Field experiments on subsurface iron removal in the Lusatian mining region

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Abstract

A series of field tests were carried out to explore the application of subsurface iron removal (SIR) for unfavourable hydrogeochemical site conditions. At two sites in the Lusatian mining region characterised by low pH (5.4 to 6.4) and low alkalinity ($K_{S4.3}$ = 0.39 to 0.85 mmol/L) together with high iron concentrations (9 to 47 mg/L) groundwater was treated using SIR. The results show that generally the technique can be successfully applied by adjusting the operational procedures to the specific site characteristics. Crucial for the application are an effective mechanical deacidification of the extracted groundwater, the use of technical oxygen and optimised interim periods between infiltration and abstraction. The application of sodium hydroxide to increase the pH and enhance the oxidation of iron was found to be of critical economic viability.

Key words: subsurface iron removal, pH, alkalinity, field test, efficiency coefficient

Introduction

Iron and manganese are commonly present in anoxic groundwater worldwide. Iron concentrations up to 3 mg/L are normally not harmful to human and animal health, but result in technical problems: clogging of production wells, precipitation and incrustation in the water supply distribution systems and orange/brown colour of water. According to the drinking water guidelines in many countries the total iron concentration should be less than 0.2 mg/L. As a result of pyrite weathering due to dewatering during mining activities very high iron concentrations of more than 100 mg/L can be observed. If groundwater has to be used for drinking water supply, industrial/agricultural water or so called eco-water for feeding wetlands in areas affected by mining, often iron removal is required. As an alternative to conventional iron removal, which uses filters in a treatment unit above ground, there is also the low-cost option of subsurface iron removal (SIR), which takes place directly in the groundwater (DVGW 2005).

As the efficiency of SIR depends on hydrogeological and hydrogeochemical site conditions, a reliable data base is required to design the scheme or it is advisable to conduct a small-scale pilot experiment to determine the suitability of the aquifer for the application of this technique (Ebermann et al. 2012; Rott et al. 2002). The process of subsurface iron removal is based on interacting redox reactions and ion exchange processes in a reaction zone formed around wells. When aerated or oxygenated water is infiltrated into a well, the oxidation process changes dissolved Fe(II) into less soluble Fe(III), mainly precipitating in the aquifer as iron(hydr)oxide. The iron hydroxide is stored in the pore space of the aquifer, providing adsorption sites. These sites are occupied mainly by calcium ions. When further Fe(II) ions enter the reaction zone during extraction, the adsorbed calcium ions are replaced. Infiltrated oxygen-enriched water leads again to oxidation of the adsorbed Fe(II) ions. Thus, a high adsorption capacity for Fe(II) is built up within the so-called reaction zone around the well. Periodic alternation between infiltration and abstraction eventually results in the production of iron-free water.

With atmospheric oxygen and concentrations up to 10 mg/L, a portion of the abstracted groundwater from one well is infiltrated into another well. A typical tool for the aeration unit is a water jet air pump. The selection of the oxygenation technique is based on the oxygen consumption in the reaction

zone during the infiltration. The main oxygen consumers are Fe(II), Mn(II), ammonium and easily degradable organic compounds. Additionally, nitrite and sulphide consume oxygen depending on their concentrations. Conditions that hinder subsurface iron removal are low pH, low hardness, and high Fe(II), Mn(II), ammonium and sulphide concentrations.

The oxidation of Fe(II) to Fe(III) requires a pH value greater than 5.5 (Eichhorn 1987). During iron oxidation the pH decreases in accordance with the buffering capacity of the water-soil system. The efficiency of the SIR technique is determined as the volumetric ratio of the water extracted to the water infiltrated, which commonly is between 3 and 5, but could reach 10. This ratio is called the "efficiency coefficient" (DVGW 2005). A high efficiency coefficient is the aim of optimizing design and operation of the technique.

In 2014 and 2015, field experiments were conducted at monitoring wells at two sites in the Lusatian mining region to test if subsurface iron removal was applicable at low buffering capacities and low pH found in the groundwater. At the site Schleife the aim was to produce so called eco-water to feed a small pond during mining operations and groundwater lowering (Koch 2012). Eco-water should have an iron concentration of less than 1 mg/L.

At the site Spreewitz high iron concentrations of more than 100 mg/L occur in the groundwater, which discharges to a natural stream and causes iron sludge deposits, brown colour of surface water and limitation of aquatic life. Different remediation measures are planned to control the iron load to the stream. A field test was conducted at a single monitoring well to gain experiences with subsurface iron removal under hydrogeochemically unfavourable conditions.

Materials and Methods

At the site Schleife, a field test was conducted using two new observation wells (OW 1 & 2). The observation wells were used both as extraction and as infiltration wells. Extracted groundwater from OW 1 ($Q_{max} = 8.4$ m^3/h) was discharged as eco-water to a nearby creek. A portion of the pumped water was treated in an aeration tower (d = 0.6 m, h = 3.1 m), enriched with technical oxygen using static mixing units (Sulzer chemtech GmbH, SMV DN 25, PP) and infiltrated into OW 2 (V = 50 m^3). Following an interim period during which dissolved and adsorbed iron was oxidized and immobilized, water with a lower iron concentration was extracted from OW 2. A portion of the pumped water was enriched with technical oxygen and infiltrated into OW 1. Thus, by switching between extraction and infiltration, a continuous treatment and supply of eco-water was possible.

Temperature, pH, electrical conductivity and O$_2$ concentration were continuously measured using Multi 3430 and Multi 350i devices (WTW Weilheim, Germany). To gain first information on site, a field test kit (Merck-Aquaquant) to determine iron has been used. The analysis of total iron (Fe$_{tot}$), dissolved iron and major cations and anions was performed parallel in two independent laboratories (DIN EN ISO 11885 and DIN 38406-E1). Water was filtered through a 0.45 µm membrane filter (GD/X Whatman) directly after sampling to determine dissolved iron. All cations were determined by ICP-OES (Spektrometer Optima 4300 DV, Perkin Elmer). Anions were determined using ion chromatography (ICS 900, Dionex). Titration was used to determine alkalinity (K$_{S4.3}$; automated titration, G20 Compact Titrator, Mettler Toledo) and acidity (K$_{B8.2}$; manual titration with phenolphthaleine. Determination of NH$_4^+$ was by photometry (DIN EN ISO 11732, E32).

Selected groundwater quality parameters are shown in Table 1. The hydrogeochemical conditions were critical with low buffering capacity and a low pH (6.1 to 6.5). In total 30 cycles of infiltration and extraction were run. The oxygen concentration was controlled (c(O$_2$) = 10 – 30 mg/L), pH adjusted using NaOH (pH = 5.9 – 11.1) and the reaction time between infiltration and extraction varied (t = 0.2 – 15 h).

Table 1 Groundwater quality data (Schleife 26/08/2013, Spreewitz 28/08/2014).

Parameter	Unit	Schleife OW 1	Schleife OW 2	Spreewitz OW 6348
pH	-	6.4	6.1	5.4
EC	µS/cm	367	416	505
$K_{S4.3}$	mmol/L	0.75	0.39	0.85
$K_{B8.2}$	mmol/L	1.3	1.5	5.8
DOC	mg/L	2.1	1.7	8.2
NO_3-N	mg/L	<0.05	<0.05	0.3
NH_4-N	mg/L	0.26	0.12	0.4
SO_4^{2-}	mg/L	103	141	228
Fe_{tot}	mg/L	8.61	12.5	46.6
Fe_{diss}	mg/L	8.46	12.4	46.0
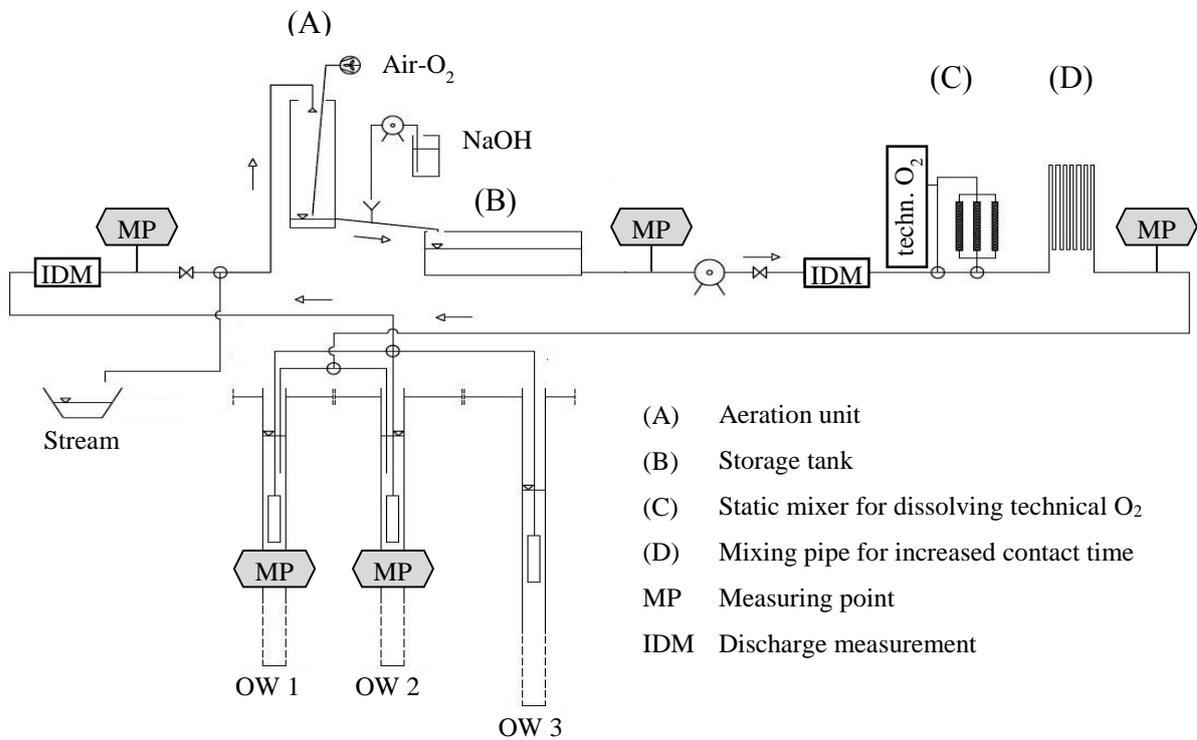
Figure 1 Schematic of field test set-up.

(A) Aeration unit

(B) Storage tank

(C) Static mixer for dissolving technical O_2

(D) Mixing pipe for increased contact time

MP Measuring point

IDM Discharge measurement

In Spreewitz, an experiment was carried out to test chemical deacidification using $Ca(OH)_2$. A 2-inch diameter observation well (OW 6348) was used for the experiment with permission from LMBV. The aquifer consists of coarse sand and gravel, covered by a 1.4 m thick silty fine sand layer. The filter screen is located between 2.3 and 4.3 mbgl. The groundwater level was found between 1.5 and 2.1 mbgl. The upper meter of the filter screen was separated using a packer system to achieve a more horizontal reaction zone during infiltration and an increase in radius. Groundwater and infiltrate was pumped using a centrifugal pump (Alko TDS 1001/3). Discharge was measured using an IDM (Siemens Sitrans FM MAG 5100 W). Technical oxygen from a pressurized gas bottle was added before a static mixer (PVC pipe, L = 50 cm, 4 static mixing elements, Sulzer chemtech GmbH, SMV DN 25, PP). The oxygenated water was passing a 100 L degassing tank (contact time 150 s) to further dissolve oxygen and to separate non-dissolved gas. The water was injected into OW 6348 via a PE hose connected to the lower end of the installed packer. If treatment of local groundwater is costly to run such an experiment, other water sources could be an alternative, as for example described by Rößner et al. (2013). In Spreewitz public drinking water from a nearby house was used as infiltrate, having a $K_{S4.3}$ of 2.3 mmol/L. In total 10 cycles of infiltration and extraction were monitored.

Results

At the site Schleife subsurface iron removal worked resulting in iron concentrations in the extracted water mainly below 1 mg/L (threshold value for eco-water), but higher than the technically required concentration of < 0.5 mg/L to prevent well clogging during long-term operation of such a scheme.

The development of iron concentrations in the pumped water of OW 1 shows characteristics atypical for the subsurface removal of iron (Fig. 2). Typically, the concentration of iron increases continuously during extraction. At Schleife, an initial increase was followed by a decrease in the concentration of iron then remaining at a level of 0.3 – 0.5 mg/L. During the initial phase of extraction the threshold value of 1 mg/L was partly exceeded. Increasing iron concentrations after reaching low values only occurred at pumped volumes of 200 – 250 m^3 corresponding to an efficiency coefficient of 4 to 5. The presence of pyrite indicated in the borehole profiles was confirmed by the analysis of sulphate together with the consumption of oxygen for processes other than the oxidation of iron. Fe(II) released as result of the oxidation of pyrite is the cause of the observed temporary increase in the concentration of iron during extraction. With the number of cycles the oxygen consumption for processes other than the oxidation of iron decreased. The stoichiometric comparison of the decrease in oxygen consumption against the decline in the sulphate concentration confirmed, that the oxidation of pyrite was the dominating process.
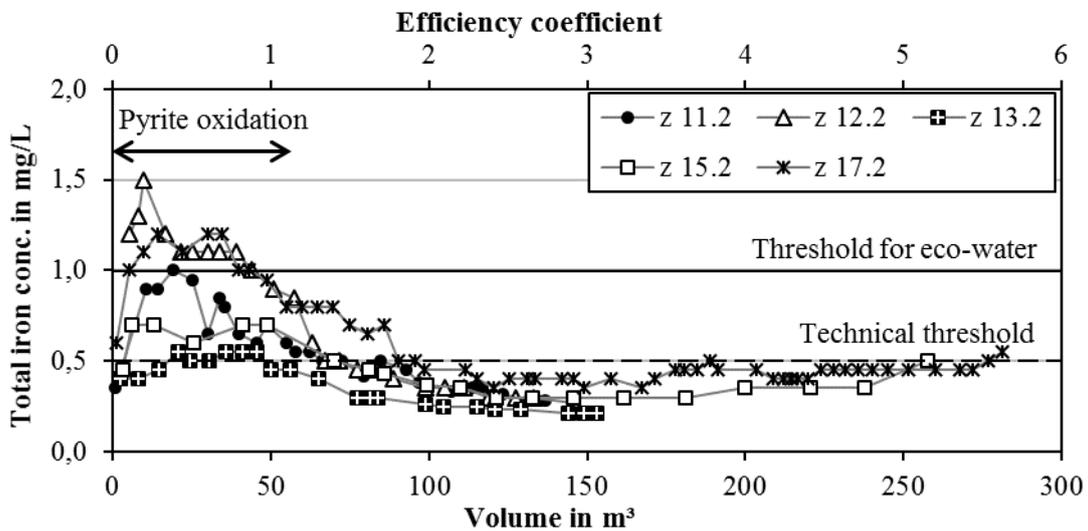

Figure 2 Efficiency coefficients for cycles with technical oxygen at OW 1.

The iron concentrations at OW 2 are characterised by the continuous rise in concentrations representative for the subsurface iron removal and are not affected by the oxidation of pyrite. Despite the application of technical oxygen, at an infiltration volume of 50 m^3 the threshold of 1 mg/L for ecological safe water was exceeded after only 45 m^3 (Fig. 3). Consequently the site represented by the observation well OW 2 has been considered unsuitable for the production of eco-water using subsurface iron removal techniques.

During cycles with aeration of the infiltrating water (O$_2$ = 9 – 10 mg/L) the oxygen consumption was independent from the contact time during the interim period between infiltration and extraction. About 94 % of the oxygen dissolved in the infiltrate was consumed. During cycles with added technical oxygen (O$_2$ = 26 – 33 mg/L) only 20% of the infiltrated oxygen was consumed for oxidation of iron, but 80% for other processes or was extracted back. A longer reaction time between infiltration of oxygen-rich water and abstraction of treated groundwater resulted in an increase in oxygen consumption for other processes, whereas for iron oxidation no more oxygen was consumed (Fig. 4).

Despite the unfavourable hydrogeochemical conditions, OW 1 is suitable for the application of subsurface iron removal using it alternately with a second well. Through a prolonged start-up phase with extended interim periods between infiltration and extraction, a decline of ancillary processes such as the oxidation of pyrite can be achieved resulting in the gradual reduction of the atypical high iron concentrations at the beginning of the extraction phase. During the start-up phase, the technical

threshold for the operation of the system of 0.5 mg/L should be applied as criterion for the termination of the extraction phase. This criterion can be further adjusted, i.e. reduced once operating conditions have been established. For normal operation the interim periods between infiltration and extraction should be short as extended periods do not enhance the oxidation of iron. The application of sodium hydroxide to increase the pH and improve the oxidation of iron is not an economical viable solution. The effective mechanical deacidification of the extracted groundwater was found to be crucial for the application of the technique of subsurface iron removal. The long-term use of filter media (calcite, dolomite) to increase the buffer capacity of the infiltrate needs to be further explored in the context of the residual iron concentrations of > 0.2 mg/L which might lead to clogging of the filter.
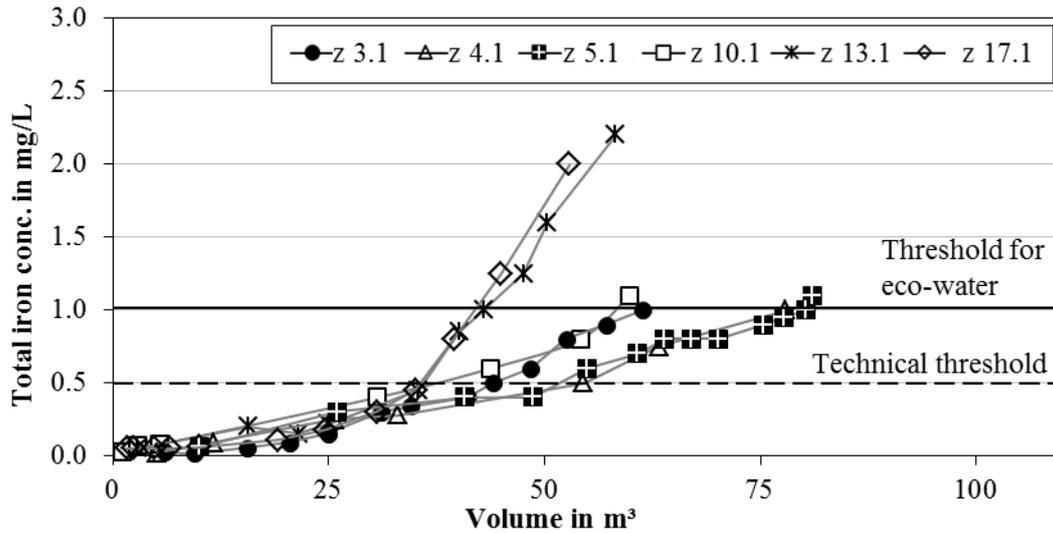

*Figure 3 Iron concentrations in extracted water from OW 2 in cycles with technical oxygen.*
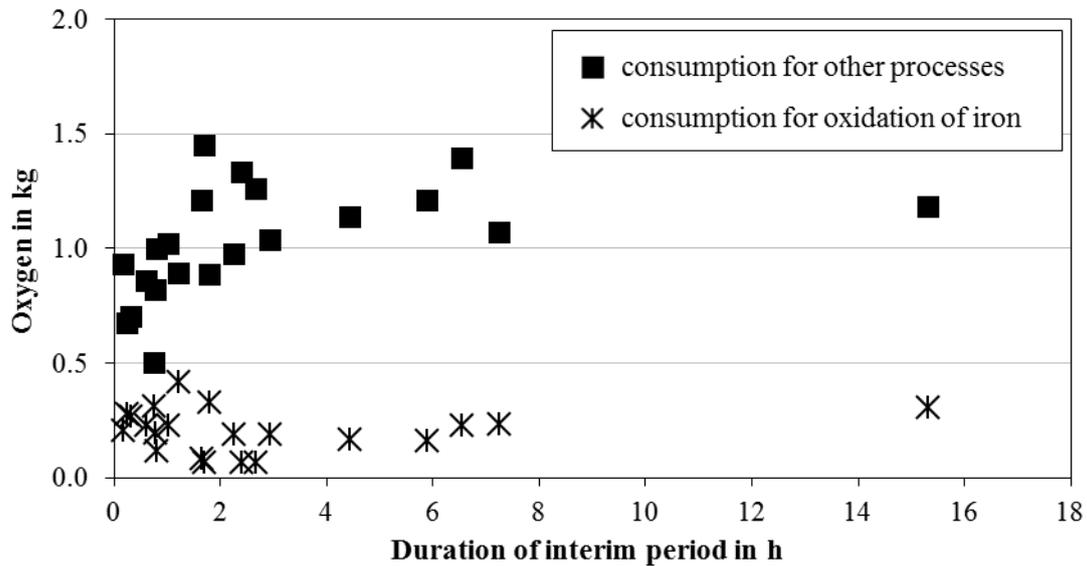
Figure 4 Dependence of oxygen consumption for iron oxidation and other processes
from duration of interim period at OW 1.

In Spreewitz, where $Ca(OH)_2$ was added to the infiltrate to increase the buffering capacity, during all 10 cycles a high quantity of iron was removed in the subsurface. The iron concentration in the pumped groundwater was significantly reduced. After 10 cycles and a criterion of $Fe_{tot} < 1$ mg/L, the efficiency coefficient was still below 1. But there was a trend of a further decreasing iron concentration in the pumped water. A major portion of the infiltrated oxygen ($O_{2, pumped}/ O_{2, infiltrated} = 44 - 80$ %) was pumped back, indicating that sufficient oxygen was available. There was no limitation caused by oxygen consumption for pyrite oxidation or other processes. As the CO_2 concentration in the infiltrate was low, no significant increase in alkalinity could be achieved by just adding $Ca(OH)_2$. Thus, the

formation of a reaction zone around the well was limited due to low pH and low buffering capacity of the infiltrate. At the same time addition of $Ca(OH)_2$ increases the risk of calcite precipitation in the well or its vicinity.

Conclusions

The results of the described and other field experiments prove that subsurface iron removal can be applied even under critical boundary conditions such as iron concentrations > 10 mg/L, pH < 6 and alkalinity $K_{S4.3} < 1$ mmol/L. But such application requires additional treatment of the infiltrating water to increase its alkalinity, thus causing additional costs (Musche et al. 2015). Further research is required to increase alkalinity and prevent well clogging especially during infiltration.

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