MODELING OF WETLANDS AND REACTOR SYSTEMS USED

FOR MINE DRAINAGE TREATMENT[1]

by

R.W. Klusman,[2] D.H. Dvorak[3], and S.L. Borek[3]

Abstract. A computer code, MINTEQAK, has been developed to model the composition of an acid drainage as it flows through wetland/reactor systems. The code was developed under U.S. Bureau of Mines sponsorship from the previous code MINTEQA2, which is distributed by EPA. The MINTEQAK code models the change of aqueous composition, and the precipitation of solids by a pseudo-kinetic method. Both geochemical and biogeochemical processes can be modeled simultaneously during flow through an anaerobic wetland/reactor in series with an aerobic wetland. The application of this code to anaerobic wetlands and reactors is described. The wetlands at French Coulee, MT, Friendship Hill, PA, Somerset, PA, and the reactors at Pittsburgh and Palmerton, PA are modeled. The results are used to understand the processes occurring in each system. These results also demonstrate the power of modeling in suggesting processes which may be occurring in such systems, and the rates of these processes.

[2] Professor of Chemistry and Geochemistry and Professor of Environmental Science and Engineering, Colorado School of Mines, Golden, CO 80401.

[3] U.S. Bureau of Mines, Pittsburgh Research Center, Pittsburgh, PA 15236

Introduction

Treatment of mine drainage by wetlands to remove metals and neutralize acidity was initiated in the 1980s. This passive mode of treatment attracted attention because of its potential for low-cost, long-term treatment, especially at the large numbers of abandoned mining sites throughout the United States. Treatment of acidic waters at active mines and power stations was initiated by the TVA in the southeastern U.S. because of the low-maintenance, low-cost potential. Observation of improvement in water quality when drainage from coal mines passed through natural wetlands was described by Wieder and Lang (1982) for a wetland in West Virginia. More quantitative studies of acidity reduction and metal removal in

natural wetlands were described by Wieder and Lang (1982), Wieder (1985), and Wieder and Lang (1986). Modification of existing wetlands or construction of wetlands for the treatment of coal mine drainage was described for early systems by Kleinmann et al. (1983;1985) and Brodie et al. (1986;1987). Kleinmann et al. (1985) described the difficulty of removing manganese from mine waters, but recognized the potential for wetlands in treating relatively small flows.

Many additional studies of experimental constructed wetlands were described in U.S. Bureau of Mines (1988) and in the international symposium proceedings edited by Hammer (1989). Girts and Kleinmann (1986) summarized performance data on approximately 20 wetlands treating coal mine drainage in the Appalachian region of the U.S. These performance data were updated by Wieder (1989) for 142 wetlands, primarily in the Appalachian region. Wieder found no identifiable relationship between wetland performance and design. It was clear from these data that there was insufficient understanding of the processes operating in a wetland to allow effective design. The construction and operation of these first generation wetlands was clearly an empirical, trial and error process.

The potential importance of microbial sulfate reduction for the reduction of acidity was described by Tuttle et al.(1969a,b) and demonstrated by Wieder and Lang (1982) (Table 1). This is an anaerobic process, requiring a complete absence of oxygen. A portion of the benefits of microbial sulfate reduction may be lost when the effluent becomes oxidized, unless the metal removal reactions have gone to near completion. If removal of iron and manganese is not complete, oxidation will produce mineral acidity, reducing pH and possibly mobilizing other metals. This has suggested to a number of researchers that the anaerobic and aerobic processes should be separated. A second generation of constructed wetlands has attempted to capitalize on enhancing the anaerobic processes with as much exclusion of aerobic processes as practical. Systems of this type have

been described by Hedin et al.(1988); Wildeman et al. (1988); Wildeman and Laudon (1989); Hedin et al. (1989); Batal et al. (1989); Nawrot (1989); McIntire and Edenborn (1990); and Wildeman et al. (1990). Wetlands with a surface exposed to the atmosphere have a thin aerobic layer on the surface and a deeper anaerobic layer. The proportion of flow through the two portions of the system is generally unknown.

Attempts have been made to optimize systems for anaerobic treatment by installing closed tank or reactor systems in place of wetlands. This modification continues to operate in a passive mode, but completely eliminates the competition of aerobic processes by enclosing the substrate in a tank, trough, or other large container. Dvorak et al. (1992) described the construction and operation of two such systems, one located in an underground coal mine in Pennsylvania and the other at a Pennsylvania smelter site. Bolis et al. (1992) used laboratory-scale reactors to evaluate metal removal by anaerobic processes for the National and Quartz Hill mine drainages in the Central City district of Colorado. Staub (1992) and Staub and Cohen (1992a,b) compared metal removal by single-stage and two-stage reactor systems in an underground zinc mine in Colorado. The results of these studies confirm the importance of the volume of an anaerobic treatment system in assessing performance.

Potential Application of Computer Modeling to Wetlands and Bioreactors

Much of the research which has been done on wetland and reactor remediation of acid drainages has been confined to measurement of influent and effluent compositions. Some of the research on the second generation anaerobic wetlands has estimated rates of microbial sulfate reduction. Actual measurement of microbial sulfate reduction rates in small containers based on sulfide generation has been done, but actual rates of sulfate reduction in larger pilot systems or constructed wetlands have not been determined. The heterogeneity in such systems

Table 1. Geochemical and biogeochemical reactions of importance in wetland and reactor systems.

REACTION	STOICHIOMETRY	SYSTEM	REFERENCE
Organic Exchange	$2RCOOH + M^{2+} \rightleftharpoons (RCOO)_2 M + 2H^+$	Anaerobic	Wieder and Lang (1986) Wieder et al. (1988; 1989, 1990) Klusman and Machemer (1991) Machemer and Wildeman (1992)
Sulfate Reduction	$SO_4^{2-} + 2"CH_2O" \rightarrow HS^- + 2HCO_3^- + H^+$	Aerobic	Herlihy and Mills (1985) Hedin et al. (1988) McIntire and Edenborn (1990) Wildeman et al. (1990) Klusman and Machemer (1991)
Sulfide Precipitation	$Fe^{2+} + HS^- \rightleftharpoons FeS + H^+$	Anaerobic	Hedin et al. (1988) McIntire and Edenborn (1990) Wildeman et al. (1990) Klusman and Machemer (1991)
Denitrification	$5"CH_2O" + 4 NO_3^- \rightarrow 4 HCO_3^- + CO_2 + 2 N_2 + 3 H_2O$	Anaerobic	Ehrlich (1990) Klusman and Machemer (1991)
Methano-genesis	$CH_3COO^- + H_2O \rightarrow HCO_3^- + CH_4$ or $CO_2 + 4 H_2 \rightarrow CH_4 + 2 H_2O$	Anaerobic	Ehrlich (1990) Klusman and Machemer (1991)
Iron Reduction	$2 Fe^{3+} + H_2 \rightarrow 2 Fe^{2+} + 2 H^+$	Anaerobic	Lovely and Phillips (1988) Lovely et al. (1989)
Carbonate Precipitation	$Mn^{2+} + HCO_3^- \rightleftharpoons MnCO_3 + H^-$	Anaerobic	Klusman and Machemer (1991)
Iron Oxidation	$4 Fe^{2+} + O_2 + 4H^- \rightarrow 4 Fe^{3+} + 2 H_2O$	Aerobic	Wildeman (1991) Klusman and Machemer (1991)
Iron Precipitation	$Fe^{3+} + 3 H_2O \rightleftharpoons Fe(OH)_3 + 3H^+$	Aerobic	Wildeman (1991) Klusman and Machemer (1991)
Manganese Oxidation	$2 Mn^{2+} + O_2 + 4 H^- \rightarrow 2 Mn^{4+} + 2 H_2O$	Aerobic	Marshall (1979) Watzlaf (1985) Klusman and Machemer (1991)
Manganese Precipitation	$Mn^{4+} + 2 H_2O \rightleftharpoons MnO_2 + 4H^+$	Aerobic	Watzlaf (1985) Klusman and Machemer (1991)
Adsorption- non electrostatic	$SOH + M \rightleftharpoons SOH\bullet M$	Both	Allison et al. (1990)
electrostatic	$SOH + M^{2+} \rightleftharpoons SO\bullet M^+ + H^+$	Both	Allison et al. (1990)
Metal Exchange	$SOH\bullet M1 + M2 \rightleftharpoons SOH\bullet M2 + M1$	Both	Allison et al. (1990)
Limestone Dissolution	$CaCO_3 + H^+ \rightleftharpoons Ca^{2+} + HCO_3^-$	Both	

will result in large temporal and spatial variability. The decrease in sulfate concentration between influent and effluent, coupled with the hydraulic residence time has been used as a surrogate measure of the overall effective sulfate reduction rate. This assumes no other operative mechanisms for removal of sulfate. A range of rates of 100-2000 micromoles of sulfate reduction /L•day can be expected based on some experimentally measured rates and effluent composition.

Other microbial reactions may be operative in a wetland or reactor, depending on the availability of suitable nutrients. These generally have not been considered significant in the overall removal process. Other inorganic processes such as precipitation of sulfide-containing minerals or carbonate minerals have been proposed. Experimental verification of a specific mineral is difficult because of amorphous character and/or the presence of the bulk substrate. Also, the rate of sulfide mineral precipitation is not readily determined. If an anaerobic wetland is operated for a long period, evidence for amorphous metal sulfides, and possible pyrite, is found.

Equilibrium geochemical modeling has been applied to understanding the chemistry of natural waters, including whether the water is in an equilibrium condition or not, degree of saturation of solid phases, and complexation of components. Application of one of these modeling codes to the equilibrium condition of a mine drainage, and to the wetland effluent does not provide much information about the processes operative in the wetland or reactor.

Much of the trial-and-error construction and testing could be eliminated if the processes hypothesized to be operative in a wetland or reactor could be modeled. Modeling will allow more rapid improvement of wetland/reactor designs. A computer model based on the system trending toward equilibrium conditions during flow through the system would offer a number of advantages in the design of a passive wetland or reactor treatment system.

There are a number of relevant reactions and processes potentially operating in a wetland or reactor system which can be modeled. Some of these reactions may be operational in anaerobic systems, and others in aerobic systems. Some of the inorganic reactions, such as dissolution, precipitation and adsorption may occur in both types of systems. Table 1 summarizes some of these reactions, the type of system where the reactions may be operational, and some references which describe the reactions. This table includes the important reactions which have been identified and a computer code should be able to simultaneously model the compatible reactions.

Computer Modeling of Processes Operating in Wetlands/Reactors

A relatively large number of computer models have been developed starting with Garrels and Thompson (1962). The number of computer models grew rapidly in the 1970s. During the 1980s the number of models did not increase, but improvements and increased capabilities were added to existing models (Bassett and Melchior, 1990). The adaptation of these increasingly complex codes from mainframes to personal computers also occurred in the 1980s.

An early code which incorporated a solution for a system containing a relatively large number of components and species was REDEQL (Morel and Morgan, 1972) which evolved into MINEQL (Westall et al. 1976). Another approach to the solution of the simultaneous equations involved in the problem was taken by the program WATEQ (Truesdell and Jones, 1973). The best features of MINEQL and later versions of WATEQ (Ball et al. 1987) were combined into MINTEQ (Allison et al. 1990). MINTEQ is a code which computes the equilibrium condition of a water, allowing for precipitation/dissolution of selected solids, and a much improved capability for modeling of adsorption and exchange processes. It does not have the capability of modeling reaction paths as originally written, nor does the later MINTEQA2 version.

PHREEQE (Parkhurst et al. 1980) can simulate several situations of which one of the most important is "path-following." In this mode, it can follow a boundary between two solid phases, dissolving or crystallizing the solids as needed. The pH and pE and the aqueous composition are calculated as the code follows the boundary. The EQ3/6 (Wolery et al. 1990) code is a combination of EQ3NR which computes the equilibrium condition of a solution, including speciation, and crystallization of supersaturated solids. The EQ6 portion of the code has the capability of modeling reaction paths. The crystallization and/or dissolution of minerals can be modeled allowing it to follow a phase boundary between two minerals in equilibrium. A more advanced modeling is to model change in composition in a "plug-flow" mode.

Requirements of a Computer Code in Terms of Modeling and Predictive Capability for a Wetlands/Bioreactor System

A computer code which can model the processes in a constructed wetland or reactor system must have a number of capabilities, not available in either PHREEQE, EQ3/6, or MINTEQ. Some of the capabilities are present in these codes, but not all. A summary of the capabilities of a modeling code for wetlands/reactors, and developed as part of this research should include:

o Computing an equilibrium condition for a mine drainage at a fixed pH and pE, and allow, or not allow precipitation of supersaturated solids as an option.
o Allow for an adjustment of pH and pE
o Change the list of allowed solids because of the possible drastic change in pH and pE.
o Change the temperature of the system.
o Increment the stoichiometric reactions represented by the geochemical and biogeochemical processes described in the Table 1. Several processes must be allowed to operate simultaneously.
o Allow for the precipitation of user-selected solids.

o Allow the flow through the wetland/reactor to be equilibrated in as many time slices as desired.
o Allow for equilibration with gaseous phases, including degassing to the atmosphere or gaseous flow into the system.
o Allow for a choice of adsorption/exchange reactions to operate.
o Drive the pH in increments to a user-selected final value.
o Allow for automatic charge balance, or not, as an option. The code should be able to automatically compensate, or to ignore imbalance.
o Allow for the user to remove selected components and associated solids from the computation while in progress in order to simulate the "complete removal" of that component in the wetland/reactor.
o At the end of the plug-flow operation of an anaerobic system, the effluent can be "treated" in an aerobic system, which is in series with the anaerobic system.
o All of the options described above must be available with a completely new set of conditions, process reactions, and rates. This allows for the modeling of an anaerobic-aerobic system constructed in series. Alternatively, the user should have the option of jumping directly to an aerobic system after the first two steps with all of the features described in subsequent steps available.
o Be able to operate the code on a personal computer without a requirement of a high powered work station or mainframe computer.

Results of Modeling Real Wetlands/Reactors Using Anaerobic Processes

During the development of this code, called MINTEQAK, a number of real wetlands and reactors were modeled. This is retrospective modeling, where hypothesized geochemical and biogeochemical reactions are occurring, with or without adsorption and exchange. The authors have experimented with different reactions, different rates, different allowed solids, and

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different adsorption models. In many cases, the experimental verification of the hypothesized processes and rates has not been done. Generally, there is inadequate experimental data collected in wetland studies to allow complete verification. The modeling does allow the user to determine what is within the realm of reality. The modeling also allows the identification of parameters in need of experimental measurement in order to gain a better understanding of the operation of constructed wetlands/reactors.

The results presented in this section were primarily obtained for purposes of developing and testing of the computer code. The results may not represent the "best" modeled solution to the problem. Most of the runs on anaerobic systems were done with an initial removal of allowed supersaturated solids, a pH/pE adjustment, followed by ten time increments through the anaerobic cell with selected rates of biogeochemical reactions. This allows the determination of the sequence of removal of regulated constituents and the changes in aqueous composition as the drainage flows through the system in a "plug-flow" model. By testing the code on a relatively large number of real wetland/reactor systems, new "bugs" in the code may appear which would subsequently allow for their correction. Other problems related to the formulation of the plan for the computer run may have to be solved by varying some of the optional parameters. Codes this complex never reach a final version, but approach it as more modeling is done for different situations by a multiplicity of users.

As experience is gained with a new code, and an inferred understanding of the geochemical and biogeochemical processes develops, forward modeling can be attempted. This is where the code is used to model the wetland/reactor processes prior to the construction of a system. Using only the acid drainage composition and flow rates, the potential performance of a hypothetical wetland/reactor can be modeled. By a series of interactive steps with design engineers, the optimum configuration can be achieved. The proposed system can be modeled at various

hypothesized rates of metal and acidity removal processes, different hydraulic loading rates, the optimum performance determined, while allowing for a margin of error. The subsequent sections briefly describe the modeling of the operation of a number of wetlands/reactors. Early research in the development of this code was described by Klusman (1991). This modeling focused on the Big Five Tunnel wetland, Idaho Springs, CO.

French Coulee Wetland, Belt, Montana

The French Coulee wetland is a large wetland constructed as three cells to treat a drainage near Belt, Montana which averages about 75 L/min. The data were obtained from John Koerth of the Reclamation Division of the Montana Department of State Lands. The first two cells operate more as a conditioning step, filtering out ferric hydroxide and chemically reducing the dissolved ferric iron, whereas the third cell is most active in treatment.

Data from the 10 September, 1991 sampling was used for the experimentation, except for calcium and magnesium. The 10 September date was a time when the effluent from Cell 3 suggested that bacterial sulfate reduction was active. The average of the 7 August and 22 August samplings were used for calcium and magnesium since these were unavailable for 10 September. An initial run determined the possible solids which are likely supersaturated, so they could be allowed to precipitate during a Step "Zero," which was assumed to be completed within Cells 1 and 2. The residence time, temperature, and influent pH for Cell 3 were 276 hr, 13.8°C, and 3.22, respectively.

Cell 3 of the French Coulee wetland was modeled at microbial sulfate reduction rates of 100 and 50 micromoles SO_4^{2-}/L•day. The calcium, magnesium, and manganese were incremented from the dissolution of limestone at a rate which would match the effluent of Cell 3, if no precipitation of solids occurred. The carbon dioxide pressure was modeled at $10^{-3.50}$ atmospheres which may allow some loss of

carbon dioxide to the atmosphere. Table 2 illustrates the composition of the mine drainage and the final results for the modeling at the two rates and the measured effluent. Table 3 shows the total amount of each "allowed solid" precipitated during the transit through Cell 3.

There are several possible conclusions suggested by the computer modeling of the French Coulee wetland. Gypsum is possibly the dominant control on major element composition through most of the wetland, but may not be the case near the effluent end. Sulfate reduction is likely the dominant biogeochemical process operating in Cell 3. There may be some removal as sulfides, though the pH of the effluent from Cell 2 is too low for microbial sulfate reduction to be operating on a significant scale. The pH of the substrate may be somewhat higher than the aqueous effluent, allowing some microbial sulfate reduction to operate. A sulfate reduction rate of 100 micromoles SO_4^{2-}/L•day effectively removes the metals by Step 8 which is 80% of the way through Cell 3. A sulfate reduction rate of 50 micromoles SO_4^{2-}/L•day fails to remove sufficient ferrous iron. If there was not bleeding of calcium and magnesium from the substrate, less gypsum would be precipitated and the final sulfate concentration may match better. Removal of gypsum and $AlOHSO_4$ from the allowed solids list may allow the modeled calcium and sulfate to increase to values closer to that of the measured effluent. The modeled aluminum concentration would likely remain low as amorphous $Al(OH)_3$ is available as an allowed solid to precipitate aluminum.

Pittsburgh Reactor, Pittsburgh, Pennsylvania

The Pittsburgh Reactor system consists of three 200 liter reactor barrels operating in series and receiving acid drainage from the Experimental Mine at the U.S. Bureau of Mines Research Center in Pittsburgh, PA (Dvorak et al. 1992). The reactor barrels are filled with mushroom compost, which is a composted mixture of various organic materials, with added limestone and gypsum. The reactor system is located underground which maintains a constant operating temperature of approximately 13°C. Dvorak et al. (1992) described some of the results from the operation of this system.

Microbial sulfate reduction was estimated by Dvorak (personal communication) to operate in the range of 100-750 micromoles SO_4^{2-}/L•day. Limestone added to the substrate was dissolving at a rate to change the influent from 328 mg Ca/L to 431 mg Ca/L in the effluent, if no calcium containing mineral is allowed to precipitate. The acidic water would be assumed to enhance dissolution of limestone because of low aqueous carbonate content. The mine drainage would be expected to increase the likelihood of gypsum precipitation, due to both dissolution of limestone and the high sulfate content of the water. All of the measured ferric iron in the influent was believed to have been reduced by organic matter to ferrous iron during the traverse through the reactor. Mine drainage influent water quality from three different dates was used in the modeling. The pore volume was assumed to be constant at 421 L and the residence time was calculated for each influent and measurement date, based on the measured flow rates. The compositions and residence times on the three dates are quite different and are modeled separately.

Table 4 shows the influent composition for the 15 April 1990 sample, the modeled effluent composition for a sulfate reduction rate of 100 micromoles SO_4^{2-}/L•day and 700 micromoles SO_4^{2-}/L•day, and the measured effluent composition. There was not a preliminary precipitation step (Step 0), but pH was adjusted to 5.00 prior to flow through the reactor. The residence time was 10.0 days and the temperature was 13.0°C.

The modeled composition suggests that the higher rate of microbial sulfate reduction is more realistic, if the final modeled metals concentrations are a guide. The discrepancy between the modeled aqueous concentration of sulfate and the measured effluent suggests that even larger amounts of gypsum may have precipitated than the modeling indicated. A

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Table 2.-Modeled and measured concentration of dissolved components in French Coulee
mine drainage (mg/L; pH in standard units).

	Mine Drainage	Cell 3 Effluent		
		Modeled		
		--SO_4^{2-} reduction rate (micromol/L•Day)--		Measured
		50	100	
Total				
Fe	1093.			
Fe(II)	445.	131.	.57	< .1
Fe(III)	648.	[2]UF	UF	[1]NA
Mn(II)	.1	11.4	11.4	10.4
Al	518.	.23	.26	< 1
Zn	4.8	.001	.24	1.2
SO_4^{2-}	5000.	1643.	1272.	2000.
HCO_3^-	0.0	4.43	3.20	-
Ca	249.	326.	402.	684.
Mg	114.	248.	248.	234.
pH	2.51	7.12	7.02	7.12

[1] NA - not analyzed.
[2] UF signifies an activity of $< 10^{-20}$m, or a numerical underflow and the component was
removed.

Table 3.-Predicted amount of solids precipitated per liter of pore water
during transit through the French Coulee wetland (mg/L).

	Modeled	
	----SO_4^{2-} reduction rate (micromol/L•Day)----	
	50	100
goethite-FeOOH	1015.	1015.
ferrihydrite-Fe(OH)$_3$	0	0
gypsum-CaSO$_4$•2H$_2$O	1762.	1436.
rhodochrosite-MnCO$_3$	0	0
siderite-FeCO$_3$	0	0
amorphous Al(OH)$_3$	0	0
ALOHSO$_4$	2706.	2706.
greigite Fe$_2$S$_3$	0.04	0.03
amorphous FeS	487.6	688.4
amorphous ZnS	7.26	6.81

Table 4.-Concentration of dissolved components in Pittsburgh Reactor influent, modeled concentrations, and measured effluent composition for the 15 April 1990 sample (mg/L; pH in standard units).[1]

| | Mine Drainage | Pittsburgh Reactor Effluent SO_4^{2-} reduction rate (micromol/L•Day) Modeled | | Measured 15-Apr-90 |
		100	700	
Ca	328.	423.	433.	431.
Mg	92.6	92.8	92.8	93.0
K	5.3	4.5	4.5	11.6
Fe(III)	3.6	10^{-11}	[2]UF	[3]NA
Fe(II)	25.7	21.5	.10	< .2
Mn	1.7	1.7	1.7	1.3
Al	13.0	.52	.52	[4](0)
SO_4^{2-}	1100.	1041.	1005.	550.
CO_3^{2-}	0	2.28	2.17	[5]360.
HS⁻	0	.013	7.17	81.2
pH	3.5	6.8	6.8	6.8
pE	-	0.0	0.0	-

[1] Allowed solids include: amorphous Al_2O_3, gypsum, K-jarosite, siderite, rhodochrosite, amorphous FeS, greigite.
[2] UF signifies an activity of $< 10^{-20}$m, or a numerical underflow and the component was removed.
[3] not analyzed.
[4] less than an unspecified detection limit.
[5] Estimated from measured alkalinity and assuming aqueous carbonate was the only source of alkalinity.

complication occurs with the aqueous carbonate. The data were modeled with a carbon dioxide partial pressure of $10^{-3.50}$ atm. This is in effect allowing some aqueous carbonate produced by sulfate reduction and dissolution of limestone to bleed to the atmosphere as carbon dioxide. Since the reactor is a closed system, rather than an open wetland as in the Big Five and French Coulee examples, another way of handling aqueous carbonate may be appropriate.

An update on the Eh for the Pittsburgh reactor resulted in an average effluent value of -245 mV or a pE of -4.31 for the temperature of 13.0°C. Additional experimentation was done with the modeling of the partial pressure of carbon dioxide and the aqueous carbonate. Because of the closed nature of the Pittsburgh

system, carbon dioxide cannot readily be lost to the atmosphere. If methanation is occurring in the system there may be additional carbon dioxide produced, other than that produced by microbial sulfate reduction. Modeling was done at two higher pressures of carbon dioxide, and a third run not allowing any interaction with the atmosphere. All aqueous carbonate produced by sulfate reduction then becomes available for aqueous reactions. Table 5 compares the results of these runs for the 15 April 1990 data, using the same influent data and residence time, the new Eh data, and only the 700 micromoles SO_4^{2-}/L•day sulfate reduction rate.

The sulfate reduction rate of 700 micromoles SO /L• day does not result in a sufficient decrease in sulfate to match the effluent

Table 5.-Concentration of dissolved components in Pittsburgh Reactor influent,
modeled concentrations, and measured effluent composition for
the 15 April 1990 sample (mg/L; pH in standard units).[1]

| | Mine Drainage | Pittsburgh Reactor Effluent | | | Measured 15-Apr-90 |
| | | Modeled | | | |
		$P_{CO_2} = 10^{-2.2}$	$P_{CO_2} = 10^{-1.0}$	No Atm. Inter.	
Ca	328.	434.	444.	437.	431.
Mg	92.6	92.8	92.8	92.8	93.0
K	5.3	4.5	4.5	5.3	11.6
Fe(III)	3.6	[2]UF	UF	UF	[3]NA
Fe(II)	25.7	.10	.10	.10	< .2
Mn	1.7	1.7	1.7	1.7	1.3
Al	13.0	.52	.52	.52	.52
SO_4^{2-}	1100.	1009.	1031.	1019.	550.
CO_3^{2-}	0	66.9	771.	256.	[4]360.
HS^-	0	7.17	7.17	5.58	81.2
pH	3.5	6.8	6.8	6.8	6.8
pE	NA	-4.31	-4.31	-4.31	-4.31

[1] Allowed solids include: amorphous Al_2O_3, gypsum, K-jarosite, siderite, rhodochrosite, amorphous FeS, greigite.
[2] UF signifies an activity of $< 10^{-20}$m, or a numerical underflow and the component was removed.
[3] NA–not analyzed.
[4] Estimated from measured alkalinity and assuming aqueous carbonate was the only source of alkalinity.

concentration. It is sufficient to remove iron to near that of the observed effluent concentration. Aluminum removal does match, but is not dependent on sulfate reduction, as aluminum removal is related to the solubility of the aluminum hydroxide. The computed aqueous carbonate and aqueous sulfide concentrations are less than that observed in the effluent. This suggests that increasing the sulfate reduction rate above the postulated 700 micromoles SO_4^{2-}/L•day would result in a better fit to the measured effluent. Since there are two moles of aqueous carbonate produced for every mole of sulfate reduced, a simultaneous match of aqueous sulfate, carbonate, and sulfide would not be possible using mirobial sulfate reduction alone. Some other mechanism may be necessary for the

removal of sulfate, other than sulfate reduction and precipitation of gypsum.

Palmerton Reactor, Palmerton, Pennsylvania

The Palmerton system is two independent 4500 liter tanks treating metal-laden drainage from smelter tailings at Palmerton, Pennsylvania and is described by Dvorak et al. (1992). An initial run revealed some difficulty with the trace constituents cadmium and nickel, and they were removed from the computation in later runs. The modeling demonstrated complete removal of cadmium and nickel.

The data from Tank 1 on the 26 August

1991 sampling are summarized in Table 6. The residence time remains at 473 hours, and a range of sulfate reduction rates from 100 to 350 micromol/L•day were used. The pE was adjusted from 2.99 to -5.33 during the pH/pE adjustment step, and the pH was not adjusted, but incremented by 0.10 standard units/step. The calcium and aqueous carbonate were incremented by dissolution of 4.60×10^{-4} moles of limestone/L•day. The aqueous carbonate was also incremented by the appropriate amount for the chosen microbial sulfate reduction rate.

Table 6.-Concentration of dissolved components in Palmerton Tank 1 influent, modeled concentrations, and measured effluent composition for the 26 August 1991 sample (mg/L; pH in standard units).[1]

	Influent Mine Drainage	----------Palmerton Tank 1 Effluent----------				Measured
		----------Modeled----------				
		----------Partial Pressure CO_2----------			No atm. Inter.	
		0.00035 atm.	0.1 atm.	0.1 atm.		
		----------SO_4^{2-} reduction rate (micromol/L• Day)----------				
		100	100	350	350	
Ca	323.	445.	342.	594.	399.	650.
Mg	464.	466.	466.	466.	466.	465.
[2]Fe	4.5	.18	.12	.52	.66	< .2
Mn	32.4	32.4	1.4	2.4	1.0	5.7
Zn	324.	[3]UF	.025	UF	UF	.61
Ni	1.00	UF	UF	UF	UF	.04
Cd	.37	UF	UF	UF	UF	.28
SO_4^{2-}	3600.	1726.	2605.	1367.	2261.	3100.
HS-	0	17.0	12.0	180.	203.	[4]14.
CO_3^{2-}	[5]26.8	4.30	1384.	658.	1895.	[5]1120.
pH	6.0	6.9	6.9	6.9	6.9	6.9
pE	2.99	-5.33	-5.33	-5.33	-5.33	-5.33

[1] Allowed solids include: gypsum, siderite, rhodochrosite, $ZnCO_2•1H_2O$, amorphous FeS, amorphous ZnS.

[2] Reported as total iron. Modeled as iron entirely existing as ferrous iron.

[3] UF signifies an activity of $< 10^{-20}m$, or a numerical underflow and the component was removed.

[4] Unreliable measurement.

[5] Estimated from measured alkalinity and assuming aqueous carbonate was the only source of alkalinity.

The regulated metals are predicted to be removed, including manganese as rhodochrosite. There are still problems in the final predicted amount of sulfate being lower than measured in the effluent. The presence or absence of gypsum, and the rate of dissolution of limestone are only estimated. This complication will be further experimented with in the modeling of Tank 2 of the Palmerton system. Further experimentation with carbon dioxide partial pressure and gypsum precipitation was modeled with the 28 September 1991 data from Palmerton, Tank 2. The residence time was estimated at 211 hours. The limestone dissolution rate was estimated at 1.04×10^{-3} moles $CaCO_3/L \cdot$ day. Both the microbial sulfate reduction rate and the carbon dioxide partial pressure were varied. The last modeled column in Table 7 compares a run with and without gypsum precipitation.

The run in Table 7 where there was no atmospheric interaction of the carbon dioxide with the substrate of Tank 2, the microbial sulfate reduction rate was 250 micromoles SO_4^{2-} /L·day, and no gypsum precipitation best matches the measured effluent. This is a marked improvement for aqueous sulfate concentration, but is not particularly close for aqueous carbonate. This could be improved only slightly by adjusting the amount of calcium carbonate which is allowed to dissolve. The modeling could be continued, adjusting various parameters to obtain a slightly better fit, but may not be any more realistic than the data in Table 7.

Some of the runs in Tables 6-7 precipitated zinc carbonate as well as amorphous zinc sulfide in the modeling. This is consistent with the observations of Dvorak et al (1992) of a non-sulfide form of zinc being present. The amount of zinc carbonate predicted to form was in the same order of magnitude as the non-sulfide zinc found by Dvorak et al. (1992). The data from the Palmerton runs in particular indicate the importance of aqueous carbonate in the prediction of effectiveness of removal of zinc and manganese. The advantage of retaining all aqueous oxidized carbon species in solution and not allowing it to escape to the atmosphere is obvious. The slowness of heterogeneous reaction such as aqueous carbon dioxide escaping

to the atmosphere probably allows anaerobic wetlands to be reasonably effective. The retention of aqueous carbon dioxide will be important in the precipitation of carbonate-containing solids such as manganese carbonate, zinc carbonate, and to a lesser extent, iron carbonate. The formation of these solids may be important in the removal of these metals, particularly manganese, in anaerobic systems. The interaction of limestone dissolution, increasing aqueous calcium concentration, followed by precipitation of gypsum, decreasing calcium concentration is difficult to model. The location of gypsum precipitation in a plug flow reactor, if it occurs, will be important to know if modeling is to be more accurate.

RESULTS OF MODELING REAL WETLANDS/REACTORS - ANAEROBIC PROCESSES COUPLED WITH ADSORPTION AND EXCHANGE REACTIONS

Somerset, Pennsylvania Wetland

The modeling of the Somerset, PA wetland incorporated additional complexities in the modeled processes, including dilution and adsorption of metals by the substrate. Hedin and Nairn (1991) summarized the characteristics of this wetland and others being studied by the U.S. Bureau of Mines at the Pittsburgh Research Center. Sulfate reduction and ferric iron reduction was postulated to occur. Adsorption of iron by an activity K_d model was incorporated in some of the runs which modeled the Somerset wetland.

The pore volume for Somerset was calculated from past retention time and dimensions (Hedin and Nairn, 1991). During the winter, influent and effluent flows are substantially different, with an increase in the effluent flow. This indicates dilution occurring either from precipitation and/or groundwater inflow. Calculated residence time was only 53.9 hours based on the effluent flows. The

Table 7.-Concentration of dissolved components in Palmerton Tank 2 influent, modeled concentrations, and measured effluent composition for the 28 September, 1991 sample (mg/L; pH in standard units).[1]

	Influent Mine Drainage	Palmerton Tank 2 Effluent				Measured
		Modeled				
		Partial Pressure CO_2		No atm. Inter.	No atm. Inter.	
		0.00035 atm.	0.1 atm.			
		SO_4^{2-} reduction rate (micromol/L•Day)				
		100	100	250	250	
		gypsum allowed				
		yes	yes	yes	no	
Ca	288.	343.	364.	356.	658.	619.
Mg	415.	417.	417.	417.	417.	397.
[2]Fe	2.1	.48	.17	.16	.14	< .2
Mn	24.9	1.8	1.7	2.6	2.9	.38
Zn	340.	.37	.64	1.0	.44	< .02
Ni	.95	[3]UF	UF	UF	UF	< .02
Cd	.33	UF	UF	UF	UF	< .02
SO_4^{2-}	3103.	2278.	2116.	2101.	2819.	2988.
HS⁻	0	.51	37.2	32.3	25.5	[4]< .1
CO_3^{2-}	[5]18.3	1149.	1152.	733.	736.	[5]293.
pH	6.1	6.9	6.9	6.9	6.9	6.9
pE	[6]2.99	[6]-1.82	-1.82	-1.82	-1.82	-1.82

[1] Allowed solids include: siderite, rhodochrosite, $ZnCO_3 • 1H_2O$, amorphous FeS, amorphous ZnS, gypsum except the column noted.

[2] Reported as total iron. Modeled as entirely existing as ferrous iron.

[3] UF signifies an activity of $< 10^{-20}$m, or a numerical underflow and the component was removed.

[4] Unreliable measurement.

[5] Estimated from measured alkalinity and assuming aqueous carbonate was the only source of alkalinity.

[6] Not reported. The same pE as measured for the 15 July 1991 was used for modeling the 28 September 1991 data.

composition of the added water is unknown, but if assumed to be precipitation, added ions are negligible, compared with the mine drainage. Precipitation in western Pennsylvania is also considered to have no residual alkalinity, which is consistent with the pH of precipitation for that region. The measurement of pE was not made, and the modeling was done at a fixed value of 0.00. The pH actually decreased during flow through the wetland, indicating a low level of sulfate treatment. This suggests another mechanism of iron and aluminum is removal is

probable. A temperature of 5°C was used in the modeling. Table 8 summarizes the results from the winter modeling of the Somerset wetland at two different microbial sulfate reduction rates, dilution by rainfall, partial pressure of carbon dioxide at atmospheric concentration of $10^{-3.50}$ atm, and adsorption. The initial run at a microbial sulfate reduction rate of 100 micromoles SO_4^{2-}/L•day is consistent with what may be expected in an outdoor environment.

The change in calcium, magnesium, sodium, iron, manganese, and aluminum is only due to dilution. None of the allowed solids in the list precipitated during the modeling run. The change in aqueous sulfate is due both to dilution and to sulfate reduction. Bisulfide and aqueous carbonate increase is due to sulfate reduction. A component such as magnesium is expected to be conservative in the flow through the wetland, and the modeling is consistent with this result.

Table 8.-Concentration of dissolved components in Fetterolf wetland influent, modeled concentrations, and measured effluent composition for the 15 February 1990 sample mg/L; pH in standard units; flow in liters/minute).[1]

	Influent Mine Drainage	----------Fetterolf Wetland Effluent----------			
		----------Modeled----------			Measured
		----------SO_4^{2-} reduction rate (micromol/L•Day)----------			
		100	1000	1000	
	Adsorption	No	No	[2]Yes	
Ca	220.	136.	136.	136.	160.
Mg	205.	127.	127.	127.	123.
Na	5.0	4.8	4.8	4.8	3.8
[3]Fe	178.	110.	110.	33.9	34.5
Mn	56.9	35.1	35.1	35.1	33.2
Al	3.0	1.9	1.9	1.9	.9
SO_4^{2-}	1850.	1778.	923.	923.	1025.
HS⁻	0	7.4	74.4	74.4	[4]NA
CO_3^{2-}	0	.4	.4	.4	NA
pH	4.63	3.65	3.65	3.65	3.65
flow	30.7	46.9	46.9	46.9	46.9

[1] Allowed solids include: gypsum, rhodochrosite, siderite, amorphous Al_2O_3, amorphous FeS.
[2] Adsorption of ferrous iron using an activity K_d model and a K_d value of $10^{+3.5}$.
[3] Entirely ferrous iron, based on influent measurement.
[4] Not analyzed.

The microbial sulfate reduction rate was increased to an improbable value of 1000 micromoles/L•day. Still no solids precipitated and the modeled concentrations for the major cations are consistent with a "dilution-only" process being operative. The fourth column of Table 8 incorporates adsorption of ferrous iron by an activity K_d model. The K_d value and the amount of adsorber for such a system is unknown. A hypothetical 10.0 mg/L of adsorber was used and a realistic K_d value of $10^{+3.5}$ was used in the modeling. No inorganic solids precipitate, but the iron is reduced to a concentration close to that observed in the effluent.

Considering the pH of the system, it is reasonable to assume microbial sulfate reduction is a minor process, relative to other processes. The decrease in iron can be accounted for by adsorption alone. The observed decrease in aqueous sulfate is primarily due to another unidentified process. The gypsum saturation index decreases from -0.12 in the first step to -0.42 in Step 10. This is consistent with a gradually decreasing pH, and gypsum precipitation cannot be invoked as a mechanism for the removal of sulfate.

Friendship Hill, Pennsylvania Wetland

The Friendship Hill wetland was described by Hedin and Nairn (1991). The wetland is constructed of three lanes or treatment systems operating in parallel. These are designated Lanes A, B, and C. The residence times for Lanes A, B, and C are 53.4, 81.6, and 67.7 hours, respectively for the measurements on 12 February 1992. Ferric iron was reduced in the modeling. Gypsum was allowed to precipitate and a microbial sulfate reduction rate which would result in the best match for the final aqueous sulfate was used in Table 9. The pE was not measured and a fixed value of 0.00 was used in the modeling. The partial pressure of carbon dioxide used in the modeling was the ambient atmospheric concentration of $10^{-3.50}$ atm. The measured temperature of 9.8°C was used in the modeling. Both aluminum and ferric iron

were allowed to be exchanged with calcium which is on the substrate. The exchange constant for both aluminum and ferric iron were modeled at $10^{+6.0}$. Table 9 summarizes these runs based on the Friendship Hill wetland. These runs couple exchange reactions with both microbial sulfate reduction and reduction of ferric iron.

The modeled results of Table 9 show good agreement with the measured effluents for each lane with the exception of ferrous iron in Lane C. The low pH observed in the Friendship Hill wetland precludes the formation of carbonate minerals. Modeling not shown here at high partial pressures of carbon dioxide demonstrated that carbonate minerals do not form as a possible mechanism for removal of iron and manganese.

Modeling was done on summer data from the Friendship Hill wetland. Little change in aqueous sulfate concentrations suggested microbial sulfate reduction was not operative at significant rates. Ferric iron reduction and exchange were the primary processes which were modeled. Due to the higher temperatures, exchange coefficients are expected to be lower. The exchange coefficient was decreased by a factor of 10 for the trivalent ions and a factor of 100 lower for ferrous iron. This resulted in effective modeling of the measured effluents but the results will not be shown.

The results in the previous Tables 2-9 indicate the probable complexity of the processes operating in anaerobic wetlands. Processes such as microbial sulfate reduction and ferric iron reduction are operating simultaneously. The fate of carbon dioxide and the potential for leakage to the atmosphere are critical in predicting the precipitation of carbonate minerals. The presence or absence of gypsum is also critical in estimating the final aqueous sulfate concentration. Finally, adsorption and exchange processes can either increase or decrease the concentration of a measured constituent. All of these processes couple together at various rates that are currently unknown. The modeling suggests by tweaking of a large number of parameters on rates, adsorption, ion exchange,

Table 9.-Concentration of dissolved components in Friendship Hill wetland influent, modeled concentrations, and measured effluent composition for the 12 February 1992 sample (mg/L; pH in standard units).[1]

	Influent Mine Drainage	Friendship Hill Wetland Effluent					
		Mod.	Meas.	Mod.	Meas.	Mod.	Meas.
		SO_4^{2-} reduction rate (micromol/L•Day)					
		300		100		1000	
		Lane					
		A	A	B	B	C	C
Ca	155.	204.	193.	195.	201.	208.	236.
Mg	62.1	62.2	64.0	62.2	64.2	62.2	57.9
Na	6.4	6.4	8.3	6.4	7.6	6.4	7.6
Fe(III)	121.	61.	61.6	76.8	77.8	65.4	73.8
Fe(II)	5.9	34.4	34.7	31.0	35.2	61.5	2.8
Mn	7.7	7.7	8.3	7.7	7.8	7.7	7.2
Al	47.2	40.8	40.2	38.8	37.7	23.4	23.8
SO_4^{2-}	1350.	1286.	1250.	1323.	1325.	1083.	1150.
HS^-	0	22.1	[2]NA	11.2	NA	93.3	NA
CO_3^{2-}	0	.47	NA	.47	NA	.47	NA
pH	2.64	2.89	2.89	2.84	2.84	3.13	3.13

[1] Allowed solids include: gypsum, rhodochrosite, siderite, amorphous Al_2O_3, amorphous FeS.
[2] Not analyzed.

and gas partial pressures almost any desired result may be obtained. The data suggest that many more parameters would have to be measured to verify what a model suggests is within the realm of reality.

Conclusions

The objective of this study was to develop and test a computer code to model geochemical and biogeochemical processes as a mine drainage moves through a wetland/reactor as a "plug flow." The computer code MINTEQAK was developed from the equilibrium code MINTEQA2. The MINTEQAK code can model several geochemical processes simultaneously during flow through an anaerobic wetland/reactor, an aerobic wetland, or an anaerobic-aerobic system in series.

The application of the MINTEQAK code to

the modeling of geochemical and biogeochemical processes operating in anaerobic wetlands and reactors was described. The code has demonstrated an ability to estimate rates of reactions and possible precipitation of solids as a mechanism for removal of regulated metals. In cases where a wetland was performing poorly, dilution and possibly adsorption processes were consistent with the observed effluent composition.

Use of the difference in aqueous sulfate concentration between the mine drainage and the wetland/reactor effluent as a means of estimating rates of microbial sulfate reduction may be inaccurate. The modeling results indicate that gypsum precipitation may also remove aqueous sulfate. Allowing gypsum to precipitate in the model may result in a predicted effluent being reasonably accurate, or too low. The difference suggests that gypsum precipitation is occurring in some systems, but not others.

Metal removal is primarily as solid sulfides. The modeling demonstrates that removal of manganese, iron, and zinc as solid carbonates is also likely. In the case of iron and zinc, both sulfide and carbonate phases are possible if the pH of the system approaches neutrality. Adsorption of metals by the organic substrate is also likely, and can serve as an important buffer of effluent metal concentration if the system is shocked by sudden changes in loading. The metal adsorption and exchange characteristics of a system's organic substrate are almost completely unknown. The modeling has demonstrated that these processes may be operational in some wetland systems.

A better understanding of the processes which are operating inside a wetland/reactor system is needed. The modeling can guide the researcher as to what parameters are most important to measure. Measurement of aqueous sulfate, carbonate, and sulfide at different positions along the flow path are critical. The presence or absence of predicted solid phases in systems which have operated for extended periods of time will also aid in the understanding of the processes occurring.

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Guidelines for Gravel Pit Wetland Creation
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Passive Treatment Methods for Manganese: Preliminary Results from Two Pilot Sites
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Modeling of Wetlands and Reactors Systems for Mine Drainage Treatment
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