

Original Research

Modeling Water Quality of AMD along the Flow Path

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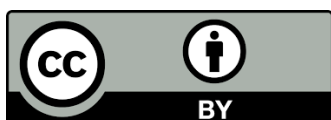
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Abstract

The water balance is severely disturbed in post-mining landscapes like Lusatia/Germany. Mine waters (amd) enter the environment and spread in groundwater and surface waters. Groundwater containing high amounts of pyrite weathering products flows into receiving waters due to lignite mining for several years. The Chair of Wassertechnik & Siedlungswasserbau at the Brandenburg University of Technology Cottbus-Senftenberg/Germany has developed a subsurface rehabilitation method using microbial sulfate reduction over the past 25 years. A continuation of the research is unlikely. This paper has presented some research results on the behavior of groundwater acidified by mining. The acidity in the surface and groundwater is specified via the negative neutralization potential. The dominant reactions in AMD genesis and migration through the aquifer are evaluated about their acidity formation or their buffering behavior. The behavior of AMD can be summarized in a simplified way in the acidity-sulfate diagram. A flow section model (PhreeqC2) was developed and parameterized based on this. This can describe the migration of quality changes in the groundwater/aquifer system. The aquifer passage is reduced to a filtration process, analogous to water treatment. The processes occurring at compartment transitions (dump-lake-aquifer-...) can be modeled from anoxic to oxic. A first case study produces the infiltration of neutralized opencast mining lake water into an aquifer influenced by mining.



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Measured absorption effects during a microbiological sulfate reduction are interpreted in the second case study with an extended flow path model. The results presented are recommended for use. A comprehensive summary of the results obtained over 25 years of research is being prepared.

Keywords

Acid mine drainage; acidity; PHREEQC; migration; adsorption

1. Introduction

After the cessation of lignite mining in the Lusatian coalfield (Germany), groundwater levels slowly approached pre-mining conditions. The highly enriched pyrite weathering products (Fe, SO₄) groundwater in the dumps and the former aerated layers also flow through previously unaffected aquifers.

While the opencast mining lakes acidify due to lack of buffering, the introduced iron is precipitated as brown hydroxide turbidity in the weakly buffered rivers. The precipitation products affect the natural habitats by silting. If the anaerobic AMD gets into drinking water catchment areas, the water treatment is overwhelmed by the increased iron concentrations. Sulfate concentrations above the drinking water limit of 250 mg/L can no longer be treated with reasonable effort.

While the regional distribution of AMD can be predicted using hydrogeological modeling, the migration of AMD leads to complex changes in the composition of AMD. These processes were investigated at individual locations, partly in connection with remediation interventions. This article summarizes the generalizable results determined in many years of research. With the methods presented, forecasts of migrating property jumps can be carried out more precisely.

2. Theoretical Basics

2.1 Use of Neutralization Potential to Characterize AMD

The oxidation of pyrite and other sulfides generates the acidity of AMD. Using the sum parameter of acid capacity $K_{S4,3}$ the neutralization potential is defined by equation (1) [1] modified by Schöpke & Preuß [2].

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

Ferrous ions, manganese and aluminum, are not included in the titration of $K_{B4.3} = -K_{S4.3}$. Therefore, they must be analyzed separately and added to equation (1). Other hydrolyzing cations must also be taken into account. For example, Zn²⁺ must be considered if its occurrence is important in the investigated groundwater.

The change in the neutralization potential due to a reaction is specified as $\Delta_R NP$, equation (2).

$$\Delta_R NP = NP(\text{products}) - NP(\text{educts}) \quad (2)$$

Different definitions of acidity (e.g., net acidity, mineral acidity, hot peroxide acidity [3]) become superfluous in conjunction with the reactions on which they are based.

2.2 Geochemical Calculations

The geochemical calculation program PHREEQC2 [4]) simulates chemical equilibrium reactions such as complex formation, dissolution, precipitation, gas exchange, redox, and surface complexing.

The basis for all further model considerations and simulation calculations is configured model cell. Equilibria with mineral phases and their surfaces primarily characterize the change of composition. The equilibria constants of solution complexes and important minerals are known. Surface complexes on the surface of the rock matrix describe the adsorption [5]. The two-dimensional polyelectrolyte surfaces of quartz, aluminosilicates and organic matter will be combined to the representative surface defined in PHREEQC. The equilibrium constants of surface complexes were adjusted using groundwater monitoring data during treatment experiments.

2.3 Modelling of Groundwater Flow

The processes in the groundwater flow are described by rapid filter processes [6]. The spatiotemporal location in the mountains only plays a subordinate role (Figure 1). The flow distance L [m] through porous material with a flow rate Q_R [m³/d] on a cross-sectional area A_F [m²] in equation (3) to equation (6). The filter/reactor volume V_R [m³] only flows through the pore volume V_P [m³]. The porous filter material mass m_{PR} [kg] has the bulk density ρ_s [kg/m³].

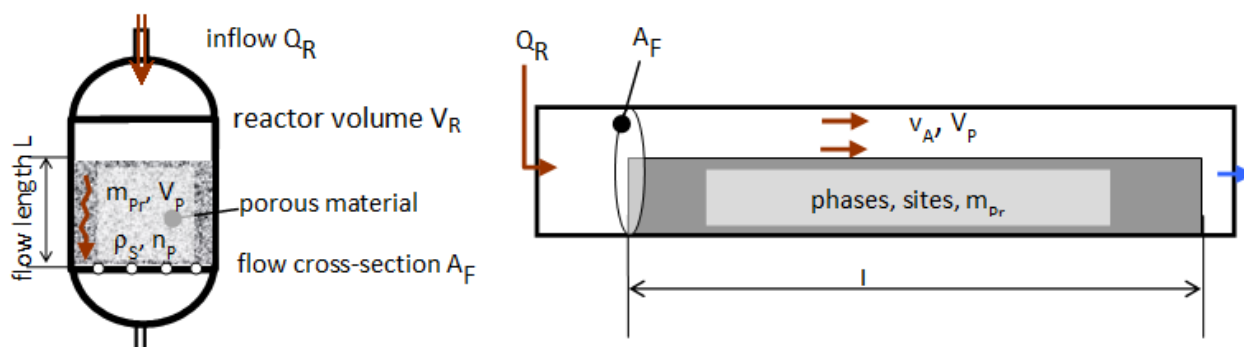


Figure 1 Analogies between the parameterization of water treatment filters and defined stream tubes through pore aquifers.

The filtration velocity v_f [m/d] is related to the empty pipe cross-section A_F , equation (3).

$$v_f = \frac{Q_R}{A_F} \quad (3)$$

The ratio between the pore volume V_P and the reactor volume V_R indicates the porosity n_P [1].

$$n_P = \frac{V_P}{V_R} \quad (4)$$

The pore solution moves through the filter material at a higher distance velocity, accordingly, equation (5).

$$V_A = \frac{V_f}{n_p} \quad (5)$$

PHREEQC relates all reactions to the pore solution V_p . The phase ratio z [L/kg] describes the proportion of the mass m_{pr} of the solid matrix in the pore volume, which can also be derived from the bulk density ρ_s , equation (6).

$$z = \frac{V_p}{m_{pr}} = \frac{n_p}{\rho_s} \quad (6)$$

Ions migrate with different specific velocities because of the interaction between the original pore solution and the aquifer matrix during the displacement of the original pore solution. These chromatographic effects can be simulated using a transport model based on PHREEQC.

3. Materials and Methods

3.1 Exploration and Test Sites

After the closure of opencast mines in the Lusatian lignite mining area (Figure 2), further development of the quality of the groundwater acidity was examined at the locations in Table 1.

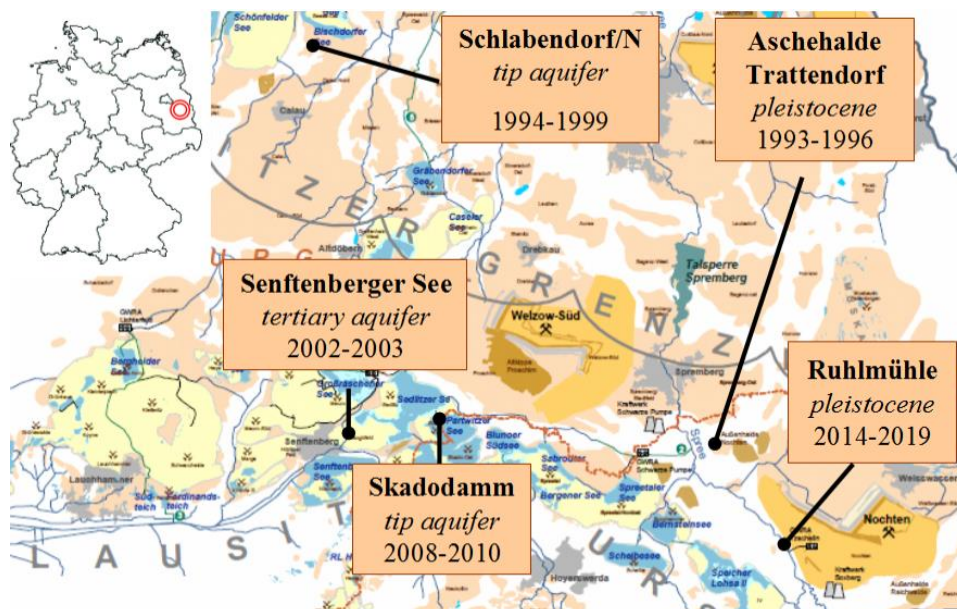


Figure 2 Lusatian lignite mining area in Germany and location of the evaluated study sites.

Table 1 Research and test sites.

Location	treatment time	Aquifer	Specifics	Reference
Aschehalde Trattendorf	1993-1996	pleistocene	legacy, gypsum-water	[7]
Schlabendorf-Nord	1994-1999	old tip	exploration tip groundwater	[1, 8, 9]
Senftenberger See	2002-2003	tertiary	sulphate reduction	[10]
Skadodamm	2008-2010	old tip	sulphate reduction	[11, 12]
Ruhlmühle	2014-2019	pleistocaene	sulphate reduction	[6]

The acidity-forming properties of sediments were investigated using various batch and laboratory filter tests using the methods described in Table 1. At the locations listed in Table 1, aquifers and groundwater were explored and the migration of treated groundwater was tracked.

The company's investigations began as part of a DFG-funded project at sites in the Lusatian post-mining landscape [1, 8, 9]. The inflow of an opencast mining lake at the Schlabendorf-Nord dump was investigated via two groundwater measuring points that had been expanded several times. The investigation methods described here were designed.

Prior to this, the groundwater impairment in a Pleistocene aquifer was observed by penetration of gypsum-saturated water from a power plant ash landfill (Aschehalde Trattendorf). The alkaline infiltrate was neutralized there after a short flow path. The high calcium concentration mobilized adsorbed ferrous iron, which threatened the water treatment of the nearby waterworks. The description of displacement fronts was developed [7, 13].

The development of the remediation process for subsoil sulfate reduction began in a tertiary aquifer layer in the southern upstream of Lake Senftenberg [10]. The results were first continued on a pilot plant at the Skadodamm (tip aquifer) and finally on a demonstration test at the Ruhlmühle (Pleistocene GWL on the Spree) [6]. Underground sulfate reduction can remediate AMD groundwater streams [11, 14].

3.2 Methods of Investigation

The water analyses were carried out according to state of the art in our cooperating laboratories. Batch and filter tests were carried out with tipping sands in the laboratory and pilot plant. A methodology [2] was designed and continuously developed for investigations in flow-through circulation filter systems [11, 12]. In addition to structural aspects, elemental analyses (EDX system) were carried out with a *ZEISS DSM 962 scanning electron digital microscope*.

3.3 Geochemical Simulation

The geochemical model PHREEQC [4] allowed the calculation of complex chemical equilibria and reaction systems. Thus, the developed investigation methods were optimized and processes in the aquifer were simulated [6, 10-12]. New master species with associated constants had to be introduced, adapted to experimental and monitoring results.

4. Selected Results of 25 Years of Research

4.1 Formation of AMD in the Aerated Rock and Transition to Anoxic Groundwater

Groundwater recharge seeps into a soil column from above while atmospheric oxygen penetrates the unsaturated pore system. The finely distributed pyrite there is oxidized to sulfate and hydrogen ions according to the reactions in Table 2. Iron hydroxide precipitates in the neutral medium, equation (12). In the presence of oxygen, the ferrous iron formed is microbially oxidized to ferric iron. This reaction determines the rate of pyrite weathering (autocatalysis). The ferrous iron formed will be oxidized back to ferric iron microbially in the presence of oxygen. This reaction determines the rate of pyrite weathering (autocatalysis). Further follow-up reactions then determine the leachate quality, Table 3.

Table 2 Pyrite oxidation and their formation of acidity as Δ_{RNP} .

Pyritoxidation			Δ_{RNP}	Gl.
$\text{FeS}_2 + 3.75\text{O}_2 + 3.5\text{H}_2\text{O}$	$\rightarrow$	$\text{Fe}(\text{OH})_3 + 2\text{SO}_4^{2-} + 4\text{H}^+$	-4	(7)
$\text{FeS}_2 + 2.8\text{NO}_3^- + 0.8\text{H}^+$	$\rightarrow$	$\text{Fe}^{2+} + 2\text{SO}_4^{2-} + 0.4\text{H}_2\text{O} + 1.4\text{N}_2$	-1.2	(8)
$\text{FeS}_2 + 14\text{Fe}^{3+} + 8\text{H}_2\text{O}$	$\rightarrow$	$15\text{Fe}^{2+} + 2\text{SO}_4^{2-} + 16\text{H}^+$	-4	(9)

Table 3 Selection of relevant subsequent reactions of sulphide weathering with their respective Δ_{RNP} (blue = buffering, red = acidity generating).

Reaction		Δ_{RNP}	Eq.
Pufferung			
$\text{MeCO}_3 + 2\text{H}^+$	$\leftrightarrow$	$\text{Me}^{2+} + \text{H}_2\text{O} + \text{CO}_2$ $\text{Me} = \text{Ca}^{2+}, \text{Mg}^{2+}, \dots$	2 (10)
Ionen exchange			
$\text{X-Me} + \text{H}^+$	$\leftrightarrow$	$\text{X-H} + \text{Me}^+$	1 (11)
Acidity-neutral reactions			
$\text{Fe}(\text{OH})_3 + 3\text{H}^+$	$\leftrightarrow$	$\text{Fe}^{3+} + 3\text{H}_2\text{O}$	0 (12)
$\text{Al}(\text{OH})_3 + 3\text{H}^+$	$\leftrightarrow$	$\text{Al}^{3+} + 3\text{H}_2\text{O}$	0 (13)
$\text{Fe}^{2+} + 0.25\text{O}_2 + \text{H}^+$	$\rightarrow$	$\text{Fe}^{3+} + 0.5\text{H}_2\text{O}$	0 (14)
$\text{Fe}(\text{OH})_3 + 2\text{H}^+ + 0.25\{\text{CH}_2\text{O}\}$	$\rightarrow$	$\text{Fe}^{2+} + 0.25\text{CO}_2 + 2.5\text{H}_2\text{O}$	0 (15)
FeCO_3	$\leftrightarrow$	$\text{Fe}^{2+} + \text{CO}_3^{2-}$	0 (16)
H_4SiO_4	$\leftrightarrow$	$\text{SiO}_2 + 2\text{H}_2\text{O}$	0 (17)
clay wethering			
Kaolinite			
$\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 + 6\text{H}^+$	$\leftrightarrow$	$2\text{Al}^{3+} + 2\text{H}_4\text{SiO}_4 + \text{H}_2\text{O}$	0 (18)
Montmorillonite-Ca			
$\text{Ca}_{0.165}\text{Al}_{2.33}\text{Si}_{3.67}\text{O}_{10}(\text{OH})_2 + 12\text{H}_2\text{O}$	$\leftrightarrow$	$0.165\text{Ca}^{2+} + 2.33\text{Al}(\text{OH})_4^- + 3.67\text{H}_4\text{SiO}_4 + 2\text{H}^+$	0.33 (19)
Illite			
$\text{K}_{0.6}\text{Mg}_{0.25}\text{Al}_{2.3}\text{Si}_{3.5}\text{O}_{10}(\text{OH})_2 + 11.2\text{H}_2\text{O}$	$\leftrightarrow$	$0.6\text{K}^+ + 0.25\text{Mg}^{2+} + 2.3\text{Al}(\text{OH})_4^- + 3.5\text{H}_4\text{SiO}_4 + 1.2\text{H}^+$	1.1 (20)
Albite			
$\text{NaAlSi}_3\text{O}_8 + 8\text{H}_2\text{O}$	$\leftrightarrow$	$\text{Na}^+ + \text{Al}(\text{OH})_4^- + 3\text{H}_4\text{SiO}_4$	1 (21)
storage minerals of Sulphate and acidity			

Reaction		Δ_{RNP}	Eq.
Gypsum $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	$\leftrightarrow \text{Ca}^{2+} + \text{SO}_4^{2-} + 2\text{H}_2\text{O}$	0	(22)
Melanterite $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	$\leftrightarrow \text{Fe}^{2+} + \text{SO}_4^{2-} + 7\text{H}_2\text{O}$	-2	(23)
Jurbanite $\text{Al}(\text{OH})\text{SO}_4 + \text{H}^+$	$\leftrightarrow \text{Al}^{3+} + \text{SO}_4^{2-} + \text{H}_2\text{O}$	-2	(24)
Alunite $\text{KAl}_3(\text{SO}_4)_2(\text{OH})_6 + 6\text{H}^+$	$\leftrightarrow \text{K}^+ + 3\text{Al}^{3+} + 2\text{SO}_4^{2-} + 6\text{H}_2\text{O}$	-3	(25)
Jarosite-Na $\text{NaFe}_3(\text{SO}_4)_2(\text{OH})_6 + 6\text{H}^+$	$\leftrightarrow \text{Na}^+ + 3\text{Fe}^{3+} + 2\text{SO}_4^{2-} + 6\text{H}_2\text{O}$	-3	(26)
Schwertmannite $\text{Fe}_8\text{O}_8(\text{OH})_{4.8}(\text{SO}_4)_{1.6} + 20.8\text{H}^+$	$\leftrightarrow 8\text{Fe}^{3+} + 1.6\text{SO}_4^{2-} + 12.8\text{H}_2\text{O}$	-3.2	(27)

The cations and anions highly enriched in the acidic leachate can temporarily store acidity and sulfate in the leachate area as secondary minerals. In addition, the exchange of cations adsorbed on the solid matrix for hydrogen ions characterizes the seepage water. After the dissolved oxygen has been consumed, the ferric iron is reduced to ferrous iron via the decomposition of organic substances, Equation (15). Part of the ferrous iron formed precipitates as iron carbonate (siderite), Equation (16). The result is the typical anoxic, hydrogen carbonate-buffered landfill groundwater with a high iron, calcium and sulphate concentration.

The hydroxide precipitation and the redox reactions of the iron Equation (12) to Equation (15) do not change the neutralization potential ($\Delta_{\text{RNP}} = 0$), but the pH value does. The siderite and silicate equilibria affect the pH slightly via their downstream buffer systems. The weathering of feldspars and clay minerals Equation (18) to Equation (22) have different buffering effects. Sulfate can temporarily be stored as gypsum neutral regarding acidity and pH Equation (22). Acidity-storing minerals Equation (23) to Equation (27) can temporarily precipitate from the pH-acidic leachate, which is dissolved again by the rising groundwater and release the stored acidity again, Figure 3.

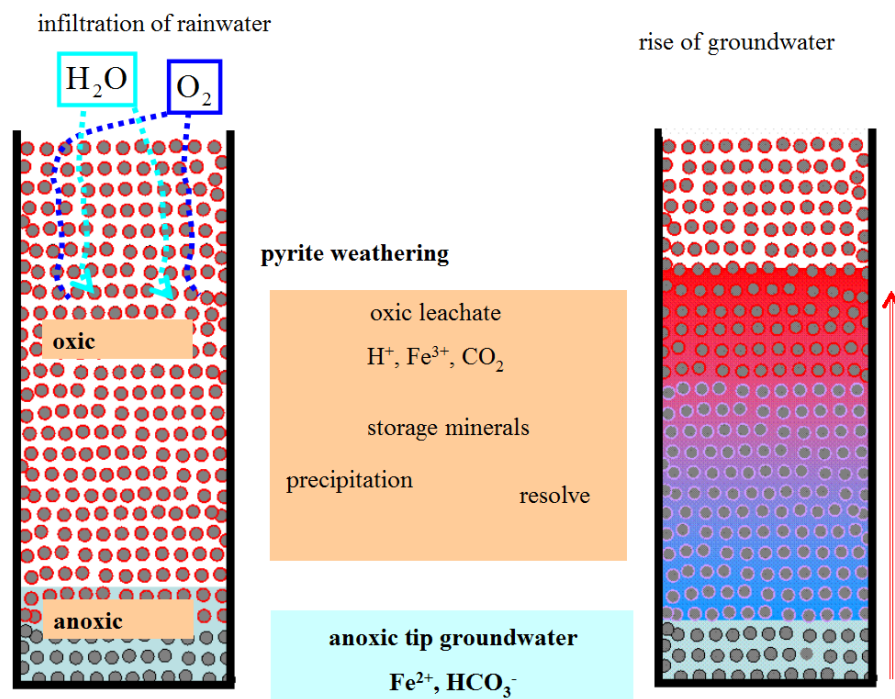


Figure 3 Reaction areas during seepage formation (left) and groundwater resurgence (right).

4.2 Combination of Genesis Processes

Reactions forming AMD (e.g. pyrite weathering), buffering effects and other reactions can be presented as vectors in an acidity/sulphate concentration plane, representing acidity–NP (Figure 4). Additionally, the processes can be demonstrated in an acidity/pH plane. The genesis of groundwater can be simulated with PHREEQC by combining pyrite weathering Equation (7) with selected subsequent reactions from Table 3 [6].

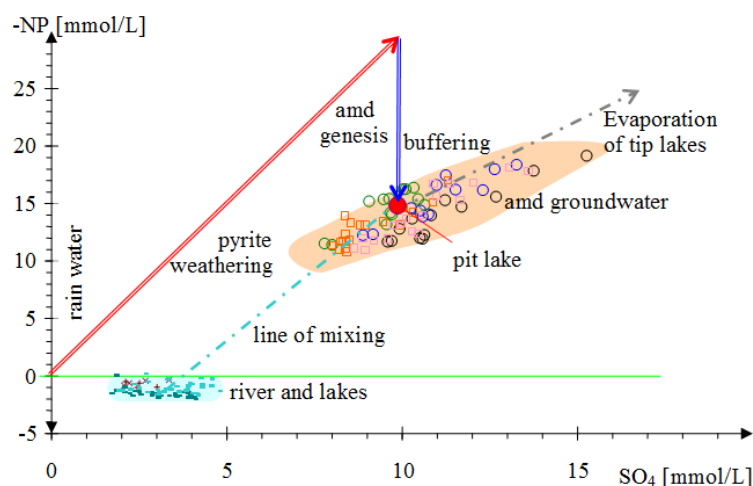


Figure 4 Acidity (-NP)-sulphate plot for the development of groundwater AMD (anoxic AMD) by sulphide weathering and buffering (red and blue vector) and an attached mining lake resulting from the mixture of spatially and temporally varying groundwater compositions.

A regionally typical linear relationship between the groundwater acidities and the sulfate concentrations can often be seen, Equation (28). Schöpke & Preuß [13]) found this connection in published AMD characteristics.

$$NP = A + B \cdot c_{SO_4} \quad (28)$$

Such a site-specific relationship limits the variety of water properties to be considered.

4.3 Surface Complexes on the Solid Phase Surface of the Aquifer

The adsorption properties of the solid phase surface are made up of very different substances, Figure 5. That would be:

- Quartz grains form the pore structure,
- clay minerals,
- Humic substances,
- Biomass and extracellular substances,
- Pyrite and other mineral traces.

These are combined into a representative surface for modeling as Sand_wOH for the weakly acidic to neutral pH range. The equilibrium constants were adjusted to local test results based on the iron hydroxide surface (Hfe_wOH), Table 4.

The Pleistocene aquifer at the Ruhlmühle [6]) consists mainly of quartz sand. The Pleistocene aquifer at the Ruhlmühle [6]) consists mainly of quartz sand. Clay minerals from layers of marl were added to the Skadodamm dump ([12]) during the dumping process. Its calcite content has already been dissolved. The surface complexation of ammonium and phosphate ions was determined during nutrient additions for microbial sulfate reduction. High aluminum concentrations in competition with ferrous iron and calcium ions in the groundwater inflow from the Ruhlmühle also required their consideration.

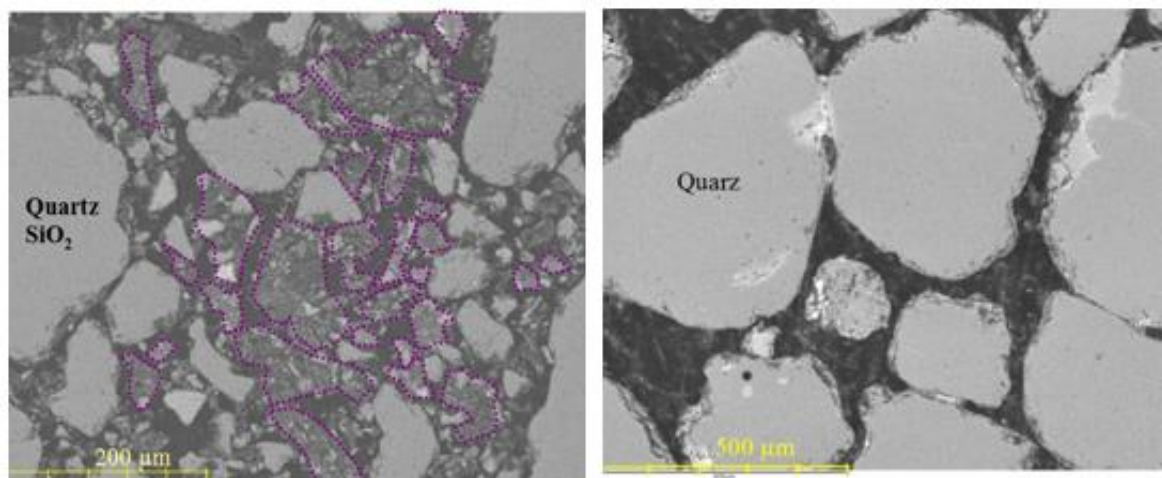


Figure 5 Electron microscopic sections from the tip aquifer with pseudo-marl particles (left) and the Pleistocene aquifer of the Ruhlmühle (right).

A greatly increased adsorption capacity for hydroxyl ions was observed in the strongly alkaline range after mixing in lime products. Silicate complex sites at high pH values were definite as

Sand_IOH. However, Sand_IOH is incompatible with the surface configuration Sand_wOH in sulfate-reducing processes.

Table 4 Optimized surface complex formation constants log_K of the Ruhlmühle (Ruhl) compared to those of the Skadodamm underground reactor (Skado) and the Skadodamm ash wall (Skado-A). (# not used, bold significant difference).

site	equation	log_K		
		Ruhl [6]	Skado [12]	Skado-A [11]
Sand_IOH	$\text{Sand_IOH} = \text{Sand_IOH}$	#	#	0
Sand_IO-	$\text{Sand_IOH} = \text{Sand_IO-} + \text{H+}$	#	#	-6
Sand_IOC _a OH	$\text{Sand_IO-} + \text{Ca}^{+2} + \text{OH-} = \text{Sand_IOC}_a\text{OH}$	#	#	4
Sand_IOMgOH	$\text{Sand_IO-} + \text{Mg}^{+2} + \text{OH-} = \text{Sand_IOMgOH}$	#	#	#
Sand_wOH	$\text{Sand_wOH} = \text{Sand_wOH}$	0	0	#
Sand_wOH ₂ ⁺	$\text{Sand_wOH} + \text{H+} = \text{Sand_wOH}_2^+$	5,50	5,50	4,5
Sand_wO-	$\text{Sand_wOH} = \text{Sand_wO-} + \text{H+}$	-8,20	-8,20	-7,2
Sand_wOAl ⁺ ₂	$\text{Sand_wOH} + \text{Al}^{+3} = \text{Sand_wOAl}_2^+ + \text{H+}$	5,20	9,50	#
Sand_wOAmmH	$\text{Sand_wOH} + \text{AmmH+} = \text{Sand_wOAmmH} + \text{H+}$	0,00	-3,99	#
Sand_wOCa ⁺	$\text{Sand_wOH} + \text{Ca}^{+2} = \text{Sand_wOCa}^+ + \text{H+}$	#	#	-3
Sand_wOFe ⁺	$\text{Sand_wOH} + \text{Fe}^{+2} = \text{Sand_wOFe}^+ + \text{H+}$	#	#	-3
Sand_wOMg ⁺	$\text{Sand_wOH} + \text{Mg}^{+2} = \text{Sand_wOMg}^+ + \text{H+}$	#	#	#
Sand_wOMn ⁺	$\text{Sand_wOH} + \text{Mn}^{+2} = \text{Sand_wOMn}^+ + \text{H+}$	#	#	#
Sand_wONa	$\text{Sand_wOH} + \text{Na+} = \text{Sand_wONa} + \text{H+}$	-5,27	-5,27	#
Sand_wOK	$\text{Sand_wOH} + \text{K+} = \text{Sand_wOK} + \text{H+}$	-4,02	-4,02	#
Sand_wOH ₂ Cl	$\text{Sand_wOH}_2^+ + \text{Cl-} = \text{Sand_wOH}_2\text{Cl}$	0,00	0,54	#
Sand_wOH ₂ H ₂ PO ₄	$\text{Sand_wOH}_2^+ + \text{H}_2\text{PO}_4^- = \text{Sand_wOH}_2\text{H}_2\text{PO}_4$	0,50	1,61	#
Sand_wOH ₂ HCO ₃	$\text{Sand_wOH}_2^+ + \text{HCO}_3^- = \text{Sand_wOH}_2\text{HCO}_3$	0,86	0,86	#
Sand_wOH ₂ HSO ₄	$\text{Sand_wOH}_2^+ + \text{HSO}_4^- = \text{Sand_wOH}_2\text{HSO}_4$	#	#	#
Sand_wOHSO ₄ ⁻²	$\text{Sand_wOH} + \text{SO}_4^{-2} = \text{Sand_wOHSO}_4^{-2}$	-3,76	-3,76	1
Sand_wOH ₃ S	$\text{Sand_wOH} + \text{H}_2\text{S} = \text{Sand_wOH}_3\text{S}$	1,75	#	#
Sand_wOHCa ⁺ ₂	$\text{Sand_wOH} + \text{Ca}^{+2} = \text{Sand_wOHCa}_2^+$	7,00	7,50	1
Sand_wOHFe ⁺ ₂	$\text{Sand_wOH} + \text{Fe}^{+2} = \text{Sand_wOHFe}_2^+$	7,54	7,54	1
Sand_wOHMg ⁺ ₂	$\text{Sand_wOH} + \text{Mg}^{+2} = \text{Sand_wOHMg}_2^+$	6,75	7,25	#
Sand_wOHMn ⁺ ₂	$\text{Sand_wOH} + \text{Mn}^{+2} = \text{Sand_wOHMn}_2^+$	6,80	7,30	#

The parameter sets in Table 4 were adapted to the monitoring data from the tests. Free and protonated adsorption sites elude adaptation.

4.4 Compartment Transitions

Changes from anoxic to oxic conditions and vice versa occur by transitioning from one environmental compartment to another. These compartment transitions and the intrusion of AMD in natural groundwater reservoirs are the focus of the developed model approaches; Figure 6 shows

the possible flows of AMD through different compartments schematically. The redox conditions change during the transition from one compartment to the other (A to D). As a result of these transition processes, several fundamental shifts in water quality occur. The displacement of the pore solution of one compartment by the water from an adjacent compartment also provokes changes in water quality (E). The migration of the displacement front describes this process.

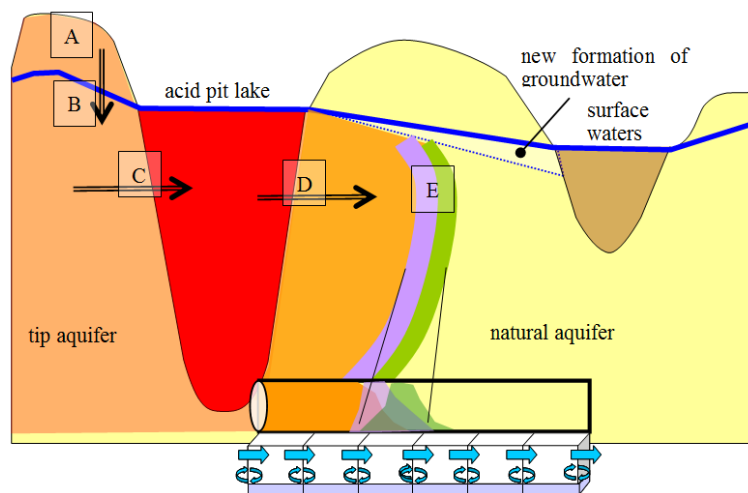


Figure 6 Scheme of creation and conversion sectors of AMD in the compartments.

The transitions A-E in Figure 6 and Figure 7 illustrate:

- A. Initial reactions: Pyrite oxidation and secondary reactions with the formation of toxic leachate AMD.
- B. Compartment transition: Conversion of oxic AMD in anoxic AMD-groundwater.
- C. Compartment transition: Conversion of anoxic tip groundwater in acid pit lake water.
- D. Acid pit lake water infiltration into the aquifer and reconversion in anoxic AMD-groundwater.
- E. Migration: Intrusion of anoxic tip groundwater in a natural aquifer with a displacement of the original pore solution.
- F. Migration: Intrusion of natural groundwater in tip aquifer (not present in Figure 6).

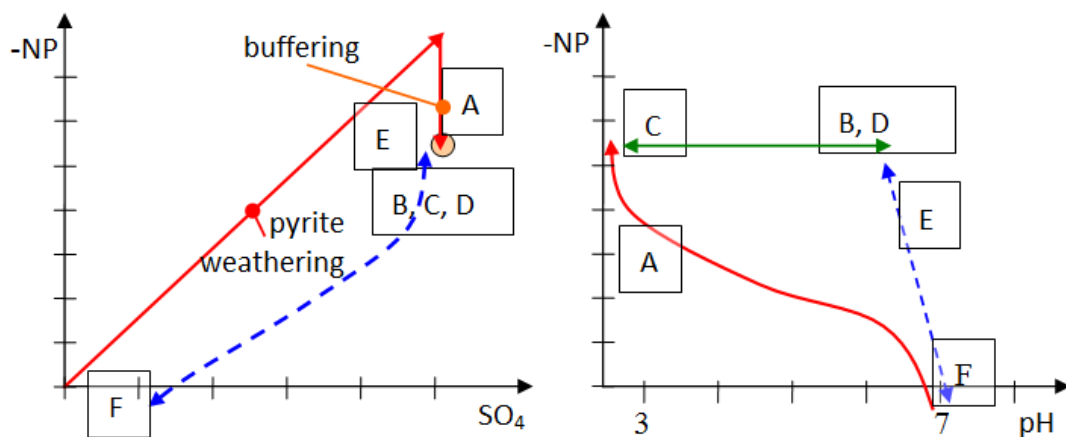


Figure 7 Development of a dump groundwater from low-ion source water (rainwater) through a combination of acid-forming and buffering reaction vectors (left) and changes in the subsequent processes A-F.

The oxic AMD with low pH, elevated acidity and high sulfate concentration will be converted to AMD-groundwater (B) by leaching. Thus, the acidity will be transformed into ferrous ions and the pH will increase. The produced groundwater will be buffered by hydrogen carbonate while acidity does not change. A linear statistical relationship between the acidity (-NP) and the sulfate concentration is frequently observed in studied areas. Such a statistical relation is found for oxic and anoxic AMD, Figure 4 ([2]).

At the conversion of anoxic tip groundwater in acid pit lake water (C) and the reconversion in anoxic AMD-groundwater the acidity and the sulfate concentration remain constant while the pH decreases or increases. During the microbial reduction of ferric hydroxides, the acidity and the sulfate concentration change slightly.

After processes B or D, groundwater migrates to a natural aquifer. Thus, the original pore solution of the natural aquifer will be displaced. Naturally, the pore system consists of sand (particles of quartz), silt, clay and natural organic matter (NOM). A chemical equilibrium between the pore solution and the solid matrix will establish only at low flow rates. The decomposition of organic matter is largely completed in natural aquifers. Equilibria with mineral phases and their surfaces primarily characterize the change of composition. The equilibria constants of solution complexes and important minerals (calcite, siderite, etc.) are known. For simplification, the surfaces of quartz, aluminosilicates (silt, clay) and organic matter will be combined to the representative surface sand_wOH.

4.5 Modeling of a One-dimensional Displacement Front

Mobile regional water bodies in contact with the stationary aquifer solids can be assigned uniform water properties. Stable flow patterns have develop over several decades in natural aquifers. A volume element that moves on a predictable streamline can be reduced to a one-dimensional case. Reactive mass transport processes are described using the general balance equation [15], consisting of the convection, diffusion, dispersion and reaction terms, Equation (29).

$$\left(\frac{\partial}{\partial t} \vec{c}\right)_L = \frac{v_f}{n_p} \cdot \frac{\partial}{\partial L} \vec{c} + \frac{\partial c}{\partial L} \left(D \cdot \frac{\partial}{\partial L} (\vec{c}) \right) + \vec{r} = \frac{v_f}{n_p} \cdot \frac{\partial}{\partial L} \vec{c} + D \cdot \frac{\partial^2}{\partial L^2} \vec{c} + \vec{r} \quad (29)$$

with

$\vec{c}$ = Vector of concentrations [mmol/L]

D = diffusion coefficient [m²/s]

$\vec{r}$ = Vector of reaction rates and source terms [mmol/(L·s)]

L = flow path [m]

v_f = filtration velocity [m/s]

n_p = porosity [1]

A second-order linear partial differential equation system results for the one-dimensional case of a homogeneous flow tube, Equation (30). The source/sink term $\vec{r}$ describing the reactions contains the complicated interactions between the substances.

$$\dot{c} = v_A \cdot \frac{\partial c}{\partial L} + D_L \cdot \frac{\partial^2 c}{\partial L^2} \quad (30)$$

The filtration velocity was replaced by the distance velocity v_A , Equation (31).

$$c(L, t) = \frac{c_0}{2} \operatorname{erfc}\left(\frac{L - v_A \cdot t}{2 \cdot \sqrt{D \cdot t}}\right) \quad (31)$$

And the Gaussian error integral Equation (32).

$$\operatorname{erfc}(x) = 1 - \operatorname{erf}(x) = 1 - \frac{2}{\sqrt{\pi}} \int_0^x e^{-\xi^2} d\xi \quad (32)$$

The EXCEL spreadsheet provides the function Equation (33)

$$c(L, t) = \Delta c \cdot \operatorname{NORM.VERT}(t; t_i; \sigma \cdot \sqrt{t}; wf) \quad (33)$$

With $wf = \text{true}$ for the integrated normal distribution (jump i at $t = t_i$) and $wf = \text{false}$ for the Gaussian function (maximum at $t = t_i$), as well as the variance σ , which includes the longitudinal diffusion coefficient.

For the reactive transition of a phase equilibrium with the stationary phase, Equation (31) proves to be a particulate solution from whose sums the concentration curves of each mobile component within the displacement front can be composed. Equation (34) describes a transition front from three concentration jumps.

$$\begin{aligned} c(t) = c_0 &+ \Delta c_1 \cdot \operatorname{NORM.VERT}(t, t_1; \sigma_1 \cdot \sqrt{t}; \text{true}) \\ &+ \Delta c_2 \cdot \operatorname{NORM.VERT}(t, t_2; \sigma_2 \cdot \sqrt{t}; \text{true}) \\ &+ \Delta c_3 \cdot \operatorname{NORM.VERT}(t, t_3; \sigma_3 \cdot \sqrt{t}; \text{true}) \end{aligned} \quad (34)$$

The parameters t_i and σ_i of each partial jump i and for each component must be determined using an adjustment calculation from simulation calculations (PHREEQC) and/or from monitoring data. Under ideal conditions, the individual partial jumps migrate through the flow tube with different constant distance velocities (retardation), which causes the concentration front to broaden on the flow path. The model can be calibrated by comparing monitoring and simulation.

The particular solution Equation (32) or Equation (33) can be transformed back into a step function at t_i . From this follows a simple material balance as a function of the water column H that has flowed through, Equation (35).

$$H(t) = \int_{t_0}^t v_f dt \quad (35)$$

Equation (36) describes the amount of substance $\Delta n_i/A_F$ normalized to the flow cross-section up to breakthrough $H(t_i)$.

$$\frac{\Delta n}{A_F} = \Delta c \cdot H(t_i) \quad (36)$$

The chemical equilibrium breakthroughs transformed into square-wave functions are time-independent, reversible and only dependent on the phase relationship z_i [L/kg], Equation (37). These are related to the solid mass with the bulk density ρ_s .

$$z_i = \frac{A_F \cdot H(t_i)}{A_F \cdot \rho_s \cdot L} = \frac{v_f \cdot t_i}{\rho_s \cdot L} \quad (37)$$

The retardation R_F indicates the relationship between the distance velocity and the propagation velocity of the concentration jump i , Equation (38).

$$R_F(i) = \frac{v_A}{v_A(i)} = \frac{v_A \cdot t_i}{L} = \frac{v_f \cdot t_i}{n_p \cdot L} = \frac{z(i)}{n_{cell} \cdot z_{cell}} \quad (38)$$

The respective simulated number of cells n_{cell} and variance σ_i determine the resolution of the concentration curves. The retardations of the transformed concentration jump t_i or z_i converge as the number of cells n_{cell} increases. Simulated or observed concentration jumps of a breakthrough front can be transferred to other flow sections via R_F , Equation (39).

$$t_i = \frac{L}{V_A} \cdot R_F(i) \quad (39)$$

By transforming the jumps into rectangular functions, the associated integral material conversions can also be recorded, Equation (40).

$$\Delta n(i) = A_F \cdot \Delta c_i \quad (40)$$

4.6 Simulation Approach for the Calculation of an AMD Breakthrough Front

The complicated concentration curves within a breakthrough front can be simulated with the mixed cell model (PHREEQC, *keyword* transport) and the solutions in Table 5.

For the discussed example, a flow tube of $L = 100$ m was divided into 100 cells of 1 m and calibrated based on exploration results. With a bulk density $\rho_s = 1.67$ kg/L and a porosity $n_p = 0.3$, the phase ratio per cell is $z_{cell} = 0.17$ L/kg. The adsorption surface, which determines the electrical term, has been calculated to be 71000 m²/L at 0.6 nm²/site on the base of cation exchange capacity $cec = 12.1$ mmol/kg or 29.3 mmol/L related to the pore solution. Equilibrated with the solid matrix, the pore solution will be the pore solution, which is equilibrated with the solid matrix, will be displayed in the simulation with a distance velocity $v_A = 0.17$ m/d ($v_f = 0.5$ m/d). This corresponds to 48 hours per cell or 200 days for the column. The times are only important for additionally defined irreversible reactions.

Table 5 Pore- and input solution and their boundary conditions in PHREEQC. Analysis of the tipping aquifer Schlabendorf/N (input) and the tertiary aquifer (pore solution) below from 03.06.2004 ([1]).

Parameter		input solution	pore solution	input options PHREEQC
temp	°C	13	13	
pH	1	4.23	7.12	

redox				Fe(2)/Fe(3)
Na	mg/L	16	4.4	
K	mg/L	3.6	0.6	
Ca	mg/L	431	32	
Mg	mg/L	29.4	1.9	
Fe(2)	mg/L	342	2.70	
Fe(3)	mg/L	0.000001	0.000001	Fe(OH)3(a) 0.00
Mn	mg/L	0.54	0.07	
NH4-N	mg/L	0.0	0.2	as N
Cl	mg/L	13	2.4	
S(6)	mg/L	1783	21	as SO4
C	mg/L	71.1	21.9	as C

The aquifer matrix was configured analogously to Skado in Table 4. The Ruhlmühle aquifer configured for microbial sulfate reduction with nutrient dosing produced implausible ammonium curves.

4.7 Simulation Results of a Breakthrough Front of AMD Groundwater

The passage of a complete breakthrough front has not yet been documented. Various groundwater conditions measured in post-mining landscapes indicate the advance of mining-acidified groundwater. These model calculations are intended to establish the causal connection between displacement groundwater. The complete displacement front forms between $z = 0.1$ L/kg and $z = 1.5$ L/kg, Figure 8. The pH value and the hydrogen carbonate concentration reach the input values. However, the most noticeable fluctuations in concentration occur between $z = 0.1$ L/kg and $z = 0.7$ L/kg. The calculated maximum pH > 7.3 and the adjustment to the amd groundwater have not been observed. Buffer buffer systems not considered in the simulation stabilize the pH value. The breakthrough front begins with the increase in sulfate concentration. While sulfate is hardly adsorbed, the divalent cations calcium, magnesium, iron and manganese are adsorbed on the solid matrix with a simultaneous increase in pH. The temporary precipitation of siderite and calcite in the simulated case follows this. The different affinity for the surface phase determines the distance velocities of these cation fronts. According to observations, the hardeners breakthrough before the ferrous iron. The bicarbonate buffering reaches a maximum between the increase in hardness and the iron concentration. The simulated hardness in the aquifer temporarily increased by 5 mmol/L above the initial concentration. Up to 8 mmol/L were observed. The complex sequence of concentration fluctuations can be explained by competing sorption on the solid and temporarily formed mineral phases, Figure 8.

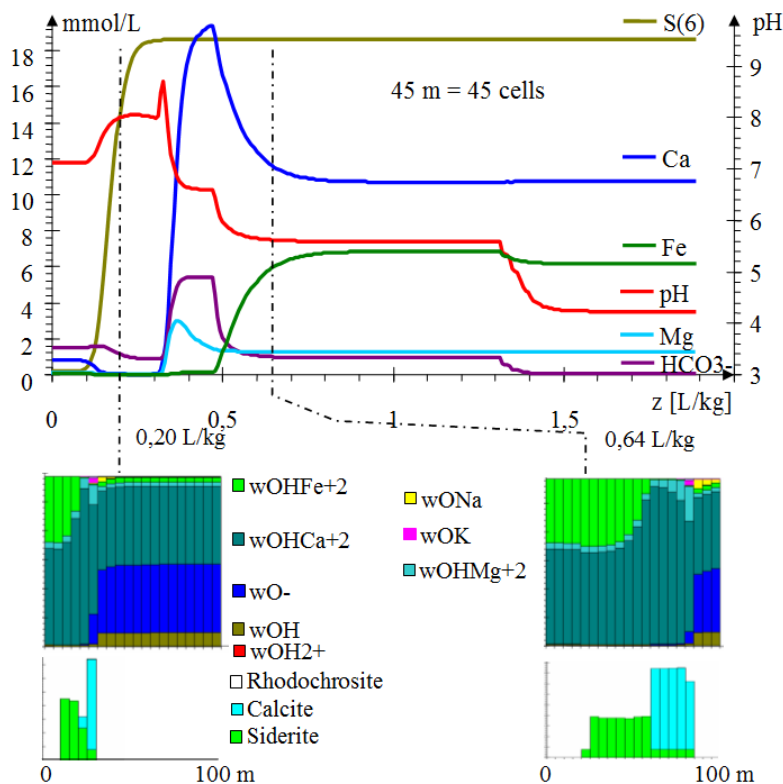
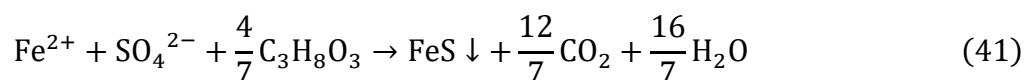


Figure 8 Breakthrough curves depending on the phase ratio z of sulphate, calcium, magnesium, hydrogen carbonate (top, left) and course of the pH value (right) after a flow path of 45 m (45 cells). Below are the respective longitudinal sections of the surface phase and the precipitated mineral phases for $z = 0.2$ L/kg and $z = 0.64$ L/kg.

The iron concentration is about to increase if the groundwater is heavily bicarbonate-buffered with higher sulfate concentrations.

4.8 Modeling Related to Irreversible Reactions

The simulation models were expanded to include reaction terms for microbiological sulfate reduction with glycerol, Equation (41) and calibrated via monitoring, Table 4.



Alternating jumps in the concentration of ferrous iron, sulfate and hydrogen sulfide were generated by intermittent substrate additions, which then migrated through the aquifer. Treated groundwater was alternately displaced by untreated groundwater. A weather-related longer break in treatment (day 350-480) allowed the active adsorption effects to be studied. The observed concentration curves, including the microbial ones, could be reproduced with the extended model, Figure 9.

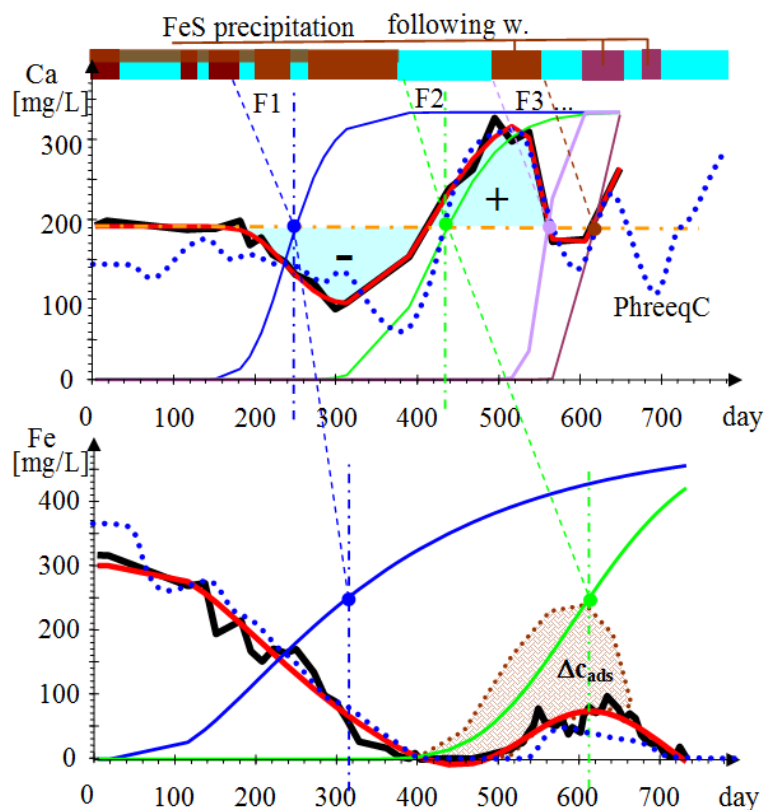


Figure 9 Development of the calcium and ferrous iron concentration after iron sulphide precipitation in the effluent of the substrate dosing (black). The concentration curves will be reproduced (red) with the sum of step functions F1 (blue), F2 (green), F3 (violet), Equation (34). Dotted in blue: Simulation with PHREEQC. The calcium exchanged for calcium (area -) is displaced again by the inflowing iron (area +). The temporarily stored iron concentration is shown as a hypothetical peak (area ΔC_{ads}) that would be expected without exchange [10].

The short dosing intervals up to day 350 are superimposed on the concentration jump F1 in which adsorbed ferrous iron is exchanged for calcium. As a result, the ferrous iron jump F1 developed flatter and more slowly than the lime jump F1. During the long break in treatment, the adsorbed calcium is exchanged back again (F2). Subsequently, the concentration curves become confusing due to shorter treatment intervals. The measured treatment effects can still be adjusted using step functions and simulated with PHREEQC.

5. Discussion and Conclusions

The results of 25 years of research supplement the methods for mine water purification described by Wolkersdorfer [16]. The genesis of amd groundwater can be explained by a combination of pyrite weathering with selected subsequent reactions. Their acidity does not change during unbuffered migration through lakes and aquifers. As oxic amd enters the anoxic aquifer, the pH increases and the acidity appears as ferrous iron. A complex structured concentration front forms between the inflowing anoxic amd and the original groundwater. The sequence of concentration changes within this displacement front can be simulated with PHREEQC. Precise information on the characteristics of the course can only be given with a regionally calibrated model.

Laboratory tests for calibration are difficult under anoxic groundwater conditions. On the other hand, sampling from measuring points along the groundwater flow can provide the information required for calibration. Despite several publications (e.g. [17] and more), these results have gone largely unnoticed.

Based on these methods, a treatment of acidified groundwater by sulfate reduction in a subsoil reactor could be developed ([6, 14, 18]). A comprehensive summary of the results obtained over 25 years of research is being prepared.

Abbreviations and Symbols

A_F	m^2	cross-section
AMD		acid mine drainage
c	mmol/L	concentration
$\vec{c}$	mmol/L	vector of concentrations
D	m^2/s	diffusion coefficient
$F1, F2, F3$	1	functions
H	m	water column that has flowed
H_{fe_wOH}	mmol/kg	surface site of $Fe(OH)_3(a)$
L	m	flow length
n	mol, mmol	amount of substance
NP	mmol/L	neutralization potential
$\Delta_R NP$	mmol/L	change in neutralization potential caused by a reaction
n_p	1	porosity
Q_R	m^3/d	inflow/outflow
$\vec{r}$	mmol/(L·s)	vector of reaction rates, source and sink terms
R_F	1	retardation coefficient
$Sand_IOH$	mmol/kg	surface site of quartz in the strongly alkaline
$Sand_wOH$	mmol/kg	surface site of quartz in the neutral
t	d, h, s	time
v_A	m/d	distance velocity
v_f	m/d	filtration velocity
V_P	m^3	pore volume
V_R	m^3	reactor volume
z	L/kg	phase relationship
ρ_s	kg/L	bulk density
σ		variance

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Author Contributions

The Author is solely responsible for this work.

Competing Interests

The author has declared no competing interests exists.

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