Experimental Development and Testing of an in Situ Technology to Reduce the Acidity of AMD-laden Groundwater in the Aquifer

Ralph Schöpke

Brandenburgische Technische Universität Cottbus, Lehrstuhl Wassertechnik und Siedlungswasserbau, 03046 Cottbus, Germany, e-mail: schoepke@tu-cottbus.de

Abstract

The oxidation of pyrite and other sulphides generates AMD as a result of mining activities. STUMM & MORGAN (1996) define acidity based on an ion balance concept. The application of this acidity-concept is limited due to analytical difficulties. One has to analyse all ionic parameters and their measurement errors. Hence, titration can be used as approximation in form of a modified neutralisation potential NP. The genesis of the groundwater and therefore the remediation of AMD can be demonstrated in -NP-sulphate-diagrams.

Sulphate-reducing processes were initiated in an aquifer with AMD-laden groundwater. Substrates were injected orthogonally to the located main groundwater flow direction. Groundwater was intermittently circulated between two wells. As substrate, methanol and nutrients were added to this circulation flow. After one year a sulphate-reducing reactor was formed within the aquifer. It could be prooved that FeS precipitation took place and acidity decreased. These effects could still be observed one year after termination of substrate injection.

Key words acid mine drainage, remediation, restoration, saturated groundwater, microbial sulphate reduction

Introduction

As a result of mining activities in the region Lausitz AMD is formed within mining dumps. Surface water bodies are influenced by migrating AMD and form acidic post mining lakes. An anaerobic sub-surface treatment plant using sulphate reduction was developed for in-situ treatment of the potentially acidic groundwater. The treatment plant was constructed and built as a pilot scale experiment at Lake Senftenberg. The pilot scale experiment run for two year with promising results-

Theoretical background

The oxidation of pyrite and other sulphides generate AMD as a result of mining acitvities. STUMM & MORGAN (1996) defined acidity (Aci) as the equivalent sum of acids that are titrable with a strong base.

$$\mathrm{Aci} = \sum \text{strong acids} - \sum \text{strong bases} \qquad \text{eq. (1)}$$

EVANGELOU (1995) definied the neutralisation potential **NP** eq.eq. (2) based on eq. eq. (1).

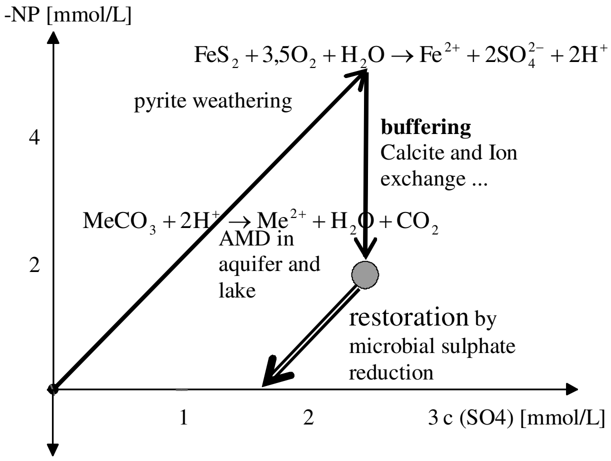
$$-\mathrm{Aci} = \mathrm{NP} = 2c_{\mathrm{CO3}} + c_{\mathrm{HCO3}} + c_{\mathrm{OH}} - c_{\mathrm{HSO4}} - c_{\mathrm{H+}} - 2c_{\mathrm{Fe2+}} - 3c_{\mathrm{Fe3+}} - 3c_{\mathrm{Al3+}} - 2c_{\mathrm{Mn2+}} \qquad \text{eq. (2)}$$

After summarizing Parameters of acid capacitiy $K_{S4,3}$, SCHÖPKE (1999) formed eq. eq. (3).

$$\mathrm{NP} \approx K_{\mathrm{S4.3}} - 3c_{\mathrm{Al3+}} - 2c_{\mathrm{Fe2+}} - 2c_{\mathrm{Mn2+}} \qquad \text{eq. (3)}$$

Ferrous Iron, manganese and aluminium are not included in the titration of $K_{B4.3} = - K_{S4.3}$. Therefore, they must be analysed separately and added to eq. eq. (3). Other hydrolyzing Cations must be included too. For example Zn^{2+} has to be considered if its occurrence plays an important role in the investigated groundwater. Eq. (3) does not take into account concentrations of hydroxo-complexes of cation-acids. These occur (pH depended) only in minor concentrations. Reactions forming AMD (e.g. pyrite weathering) and buffer reactions (e.g. calcite dissolution) can be presented as vectors in an acid/sulphate concentration plane, where acid equals –NP (see Figure 1).

Figure 1 *Vectors of pyrite weathering and carbonate buffering wich generate amd and vector of restoration, eq.(4)*



Microbial sulphate reduction can be expressed using eq.(4). As a substrate methanol is chosen. The reaction vector in the acid/sulphate plane is antiparallel compared to the vector of pyrite weathering in Figure 1.

$$Fe^{2+} + SO_4^{2-} + \tfrac{4}{3}CH_3OH \rightarrow FeS + \tfrac{4}{3}CO_2 + \tfrac{8}{3}H_2O \qquad (4)$$

Eq. (4) is limited due to the available concentration of iron in solution. Hydrogen sulphide is formed in absence of iron.

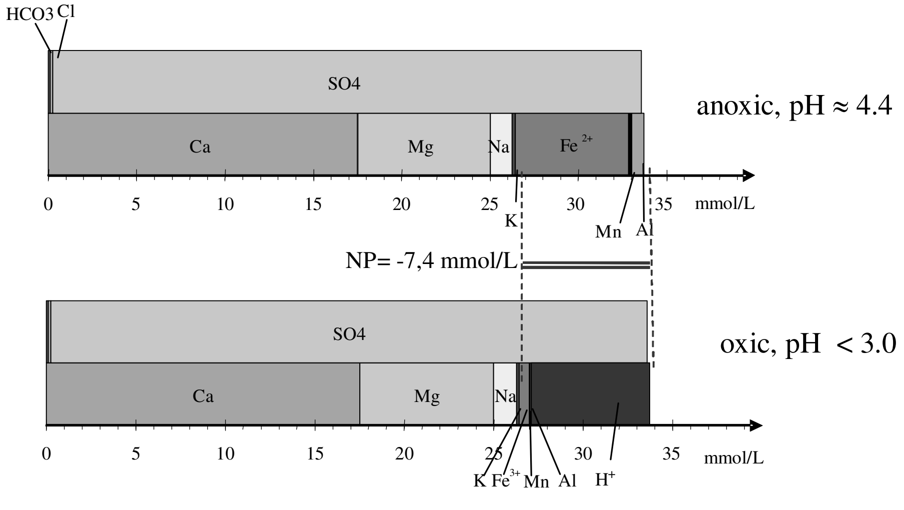
$$2H^+ + SO_4^{2-} + \tfrac{4}{3}CH_3OH \rightarrow H_2S + \tfrac{4}{3}CO_2 + \tfrac{8}{3}H_2O \qquad (5)$$

The formation of H_2S expressed in reaction eq.(5) is not desired in the remediation process.

Experiments

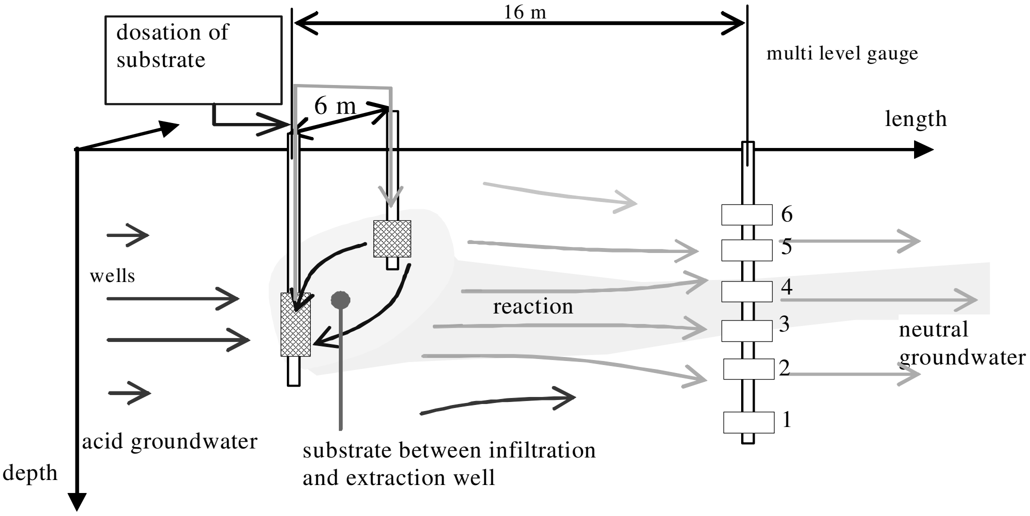
The Pilot scale setup was installed in an aquifer at the south of Lake Senftenberger (Lausitz, Germany). A layer of anoxic acidic groundwater migrating towards Lake Senftenberg had been treated (Figure 2, Table 1) by microbial sulphate reduction. The composition of the untreated and treated groundwater is contained in Table 1. Fig. 2 demonstrates the oxidation of groundwater.

Figure 2 *Ion* ***b****alance (composition) of groundwater in anoxic and oxidised form (equilibrium with atmosphere in lake)*



The setup of the pilot scale experiment for remediation is shown in Figure 3. Methanol and nutrients were injected as substrate for sulphate reducing bacteria. The injection was conducted orthogonally to the located main groundwater flow direction. Groundwater was intermittently circulated between two wells. The time for short circuit of substrate between infiltration and extraction well was estimated to be about 48 h.

***Figure 3** Pilot scale setup for remediation of AMD bearing groundwater by microbial sulphate reduction*

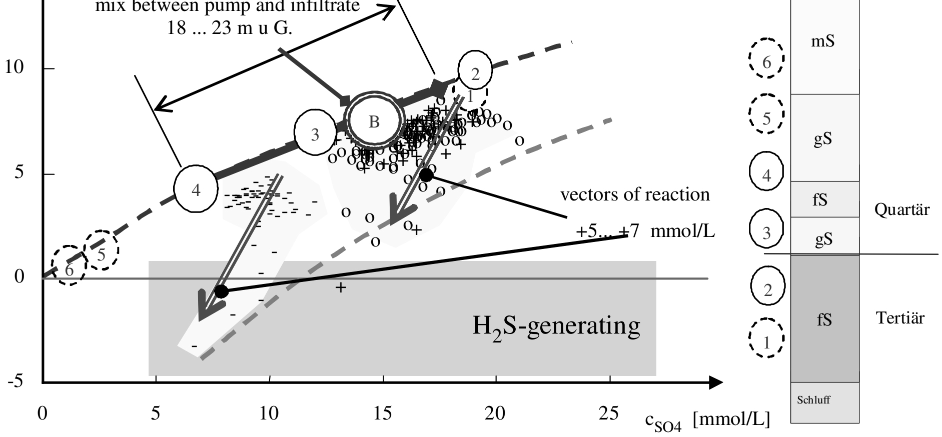


After one year a sulphate-reducing reactor was formed within the pore space of the aquifer with a cross-section of approximately 50 m^2. It could be prooved that FeS precipitation took place and that hydrogen sulphide was formed. It can be stated that the acidity of the treated groundwater decreased. The initial injection was continuously conducted over three months. The treatment effects could still be observed one year after termination of substrate injection.

Results

Groundwater composition at the test site is a function of aquifer depth. The groundwater properties are vertically distributed. As shown in figure 4 deeper tertiary layers are characterised by higher aciditiy than quaternary layers. Due to the genesis of the groundwater a statistical correlation between the measured acidity using the -NP concept of Schöpke (1999) and the groundwater sulphate concentration exists (see figure 4).

***Figure 4** results of the pilot scale experiment*



Considering reaction vectors (see Figure 1) for sulphate reduction, groundwater from different layers can be separated and characterised by initial boundary conditions based on statistical analysis. Figure 4 shows the groundwater properties at the observation well (sampling points 2 to 4 in Figure 3) downstream of the substrate injection compared to the treated groundwater (end of reaction vectors in Figure 4).

***Table 1** Two representative analysis of reactor inflow and outflow*

Parameter		inflow 1	outflow 1 with iron	inflow 2	outflow 2 with lack of iron
PH	1	4.40	5.26	4.30	6.2
$K_{S4.3}$	mmol/L	≈0	0,46	0	2,8
Fe	mg/L	180	102	120	<1
Sulphid-S	mg/L	<0.01	<5	<0,01	60
SO_4	mg/L	1 900	1 200	1 100	600
NP	mmol/L	-7.4	-2.2	-4,8	+2
ΔNP≈	mmol/L	+5		+7	

The mean reduction of the acidity (ΔNP) of the groundwater was calculated and is about 5-7 mmol/L.

Conclusions

The results of the pilot scale experiment show that it is possible to treat anoxic AMD. The treatment result of sulphate reduction is limited due to available dissolved iron. If the available dissolved iron is depleted, hydrogen sulphide is formed. To use the pore space of the aquifer as a reactor, a period of adjustment of about 3 months is necessary. A statistical approach calculating the results of the treatment is possible considering a reaction vector analysis. Currently a pilot scale experiment is on its way applying glycerine as substrate

Acknowledgements

We would like to thank the German Ministry for Education and Research (BMBF) and the LMBV for funding and supporting the project.

Project details

„Experimentelle und modellgestützte Entwicklung von Verfahren der geochemischen Grundwasser- und Untergrundbehandlung zur Gefahrenabwehr im Nordraum des Senftenberger Sees" (Kennzeichen: BMBF 02-WB 0068, Laufzeit: 01.09.2000 – 31.08.2003 mit Verlängerung bis 31.12.2003, BTUC 2003). The project is documented in Koch et al. (2006) and Schöpke et al. (2006)

References

Evangelou (1995): Pyrite oxidation and its control; CRC Press Boca Raton New York London Tokio

Koch, R.; Schöpke, R.; Mangold, S.; Regel, R.; Striemann A. (2006): Entwicklung und Erprobung eines Verfahrens zur Untergrundentsäuerung von Kippengrundwässern; Schriftenreihe Siedlungswasserwirtschaft und Umwelt, Bd.11

Schöpke, R.(1999): Erarbeitung einer Methodik zur Beschreibung hydrochemischer Prozesse in Kippengrundwasserleitern; Dissertation BTU Cottbus LS Wassertechnik, Schriftenreihe Siedlungswasserwirtschaft und Umwelt, Heft 2

Schöpke, R.; Koch, R.; Mangold, S.; Preuß, P.; Regel, R.; Striemann, A. (2006): Entwicklung und Erprobung eines Verfahrens zur Untergrundentsäuerung von Kippengrundwässern; Grundwasser 11 (2006) 4, S.270-275

Stumm & Morgan (1996): Aquatic chemistry - Chemical Equilibria and Rates in Natural Waters; third edition John Wiley, New York