Numerical modelling of the iron/sulphur-cycle in the sediments of lakes affected by acid mine drainage

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The oxidation of anoxic materials during open pit brown coal mining leads to appreciable chemical changes in these materials and the adjacent groundwater. Especially the weathering of accompanying pyrite leads to acid mine waters rich in sulphate and iron and very low in pH. If mining operation is ceased, the mining pits are flooded with groundwater, and the water of the residual lakes shows typically a pH value of about 3. Because of this low pH the lakes can not be used for fishery or leisure activities. Assessment of the long-term behaviour of such lakes and especially of potential neutralization mechanisms are therefore of public interest. In the following we present a numerical study on the chemical and biochemical processes taking place in the sediment of an 30 yeras old acidic lake in the Lusatian mining area near Lauchhammer, Germany. The objective of this study is to describe and quantify possible in situ neutralization processes in the sediment of these lakes.

(Bio)Chemical reactions

The partly oxidized pyrite bearing mining dumps continously release sulphate- and Fe^{2+}-rich groundwater. If this still anoxic water reaches the surface (e.g. in a river or a lake) the reaction with atmospheric oxygen leads to the oxidation of reduced iron and the subsequent precipitation of iron oxyhdroxides, such as goethite (γ-FeOOH) or schwertmannite ($Fe_8O_8(OH)_6SO_4$). This process leads to further acidification according to the following reaction:

$$Fe^{2+} + \tfrac{1}{4}O_2 + \tfrac{3}{2}H_2O \rightarrow FeOOH + 2H^+ \qquad (1)$$

Possible neutralization processes may occur in the sediment, where iron reduction and sulphate reduction by bacteria can lead to the formation of iron monosulphides or pyrite:

$$2CH_2O + 8FeOOH + 16H^+ = 2CO_2 + 8Fe^{2+} + 14H_2O \qquad (2)$$

$$2CH_2O + SO_4^{2-} + H^+ = HS^- + 2CO_2 + 2H_2O \qquad (3)$$

$$Fe^{2+} + HS^- = FeS + H^+ \qquad (4)$$

CH_2O denotes the microbially available organic carbon of the sediment. Equations (2), (3), and (4) express iron and sulphate reduction and iron monosulphide formation, resp. Peine and Peiffer (1996) have shown that the formation of iron sulphide is an indicator of in-lake neutralization.

Measurements

The measurements were performed for the residual lake 77 (RL 77) by S. Peiffer and A. Peine and coworkers from the Limnological Research Station of the University of Bayreuth, Germany. RL 77 covers a surface area of 0.24 km^2 and the water reaches a maximum depth of 7 m. About 30 years have been elapsed since initial flooding and the pH of the lake water is about 2.9. The water shows a sulphate content of about 10 mM and a dissolved iron Fe^{3+} content of 1 mM. While the epilimnion contains almost no reduced iron, the hypolimnion is anoxic during summer stratification and shows Fe^{2+} concentrations up to 10 mM. Furthermore the pH value is increased to 3.5 during this period.

The porewater of the sediment shows a rapid increase of pH up to nearly neutral values in a sediment depth of about 10 cm. Microbial sulphate reduction, which was measured in a sediment core by a ^{35}S-tracer technique, and an increasing concentration of Fe^{2+} appear in a sediment zone between 5–20 cm below sediment-water-interface. Batch experiments did not show bacterial iron reduction in the neutral sediment zone. The sediment material of the lake consists of the former mining pit surface, overlayn by about 15 cm of newly precipitated sediments, which are composed nearly exlusively of iron hydroxides. A weak accumulation of reduced sulphur could be observed in some of the sediment cores.

The numerical model

We used the numerical model TBC (*T*ransport, *B*iology and *C*hemistry, Schäfer *et al.*, 1998) to simulate the reactive transport in the sediment. The model allows to calculate multi-species transport including biochemical and chemical reactions. Biochemical reactions are simulated via microbial growth controlled by Monod kinetics, while chemical reactions may be either handeled as fast equilibrium or slow kinetic reactions.

TBC is very flexible model as it is not limited to a fixed set of equations but supports the reproduction of a large variety of possible reactions. The model provides the general structure of the reactive transport processes, whereas the user assembles the specific reactive model for the site under investigation. To embed the residual lakes in the regional flow system, large scale groundwater flow was modelled with MODFLOW (McDonald and Harbaugh 1988).

Results

To assess the reactive pathways in the sediments we considered a number of different possible reactions in the numerical modelling process. Preliminary calculations showed, that the sulphide produced by sulphate reduction would lead to a larger accumulation of iron sulphides, if precipitation was the relevant long-term sulphide sink in the sediment porewater. According to the observations, the reactive system had to fulphill the conditions that only minor amounts of iron sulphide will accumulate and that pH and Fe^{2+}-concentrations will increase in the sediment.

Two different situations concerning the fate of sulphide were taken into account:

(1) Initial formation of iron sulphides and subsequent oxidation of the sulphides with Fe^{3+} from the lake water as oxidant.,

(2) Reductive dissolution of iron hydroxides with dissolved sulphide as reducing agent.

The simulation results suggest that sulphate reduction should be the major biochemical redox reaction in the sediments. Sulphide produced during sulphate reduction will be re-oxidized by iron hydroxides:

$$8FeOOH + H_2S + 14H^+ = 8Fe^{2+} + SO_4^{2-} + 12H_2O$$

Initial formation of iron sulphides and subsequent oxidation with dissolved Fe^{3+} should be of minor importance, as the diffusive transport of Fe^{3+} from the overlaying lake water is too slow. Furthermore protons are produced during the oxidation of iron sulphides, which is not consistent with the observered increase in pH.

Thus the dominating sulphide consuming process seems to be the chemical reduction of iron hydroxides by dissolved sulphide. Obviously the fast sulphide oxidation via iron hydroxide reduction keeps porewater sulphide concentration too low for the precipitation of iron sulphides even in the neutral zone of the sediment.

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