

THEORETICAL TECHNIQUE FOR PREDICTING THE CUMULATIVE IMPACT OF IRON AND  
MANGANESE OXIDATION IN STREAMS RECEIVING DISCHARGE FROM COAL MINES

by Keith E. Bobay

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DONALD PAUL HODEL, Secretary

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Dallas L. Peck, Director

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For additional information write to:

U.S. Geological Survey  
6023 Guion Road, Suite 201  
Indianapolis, Indiana 46254

Copies of this report  
can be purchased from:

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U.S. Geological Survey  
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FACTORS FOR CONVERTING INCH-POUND UNITS TO METRIC  
(INTERNATIONAL SYSTEM) UNITS

<u>Multiply inch-pound unit</u>	<u>by</u>	<u>To obtain Metric units</u>
foot (ft)	0.3048	meter (m)
square foot (ft <sup>2</sup> )	0.0929	square meter (m <sup>2</sup> )
mile (mi)	1.609	kilometer (km)
cubic foot per second (ft <sup>3</sup> /s)	0.0283	cubic meter per second (m <sup>3</sup> /s)

To convert degree Fahrenheit (°F) to degree Celsius (°C)

$$(0.556) (°F - 32°) = °C$$

To convert degree Celsius (°C) to degree Kelvin (°K)

$$°C + 273.16 = °K$$

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THEORETICAL TECHNIQUE FOR PREDICTING THE CUMULATIVE IMPACT  
OF IRON AND MANGANESE OXIDATION IN STREAMS RECEIVING  
DISCHARGE FROM COAL MINES

By Keith E. Bobay

ABSTRACT

Two U.S. Geological Survey computer programs are modified and linked to predict the cumulative impact of iron and manganese oxidation in coal-mine discharge water on the dissolved-chemical quality of a receiving stream. The coupled programs calculate the changes in dissolved-iron, dissolved-manganese, and dissolved-oxygen concentrations; alkalinity; and, pH of surface water downstream from the point of discharge. First, the one-dimensional, steady-state stream, water-quality program uses a dissolved-oxygen model to calculate the changes in concentration of elements as a function of the chemical reaction rates and time-of-travel. Second, a program (PHREEQE) combining pH, reduction-oxidation potential, and equilibrium equations uses an aqueous-ion association model to determine the saturation indices and to calculate pH; it then mixes the discharge with a receiving stream. The kinetic processes of the first program dominate the system, whereas the equilibrium thermodynamics of the second define the limits of the reactions.

A comprehensive test of the technique was not possible because a complete set of data was unavailable. However, the cumulative impact of representative discharges from several coal mines on stream quality in a small watershed in southwestern Indiana was simulated to illustrate the operation of the technique and to determine its sensitivity to changes in physical, chemical, and kinetic parameters. Mine discharges averaged 2 cubic feet per second, with a pH of 6.0, and concentrations of 7.0 milligrams per liter (mg/L) dissolved iron, 4.0 mg/L dissolved manganese, and 8.08 mg/L dissolved oxygen. The receiving stream discharge was 2 cubic feet per second, with a pH of 7.0, and concentrations of 0.1 mg/L dissolved iron, 0.1 mg/L dissolved manganese, and 8.70 mg/L dissolved oxygen. Results of the simulations indicated the following cumulative impact on the receiving stream from five discharges as compared with the effect from one discharge: 0.30 unit decrease in pH, 1.82 mg/L increase in dissolved-iron, 1.50 mg/L increase in dissolved-manganese, and 0.24 mg/L decrease in dissolved-oxygen concentration.

## INTRODUCTION

### Background

The Surface Mining Control and Reclamation Act requires that before a permit to mine is issued, an assessment must "be made by the regulatory authority of the probable cumulative impacts of all anticipated mining upon the hydrology of the area ." (Public Law 95-87, 1977, Sec. 507 (b)(11))

The cumulative impact area is defined as "the area in which there would be an interaction between the hydrologic impacts of the proposed mine and all other anticipated mining." (Federal Register, 1983, p. 43957)

The section on background and legislative intent further states "if any material damage would result to the hydrologic balance from the cumulative impacts of a newly proposed and any previously permitted operation, the new operation could not be permitted." (Federal Register, 1983, p. 43957)

Therefore, the regulatory authority is required to make a cumulative assessment of every permit, prior to issuance, as to whether material damage will occur. But the regulations and statements of intent allow a wide latitude and do not specify the analytical technique to make the assessment. Currently, the most common cumulative hydrologic impact assessment (CHIA) performed by regulatory authorities is based on a qualitative analysis. Many assessments simply state 'No Impact' by summing the determinations in the probable hydrologic consequence (PHC) sections of the permit applications (Nadolski and others, 1983, p. 210).

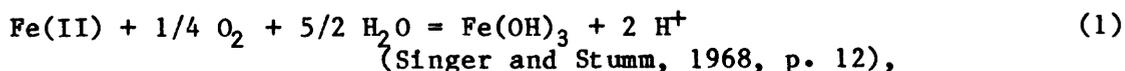
### Purpose and Scope

This report presents a quantitative, reproducible technique for assessing the cumulative impact on a receiving stream from the oxidation of dissolved ferrous iron and dissolved manganous manganese in coal-mine discharges. The technique predicts dissolved-oxygen, dissolved-iron, dissolved-manganese, and alkalinity concentrations and pH of the receiving stream. Although criteria such as depositional and biological effects, and changes in suspended sediment loads are needed to make a thorough judgment of material damage, the present technique is limited to impacts to the chemistry of the water column.

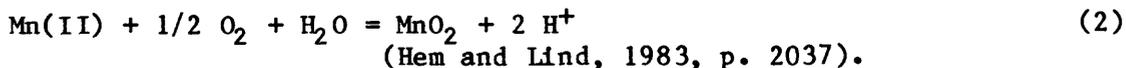
The proposed technique does not require chemical equilibrium; it explicitly solves the nonlinear effects of the kinetically modeled oxidation on the general chemistry of the receiving stream. The technique uses two existing public-domain U.S. Geological Survey computer programs, making availability easy to regulatory authorities. Although the technique is theoretically applicable to a wide range of hydrologic settings, simulations were performed with representative data from a small watershed in southwestern Indiana.

### Approach

The simple stoichiometry of ferrous iron and manganous manganese oxidation and precipitation forms the basis of this theoretical technique:



and



As one mole of Fe(II) is oxidized to Fe(III) and precipitated as ferric hydroxide, one-quarter mole of oxygen is consumed and two moles of hydrogen ion are produced. Similarly, as one mole of Mn(II) is oxidized to Mn(IV) and precipitated as MnO<sub>2</sub>, one-half mole of oxygen is consumed and two moles of hydrogen ion are produced.

Therefore, to determine the cumulative impact on a receiving stream as a result of these chemical reactions, the following questions must be addressed:

- 1) How many moles of the reduced forms of the metals are oxidized, given thermodynamic and kinetic constraints?
- 2) How much of the oxygen which has been consumed is replaced by reaeration?
- 3) Of the total hydrogen ions produced, how many moles are free, thus able to reduce pH?
- 4) What are the effects from mass balance when two waters are combined?

The kinetics of oxidation and reaeration in the one-dimensional, steady-state stream, water-quality program (Bauer and others, 1979) are combined with the equilibrium thermodynamic, pH, and mass-balance calculations in the PHREEQE (acronym for pH, redox, and equilibrium equations) program (Parkhurst and others, 1980) to simulate the reactions and answer these questions.

Chapman (1982) constructed a complex program, RIVEQL II, to similarly combine a chemical equilibrium model with a physical transport model which included a pseudo-kinetic treatment of redissolution. However, chemical reactions other than redissolution of precipitates and dissociation of surface species were treated as equilibrium reactions. Bencala (1983) coupled a physical mass transport model and a kinetic model to simulate solute transport processes in a mountain pool-and-riffle stream. This strictly deterministic model was applied primarily to understand the physical and chemical processes in the system. Lumb (1982) presented a procedure for the assessment of cumulative impacts from coal mining based on a qualitative matrix to determine the magnitude of the impact. Then, techniques ranging from simple mass balance to data-intensive hydrologic models were used to quantify the impacts.

The theoretical technique presented here is a more simplified effort which combines many of the physical, chemical, and biological processes into lumped parameters. However, it has the advantage of not requiring intensive data collection. Most chemical and physical parameters are available in coal-mine permit applications (Nadolski and others, 1983, p. 209). Kinetic rates, if not determined empirically, must be estimated from a range of values in the literature. In order to determine the maximum potential damage, a worst case scenario could be represented by fast oxidation and slow reaeration.

## DESCRIPTION OF TECHNIQUE

Two U.S. Geological Survey computer programs are modified and coupled to perform the calculations in the technique. In addition, 11 subprograms are used to enter and reformat the data, and to perform simple calculations. A Command Procedure Language (CPL) program combines the two primary FORTRAN programs and 11 subprograms into one system. Simplifying assumptions, program options, and program interactions are presented below.

### Computer Programs Used

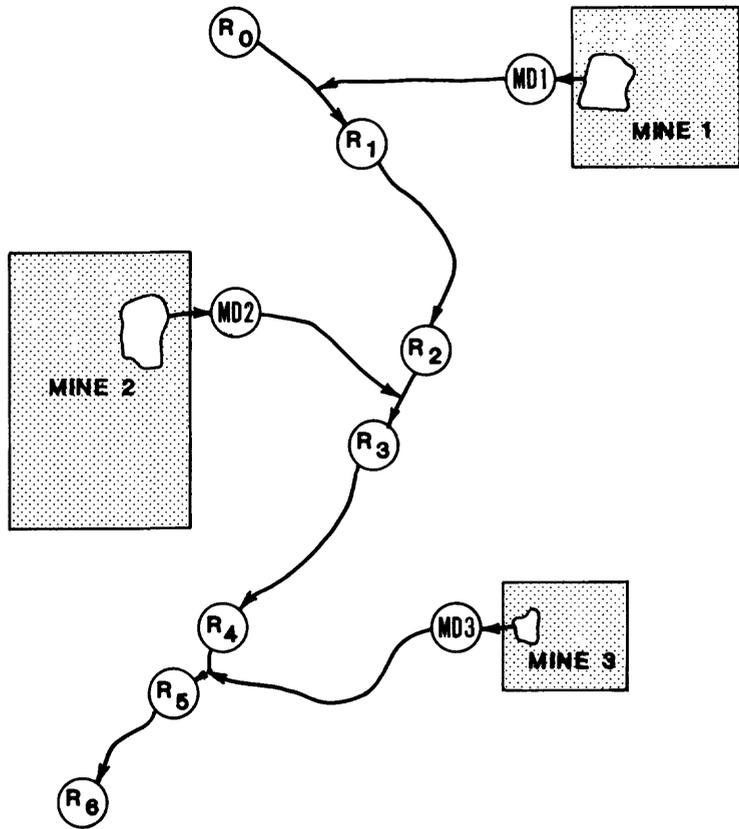
#### One-dimensional, Steady-state Stream, Water-quality Program

The one-dimensional, steady-state stream, water-quality program predicts the receiving stream response to waste inputs, such as coal-mine discharge or sewage effluent. It calculates the response of dissolved oxygen, biochemical oxygen demand (BOD), nitrogen, phosphorus, coliform bacteria, and three user-defined conservative constituents (Bauer and others, 1979, p. 1).

The one-dimensional analysis is ideally applied to narrow, low-order streams. Some accuracy is lost when it is used on wide, turbulent rivers. The steady-state assumption requires that the receiving stream is divided into subreaches defined by the location of inflows. Therefore, the flow remains constant through each subreach of the system (Bauer and others, 1979, p. 2-15).

The framework for this FORTRAN IV program is derived from a dissolved-oxygen (DO) model based on a modified Streeter-Phelps oxygen-sag equation. The DO deficit is calculated as a function of the initial deficit, oxygen sources (atmospheric reaeration and photosynthesis), and oxygen sinks (BOD, algal respiration, and sediment oxygen demand). The deficit is computed for the time-of-travel through each subreach. The DO concentration at any point in the subreach is equal to the saturated DO concentration minus the DO deficit (Bauer and others, 1979, p. 9-11).

Figure 1 is a diagram showing the location of three coal-mine discharges into a receiving stream. The discharges are modeled from the sediment ponds to the confluence and then mixed with the stream. The stream is divided into three subreaches ( $R_1-R_2$ ,  $R_3-R_4$ ,  $R_5-R_6$ ); each begins at the confluence with a discharge. The mixed solution is modeled for each subreach. The final solution is shown as  $R_6$  at an arbitrary point downstream from the last inflow. The mine discharges are assumed to be the only inflows to the stream between  $R_0$  and  $R_6$ .



EXPLANATION

- MD Mine discharge
- $R_0$  Original receiving water
- $R_{1-6}$  Resulting mixed receiving waters

Figure 1.-- Hypothetical inflows and subreaches of a receiving stream.

## pH, Redox, and Equilibrium Equations (PHREEQE) Program

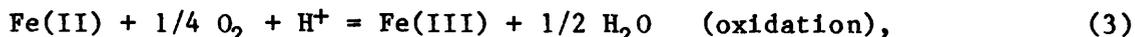
PHREEQE is a FORTRAN IV computer program designed to simulate geochemical reactions. The program is similar to the Survey's WATEQ family of programs based on aqueous-ion association models; yet, the functions and capabilities of PHREEQE are much broader and more sophisticated. It can calculate pH, pE, alkalinity, total concentration of elements, amounts of minerals exchanging with aqueous phases, the distribution of aqueous species, and the saturation state of the aqueous phase with respect to specified mineral phases (Parkhurst and others, 1980, p. 1-3).

The thermodynamic data base of the aqueous model includes 120 aqueous species from 19 elements, and 38 minerals. The model is completely user-definable. The program uses equilibrium equations based on five fundamental concepts: electrical neutrality, conservation of electrons, mass balance, mineral equilibrium, and mass action. Iteration techniques are used to solve a set of nonlinear equations. Several types of reactions can be simulated, including mixing, titration, evaporation, and equilibration. The reactions can also be used in various combinations (Parkhurst and others, 1980, p. 1-7, 42).

### Assumptions and Modifications of the Programs

Specific assumptions are made prior to running either program (PHREEQE or water-quality program). The one-dimensional analysis requires complete mixing of constituents within any cross-section. The steady-state assumption requires constant flow rate through each subreach. Constant stream morphometry is also assumed through each subreach. Thus, major changes in hydraulic characteristics, stream temperature, or reaction coefficients require a new subreach division (Bauer and others, 1979, p. 1-2). Additional assumptions and modifications to the primary subprograms are made with oxygen sources and sinks, reaction rates, reduction-oxidation potential, nonequilibrium, and kinetic dominance.

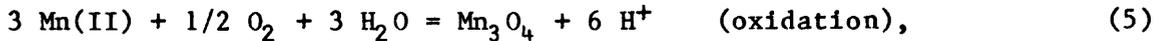
The technique addresses only the reduced states of iron and manganese as the dominant dissolved forms in most natural waters (Hem, 1963, p. A8; Hem and Cropper, 1959, p. 10). Because the technique is concerned with the maximum potential effects from the oxidation of these reduced forms, decreases in concentrations of the metals owing to complexation and adsorption are assumed to be insignificant. As the reduced states are oxidized to iron (III) and manganese (IV) and then precipitated, oxygen is consumed and the pH is lowered. Precipitation of the aqueous phase to the solid phase is modeled in the technique as an equilibrium process. The oxidation and precipitation of iron is shown in two steps (Singer and Stumm, 1968, p. 12):



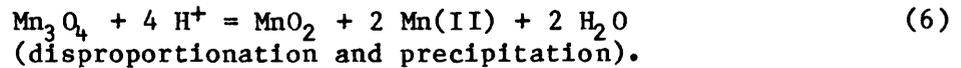
and



In the laboratory, Hem and Lind (1983, p. 2037) have shown that the oxidation of Mn(II) results in the formation of metastable intermediate products. Two possible intermediates are hausmannite ( $Mn_3O_4$ ) and feitknechtite ( $8MnOOH$ ). The pyrolusite ( $MnO_2$ ) end-product results from the disproportionation of the intermediates. The following stoichiometry shows this two-step process for hausmannite:



and



The modified Streeter-Phelps equation in the DO model has been simplified for the technique. The sum of effects from photosynthesis, respiration, sediment oxygen demand, and biochemical oxygen demand (BOD) are assumed to be zero. This could occur in a low-order stream receiving little sunlight where a minimum amount of algae and sludge deposits are present. Biochemical oxygen demand is a measure of the dissolved oxygen required by microorganisms in the biochemical oxidation of organic matter. In the theoretical technique, the BOD terms are replaced by ferrous oxygen demand (FOD) and manganous oxygen demand (MOD). The following equation describes the dissolved oxygen sources and sinks:

$$dD/dT = -1/A \, d(QD)/dx - K_a D + 1/4 K_f F + 1/2 K_m M, \quad (7)$$

where

- D is dissolved oxygen deficit, in milligrams per liter;
  - T is time-of-travel, in days;
  - x is downstream distance, in feet;
  - A is cross-sectional area, in square feet;
  - Q is discharge, in cubic feet per second;
  - $K_a$  is atmospheric reaeration rate, in  $\text{day}^{-1}$ ;
  - $K_f$  is ferrous deoxygenation rate, in  $\text{day}^{-1}$ ;
  - $K_m$  is manganous deoxygenation rate, in  $\text{day}^{-1}$ ;
  - F is dissolved-iron (II) concentration, in milligrams per liter;
  - M is dissolved-manganese (II) concentration, in milligrams per liter;
- and 1/4 and 1/2 are the stoichiometric mole ratios from equations 1 and 2.

At steady-state conditions,  $dD/dT=0$ . Upon integration with boundary conditions,  $C=C_0$  (any solute concentration) at  $x=0$ ,

$$D = D_0 (e^{-K_a T}) + 1/4 K_f F_0 / (K_a - K_f) (e^{-K_f T} - e^{-K_a T}) + 1/2 K_m M_0 / (K_a - K_m) (e^{-K_m T} - e^{-K_a T}). \quad (8)$$

This equation is used in the model calculations. It can be simplified to show the effects of FOD and MOD without reaeration by setting  $K_a$  equal to zero:

$$D = D_0 + 1/4 F_0 (1 - e^{-K_f T}) + 1/2 M_0 (1 - e^{-K_m T}). \quad (9)$$

The results of the two equations can be compared to show the relative importance of atmospheric reaeration.

The theoretical rate of reaction for ferrous iron oxidation can be calculated using values for DO, pH, a constant ( $k_1$ ) from the literature, and adjustment for calibration (Stumm and Lee, 1961, p. 145; Singer and Stumm, 1970, p. 1122; Stumm and Morgan, 1970, p. 534; Sung and Morgan, 1980, p. 562). The following equation defines the kinetic relationship for iron in the pH range 5 to 8 (Stumm and Lee, 1961, p. 145):

$$-d[\text{Fe(II)}]/dT = k_1[\text{Fe(II)}]p\text{O}_2 [\text{OH}^-]^2, \quad (10)$$

where  $[\ ]$  denotes activity,  $p\text{O}_2$  is the partial pressure of oxygen, and  $k_1$  is a constant.

Equation 10 shows that the reaction rate is first order with respect to the partial pressure of oxygen and second order with respect to the hydroxyl ion activity. Because the pH is directly proportional to the activity of the hydroxyl ion, the reaction rate increases two orders of magnitude for every unit increase in pH. At constant DO and pH, the entire rate becomes first order (Singer and Stumm, 1968, p. 13):

$$-d[\text{Fe(II)}]/dT = k[\text{Fe(II)}]. \quad (11)$$

Manganese is not so easily removed from water as iron; the kinetics of the reaction are much slower. Also, the oxidation reaction is much more complex than iron and not fully understood because Mn(II) can be oxidized to Mn(III) or Mn(IV) (Hem, 1963, p. 2, 54). However, the reaction is similarly second-order dependent upon  $[\text{OH}^-]$  and first-order dependent on  $\text{O}_2$  (Morgan, 1967, p. 606-618; Stumm and Morgan, 1970, p. 536). Manganese has been shown to precipitate with other elements and compounds, but coprecipitation with ferric hydroxide does not normally occur at pH less than 6.7 (Hem, 1963, p. 59-61). Although the oxidation of reduced manganese is autocatalytic (Morgan, 1967, p. 613-614; Stumm and Morgan, 1970, p. 535), pseudo first-order kinetics can be assumed if a substantial area of oxide surface is available (Lewis, 1976, p. 139-144; Hem, 1981, p. 1373). Because substantial oxidation of Mn(II) does not occur at pH much less than 8.0 (Coughlin and Matsui, 1976, p. 108), and in order to simplify the kinetics for the water-quality program, manganese oxidation is assumed to be pseudo first-order in the technique. The rate law takes the same form as iron in equations 10 and 11.

Whereas substantial oxidation of ferrous iron in natural waters will normally occur in minutes to hours, manganese (II) requires hours to days (Pankow and Morgan, 1981a, p. 1157-1158; Sung and Morgan, 1981, p. 2377). The constant ( $k$ ) in equation 11 will normally differ one-to-three orders of magnitude between the two metals.

Reaeration rates can be calculated within the water-quality program or entered directly. Eight reaeration equations, including the Bennett-Rathbun and Tsivoglou-Wallace equations, are available. The user enters the equation number and stream parameters that are required. All reaction coefficients are adjusted for water temperatures other than 20 degrees Celsius (Bauer and others, 1979, p. 14; Terry and others, 1983, p. 49).

According to Stumm and Lee (1961, p. 144), fifty percent of the acidity in acid-mine drainage originates from the oxidation of ferrous iron. This oxidation is accompanied by the release of protons ( $\text{H}^+$ ) which tend to reduce the pH

of the solution. The iron, manganese, and oxygen lost in the reaction are removed from the solution in PHREEQE by a negative reaction. The resulting pH reflects the change owing to oxidation and precipitation as shown in equations 1 and 2.

The concept of reduction-oxidation (redox) potential is addressed in PHREEQE as pE (negative logarithm of the electron activity). The redox conditions in the initial solution must be specified for PHREEQE calculations to begin (Parkhurst and others, 1980, p. 32). Because the absolute value of the pE is meaningless (Thorstenson, 1984, p. 34-38) and usually unknown, a high positive number is input as pE to indicate nearly saturated oxidation conditions in flowing waters. Only a relative value is required because dissolved oxygen is explicitly solved in the water-quality program.

The chemical composition of a solution is influenced significantly by the dissolution and precipitation of mineral phases interacting with the solution. Therefore, the chemical model must be tailored to characterize the particular geologic setting, such as including calcite to reflect the buffering potential of a carbonate bearing terrane. These phase interactions are affected by kinetic processes and geochemical equilibrium. While the equilibrium thermodynamics determine the direction of the reaction and what the equilibrium concentration will be under given conditions, the kinetics indicate how fast the reaction will proceed or how much time is required. If the kinetics are fast enough, the reaction can be treated as an equilibrium process. If the reaction proceeds at a slow rate, then kinetics is the controlling process (Stumm and Morgan, 1970, p. 12; Hoffman, 1981, p. 352). In the theoretical technique proposed here, the kinetics of the reactions dominate the system and the equilibrium thermodynamics define the limits of the reaction.

### Coupling of the Programs

A CPL (Command Procedure Language) utility program was written to link the water-quality and PHREEQE programs that form the basis of this technique. The CPL program is currently on the PRIME computer system of the Indiana District of the U.S. Geological Survey. Figure 2 schematically shows the physical interactions of these two programs for three coal-mine discharges. The mine discharge solution (MD) is modeled from the point of discharge (see figure 1) to its confluence with the receiving stream. The water-quality program (Q.W.) calculates downstream values for dissolved oxygen, iron, and manganese. The changes in concentrations are entered into PHREEQE as a negative reaction and removed from solution. The moles of oxygen lost due to ferrous and manganous oxidation ( $X_{DO}$ ) are calculated in a subprogram. The calculations within PHREEQE are performed as stated in the previous section. The output solution from PHREEQE, including pH, pE, and alkalinity, is combined in a subprogram with the downstream concentrations of dissolved iron, dissolved manganese, and dissolved oxygen from the water-quality program. These solution characteristics of the discharge channel are mixed in PHREEQE with the solution characteristics of the receiving stream ( $R_0$ ). This mixed solution is returned to the water-quality program while treating the total metals as reduced because PHREEQE 'oxidizes' the reduced forms if the solution conditions are oxidizing.

This does not affect any characteristic of the solution except the meaningless variable, pE. This solution is entered into the water-quality program and the cycle is repeated.

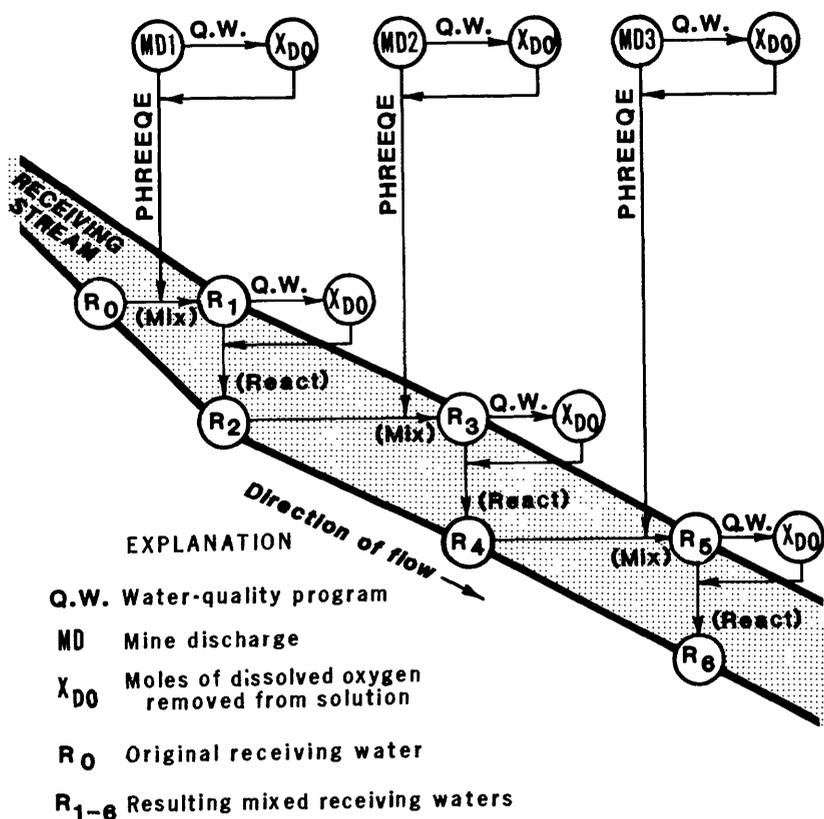


Figure 2.-- Interaction of the primary programs.

In addition to the two primary programs, the CPL program includes three data-entry subprograms and eight data-handling subprograms. The subprogram called PHRQINPT sets up the input file for PHREEQE by prompting the user for parameter values (G.W. Fleming and L.N. Plummer, written commun., 1984). The CPL program includes two other data-entry subprograms to set up the input file for the water-quality program.

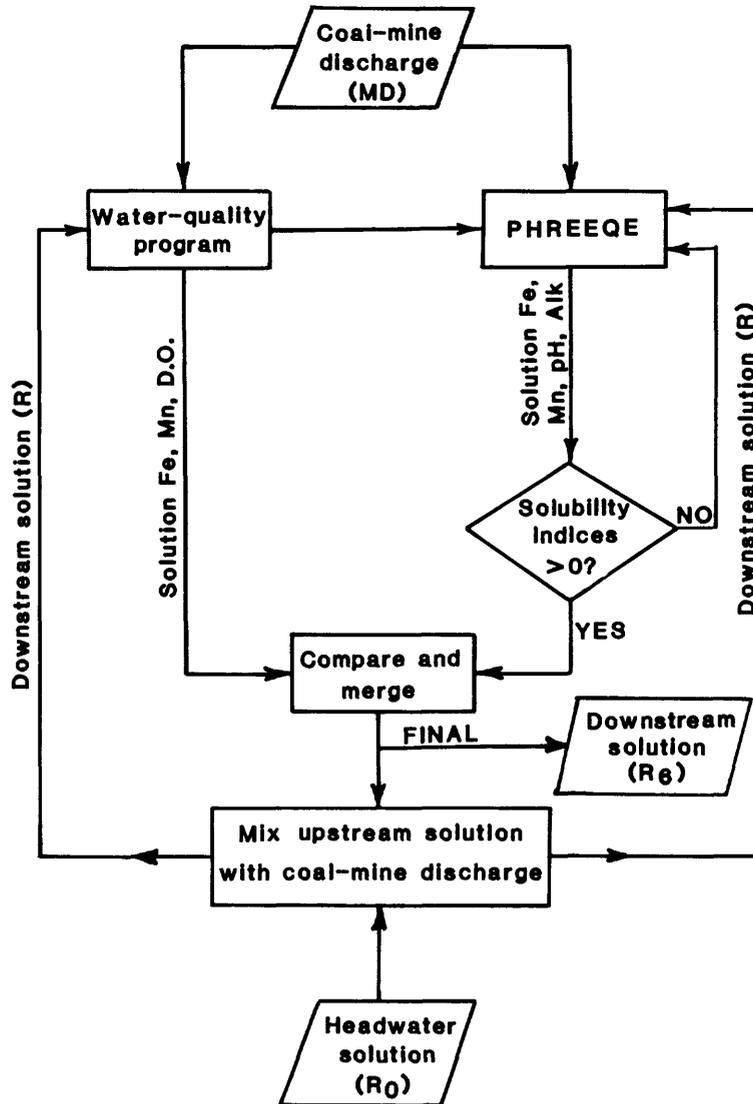


Figure 3.-- Flowchart of the primary programs.

Figure 3 is a flowchart of the program inputs, outputs, operations, and decisions. As shown in figure 2, the coal-mine discharge (MD) is modeled initially in PHREEQE and the water-quality program. A subprogram accesses the solubility indices in PHREEQE to determine whether precipitation conditions exist ( $SI > 0$ ) for  $Fe(OH)_3A$  (amorphous) and  $MnO_2$ . If dissolution conditions exist ( $SI < 0$ ) or if the calculated concentrations in solution are less than the equilibrium concentrations, then the user must re-enter PHREEQE and obtain the equilibrium value for the species. The concentration in the water-quality program must be replaced by this equilibrium or limiting value before the

program can continue. Another data-handling subprogram compares the output from the two primary programs and merges the data into a PHREEQE input file so that the mine-discharge solution can be mixed with the headwater solution ( $R_0$ ). When the output solutions from the two primary programs are compared, they should be equal, except for dissolved oxygen; PHREEQE only lowers the pE when oxygen is removed. The mixed downstream solution (R) is entered into the programs, modeled over the reach, and mixed with the next mine discharge. This cycle continues until the final downstream solution ( $R_6$ ) is obtained.

### Physical and Chemical Options of the Programs

The coupling of the programs provides a variety of options for the user. These include the general hydrologic configuration, the types of aqueous species in solution, and the use of different mineral phases as oxidation products.

A typical hydrologic configuration is shown in figure 1 where three coal-mine discharges are modeled. Several discharges or inflows can be included in the model. Any distance between inflows is acceptable as long as the steady-state assumption is not violated. If the hydrologic setting includes two or more watersheds, the watersheds must be modeled separately, and then mixed at the point of confluence.

Although the technique addresses the kinetics of only ferrous and manganese oxidation, PHREEQE can solve initial solutions of up to 120 aqueous species. At present, though, the CPL program is capable of treating only two other species as non-conservative, and three species as conservative constituents chosen by the user. This limitation is imposed by the capacity of the water-quality program's data-input file. A mass-balance approach is used in the program to calculate the downstream concentrations after mixing. Therefore, inaccurate results will occur if non-conservative species are input as conservative constituents.

Thirty-eight mineral phases are available in the pre-constructed PHREEQE data base. Pyrolusite,  $MnO_2$ , has been added from the data base in WATEQF (Plummer and others, 1976, p. 13, 60) as the final oxidation product of Mn(II). Although intermediate oxidation products from Fe(II) and Mn(II) are possible (eg.  $MnCO_3$ ,  $Mn_3O_4$ ,  $Mn(OH)_2$ ,  $Fe(OH)_2$ ,  $Fe_3O_4$ , and  $FeOOH$ ), pyrolusite and amorphous ferric hydroxide are the most likely oxidation end products. Therefore, their equilibrium thermodynamics are used in the calculations.

SIMULATIONS OF CUMULATIVE IMPACTS OF IRON AND MANGANESE OXIDATION USING  
REPRESENTATIVE DATA FROM A SMALL WATERSHED, SOUTHWESTERN INDIANA

Characteristics of the Data

The validity of the theoretical technique could not be tested because a complete set of data was not available. However, simulations were run with data representative of a small watershed in southwestern Indiana to illustrate the operation of the technique and to determine its sensitivity to changes in parameters, such as reaction rates, initial water quality, discharge quantity, and distances.

Stream morphometric characteristics are available from previous studies and topographic maps (Peters, 1981; Renn, 1983). The stream characteristics used in the simulations are shown in table 1. A range of values is given for the receiving-stream data because certain parameters increase in the downstream direction. For example, the quantity of each succeeding stream reach increases by 2.0 cubic feet per second (ft<sup>3</sup>/s) at the confluence with each mine discharge. Coal-mine discharge and receiving-stream data are available from permit applications for many areas in southwestern Indiana (SIECO, Inc., 1982, p. 38-40; Geosciences Research Associates, Inc., 1983, p. A3-A4). Commonly collected parameters in permit applications include iron, pH, alkalinity, sulfate, total dissolved solids, total suspended solids, and major cations and anions (Nadolski and others, 1983, p. 209).

The initial quality and chemical characteristics of the coal-mine discharges and receiving stream used in the simulations are shown in table 2. A range of values is given for the rates of reactions in the receiving stream. The rates decrease downstream as pH and dissolved-oxygen concentration decrease. The remaining receiving-stream data represent the water quality before mixing with the first mine discharge.

Simulations were run as worst case scenarios; the discharge quality was assumed to be the poorest permissible under the laws. The maximum daily legal discharge concentrations of total iron and total manganese from a coal-mine sediment pond are 7.0 milligrams per liter (mg/L) and 4.0 mg/L, respectively. The pH must remain between 6.0 and 9.0 with minor exceptions (Federal Register, 1982, p. 45395). In order to determine the maximum impact from oxidation, the metals are assumed to be in the reduced, dissolved state. This assumption requires that the original coal-mine discharge be in a state of nonequilibrium.

Table 1.--Morphometric characteristics of the simulated streams and mine discharges

Solution	Quantity (ft <sup>3</sup> /s)	Reach length (mi)	Average depth of reach (ft)	Average cross-sectional area of reach (ft <sup>2</sup> )	Average slope of reach (ft/ft)	Reach time-of-travel (hr)
Mine discharge	2.0	0.50	0.50	2.0	0.0050	.51
Receiving stream	2.0-12.0	.50	.50-.75	4.0-12.0	.0005	.73 3.65 hrs total

Table 2.--Initial quality and chemical characteristics of the simulated streams and mine discharges

Solution	Dissolved oxygen (mg/L)	[Fe <sup>+2</sup> ] (mg/L)	[Mn <sup>+2</sup> ] (mg/L)	pH	Alkalinity (mg/L as CaCO <sub>3</sub> )	Temp (°C)	Iron oxidation rate (day <sup>-1</sup> )	Manganese oxidation rate (day <sup>-1</sup> )	Atmospheric reaeration rate (day <sup>-1</sup> )
Mine discharge	8.08	7.0	4.0	6.0	60.0	25.0	10.0	0.2	23.2
Receiving stream	8.70	.1	.1	7.0	150.0	22.0	10.0 - 50.0	.2 - 1.0	2.3

The reaction rate for iron was calculated by means of equation 10. At 25 degrees Celsius, pH of 6, 8.08 mg/L dissolved oxygen (saturation), and kl of  $14 (\pm 5) \times 10^{13}$  ( $L^2 \text{mole}^{-2} \text{atm}^{-1} \text{min}^{-1}$ ) (Stumm and Lee, 1961, p. 145; Singer and Stumm, 1968, p. 13; Stumm and Morgan, 1970, p. 534), the iron reaction rate for the mine discharge is approximately 10 per day. In the case of manganese, however, similar reaction constants are not available for pseudo first-order rates. Instead, reaction rates measured in near-neutral waters were obtained from the literature. Reported values for pseudo first-order reaction rates range from 0.7 to 0.9 per day (Lewis, 1976, p. 152; Hem, 1981, p. 1373). These rates were adjusted in the simulations owing to differences in pH and temperature. At pH 6.5 and 23.5 degrees, a value of 1.0 per day was assigned to k. At pH 6.0 and 25 degrees, a value of 0.2 per day was used in the simulations. The Tzivoglou-Wallace equation was used to calculate the atmospheric reaeration rate (Bauer and others, 1979, p. 17; Terry and others, 1983, p. 49). The rate for the mine discharge is 23.2 per day. The reaeration rate for the receiving stream is an order of magnitude less owing to the difference in slope.

The maximum effect from the complete oxidation and precipitation of 7 mg/L dissolved ferrous iron and 4 mg/L dissolved manganous manganese can be calculated using the stoichiometry in equations 1 and 2. First, the units are converted to moles per liter (M):

$$\begin{aligned} & 7 \text{ mg/L Fe(II)}/55847(\text{mg/mole}) = 1.25 \times 10^{-4} \text{ M Fe(II)}, & (12) \\ \text{and} & 4 \text{ mg/L Mn(II)}/54938(\text{mg/mole}) = 7.28 \times 10^{-5} \text{ M Mn(II)}. & (13) \end{aligned}$$

Then, to determine the amount of oxygen consumed as a result of the complete oxidation, the mole ratios must be introduced:

$$\begin{aligned} & 1.25 \times 10^{-4} \text{ M Fe(II)} \times 1/4 = 3.13 \times 10^{-5} \text{ M O}_2, & (14) \\ \text{and} & 7.28 \times 10^{-5} \text{ M Mn(II)} \times 1/2 = 3.64 \times 10^{-5} \text{ M O}_2. & (15) \end{aligned}$$

Therefore, the concentration of dissolved oxygen depleted owing to the complete oxidation of 7 mg/L Fe(II) and 4 mg/L Mn(II) is  $6.77 \times 10^{-5}$  moles/L or 2.17 mg/L. It is interesting to note that the dissolved manganese has a greater potential for depleting the oxygen than does dissolved iron.

Similarly, to determine the amount of hydrogen ions produced as a result of the complete oxidation and precipitation of the iron and manganese, different mole ratios are applied:

$$\begin{aligned} & 1.25 \times 10^{-4} \text{ M Fe(II)} \times 2 = 2.50 \times 10^{-4} \text{ M H}^+, & (16) \\ \text{and} & 7.28 \times 10^{-5} \text{ M Mn(II)} \times 2 = 1.46 \times 10^{-4} \text{ M H}^+. & (17) \end{aligned}$$

Therefore,  $3.96 \times 10^{-4}$  moles/L hydrogen ions are produced. In a dilute solution with no buffering capacity, these would all be free protons resulting in a pH of 3.40.

However, complete oxidation of the reduced forms may or may not occur in natural waters. As stated earlier, other factors, such as kinetics, thermodynamics, reaeration, buffering capacity, and mass balance are included in the theoretical technique to determine the cumulative impact of iron and manganese oxidation on the receiving stream.

Simulations With Discharges from Zero to Five Coal Mines

The coal-mine water was modeled from its point of discharge to its mouth one-half mile downstream. The solution characteristics are shown in table 3 as the original mine discharge and discharge at the mouth. As shown in the table, very little change occurred over the reach because not enough time was available for the reactions to proceed. Dissolved-oxygen concentration decreased 0.10 mg/L and dissolved-iron concentration decreased 0.99 mg/L. These solution characteristics were used for all of the mine discharges in the subsequent simulations.

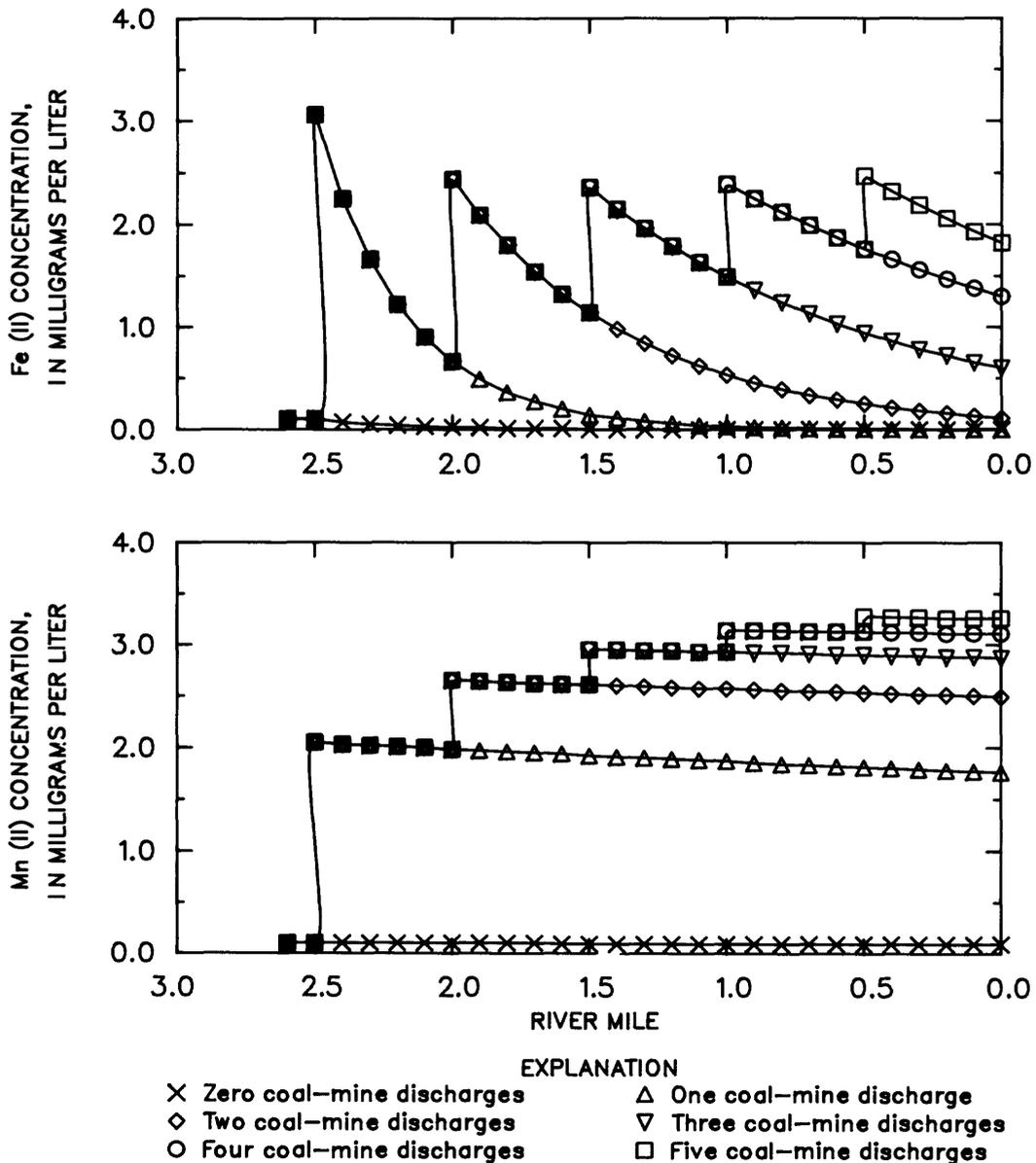
Table 3.--Initial solution characteristics and results of the hypothetical simulations with from zero to five coal mines discharging at half-mile intervals<sup>1</sup>

Number of discharges	Dissolved oxygen <sup>2</sup>	Dissolved iron (II)	Dissolved manganese (II)	pH	Alkalinity as CaCO <sub>3</sub>	Temp (°C)	Discharge (ft <sup>3</sup> /s)
0	8.64	0.001	0.09	7.00	150	22.0	2
1	7.96	.004	1.76	6.42	101	23.5	4
2	7.74	.11	2.49	6.26	86	24.0	6
3	7.69	.60	2.87	6.19	78	24.2	8
4	7.70	1.30	3.11	6.15	74	24.4	10
5	7.72	1.82	3.26	6.12	71	24.5	12
Original receiving stream (R <sub>0</sub> )	8.70	.10	.10	7.00	150	22.0	2
Original mine discharge	8.08	7.00	4.00	6.00	60	25.0	2
Mine discharge at mouth	7.98	6.01	3.99	5.99	59	25.0	2

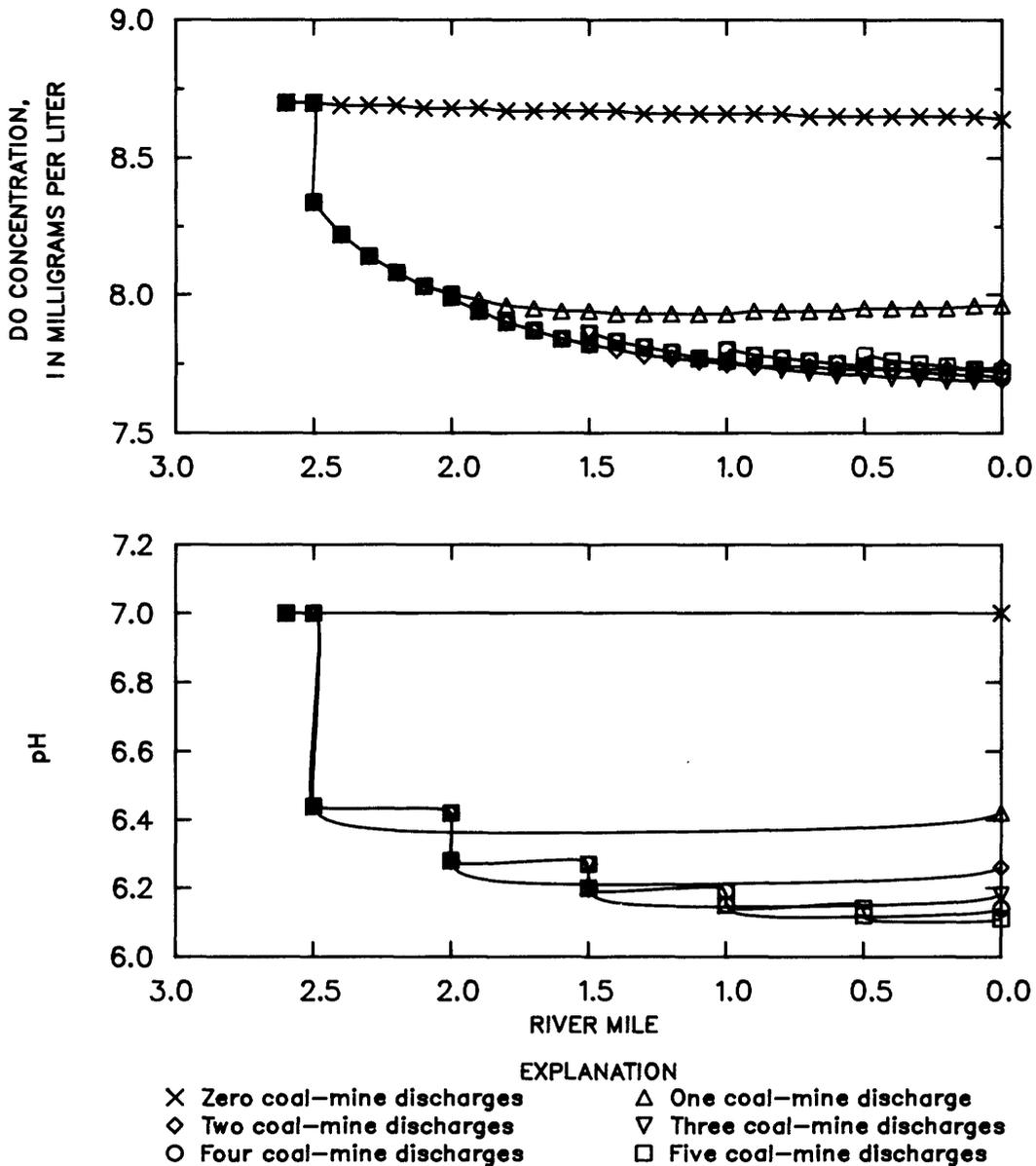
<sup>1</sup>Results are shown for the furthest downstream point for 0-5 discharges (RM 0.0 in figures 6, 7, and 8).

<sup>2</sup>All units in milligrams per liter unless otherwise specified.

The oxidation of iron and manganese in a stream not receiving coal-mine discharge was simulated to establish baseline water quality. The stream was modeled under steady-state conditions for 2.5 miles. Downstream water quality is summarized in table 3 and in figures 4 and 5. As shown in the figures, very little change occurs over the reach. Compared to the original receiving-stream quality in table 3, dissolved iron decreased 0.099 mg/L to equilibrium, dissolved manganese decreased 0.01 mg/L, dissolved-oxygen concentration remained near saturation, and the pH remained at 7.00.



**Figure 4.** -- Simulated cumulative impact of iron and manganese oxidation on concentrations of dissolved iron (II) and dissolved manganese (II) in streams receiving discharge from zero-to-five coal mines at half-mile intervals.



**Figure 5. -- Simulated cumulative impact of iron and manganese oxidation on concentrations of dissolved oxygen (DO) and pH in streams receiving discharge from zero-to-five coal mines at half-mile intervals.**

Simulations were run to determine the effect on a stream receiving identical discharges from one to five coal mines. The discharges flowed into the stream beginning at river mile (RM) 2.5 and at half-mile intervals thereafter, depending on the number of coal mines modeled. For example, with three coal mines, discharges would enter the receiving stream at RM 2.5, RM 2.0, and RM 1.5, then the stream would be modeled under steady-state conditions to

RM 0.0. Results at the furthest downstream point are shown in table 3 and in figures 4 and 5. After the initial rises from mixing, a logarithmic decay of dissolved iron is shown in figure 4 for each of the simulations. Dissolved manganese increases initially upon mixing, then decreases linearly owing to the extremely slow kinetics. The first discharge accounts for 53 percent of the total increase in dissolved manganese between the initial concentration and the concentration resulting from five discharges.

The dissolved-oxygen concentration at the upstream site ( $R_0$ ) drops sharply after mixing with the first mine discharge at RM 2.5, then slowly decreases as the oxygen is lost to FOD and MOD. The results obtained from simulating one discharge is unique; oxygen concentration begins to increase after RM 1.5. Reaeration is greater than oxidation because almost all of the iron has been oxidized and very little MOD has taken place. The first discharge accounts for 74 percent of the total decrease in dissolved oxygen between zero and five coal-mine discharges. The remaining four discharges account for only 26 percent of the decrease at RM 0.0. Similar results are shown for the pH. The first discharge accounts for nearly two-thirds of the total decrease in pH.

In general, the curves show that for relatively conservative species (Mn(II)), as well as oxygen and pH, the cumulative impacts of iron and manganese oxidation from additional discharges is degressive. That is, as more coal mines discharge to a receiving stream, the incremental change in concentration at a point downstream becomes less. In these simulations, the first discharge accounted for 50 to 75 percent of the change in concentration. For reactive species, such as dissolved ferrous iron, the first few discharges may result in equilibrium concentrations at the furthest downstream point (RM 0.0), depending on the magnitude of the oxidation rate. Additional discharges increase the downstream concentration in fairly uniform increments once equilibrium is achieved.

Comparing the downstream values from only one coal-mine discharge with the values from five discharges shows that dissolved iron increased 1.82 mg/L, dissolved manganese increased 1.50 mg/L, dissolved-oxygen concentration decreased 0.24 mg/L, and pH decreased 0.30 units. Compared with the baseline simulation, dissolved iron from five discharges increased the same, 1.82 mg/L, whereas, dissolved manganese increased 3.17 mg/L, dissolved-oxygen concentration decreased 0.92 mg/L, and pH decreased 0.88 units.

Comparing the downstream values from five discharges with the representative mine discharge characteristics in table 3 shows that nearly 75 percent of the dissolved ferrous iron from all five discharges oxidized to ferric iron and precipitated theoretically. Only 19 percent of the dissolved manganese (II) oxidized. Therefore, manganese builds up in the receiving stream.

## Sensitivity Analyses

Several simulations were run in order to determine the sensitivity of the technique to changes in parameter values. The simulations were grouped according to the parameter types: chemical, physical, and kinetic. Results of these simulations are shown in table 4 and in figures 6, 7, and 8. All of these simulations were run with five coal mines discharging into the receiving stream and, therefore, can be compared to the original simulation with five discharges. The pH is relatively insensitive to the parameter changes shown, except alkalinity and dilution. Therefore, pH has not been included in the figures.

Effects from varying certain chemical parameters are shown in table 4 and in figure 6. Dissolved-oxygen concentration in the discharge was set to 0.0 mg/L in one simulation. Consequently, the oxidation rate was initialized at 0 per day, then gradually increased as oxygen was produced from reaeration. This anaerobic state could result from discharges originating at or near the bottom of a stagnant sedimentation pond. Dissolved-iron concentration was thirty percent greater as a result of the low oxygen and the slow oxidation. Dissolved oxygen was 2.65 mg/L lower at RM 0.0 than the original simulation (see table 4) owing to the lower initial concentrations and less FOD and MOD. This is a significant decrease in oxygen in the receiving stream and implies that these discharges should be aerated. Oxygen concentrations could be increased by installing splash blocks to aerate the solution below the point of discharge or by discharging from the pond surface.

The regulated 30-day averages for total iron and total manganese (3.5 mg/L and 2.0 mg/L, respectively) were input as discharge concentrations (Federal Register, 1982, p. 45395). As shown in table 4, values at RM 0.0 are 0.91 mg/L and 1.63 mg/L, respectively, or exactly half of the final concentrations in the original simulation. In the next simulation, the alkalinities of the discharge and the receiving stream were decreased an order of magnitude. Although the equilibrium concentrations of iron (II) and manganese (II) are normally affected by the alkalinity of a solution, the simulated iron and manganese concentrations at RM 0.0 did not change. The pH of the stream dropped from 6.12 to 5.74 as a result of the reduced capacity of the stream to buffer the increased hydrogen ion activity.

The amount of discharge and the distance were varied as the physical parameters of the sensitivity analyses. Additionally, a simple mass balance was calculated and included in figure 7. In the first simulation, the results for the reactive species, dissolved iron, are much higher because mass balance treats all elements as strictly conservative. The mass balance approximation for a relatively conservative species, such as dissolved manganese, is fairly accurate. Results for dissolved oxygen are only 0.46 mg/L greater (see table 4). Although not shown, the pH is within one percent of the value produced with the theoretical technique.

The receiving stream was increased to 20 ft<sup>3</sup>/s in the next simulation. The iron and manganese concentrations in figure 7 show the effects from this dilution. The oxidation rates in the receiving stream were increased as a

result of the higher pH and oxygen concentration. At RM 0.0, the dissolved-iron concentration is near equilibrium, whereas dissolved manganese is less than one-third of the concentration of the original simulation.

The distance from the point of discharge to the receiving stream (see figure 1) was decreased from 0.5 miles to 0.05 miles or 264 feet. Very little change is seen in the results at RM 0.0. Coal-mine discharges were located at 0.1 mile intervals instead of 0.5 miles in the next simulation. As shown in figure 7, the increase in dissolved iron and dissolved manganese in the first half-mile was very large. But after reaching a peak concentration of 4.09 mg/L, the iron decreased to a value 0.69 mg/L below the original simulation owing to the long time-of-travel available for oxidation. Manganese concentrations peaked after the last discharge at RM 2.1, then oxidized very slowly and decreased nearly to the original concentration.

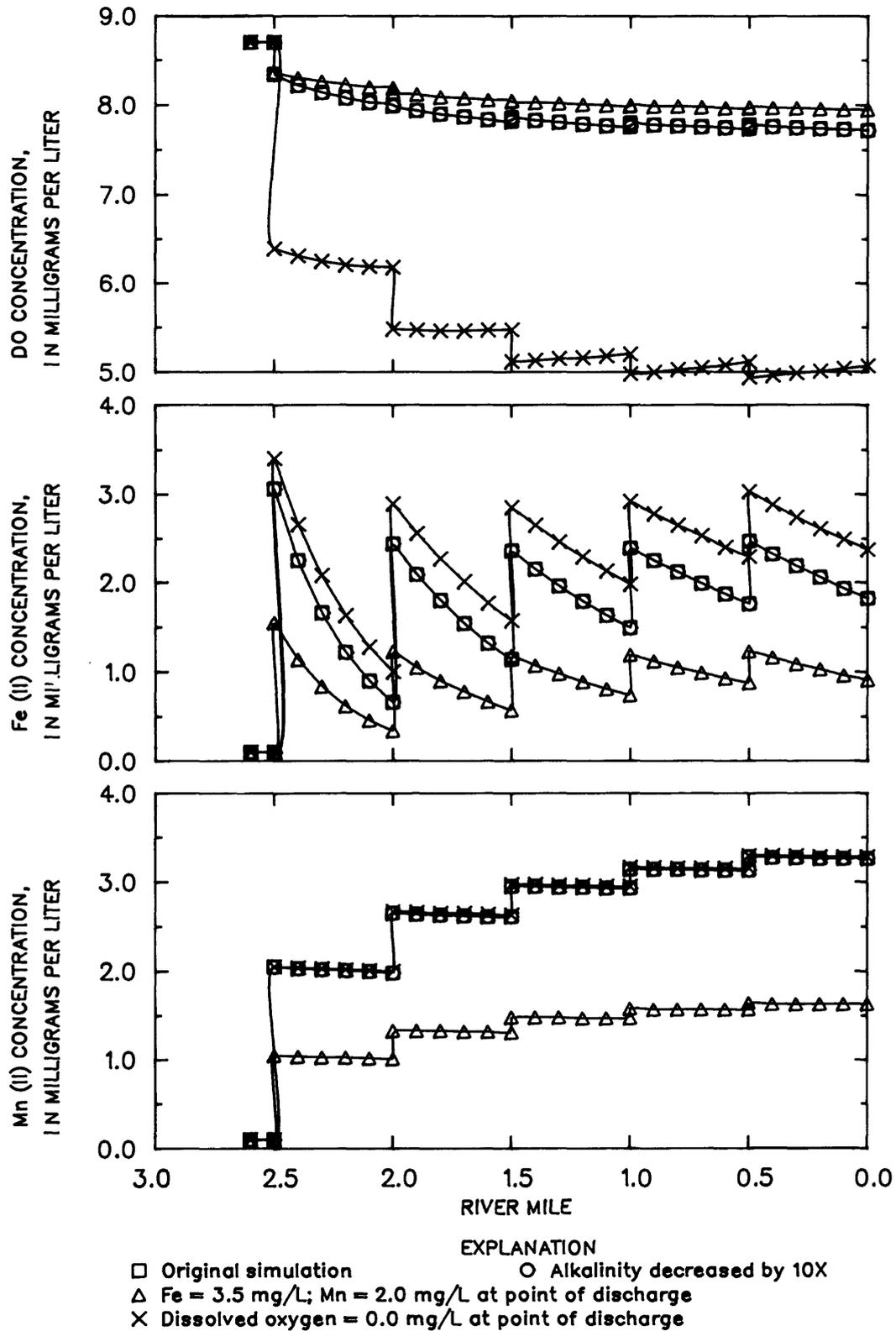
Table 4.--Simulated stream characteristics resulting from the sensitivity analyses with five coal mines discharging at half-mile intervals<sup>1</sup>

Parameter changes	Dissolved oxygen <sup>2</sup>	Dissolved iron (II)	Dissolved manganese (II)	pH	Alkalinity as CaCO <sub>3</sub>
Original simulation	7.72	1.82	3.26	6.12	71
DO=0.0 mg/L <sup>3</sup>	5.07	2.37	3.28	6.13	72
Fe=3.5 mg/L; Mn=2.0 mg/L <sup>3</sup>	7.95	.91	1.63	6.14	73
Alkalinity decreased 10X	7.72	1.82	3.25	5.74	4
Flow at R <sub>0</sub> =20 cfs	8.13	.03	1.05	6.58	117
Distance=0.05 miles <sup>3</sup>	7.71	2.09	3.25	6.12	71
Discharge interval=0.1 mile	7.66	1.13	3.24	6.11	71
Mass balance	8.18	5.85	3.35	6.17	75
Oxidation rate decrease 10X	8.10	5.02	3.34	6.15	74
Oxidation rate increase 10X	7.48	.01	2.49	6.09	68
Reaeration rate decrease 10X	7.59	1.82	3.26	6.12	71
Reaeration rate increase 10X	8.08	1.82	3.26	6.12	71

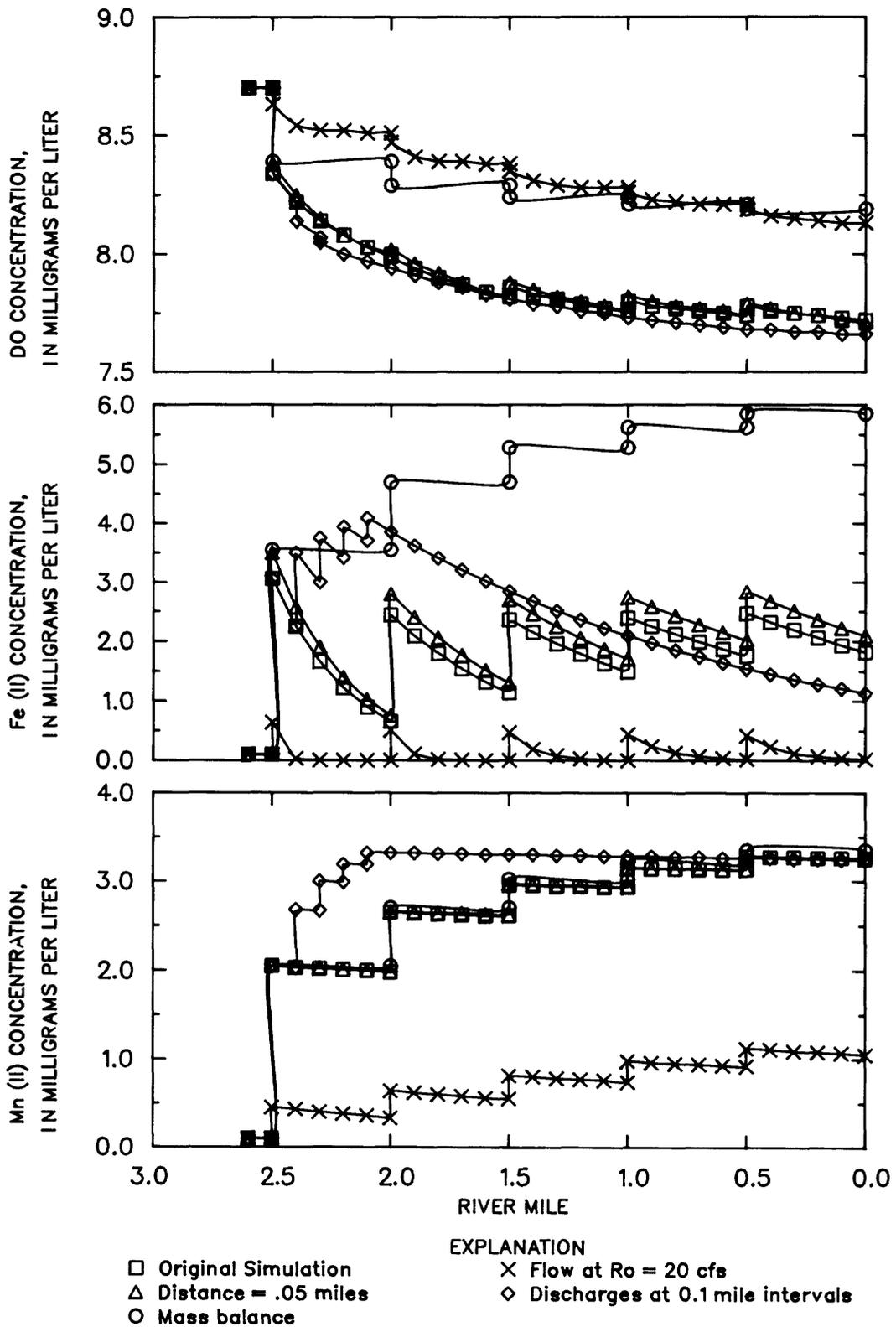
<sup>1</sup>Results are shown for the furthest downstream point (RM 0.0 in figures 6, 7, and 8).

<sup>2</sup>All units are in milligrams per liter except pH.

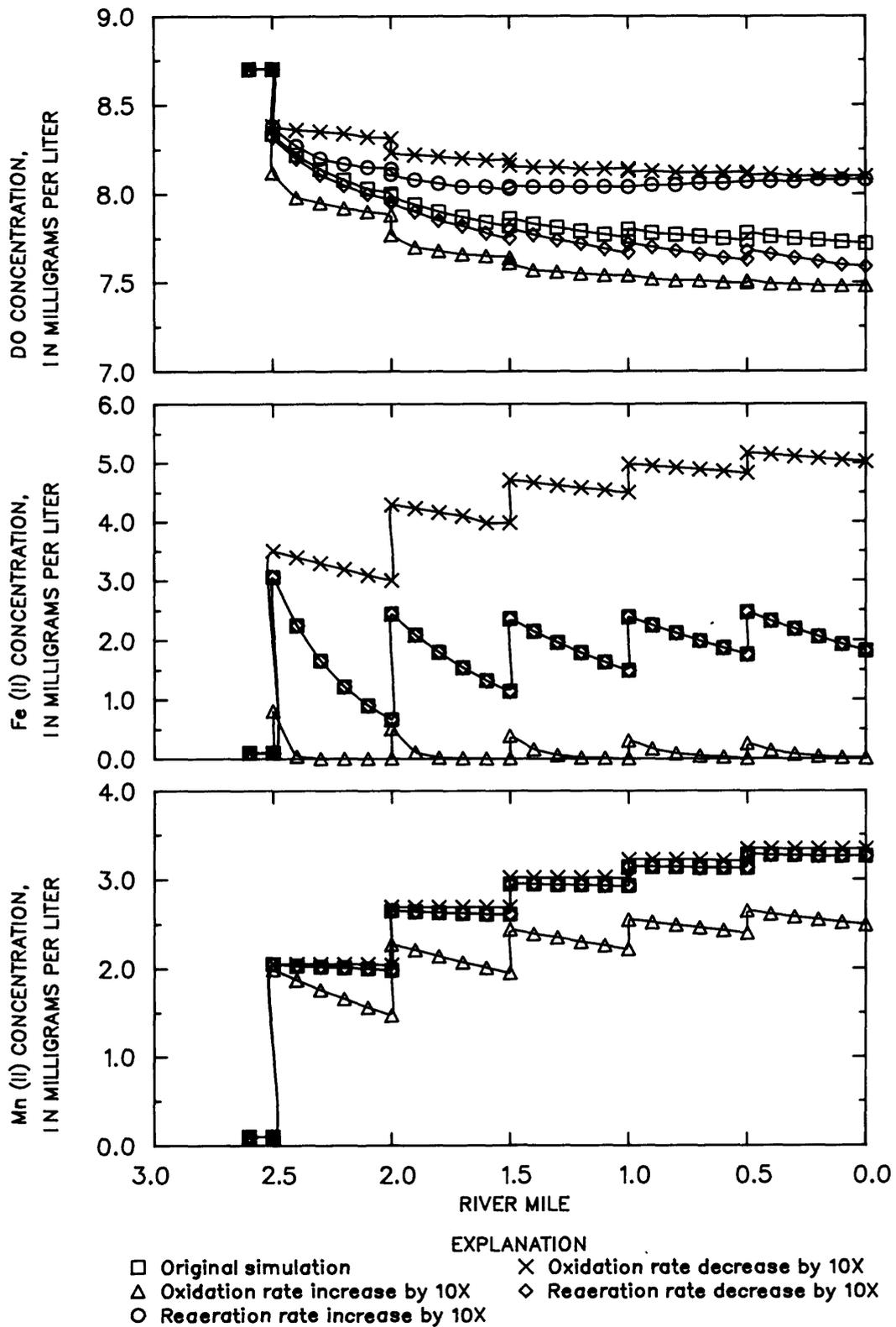
<sup>3</sup>These parameter changes pertain to the coal-mine discharge only.



**Figure 6.** -- Results of the chemical sensitivity analyses on concentrations of dissolved oxygen (DO), dissolved iron (II), and dissolved manganese (II) in streams receiving discharge from five coal mines at half-mile intervals.



**Figure 7. -- Results of the physical sensitivity analyses on concentrations of dissolved oxygen (DO), dissolved iron (II), and dissolved manganese (II) in streams receiving discharge from five coal mines at half-mile intervals.**



**Figure 8.** -- Results of the kinetic sensitivity analyses on concentrations of dissolved oxygen (DO), dissolved iron (II), and dissolved manganese (II) in streams receiving discharge from five coal mines at half-mile intervals.

The oxidation and reaeration rates were varied by an order of magnitude in the final group of sensitivity analyses. The ferrous and manganous oxidation rates were decreased by a factor of 10 in the first of these simulations. The results in figure 8 show dissolved iron as a fairly conservative species with little oxidation taking place. The final concentration is 3.20 mg/L greater than the original simulation (see table 4). When the rates were increased an order of magnitude, the dissolved iron decreased nearly to the equilibrium concentration. Dissolved manganese decreased approximately 25 percent compared with the original simulation. Iron and manganese concentrations were not affected by changes in the reaeration rate. Increased reaeration and decreased oxidation rates resulted in similar dissolved-oxygen concentrations at RM 0.0. Increased oxidation and decreased reaeration also resulted in similar oxygen concentrations. In these simulations though, the net change in dissolved oxygen was less than 0.4 mg/L.

In summary, iron oxidation rate, dilution, and low initial concentrations of the dissolved constituents in the mine water had the most pronounced effect on stream quality at RM 0.0. Dissolved iron was fairly sensitive to direct changes in the oxidation rate and indirectly through decreased oxygen concentrations. Changes in the reaeration rate had a negligible effect on all downstream constituents. As long as some oxygen was available, iron and manganese were not affected. Mass balance calculations gave a good approximation for concentrations of oxygen and manganese. pH was relatively insensitive to parameter changes.

#### SUMMARY AND CONCLUSIONS

A theoretical technique is proposed for predicting the maximum cumulative impact from the oxidation of iron and manganese on the dissolved-chemical quality of streams receiving discharge from coal mines. Regulatory agencies are required to consider the probable cumulative impact of anticipated coal mining before granting a permit. Although this includes chemical, physical, and biological impacts on the hydrology of the area, the technique is limited to the theoretical chemical effects of iron and manganese oxidation.

The technique is based on the stoichiometry of ferrous iron and manganous manganese oxidation and precipitation. As one mole of Fe (II) is converted to Fe (III) and as one mole of Mn (II) is converted to Mn (IV), three-quarters of one mole of oxygen is consumed and four moles of hydrogen ion are produced. The amount of metals oxidized and precipitated, the effects on pH and dissolved oxygen, and the changes in concentration of elements owing to mass balance and chemical reactions are calculated in the technique.

A coupling program dynamically links two existing U.S. Geological Survey computer programs: the one-dimensional, steady-state stream, water-quality program and the pH, redox, and equilibrium equations (PHREEQE) program. The water-quality program calculates concentration changes in iron, manganese, and dissolved oxygen as a function of reaction rates and time-of-travel. PHREEQE simulates geochemical reactions; calculates saturation indices, alkalinity, and pH; and mixes two solutions. The reaction kinetics drive the system, whereas thermodynamics provide the limiting situation.

Although data were not available to test the technique, simulations with data representative of southwestern Indiana were run to illustrate the operation of the technique and to determine its sensitivity to changes in chemical, physical, and kinetic parameters. The theoretical impact on streams receiving identical discharges from zero to five coal mines was simulated. Results showed that the discharge from the first coal mine accounted for 50 to 75 percent of the total changes in pH, dissolved oxygen, and dissolved manganese for the entire system of five coal mines. For dissolved iron, additional discharges resulted in fairly uniform increases above equilibrium in concentrations downstream. Comparing the results from five coal-mine discharges with the ambient water quality shows a decrease of almost 1 mg/L in dissolved oxygen and 1 pH unit due to ferrous and manganous oxidation and mass balance.

In general, the simulations showed that the oxidation of the maximum legal concentrations of iron and manganese (assuming the reduced, dissolved state) in the discharge from five coal mines does not have a dramatic cumulative impact on downstream concentrations of dissolved oxygen or pH. Enough oxygen is transferred into solution as a result of atmospheric reaeration to offset most of the oxygen lost to ferrous and manganous oxidation. The carbonate system in solution provides enough alkalinity to minimize pH effects. Approximately 75 percent of the ferrous iron in the mine discharge oxidized to ferric iron and precipitated theoretically as amorphous ferric hydroxide. On the other hand, over 80 percent of the dissolved manganese remained in solution as a result of the slow kinetics. Therefore, manganese builds up in the receiving stream.

The technique is most sensitive to changes in iron oxidation rate, amount of flow in the receiving stream, and low initial constituent concentrations in the mine discharge. Changes in atmospheric reaeration rate had a negligible effect on water quality at RM 0.0 because oxygen was never limiting. Mass balance approximations for dissolved oxygen and dissolved manganese were close to the original results of the simulations. pH was relatively insensitive to changes in parameters.

This theoretical technique is readily available and is flexible enough to be used by any regulatory agency. Although the technique is presented on a theoretical basis, reasonable results have been produced with various simulations. However, validation is required in order to apply the technique to real systems. This should be accomplished in subsequent work.

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