Modeling the Iron Cycle in Stream Systems

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ABSTRACT

An unsteady, dynamic receiving water quality simulation model was developed which includes three trophic levels and the iron cycle. This model was applied to a river system in which the greatest portion of the dry-weather flow is mine drainage water from open-pit soft-coal mines. This drainage water contains very high concentrations of iron. The simulation results show that the contribution of iron discharged out of the streambed sediments into the water column is very significant and that future simulation models must describe this process more accurately than to date.

INTRODUCTION

Mining activities are usually associated with massive alterations of the water balance and the aquatic ecosystem. The following paper covers the unique problems resulting from mining activities in the watershed of a tributary of the Rhine River in Germany. Further, procedures for quantifying the impacts of pit water on the aquatic environment are described.

STUDY AREA

The river considered here is a left bank tributary of the Rhine River in Northrhine-Westphalan, Germany. It is about 100 km long and has an area of around 1800 km^2. In the lower reaches soft coal is mined in extremely large open-pit mines. These pits require a regional lowering of the watertable, in places up to 200 meters. The greatest portion of this pumped ground water is discharged into the river. This ground water accounts for about two-thirds of the total discharge of the river.

The organic pollution-load of this mine drainage water is quite low, in fact, the drainage waters dilute the urban discharges into the river system. The nutrient loading is negligible, and the pH varies between a very reasonable 6.5 and 9. The low dissolved oxygen concentrations (<5 mg/l) and the high temperatures (between 13°C and 26°C) present some problems.

The main problem, however, is the high total iron concentrations, they lie between 2 mg/l and 8 mg/l. The iron precipitates with the presence of oxygen in the stream water, which covers the streambed with a crust. This aggravates the benthic ecosystem. There are grounds for the assumption that the precipitated iron influences the natural metabolism of the benthic animals. Crusts of iron on the gills of fish have been observed which contributed to their death.

Extensive water resources measures are planned in the watershed. A planning tool which could predict the impacts of these measures on the stream water quality in the watershed was needed to optimize these investments. Included in the planned measures are the enlargement of wastewater

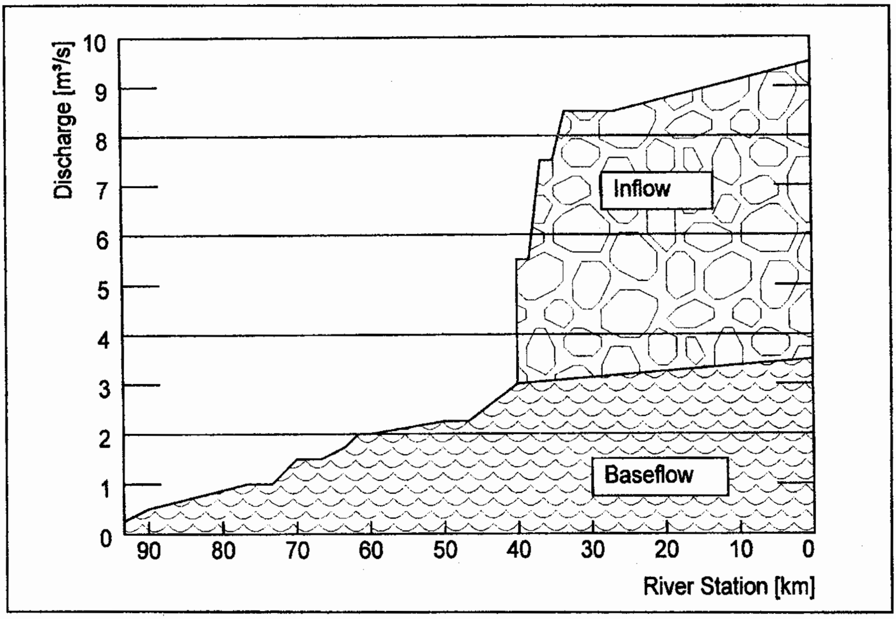

Figure 1: Hydrologic longitudinal section

treatment facilities, the new construction of stormwater retention basins and the rehabilitation of the river and its tributaries. This rehabilitation process is sometimes referred to in Germany as an *unleashing* of the river system. A stream water quality model was developed for this reason which included the influences of iron in the mine drainage waters.

MODEL PROCEDURES

Kinetics of the Iron Cycle

Iron under reduced conditions is found in the ferrous (Fe^{2+}) form. These conditions are almost always found in ground water as in the study area. In the presence of oxygen Fe^{2+} oxidizes to Fe^{3+} (Sigg and Stumm, 1991, pg. 265)

$$Fe^{3+} + e = Fe^{2+} \quad . \tag{1}$$

The kinetics of the iron-oxidation is a function of oxygen concentration and pH (Sigg and Stumm, 1991, pg. 282)

$$\frac{d[Fe^{2+}]}{dt} = -k_H \frac{[O_2(aq)]\,[Fe^{2+}]}{[H^+]^2} \tag{2}$$

where

$[Fe^{2+}]$ = concentration of the ferrous iron [mol/l],

$[O_2\,(aq)]$ = concentration of the dissolved oxygen [mol/l],

$[H^+]$ = concentration of the hydrogen ion (corresponds to pH) [mol/l] and

k_H = kinetic coefficient [mol/l/min],

= 3×10^{12} mol/l/min at 20°.

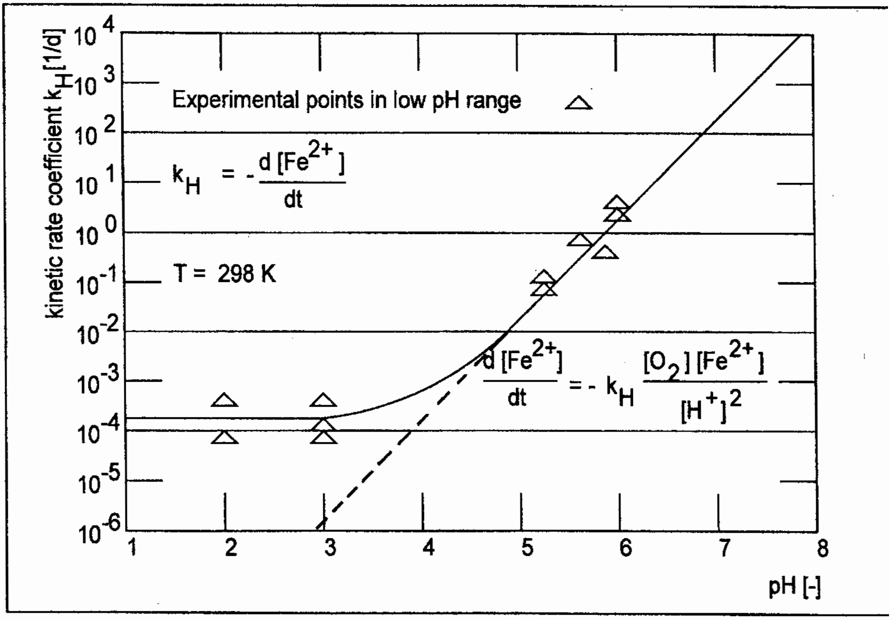

Figure 2: Oxidation rate of ferrous iron as a function of pH (after Stumm and Morgan, 1981, pg. 467)

Figure 2 represents the rate of oxidation of iron as a function of pH. It can be seen here tha the oxidation rate is constant at low values of pH while at higher values it is inversely proportiona to the square of the pH.

The mass of the produced ferric iron can also be derived from Equation [2] with a smal modification. The ferric iron forms flocks which sink to the streambed. Here a crust is forme which is very hard. This is the process of ferric incrustation. The kinetic differential equations fo this process are

$$\frac{d\left[Fe^{3+}\right]}{dt} = + k_H \frac{\left[O_2(aq)\right]\left[Fe^{2+}\right]}{\left[H^+\right]^2} - k_{PRECIP}\left[Fe^{3+}\right] \qquad [3]$$

and

$$\frac{d\left[Fe(s)^{3+}\right]}{dt} = + k_{PRECIP}\left[Fe^{3+}\right] - k_{SETT}\left[Fe(s)^{3+}\right] \qquad [4]$$

where

$[Fe^{3+}]$ = concentration of the dissolved ferric iron [mol/l],

k_{PRECIP} = precipitation rate of the ferric iron into flocks [1/h],

$[Fe(s)^{3+}]$ = concentration of the precipitated ferric iron [mol/l] and

k_{SETT} = settling rate of the ferric iron flocks to the streambed [1/h].

The other terms are defined above.

Oxygen is consumed with the ferrous oxidation process. The kinetic differential equation for the modeling of oxygen requires an additional sink term (Smith, 1978)

$$\frac{d\left[O_2\right]}{dt} = \ldots - FekO_2\, k_H \frac{\left[O_2(aq)\right]\left[Fe^{2+}\right]}{\left[H^+\right]} \qquad [5]$$

where

$FekO_2$ = stoichiometric constant between ferrous iron and the dissolved oxygen [-],

= 0.143 mg O_2/mg Fe^{2+}.

It is commonly conceived that pore water in streambed sediment is anaerobic or anoxic. It can, therefore, be assumed that the redox potential in the sediment is negative. This situation provides the conditions where the ferric iron can be reduced to ferrous iron and discharged back into the water column again.

The redox potential can be calculated with the Nernst Equation (Sigg and Stumm, 1991, pg. 263)

$$E_h = E_h^o + 2.3\,\frac{R\,T}{F}\log\frac{\left[Fe^{3+}\right]}{\left[Fe^{2+}\right]} \qquad [6]$$

where

E_h = redox potential [V],

E_h^o = redox potential for standard conditions [V],

= 0.77 V at 25°,

R = universal gas constant, 8.314 J/mol/K and

F = 1 Faraday.

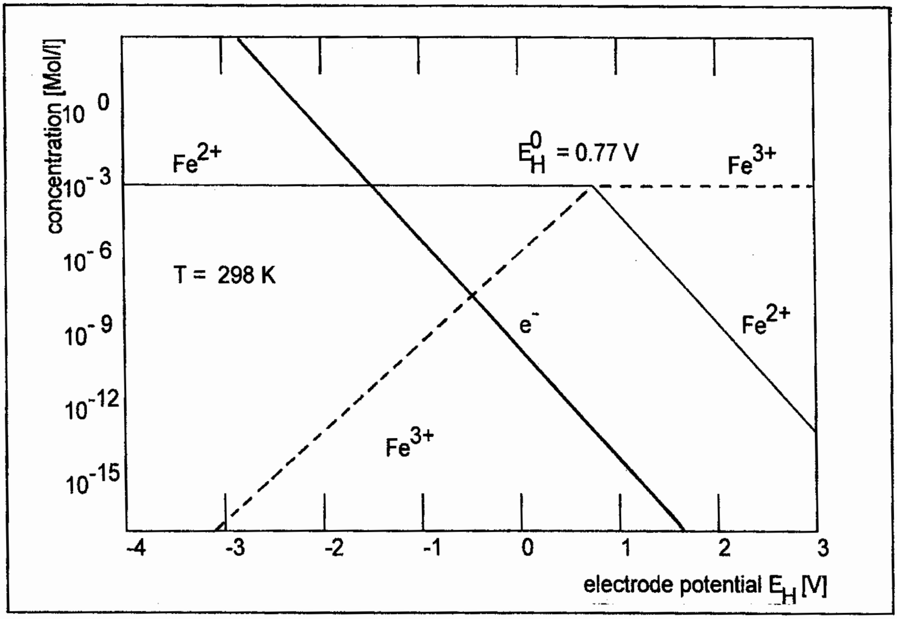

Figure 3: Redox equilibrium Fe^{3+} / Fe^{2+} (after Sigg and Stumm, 1991, pg. 266)

Figure 3 is an example redox equilibrium for a solution of 10 mol/l.

The resolution of ferric iron out of the streambed sediment can be approximated with the kinetic equation

$$\frac{d\left[Fe(s)_{sed}^{3+}\right]}{dt} = -\,k_r\left[Fe(s)_{sed}^{3+}\right] + k_{SETT}\left[Fe(s)^{3+}\right] \qquad [7]$$

where

$[Fe(s)_{sed}{}^{3+}]$ = equivalent concentration of ferric iron in the sediment [mol/l] and

k_r = rate coefficient for the resolution of sediment ferric iron to ferrous iron [1/h].

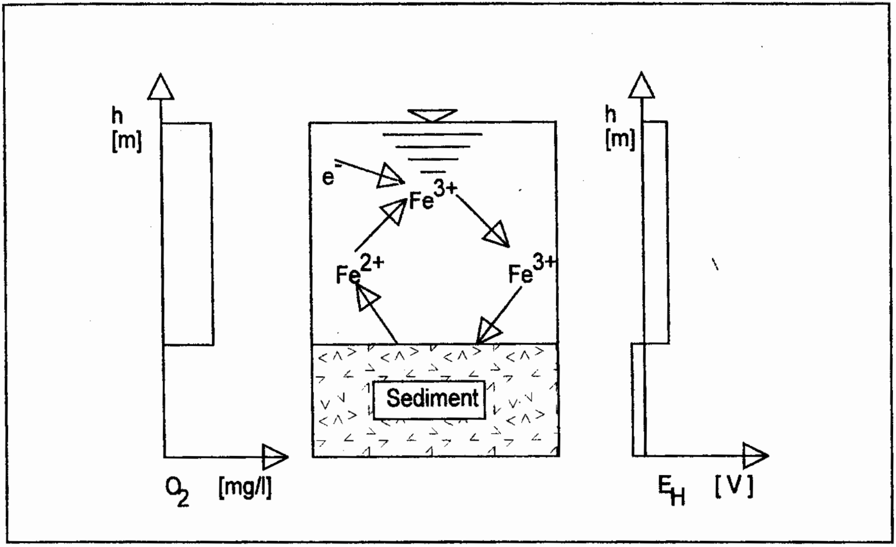

Figure 4: Schematic description of the iron cycle

The kinetic iron-oxidation equation, Equation [2], must be expanded to represent the complete instream ferrous iron-cycle dynamics

$$\frac{d[Fe^{2+}]}{dt} = - k_H \frac{[O_2(aq)]\,[Fe^{2+}]}{[H^+]^2} + k_r \left[Fe(s)^{3+}_{sed}\right] \qquad [8]$$

For the sake of completeness it should be mentioned that ferric iron forms precipitates with orthophosphate. Here 1.8 mg Fe^{3+} combines with 1.0 mg oPO_4-P. This process was not considered in this study as it was not considered to be of significance in the river system studied.

Modeling Approach

A stream water quality model was set up to analyze the impacts of the mine drainage on the aquatic ecosystem and to plan mitigation measures. The Water Quality for River - Reservoir Systems (WQRRS) model of the Hydrologic Engineering Center (Smith, 1978) was expanded to include an iron-cycle module. WQRRS is an unsteady, dynamic receiving water model. It can simulate the *unsteady* discharge as well as *dynamic* physical, chemical and biological processes in the stream system.

The model is modular in character. This allows for the easy modification of the simulated processes dependent on the dominant ecosystem processes and the availability of input data. The water chemistry section of the model allows for the dynamic calculation of pH dependent on the water hardness in each computational element in the system. The dissolved oxygen concentration is dependent on the C-BOD, nitrification, algae growth and decay and the reaeration. If sufficient data are available, a second (zooplankton, benthic animals and aquatic insects) and third (fish) trophic level can be included in the simulation.

The model simulates components in the water column with the complete advection-dispersion equation and the various kinetic transfers of one component to another. The contribution of substances out of the streambed sediment in only simulated with simple transfer functions. In order to reduce the programming effort to an acceptable level it was decided to represent the iron precipitation process as a first-order decay process. This is a classical algorithm in water quality simulation. The reaction of ferrous to ferric iron and its resulting oxygen demand were neglected in this model development phase. This assumption is quite realistic as the reaction times for these processes are very fast (minutes) at the instream pH values in comparison with the simulation time steps (hours). The simplified model equations used were

$$\left[Fe_{total}\right] = \left[Fe^{2+}\right] + \left[Fe^{3+}\right] + \left[Fe(s)^{3+}\right] \qquad [9]$$

and

$$\frac{d\left[Fe_{total}\right]}{dt} = -\,k\left[Fe_{total}\right] \qquad [10]$$

where

$[Fe_{total}]$ = total iron concentration in the water column [mg/l] and

k = removal rate of total iron due to settling [1/h].

RESULTS

Extensive preliminary investigations were carried out before beginning with the simulations. A large effort was made to see that the water balance in the stream system was correct. This was accomplished by comparing base flow plus all of the discharges to the stream system with instream discharge records. A very good water balance was achieved as a result of a calibration measurement campaign.

Subsequently, a chloride balance was carried out. The instream chloride concentrations (ca. 60 mg/l) were at a level where chloride can be considered as a conservative substance. The chloride balance was also very good which leads to the conclusion that the base and discharge flows used were correct.

The simulations showed lower concentrations of total iron in the water column than the stream samples. The results of the water and chloride balances exclude the possibility of measurement or data errors as the origin of this discrepancy. Even with a total iron removal rate $k = 0.0$ / h the simulated concentrations were lower than those measured. Numerically it would have been necessary to have a negative removal rate in order to achieve a compatibility between simulated concentrations and those measured. Physically this means in reality the so called "decay rate" is a "production rate". This is only explainable when iron is redissolved in the sediment and released into the water column at a rate much higher than originally assumed. For the sake of the acceptance of the model it was decided at this time not to use a negative decay rate in further

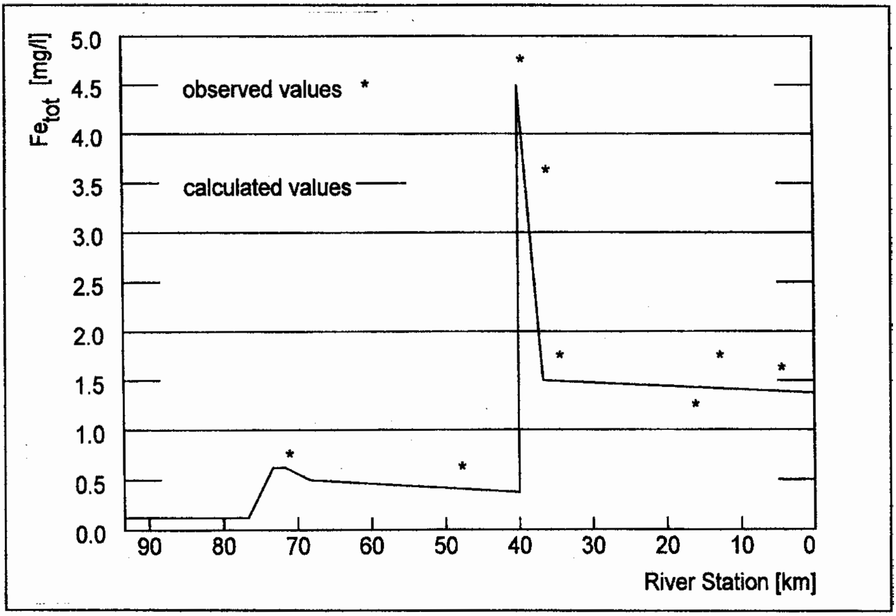

Figure 5: Comparison of measured and simulated total iron concentrations

simulations.

CONCLUSIONS

It must be concluded that the movement of iron out of the streambed sediments has a very significant influence on the water column iron concentrations. There are two possibilities for the source of this iron. The resolution of ferrous iron in the reductive environment of the streambed sediments, Equation [7], is the most obvious source. A further source of this iron is the erosion and resuspension of the iron sediments. Preliminary calculations indicate that even during high flows conditions the streambed shearstress would not be high enough to remove the ferric incrustation. The shearstress levels needed to breakup these kinds of incrustations must be studied with experiments in hydraulic laboratory flow channels.

The next step in the model development would be the incorporation of a more detailed module for the streambed sediments. This module would consider the dissolved oxygen and redox potential in the sediment pore water. With such a module and the kinetic relationships described above it will be possible to simulate the iron cycle correctly in stream systems.

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