

Process for the Subsoil Treatment of Acidified Groundwater through Microbial Sulfate Reduction

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Abstract

Sulphate and the acidity formed mainly from ferrous iron ions are the main contaminants of groundwater affected by mining. The Chair of Wassertechnik & Siedlungswasserbau at BTU Cottbus-Senftenberg has developed a subsurface rehabilitation method using microbial sulfate reduction over the past twenty years. The basis for dimensioning this technology is now available after a successful demonstration test at the Ruhlmühle in the Lusatian mining district. The used substrate guarantees complete implementation and does not trigger any further damaging effects. Nutritional supplements (N, P) are kept to a minimum. The concentration of hydrogen sulfide in equilibrium with the precipitated iron sulfides limits the treatment effect in the incorporation phase.

Keywords: Technology, Reclamation, Dimensioning, Modelling

Introduction

Iron sulfides are oxidized in the ventilated areas of the lowering funnel and the dump during open-cast mining operations. Their acidic reaction products are dissolved by seepage water or rising groundwater and form the amd. The acid mine drainages flows into the acidic pit lake that is being formed during the filling of the remaining open pit. In anoxic groundwater, the acidity (-NP) is presented as dissolved ferrous iron.

$$NP \approx K_{S_{4,3}} - 3c_{Al^{3+}} - 2c_{Fe^{2+}} - 2c_{Mn^{2+}} \quad (1)$$

After the groundwater flow conditions have been restored before mining, the groundwater enriched with pyrite weathering products flows into adjacent surface waters. Rivers such as the Spree in Germany buffer the acidity that has been introduced. The iron carried along affects the waters as brown turbidity.

The drinking water supply sometimes can also be impaired by exceeding the sulphate limit values.

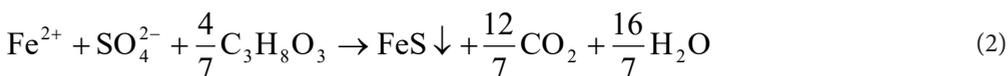
Table 1 Analysis of groundwater inflow in beginning, end and the best effect.

Parameter	Dimension	start	end	best effect
Temp	°C	11	11	11
pH	1	4,02	4,45	5,3
LF	µS/cm	1919	1295	700
NP	mmol/L	-18,0	-10,6	+1
Fe	mg/L	437	291	50
SO ₄	mg/L	1240	812	< 100
NH ₄ -N	mg/L	2,6	2,5	0,2*)
PO ₄	mg/L	0,59	0,47	0,2*)

*) with nutritional supplements

Aims

The aim of the subsoil treatment is to bind ferrous iron as iron sulfide by reducing the sulfate to sulfide sulfur, eq. 2. This lowers the acidity, the iron and sulphate concentration.



This process can be done on the path through the aquifer or in the source of contamination.

The process was developed for the treatment of a groundwater flow but can also be used on tip aquifers with an almost dormant solution phase. 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 bioaccumulating substances.

ok6 Limitation of inert substances.

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

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.

The sulphate conversion depends on the microbiological activity, the amd quality, the substrate concentration, the available nutrients and possible inhibitors. The mortality rate must also be taken into account. Orientation reaction parameters are available for the kinetics. They must be specified at each location. The pore structure of the aquifer has a very large reactive surface. This also triggers various chromatography effects.

$$c_{\text{Substrat}} = v_{\text{O}_2} \cdot \Delta c_{\text{O}_2} + v_{\text{Fe}_3} \cdot \Delta c_{\text{Fe}_3} + v_{\text{Fe}_2} \cdot \Delta c_{\text{Fe}_2} + v_{\text{H}_2\text{S}} \cdot \Delta c_{\text{H}_2\text{S}} \quad (3)$$

Tab. 1 Stoichiometric coefficients for the conversion of oxygen, ferrous and ferric iron, as well as conversion factors for the specification as BOD (Schöpke et al. 2017).

Substrat		Faktor for BOD	M	stoichiometric coefficients			
		mol/mol	g/mol	nO2	nFe3	nFe2	nH2S
Carbohydrate	{CH ₂ O}	1,00	30	1,00	2,25	2,00	
Methanol	CH ₃ OH	1,50	32	0,67	1,50	1,33	1,66
Glycerol	C₃H₈O₃	3,50	92	3,5	0,64	0,57	0,71
Ethanol	C ₂ H ₅ OH	3,00	46	3,00	0,75	0,67	
Acetic acid	CH ₃ COOH	2,00	60	2,00	1,13	1,00	
calculated BOD	O ₂		32	1	2,25	2	

Exploration and rehabilitation test

The last demonstration test proceeded over 31 months (2014-2019) with a groundwater treatment of around 6 m³/h over a width of 100 m and a follow-up observation over 30 months. The effect is 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. Fig. 1 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 (Table 1).

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,

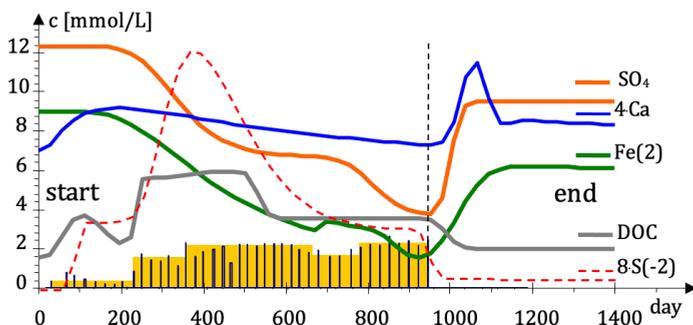


Fig. 1 Concentration curves of process-characterizing ingredients during the remediation attempt after a 25.5 m flow path through the aquifer. The substrate additions are marked as bars, not to scale.

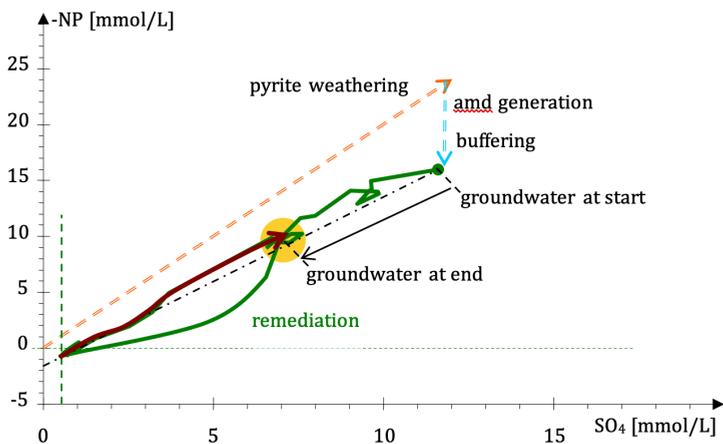


Fig. 2 Acidity (-NP) -sulphate diagram of amd formation through pyrite weathering and buffering in the aquifer (dashed) and its remediation process through microbial sulphate reduction. The reaction (green) runs along its line of action up to best effect (Table 1). The deviations are caused by various 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).

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.

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 are sufficient to smooth the sulfate concentration curve. The material balance is obtained by integrating the material flows of the inflow minus that 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 known from water treatment. All effects has been prognosted using PHREEQC with a mixed cell flow path in Schöpke *et al.* (2020).

Model

A PHREEQC mixed cell model 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

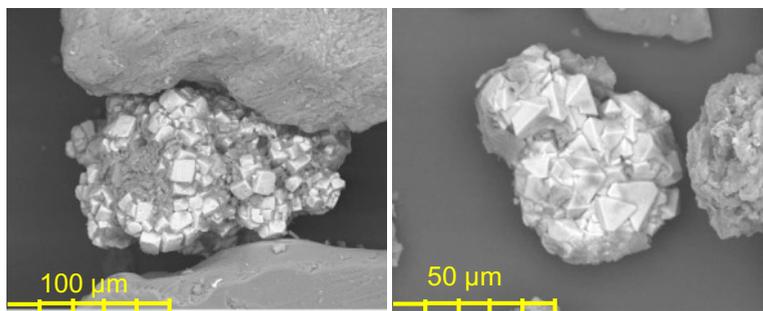


Fig. 4 Pyrite crystals in pore system.

$$\frac{\partial c_{\text{Su}}}{\partial t} = \mu_0 \cdot c_{\text{Biomasse}} \cdot f(\text{Temp}) \cdot f(\text{pH}) \cdot f_{\text{Su}}(c_{\text{Su}}) \cdot f_{\text{SO}_4}(c_{\text{SO}_4}) \cdot f_{\text{N}}(c_{\text{N}}) \cdot f_{\text{P}}(c_{\text{P}}) \cdot f_{\text{I}}(c_{\text{I}}) \quad (4)$$

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 eq. 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. Orientation reaction parameters are available for the kinetics and surface complexation (Schöpke *et al.* 2016). They must be specified at each location.

Dimensioning

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 (Schöpke *et al.* 2020).

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References

- Parkhurst, D. L., Appelo, C.A.J. (2013): Description of Input and Examples for PHREEQC Version 3—A Computer Program for Speciation, Batch-Reaction, One-Dimensional Transport and Inverse Geochemical Calculations. U.S. Geological Survey, Denver, Colorado, Chapter 43 of Section A, Groundwater Book 6, Modeling Techniques
- Schöpke, R.; Preuß, V.; Zahn, L.; Thürmer, K. (2016): Modelling the changes in water quality of AMD along the flow path. In: Drebenstedt, C.; Paul, M. (Hg.): Mining Meets Water - Conflicts and Solutions; IMWA Leipzig; Proceedings, IMWA 2016 in Leipzig, Germany, July 11-15
- Schöpke, R.; Preuß, V.; Thürmer, K.; Zahn, L.; Walko, M.; Totsche, O. (2017): Control of the remediation of anoxic AMD groundwater by sulphate reduction in a subsoil reactor. In: Wolkersdorfer, C.; Sartz, L.; Sillanpää, M. & Häkkinen, A.: Mine Water & Circular Economy (Vol I). – p. 502 – 510; Lappeenranta, Finland (Lappeenranta University of Technology).
- Schöpke, R.; Walko, M.; Regel, R.; Thürmer, K. (2020): Bemessung der mikrobiellen Sulfa-treduktion zur Behandlung von pyritver-witterungsbeeinträchtigten Grundwasserströmen – Ergebnis eines Demonstrationsversuches am Standort Ruhlmühle; Schriftenreihe Siedlungswasserwirtschaft und Umwelt, Bd.27; <https://www-docs.b-tu.de/fg-wassertechnik/public/Publicationen/Schriftenreihe/Heft27.pdf>