ORIGINAL ARTICLE

Felix Bilek

Column tests to enhance sulphide precipitation with liquid organic electron donators to remediate AMD-influenced groundwater

F. Bilek
Grundwasserforschungszentrum e.V.,
Meraner Str. 10, Dresden, Germany
E-mail: fbilek@dgfz.de
Tel.: +49-351-4050674
Fax: +49-351-4050679

Abstract Dump groundwaters in the former East-German lignite-mining district are characterized by high amounts of ferrous iron and sulphate. Both the pyrite weathering products endanger the surface water quality when discharged into lakes. Only the precipitation of both contaminants in the subsurface can prevent the further contamination of surface waters. The two-step process of microbial catalyzed sulphate reduction and iron sulphide precipitation is limited by the low availability of natural organic substances as electron donators. Therefore, a new remediation technique is developed based on the injection of a liquid organic electron donator (methanol) into the contaminated aquifer. The saturated aquifer is used as a bioreactor, where iron monosulphides are precipitated in the groundwater-filled pore space. Column experiments were performed under natural pressure and temperature conditions with natural anoxic groundwater and original sediments to test the remediation technology. The test showed that a complete iron removal (4 mmol/l), even under rather acid conditions (pH 3.8), is possible after having established an active sulphate reducer population. The turnover of the added organic substance with sulphate is complete and the amount of the resulting sulphide controls the effluent pH. In addition, intensified microbial activity triggers the turnover of natural organic substances. Also, natural Fe(III) hydroxides react with the sulphide produced. Considering the long natural retention times (decades), artificially enhanced FeS precipitation is spontaneous, although it shows kinetic behaviour in the range of days. In light of the promising results, the development of a field scale application of this technique is considered to be necessary. It will have to focus on the improved precipitation control of the FeS in the subsurface.

Keywords Sulphate reduction · Sulphide precipitation · Acid mine drainage · Remediation technology · Germany · Lausitz

Introduction

Most of the primary energy production in former Eastern Germany was based on lignite. The former East-German open cast lignite mining district covers an area of about 70×70 km^2. The groundwater table had been lowered up to 100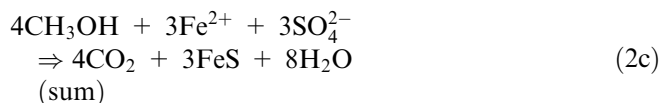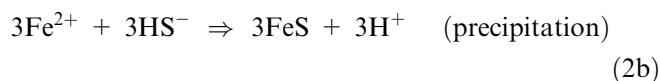 m to run 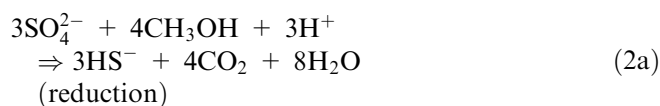the mines. The coal seams had been overlain by pyrite-rich silt and clay layers. During the mining process, the overburdened sediments had been strip-mined and thereby were aerated. Pyrite oxidation occurs because this mineral is not in thermodynamic equilibrium with atmospheric conditions (Eq. 1). Pyrite weathering products are stored in the pore water of the unsaturated zone. Most of the mines

were shut down after the German reunification for economical reasons. The former groundwater table is currently re-established reducing ongoing pyrite oxidation in the dumps. This causes the dissolution of the pyrite weathering products in the rising groundwater. This water, which eventually leaves the dump because of the natural hydraulic gradient, is characterized by high amounts of acidity, which is mainly transported by ferrous iron and sulphate concentrations of up to 30 mmol/l.

$$FeS_2 + 3.5O_2 + H_2O \Rightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+ \quad (1)$$
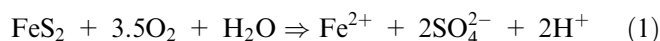
Adjacent lakes and rivers suffer from low pH-values due to Fe(III)-hydroxide precipitation and high sulphate inputs. Their shores are contaminated by ferric iron hydroxide sludge. Although neutralization of the surface water bodies by addition of carbonates or soda would raise the pH, it does not protect the surface waters from high amounts of sulphate and the deposition of the hydroxide sludge.

Sulphate reduction (Eq. 2a) and consecutive sulphide precipitation (Eq. 2b) would present an attractive natural attenuation process because it eliminates the acidity transported by Fe(II) from solution as well as sulphate. Unfortunately, most natural rates of sulphate reduction cited in literature do not support the hope for the establishment of an effective self-healing process in the acidified aquifers (Chapelle et al. 1987; Leuchs 1988; Schulte 1998; Chapelle and McMahon 1991; Bilek 2004).

$$3SO_4^{2-} + 4CH_3OH + 3H^+$$
$$\Rightarrow 3HS^- + 4CO_2 + 8H_2O \quad (2a)$$
(reduction)

$$3Fe^{2+} + 3HS^- \Rightarrow 3FeS + 3H^+ \quad (precipitation)$$
$$(2b)$$

$$4CH_3OH + 3Fe^{2+} + 3SO_4^{2-}$$
$$\Rightarrow 4CO_2 + 3FeS + 8H_2O \quad (2c)$$
(sum)

In lignite mining dump, aquifers ferrous iron and sulphate are abundant in solution and do not represent limiting factors for sulphide precipitation. Although East-German dump aquifers show high amounts of tertiary organic carbon of up to 5 mass% (Berger 2000), which originate from the tertiary lignite, the lack of a bioavailable electron donor seems to be the rate limiting step for sulphide production (Wisotzky 1998, 2003). Its bioavailability is low probably due to its structure, which is a key factor for the microbial mineralization process (Giblin et al. 1990; Cook and Schindler 1983; Kelly and Rudd 1984; Lovley and Klug 1986). Continuous addition of bioavailable organic substances, therefore, is considered to be a promising way to enhance natural sulphate reduction- and precipitation rates and to reduce the acidity load of the dump groundwaters by this way.

Elimination of 1 mol of ferrous iron by the precipitation of iron monosulphide leads to the storage of 2 mol acidity, but it will not eliminate the other 2 mol of protons, which are released during weathering of 1 mol of pyrite (Eq. 1). Most unoxic dump groundwaters show pH-values between 4 and 6 due to carbonate or silicate dissolution (Bilek 2004). Thus precipitation of iron monosulphides is sufficient to bind the remaining acidity of the dump groundwater.

Mass balance calculations showed that the huge matter fluxes, which have to be treated in the area of investigation, require large amounts of electron donators, which cannot be stored in the aquifer itself, by constructing a reactive wall with organic solids as described by Benner et al. (2002), Blowes et al. (1995) and Herbert et al. (1998). Also the pore volume of a reactive wall would be filled with precipitates within a short time and would reduce the hydraulic flux through the wall. Moreover, tests with solid organic material showed declining reaction rates after a few months due to the selective consumption of solid organic material (Benner et al. 2002; Blowes et al. 1995; Herbert et al. 1998). Thus, the continuous injection of liquid organic material into the reaction zone in the aquifer and the use of the whole aquifer pore space as room for precipitation seem to be rather promising.

Enhanced sulphate reduction for water treatment has been investigated in laboratory studies for many years. Batch-tests (Hard et al. 1997) or experiments in fluidized bed reactors have been performed (Barnes et al. 1992; Govind and Yang 1999). Fixed bed column tests have been studied by Tuttle et al. (1969), Wakao et al. (1979) and Tsukamoto and Miller (1999), which used material that consisted partly or completely of solid organic material or was previously spiked with buffering substances (Maree et al. 1986). In some investigations no iron sulphide precipitation was aspired after sulphate reduction (Reis et al. 1988; Elliot et al. 1998). Oxidized mine waters are treated in pond-systems (Rose et al. 1998) and up-flow anaerobic sludge blanket reactors are used to precipitate metal sulphides (Diaz et al. 1997). No investigation is known to the author that combines most of the conditions that are relevant for the remediation technique to be developed. Therefore, column tests were performed to represent the natural conditions as close as possible. In this paper, the results of these tests are represented, which were performed accompanying in situ tests (LMBV 2003). The main elements of the experimental design are:

– Combining the two processes *sulphate reduction* and simultaneous *iron sulphide precipitation* in a fixed bed reactor.

– The use of natural sediment from the test site (poorly sorted sands with 80 mass% between 0.1 and 2 mm grain size) without any organic or buffering additives.
– The use of natural anoxic (Standard redox-potential 500 ± 100 mV) ferrous iron-rich groundwater from the field test site with an acidity of about 7.0 mmol/l and a pH of about 3.8.
– The use of methanol as an electron donator. Its availability for sulphate-reducing bacteria is well documented (e.g. Tsukamoto and Miller 1999; Lyew et al. 1994; Hard et al. 1997).
– Pressure (2 atm) and temperature (10–15°C) conditions typical for the test site.
– The use of natural sulphate reducer populations [inoculation procedure is described in Bilek (2004)].

The purpose of this research was to investigate if sufficient sulphate reduction and precipitation was achievable under the mentioned rather realistic conditions in order to reduce the remaining acidity of the groundwater to levels that allow the discharge into public surface waters. The low pH of 3.8 of the water was expected to post the most severe problem for the
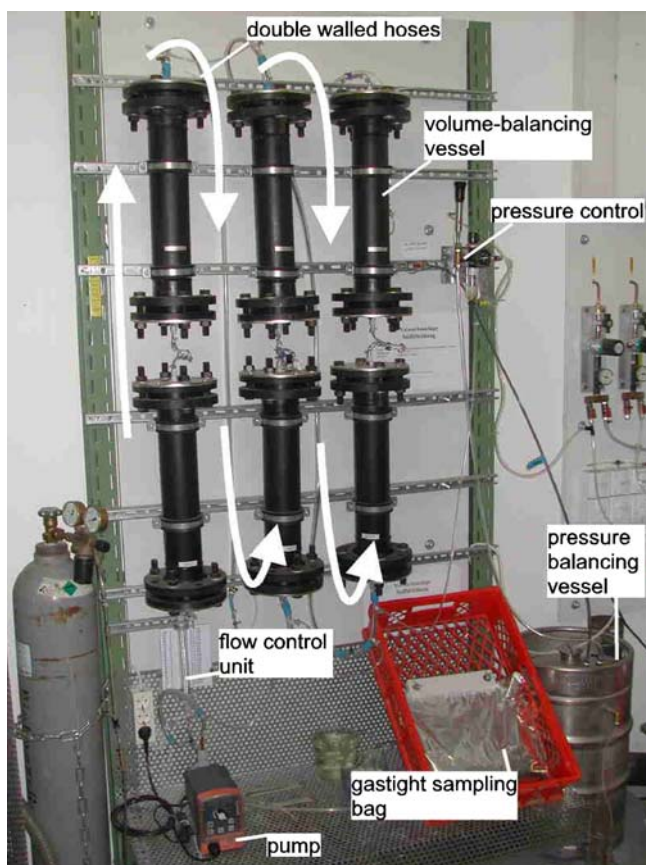

Fig. 1 Construction of the column consisting of five sections, one vessel to balance the liquid volume during sampling and one nitrogen-filled pressure balancing vessel

establishment of an active sulphate-reducing bacteria (SRB) population.

Materials and methods

A HDPE column consisting of five 50-cm-sections and five sampling ports was used for all the experiments (Fig. 1, Table 1). In the field test (LMBV 2003), the injection of the methanol occurred about 20 m below the groundwater surface. Under these conditions, the naturally dissolvable CO_2 contents were significantly higher than under atmospheric conditions. Total inorganic carbon (TIC) is a product of the sulphate reduction (Eq. 2c), it contributes to the buffer capacity of the water and the solubility product of siderite is dependent of the CO_3^{2-} content. This necessitated a column-construction, which enabled the relative pressure to be kept constant at about 2 bar. This was realized with a pressure-balancing vessel at the column outlet, which also served to take up the waste water discharged.

The sediment was taken from the drilling cores of the injection well at the field test site from the saturated zone. It was homogenized and filled into the columns under nitrogen atmosphere in a glove box while being saturated with anoxic groundwater from the site.

Native groundwater was percolated through the column. It was stored under anoxic conditions in flexible gastight aluminium/plastic bags. The groundwater at the site was in equilibrium with about 7,000 Pa of CO_2. To prevent degassing under atmospheric conditions in the bags, an artificial atmosphere of 93,000 Pa N_2 and 7,000 Pa CO_2 was placed in the bags before filling them with groundwater. To stabilize the Fe(II) concentration in the storage bags, they were spiked with 50 mg/l of the reducing agent sodiumdithionite ($Na_2S_2O_4$).

The weekly sampling was done by connecting a valve, a 0.2 µm filter and a syringe to one of the sampling ports. The internal pressure of the system pressed the pore water slowly into the syringe without contact to the atmosphere. The sample was then divided up for analytic purposes. The cations were analysed with an ICP (Spectro CIROS[CCD]), and ferrous iron and sulphate were analysed separately by liquid ion chromatography (Dionex). Sulphide was measured with a sulphide electrode (AMT Analysenmeßtechnik GmbH) under anoxic acid conditions, dissolved organic carbon (DOC) was measured according to DIN EN 1484(H3) with a TOC5000 (Shimatzu). The same technique was adapted to measure TIC. Seven successive experimental steps (Table 2) were performed during the operation of the column.

Acidity was calculated by numerically titrating the samples with the speciation program PHREEQC vers. 2.8 (Parkhurst and Appelo 1999). Atmospherical conditions (gas partial pressures for CO_2 and O_2) and a

Table 1 Geometric and hydraulic data of the column

Column		
Length	2.5	M
Diameter	0.075	M
Area	$4.42 \cdot 10^{-3}$	m2
Total volume	$1.10 \cdot 10^{-2}$	m3
Flux		
Pore water velocity	$2.25 \cdot 10^{-1}$	m/d
Darcy velocity	$6.52 \cdot 10^{-2}$	m/d
Pore space	0.29	
Flow rate	0.2	ml/min
Retention time	11.1	D

pH-value of 7.0 were used as a reference state because the future seepage of the treated water into a neutral surface water body was expected. Also, the precipitation of iron- and aluminium hydroxides was numerically enabled using the equilibrium constants K of the PHREEQC standard database.

Results

The inflow concentrations of all ions given in Table 3 stayed constant throughout the whole experiment except for aluminium, which showed a clear pH-dependence due to Al-hydroxide precipitation. The increase of the DOC concentration above the background level of 6 mg/l represents the addition of methanol in the groundwater storage bags (Table 2). All experimental steps show a complete reduction of the added DOC to its background level between the inflow and port 1 (Fig. 2).

This documents the complete microbial oxidation of the methanol within the first 50 cm and within 2.2 days. The only exception occurred after changing the inflow pH-value from 4.8 to 3.8 (experimental step 6): The DOC temporarily showed elevated concentrations compared to the background level: Methanol was therefore not oxidized completely for a 2-3 weeks period (Fig. 2) due to the reduced microbial activity. After that, the original microbial activity was restored again.

Although FeS is oversaturated at port 1 in *experimental step 1* and iron(II) elimination is incomplete (Fig. 3), no further decline of the ferrous iron

Table 3 Averaged water quality at the inflow

	Inflow	Port 1
pH	3.8 Conc. [mmol/l]	6.3 Conc. [mmol/l]
Fe(TOT)	3.19	0.00
Fe(II)	3.14	0.00
Mn(TOT)	0.22	0.22
Al(TOT)	0.14	0.00
Ca(TOT)	6.93	7.11
MgTOT)	4.07	4.32
Na(TOT)	0.89	0.56
K(TOT)	0.18	0.16
Si(TOT)	0.65	0.54
Sulphate	15.0	8.63
Sulphide	0.03	0.70
Cl(TOT)	< 0.36	0.44
TIC	2.37	13.1
DOC (mg/l)	5.65	13.0
O_2	0.00	0.00
	$K_{B7.0}$: 7.0	$K_{A7.0}$: 4.4

concentration occurred along the flow path between ports 2 and 5.

In *experimental step 2*, the inflow pH-value was raised to reduce the solubility of the iron monosulphide (Eq. 2b). This pH- increase had no visible effect on the pH-value at port 1 and only a very small decrease of iron concentration was observed (Fig. 3).

Therefore, the methanol concentration was raised to 200 µl/l in *experimental step 3*, which led to an immediate small pH-increase from 5.2 up to 5.5 (Fig. 4). The sulphide concentration declined and the sulphate as well as the ferrous iron concentration showed a marked decline (Figs. 3, 5).

In *experimental step 4*, fresh groundwater with a lower redox-potential was used. This resulted in a sulphate- and ferrous iron concentration decline at port 1 and a raise of the pH-value from 5.3 up to 6.

In *experimental step 5*, 400 µl/l methanol was added, which again was oxidized completely within the first 50 cm of the column. The pH-value was raised up to 6.3, the standard redox-potential was lowered below 0 mV (Fig. 4). In this step, ferrous iron was eliminated completely.

In *experimental step 6*, the methanol-inflow concentration stayed at 400 µl/l, but the pH was not increased artificially any more. This step was performed to test
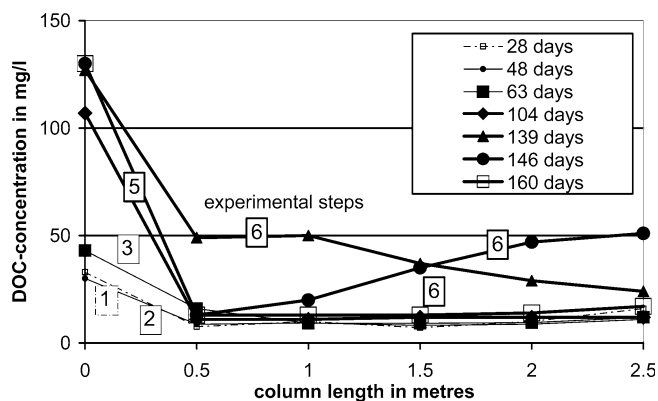
Table 2 Experimental steps and changes of the injected ground water

Experimental step	pH value	Methanol concentration (µl/l)	Redox potential (mV)	Duration (days)
1	3.8	100	500–600	35
2	4.8	100	400–500	13
3	4.8	200	400–500	42
4	4.8	400	100–200	14
5	4.8	400	100–200	35
6	3.7	400	500–600	28
7	3.8	0	400–500	35

Fig. 2 Selected DOC-concentration profiles along the column in the course of the experimental steps

how stable the well-established microbial fauna behaves under the increased environmental stress of the natural pH-conditions. After having lowered the pH, sulphide- and TIC concentration declined immediately. Both concentrations re-approached their former levels within a period of 3 weeks (Figs. 5, 6). Methanol was not completely used up during this period (Fig. 2).

In *experimental step 7*, methanol was not added any more and the pH was not raised artificially. This step was performed to test how long the established SRB population would be active under these conditions and if re-dissolving iron sulphides would lead to an unwanted increase of iron- and sulphur species. Sulphide- and TIC concentration declined immediately, sulphate- and ferrous iron concentration rose up to their inflow levels within 3 weeks.

Iron disulphides have neither been found in the original sediment nor after termination of the laboratory experiment. Iron monosulphides have been visible as black coatings on the sediment surface. This coating was rather homogenous within the first 50 cm of the column and showed increasingly heterogeneous distribution along the further flow path. Almost no coatings were visible any more after 2 m of the flow path (Fig. 7).

Discussion

Electron transfers

The described results show that it is possible to achieve a significant reduction of groundwater acidity by artificially enhancing the precipitation of iron sulphides. The microbial population in the column and the turnover measurable as DOC-, TIC-, sulphate-, sulphide- and iron concentration adapt in every step of the experiment to the added amount of electron donor. This clearly shows that the easily bioavailable electron donor is the limiting factor for sulphate reduction in the investigated system.

Sediment analysis (Bilek 2004) showed that the observed decline of the iron concentration is due to the formation of iron monosulphide. Comparing the stoichiometry of the governing redox reactions with the change in concentration of reactants and products showed that additional sediment-born organic carbon was transformed into TIC (Fig. 8). The quantity of this turnover seems to be correlated with the microbial activity because the excess of TIC increases with the increasing turnover of methanol. A complete non-availability of the sediment-born organic carbon for SRB cannot thus be deduced from the constant DOC

Fig. 3 Ferrous iron and aluminium concentration at the inflow and port 1
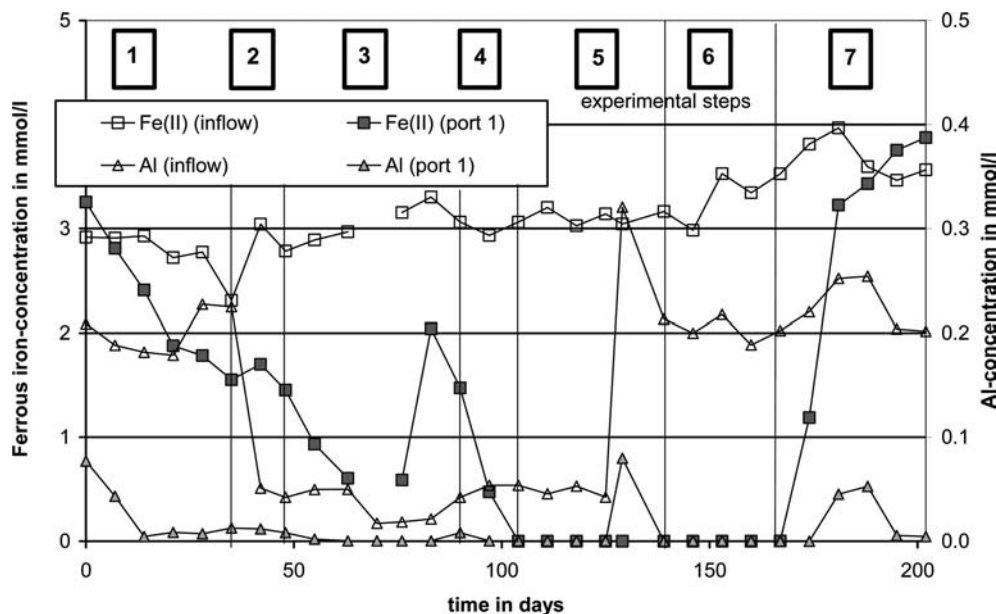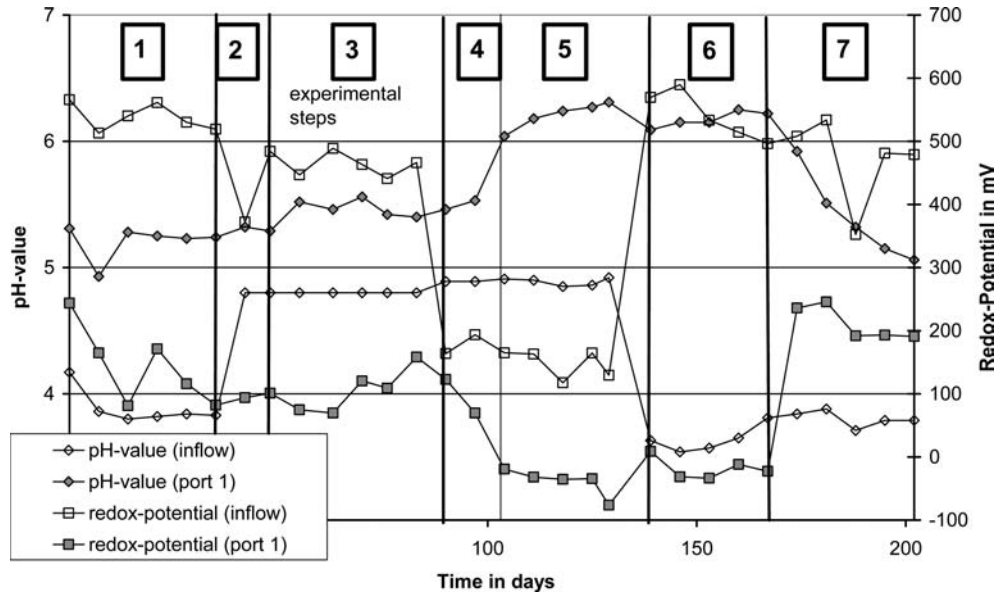
Fig. 4 pH-value and standard redox-potential at the inflow and port 1

concentration. The sediment analysis confirmed the consumption of sediment-born organic carbon during sulphate reduction (Bilek 2004) and also showed that the reductive dissolution of ferric hydroxides by sulphide (described by van Gunten and Zobrist 1993; Pytzik and Sommer 1981) must be a major sink for sulphide.

pH-control

The establishment of the SRB population in experimental step 1 was successful even at an inflow pH-value of 3.8. The artificial increase of the pH-value (experimental steps 2 through 5) did not result in a measurable pH-increase at port 1 and hence no

measurably increased precipitation of iron monosulphide and thus was not necessary. This finding was supported by experimental step 6 with no artificial pH increase: After a temporary decline of the sulphide reduction (Figs. 2, 8), the former reaction rates were achieved again. This shows the adoption process of the SRB to the new environmental conditions. Thus, even the rather acid groundwater from the site seems to be treatable by the new technology of injecting liquid electron donors into the aquifer.

If all sulphide generated was used up by FeS precipitation, no pH-increase would result (Eqs. 2a–c). Only if the sulphide production exceeds sulphide precipitation, a pH-increase can occur, as can be seen from the correlation of sulphide concentration and pH-value (Figs. 4, 5).

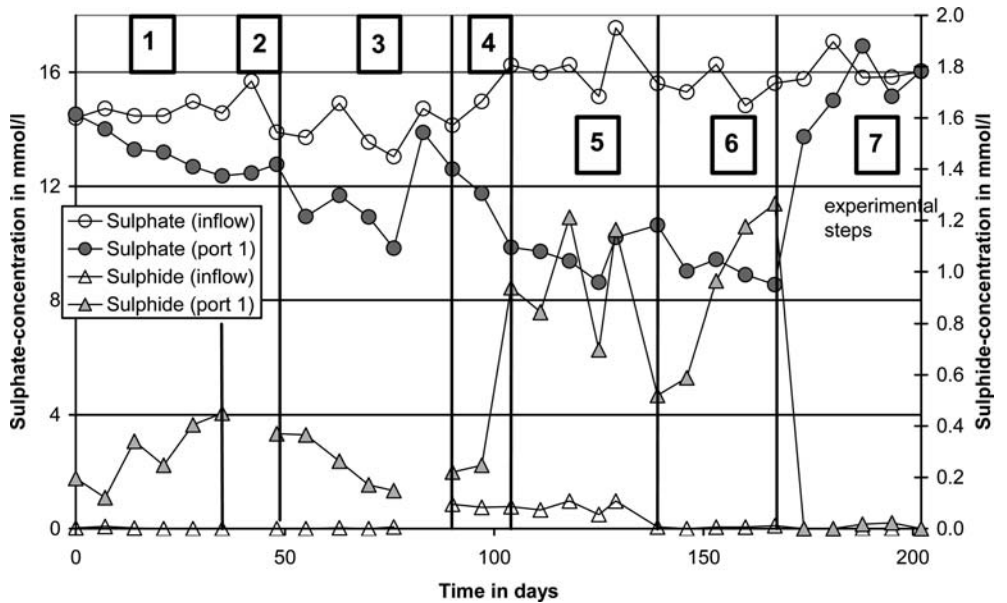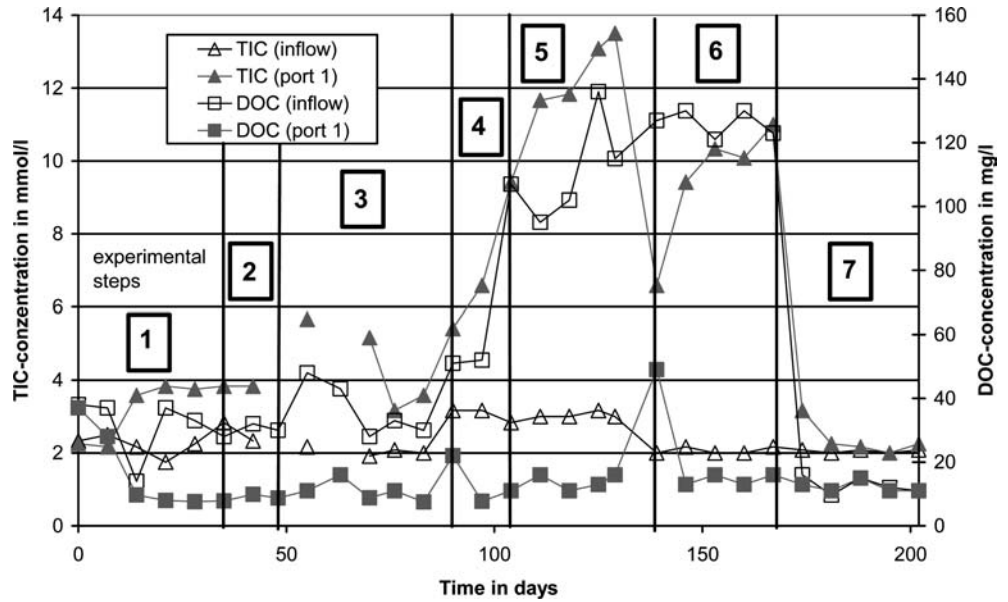**Fig. 5** Sulphate- and sulphide-concentration at the inflow and port 1

Fig. 6 DOC- and TIC-concentration at the inflow and port 1

Space for precipitates

The complete oxidation of all the artificially added electron donor occurs somewhere within the first 50 cm of the flow path and within 2.2 days after the methanol-enriched groundwater is infiltrated into the sediment column. Transferred to the field scale the desired reaction occurs immediately and rather completely when the dissolved reactants methanol and sulphate get into contact with the sediment colonized by SRB. It is therefore expected that in case of an injection of methanol in an aquifer the precipitation would take place only in the nearest vicinity to the injection well. The void pore space, which is available for precipitation, is thus considered to be rather small. The resulting clogging of the pore space by precipitation products, thus. might represent a hindrance for the long-term use of the infiltration device.

Control of the iron monosulphide precipitation

Iron monosulphide precipitation seems to be correlated with the pH and the sulphide concentration (compare Figs. 3, 4, 5). Both correlations suggest that the precipitation of the iron monosulphide is controlled by its solubility product (Eq. 2b). On the other hand, the pore water shows up to ten times oversaturation of iron monosulphide at port 1 in experimental steps 1–4 compared to the solubility product given in the PHREEQC-database (Fig. 9). The oversaturation at port 1 does not show a dectable trend in the course of the experiment. A decline of the oversaturation, for example, because of an increasing number of crystalization cores is not observed. Also, the (strongly scattered) saturation indices at the other ports do not show any clear trend or relation to the experimental steps.

Fig. 7 Sediment samples from various positions along the flow path

Fig. 8 Comparison of the concentration of electron donors and -acceptors in all experimental steps. To compare the electron releasing and the electron consuming processes better in light of the redox reaction stoichiometries, the concentrations are presented in moles of electrons which are consumed or are released, respectively
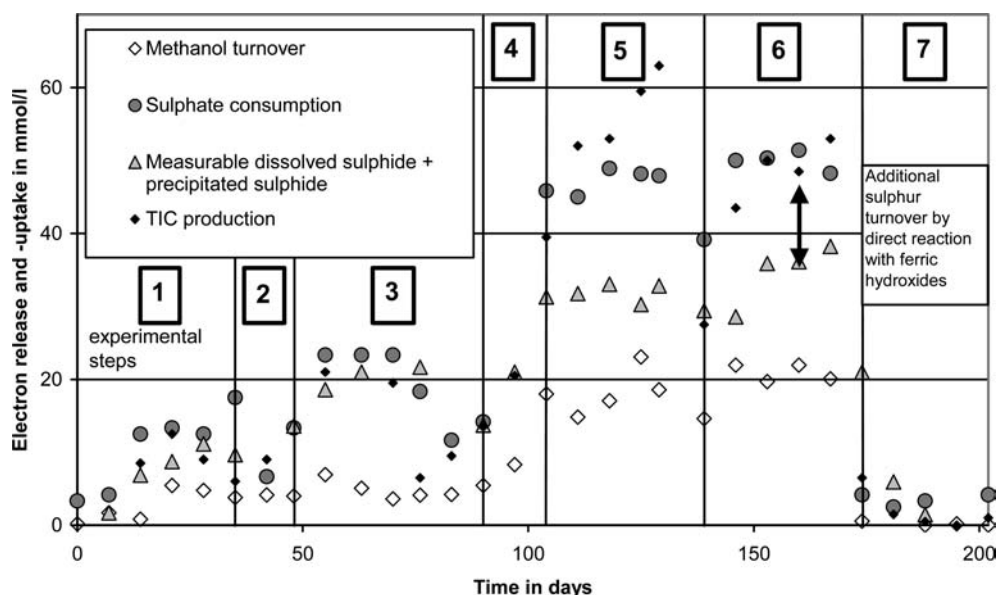
However, the saturation indices (SI = log[ion activity product/K]) decline from port 1 through 4 to about 0 (saturation), although the values are widely scattered (Fig. 9). Thus, the precipitation process also shows a certain kinetic behaviour. After the very fast increase of sulphide concentration and pH between inflow and port 1 ongoing FeS precipitation occurs until the solution shows the theoretically expected concentrations. Ongoing but declining precipitation between ports 1 and 4 was also observed after opening the column at the continuously diminishing black coatings on the sand grains (Fig. 7).

pH and sulphide concentration (Figs. 4, 5) are controlled by the amount of methanol added and its complete turnover according to Eq. 2a. Because both parameters are included in the solubility product of iron monosul-phide, they in turn control the amount of its precipitation. Thus, the amount of precipitating iron monosulphide can be controlled by the amount of methanol added, which can be seen by comparing Fig. 3 and Table 2.

$$c(Methanol) \Rightarrow \text{controls} \Rightarrow pH, c(sulphide)$$
$$\Rightarrow \text{controls} \Rightarrow c(iron\ monosulphide_{prec.})$$

This control is essential because excess addition of organic electron donors results in an excess production of sulphide (Fig. 5), which is not wanted downstream of the reactive zone in the aquifer. The amount of organics has to be adjusted to the amount of ferrous iron to be precipitated and the pH-increase that is necessary to establish an active SRB population.

Fig. 9 Saturation indices of iron monosulphide along the column profile for the experimental steps 1–4
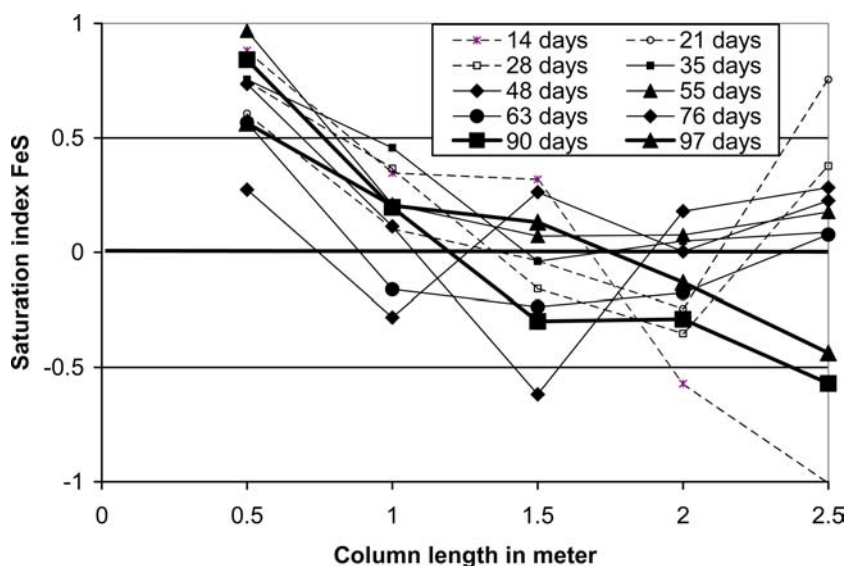
Stability of iron monosulphides

As discussed above, the precipitation of iron disulphides in the aquifer is not necessary to produce an acidity-free groundwater. Due to the rising groundwater tables in most areas of the former East-German lignite-mining district, widespread reoxidation of the monosulphides is not expected. Re-dissolution under anoxic and equilibrium conditions would lead to an iron concentration increase of 0.17 mmol/l and the same concentration increase of sulphide that could be tolerated.

To test the stability of the precipitated iron monosulphides under anoxic conditions, experimental step 7 was performed with no methanol addition at all: After 5 weeks of flushing the columns with untreated unoxic groundwater, iron-, sulphide- and sulphate concentrations reached their background levels, but did not exceed them by amounts higher than the inflow concentration standard deviation. Thus, no significant amounts of additional iron or sulphur were added to the aquatic phase. This confirms the theoretical considerations and shows that even the iron monosulphides are rather stable in the anoxic subsurface.

Conclusions

Column experiments were performed to investigate iron sulphide precipitation triggered by addition of methanol to natural anoxic and acidified groundwater. The experiments differed from other similar experiments documented in the literature by the use of natural sediments as fixed bed, not using other solid organic or buffering material, natural flow velocities, natural pressure conditions and no addition of nutrients. The experiments showed that under these near natural conditions, a complete precipitation of iron as iron monosulphide was achievable. The added amount of methanol was used up completely and all released electrons were transferred to sulphate, which is the dominant electron acceptor in the investigated system. Thus, the amount of sulphide produced can be controlled by the amount of methanol added. The pH-value is dependent on the amount of the sulphide concentration in the solution and the precipitation of iron monosulphide is controlled by its solubility product. Thus, the amount of precipitating iron sulphide can be controlled by the amount of added methanol. These dependences allow complete precipitation of all ferrous iron by minimizing the sulphide concentration downstream of the reaction zone. In the investigated system, even at pH 3.8, a complete precipitation of iron monosulphide can be achieved if the SRB population is well established on the sediment surfaces.

The major part of the turnover takes place near the inflow of the column. This shows that the precipitates are not distributed homogenously in the void pore space. This might result in a fast clogging of the pore spaces by biomass or by precipitates because not much volume is used as a storage space. Future work, therefore, has to focus on techniques to distribute the precipitates better in the aquifer. Alternatively, sulphate reduction and sulphide precipitation could be established in a technical in-situ reactor, which separates the groundwater from the aquifer sediment and which enables the extraction of the iron sulphide sludge from the subsurface.

When calculating the amount of the electron donator to be injected in the field, apart from the electron consumption by the sulphate reduction, additional electron acceptors like ferric iron hydroxides and natural electron donators like bioavailable natural organic substance have to be taken into account.

To generate a water of low acidity, the precipitation of iron disulphides is not necessary for the inflow water quality used in the presented experiments. It was shown that the iron monosulphides seem to be rather stable under unoxic conditions, despite their much higher solubility product compared with iron disulphides.

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