Relevance of sulphate reduction for model based prognosis of mine water quality development with reactive mass transport concepts

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Abstract For adequate prognosis of mine water quality a reactive mass transport model has been used which allows for detailed process analysis including microbial catalysed reactions. It is obvious that bacteria activities influence mine water quality development and therefore affect water management and environmental impact. It could be shown that model results even with simplified approach give insight into process dynamics and interdependencies for sulphide formation and iron solid phases. However further studies on the microbial background are required for better model calibration and long term prognosis.

Key Words reactive mass transport, modelling, sulphate reduction, bacteria, pump scaling

Introduction

In the European coal mining area several mines show significant concentrations of sulphide in the discharged or pumped out mine water. Because of the odour nuisance related herewith such mine water requires specific treatment causing additional investment and operating costs. Technical specification and planning have to take account of the probable quality development of the mine water.

Sulphur chemistry is driven by microbial processes to a large extent. This starts in the mine environment with pyrite oxidation caused by ventilation during active mining and can continue with sulphate reduction under oxygen free conditions after mine closure. Bacteria catalyzing these processes have been found in all environments facilitating conversion of phases otherwise metastable for long time. Sulphate reduction has been subject to intensive investigation and utilisation during enhanced groundwater attenuation in the last decade and has therefore found its way into reactive mass transport modelling.

Sulphate reduction in mine water

It is obvious that such processes can influence mine water chemistry during flooding and flushing. However few systematic investigations on microbial population in coal mines exist up to now. Because sulphate reducing bacteria could be detected in such sulphide containing mine water the causal relationship is evident. Sulphate is available in many mine inflows and in nearly all mines after flooding. The reaction product sulphide will react with many metals forming nearly insoluble sulphides. Iron is the dominating metal and reaction partner in the mine water environment during and after flooding. This precipitation of iron sulphide (FeS) leads to a suppression of sulphide release and a diminution of iron concentrations.

As a result of these processes we can see at some sites after leaching of iron and hence decreasing iron concentration an emergence of sulphide in its place (fig. 1). The sulphide concentration level gives some indication for the overall reaction rate in the mine. However we can not derive information on the chemical conversion and the processes associated with. The organic carbon source is the most important factor influencing bacterial growth though we have no indication for its nature in hard coal mines up to now. Mine water is predominantly free of DOC and specific hydrocarbons respectively. Possibly anaerobic oxidation of methane plays an important role for sulphate reduction and vice versa (Basen 2009).

Beyond nutrient supply bacterial growth is controlled by different environmental factors which will remain unknown until a detailed identification of the microbial population is available.

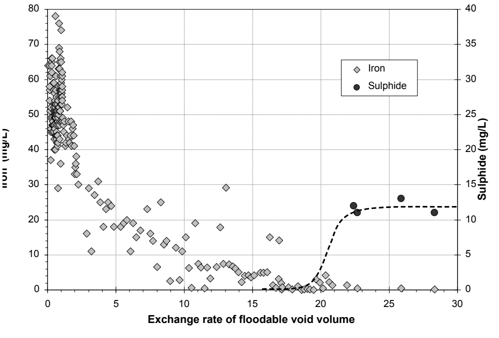

__Figure 1__ Concentration development of iron and sulphide in mine water discharge with active sulphate reduction.

Reactive mass transport concept

Numerical models have become standard tools for mine and groundwater management. As can be derived from the process analysis the interaction of flow regime, chemical reactions and microbial activity is the demand for model based prognosis of mine water quality development. All these features are combined in the DMT developed reactive mass transport model ReacFlow3D/Boxmodel enhanced during the last decade within the framework of European research projects (RFCS) in cooperation with French, Spanish and Polish partners.

The name Boxmodel refers to the potentially large areal size of the balance cells (boxes) describing hydraulically homogeneous mined areas (fig. 2). To a box all important information and components of the mine field in the hydro-geological sense are assigned: storage volume, conductivity, recharge, discharge and also information on minewater quality: pH, EH, temperature, concentrations, stored contaminants, typical minerals and more (Eckart *et al.* 2004). It is in essence a volume-balance model and uses the finite difference approach. Its features include laminar and turbulent flow, time variant input data and comfortable processing of input and output data. While developed specifically for water flow in underground mines, it can also be used for any other groundwater flow problem and can be connected with standard finite element numerical flow models like FEFLOW, ModFlow and Spring (fig. 2).

An international standard for investigation of geochemical processes in aquatic systems is the PHREEQC geochemical model, designed by Parkhurst (1995). A numerical equilibrium and reaction code (similar to PHREEQC) using the PHREEQC data set has been developed and directly integrated into the model. Approaches to couple PHREEQC with flow model codes as an external program, on the other hand, resulted in intolerably slow execution rates. ReacFlow3D has therefore been enhanced to a multi-component reactive transport model combining flow model and comprehensive reaction model.

Chemical reactions in the liquid phase do occur and make it impossible to simulate the transport of chemical components separately. Close to reality modelling requires parallel transport of the dissolved salts for each box, at the same time interval. The integration of the chemical reaction processes yields totally different results from what would have been obtained by transport modelling and application of simple mixing formulas only.

Geochemical model features

Philosophy of the reactive mass transport modelling is integration of all processes relevant for the investigated site but limitation on those really required. In spite of the flexible structure of model cells and geochemical code calculation runtime will get out of control otherwise. However RecFlow3D offers the full range of features with impact on the geochemical water evolution.

- Release of oxidation products accumulated during active mining
- Precipitation and dissolution of solid phases (= minerals)
- Reactions depending on specific reaction rates.
- Calculation of the species distribution
- pH-EH-calculation
- Consideration of reactive gas phase con-

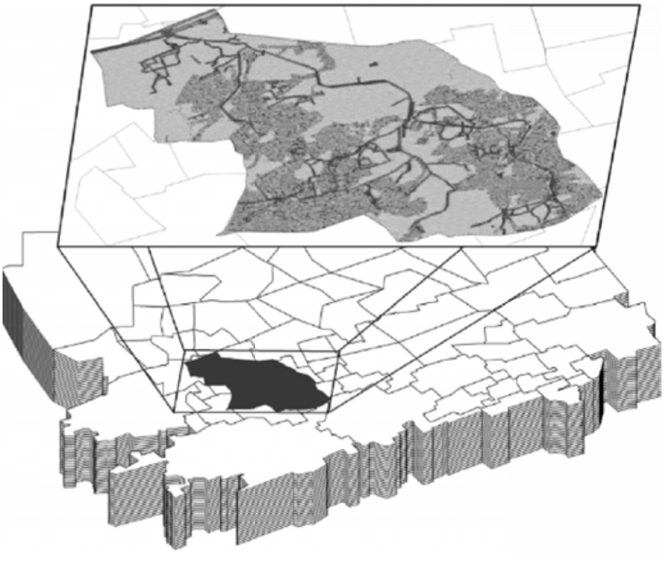

Figure 2 *ReacFlow3D example for coupling of a standard groundwater model with a mine Boxmodel.*

stituents (O_2, CO_2, CH_4)
- Sorption via exchange species on permanent surface charges of clay minerals (e.g.)
- Sorption corresponding to the surface complexation model
- Sorption with k_d coefficients
- Microbial activity given by k_d activity coefficients
- Microbial activity calculated via microbial growth and yield

Calculation of microbial growth controlled activity follows the approach of Schäfer *et al.* (2008) using the Monod kinetic concept developed for characterisation of bacteriological activities at brownfield sites.

With regard to mine water quality prognosis the described processes have different relevance in the mine environment. We distinguish three different zones especially important in terms of chemical composition and reactions:

First the flooded mine itself as reaction tank for the inflowing seepage water with products of ventilation triggered oxidation (fig. 3). Here buffering reactions with carbonate phases will take place which play an important role for mine water pH, carbonate equilibrium and subsequent reaction potential. Within a more or less closed system reactions result in elevated CO_2 partial pressures releasing CO_2 into the gaseous phase when e.g. mine water moves upwards into open voids or shafts. Therefore the gas phase has also to be considered in the reaction model. The buffering reaction stops when all acid generated is consumed depending on the geochemical equilibrium realised. In a typical mine water environment the reaction system consisting of acid–sulphate–calcium–carbonate the concentrations of calcium and sulphate are controlled by the solubility of gypsum, therefore, precipitation of gypsum is expected to occur. The enrichment of carbonate in the mine water also influences the solubility of siderite and hence the mobility of iron. The whole is system is of course differentiated by the particular salt contents and locations of the water inflows. As additional process microbial activities will superimpose this chemical evolution. As sulphate reducing bacteria require oxygen free conditions and nearly all ventilation caused oxygen will have been consumed shortly after mine closure sulphate reduction may start theoretically already during the flooding period. However some analysis taken from mine water inflows (some definitely from the rocks covering the carboniferous layer) into the active mines showed hydrogen sulphide smells and sulphide concentrations. This means that the microbial activity might be introduced from outside the mine and will grow there depending on the specific hydrochemical conditions. At present we can just refer to assumptions concerning the spatial distribution of such bacterial activities and the factors controlling the process. The chemical reactions following sulphide production can then be easily calculated as formation of hardly soluble metal sulphides.

Figure 3 *Schematic cross section with a typical mine setting.*

Secondly there is a hot spot for geochemical prognosis at the pumping stations when mine water drainage is still active. This is predominantly due to four components and the related processes:

- Iron dissolved in the mine water may (depending on pumping technology) come into contact with oxygen and precipitate as iron hydroxides in pumps and pipeworks.
- Calcite can precipitate if degasification of CO_2 results in lower partial pressure and consequently to higher pH and super saturation. However the kinetics of calcite nucleation and precipitation are quite slow. Calcite scaling is therefore quite rare but can result in objectionably hard precipitations.
- Often water from different mine fields is drained to and mixed in or near the pumps. Because of different source area or flow path and therefore differing composition those substreams can contain barium and sulphate respectively which results in spontaneous precipitation of barium sulphate. Such scalings are quite hard and cause substantial damage to pumps and limit the operating time. Objective of modelling is therefore prediction of mixing scenarios and deduction of alternative flow conditions which keep the reaction zone distant to the drainage stations.
- Similarly the mixing of sulphide and iron containing water results in iron sulphide precipitation. It seems however that FeS because of its fine grain size sticks to pump and pipe walls only to a small rate. Correct prognosis of hydrogen sulphide content is of additive importance because all sulphide species are very aggressive for corrosion of steel and even stainless steel

and may therefore cause cracking of pumps and pipes.

Because the flooded mine does not allow for subsequent changes in flow conditions the model prognosis has to provide a comprehensive evaluation of all processes described. This must be based on an accurate review of the inflows and the primary processes in the mine voids (see above) and sensitive analysis of the pump station zone. Relevant geochemical processes confine basically to precipitation processes.

Third zone of interest is the upper groundwater layer which can be affected by mine water in a future period of post-mining development or in case of collapse of hydraulic connection and hence uncontrolled rise of the water level. In contrast to the mine itself where during the flooding a quasi-equilibrium could establish mine water infiltrating here meets rocks with often totally different composition filled with water containing different salt loads. So beside water-rock interactions additionally sorption processes are to taken into account selectively retarding metals for example.

Model results

For modelling of sulphate reduction the following processes have been activated for the calculations:

- Multi-component transport with EH-pH calculation
- Bacterial sulphate reduction
- EH controlled iron dissolution from an iron hydroxide reservoir with following reduction to Fe(II)
- Precipitation of iron sulphide

This relatively simple model setup has been chosen due to the considerable lack of knowledge on the bacterial processes. As explained above we still have no detailed information on the carbon source which therefore has been given as undefined carbon. Because we have no better approach up to now the bacterial growth has been controlled by limiting the carbon source. This assumption seems not plausible taking methane or other substances derived from the all-round coal layers into account. Bacterial growth must therefore serve as a provisional universal factor controlling the reaction rate.

According to all these uncertainties it proved very demanding to get sufficient model results. Because the bacterial growth is given as a time depending rate the time of exposure of the water in the mine fields (boxes) influences directly the resulting sulphide concentration. Because of implausible high values in some mine fields we can conclude that there must be additional growth or yield limiting factors which we don not know up to now.

Reductive dissolution of iron hydroxides has been calculated as solely chemically driven in spite of evidence from other studies that this process is generated by bacterial activity too. But because of no input data a bacterial based modelling of this process has been neglected up to now.

Despite all these deficiencies of the input data the overall process and geochemical interactions in a flooded mine can be reproduced in a satisfactory manner (fig 4). Even though the flushing of iron follows a well-known dynamic (Younger & Blachère 2003) this process had to be revised because of removal of iron by FeS precipitation and release of iron via $Fe(OH)_3$ dissolution. The graphs show that iron and sulphide are mutually exclusively in mine water discharge so that sulphide can only emerge when its production rate exceeds the iron concentration or iron is completely flushed out. Time of this change in the environment and the final sulphide concentrations can be manipulated by the iron reservoirs and the sulphate reduction rate.

Conclusions

When mine water quality prognosis demands for more than a concentration development of iron with respect of water treatment strategy and additional geochemical processes in the mine are evident there is an increasing demand for reactive mass transport modelling. A further challenge is an obvious occurrence of biologically controlled processes like sulphate reduction.

For practical use in large scale models and in consequence of the often limiting availability of input data it is reasonable to limit chemical reactions considered and to simplify the supposable processes. It could be shown that this selected chemistry suffices to reproduce the dominating processes resulting in the mine water quality

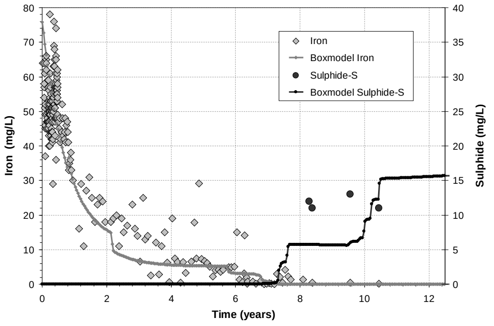

Figure 4 *Comparison of measured and calculated concentration development for iron and sulphide-S.*

monitored. This represents a major achievement for the practical application of the geochemical reaction model for mine water rebound.

With respect to sulphate reduction in the coal mine environment there are still large lacks of knowledge to find sufficient input data for the model. The Reacflow3D/Boxmodel however presently provides all geochemical features required also for more ambitious and detailed process description. Currently continuative studies are planned for better understanding of the microbial population in abandoned European hard coal mines.

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