Simultaneous In-Situ Immobilisation of Uranium and Arsenic by Injectible Iron and Stimulated Autotrophic Sulphate Reduction

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Abstract. The combination of injectible grey cast iron (gcFe) and nano-scale iron (naFe) corrosion with autotrophic sulphate reduction (aSR) for simultaneous U and As immobilisation was investigated in column experiments. NaFe resulted in an intensive corrosion, the formation of a homogenous reactive zone, a distinct aSR and complete U and As immobilisation. At the gcFe column, a particle displacement resulted in the formation of reactive gcFe clusters, which were partly bypassed by the influent groundwater. Nevertheless, the lasting gcFe corrosion caused a complete As, but only partial U immobilization.

Introduction

The intensive uranium ore mining which took place until the mid-seventies has devised many abandoned mine processing sites in Eastern Germany. Hydraulic connections to aquifers, which are present at many sites, resulted in numerous, smaller and decentralised groundwater run-offs contaminated with heavy metals, arsenic (As) and radionuclides including uranium (U). Their concentrations frequently exceed groundwater standards for remedial actions at inactive U processing sites (Schneider et al. 2001). For Germany, this standards are recommended with 0,3 mg U/L (SSK 1992) and 0,02-0,06 mg As/L (LAWA 2000)

In order to prevent an ongoing contamination of ground- and surface water, many abandoned mine processing sites need restoration. In Germany, classical pump-and-treat technologies and conventional water treatment methods are common remediation practice. This is a cost intensive approach which leaves in addition concentrated residues for disposal (Neitzel et al. 2000) Therefore, the development of long term active and inexpensive in-situ treatment methods has become a research topic of major importance and interest.

The use of zero valent iron (ZVI) for in-situ containment of uranium within permeable reactive barriers (PRB) is already almost standard approach in the US. The activity of sulphate reducing bacteria within ZVI-PRB is well known (Gu et al.1999). It is considered much than a problem instead a chance to improve clean-up efficiency especially for contaminant mixtures by providing additional immobilisation reactions. Those reactions can be of major concern for remediation of contaminant mixtures such as groundwater runoffs from uranium mine processing sites. Moreover, the application of PRB requires excavation and is still limited to shallow aquifers (Simpkin 2003), whereby this method is often ineffective for smaller, decentralised groundwater run-offs.

A potential alternative to PRB are reactive zones (RZ). They are created by installing a line of overlapping injection points perpendicular to the groundwater flow direction. For this purpose, metallic iron to be injected is necessary in relative small quantities (≤ 1wt% of aquifer material) (Simpkin 2003) and very small size (usually <<100 µm in diameter, depending on aquifer's pore channel size). Because of small quantities of metallic iron, reducing conditions and contaminant removal capacity of RZ are not as high as PRB, whose iron content is usually greater than 20 wt% of aquifer material. However, due to the use of injection lances, the RZ technology is more flexible and is only limited by achievable depth of drilling equipment used. Therefore, this innovative technology seems to be more economic to sites with smaller, decentralised run-offs and was focused in this study.

The combination of anaerobic iron corrosion and biological sulphate reduction for an in-situ immobilisation of arsenic and uranium has some further advantages in reactive treatment zone applications of metallic iron. Hydrogen, generated by the anaerobic iron corrosion (Equation 1), accumulates at the iron surfaces and causes their passivation. Autotrophic sulphate reducing bacteria may consume this hydrogen (Equation 2), thereby promoting a continuation of the corrosion process. The produced sulfide precipitates with ferrous iron as patches of iron sulphide at anodic areas of the iron surfaces (Equation 3). This process also promotes corrosion, since iron sulphide does not precipitate on the iron surface as a uniform, passivating film (Ehrlich 1997). Finally, the stimulation of sulphate reduction by gaseous H_2 and CO_2 seems very attractive for in-situ treatment methods because of the more evenly and efficiently in-situ storage of gases compared to liquid and solid carbon source. Therefore, an anerobic corrosion of injectible iron materials combined with an autotrophic sulphate reduction was favoured in this study.

$$Fe^0 + 2\,H_20 \rightarrow Fe^{2+} + H_2 + 2\,OH^- \qquad (Eq.1)$$

$$SO_4^{2-} + H^+ + 4\,H_2 \rightarrow HS^- + 4\,H_20 \qquad (Eq.2)$$

$$Fe^{2+} + HS^- \rightarrow FeS(s) + H^+ \qquad (Eq.3)$$

Materials and Methods

Zero valent iron materials (ZVI), which were often used in PRB technologies (US-EPA 1998), tend to surface passivation by formation of precipitates due to their high purity (Friedrich and Knappik 2001). Therefore, a particulate, impure grey cast iron (gcFe) was selected for the column tests. Impurities like carbides counteract an early passivation of the iron surface and promote iron corrosion. The gcFe was obtained from Maier Metallpulver GmbH, Rheinfelden (Germany). The particles were gas classified < 30 µm before use. Nano-scale iron (naFe) was selected as alternative iron material. Injectible naFe is a promising new material for groundwater remediation. A markedly improved reactivity due to much greater surface area for reductive dehalogenation was described by (Vance 2003). NaFe (colloid size 0,1 µm) was obtained from the Toda Kogyo Europe GmbH, Japan.

The influent groundwater (Table 1) was collected at the abandoned mine processing site in Lengenfeld (Eastern Germany). Originally, it contained about 0,14 mg U/L and 0,09 mg As/L. Oxygen, possibly diffusing into the groundwater during storage, was removed by vacuum degasification. Subsequently, the groundwater was transferred into gas-tight bags (PP/Al/PE, Tesseraux GmbH, Germany) and enriched with about 15 mg U/L (as $UO_2(NO_3)_2{*}6H_2O$) and 5 mg As/L (as $NaAsO_2$) for a better quantification of the pollutant immobilisation. To maintain CO_2 partial pressure at groundwater conditions, a defined CO_2/ N_2 atmosphere (30 ml CO_2 and 470 ml N_2 according Henry’s law) was kept within the influent bags.

For the flow experiments, three columns (length: 50 cm, diameter 10cm) were operated for 112 days at 12°C. Preceding to the column tests, injection tests in 60 L -test barrels as well as hydraulic conductivity-tests were performed to determine optimal amounts of injectible iron application. About 2 g/kg (0,2 wt%) gcFe or naFe could be injected without hydraulic conductivities within the reactive zones, which is well below 1 wt% denoted for RZ by (Simpkin, 2003). According to injection test results, in two columns 0,2 wt% gcFe, in the third column 0,2 wt% were used. Autotrophic sulphate reducing bacteria, raised in separate microcosms from the native groundwater, were added to a gcFe column (column 1) and a naFe column (column 2). The second gcFe column (column 3) remained abiotic, providing a reference. The gas saturation of the pore volume was estimated to about 3 % for H2 and about 0.6 % for CO_2 in gas storage tests under flow conditions. To keep gas content close to saturation, the two biotic columns 1 and 2 were supplied with 20 ml H2 and 10 ml CO_2 two times a week. After 56 days, H2 injection was performed three times a week. The abiotic column 3 received 10 ml CO_2 two times a week.

Table 1. Average composition of influent groundwater used for the column tests.

pH	E_h	O_2	TOC	TIC	As	U	SO_4
[-]	[mV]			[mg/L]			
6,6	309	1,3	5,4	69	5,0	15,0	236

To estimate effective porosities, tracer tests with 1 g NaCl/L groundwater were carried out preceding the flow experiments. According to the determined effective porosity, the influent flow rate was set to about 0,2 L/d using a peristaltic pump (ISMATEC IPC-N) in order to ensure a residence time of 7 days. Thereby, the reaction time for autotrophic sulphate reduction was optimised and every replaced pore volume could be sampled. To avoid O_2 uptake, influent tubes were equipped with PP mantles flushed continuously with N_2.

The column effluent was passed through 100-mL glas vials, which were replaced for sampling. Every replaced pore volume was analysed for pH, redox, major and trace elements (ICP-OES, Spectro), sulphate (IC, Dionex), ferrous iron (photometer), inorganic carbon (TOC/TIC -Analyzer, Shimadzu) as well as for the isotopic composition of sulphate ($^{18}O/^{16}O$ and $^{34}S/^{32}S$). Isotope measurements (IRMS) were carried out at the UFZ Centre for Environmental Research Leipzig-Halle, department of isotope hydrology. The influent groundwater was analysed for the same parameters. A change of the hydraulic head due to mineral precipitation or bioclogging was continuously monitored at the column influent by piezometer tubes. According to Darcy' Law, hydraulic heads were used for calculation of hydraulic conductivities.

Subsequent to column tests, pore water and sediment samples were collected from the sediment columns along the flow path in distance of 5, 15, 25, 35, 45 cm from the influent inlet. Thereby, a nitrogen-pressure filtration of sediment samples was used to collect pore waters in gas-tight plastic syringes. To protect sulphate reducing bacteria and reduced mineral phases, the biotic columns 1 and 2 were dismantled under nitrogen atmosphere. Pore waters were analysed for pH, redox and major and trace elements (ICP-OES) as well as microbial counts of sulphate reducing bacteria (MPN-method). MPN counts were performed by the G.E.O.S mbH Freiberg. After pore water extractions sediment samples were used for acid volatile sulphur digestions and sequential extractions in order to identify uranium and arsenic binding forms. Sequential extractions were carried out according the method of (Zeien 1995).

Results and Discussion

At column 1 (biotic, grey cast iron), a particle displacement was observed after the fifth replaced pore volume (Fig. 1a). This process was accompanied by an increase of hydraulic conductivity. In contrast, the homogenous blackening of the biotic nano scale iron column remained till the end of the test period (Fig.1b). This observation is explained by different particle retention mechanisms. Whereas grey cast iron (particle size ≤ 30 µm) was deposited in the pore space by sedimentation, nano scale iron (colloid size ≈ 0,1 µm) and its transformation products were retained by adsorption to the sediment surface.

Grey cast iron showed a lasting and constant corrosion, which resulted in an increase of effluent pH (from pH 6,5 to maximal pH 8) and a decrease in redox potential (from 480 mV to about 80 mV) in column 1 (biotic, grey cast iron).

Because of iron hydroxide formation and the lack of sulphate reducing bacteria, only a slight environmental change was observed in column 3 (abiotic, grey cast iron) until the seventh replaced pore volume. The redox potential decreased about 100 mV, pH increased from pH 6.5 to maximal pH 7.4. In contrast, naFe showed a temporary and intensive corrosion. Until the third replaced pore volume, the effluent pH was above 9. To the end of the test, the pH remained between 8 and 8.5 and the redox potential decreased from 480 to about 100 mV.

During the whole test time, U and As were completely immobilised in column 2 (biotic, nano scale iron). In both grey cast iron columns (1 and 3) arsenic was also completely immobilised, while uranium retention was incomplete (Fig. 2). The U peak after seven replaced pore volumes correlated with a temporary redox reduction in the influent groundwater. Due to those redox fluctuations, no iron hydroxide formation and the subsequent uranium sorption was possible. However, uranium retention in the reduced column 1 (biotic, grey cast iron) was clearly better than in column 3 (abiotic, grey cast iron).

Significant amounts of ferrous iron were discharged from the reduced column 1 (biotic, grey cast iron). Despite a reducing redox potential, no ferrous iron was detected in the effluent of column 2 (bio-naFe). Due to iron hydroxide formation, no ferrous iron was measured in the effluent of column 3 (abiotic, grey cast iron). (Fig. 3). During the test period, the effluents of both grey cast iron columns (1 and 3) showed no decrease in sulphate concentrations. A significant sulphate reduction (5 to 8,5 mg/L*d) was observed at column 2 (bio- naFe). Performing a balance between H_2 required for measured sulphate decrease (see Equation 2) and injected H_2, it could be evidenced that autotrophic sulphate reduction was limited by available (injectible) H_2 amounts.

One line of evidence for the occurrence of bacterial sulphate reduction was the enrichment of ^{34}S isotope in the dissolved sulphate during its passage through column 2 (biotic, nano scale iron). The preferential utilization of ^{32}S by bacteria leads to increasing $\delta^{34}S$ values in the residual sulphate and very low $\delta^{34}S$ values in the produced sulphide. Assuming piston-flow conditions with no preferential flow occurring in the columns, the enrichment of ^{34}S follows a Rayleigh type fraction-

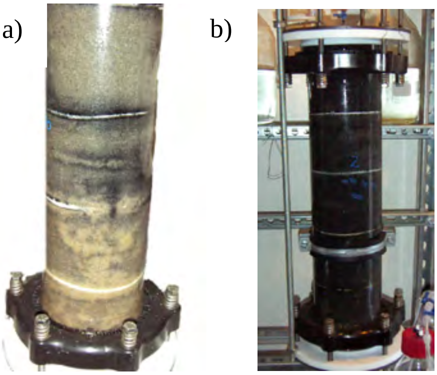

Fig. 1. Column tests: a) Column 1, b) Column 2

ation model. Applying this model, an enrichment factor ($^{34}\varepsilon$) of -30 ‰ (between residual aquatic sulphate in the column effluent an freshly formed sulphide) was determined for column 2 (Fig. 5). This value is in the medium range of natural, heterotrophic sulphate reduction (Knöller and Trettin 2003). However, no data are known for autotrophic sulphate reduction so far. Although no significant decrease of the sulphate concentration was measured in the effluent of column 1 (biotic grey cast iron), a slightly negative correlation between $\delta^{34}S$ and residual sulphate was present, yielding a theoretical enrichment factor ($^{34}\varepsilon$) of about -5 ‰ (Fig. 4) This very low enrichment factor indicates a mixing of reduction-influenced sulphate and unreduced influent sulphate.

The findings of aqueous phase analyses were supported by pore water and sediment analyses subsequent to the column experiments. Similar microbial counts of autotrophic sulphate reducing bacteria were obtained for column 1 (biotic gcFe) and column 2 (biotic naFe). In column 1, the first third of the flow path showed the highest microbial counts of sulphate reducing bacteria and decrease in sulphate concentrations within the pore water of about 30 mg/L (Fig.6a). Correlat-

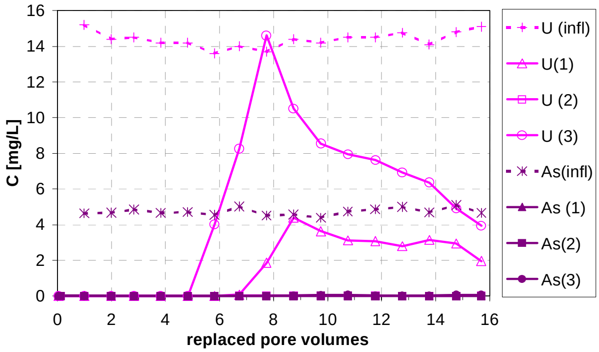

Fig. 2. U and As concentration changes.

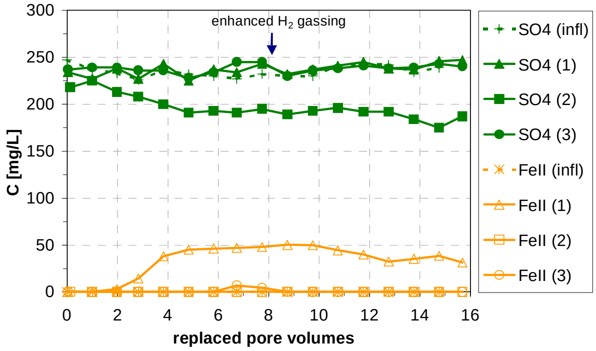

Fig. 3. SO_4^{2-} and Fe^{2+} concentration changes.

ing with this, iron monosulphide and the main part of immobilised U and As were found in sediment samples taken at 5 cm and 15 cm of the flow path of column 1 (biotic gcFe). The pore water analyses and the iron monosulphide contents of column 2 (biotic naFe) prove the occurrence of an effective autotrophic sulphate reduction. U and As were nearly completely immobilised within the first entimeters of the flow path, correlating with the highest biological activity (Fig. 6b). Pore water analyses showed no signifycant sulphate decrease in column 3 (abiotic gcFe). Most uranium and arsenic was retained in the influent area, where an iron hydroxide formation was analysed by sequential sediment extraction.

To verify geochemical and microbial processes within the most effective column 2 (biotic naFe, compare Fig. 2), a phreeqC- transport modelling was carried out. Metallic iron was defined as a new mineral phase according to equation 1. To ensure a complete oxidation, a positive equilibrium constant (log_k 10) was used. Two versions of iron corrosion kinetics were modelled. In version (1), a constant

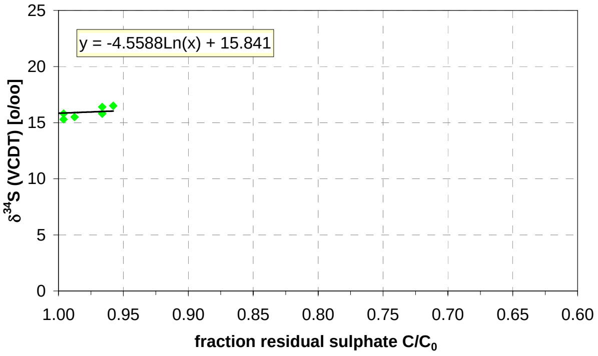

Fig. 4. Column 1: ^{34}S and residual SO$_4$.

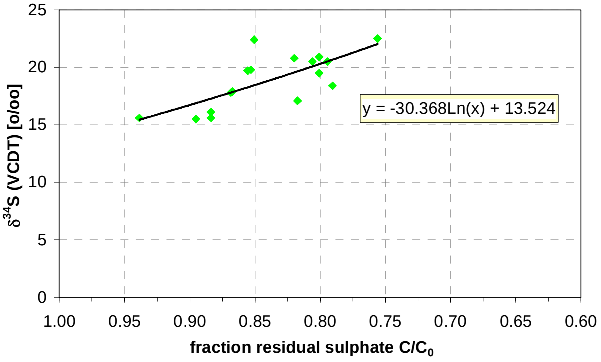

Fig.5. Column 2: 34S and residual SO$_4$.

iron corrosion rate (2.2 $*10^{-8}$ mol/s) was used for the duration of the experiment. To simulate a surface passivation, the corrosion rate was decreased marginally in each time step using the ‘Put’ and ‘Get’ functions. In version (2), a short, intensive iron corrosion rate ($5.1*10^{-7}$ mol/s) without surface passivation was simulated. The kinetic of autotrophic sulphate reduction was obtained by the measured sulphate concentration decrease. For both versions, the precipitation of siderite and iron monosulphide were the main OH- and Fe(II) consuming processes. Thereby, siderite was dissolved in favour of a biological induced iron monosulphide precipitation accompanied by a HCO_3^- release. The measured concentrations of inorganic carbon could only be fitted with version 2, where significant siderite amounts were precipitated at the initial stage of the test. Hence, an intensive iron corrosion with Fe(II)- storage by precipitation and subsequent sorption of ferrous iron mineral phases (e.g. siderite) on the sediment surface is more probable than a lasting and constant corrosion of nano scale iron. A clear identification of uranium and arsenic immobilisation processes was not possible due to amorphous character of freshly formed mineral phases and the lack of corresponding thermodynamic data. Furthermore, surface complexation sites for FeS are not implicated in phreeqC- databases.

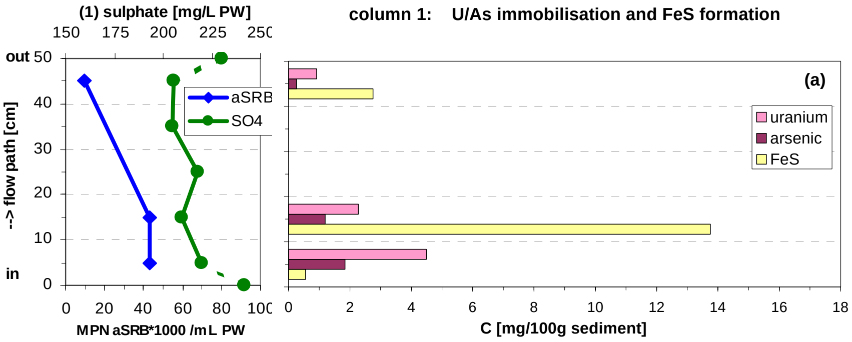

Fig. 6a. Pore water and sediment analyses analyses in column 1.

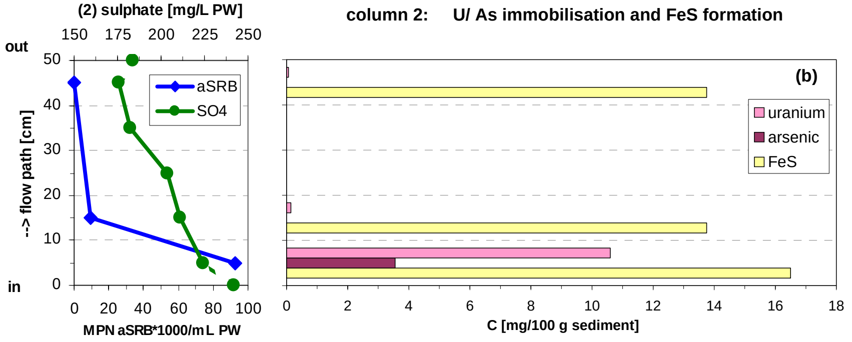

Fig. 6b. Pore water and sediment analyses analyses in column 2.

Conclusions

In this study, the long term reactivity of injectible iron particles and the contribution of autotrophic sulphate reduction for uranium and arsenic immobilisation under flow conditions was investigated. In two (biotic and abiotic) columns, 2 g particulate grey cast iron, in a third (biotic) column, 2 g colloidal nano scale iron per kg silica sand were used.

Firstly, we found the combination of anaerobic iron corrosion and autotrophic sulphate reduction have proven most effective for uranium and arsenic immobilisation. While an iron hydroxide formation resulted in a full arsenic and only partial uranium immobilisation in the abiotic grey cast iron column, the highest microbial counts of autotrophic sulphate reducing bacteria and an FeS formation were observed relating to an almost complete pollutant immobilisation in the biotic columns.

Furthermore, we found the particle retention mechanism to be important for an ‘reactive zone’ formation and their hydraulic conductivity. Due to its particle size (≤ 30 µm), grey cast iron was deposited in the pore space by sedimentation. Thus, a particle displacement caused the formation of cluster like structures in the biotic grey cast iron column. This process resulted in an increase of hydraulic conductivity. Although no sulphate decrease was measured in the effluent of this column, enhanced microbial counts of autotrophic sulphate reducing bacteria as well as iron monosulphide formation were analysed in the cluster like structures. Hence, it was concluded, that most influent water did not react in the iron enriched and reduced clusters. This result indicates the importance of optimised iron particle sizes and injection rates for the formation of homogenous RZ. Nevertheless, grey cast iron shows a lasting and constant corrosion. Due to surface passivation by iron hydroxides, the corrosion was less intensive in the abiotic grey cast iron column.

Because of its adsorptive retention on the sediment surface, the injection of nano scale iron resulted in the formation of a homogenous reactive zone without significant permeability change. A distinct autotrophic sulphate reduction was promoted by direct injection of storable H_2 and CO_2 gas to the pore space of aquifer material. Besides decreasing sulphate concentrations and increasing ^{34}S-isotope values in the column effluent, enhanced microbial counts of autotrophic sulphate reducing bacteria as well as the abundance of iron monosulphide were observed. It could be shown that autotrophic sulphate reduction was limited by available H_2 amounts. Therefore, enhanced sulphate reduction rates are possible by optimising the in-situ H_2 injection regime. In spite of the temporary and intensive corrosion of nano scale iron, no ferrous iron was detected in the column effluent. By means of a phreeqC- modelling, it was concluded that ferrous iron could be retained in the system by siderite precipitation. In favour of an iron monosulphide precipitation, siderite was dissolved stepwise. Therefore, the combination of nano scale iron corrosion and autotrophic sulphate reduction has proven suitable to achieve effective As und U immobilisation in engineered reactive zones.

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