

## Modeling the changes in water quality of AMD along the flow path

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### Abstract

Mine waters enter the environment and spread in groundwater as well as in surface waters. Sometimes they change their characteristics along the flow path several times. By modeling these processes, it is possible to forecast potential environmental damages and to avert them successfully.

AMD flows through various compartments in the environment. In the course of the transition from one compartment to the other, the redox conditions change from anoxic to oxic conditions and vice versa. These compartment transitions and the intrusion of AMD in natural groundwater reservoirs are the focus of the developed model approaches.

Due to compartment 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. This process is described by the migration of the displacement front.

Simulation calculations allow retracing the observed statistical relation between the acidity and the sulphate concentration. By the use of a connected groundwater flow model, it is possible to forecast the arrival of high iron and sulphate concentrations at sensitive points of the flow path. After the inclusion of microbiological reactions, the developed model concepts based on PHREEQC (Parkhurst & Appelo 1999) will be used for the long-term management of in-situ sulphate reduction.

Key words: Mine water, modeling, groundwater quality

### Introduction

During the migration of Acid Mine Drainages (AMD) through different environmental compartments, for example tip, lake or river, their characteristics change. Thereby, undesirable effects and risks may occur because of the acidity and high concentrations of iron, sulphate and heavy metals. Changes in water quality in the course of the spread of AMD in the environment can be understood by the use of several model concepts. In specific cases, they even allow forecasting the relevant changes in characteristics.

### Use of neutralization potential to characterize AMD

The oxidation of pyrite and other sulphides generates the acidity of AMD. Using the sum parameter of acid capacity  $K_{S4,3}$  the neutralization potential is defined by equation 1 (Evangelou 1995 modified by Schöpke & Preuß 2012).

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

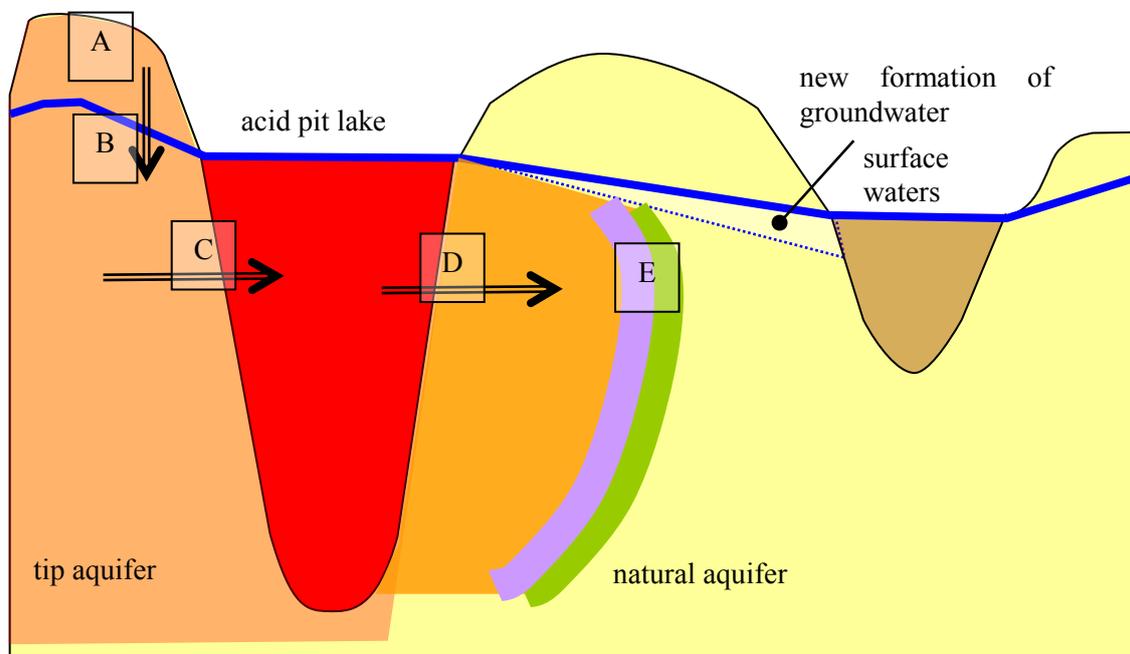
Ferrous ions, manganese and aluminum are not included in the titration of  $K_{B4,3} = -K_{S4,3}$ . Therefore, they must be analysed separately and added to equation 1. Other hydrolyzing cations must also be taken into account. For example,  $Zn^{2+}$  will have to be considered if its occurrence plays an important

role in the investigated groundwater. Reactions forming AMD (e.g. pyrite weathering), buffering effects and other reactions can be presented as vectors in an acidity/sulphate concentration plane, wherein acidity is represented by  $-NP$  (figure 2). Additionally, the processes can be demonstrated in an acidity/pH plane.

### Compartment transitions

Changes from anoxic to oxic conditions and vice versa occur by the transition from one environmental compartment to the other. These compartment transitions and the intrusion of AMD in natural groundwater reservoirs are the focus of the developed model approaches (Parkhurst & Appelo 1999).

Figure 1 shows schematically the possible flows of AMD through different compartments. In the course of the transition from one compartment to the other (A to D), the redox conditions change. 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). This process is described by the migration of the displacement front.

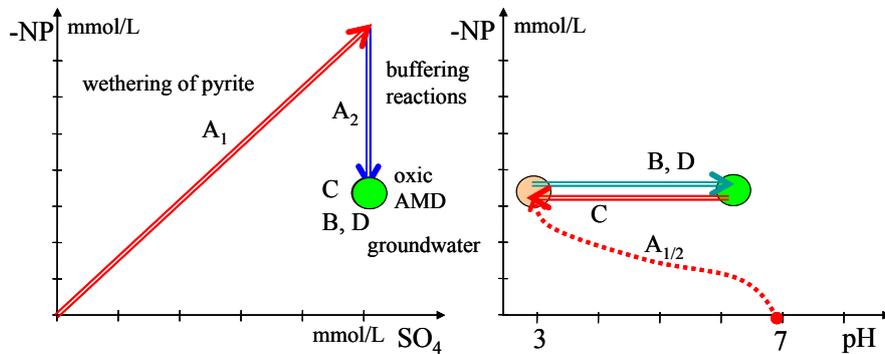


**Figure 1** Scheme of creation and conversion sectors of AMD in the compartments.

The transitions A-E in figure 1 and figure 2 illustrate:

- A: Initial reactions: Pyrite oxidation ( $A_1$ ) and secondary reactions ( $A_2$ ) with formation of oxic 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: Infiltration of acid pit lake water into the aquifer and reconversion in anoxic AMD-groundwater.
- E: Migration: Intrusion of anoxic tip groundwater in a natural aquifer with displacement of the original pore solution.
- F: Migration: Intrusion of natural groundwater in tip aquifer (not present in figure 1).

By leaching, the oxic AMD with low pH, elevated acidity and high concentration of sulphate will be converted to AMD-groundwater (B). Thus, the acidity will be transformed to ferrous ions and the pH will increase. The produced groundwater will be buffered by hydrogen carbonate while acidity does not change. A statistical linear relationship between the acidity (-NP) and the sulphate concentration is frequently observed in studied areas. Such a statistical relation is found for both oxic and anoxic AMD (Schöpke & Preuß 2012).



**Figure 2** Reaction vectors in an acidity/sulphate concentration plane.

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

**Intrusion of anoxic tip groundwater in a natural aquifer with displacement of the original pore solution (E)**

After processes B or D, groundwater migrates in 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. Decomposition of organic matter is largely completed in natural aquifers. Equilibria with mineral phases and their surfaces primary 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 defined in PHREEQC. Based on iron oxides (Hfo\_wOH in wateq4f) Schöpke et al. (2011) described the surface sand\_wOH. Using groundwater monitoring data in the course of treatment experiments the equilibrium constants of surface complexes were adjusted.

To model the relevant processes the aquifer is idealized as a flowed column based on the parameters in table 1.

**Table 1.** Parameters of the aquifer idealized as column

Parameter	symbol	unit
area of column	$A_F$	$m^2$
flow time	$t_0, t_1$	d
flow length	$L$	m
reactor (column) volume	$V_R$	$m^3$
porosity	$n_p$	1
specific discharge	$v_f$	m/d
fluid velocity	$v_A$	m/d
flowed water column	$H$	m
amount of exchanged pore volume in the column	$PV$	1
concentration in the column	$c(L)$	$mol/m^3$
amount of substance	$n$	mol
concentration of inflow	$c_0$	$mol/m^3$
capacity function based on volume	$q_v(c)$	$mol/m^3$
adsorbed concentration with respect to the volume of solution	$c_x$	$mol/m^3$

Ions migrate with different specific velocities  $v_A$  because of the interaction between the original pore solution and the aquifer matrix. These chromatographic effects can be simulated by the use of the transport model based on PHREEQC.

Via the pore volume  $n_p$ , the fluid velocity  $v_A$  is linked to the specific discharge  $v_f$ .

$$v_A = \frac{v_f}{n_p} \tag{2}$$

By integrating over the specific discharge the flowed water column  $H$  will be obtained

$$H = \int_{t_0}^{t_1} v_f \cdot dt \tag{3}$$

In the beginning,  $t = t_0$ , the pore solution ( $c_0$ ) is in chemical equilibrium with the solid phases of the aquifer ( $q_v(c_0)$ ). After influx of water column  $H$ , so when an ideal jump in concentration ( $c_0 \rightarrow c_1$ ) migrates, the new state of the solid phase ( $q_v(c_1)$ ) standing in equilibrium with  $c_1$  adjusts itself. This leads to mass transfer between the solid phase and the flowed pore solution. As a result, a concentration front differing from the quality of the infiltrated solution occurs. If the solution front has advanced to the length  $L$ , the following balance can be used for the flow path (equation 4):

$$(c_1 - c_0) \cdot H_D = \frac{v_f}{v_A(c_0 \rightarrow c_1)} = \frac{\Delta n(t_1)}{A_F} = (c_1 - c_0) \cdot L \cdot n_p + (q_v(c_1) - q_v(c_0)) \cdot L \tag{4}$$

$H_D$  is the already passed water column, when reaching concentration  $c_1$  at length  $L$  (breaking point). Thereby, the breakthrough is considered as ideal jump ( $c_0 \rightarrow c_1$ ), which migrates through the column. The amount of substances in the volume of the pore solution is calculated from the reactor length  $L$ , the area  $A_F$  and the porosity  $n_p$ . To calculate the amount of substances adsorbed to the matrix the volume-related capacities of the matrix  $q_v(c_0)$  and  $q_v(c_1)$  in their respective equilibria are necessary.

As part of the calculations, the processes in filters and in the aquifer refer to the respective reactor volume. PHREEQC indicates the concentration of the adsorbed phase with respect to the volume of the pore solution. The volume-related capacities of the matrix are linked to their concentrations in PHREEQC  $c_x$  via the pore volume  $n_p$ .

$$q_v(c) = n_p \cdot c_x \tag{5}$$

Unfortunately, the absolute volume-related capacities  $q_v$  of real aquifers cannot be indicated because of the different binding forms. However, only the changes are significant to describe the migration processes.

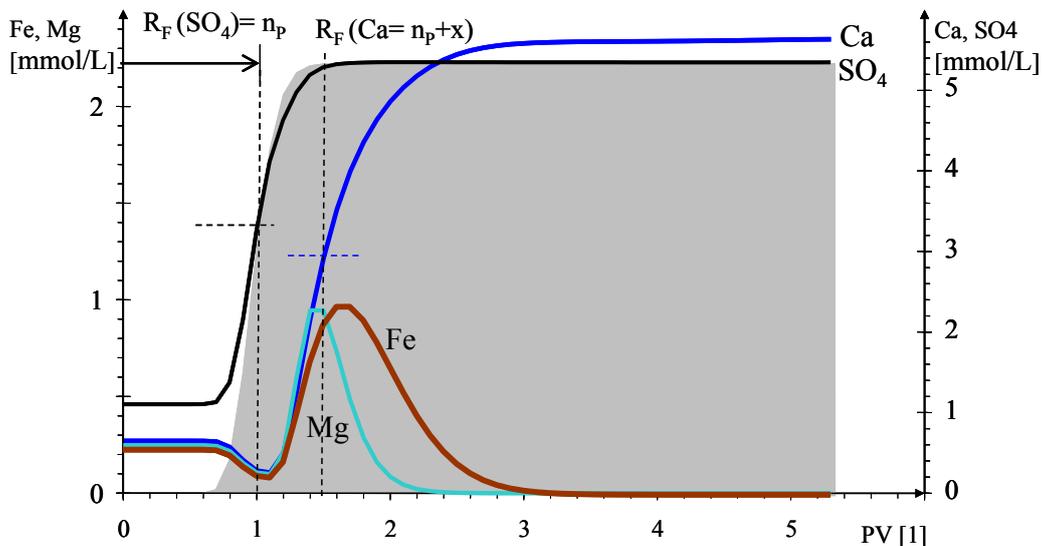
$$R_F = \frac{H_D}{L} = n_p \cdot PV = n_p + \frac{(q_v(c_1) - q_v(c_0))}{(c_1 - c_0)} \tag{6}$$

In contrast to the commonly used definition of the retardation factor  $R_F$ , here the often not exactly determinable pore volume  $n_p$  is included.

Considering several interacting components instead of just one, for example in a real water, the adjustment of the new equilibrium can take place by several jumps in concentration that occur with each other and/or successively. This transition pattern can be simulated by the use of a mixed-cell-model. For each jump in concentration, characteristic  $R_F$ -values are obtained. They allow predicting the further migration assuming defined boundary conditions.

**Examples**

A simple example is the infiltration of alkaline water from a dump of power plant ash. After infiltrating in the aquifer, the alkaline water is quickly neutralized. During the subsequent displacement of a weakly acidic groundwater by this calcium sulphate-rich infiltrate a complex transition front develops. The inflowing calcium ions thereby replace the cations ferrous and magnesium adsorbed to the matrix of the aquifer. Consequently, a transition front with increased ferrous and magnesium concentrations establishes in the infiltrate. Figure 3 shows the modeling results of this process using a mixed-cell-model. Therein, the progressions of concentrations are plotted depending on the exchanged pore volume PV. Sulphate breaks through immediately running approximately parallel to the hydraulic breakthrough. In previous investigations of pore aquifers in Lusatia, Germany, Schöpke et al. (2011) fitted the parameters of the surface complexes on the aquifer matrix.



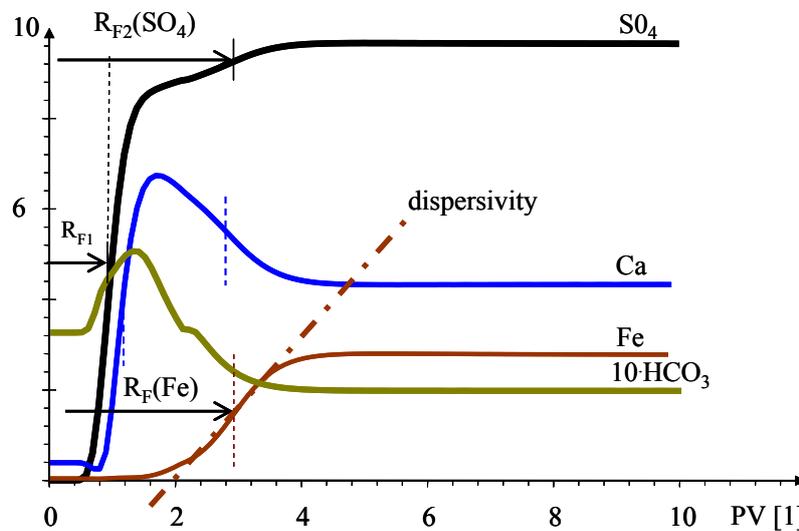
*Figure 3 Modelled concentration patterns due to the displacement of groundwater by a calcium sulphate-rich water as a function of the exchanged pore volume*

However, while the calcium concentration approaches the concentration of the inflow the magnesium and ferrous concentration increase temporarily. In particular, the high amount of ferrous is problematic (Table 2). Anyway, the developed concentration pattern is characteristic of this process. Therein the chemical parameters of the aquifer matrix determine the maximum concentrations and retardations. A result of the modeling is initially a forecast of the expected concentration pattern. The calculated concentration pattern can be divided into sequences of several jumps in concentration. Each jump in concentration migrates in accordance with its characteristic retardation factor  $R_{Fi}(X)$ . The full passage of such a front can be rarely observed at a single measuring point. To adjust the model the data of a groundwater monitoring network should be used.

**Table 2.** Different water qualities of the displacement of groundwater by a calcium sulphate-rich water

parameter	unit	neutralised infiltrate	transition front	groundwater
pH	l	5-7	5,1	5,5
$K_{S4,3}$	mmol/L	0	0,13	0,12
NP	mmol/L	0	-2,0	-0,3
Ca	mg/L	225	100 - 150	26
Mg	mg/L	0	20 - 35	6
Fe	mg/L	0	40 - 60	13
$SO_4$	mg/L	600	400	125

The second example concerns the migration of anoxic tip groundwater in a natural aquifer (E). During this migration in principle the same processes take place, except that the inflow also contains ferrous and acidity. Occasionally calcite and siderite have to be considered as mineral phases in the aquifer matrix. Therefore, the resulting concentration patterns are more complicated than shown in figure 3.



**Figure 4** Modelled concentration pattern due to the displacement of groundwater by tip groundwater as a function of the exchanged pore volume

The increase in the hydrogen carbonate concentration shown in figure 4 depends on the solution of calcite, which was present in the aquifer. After solving the calcite phase, a jump in concentration follows and a stable groundwater quality establishes. Thereby, the dispersivity of the column determines the steepness of the transitions.

By means of extensive scenario calculations, adsorptive neutralization processes can be traced in tip aquifers (Schöpke & Preuß 2013). They show linear relations between the acidity and the sulphate concentration that deviate from the pyrite weathering stoichiometry (Schöpke & Preuß 2012, Schöpke & Preuß 2015).

## Conclusions

When simply changing the redox conditions of AMD (B, C, D), the acidity changes rarely. Oxidic AMD are usually acidic, while anoxic AMD are slightly acidic to neutral. In this case, the acidity is mainly caused by ferrous.

During the intrusion of anoxic tip groundwater in a natural aquifer with the displacement of the original pore solution (E), complex quality patterns develop at the displacement front. The individual jumps in quality migrate delayed after the groundwater flow. A transport modeling can approximately predict the quality pattern and their retardation. Hazard scenarios, inter alia for water catchments, can be derived from the comparison between the modeling and the observational data.

Currently, the process of infiltration of acid pit lake water into the aquifer and the reconversion in anoxic AMD-groundwater (D) is still the least understood. In this case, the reduction processes do not end in an equilibrium. At the passage through reducing sediments, a certain pH and the corresponding iron concentration adjust themselves. They decisively determine the concentration pattern that develops during the migration through the aquifer (E).

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