Geochemical modeling of coal mine drainage, Summit County, Ohio

A. Foos

Abstract Geochemical modeling was used to investigate downstream changes in coal mine drainage at Silver Creek Metro-park, Summit County, Ohio. A simple mixing model identified the components that are undergoing conservative transport (Cl^-, PO_4^{3-}, Ca^{2+}, K^+, Mg^{2+} and Na^+) and those undergoing reactive transport (DO, HCO_3^-, SO_4^{2-}, Fe^{2+}, Mn^{2+} and Si). Fe^{2+} is removed by precipitation of amorphous iron-hydroxide. Mn^{2+} are removed along with Fe^{2+} by adsorption onto surfaces of iron-hydroxides. DO increases downstream due to absorption from the atmosphere. The HCO_3^- concentration increases downstream as a result of oxidation of organic material. The rate of Fe^{2+} removal from the mine drainage was estimated from the linear relationship between Fe^{+2} concentration and downstream distance to be 0.126 mg/s. Results of this study can be used to improve the design of aerobic wetlands used to treat acid mine drainage.

Key words Acid mine drainage · Iron-hydroxide · Wetlands

Introduction

One of the most serious problems associated with coal mining is the generation of acid mine drainage (AMD). Coal mining operations expose sulfur-bearing minerals such as pyrite (FeS_2) to oxygen and water resulting in a series of oxidation and hydrolysis reactions which produce sulfuric acid. These reactions are catalyzed by bacteria, particularly *Thiobacillus ferrooxidans* (Wildeman 1991). AMD typically has pH values as low as 2 and high concentrations of SO_4^{2-}, Fe^{2+}, Al^{3+}, and Mn^{2+}. The high acid and metal concentrations are toxic to aquatic life, wildlife and vegetation. The ocherous precipitate "yellowboy" also associated with AMD adversely affects the visual aesthetics of the environment (Michaud 1995). In addition to the reclamation needs of current coal mining operations, the United States is burdened with hundreds of abandoned sites which require remediation. Passive remediation systems such as anoxic limestone drains and constructed wetlands are increasingly being investigated as possible solutions to the AMD problem. This study focuses on the chemical processes occurring in mine drainage flowing through an oxic environment. The results of this study can be used to better improve the design of aerobic wetlands for the remediation of AMD.

Received: 4 June 1996 · Accepted: 17 September 1996

A. Foos
University of Akron, Geology Department,
Akron OH 44325–4101, USA
e-mail: afoos@uakron.edu

Study area

The study area was located in Silver Creek Metro-park, in southwestern Summit County, Ohio (Fig. 1). The area is dotted with a number of abandoned underground coal mines which date back to the turn of the century. Silver Creek lake is an artificially created lake used for recreational purposes. When the dam was built, discharge from an abandoned coal mine was diverted under the lake to flow out past the dam and channelized for a distance of over 150 m. Samples of this abandoned mine drainage were collected at the point of discharge and at 15.4 m intervals downstream. One sample was collected from the spillway which drains the lake, this sample being representative of the lake composition. A sample was also collected downstream from where the mine discharge and the lake discharge intersect (Fig. 2).

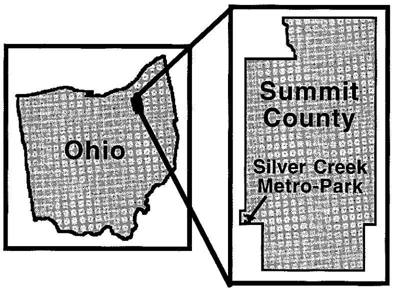

Fig. 1
Location of Silver Creek Metro-park

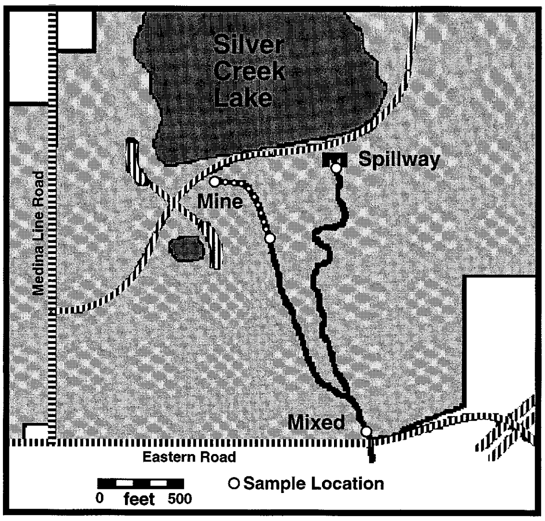

Fig. 2
Sample collection sites at Silver Creek Metro-park

The geology of the area is characterized by approximately 6 m of Pleistocene glacial deposits overlying Pennsylvanian age bedrock (Schmidt 1979). The Pleistocene deposits consist of the highly calcareous Hayesville Till plus undifferentiated outwash and lacustrine deposits (White 1984). The Sharon No. 1 Coal, which was mined in the area, is characteristically a low sulfur coal.

Analytical methods

Hydrologic parameters were measured along the mine discharge stream and the lake spillway stream. The average stream velocity was estimated by multiplying the surface velocity by a correction factor (0.85). Cross-sectional area multiplied by velocity was used to estimate the discharge.

Unless otherwise stated, standard methods recommended by the American Public Health Association (Greenberg and others 1992) and US Geological Survey (Skougstad and others 1979) were followed for sample handling, holding times, reagent purity and analytical procedures. Temperature, pH, conductivity and dissolved oxygen (DO) were measured on site. Total alkalinity and HCO_3^- were determined by titration on an untreated sample. Filtered, unacidified samples were used for determination of major anions (Cl^- and SO_4^{2-}) by ion chromatography. Metal concentrations were measured on filtered, acidified samples using inductively coupled plasma spectroscopy (Al, Ca, Fe, Mg, Mn, P and Si) and atomic absorption (K and Na). The computer program WATEQ4F (Ball and Nordstrom 1987) was used to calculate ionic speciation and saturation indexes (SI) of mineral phases.

Two samples of the yellowboy were collected for mineralogical and chemical analysis. Amorphous iron-hydroxide phases were dissolved using the ammonium oxalate extraction procedure of Schwertmann (1964). Crystalline iron-oxide and iron-hydroxide phases were dissolved using the Na citrate-dithionite procedure (Mehra and Jackson 1960). The resultant solutions were analyzed for Fe and Mn using atomic absorption spectroscopy. Samples were X-rayed with CuK-alpha radiation before and after the ammonium oxalate extraction.

Results

Water flowing from the abandoned mine was very clear and had a constant temperature of 11.5 °C. Discharge from the spillway had a more variable temperature which reflected the current air temperature and the water was more cloudy. The hydrologic properties of the two streams are given in Table 1.

The chemical composition data for the mine discharge, water from Silver Creek lake and the mixed sample are presented in Table 2. The coal mine drainage has a relatively low pH (6.4) and DO concentration (4.5 mg/l), and high Fe^{2+} (16.7 mg/l), Mn^{2+} (4.9 mg/l), SO_4^{2-} (159.1 mg/l) and Si (6.2 mg/l) concentrations relative to water from

Table 1
Hydrologic parameters of the mine discharge and spillway stream at Silver Creek Metro-park

	Mine	Spillway
Velocity (m/s)	0.213	0.399
Cross-sectional area (cm^2)	1205	776
Discharge (m^3/s)	0.0257	0.0263
Mixing factor	0.494	0.506

Table 2
The chemical composition of the mine discharge, water from Silver Creek Lake and a mixed sample from these two sources (concentrations in mg/l); *DO* dissolved oxygen, *T* °C, *Cond.* μmhos/cm)

	Mine	Lake	Mixed
pH	6.38	7.80	7.65
DO	4.48	4.96	5.78
T	11.3	20.8	16.6
Cond.	444	413	445
HCO_3	40.8	125.6	98.0
Cl	62.7	63.0	61.7
SO_4	159.1	58.3	94.2
PO_4	2.73	2.57	2.72
Ca	50.19	44.57	48.87
Fe	16.67	0.19	0.44
K	4.3	4.2	3.9
Mg	22.75	15.43	18.61
Mn	4.90	0.18	1.79
Na	20.2	33.1	28.5
Si	6.22	4.03	4.61

the lake. Aluminum concentrations were at, or below, the detection limit (0.01 mg/l) of the ICP. These values are not bad compared to other coal mine drainage in Ohio which have an average pH of 4.8 and orders of magnitude more Fe^{2+} (806 mg/l), SO_4^{2+} (3936 mg/l), and Si (14 mg/l) (Winland and others 1991). There are two possible reasons for this; first, the Sharon Coal which was mined in this area is a low sulfur coal, and second, the glacial drift is carbonate rich, which could be buffering the system. The piper diagram (Fig. 3) shows that the values of the mixed sample are between the mine discharge and lake water. The mine discharge has higher total dissolved solids (TDS) than the lake with the mixed sample intermediate between the two. The lake is enriched in both HCO_3^- and Na + K, relative to the mine drainage.

Simple mixing model

A hypothesis that the composition of the mixed sample represents mixing of the mine and lake waters, or simple dilution of the mine drainage with water from the lake, was tested with a simple mixing model. The estimated discharge was used to calculate a mixing factor for each stream (Table 1). The mixing factor is the discharge of one stream divided by the sum of the discharge of the two streams. The concentration of each component was multiplied by the mixing factor for each stream and the two values were summed to get the modeled, mixed composition. The percent error is the difference between the measured and modeled composition divided by the measured composition times 100. The results of this model are presented in Table 3. For Cl^-, PO_4^-, Ca^{2+}, K, Mg^{2+} and Na^+ the modeled composition was within 10% of the measured composition. However, for DO, HCO_3^-, SO_4^{2-}, Fe^{2+}, Mn^{2+} and Si the difference between modeled and measured concentrations was greater than 10% with the greatest difference for Fe^{2+} and Mn^{2+}.

The simple mixing model predicted the concentrations of Cl^-, PO_4^{-3}, Ca, K, Mg and Na to within 10%. These components are undergoing conservative transport, and not reacting with their surroundings. They are neither entering or leaving the system.

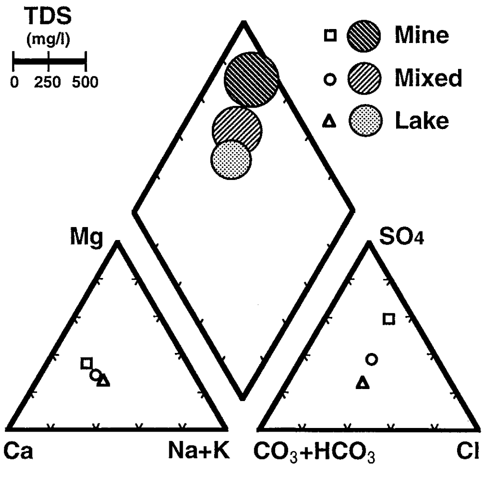

Fig. 3
Piper diagram comparing the mine discharge to water from Silver Creek lake and a mixed sample from these two sources

Table 3
Comparison of the measured and modeled composition of the mixed sample at Silver Creek Metro-park

	Measured	Modeled	% Error
pH	7.65	7.10	7
DO	5.78	4.72	18
T	16.6	15.7	5
Cond.	445	428	4
HCO_3	98.0	84.0	14
Cl	61.7	62.9	− 2
SO_4	94.2	107.7	− 14
PO_4	2.72	2.65	3
Ca	48.87	47.33	3
Fe	0.44	8.27	−1800
K	3.9	4.25	− 9
Mg	18.61	19.02	− 2
Mn	1.79	2.49	− 39
Na	28.5	26.78	6
Si	4.61	5.10	− 11

The concentrations of DO, HCO_3^-, SO_4^{2-}, Fe^{2+}, Mn^{2+} and Si were not adequately predicted with the simple mixing model indicating these components are undergoing reactive transport. They are either being added to, or removed from, the system. For DO and HCO_3^- the modeled composition is lower than the measured concentration; they have a positive error which indicates they are being added to the system. The model overestimated the concentration of SO_4^{2-}, Fe^{2+}, Mn^{2+} and Si which indicates that these components are being removed from the system.

Even though this simple mixing model did not adequately predict the composition of the mixed sample, it did tell us quite a bit about the system. It identified the components that are undergoing conservative transport and those undergoing reactive transport. The model also identified components that are being added to the system and ones that are being removed from the system.

Chemical changes downstream

In order to understand the chemical processes occurring along the mine drainage, high resolution sampling at 15.4 m intervals along the stream was conducted (Fig. 4). The concentration of the components undergoing conservative transport (Cl^-, PO_4^{3-}, Ca^{2+}, K^+, Mg^{2+} and Na^+) did not change downstream. Of the components undergoing reactive transport, DO and HCO_3^- increased downstream, Fe^{2+}, Mn^{2+} and Si decreased downstream.

The concentration of Fe^{2+} decreased from 17 to 13 mg/l over the distance of 152 m. There was an excellent correlation ($r = 0.93$) and a linear relationship between distance and Fe^{2+} concentration. Iron precipitation on the bed of the stream was observed as a yellowish-red (7.5YR 5/8) precipitate, commonly known as yellowboy. There were two types of precipitates, a very fine sediment of flocculated iron-hydroxide and clay, and a coating on

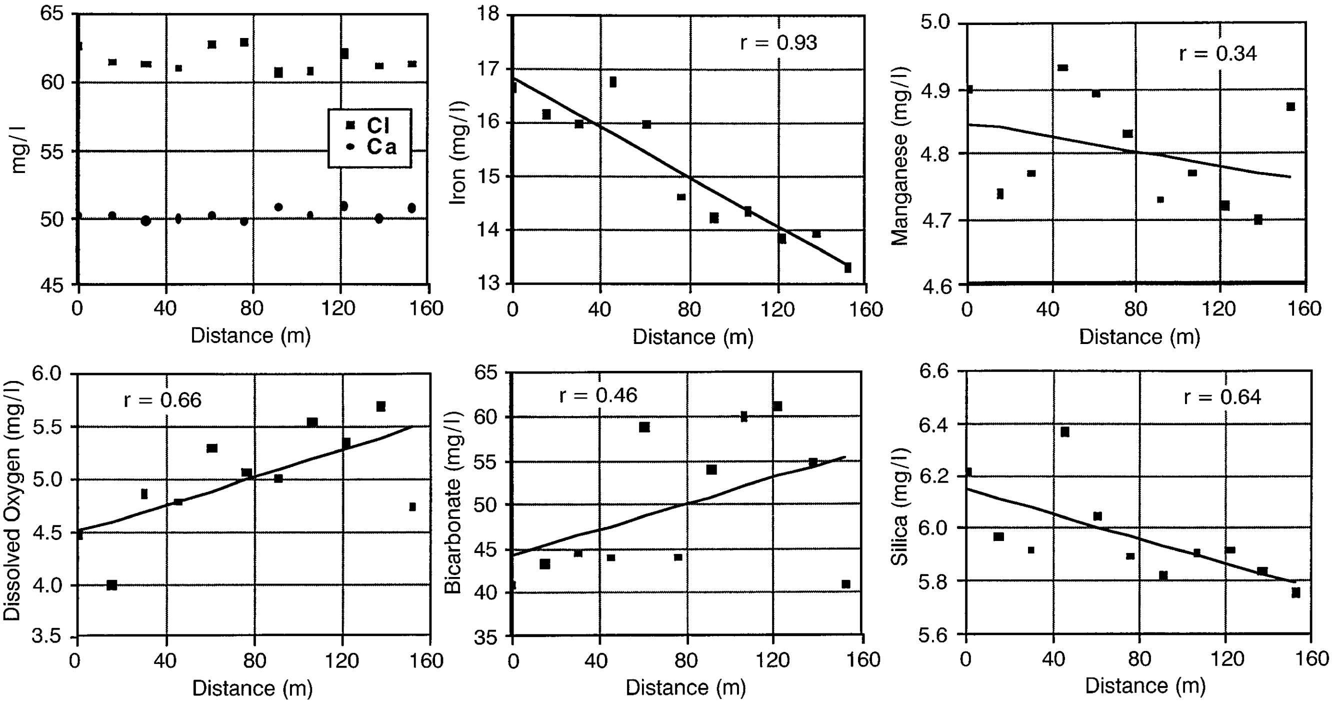

Fig. 4

Concentration versus downstream distance of selected components of coal mine discharge at Silver Creek Metro-park

pebbles, which in some places formed a hard, continuous crust on the stream bed. The major iron-oxide and iron-hydroxide phases are all supersaturated with respect to the stream discharge (Table 4). Ferrihydrite, the amorphous phase, is the most likely precipitate from the mine drainage. Its SI ranged from 0.4 to 1.4, and there was no relationship between SI and downstream distance. X-ray diffraction analysis of the iron-rich fine sediment and coatings indicated that there was a lack of crystalline iron-oxide or iron-hydroxide phases. Selective dissolution was used to further characterize the precipitate. The ammonium oxalate extraction (Fe_o) only dissolves the amorphous phases, whereas the citrate-dithionite extraction (Fe_d) dissolves both amorphous and crystalline iron-oxide and iron-hydroxide phases. Results of selective dissolutions of these two samples are given in Table 5. The Fe_o/Fe_d ratios of 0.83 and 0.87 indicate that over 80% of the precipitate is amorphous.

Manganese decreased with distance downstream, however the correlation coefficient ($r = 0.34$) is poor. The WATEQ4F analysis indicated that the manganese-oxides, manganese-hydroxides and manganese-carbonates were all undersaturated with respect to these waters (Table 4), so it is unlikely that Mn^{2+} is being removed by precipitation of these minerals. There is a fair correlation ($r = 0.51$) between Mn^{2+} and Fe^{2+} (Fig. 5). Most likely Mn^{2+} is being removed along with the Fe^{2+}. It is either substituting for Fe in the iron-hydroxides or is being adsorbed onto the surfaces of the iron-hydroxides. These observations are consistent with thermodynamic studies which indicate that Mn^{2+} is readily adsorbed onto the surfaces of freshly precipitated ferric oxyhydroxides at near neutral pH, however, a pH greater than 8.5 is necessary for oxidation and precipitation of Mn-hydroxide (Klusman and Machemer 1991). The amorphous iron-hydroxide precipitate contains a high concentration of Mn (Table 5). The average Mn/Fe ratio of the precipitate (0.04) is almost an order of magnitude lower that the average Mn/Fe ratio of the water (0.32), suggesting that the rate of Mn^{2+} removal is much lower than the rate of Fe^{2+} removal.

DO concentration increases with downstream distance, ranging from 4.0 to 5.7 mg/l. The DO saturation with respect to the atmosphere, calculated from barometric pressure (981 mbar) and water temperature (11.5 °C), is

Table 4

Average saturation index (*SI*) of selected phases calculated using WATEQ4F. $SI = \log IAP/K_T$, where IAP is the ion activity product and K_T is the equilibrium constant at 11.5 °C

Phase	Formula	SI
Hematite	Fe_2O_3	14.93
Goethite	FeOOH	6.96
Ferrihydrite	$Fe(OH)_3$	1.07
Pyrolusite	MnO_2	−14.27
Manganite	MnOOH	− 6.44
Rhodochrosite	$MnCO_3$	− 1.17
Quartz	SiO_2	0.53
Chalcedony	SiO_2	0.06
SiO_2(a)	SiO_2	− 0.83
Aragonite	$CaCO_3$	− 2.09
Calcite	$CaCO_3$	− 1.94
Dolomite	$CaMg(CO_3)_2$	− 4.61

Table 5
Results of selective dissolution analysis (Fe_0 and Mn_0 ammonium oxalate extraction, Fe_d sodium citrate-dithionite extraction)

	Crust	Sediment
Fe_0	195	35
Fe_d	233	40
Mn_0	8.9	0.98
Fe_0/Fe_d	0.83	0.87
Mn/Fe	0.046	0.028

10.5 mg/l. Therefore, the mine discharge is undersaturated in DO with respect to the atmosphere. The increase in DO is most likely due to absorption from the atmosphere.

Even though the correlation is poor ($r = 0.46$), there is a definite increase in HCO_3^- concentration downstream, with a jump in the concentration at approximately 60 m. There are three possible sources for carbonate ions in this system: absorption from the atmosphere, dissolution of carbonate minerals and oxidation of organic matter. The concentration of HCO_3^- in equilibrium with the atmosphere at an average temperature of 11.5 °C is governed by the following chemical reactions:

$$H_2CO_3 = CO_2 + H_2O \quad \log K_{11.5} = -37.97 \qquad (1)$$

$$H_2CO_3 = HCO_3^{-} - + H^{+} \quad \log K_{11.5} = -6.67 \qquad (2)$$

With atmospheric $\log[CO_2]$ equal to -3.52, the $\log [H_2CO_3]$ in equilibrium with the atmosphere can be calculated from the equilibrium expression for Eq. 1 to be -5.10. Substituting the $[H_2CO_3]$ concentration and an average pH of 6.4 into the equilibrium expression for Eq. 2 yields the HCO_3^- concentration, ($\log[HCO_3^-] = -5.37$). The average $\log[HCO_3^-]$ of -3.15 for the mine drainage is greater than the equilibrium $[HCO_3^-]$ indicating that these waters are supersaturated in HCO_3^- with respect to the atmosphere and it is unlikely that carbonate is being added from this source.

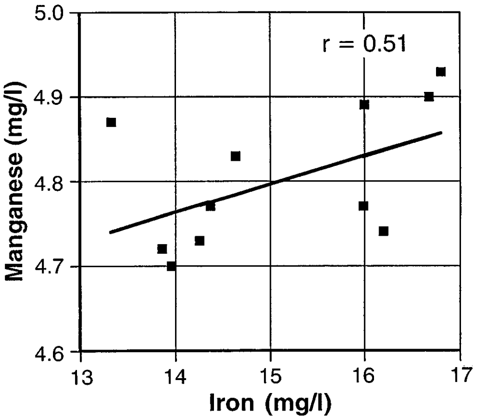

Fig. 5
Mn^{2+} versus Fe^{2+} concentrations of coal mine discharge at Silver Creek Metro-park

The second possible source of carbonate ions is dissolution of carbonate minerals. The WATEQ4F analysis indicates that the major carbonate minerals are all undersaturated (Table 4) with respect to these waters, so this is a very likely source of carbonate ions. However, Ca^{2+} and Mg^{2+} concentrations remain constant downstream and they would be expected to increase if calcite or dolomite were being dissolved.

The third possible source of carbonate ions is oxidation of organic matter. In this case, HCO_3^- concentrations would depend on the amount of plant material that is introduced to the stream, and this is most consistent with the nonlinear increase in HCO_3^-. At a distance of 60 m downstream, where the HCO_3^- concentrations increased, the stream flowed from an area of mowed lawn into a wooded area of dense vegetation where there was an increase in the input of organic matter into the stream.

Silica decreases with downstream distance. The WATEQ4F analysis indicates that the waters are near equilibrium with the silica phases (Table 4), so it is possible that one of these phases is precipitating from the mine discharge.

There was no relationship between measured SO_4^{2-} concentration and downstream distance. There was a faint “rotten egg” smell at the site which could suggest the presence of H_2S in the mine discharge. No attempt was made to preserve the H_2S or analyze for total sulfur which could account for the lack of a relationship between SO_4^{2-} and downstream distance.

Rate of Fe^{2+} removal

The linear relationship between Fe^{2+} concentration and downstream distance was used to estimate the rate of Fe^{2+} removal from the system. The best fit line from Fig. 4 relates the concentration of Fe^{2+} to distance in meters.

$$(Fe) = (-0.023)\,m + 16.65 \qquad (3)$$

Multiplying the slope of this line by the stream velocity (0.213 m/s) yields the change in Fe^{2+} concentration with respect to time ($dC/dt = 0.0049$ mg/l per s). The change in Fe^{2+} concentration with respect to time multiplied by the discharge (0.0257 m^3/s) gives the rate of Fe^{2+} removal which is 0.126 mg/s. For a steady state model the first order removal of Fe^{2+} can be expressed by the following equation:

$$V \cdot dC/dx - kC = 0 \qquad (4)$$

where V is the velocity in m/s, C is the concentration in mg/l, x is the distance in m, k is the first order rate constant for net Fe^{2+} removal. Solving this equation for k yields a rate constant of 2.9×10^{-4}. This value is similar to the rates observed by Kimball and others (1994) of 1×10^{-2} to $5 \times 10^{-5}$for mine drainage from St. Kevin Gulch near Leadville, Colorado.

Discussion and conclusions

Through a combination of iron-hydroxide precipitation and dilution, waters from the abandoned mine at Silver Creek Metro-park were shown to be within the effluent limits for mine drainage (3.5 and 2.0 mg/l for Fe and Mn respectively, US EPA 1982) when they leave the site.
The mine discharge at Silver Creek Metro-park naturally contains sufficient alkalinity to neutralize the acidity associated with dissolved iron and manganese. These waters have chemical characteristics similar to the effluent of anoxic limestone drains (ALD), low DO, high Fe^{2+} and Mn^{2+}, and near neutral pH. Limestone is frequently added to mine discharge to increase the alkalinity and neutralize the acidity. In an oxic environment precipitation of iron-hydroxides on limestone surfaces armors the limestone lowering its effectiveness. ALDs are designed to eliminate this problem by preventing the precipitation of iron-hydroxides. Discharge from ALDs has sufficient alkalinity to neutralize the acidity, however, it still has high concentrations of dissolved metals (Hedin and others 1994). For a comprehensive remediation system ALDs are coupled with wetlands which are designed to remove metals from the discharge. The dominant processes occurring along the mine drainage at Silver Creek Metro-Park are absorption of oxygen from the atmosphere, oxidation of Fe^{2+} to Fe^{3+} followed by precipitation of amorphous iron-hydroxides. The rates of these processes are most likely controlled by the rate of oxygen absorption from the atmosphere. In pilot scale treatments of synthetic AMD, Hustwit and others (1992) found that at near neutral pH, the rate-limiting step in the oxidation of Fe^{2+} is the oxygen transfer rate. Aerobic wetlands should be designed to maximize the absorption of oxygen from the atmosphere, possibly by increasing the water turbulence and the surface area to depth ratio.

Acknowledgements The data presented in this study were collected by the fall 1995 geochemistry class at the University of Akron as part of an NSF DUE-ILI project. I. Sasowsky supervised the collection of hydrologic data and T. Quick assisted in the water analysis.

References

Ball JB, Nordstrom DK (1987) WATEQ4F - a personal computer FORTRAN translation of the geochemical model WATEQ2 with revised database. U.S. Geological Survey, Open File Report 87–50, Menlo Park, Calif.

Greenberg AE, Clescerl LS, Eaton AD (eds) (1992) Standard methods for the examination of water and wastewater. American Public Health Association, Washington, DC.

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

Hustwit CC, Ackman TE, Erickson PE (1992) The role of oxygen transfer in acid mine drainage (AMD) treatment. Water Environ Res 64:817–823

Kimball BA, Broshears RE, Bencala KE, McKnight DM (1994) Coupling of hydrologic transport and chemical reactions in a stream affected by acid mine drainage. Environ Sci Technol 28:2065–2073

Klusman RW, Machemer SD (1991) Review of processes operating in constructed wetlands to attenuate acid mine drainage. In: Mallard GE, Aronson DA (eds) U.S. Geological Survey Toxic Substances Hydrology Program–Proceedings of the technical meeting, Monterey, Calif, 11–15 March, 1991. US Geological Survey Water-Resources Investigations Report 91–4034, Reston Va, pp 513–540

Mehra OP, Jackson ML (1960) Iron oxide removal from soils and clays by a dithionite-citrate system buffered with sodium bicarbonate. In: Clay and Clay Minerals Proc 7th Conf. Washington DC, Natl Acad Sci-Natl Res Council Publ, pp 317–327

Michaud LH (1995) Recent technology related to the treatment of acid drainage. Earth Miner Sci 63:53–55

Schmidt JJ (1979) Ground-water resources of Summit County. Ohio Department of Natural Resources, Division of Water, Columbus Ohio

Schwertmann U (1964) Differenzierung der Eisenoxide des Bodens durch photochemische Extraktion mit saurer Ammoniumoxalat-Lösung. Z. Pflanzenernaehr Bodenkd 105:194–202

Skougstad MW, Fishman MJ, Friedman LC, Erdmann DE, Duncan SC (1979) Methods for determination of inorganic substances in water and fluvial sediments. TWRI, Book 5, Chapter A1. U.S. Geological Survey, Washington, DC

U.S. Environmental Protection Agency (1982) Development document for effluent limitation guidelines and standards for coal mining. Document No. EPA 440/1–82/057, Washington, DC

White GW (1984) Glacial geology of Summit County, Ohio. Report of Investigations No. 123, Ohio Department of Natural Resources, Columbus OH

Wildeman T (1991) Drainage from coal mines: chemistry and environmental problems In: Mallard GE, Aronson DA (eds) U.S. Geological Survey Toxic Substances Hydrology Program–Proceedings of the technical meeting, Monterey, Calif, 11–15 March, 1991. U.S. Geological Survey Water-Resources Investigations Report 91–4034, Reston, Va, pp 499–510

Winland RL, Traina SJ, Bigham JM (1991) Chemical composition of ocherous precipitates from Ohio coal mine drainage. J Environ Qual 20:452–460