiency constructed wetlands treating AMD are needed. Such an opportunity was provided at a failed constructed wetland in McCreary Co., Kentucky, USA, which received AMD from the underground mines in the Jones Branch watershed. The U.S. Forest Service established a surface flow wetland to treat AMD emanating from two collapsed portals of a 91-ha abandoned mine at Jones Branch in the spring of 1989. The wetland substantially reduced metal concentrations and acidity of AMD during the first year of treatment. During the following three years, however, and during periods of high flow rate ($>40\,\mathrm{l\ min^{-1}}$) the efficiency of the wetland was reduced due to insufficient utilization of treatment area, inadequate alkalinity production, and metal overloading. Several other AMD treatment wetlands constructed in the Appalachian region have been confronted with similar limitations. Therefore, a project to improve the performance of the AMD treatment system at the Jones Branch wetland was implemented. The objectives of the project were: (1) to modify the design parameters of the existing constructed wetland by introducing an anaerobic/alkaline pretreatment system and by developing a subsurface drainage system that will enhance utilization of the wetland cell substrates; and (2) to evaluate the design and operating efficiency, in terms of water quality, at different stages of treatment in the renovated constructed wetland.

Materials and methods

Study site and renovated wetland design

The original surface flow wetland designed at Jones Branch consisted of two sequential ponds with 15 and 10 cells, respectively, providing 1022 m^2 of treatment area. Each cell contained a 23-cm crushed limestone substrate overlain by a 46-cm layer of spent mushroom compost in which cattails (*Typha latifolia*) were transplanted. Renovation of the wetland involved: removal of the preexisting substrate; installation of ALDs; converting the original surface flow design to an alternating surface/subsurface flow system; and addition of a new substrate. Due to topographic constraints, increasing the size of the treatment system was not possible. Seepage from the mine was collected in an anaerobic lagoon. From there it was diverted to the wetland fields via two ALDs, consisting of 12.2 m long PVC pipes of 0.5 m diameter filled with 2.5–7.5-cm crushed limestone. Both ends of the ALDs are submerged in 1.5 m of water to maintain an anoxic state (Fig. 1). Precipitation of metal hydroxides in the drain is deterred because the iron is in its reduced state; thus, armoring of limestone is prevented. Two 30-cm diameter gate valves were installed at the outlets of the ALDs to control the flow rate and water level (Fig. 2).

In the wetland fields, AMD flows through a series of five alternating aerobic/anaerobic treatment zones. Each aerobic treatment zone consists of a precipitation basin with no organic substrate or plants. Acid mine drainage collected in the precipitation basin flows into the subsurface of a wetland cell (anaerobic treatment zone) through a

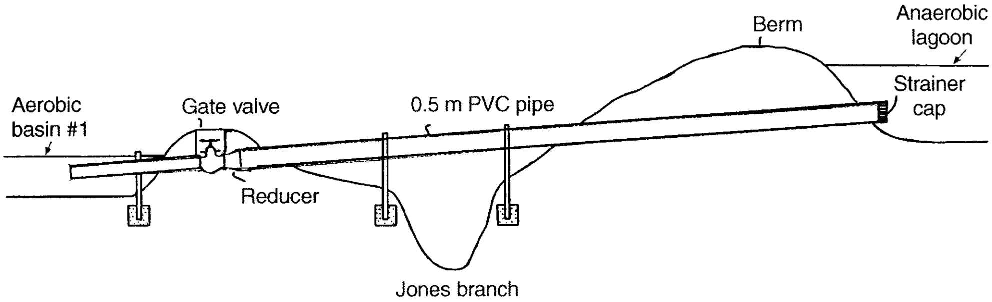

Fig 1
Cross sectional view of one anoxic limestone drain at the Jones Branch wetland

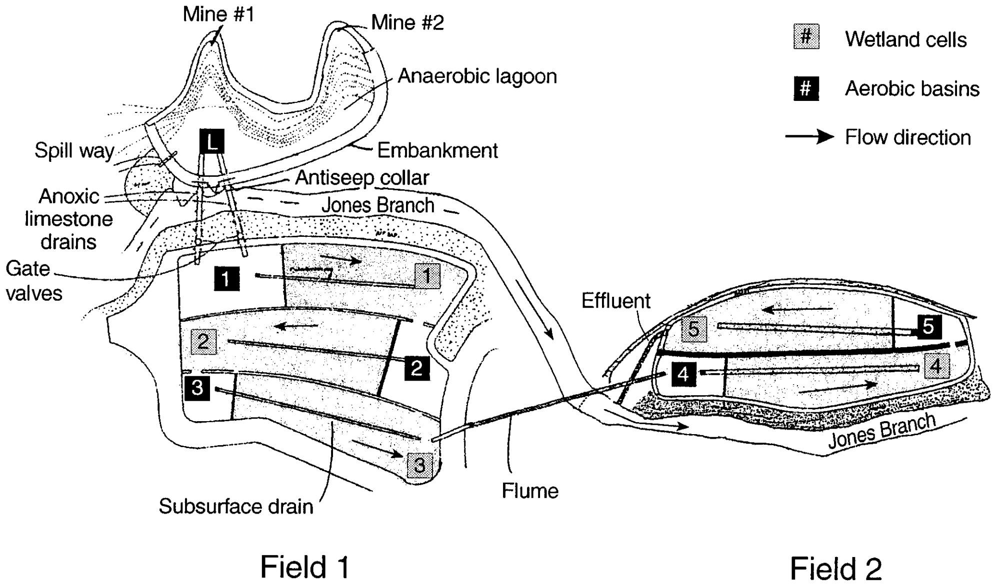

Fig 2
Site plan and sampling locations

perforated 15-cm diameter PVC pipe. The pipe is capped on one end so that AMD will percolate upward through the perforations and into a substrate composed of 30-cm crushed limestone overlain by 50 cm of hay/manure compost in which cattails are planted (Fig. 3). From the end of the first wetland cell, AMD is directed to another aerobic basin where further oxidation and metal precipitation are anticipated. This treatment process is repeated so that the drainage passes through a series of three aerobic/anaerobic treatment sequences in the first wetland field, then proceeds through a flume to a second field with two more treatment sequences. Construction of the lagoon, ALDs and alkaline subsurface flow system in field 1 (Phase I) began in May 1995 and was completed in June 1995. Renovation of field 2 (Phase II) began and was completed in September 1995.

The main treatment principle of the new design was to generate enough alkalinity in the ALDs and anaerobic wetland cells to promote metal precipitation, while compensating for acidity produced during hydrolysis in aerobic zones. With each subsequent treatment series, the amount of alkalinity produced was expected to increase as the concentration of metals decreases. In addition, the system was also expected to provide supplementary treatment through organic complexation of metals, adsorption to exchange sites, physical entrapment of solids, uptake by plants, and precipitation of metal carbonates.

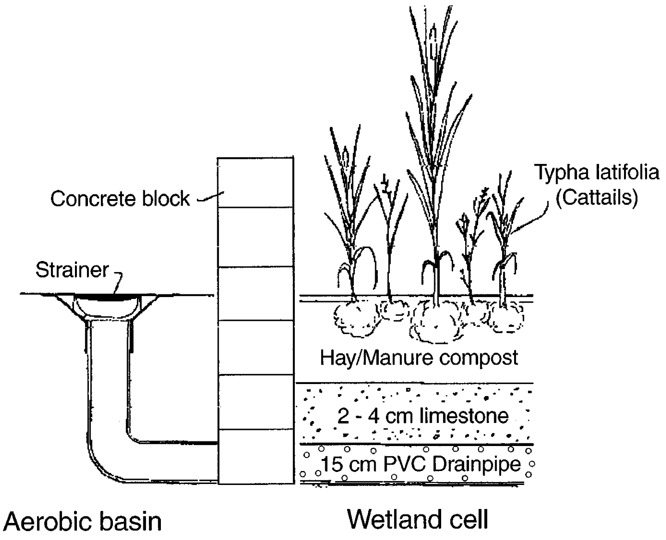

Fig 3
Detail of the subsurface flow system implemented at the Jones Branch wetland

Sample collection

Water samples were taken after renovation on a biweekly basis from June 1995 to December 1996. Surface water samples were collected at the anaerobic lagoon; aerobic basins 1–5; and wetland cells 3 and 5 (Fig. 2). Water pH, dissolved oxygen (DO), redox potential (Eh) and ferrous iron (Fe^{2+}) were measured in the field at each sampling point. Field pH and DO determinations were measured with calibrated Corning 313 and GS 1000 W meters, respectively. An Oakton ORP meter equipped with a platinum electrode was used to measure Eh. Field Fe^{2+} measurements were determined using a CHEMetrics© Ferrous Iron Test Kit. Three water samples were collected at each station. One sample was preserved with HNO_3 to $pH < 2.0$ for total Fe, Mn, Al, and Ca analyses. A second sample was preserved with 2N zinc acetate and NaOH to $pH > 9$ for sulfide analysis. The third sample was filtered through 0.2-μm filters for the determination of acidity, alkalinity and sulfate. Samples were transported with ice in coolers and stored at 4 C prior to analysis. Influent flow rate was calculated using a bucket and stopwatch. H-flumes at the outlet of wetland fields 1 and 2 were used to calculate intermediate and effluent flow rates, respectively.

Substrate samples were collected with a PVC coliwasa at each aerobic basin and wetland cell within the treatment system. The collected sludge was sealed in plastic bags and transported with ice in coolers. Interstitial solutions were collected by centrifuging the sludge at 3000 rpm for 1 h. The supernatant was filtered through 0.2 μm filters, and immediately analyzed for pH, EC, Eh, Al and Fe^{2+}. The remaining sample was preserved in a similar fashion as described above.

Solution analysis

Total Fe, Mn, Al, and Ca were analyzed using a IL S11 atomic absorption spectrophotometer. Interstitial Al and Fe^{2+} were determined colorimetrically and measured with a Bio-Tek Instruments spectrophotometer microplate autoreader. Interstitial Fe^{2+} was analyzed using the phenanthroline method; and Al by the eriochrome cyanine-R method. Acidity, alkalinity and sulfide were analyzed by titrimetric procedures using a Metrohm 665 Dosimat. Sulfate was determined turbidimetrically using the barium chloride method. All solution characterization procedures followed guidelines of the Standard methods for the examination of water and wastewater (APHA 1989) manual. Duplicate analyses were performed for 5% of the samples and exhibited $\leq 10\%$ analytical error. Geochemical modeling of aqueous-phase speciation equilibria was performed with the MINTEQA2 computer program (Allison and others 1990). Measured pH and Eh values were used as model inputs in the computer simulation.

Sediment characterization

Sediment samples were collected one year after the renovation had been completed using a soil auger. Elemental analysis was performed on finely ground air-dried samples with an EDAX-Phillips XRF Energy-Dispersive Analyzer (Phillips Electronic Instrument Co.). The instrument settings were at 25 kV and 200 μA using a Rh x-ray tube. Quantitative elemental determinations of the samples were based on above-background integrated peak intensities compared with a standard calibration curve, developed from reference materials supplied by the National Bureau of Standards. Selected precipitate samples were also examined with a Hitachi S-800 field emission scanning electron microscope equipped with a backscattered-electron detector.

Results and disscussion

Pre-renovation water quality

The original wetland design proved to be sufficient at reducing metal levels and acidity during the first six months of operation, but failed thereafter (Table 1). Average pH levels rose from an influent level of 3.05 to 7.20 in the effluent during the first year, however, effluent pH levels consistently remained below influent levels in subsequent years. Apparently, hydrated lime which was top-dressed on the substrate efficiently promoted metal precipitation and buffered acidity produced during metal hydrolysis initially, but neutralization ceased as the alkaline source was exhausted (Chalfant 1993). In the first year,

Table 1

Comparison of inflow and outflow water-quality data prior to renovation at the Jones Branch wetland. Values in mg l^{-1} except for pH which is in standard units. n = number of samples

Date	Influent															
	n*	pH			Fe			Mn			Al			SO_4		
		Min	Ave	Max	Min	Ave	Max	Min	Ave	Max	Min	Ave	Max	Min	Ave	Max
1989	8	2.89	3.05	3.33	960	1256	1420	15.8	22.2	37.3	8.1	12.4	20.6	3490	4311	5290
1990	10	2.83	3.19	3.61	560	937	1218	10.4	17.3	22.8	6.8	10.4	14.3	2700	3725	4600
1991	11	2.94	3.15	3.69	475	1017	1322	8.5	19.1	47.0	3.9	17.2	38.8	2000	3655	4800
1992	9	2.68	3.30	3.85	888	1229	1440	16.3	18.1	20.2	25.4	35.9	42.8	4100	4363	4600
94/95	5	3.24	3.47	3.87	225	739	1149	4.2	8.4	16.6	9.1	15.0	26.7	1098	2559	5385

Date	Effluent															
	n*	pH			Fe			Mn			Al			SO_4		
		Min	Ave	Max	Min	Ave	Max	Min	Ave	Max	Min	Ave	Max	Min	Ave	Max
1989	8	6.10	7.20	7.92	0.11	33.6	231	0.29	4.18	13.7	0.2	0.5	0.7	12.0	763	2460
1990	10	2.49	2.98	5.33	145	452	768	7.7	14.4	20.3	0.5	8.2	12.3	1550	3028	3800
1991	11	2.48	2.59	2.77	223	467	856	7.8	15.8	38.8	4.1	12.0	25.9	1650	2661	3900
1992	9	2.74	2.79	2.82	558	848	1038	13.1	15.4	17.8	26.5	33.8	39.7	3100	3880	4500
94/95	5	2.37	2.53	2.72	193	452	755	6.1	9.3	19.4	4.0	44.5	18.5	1572	2665	5010

[a] Analysis from 1989–1992 performed by U.S. Forest Service Northeastern experimental Station

elevated pH levels decreased the solubility of metal hydroxides and resulted in a >95% reduction of iron and aluminum. Manganese and sulfate levels also displayed a reduction of ≈80% during this period.

Several studies have suggested that adsorption and complexation of metals in organic substrates occurs only in the initial few months of AMD exposure before becoming saturated (Henrot and Wieder 1990; Kleinmann and others 1991; Wieder 1993). During the 1990–1992 period a reduction of only ≈20% Mn and Al was observed, which indicates that the metal retention processes had diminished. With continued age, increased Mn levels were observed as drainage passed through the wetland resulting in effluent concentrations that exceeded those of the influent. Apparently, the wetland substrate had become saturated with accumulated metals and desorption of chemisorbed Mn or resolubilization of Mn precipitates was occurring. In addition, reduction of sulfate declined with each passing year indicating lowered microorganism metabolism rates or inadequate infiltration and retention of AMD within the substrate zone (McIntire and Edenborn 1990). A reduction of ≈30% in Fe concentration continued from 1990 through 1995, evident by low pH levels in effluent waters and the accumulation of a ≈10-cm layer of precipitate above the substrate. Water quality parameters had significantly deteriorated by 1995, so that effluent water quality was equal to or worse than influent water quality. Deterioration of the system was also apparent through mass vegetation die-off.

Post-renovation water quality

Surface-water quality data for influent and effluent samples during the post renovation period are presented in Table 2. With the completion of Phase I renovation, influent pH levels rose from 3.10 to 6.44 at the flume (between wetland fields 1 and 2) then dropped to 5.31 in field 2. This trend remained constant until Phase II renovation was completed, which suggests that the old substrate was contributing contaminants to the Phase I partially treated mine water. Effluent pH levels increased to 6.46 and remained higher than flume pH levels for all sampling events that occurred after Phase II had been completed (Fig. 4a). Flume and effluent pH values indicate that conditions were favorable for precipitation of metal hydroxides and neutralization of the subsequent acidity generated during these reactions. The slight decline in pH during the last four months of 1996 may indicate that some of the neutralizing potential associated with limestone dust and fine particles may have been exhausted.

Post-renovation Eh values at the Jones Branch wetland indicated that both oxidizing and reducing conditions occurred within the system (Table 3). The Fe^{2+} to Fe^{3+} redox couple is often used as an arbitrary boundary between oxidizing and reducing conditions. It has been suggested that an Eh of 150–250 mv is representative of conditions necessary for Fe^{3+} reduction (Bohn 1971; Kadlec and Knight 1996). The relationship between Eh and iron redox chemistry is of great consequence to the system since $Fe(OH)_3$ has the capability to coat and armor limestone. Surface water samples collected in the aerobic basins exhibited moderately reduced to oxidized conditions, while samples from the wetland cells displayed reduced (<160 mv) Eh conditions. Differences between the two zones may be attributable to surface aeration in aerobic basins and high oxygen demand by the organic compost in anaerobic wetland cells. Interstitial solutions exhibited higher pH and lower Eh values than those observed in the surface water samples. Pore water from the wetland cell substrates displayed Eh values from 13.2 to –72.5 suggesting prevalence of Fe^{2+}. The ratio of Fe^{2+} to Fe^{3+} in the system confirms that reducing conditions prevailed

Table 2
Post-renovation influent and effluent water quality and flow data from July 1995 to October 1996 for the Jones Branch wetland. SD Standard deviation of the mean, n ‡ number of samples

Parameter	Units	Average		Minimum		Maximum		SD†		n = ‡
		Influent	Effluent	Influent	Effluent	Influent	Effluent	Influent	Effluent	
pH	std.	3.38	6.46	2.70	4.39	4.41	8.35	0.45	0.99	26
Eh	mv	260.6	159.3	146.6	−43.2	374.0	417.0	63.2	109.6	25
DO	mg/l	1.5	3.8	0.3	0.6	4.8	6.6	0.9	1.7	25
Fe^{2+}	mg/l	787	19.5	550	0.1	1007	275	109	55.5	26
Total Fe	mg/l	787	37.3	430	0.2	1031	331	121	75.2	26
Mn	mg/l	10.9	5.6	6.6	0.6	14.1	13.0	2.1	3.1	26
Al	mg/l	12.6	0.2	4.8	0	22.3	0.7	4.1	0.2	26
Ca	mg/l	261	264	157	76	337	613	47	128	26
Sulfate	mg/l	3034	1352	1944	312	4245	3390	569	730	26
Sulfide	mg/l	1.2	1.2	0	0	6.4	4.8	1.8	1.6	26
Alkalinity	mg/l[a]	0	141	0	0	0	295	0	90	26
Acidity	mg/l[a]	2244	119	1281	4	2883	915	337	206	26
Flow	LPM	37.1	26.1	10.6	1.1	57.2	57.2	14.4	18.7	26

[a] $CaCO_3$ equivalent

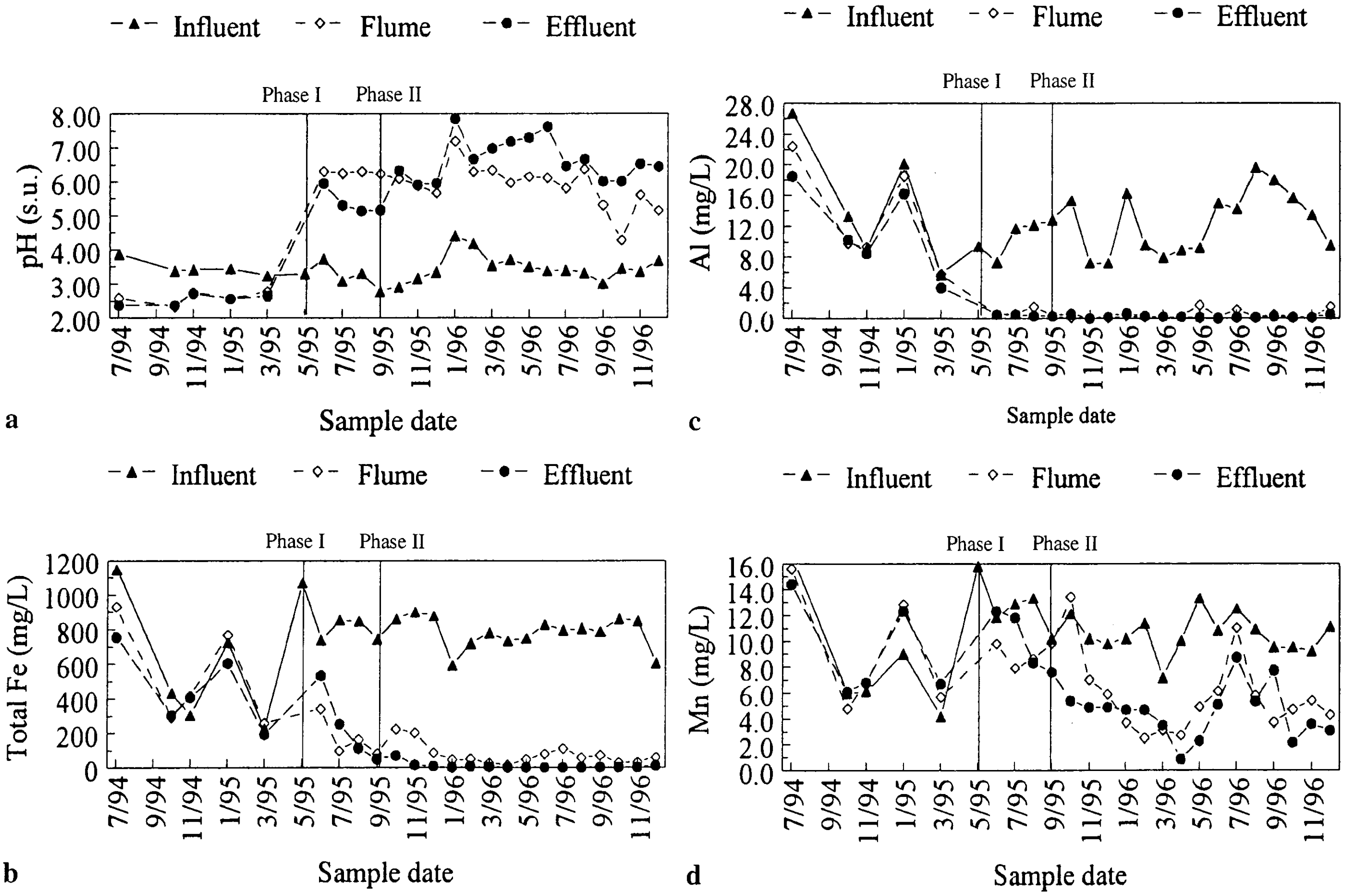

Fig 4
Surface water quality data for **a** pH; **b** total iron; **c** aluminum; and **d** manganese at the influent, flume and effluent sampling points

within the wetland substrate, while surface waters alternated between oxidizing and reducing conditions (Table 3). Thus, the armoring of limestone in the wetland cell substrates should be prevented.

Post-renovation analysis indicated Fe retention within the treatment system. Mean influent total Fe levels dropped from 787 to 110 and 37 mg l^{-1} at the flume and effluent, respectively (Fig. 4b). This accounted for an 86% removal of Fe in field 1 and a total removal of 95% for the entire system. Mean effluent Fe levels did not meet Office of Surface Mining (OSM) discharge guidelines for the entire post construction period, however, samples from November 1995 through the end of the study period contained an average of 3.3 ± 2.5 mg l^{-1} Fe which would satisfy the discharge criteria.

Iron retention in the wetland system was the result of several precipitation and/or adsorption processes at the surface and within the substrate. The hydrolysis of Fe^{3+} or microbial oxidation of Fe^{2+} usually accounts for 40–70% of the total Fe removed from AMD by wetlands (Henrot and Wieder 1990; Wieder 1993), while nearly 30% of the Fe retained may be in an iron sulfide form (McIntire and Edenborn 1990; Wieder 1993). Using X-ray diffraction and thermal analysis, Barton and Karathanasis (1998) identified Fe species in the renovated wetland treatment system. In their report, characterizations of precipitates from aerobic zones indicated the presence of crystalline Fe minerals such as hematite, lepidocrocite, goethite, and jarosite. Anaerobic wetland cell substrate characterization suggested the presence of amorphous iron minerals such as ferrihydrite and Fe-oxyhydroxysulfate. Apparently high Fe^{3+} activity and low oxygen diffusion rates in the lower biotic subsurface environment inhibited the kinetics of crystalline iron precipitation. Instead, amorphous ferrihydrite appeared to dominate the Fe precipitates within the substrate. Some goethite, lepidocrocite and hematite, however, were observed near the surface of wetland cell substrates and were attributed to increased oxygen levels from surface aeration and/or oxygen transport by plant roots.

Aluminum concentrations were reduced by 98% through the wetland after renovation and low levels (<0.7 mg l^{-1}) were observed in the effluent throughout the post renovation period (Fig. 4c). This reduction may be attributed to the solubility of Al, which is pH-dependent and forms aluminum hydroxide precipitates at pH ≈ 5.0 (Stumm and Morgan 1981). Interstitial solution analysis revealed that a pH of 5.76 is reached in the subsurface of the first wetland cell and maintained at or above this level in subsequent substrate zones (Table 3).

Table 3
Mean surface water and instertitial solution chemistry for post renovation samples collected at the Jones Branch wetland. n = 8, SD < 50% for interstitial solutions; n = 26 for surface water samples, L anaerobic lagoon; B(#) aerobic precipitation basin; C(#) wetland cell

Parameter	Sample Site‡										
	L	B1	B2	B3	B4	B5	C1	C2	C3	C4	C5
	Interstitial Solution										
pH (std.)	3.51	3.93	5.53	6.20	6.04	5.36	5.76	6.35	6.62	7.15	7.71
Eh (mv)	269.1	176.7	67.7	−10.1	48.2	97.9	78.1	−14.3	6.8	−28.1	−72.5
Fe^{2+} (mM)	10.36	10.47	7.17	4.61	2.80	0.83	3.71	1.15	1.07	0.35	0.04
Fe^{3+} (mM)	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Al (mM)	0.16	0.07	0.02	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Ca (mM)	4.28	5.62	6.24	5.81	4.60	4.78	5.45	4.74	4.85	4.22	4.81
Mn^{2+}(mM)	0.21	0.22	0.16	0.11	0.10	0.09	0.14	0.13	0.09	0.04	0.03
SO_4^{2-} (mM)	19.56	21.22	17.23	13.69	10.25	10.42	11.23	8.57	7.76	6.09	5.43
Alkalinity (mg L-$^{-1}$)^a	0	0	18.1	33.7	25.3	75.0	70.2	153.7	230.3	421.9	635.8
	Surfacce Water										
pH (std.)	3.38	3.20	3.19	4.62	5.96	4.83	–	–	6.07	–	6.46
Eh (mv)	260.6	294.8	345.4	246.8	83.8	169.1	–	–	264.3	–	159.3
Fe^{2+} (Mm)	8.95	9.39	1.01	0.41	0.15	0.11	–	–	0.40	–	0.24
Fe^{3+} (mM)	<0.01	0.02	0.10	0.01	<0.01	<0.01	–	–	<0.01	–	<0.01
Al (mM)	0.14	0.11	0.05	0.02	<0.01	0.01	–	–	<0.01	–	<0.01
Ca (mM)	3.93	4.19	4.04	3.56	3.69	3.31	–	–	3.94	–	4.32
Mn^{2+} (mM)	0.20	0.22	0.15	0.12	0.10	0.10	–	–	0.12	–	0.10
SO_4^{2-} (mM)	21.45	22.31	13.26	10.19	8.22	8.95	–	–	8.19	–	10.73
Alkalinity (mg L^{-1})^a	0	0	0	39.0	112.5	35.9			198.5		141.1

^{a} $CaCO_3$ equivalent

Manganese concentrations, on the other hand, displayed a moderate 48.6% removal through the wetland system and showed variable retention rates. Several researchers have reported similar results for Mn in wetland treatment systems (Wieder 1989; Fennessy and Mitsch 1989; Brodie 1990; Brodie and others 1993; Dietz and Stindinger 1996; Sikora and others 1996), and attributed low removal rates to several biogeochemical interactions and slow kinetic processes of Mn^{2+} oxidation (Stumm and Morgan 1981). Flume Mn concentrations displayed an initial four month reduction from influent levels after Phase I renovation, then returned to levels equal to the influent (Fig. 4d). The completion of Phase II resulted in an initial three month reduction of effluent Mn concentrations, while flume values remained consistent with influent concentrations. By November 1995, flume and effluent Mn concentrations remained relatively equal and displayed removal rates from 30 to 90%. The retention of Mn during the first four months of Phase I, when field 2 was not contributing to treatment, and the first three months of Phase II, when field 1 did not contribute to Mn treatment, may be attributed to sorption processes. It has been suggested that a majority of Mn sorption to organic matter and limestone occurs during the initial months of AMD treatment when sorption sites are plentiful (Kleinmann and others 1991; Wieder 1993; Wildemann and others 1994; Evangelou 1995).

The concentration of Mn in the flume and effluent, after November 1995, appears to be influenced by the loading rates and Fe^{2+} concentrations. After Phase II renovation, flume and effluent Mn levels gradually dropped during the first eight months, then increased in the following four months before falling again toward the end of the study (Fig. 4d). Upon observation of the analytical data for flume waters, a relationship between total Mn and Fe^{2+} was established which exhibited a correlation coefficient (R^2) of 0.72. Apparently, Mn oxidation was inhibited by the presence of ferrous iron within the system (Fig. 5). The Fe^{2+} may control Mn oxidation rates in reduced environments by contributing electrons to previously precipitated Mn oxides and producing soluble

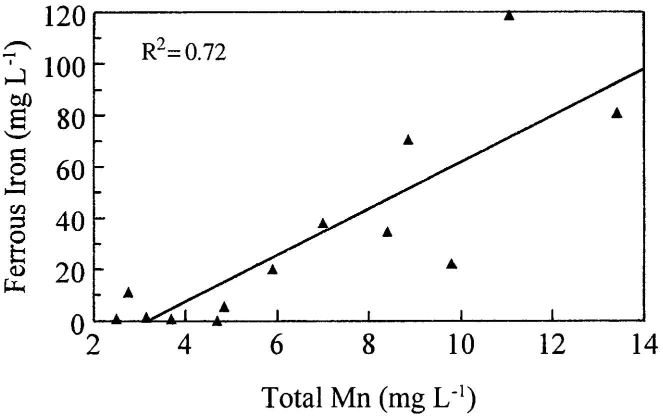

Fig 5
Influence of ferrous iron concentration on total manganese at the flume sampling point

Mn^{2+} (Burdige and others 1992). High Fe^{2+} concentrations at the flume may have inhibited Mn oxidation and resolubilized Mn oxides that had previously precipitated. This relationship can be used to explain the variable Mn treatment rates. Areas displaying low Fe^{2+} concentrations exhibited high Mn retention, while high Fe^{2+} content corresponded with low Mn treatment efficiency.

The renovation also sought additional alkalinity production from limestone dissolution and sulfate reduction. Analysis of surface waters and interstitial solutions for titratable alkalinity, SO_4^{2-}, S^{2-} and Ca were performed to identify the dominant alkalinity forming process. Following Phase I renovation, titratable alkalinity levels at the flume displayed a tremendous increase to 1268 mg $CaCO_3$ l^{-1} (Fig. 6a). Dissolution of limestone dust and fines accumulated in the system during the renovation probably elicited this response. Alkalinity generation in flume samples after Phase II renovation was erratic with values ranging from 0 to 238 mg $CaCO_3$ l^{-1}. Effluent samples, on the other hand, displayed an increase to ≈ 200 mg $CaCO_3$ l^{-1} during the first nine months then fell to ≈ 100 mg $CaCO_3$ l^{-1} during the last few months of the study. Apparently, either limestone dissolution or sulfate reduction processes, or both, peaked during the first nine months and leveled off afterwards. The instability of alkalinity measurements in the flume may be associated with metal carbonate precipitation. Using a pCO_2 value of 0.3, representative of flooded soils (Lindsay 1979) mineral speciation was performed using the MINTEQA2 program to determine the solubility of rhodochrocite ($MnCO_3$) and siderite ($FeCO_3$) within the treatment system. The resulting saturation indices indicated conditions at or near saturation for both metal carbonates in the wetland cells (Table 4). In addition, siderite precipitation in the interstitial zones of aerobic basins 2–5 is also favored. Thus, the formation of these precipitates contributed to the removal of Mn and Fe, but it also consumed some of the alkalinity produced from limestone dissolution within the system.

The concentration of SO_4^{2-} in the surface water decreased by 53.4% as it passed through the wetland, suggesting that sulfate reduction might be an active process (Fig. 6b). However, low S^{2-} concentrations (<5 mg l^{-1}) in surface and interstitial samples indicated that iron sulfide precipitates were not likely to form. Mineral speciation using the MINTEQA2 program suggested considerable undersaturation with respect to FeS and pyrite in all sampling locations. Apparently, sulfate reducing bacteria (SRB) were inactive in the system. According to Hilton and Oleszkiewicz (1988), SRB are inhibited by SO_4^{2-} concentrations above 1200 mg l^{-1}. Postgate (1984) also noted that the redox potential of the environment must be below –100 mv in order to cultivate SRB. The SO_4^{2-} concentrations and oxygen levels observed during the post renovation period were above these levels and, therefore, not suitable for dissimilatory sulfate reduction by SRB. However, geochemical modeling suggested that conditions were favorable for the formation of gypsum ($CaSO_4$) in the interstitial solution samples and surface water samples from aerobic basins 3 and 5 (Table 4). Therefore, the observed decrease in sulfates can be explained by gypsum precipitation. Resolubilization of precipitated Fe-oxyhydroxysulfates in the last wetland cell may be responsible for the observed increase in effluent SO_4^{2-} concentrations.

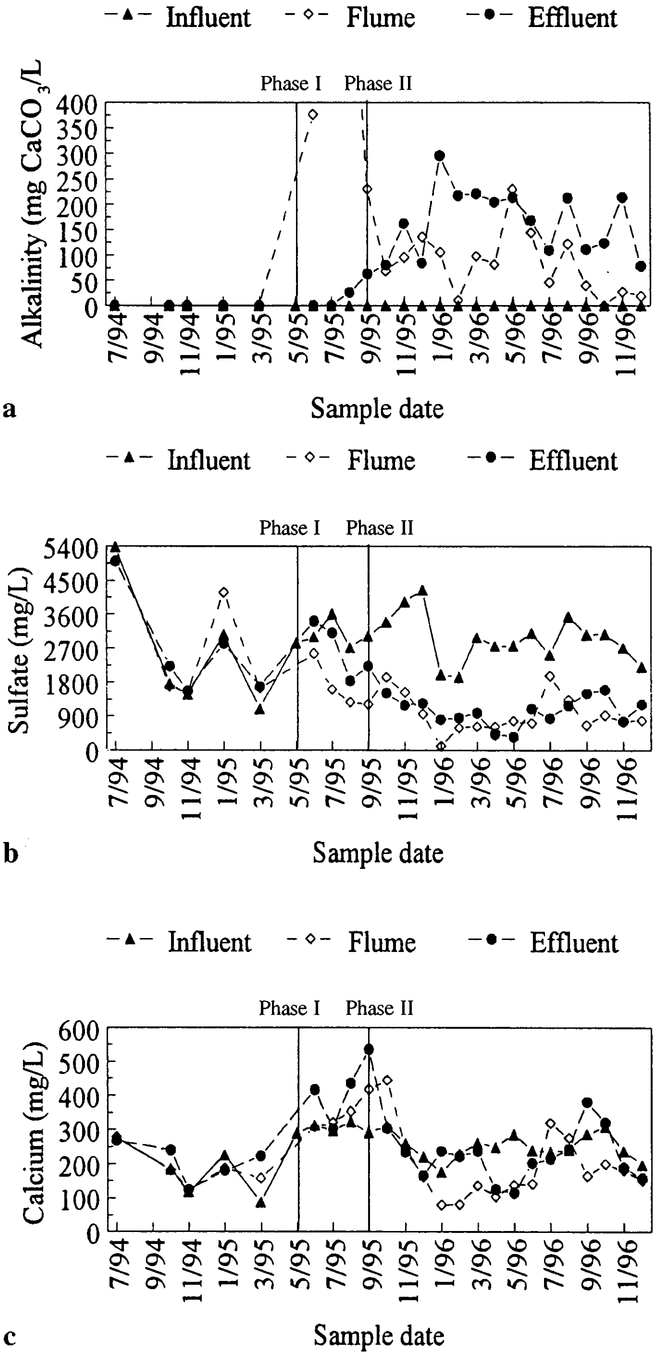

Fig 6
Surface water quality data for **a** total alkalinity; **b** sulfate; and **c** calcium at the influent, flume and effluent sampling points

The fate of Ca^{2+} in the system is closely associated to that of SO_4^{2-}. Average surface water effluent Ca^{2+} concentrations were generally higher than those observed in the

Table 4
Saturation indices (log Q/K) of interstitial and surface waters for selective minerals. Positive values indicate supersaturation and negative values undersaturation; Q ion activity product; K solubility constant, L anaerobic lagoon; B(#) aerobic precipitation basin; C(#) wetland cell

Mineral	Sample Site‡										
	L	B1	B2	B3	B4	B5	C1	C2	C3	C4	C5
	Insterstitial Solution										
FeS (precipitate)	−31.6	−22.4	−20.6	−15.7	−22.6	−24.3	−15.4	−17.0	−23.0	−22.2	−21.9
Pyrite	−40.8	−25.7	−25.6	−18.3	−29.9	−31.2	−16.8	−20.5	−30.8	−30.9	−30.8
Siderite	− 3.63	− 2.80	0.26	1.44	0.95	− 0.94	0.51	1.21	0.72	2.27	2.34
Rhodochrosite	− 5.47	− 3.62	− 1.54	− 0.34	− 0.65	− 2.05	− 1.06	0.09	− 0.56	1.01	1.66
Gypsum	− 0.04	0.09	0.10	0.03	− 0.12	0	0	− 0.14	− 0.16	− 0.29	− 0.29
	Surface Water										
FeS (precipitate)	−29.4	−32.5	−40.2	−38.7	−39.5	−43.4	–	–	−28.5	–	−41.9
Pyrite	−36.7	−41.9	−54.7	−54.6	−58.4	−62.8	–	–	−39.6	–	−63.8
Siderite	− 3.98	− 4.32	− 5.23	− 2.72	− 0.45	− 2.85	–	–	0.20	–	0.71
Rhodochrosite	− 5.77	− 6.09	− 6.20	− 3.40	− 0.78	− 3.04	–	–	− 0.48	–	0.14
Gypsum	− 9.62	− 8.49	− 7.57	− 0.11	4.49	− 0.68	–	–	5.86	–	5.87

influent, however, flume Ca^{2+} levels were consistently lower than those observed in both influent and effluent (Fig. 6c). Interstitial Ca^{2+} levels exhibited a moderate 31% increase between the lagoon and aerobic basin 2, which suggest limestone dissolution (Table 3). In subsequent treatment zones, the concentration of Ca^{2+} fell, possibly due to gypsum precipitation, then rose in the last wetland cell. Even though gypsum precipitation was favored throughout the treatment system in interstitial zones, the influence of oxygen in the upper water column may have had an impact on its stability. Based upon MINTEQA2 results, surface waters were undersaturated with respect to gypsum between the lagoon and aerobic basin 2, and saturated in later stages of treatment (Table 4).

Scanning electron microscopy

Evidence from solution analysis and geochemical modeling indicated that gypsum precipitation was probable, while FeS or pyrite formation was unlikely. Mineral identification of precipitates and substrate samples from selected aerobic basins and wetland cells were subjected to SEM analysis to gain a better understanding of S and Fe speciation. Precipitates collected in the aerobic basins consisted primarily of 0.1–0.5 μm spherical particles which were packed into 1–5 μm diameter globules (Fig. 7). This morphology is typical of amorphous ferric hydroxide or ferrihydrite, which often precipitates as globular aggregates around organic residues (Schwertmann and Taylor 1989). It has been suggested that the organic residues holding these globular aggregates together may be iron oxidizing bacteria (Lazaroff and others 1985; Ferris and others 1989). Figure 7 also reveals, to a lesser extent, the presence of thin disc-shaped particles similar in morphology to those described by Welton (1984) as hematite.

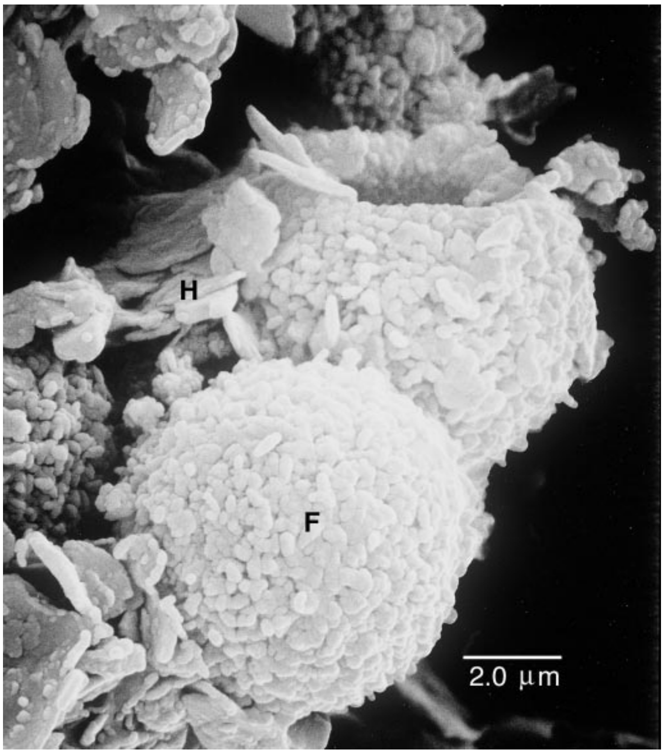

Fig 7
SEM from aerobic basin 1 showing ferrihydrite (F) and disc-shaped hematite (H)

A ferrihydrite dominated matrix was evident in all wetland cell samples. Since reducing conditions prevail in the wetland substrate and evidence was not established for ferrous iron precipitation, iron oxidizing bacteria must play a significant role in mineral formation reflected by the overwhelming abundance of ferrihydrite. Tabular gypsum crystals similar to those described by

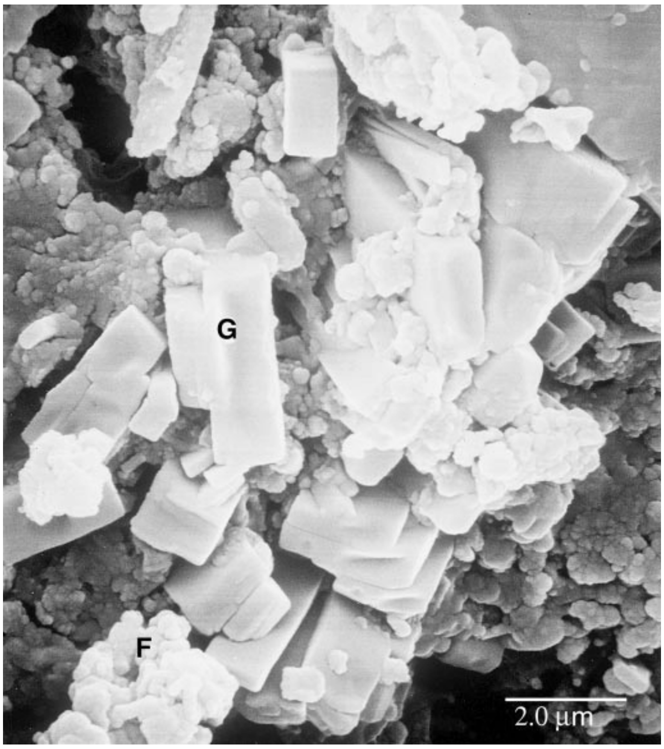

Fig 8
SEM from wetland cell 3 showing tabular gypsum (G) crystals and amorphous ferrihydrite (F)

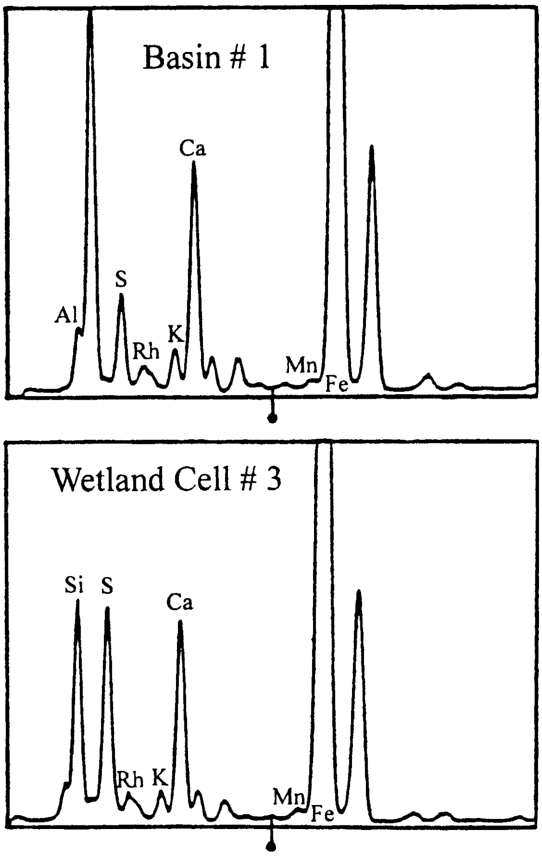

Fig 9
EDAX patterns of precipitates and sediments from the aerobic basin 1 and wetland cell 3

Karathanasis and Thompson (1995) were also observed within wetland cell substrates (Fig. 8). Iron sulfide precipitates were not observed in any wetland cell or aerobic basin.

X-ray fluorescence analysis of the sediments and precipitates supported the presence of the above mentioned minerals observed with SEM. EDAX spectrograms exhibit a large Fe band throughout the system (Fig. 9), which is consistent with the abundance of iron minerals observed. Equal amounts of calcium and sulfur in the wetland cells support the presence of gypsum (Welton 1984). Rhodium peaks emanate as background radiation from the X-ray tube.

Loading rates

Average influent and effluent flow rates after renovation were 37.1 and 26.1 l min^{-1} (LPM), respectively. The large difference in the values is attributable to evapotranspiration losses and a leak that was detected and sealed in April, 1996. After the leak was repaired, effluent flow rates varied less than 1.5 LPM from the influent rate. Prior to renovation, retention of drainage within the system was estimated to be ≈ 2 h (Chalfant 1993). A tracer study similar to the one performed by Hellier (1996) conducted to determine retention time in the renovated system showed an increased residence within the system to nearly three days.

Post-renovation influent Fe loading rates ranged from 16.5 to 59.3 kg day^{-1}, and averaged 42.0 kg day^{-1}. Post-renovation effluent Fe loading rates ranged from 10.5 to 0.03 kg day^{-1}, and averaged 1.4 kg day^{-1}. Based on these values, the wetland retained 18676 kg (18.7 metric tons) of iron during the post-renovation period. The average acidity load input was 120 kg day^{-1}, while output levels were reduced to 4.47 kg day^{-1}. Thus, 53144 kg (53.1 metric tons) of acidity were neutralized during the post renovation period. It was also estimated that the wetland retained an average of 0.37 kg Mn day^{-1}, or 170 kg of Mn over the entire study period.

Loading rates have been used to determine the optimal size for wetlands treating AMD. Design maxima for Fe and Mn removal by surface flow wetlands range from 10 to 20 and 0.5 to 1.0 g day^{-1} per square meter (GDM), respectively (Hedin and others 1994). Dietz and Stindinger (1996) have suggested design criteria of 10 GDM for Fe, and 25 GDM for acidity in subsurface flow wetland systems. During the post construction period, removal rates for Fe, Mn and acidity were 39.7, 0.37 and 113 GDM, respectively. From these results, the Jones Branch wetland system appears to have exceeded design limits for Fe and acidity removal. Moreover, Fe and acidity treatment rates were sustained during high loading periods and have been maintained throughout the post renovation period. Problems associated with Fe^{2+} concentration, water depth, vegetation and microbial activity may have contributed to inadequate Mn treatment.

Performance assessment

The ALDs appeared to have had a beneficial influence on mine water chemistry. Influent and effluent pH determinations made at the ALDs pipe openings, using a submersible pH probe, revealed an increase from 3.46 ± 0.27, at the inlet, to 4.61 ± 0.72 at the drain outlet. Apparently, acidity produced by hydrolysis as drainage entered the first precipitation basin may have moderated the pH increase. A submersible dissolved oxygen (DO) probe was used at the inlet and outlet of the ALDs to evaluate redox conditions. Dissolved oxygen levels below 2 mg l^{-1} are a necessary requirement for long term treatment by ALDs (Skousen 1991). Results indicated that DO levels were lower than 2 mg l^{-1} throughout the post renovation period. Using a porosity of 35% for limestone and average influent flow rates, retention time for each drain was determined to be 2.4 h. Faulkner and Skousen (1994) recommended a retention time of 15–20 h for optimal alkalinity generation, thus, the Jones Branch ALDs under the prevailing flow rates are not operating at maximum efficiency levels.

Elevations in calcium concentration through the ALDs were evident in twenty of the twenty six sampling events. An average Ca^{2+} increase of 18 mg l^{-1} through the drains was observed during the post renovation period, which is equivalent to the dissolution of 2.4 kg day^{-1} of limestone. Given that 7500 kg of limestone were originally placed in the drains and that the limestone is $\approx$80% $CaCO_3$, complete dissolution should theoretically occur in 6.44 years if current conditions prevail. Water quality data did not suggest retention of Fe or Mn in the ALDs, however, mineral speciation using the MINTEQA2 program suggested possible precipitation of $Al(OH)_3$ and gypsum. Potential clogging of the ALDs is a concern and has been reported by other researchers (Brodie and others 1993; Faulkner and Skousen 1994; Hedin and Watzlaf 1994; Hedin and others 1994), however, the existing 30-cm gate valves allow periodic flushing of the drain to remove unarmored precipitates. In addition, the use of PVC pipe in construction may allow for removal of spent or coated limestone with an industrial vacuum and subsequent limestone replacement. Therefore, what was lost in alkalinity generation by this design may have been replaced by long term gains involving precipitate removal and limestone recharging.

The dissolution of limestone within the wetland system contributed to the generation of alkalinity and neutralization of $\approx$42 metric tons of acidity per year. An estimate of the systems longevity, based upon exhaustion of the organic compost, is difficult to determine because many factors contribute to its saturation (Wieder 1993). However, a budget of the acidity consumed by limestone dissolution can be created to estimate the systems life expectancy. Approximately 320 metric tons of limestone were placed within the wetland system at Jones Branch. At 80% purity, the limestone can theoretically neutralize 42 metric tons of acidity per year for 6.07 years. Thus, based on the optimal conditions for dissolution, limestone would need to be replaced in the wetland substrate and in the ALDs after six years of operation.

Conclusions

Analytical results from post-renovation water quality monitoring have been very encouraging. Mean iron concentrations decreased from 787 to 37 mg l^{-1}, pH increased from 3.38 to 6.46 and acidity was reduced from 2244 to 119 mg $CaCO_3$ l^{-1}. Renovation has resulted in the retention of 98% Al, 95% Fe, 94% acidity, 56% SO_4^{2-}, and 48% Mn within the wetland. Mass loading data indicate that 18.7 metric tons of iron were retained and 53.1 metric tons of acidity were neutralized by the system during the post renovation period. Monthly performance data revealed changes in water quality after renovation and indicated consistency in treatment efficiency. A considerable amount of alkalinity from limestone dissolution was generated within the wetland substrate and metal carbonates were formed. Although bacterially mediated sulfate reduction was not evident within the system, sulfate removal was achieved through gypsum precipitation. Increased oxygen demand by the organic substrate, however, maintained reducing conditions so that armoring of the limestone could be prevented. The combination of technologies utilized in the renovation and the sequence in which they were implemented within the wetland proved to be efficient for treatment of high-metal-load AMD and exceeded the design criteria of any one technology alone. In addition, utilization of the designed subsurface flow system increased residence time, thus lowering the recommended sizing requirements for AMD treatment wetlands. Even though the system is still immature, the results suggest that the design may be suitable for AMD sites that are restricted by topography or available surface area and deemed inappropriate for treatment using constructed wetlands. With continued monitoring, information shall be accumulated to evaluate the long-term usefulness of this treatment approach.

References

Allison JD, Brown DS, Novo-Gradac KJ (1990) MINTEQA2/PRODEFA2, a geochemical assessment model for environmental systems: Version 3.0 user's manual. Athens, GA: Environ Res Lab, USEPA

APHA (American Public Health Association, 1989) Standard methods for the examination of water and wastewater, 17th edn. APHA, Washington, DC, pp 3-1–4-110

Barton CD, Karathanasis AD (1998) Aerobic and anaerobic metal attenuation processes in a constructed wetland treating acid mine drainage. Environ Geosci 5:43–56

Bohn HL (1971) Redox potentials. Soil Sci 112:39–45

Brodie GA (1990) Treatment of acid drainage using constructed wetlands, experiences of the Tennessee Valley Authority. In: Graves DH (ed) Proc of the Nat Symp on Mining. OES Publications, Lexington, KY, pp 77–83

Brodie GA, Britt CR, Tomaxzewski TM, Taylor HN (1993) Anoxic limestone drains to enhance performance of aerobic acid drainage treatment wetlands: experiences of the Tennessee Valley Authority. In: Moshiri GA (ed) Constructed wetlands for water quality improvement. Lewis Publishers, Boca Raton, FL, pp 129–145

Burdige DJ, Dhakar SP, Nealson KH (1992) Effects of manganese oxide mineralogy on microbial and chemical manganese reduction. Geomicrobiol J 10:27–48

Chalfant GR (1993) A constructed wetland for treatment of acid mine drainage. United States Department of Agriculture, Forest Service, Winchester, KY, Daniel Boone National Forest, pp 1–23

Dietz JM, Stidinger DM (1996) Acid mine drainage abatement in an anaerobic subsurface flow wetland environment: case history of the treatment system at Corsica, PA. In: Daniels WL, Burger JA, Zipper CE (eds) Proc of the 13th Am Soc for Surface Mining and Reclamation Conference, Knoxville, TN. Virginia Tech Res Div, Blacksburg, VA, pp 531–540

Evangelou VP (1995) Pyrite oxidation and its control. CRC Press, Boca Raton

Faulkner BB, Skousen JG (1994) Treatment of acid mine drainage by passive treatment systems. In: Proc of the International Land Reclamation and Mine Drainage Conference. Pittsburgh, PA, USDI, Bureau of Mines, SP 06B-94, pp 250–257

Fennessy M.J, Mitsch WJ (1989) Design and use of wetlands for renovation of drainage from coal mines. In: Mitsch WJ, Jørgensen SE (eds) Ecological engineering. J. Wiley, New York, pp 231–253

Ferris FG, Tazaki K, Fyfe WS (1989) Iron oxides in acid mine drainage environments and their association with bacteria. Chem Geol 74:321–330

Hedin RS, Watzlaf GR (1994) The effects of anoxic limestone drains on mine water chemistry. In: Proc of the International Land Reclamation and Mine Drainage Conference. Pittsburgh, PA, USDI, Bureau of Mines, SP 06A-94, pp 185–194

Hedin RS, Watzlaf GR, Nairn RW (1994) Passive treatment of acid mine drainage with limestone. J Environ Qual 23:1338–1345

Hellier WW (1996) The Bark Camp Run Demonstration constructed wetlands: findings and recommendation for future design criteria. In: Daniels WL, Burger JA, Zipper CE (eds) Proc of the 13th Am Soc for Surface Mining and Reclamation Conference, Knoxville, TN. Virginia Tech Research Div, Blacksburg, VA, pp 550–559

Henrot J, Wieder RK (1990) Processes of iron and manganese retention in laboratory peat microcosms subjected to acid mine drainage. J Environ Qual 19:312–320

Hilton BL, Oleszkiewicz JA (1988) Sulfide induced inhibition of anaerobic digestion. J Environ Eng Am Soc Civ Eng 114:1377–1385

Kadlec RH, Knight RL (1996) Treatment wetlands. CRC Press, Boca Raton

Karathanasis AD, Thompson YL (1995) Mineralogy of iron precipitates in a constructed acid mine drainage wetland. Soil Sci. Am. J. 54:1773–1781

Kepler DA, McCleary EC (1994) Successive alkalinity-producing systems (SAPS) for the treatment of acid mine drainage. In: Proc of the International Land Reclamation and Mine Drainage Conference. Pittsburgh, PA, USDI, Bureau of Mines, SP 06A-94, pp 195–204

Kleinmann RLP (1989) Acid mine drainage: US Bureau of Mines researches and develops control methods for both coal and metal mines. Engineering and Mining Journal, July 1989

Kleinmann RLP, Edenborn H Hedin RS (1991) Biological treatment of mine water - an overview. In: Proc of the Second Int Conference on the Abatement of Acidic Drainage. MEND, Montreal, Canada, pp 27–42

Lazaroff N, Melanson L, Lewis E, Santoro N, Pueschel C (1985) Scanning electron microscopy and infrared spectroscopy of iron sediments formed by Thiobacillus ferrooxidans. Geomicrobiol J 4:231–267

Lindsay WL (1979) Chemical equilibria in soils. J. Wiley, New York

McIntire PE, Edenborn HM (1990) The use of bacterial sulfate reduction in the treatment of drainage from coal mines. In: Procof the West Virginia Mining and Reclamation Conference. West Virginia University, Morgantown, WV, pp 409–415

Nairn RW, Hedin RS, Watzlaf CR (1992) Generation of alkalinity in an anoxic limestone drain. In: Proc of the American Society for Surface Mining and Reclamation Conference. ASSMR, Duluth, MN, pp 206–219

Postgate JR (1984) The sulfate reducing bacteria, 2nd edn. Cambridge Univ Pr, Cambridge

Schwertmann U, Taylor RM (1989) Iron oxides. In: Dixon JB, Weed SB (eds) Minerals in soil environments, 2nd ed. (SSSA Book Ser 1) SSSA, Madison, WI, pp 379–438

Sikora FJ, Behrends LL, Brodie GA, Bulls MJ (1996) Manganese and trace metal removal in successive anaerobic and aerobic wetlands. In: Daniels WL, Burger JA, Zipper CE (eds) Proc of the 13th Am.Soc. for Surface Mining and Reclamation Conference, Knoxville, TN. Virginia Tech Research Div, Blacksburg, VA, pp 560–579

Skousen J (1991) Anoxic limestone drains for acid mine drainage treatment. Green Lands 21:30–35

Stumm W, Morgan JJ (1981) Aquatic chemistry, 2nd ed. J. Wiley, New York

Turner D, McCoy D (1990) Anoxic alkaline drain treatment system, a low cost acid mine drainage treatment alternative. In: Graves DH (ed) Proc of the Nat Symp on Mining. OES Publications, Lexington, KY, pp 73–75

US Environmental Protection Agency (1983) Neutralization of acid mine drainage, design manual. Cincinnati, OH, USEPA-600/2–83–001

Welton JE (1984) SEM petrology atlas. Am Assoc Petrol Geol, Tulsa

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

Wieder RK (1993) Ion input/output budgets for wetlands constructed for acid coal mine drainage treatment. Water Air Soil Poll 71:231–270

Wildeman TR, Updegraff DM, Reynolds JS, Bolis JL (1994) Passive bioremediation of metals from water using reactors or constructed wetlands. In: Means JL and Hinchee RE (eds) Emerging technology for bioremediation of metals. Lewis Publishers, Boca Raton, pp 141–148