Control of the remediation of anoxic AMD groundwater by sulphate reduction in a subsoil reactor

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Abstract Groundwater containing high amounts of products of pyrite weathering in consequence of lignite surface mining flows into receiving waters for a number of years. Iron hydroxides causing turbidity and silting will strongly affect surface waters for many decades. In addition to liming acidic surface waters and the conventional treating of mine waters, microbial sulphate reduction of the inflowing anoxic acid mine drainage (AMD) groundwater is tested for long-term remediation.
During a pilot project at Lusatia / Germany glycerol as a carbon source and nutrient solutions of N and P are infiltrated in an anoxic AMD groundwater stream by lances (Hildmann et al. 2016). Planning and operation were carried out based on the model as proposed below.

Introduction

Lignite surface mining in Lusatia, Eastern Germany caused pyrite weathering due to lowering of the groundwater level. Owing to the post-mining rebound of groundwater level, iron- and sulphate-rich groundwater enters the surrounding environment for a number of years. A possible solution to remediate the groundwater and to protect receiving water courses is the use of sulphate reduction in-situ in the aquifer.

The oxidation of pyrite and other sulphides generates the acidity of acid mine drainage (AMD). Using the sum parameter of acid capacity ($K_{S4,3}$) and the concentrations of iron, aluminium and manganese the neutralization potential (NP) is defined by equation 1.

$$NP \approx K_{S4,3} - 3c_{Al3+} - 2c_{Fe2+} - 2c_{Mn2+} \qquad (1)$$

Reactions that produce AMD and their inversion as a result of remediation can be presented as vectors in an acidity/sulphate concentration plane, wherein acidity is represented by negative neutralisation potential ($-NP$) (Schöpke et al. 2016, Fig. 3). A statistical linear relationship between the acidity and the sulphate concentration is frequently observed in AMD contaminated groundwaters. Ferrous iron generates the majority of acidity. Due to aeration and oxidation, AMD forms acidic lakes. Alternatively, in buffered rivers iron hydroxides cause a brown turbidity.

Acid surface waters, e.g. lakes, can be neutralised by liming. During this process, the neutralisation potential increases and achieves positive values, whereas the concentration of

sulphate remains constant. Anoxic AMD groundwater flows can be treated by microbial sulphate reduction. As a result, acidity and sulphate concentration decrease at a stoichiometric ratio and iron sulphide precipitates. In case of lack of iron, toxic hydrogen sulphide will be formed. As the reaction progresses, precipitation of calcite may occur.

Our concept for remediation

Sulphate reduction in the aquifer – that is our concept for remediation of AMD groundwater. Analogous to microbial types of passive AMD treatment it is based on natural processes to neutralize acidity due to precipitation of iron sulphide. Constructed wetland processes require large areas to treat moderately acidic AMD. However, we don't have large areas and therefore make use of the great volume of the aquifer. The concept has been developed to treat stagnant and flowing groundwater bodies that may endanger receiving water courses. Emanating from hot spots, acidity can reach up to concentrations of NP ≈ -20 mmol/L (1000 mg/L CaCO$_3$ or ≈ 500 mg/L Fe).

To enrich the groundwater with substrate it is extracted and re-infiltrated after mixing with glycerol and nutrients (nitrogen N, phosphorus P) if necessary as shown in Fig. 1. The infiltration of the substrate-enriched groundwater happens periodically. Between two cycles of infiltration, the groundwater flows freely. Both water bodies mix in the downstream via hydrodynamic dispersion effects. A mixed culture of autochthonous sulphate-reducing microorganisms multiplies in the downstream and the subsoil reactor develops.
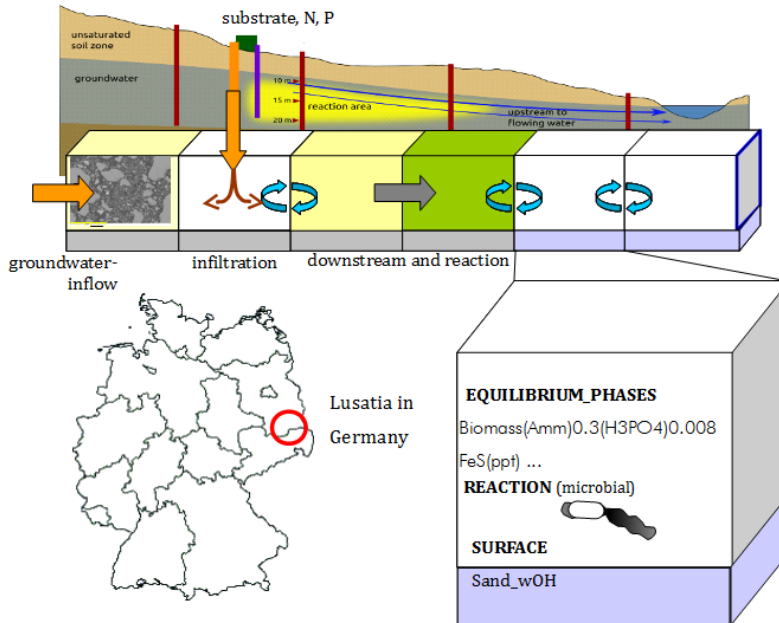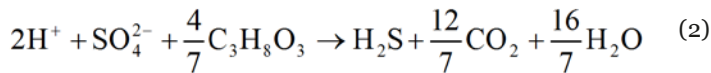

Figure 1 *Scheme and nomenclature (phreeqc) of the mixed cell model (above and right side) and position of the study area in Lusatia, Germany (left side)*

The pilot projects were prepared by laboratory experiments, field tests (Tab. 2) and modeling with phreeqc (Parkhurst & Appelo 2006). This article concentrates on geo- and biochemical problems.

Biochemical reactions

Sulphate can be reduced to hydrogen sulphide by easily degradable organic substances, Eq.(2). In Lusatia, methanol and glycerol are accepted as substrates. Together, hydrogen sulphide and ferrous iron precipitate as iron sulphide, Eq.(3). The pH value and the available concentration of iron determine the concentration of remaining hydrogen sulphide.

$$2H^+ + SO_4^{2-} + \frac{4}{7}C_3H_8O_3 \rightarrow H_2S + \frac{12}{7}CO_2 + \frac{16}{7}H_2O \quad (2)$$

$$Fe^{2+} + H_2S \leftrightarrow FeS + 2H^+ \quad (3)$$

Taking the expected conversion of ferrous iron and possibly concentrations of oxygen and ferric iron, the need for substrate is calculated according to Eq.(4) using the stoichiometric coefficients n(i) given in Tab. 1.

Table 1 Stoichiometric coefficients ν(i) of substrates used for sulphate reduction

| Substrate		M g/mol	Stoichiometric coefficients n(i)		
			n(O2)	n(Fe(3))	n(Fe(2))
Carbohydrate	{CH$_2$O}	30	1 .00	2 .25	2 .00
Methanol	CH$_3$OH	32	0 .67	1 .50	1 .33
Glycerol	C$_3$H$_8$O$_3$	92	3 .5	0 .64	0 .57
Ethanol	C$_2$H$_5$OH	46	3 .00	0 .75	0 .67
Acetic acid	CH$_3$COOH	60	2 .00	1 .13	1 .00
calculated BOD	O$_2$	32	1.00	2 .25	2.00

Alternatively, the biochemical oxygen demand (BOD) can also be specified for mixtures.

$$c_{Substrat} = v_{O2} \cdot \Delta c_{O2} + v_{Fe(3)} \cdot \Delta c_{Fe(3)} + v_{Fe(2)} \cdot \Delta c_{Fe(2)} \quad (4)$$

The growth kinetics of microbial biomass in the form of substrate consumption is determined by growth rate (μ_o), concentration of Biomass ($c_{Biomass}$), pH value, temperature (Temp) as well as monod- and inhibition terms ($f_i(i)$) as described in Schöpke et al. (2011) and in Eq. (5).

$$\frac{\partial c_{Su}}{\partial t} = \mu_0 \cdot c_{Biomass} \cdot f(Temp) \cdot f(pH) \cdot f_{Su}(c_{Su}) \cdot f_{SO4}(c_{SO4}) \cdot f_N(c_N) \cdot f_P(c_P) \cdot f_I(c_I) \quad (5)$$

Eq. 6 describes the yield of biomass. To characterize with phreeqc the consumption of nutrients and substrate the intermediate product X was defined.

$$1.75\,SO_4^{2-} + 4H^+ + Su \rightarrow 1.75H_2S + 0.08X + 3CO_2 + 11H_2O \mid Su = Glycerol \quad (6)$$
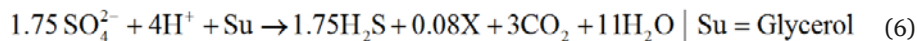
This intermediate product X condenses to the phase Biomass. The composition of the phase Biomass corresponds to the expression in Eq. (7) but can slightly differ.

$$Biomass = X(Su)_{0.33}(NH_3)_{0.3}(H_3PO_4)_{0.008} \quad = \{C_5H^7O{-}_2N_1P_{0.008}\} \quad (7)$$

The kinetic of the lysis of Biomass is defined as first-order reaction. At its decay, the phase Biomass releases again the bound nutrients and the substrate. All kinetic constants researched by Schöpke et al. (2011) were adapted to the considered processes. The Monod-constants used in the terms $f_i(i)$ only had to be changed slightly. During the model adjustment, the reaction mechanisms as well as the formation of intermediate products can still be altered. In the considered aquifers, methanogenesis can be neglected.

Pore systems

In the pore system of the aquifer, different biochemical reactions take place. The stationary solid matrix consists of quartz sand, clay minerals and organic particles. Pore solution flows through the interstices. Pseudoparticles consisting of fine grains were sometimes found in aquifers in the area of mine dumps. Their inner pore system is only accessible by diffusion. Pleistocene aquifers contain predominantly quartz particles with traces of clay and lignite. The stationary surface area of the pore system will be defined as pore gel. Surface phases, mineral phases, bacteria and extracellular substances will mainly form the pore gel. Solid humic substances can be mobilised at increasing pH value. The thermodynamics of the pore gel may differ from that of the pore solution and the process constants can slightly deviate from the macroscopically known constants. The geochemical software phreeqc can calculate all processes in the system of pore gel and pore solution. For this purpose, the tabulated values of thermodynamic constants were adjusted to test results.

Transport model

All processes of pore solution and pore gel were included in every cell of the *mixed cell* transport problem. The flow path between the infiltration and each measuring point (25 m, 30 m, 100 m, 200 m) will be described as flow tube, which takes into account the filtration processes. The flow tube consists of 1 m long *mixed cells*. The *rates* and *kinetics blocks* are adapted to the described biochemistry of sulphate reduction.

### Application of sulphate reduction in subsoil reactors

Tab. 2 gives an overview of the initial conditions at individual test sites in Lusatia/Germany. The results concerning lake RL 111 documented Preuß (2004), in the case of Senftenberger See Koch et al. (2006) and in the case of Skadodamm Schöpke et al. (2011). Experiences with sulphate reduction in acidic lake water (No. 0) will not be discussed in this article. The pilot project at the location Ruhlmühle is still running (Hildmann et al. 2016).

Table 2 Locations of application and some of the characteristics of the respective test sides

No.	location	year	aquifer	particularities
0	lake RL 111	2001-2004	lake	pH < 3.5, aerob
1	Senftenberger See	2002-2003	tertiary	Mobilisation of humic substances
2	Skadodamm	2008-2010	dump	pH > 4.8, Al < 0.2 mg/L
3	Ruhlmühle	2014-2017	quaternary	pH < 4.1, Al > 10 mg/L

At the location Ruhlmühle in the north of Saxony (Germany, No. 3), a groundwater stream of Q = 200–300 m³/d is treated by microbial sulphate reduction (Fig. 1). The groundwater is extracted by three wells and re-infiltrated intermittently after mixing with glycerol and nutrients. The infiltration line consists of 30 lances and has a width of about 100 m. Along a flow length of 300 m the subsoil reactor develops. The flowtime is 300 to 500 days. To infiltrate substrate-enriched groundwater into the entire flow cross-section the lances are arranged in three horizons.

Taking into account more than five specially selected measuring points, the model was adapted to the changes of groundwater quality. By this, the longitudinal profiles of the concentrations of iron and sulphide after 900 days of treatment in Fig. 2 were calculated. The precipitation front of iron sulphide (FeS) is located at approximately 145 m of flow path. At this point, however, already 500 m water column flowed through the subsoil reactor. The arrow in Fig. 2 indicates the retarded migrating iron front. Precipitated iron is supplied by desorption from the solid matrix. The lost iron will be exchanged for aluminium, calcium and other dissolved cations (competing adsorption). That is why the front of the iron removal migrates more slowly than the infiltration front.
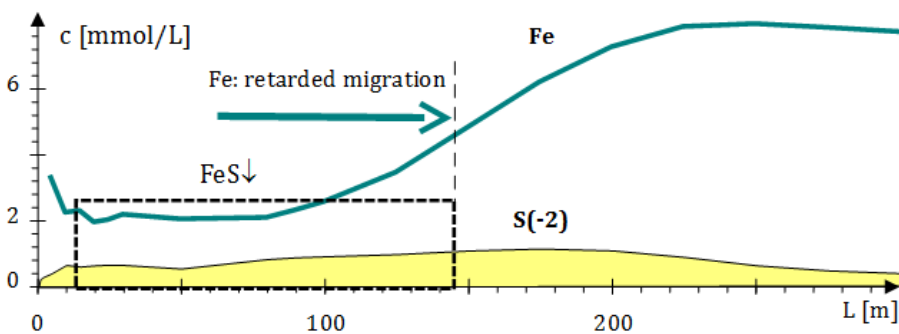
Figure 2 Modeled longitudinal sections of iron (Fe) and sulphide (S(-2)) concentrations after 900 days of treatment based on monitoring data at the location Ruhlmühle (No. 3).

Fig. 3 demonstrates the development of the acidity (-NP) and of the sulphate concentration (SO$_4$) due to the treatment at the measuring points after 20 and 30 m of flow path as described in Schöpke et al. (2016). The change of groundwater quality over 900 days of

treatment (dark blue) can be explained as a combination of the theoretical vector of sulphate reduction (black) and the vector of a slight buffering by the aquifer matrix (light blue). According to Eq. 1, the acidity correlates with the remaining concentration of iron (brown, dashed).
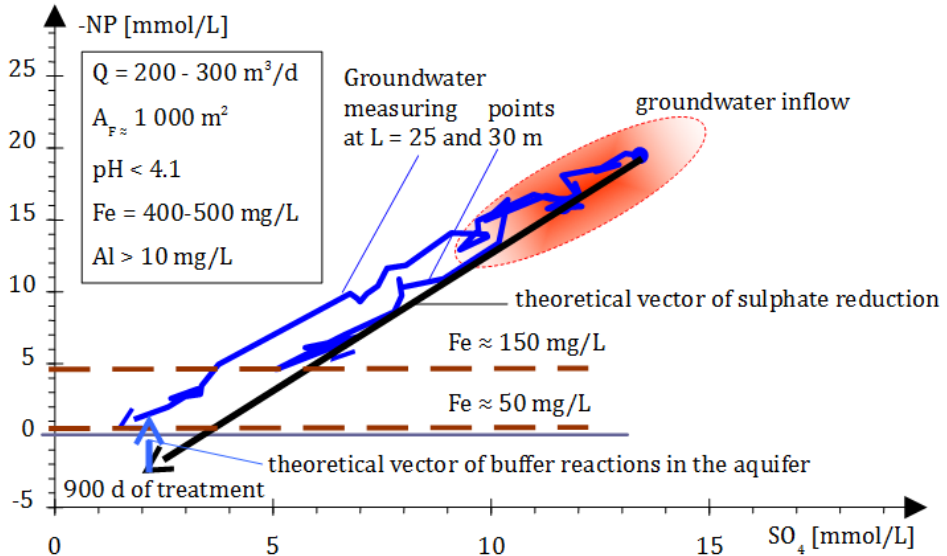
Figure 3 *Effects of microbial sulphate reduction in the aquifer at the location Ruhlmühle shown in the acidity/sulphate concentration plane as well as treatment parameters and the original groundwater quality.*

After 900 days of treatment, the residual concentration of iron approaches 50 mg/L. As mentioned, the remaining concentration of hydrogen sulphide depends on the iron concentration and the pH value. Close to the infiltration point, the success of the remediation with low sulfide residues is already achieved. At the location No. 2 (Tab. 2, Skadodamm), on a width of 20 m a groundwater stream of only 13 m³/d and with a higher pH value was treated. After the period of adaption, the sulphate reduction already took place in the first ten meters. Several developed concentration fronts migrate at different speeds through the aquifer because of competing adsorption as just described. Due to substrate overdose during the phase of infiltration at this location hydrogen sulphide was formed. The hydrogen sulphide migrated with the groundwater stream and on its further flow path caught up with the retarded migrating ferrous iron. At the location No. 1 (Tab. 2, Senftenberger See) the mobilisation of humic substances in the groundwater was observed as consequence of increasing pH value. This process can also be described by means of the proposed model (phreeqc).

Conclusions

Microbial sulphate reduction allows long-term treatment of AMD sources and migration pathways. Tab. 3 shows the specific reduction of acidity and other performance parameters

of individual sulphate reducing reactors. Skousen et al. (2017) specify for a vertically flowed through wetland a specific reduction of acidity of maximal 35 g/(m²·d). Regarding their performance, subsoil reactors are comparable to constructed wetlands. However, a larger reaction space is available.

Table 3 Performance parameters of differently working sulphate reducing reactors

Reactor	DNP mol/(m²·d)	Dacidity g/(m²·d)	flow length L m	running time d
vertically flowed wetland	0 .7	max. 35	» 0 .5 − 2	no information
Skadodamm (No. 2)	0 .45	23	9	360
Ruhlmühle (No. 3)	1 .8	90	25 − 30	> 850

So far in case of subsoil sulphate reduction, the test times were not sufficient to indicate long-term concentrations of hydrogen sulphide and residual substrate. Obstructions by reaction products and gas bubbles were observed in no event. The basics of the preparation and assessment of these treatment methods were developed. An important element is geochemical modeling. The model can describe the biochemistry, the competing sorption on the aquifer matrix and the mobilisation of humic substances on the flow path. Important input parameters are the pH value as well as the concentrations of iron, aluminium, sulphate and nutrients. The site-typical conditions have to be explored accurately. Adapted simulations (phreeqc) can also describe the different velocities of migration and effects of mobilisation of humic substances at increasing pH values.

So far, the strict German and European environmental legislation result in the use of pure chemicals as substrates and therefore cause high costs. Alternative substrates should be selected on the following conditions:

- Prohibition of deterioration.
- Criteria for the assessment of good chemical status.
- No danger of eutrophication in adjacent waters.
- The treated groundwater has to be suitable for drinking water treatment.

Depending on the geochemical conditions, the treatment measures require several years of adaption of the autochthonous microorganisms. By means of a model-supported process control, complete substrate consumption can be aimed at and the residual concentration of hydrogen sulfide can be minimized. Unanswered questions of detail have to be clarified by monitoring and modeling during future applications. The proposed principles of sulphate reducing reactors can be adapted to technical systems (end of pipe).

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