



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 as a consequence of lignite mining flows into receiving waters for a number of years. Iron hydroxides causing turbidity and silting will strongly affect the river Spree for many decades. In addition to liming acidic surface waters and the conventional treating of mine waters, microbial sulphate reduction of the inflowing anoxic AMD groundwater is tested for long-term remediation. During a pilot project at Lusatia / Germany, glycerin as a carbon source and nutrient solutions of N and P are infiltrated into an anoxic AMD groundwater stream by lances. Planning and operations were carried out based on the model as proposed below.

Keywords: Groundwater; Acid Mine Drainage (AMD); Treatment; Biochemical Reactions.

1. Introduction

Groundwater containing high amounts of products of pyrite weathering as a consequence of lignite mining flows into receiving waters for a number of years. A possible method of groundwater remediation is sulphate reduction in the aquifer. The oxidation of pyrite and other sulphides generates the acidity of AMD [1-3]. Using the sum parameter of acid capacity $K_{S4,3}$ and the concentrations of iron and manganese, the neutralization potential is defined by Equation 1.

$$NP \approx K_{S4,3} - 3c_{Al^{3+}} - 2c_{Fe^{2+}} - 2c_{Mn^{2+}} \quad (1)$$

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 neutralization potential ($-NP$) [4-6]. A statistically linear relationship between the acidity and the sulphate concentration is frequently observed in AMD contaminated groundwater. Ferrous iron generates the majority of acidity. Due to aeration and oxidation, AMD forms acidic lakes. Alternatively, in buffered rivers such as the Spree, iron hydroxides cause brown turbidity.

Acid surface waters, e.g., lakes, can be neutralized by liming. During this process, the neutralization potential increases and achieves positive values, whereas the concentration of sulphate remains constant. Anoxic AMD

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groundwater flows can be treated by microbial sulphate reduction. As a result, acidity and sulphate concentrations 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, the precipitation of calcite may occur.

The pilot projects were prepared by laboratory experiments, field tests (Table 1), and modeling with PHREEQC [7]. This article concentrates on geo- and biochemical issues.

Table 1. Locations of application

No.	Location	Year	Aquifer	Particularities
0	lake RL 111	2001-2004	lake	$pH < 3, 5, aerob$
1	Senftenberger See	2002-2003	tertiary	Mobilization of NOM
2	Skadodamm	2008-2010	tip	$pH > 4.8, Al < 0.2 \text{ mg/L}$
3	Ruhlmühle	2014-2019	quaternary	$pH < 4.1, Al > 10 \text{ mg/L}$

Table 1 gives an overview of the initial conditions at individual test sites. The results concerning lake 111 documented Preuß (2004) [8], in the case of Senftenberger See Koch et al. (2006) [9] and in the case of Skadodamm Schöpke et al. (2011) [10]. The pilot project Ruhlmühle is still running [1-3]. Sulphate reduction of acidic lake water (No. 0) will not be discussed in this article.

At the location Ruhlmühle in the north of Saxony (Germany), a groundwater stream is treated by microbial sulphate reduction as shown in Figure 1. To enrich the groundwater with substrate it is extracted and re-infiltrated after mixing with glycerin and nutrients if necessary. 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.

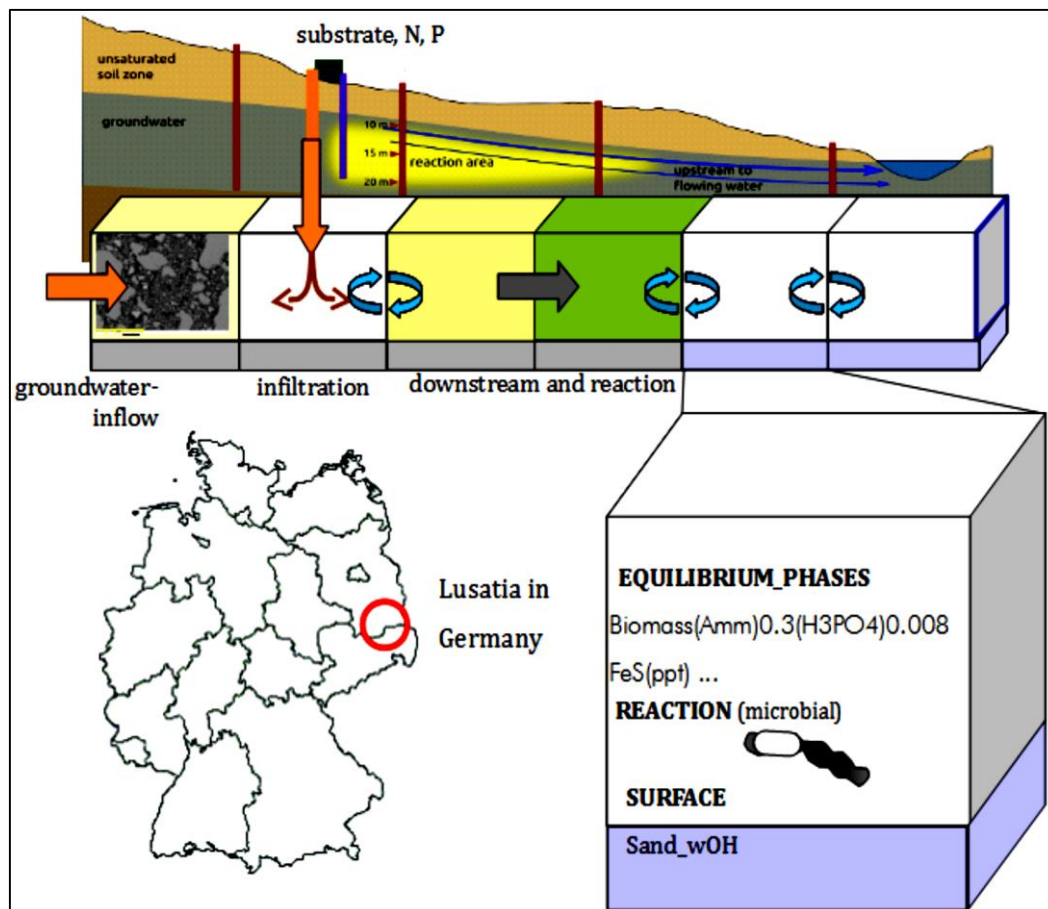
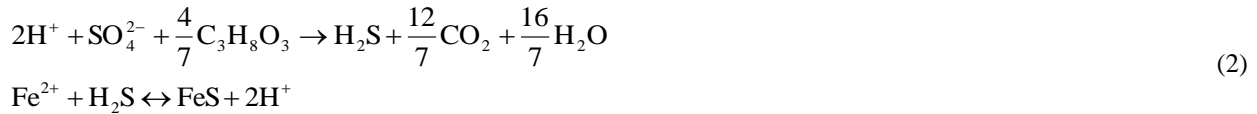


Figure 1. Pilot projects in Lusatia/Germany and scheme of the mixed cell

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. Emanating from hot spots, acidity can reach up to concentrations of $NP \approx -20 \text{ mmol/L}$ (1000 mg/L CaCO_3 or $\approx 500 \text{ mg/L Fe}$).

2. Biochemical Reactions

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



Taking the expected conversion of ferrous iron and possibly concentrations of oxygen and ferric iron, the need for substrate is calculated using the stoichiometric coefficients given in Table 2.

Table 2. Stoichiometric coefficients of substrates for sulphate reduction

Substrate		M	Stoichiometric Coefficients		
		g/mol	v(O ₂)	v(Fe(3))	v(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	2,25	2

Alternatively, the BOD can also be specified for mixtures. According to Equation 3 the required amount of substrate is calculated. The general requirements for the rehabilitation process are compiled in a checklist as criteria ok1 to ok6:

Ok1 Proof of the intended effect.

Ok2 No eutrophication effect of the treated water.

Ok3 No higher oxygen consumption in surface waters.

Ok4 No acute toxicity of the treated water.

Ok5 Limitation of potentially bio-accumulating substances.

Ok6 Limitation of inert substances.

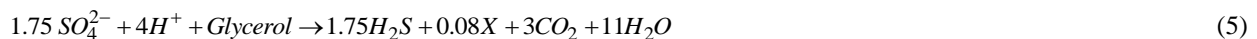
$$c_{\text{Substrat}} = v_{O_2} \cdot \Delta c_{O_2} + v_{Fe(3)} \cdot \Delta c_{Fe(3)} + v_{Fe(2)} \cdot \Delta c_{Fe(2)} \quad (3)$$

The use of drinking water after conventional treatment of the treated groundwater flow will be guaranteed.

The growth kinetics of microbial biomass is determined by growth rate μ_0 , pH value, temperature, monod- and inhibition terms $f(i)$.

$$\frac{\partial c_{Su}}{\partial t} = \mu_0 \cdot c_{\text{biomass}} \cdot f(\text{Temp}) \cdot f(\text{pH}) \cdot f_{Su}(c_{Su}) \cdot f_{SO_4}(c_{SO_4}) \cdot f_N(c_N) \cdot f_P(c_P) \cdot f_I(c_I) \quad (4)$$

As described in Schöpke et al. (2011) [10]. In accordance with Equation 5 the intermediate product X will be formed at microbial sulphate reduction.



Subsequently, the intermediate product X condenses to the phase biomass according to Equation 6. The composition of the phase biomass follows the expression in Equation 7 but can slightly differ.



$$\log_k = -30$$

$$\text{Biomass} = X(\text{Substrat})_{0.33}(\text{NH}_3)_{0.3}(\text{H}_3\text{PO}_4)_{0.008} = \{C_5H_7O_2N_1P_0.008\} \quad (7)$$

The kinetic of the lysis of biomass is defined as first-order reaction. In the considered aquifers, methanogenesis can be neglected.

3. 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. 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.

4. Transport Model

A PHREEQC mixed cell model (Figure 1) was adapted to the measured concentration curves in the downstream flow of the substrate addition, especially for dimensioning and operational management. This also included adsorption processes on the solid matrix and the hydraulic effect of separated reaction products and possible gas excretions in addition to the biochemical reactions. Gas excretions could be excluded in the previously treated groundwater lamellae. An impairment of the permeability (k_f) has not yet been proven, which the flow route model also predicts for the next two decades.

The underground reactor will be represented by a few characteristic flow tubes. Each flow tube is described using a mixed cell model. The infiltration facilities and measuring points are determined on model basis. The exploration is made more precise with the construction of the infiltration and monitoring systems. The operating regime is then determined by PHREEQC modeling. The microbial sulphate reaction describe Equation 4.

The mortality rate must also be taken into account. A large number of side reactions also must be taken into account. The pore structure of the aquifer has a very large reactive surface. This triggers various chromatographic effects. The reaction products deposited in the pore system can be predicted. Reaction parameters for the kinetics and surface complexation had been specified at location.

The methodological bases of the dimensioning of an underground reactor is created:

- A thorough exploration is required at first.
- The dimensioning takes place by means of hydrogeological modelling and the use of the flow route model.
- This can be used to construct statistical distributions over the properties of the aquifer about the heterogeneity of the groundwater flow and the properties of the sediment matrix. Tracer tests can also be used.
- It will be parameterized a mixed cell model in PHREEQC for the operating regime.
- The renovation operation itself is optimally designed through the combination of monitoring and modelling.
- The profitability can only be calculated on the property.

Recommendations for approval and exploration are available for the preparation of underground reactors [4].

5. Technology

The substrate is mixed into the groundwater flow intermittently using infiltration lances or equivalent methods. For treatment, the substrate required for sulphate reduction must be added to the groundwater flow and allowed to react on the further course of the flow.

The simplest substrate dosage would be by pump and addition. Then you could leave out the further treatment in the aquifer. So only an intermittent injection with substrate-enriched groundwater is possible. The distribution of the substrate takes place on the further flow path by dispersion processes. The substrate must be entered into the entire flow cross-section.

- Low AMD currents are already treated through passive reactive walls. Various solid substrates are used there, mostly for sulfidic heavy metal binding. The requirements placed on the treated water cannot be met with this.
- The combination of infiltration and injection wells creates a gradient across the direction of the groundwater flow, via which the enriched water reaches the flow area between the wells.
- Another possibility is the ADAG system, in which the groundwater is collected via the collector well and then redistributed via the distributor.
- In the demonstration experiment, lances at different depths were charged with substrate-enriched groundwater. The costly infiltration wells are replaced by infiltration lances.

6. Results

A groundwater stream of $Q = 200\text{--}300 \text{ m}^3/\text{d}$ was treated by microbial sulphate reduction at the location Ruhlmühle (Table 1, No. 3, and Figure 1). The demonstration test proceeded over 31 months (2014-2019) with a groundwater treatment of around $6 \text{ m}^3/\text{h}$ over a width of 100 m and a follow-up observation over 30 months. The effect was monitored and controlled by a monitoring program.

The groundwater flow field is determined through geological exploration. The sulphate conversion depends on the microbiological activity, the AMD quality, the substrate concentration, the available nutrients and possible inhibitors. The sulfate reducing bacteria must be grown slowly at first.

Figure 2 shows the course of the sulphate concentration after 900-day remediation operation. During the start-up phase, substoichiometric substrate is added in order to grow the sulphate reducers. In the following time the sulphate concentration decreases. After completion of the measure, it rises again to the inflow concentration. The sulphate concentration at inflow slightly decreases during the remediation operation.

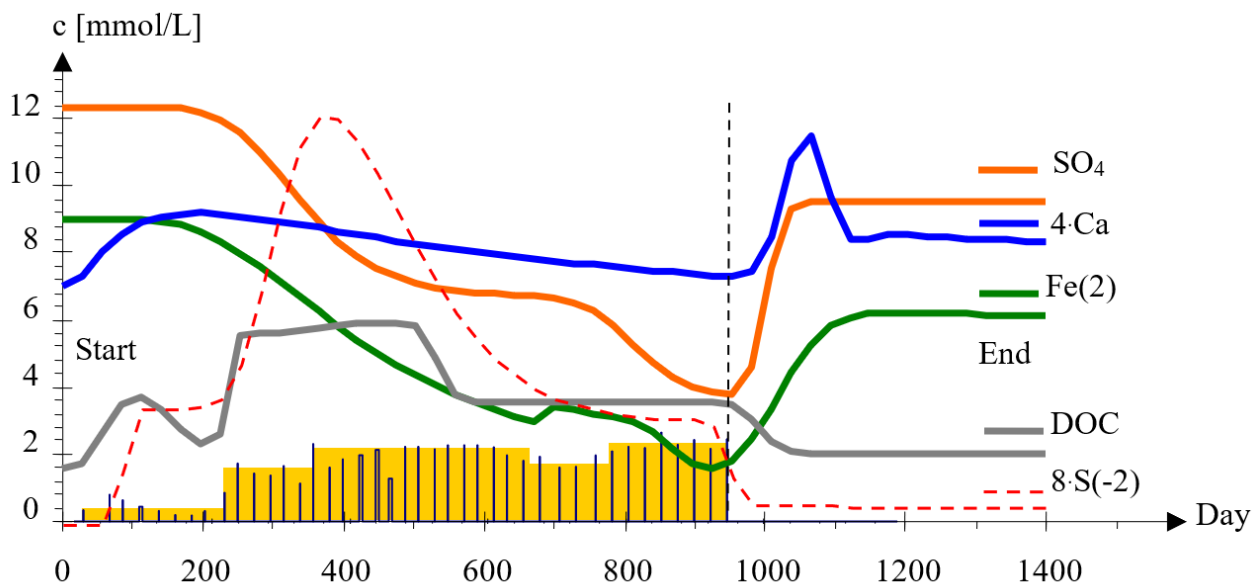


Figure 2. Concentration curves of process-characterizing ingredients during the remediation attempt after a 25.5 m flow path through the aquifer. The substrate additions are marked as bars, not to scale

The maximum sulfate degradation is limited by the substrate dose. The increase after the addition of the substrate corresponds to that of a conservative tracer. The ferrous concentration will be delayed. During the incorporation of the underground reactor, ferrous iron on the solid matrix is exchanged for other cations. These cations are displaced again by the inflowing ferrous iron after the renovation is completed. These cations are displaced again by the inflowing ferrous iron after the renovation is completed. The added substrate is only used incompletely in the beginning. Therefore, the substrate dose should be increased slowly up to the desired maximum dose. The slowly rising pH values can mobilize humic substances that are fixed in the subsoil.

The beginning of the sulphate reduction immediately increases the hydrogen sulphide concentration. Hydrogen sulphide concentration decreases again with the slowly increasing pH value and the aging of the precipitated products. A low sulphide concentration remains after the renovation has been completed. The aging behavior of the sulphide precipitated products is currently insufficiently known. The predicted hydrogen sulfide concentration at the end of the flow section represents, in addition to the remaining substrate concentration, an important control variable for process control. Due to the increasing pH value during the treatment, humic substances can also be mobilized from the subsoil and simulate substrate residues via the DOC. The remaining hydrogen sulfide concentration is in equilibrium with ferrous iron, the pH value and aging iron sulfide phases (Figure 3).

Under the conditions of the low pH values at the location Ruhlmühle (No. 3), the iron sulphide precipitation was delayed and extended to more than 100 m of flow path. The aluminum concentration decreases before the content of iron diminishes.

Obstructions by reaction products and gas bubbles were observed in no event. Adapted simulations (PHREEQC) can describe the different velocities of migration and effects of NOM mobilization at increasing pH values. This effect could

be described as a *solid solution* by a system of humic substances. The residual concentration of hydrogen sulphide depends on the iron concentration and the pH value. So far, the test times were not sufficient to indicate long-term concentrations of hydrogen sulphide and residual substrate.

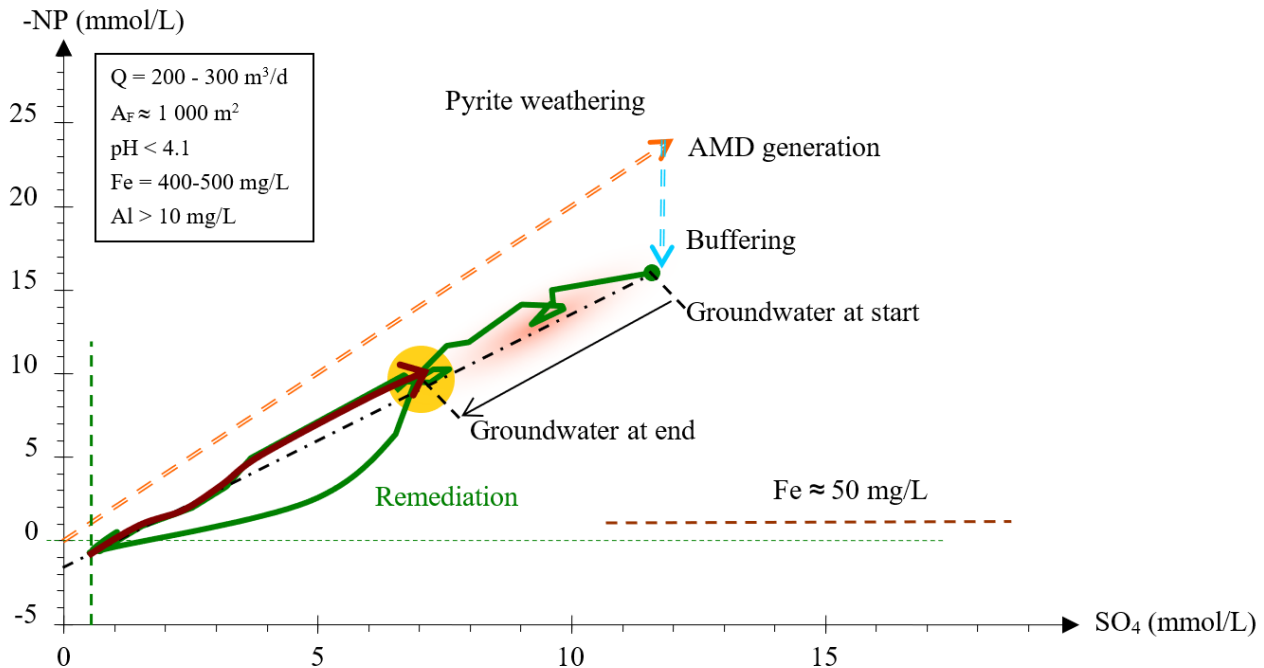


Figure 3. Acidity (-NP) -sulphate diagram of AMD formation through pyrite weathering and buffering in the aquifer (dashed) and its remediation process through microbial sulphate reduction. The reaction (green) runs along its line of action up to *best effect*. The deviations are caused by various side reactions. After the addition of the substrate, the condition of the inflow is restored (brown). The inflow condition changes during operation (groundwater at end).

The fluctuations in the nature of the intermittent mode of operation are largely compensated for on the flow path by dispersion processes. The particular solution of the one-dimensional general balance equation describes a jump in concentration. Excel offers a function for this purpose. A summary of jump functions is sufficient to smooth the sulfate concentration curve. The material balance is obtained by integrating the material flows of the inflow minus those of the rehabilitated groundwater flow. The jump functions have the property that they can be transformed into rectangular functions of equal area. That makes the balance calculation easier.

The flow resistance will be increased by the reaction products iron sulfide and biomass. Iron sulfide particles from the treatment could not yet be determined using an electron microscope. Iron sulfides can also be deposited on existing pyrite concretions. The diameter of their crystals are from 10 μm . The hydraulic effects resulting from the deposition of reaction products can be calculated with the Kozeny-Carmann Equation [11, 12], known from water treatment. All effects have been predicted using PHREEQC with a mixed cell flow path in Schöpke et al. (2020) [4].

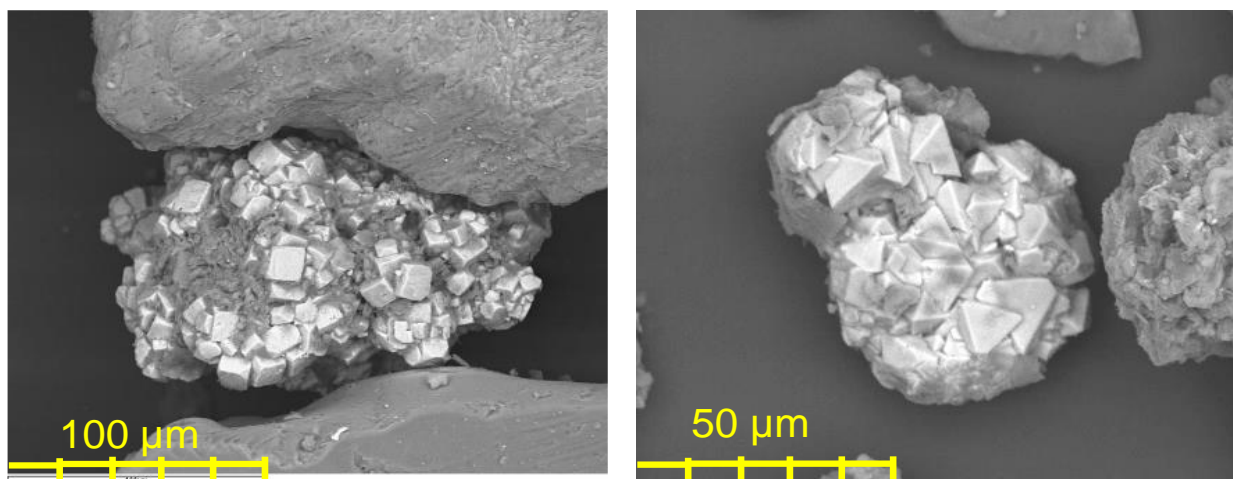


Figure 4. Pyrite crystals in pore system

7. Conclusions

As shown in Figure 3, the development of the quality of the groundwater at a flow path of 20–30 m at Ruhlmühle is made up of the vector of sulphate reduction and the buffering by the solid matrix. Tab. 3 shows the specific reduction of acidity and other performance parameters of individual sulphate reducing reactors. Skousen et al. [13, 14] specify for a vertically flowed through wetland a specific reduction of acidity of maximal 35 g/(m²·d) (Table 3). Regarding their performance, subsoil reactors are comparable to constructed wetlands. However, a larger reaction space is available.

At the location Skadodamm (No. 2), on a width of only 20 m, a groundwater stream of only 13 m³/d was treated. After the period of adaption, the sulphate reduction had already taken place in the first ten meters. The precipitation of iron sulphide already begins during the growth phase of the microorganisms. Precipitated iron is supplied by desorption from the solid matrix. The lost iron will be exchanged for aluminum, calcium, and other dissolved cations. That is why the front of the iron removal migrates more slowly than that of the formed hydrogen sulphide. Several developed concentration fronts migrate at different speeds through the aquifer. At the location Skadodamm, due to substrate overdose during the phase of infiltration, 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. They both precipitated as iron sulphide (Figure 2). Thus, the intermittent operation is made uniform.

Table 3. Performance parameters of sulphate reducing reactors

Reactor	ΔNP	Δ Acidity	Flow length L	Running time
	mol/(m ² ·d)	g/(m ² ·d)	m	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

Microbial sulphate reduction allows long-term treatment of AMD sources and migration pathways. The basics of the preparation and assessment of these measures were developed. An important element is geochemical modeling. The model can describe the biochemistry, the competing sorption on the aquifer matrix, and the mobilization of humic substances on the flow path. Important input parameters are the pH value as well as the concentrations of iron, aluminum, sulphate and nutrients. The site-typical conditions have to be explored accurately.

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 based 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.

The proposed principles of sulphate reducing reactors can be adapted to technical systems (end of pipe).

8. Declarations

8.1. Author Contributions

R.S. and M.W. contributed to the design and implementation of the research, to the analysis of the results and to the writing of the manuscript. All authors have read and agreed to the published version of the manuscript.

8.2. Data Availability Statement

The data presented in this study are available in the article.

8.3. Funding

The authors received no financial support for the research, authorship, and/or publication of this article.

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8.5. Institutional Review Board Statement

Not applicable.

8.6. Informed Consent Statement

Not applicable.

8.7. Declaration of Competing Interest

The authors declare that there is no conflict of interests regarding the publication of this manuscript. In addition, the ethical issues, including plagiarism, informed consent, misconduct, data fabrication and/or falsification, double publication and/or submission, and redundancies have been completely observed by the authors.

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