Microbial Iron Retention in the Groundwater upstream to a River

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Abstract

High iron and sulphate concentrations are observed in several surface waters of the Lusatian mining district. Especially iron affects the freshwater fauna (fish, insect larvae) and aquatic plants by lowered pH or high turbidity. Both iron and sulphate are mobilized from iron sulfides like pyrite and marcasite, which are decomposed under oxic conditions. These conditions appear in the underground of large areas after lowering the groundwater table to enable the opencast lignite mining. To develop a treatment technology, we built a pilot plant at the location "Ruhlmühle" (north Saxony) in 2014, where an iron hot spot (about 400 to 550 mg/L Fe) in groundwater was detected. At the pilot plant, groundwater is extracted by 3 wells, mixed with glycerin and re-infiltrated. The infiltration line consists of 30 lances and has a width of about 100 m. The infiltrated glycerin serves as a carbon source for sulphate-reducing bacteria (SRB). Although the microbes operated under the difficult starting conditions (pH-value of about four), it took a longer time than expected to rise the pH above five by bacterial metabolism. Under these conditions, the iron could precipitate as iron sulfide, generating additional alkalinity. Up to now, the iron concentration has been reduced to about 200 to 300 mg/L. Sulphate and electrical conductivity have decreased (SO_4 from about 1100 mg/L to about 500 mg/L) too, and the neutralization potential has risen from between -15 to -20 mmol/L to above -10 mmol/L. We expect a further decrease of the iron concentrations down to 30 mg/L during the continued operation.

Key words: groundwater, remediation, pyrite oxidation, iron hydroxides, iron sulfides, glycerin, glycerol

Introduction

Pyrite and marcasite oxidation is a common consequence of opencast lignite mining. However, the oxidation of iron sulfides is not only restricted to the mine dumps but it also occurs in the adjacent areas with lowered groundwater tables. As a consequence, some rivers of the Lusatian mining district, e. g. the rivers Spree, Schwarze Elster and most of their tributaries contain high and visible iron concentrations. If reduced iron from the groundwater is transformed into iron hydroxides in an oxygen rich environment like a river, it has severe negative effects for the water biocenosis (e.g. lowered pH, high turbidity). Therefore, a reduction of the iron mass flow is necessary.

Study area - subsurface conditions

The groundwater treatment is located southwest of river Spree near the small town Neustadt in the North of Saxonia in a FFH reserve area. The treated groundwater flows almost perpendicular to an abandoned river course (“Altarm”). The “Altarm” flows into river Spree downstream outside of the study.

Geological, the area is characterized by the glacial trough structure "Spreewitzer Rinne". Quaternary deposits in the study area consist of fine to coarse sands or gravel with thin silty or clayey layers, partly with a high share of lignite. Glaciofluvial variations in water discharge and flow direction formed small-scale heterogeneous sediment structures (Hildmann et al. 2016). The sediments have a porosity of about 30 % and an average hydraulic conductivity of $6.6 \cdot 10^{-4}$ m/s. The longitudinal dispersivity is approximately 0.2 m.

The lower limit of these aquifer forms glacial till. This zone of low hydraulic-conductivity rises from 25 m to 15 m below the terrain surface downslope the first row of observation wells. The thickness of the aquifer decreases, which corresponds to faster groundwater flow in the surroundings of the second and third row of observation wells.

Knowledge about the subsurface is exclusively based on the information of drillings and sediment analysis. Some suppositions have been defined and specified by the hydraulic modeling and were confirmed by the results of a tracer experiment.

A tracer experiment with sulfur hexafluoride (SF_6) was conducted from November 2014 to march 2016. Tracer was injected into six DSI-lances in the middle of the infiltration line. It was detected at the first row of observation wells after 35 days (distance: 20 - 25 meters), at the second row after 100 days (distance: 85 - 95 meters) and at the third row after more than 235 days (distance: 185 - 205 meters). Based on these data, we calculated flow rates between 0.45 - 0.6 m/d in the surroundings of the first row of observation wells and 0.7 - 0.95 m/d further in the downgradient area.

Groundwater level has risen steadily in consequence of the termination of lignite mining in the past. A considerable acid and salt input into the aquifer was triggered due to the ascending groundwater. However, the level remained relatively stable since the beginning of this experiment. The current water table fluctuates between 8.0 and 8.3 meters below ground in the area of the first row of observation wells. Hence, there is a thick unsaturated layer with a high potential of acid inflow into the aquifer.

Untreated groundwater in this investigation area is characterized by pH-conditions lower than four, an electrical conductivity of about 1800 µS/cm, iron concentrations > 400 mg/L, and sulphate concentrations between 1100 - 1500 mg/L. Caused by the high acid content, iron and manganese concentrations, neutralization potentials are below -15 mmol/L (Schöpke et al. 2015).

Method

The project started in 2014 to evaluate reduction potential of the iron mass flow while passing an active subsurface zone. A carbon source (glycerin = glycerol) is infiltrated into the subsurface to enhance the biochemical reduction sulphate in the aquifer (fig. 1). Anaerobic sulphate-reducing bacteria (SRB) use the oxygen of sulphate for oxidation of the organic matter. As a consequence, sulfide and solute iron(II) precipitate as iron-monosulfides within the aquifer and the transport into the surface water is reduced.

The following chemical equation describes the process:

$$Fe^{2+} + SO_4^{2-} + \frac{4}{7}C_3H_8O_3 \rightarrow FeS \downarrow + \frac{12}{7}CO_2 + \frac{16}{7}H_2O$$

The groundwater treatment is only conducted in the saturated zone with anoxic, reducing conditions and operates in accordance with the water approval of the mining authority of the Free State of Saxony.

The pilot system plant (fig. 1) is composed of pumping wells for extracting a part of the groundwater, a container for the dosage unit plus system control and 30 injection lances (DSI-lances) for infiltration of a water-glycerin-mixture for treatment. Depending on the monitoring results, additional nutrients can be supplied for the metabolism of microorganisms (phosphate, nitrogen).

The technical process of groundwater extraction, dosage and re-infiltration operates automatically. The plant operates as a closed system without oxygen input.

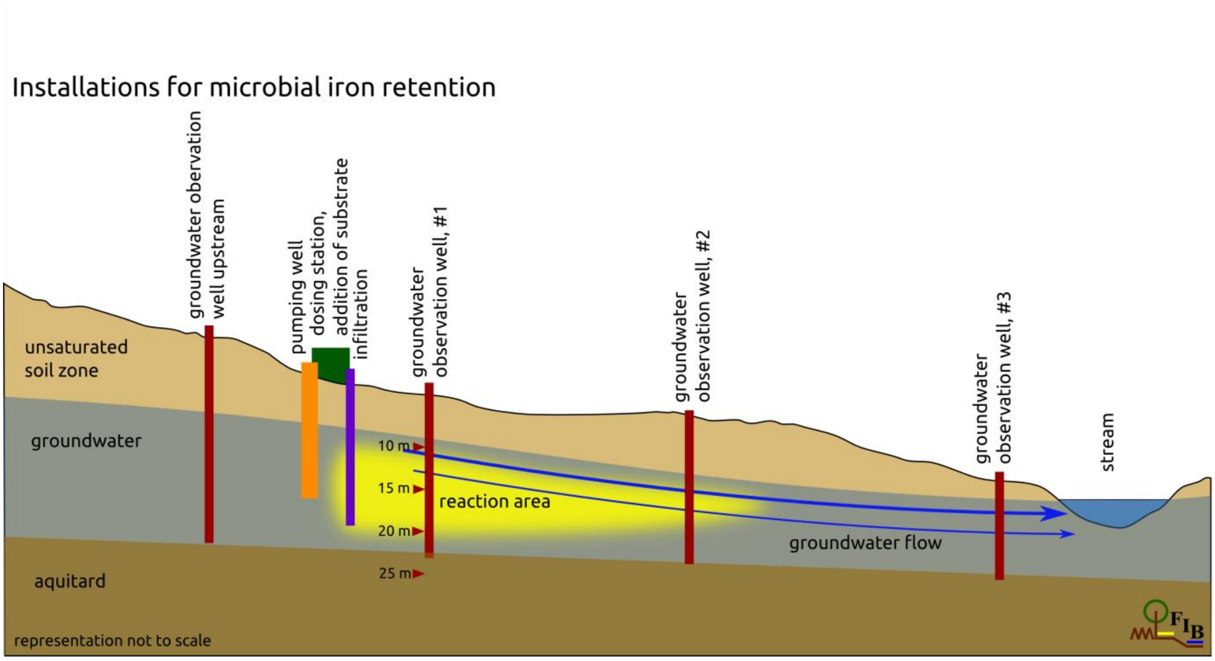

Figure 1 *Vertical section through the test area.*

The active subsurface zone is positioned in a line of about 100 meters length and captures a 9 meters thick part of the aquifer. Treatment is discontinuous: infiltration cycles alternate with undisturbed groundwater flow, which enhances the mixing of treated and untreated water. 18 observation wells (in 3 rows perpendicular to the groundwater flow direction) are used for monitoring.

Results

System operation

48.680 m³ of groundwater was extracted during 23 infiltration cycles from December 2014 to April 2016, charged with 16.500 liter of glycerin and 3.580 liter of phosphate solution and re-infiltrated.

The quantities of glycerin and phosphate are dosed based on the monitoring results. Especially in the beginning, the dosage was rather low to avoid unmetabolized outflow. Currently, 6 L/h of glycerin and 6 g/h of phosphate are infiltrated.

The sulphate-reducing bacteria currently use a large proportion of the natural nitrogen reserve for their metabolism. Another part is adsorbed on the rock matrix. Therefore, an additional infiltration of nitrogen is necessary in the near future.

The technical installations have operated reliably. During installation of the plant, the exact automatic measurement of the infiltrated glycerin volume was a challenge. This problem was solved by the subsequent integration of a water pressure device and temperature sensor with a feedback to the stored program control (SPC).

Groundwater treatment

The low pH-conditions retarded the iron(II) precipitation at the beginning of the treatment process. However, the rate of SRB increases slowly and through their metabolism the pH rose to values above pH 5 (fig. 2).

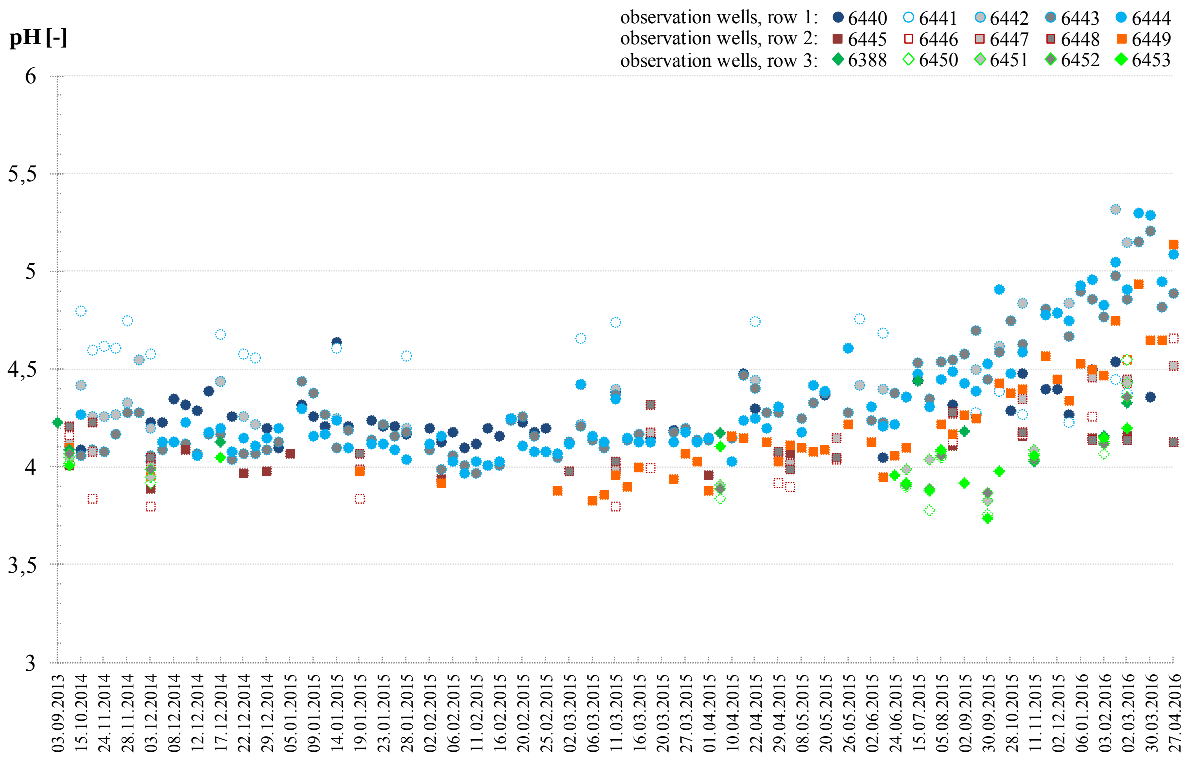

Figure 2 *Development of pH- conditions in the downgradient area of the pilot plant.*

After 16 months of treatment, the pH values enabled the removal of iron from groundwater by sulfide precipitation in a relevant degree. Electrical conductivity decreased depending on concentrations of iron and sulphate, and also calcium and aluminum decreased significantly.

Acid load in groundwater decreased at low level analogous to improved pH conditions. This effect was detected in the observation wells directly downstream to the infiltration line first and arrived at the second and third row in the beginning of the year 2016.

The best remediation successes were observed at the measuring points 6443, 6444, 6449 and 6451. The iron concentrations decreased by 32 - 61 % from concentrations of 420 to 560 mg/L to values between 195 to 330 mg/L in this monitoring area. This indicates that iron is precipitated in the subsurface. The sulphate concentrations in the aforementioned observation wells changed from values of 1120 to 1455 mg/L to values between 480 to 900 mg/L, which corresponds to a reduction of 38 - 57 %. Depending on the acid potential, decreasing iron (II), aluminum and manganese concentrations increased the neutralization potential by 8.1 - 10.9 mmol/L. This represents an improvement of 39 - 58 %. The concentrations of calcium dropped from values around 100 mg/L to values around 70 mg/L. Aluminum decreased from average concentrations of 25 mg/L to 3,5 mg/L.

In the following, the developments in the observation well 6444 are described in detail. Groundwater at this measuring point showed iron concentrations of 500 mg/L, sulphate concentrations of 1100 mg/L and a neutralization potential of -16 mmol/L at the beginning of the study. The iron concentrations could be reduced to below 200 mg/L (fig. 3), the sulphate concentrations decreased to 480 mg/L (fig. 4) by the groundwater treatment up to now.

Figure 3 *Decrease of iron concentrations at groundwater observation well 6444.*

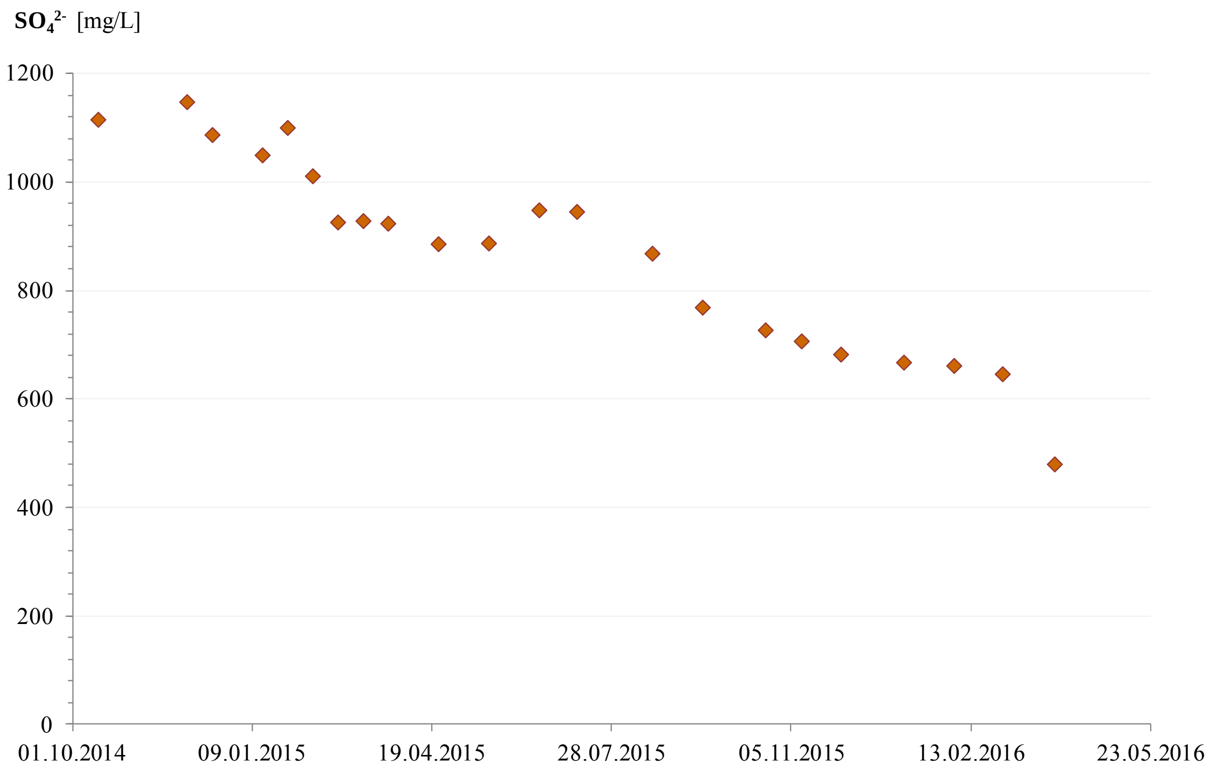

Figure 4 *Decrease of sulphate concentrations at groundwater observation well 6444.*

Evangelou (1995 in Schöpke et al. 2011) defined the neutralization potential (NP) as a measure of the acidity of water, particularly for acid mine drainage. Schöpke et al. (2011) simplified the formula as follows:

$$\mathrm{NP} \approx \mathrm{K}_{\mathrm{S4,3}} - 3\mathrm{c}_{\mathrm{AL3+}} - 2c_{Fe2+} - 2\mathrm{c}_{\mathrm{Mn2+}}$$

A neutralization effect results from precipitating again the reaction products of the pyrite oxidation, particularly iron. In the area of the observation well 6444 the neutralization potential improved by 9.2 mmol/L during the groundwater treatment (fig. 5).

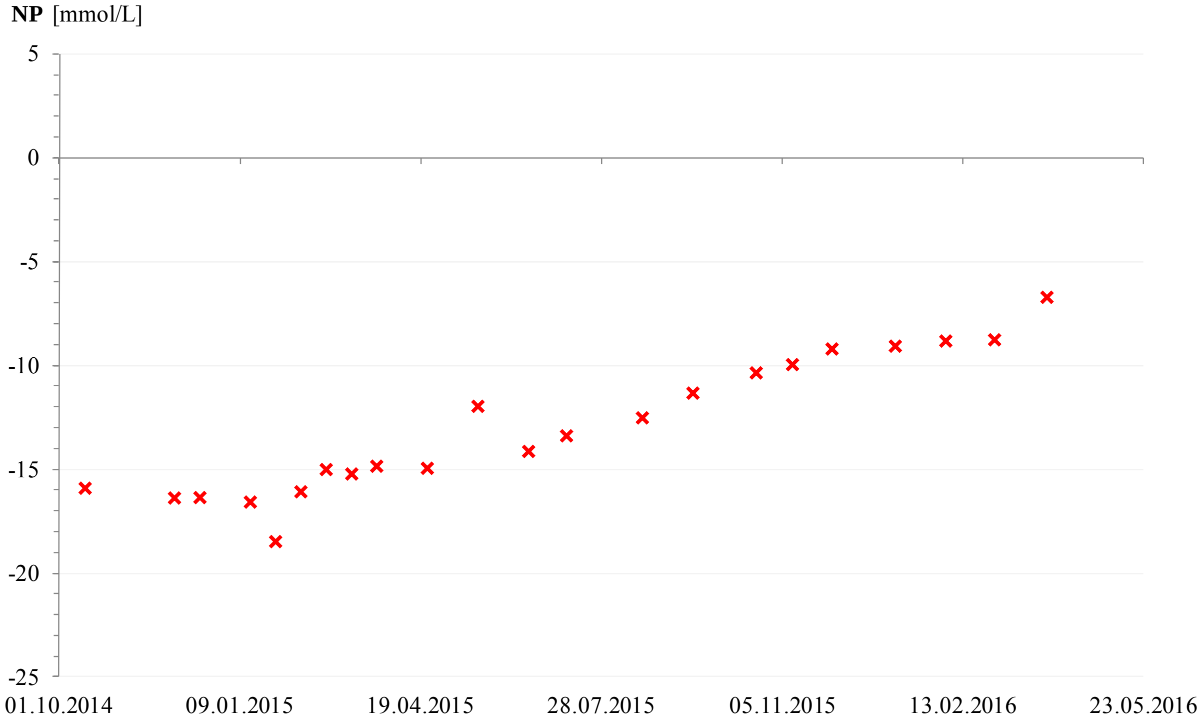

Figure 5 *Increase of neutralization potential at groundwater observation well 6444.*

Reaction area

Not all observation wells are affected equally. No changes could be detected at the measuring points 6440, 6445, 6448 and 6388. A possible reason is that the measuring points 6440, 6445 and 6388 do not receive the treated groundwater (fig. 6). An improvement of groundwater quality is detectable at all other observation wells. These results of the operation monitoring correlate with the results of the tracer experiment.

The best results could be observed at the measuring points 6443, 6444, 6449 and 6451. It can be assumed that the reaction zone further expands during the continued groundwater treatment. Additionally, through diffusion, dispersion and retardation in the flow path an increasing mixing of untreated and treated groundwater can be achieved.

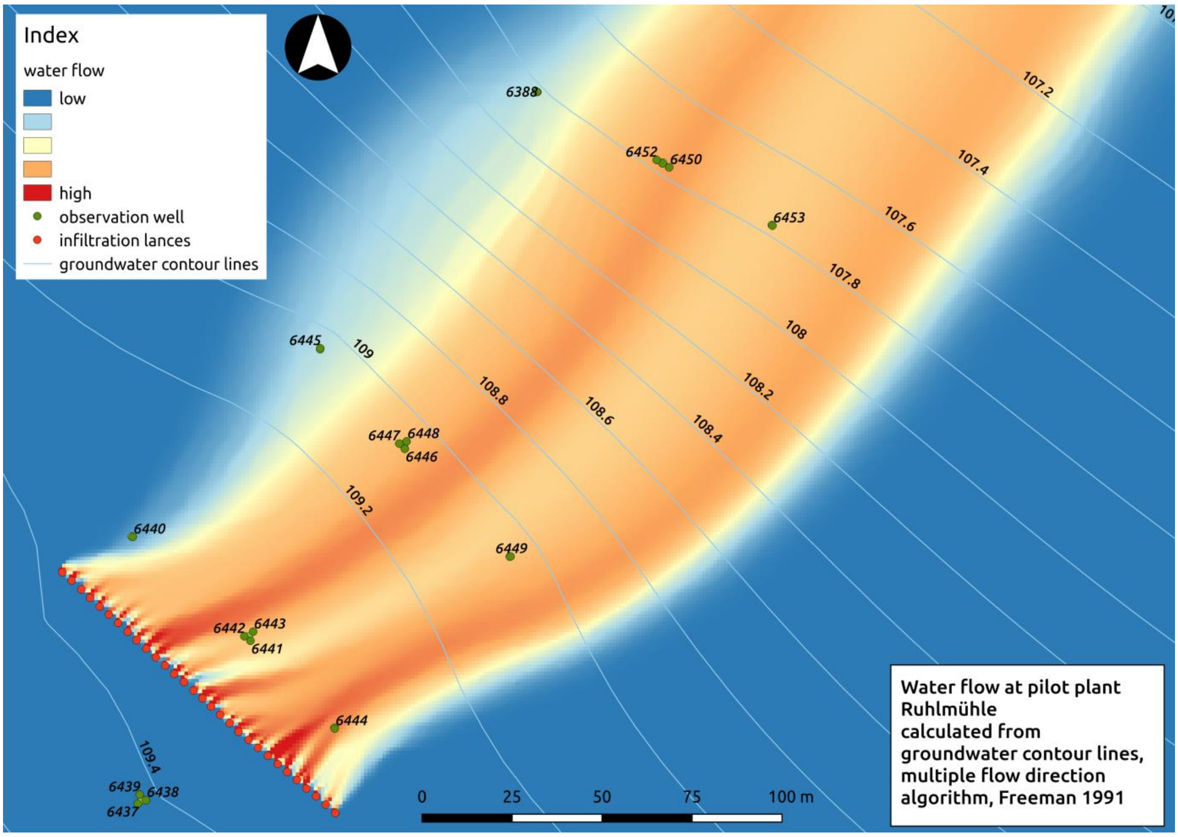

***Figure 6** Water flow at pilot plant Ruhlmühle. Shown is the direction of water flow from the infiltration lances to the stream, derived from the groundwater contour lines.*

Discussion

Sulfate reducing bacteria were stimulated with the infiltration of glycerin, while very low pH values of the groundwater indicate difficult living conditions. Experimental work of Tuttle et al. (1969) and Johnson et al. (1993) showed that SRB are able to reproduce even at pH 2.9, but not at lower pH. Our results indicate the growth of SRB about three month after stimulation by the occurrence of sulfide at the field scale, too. Even if their growth is delayed, stimulation of SRB seems to be a robust process.

Compared to a former pilot plant (Gast et al. 2010, Schöpke et al. 2013), the whole process was scaled up for the use as remediation technology. Extraction of water, dosing and infiltration is fully automated and worked reliably.

Other approaches use the process of sulfate reduction, too. Water treatment within tubes with sand could be used (example Hainer See), but all water need to be extracted, performance in winter is low and the remaining iron sulfide has to be deposed. Autotrophic sulfate reduction supports the microbes with hydrogen instead of a carbon source (Bilek et al 2007, Bilek 2012). In this case, control of the multi-level process in artificial reactors, with removal of iron sulfide and partially with pH control by CO_2 fumigation, is much more costly.

Reduced iron could be precipitated by aeration, both if oxygen is brought into the underground (as done for iron removal for drinking water pumping wells) and if the water is extracted. However, the underground may be clogged or iron hydroxide sludge has to be removed, and sulfate remains untreated. Iron precipitation without sulfate reduction is provoked during neutralization of mining lakes (Grünewald et al 2012), with remaining high sulfate concentrations at the lake outflow. Bilek (2012) gives an overview about further approaches.

In comparison, the pilot plant Ruhlmühle has some important advances. The process could reduce both iron and sulfate concentrations, and the precipitated iron sulfide remains in the subsurface.

Conclusions

Low pH-values about four of the upstream groundwater are regarded as difficult for SRB. However, the SRB have been capable to use the infiltrated glycerin for their metabolism, as indicated by sulfide formation and decreasing sulphate concentrations. Low pH-values inhibit the precipitation of iron and sulfide as iron(mono)sulfide. During the operation of the pilot plant, pH-values rose slowly due to sulphate reduction, and finally the precipitation of iron sulfide get started, as decreasing concentrations of iron indicates. Coupled to this process, pH-values rises up to 5 and accelerate the precipitation process. Nevertheless, the process needed about 16 months to show significantly decreasing iron concentrations and will still take some time, until iron concentrations < 100 mg/l are reached.

Although the process took a long time to start, the operation of the pilot plant shows already achievements of remediation. Retention of iron and sulphate in the underground are an important advantage of the process, because there are no remaining disposals. The aquifer provides constantly reduced conditions avoiding recurrent iron mobilization. Experiences from an earlier project show that the pore volume will not block, also because the iron sulfide is much smaller then iron hydroxide, which is often causes problems in wells.

In summary, the process is suitable to treat groundwater with high iron and sulphate concentrations, so called hot spots. Hot spots upstream of rivers and lakes in former mining areas are the result of the heterogeneity of the pyrite and marcasite deposits. Efforts are still needed to reduce the environmental costs of the process, for instance by identifying alternation carbon sources.

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