Design of a treatment zone technology for in-situ immobilisation of uranium and arsenic

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Abstract

In this study we investigated the geochemical and microbial as well as the technical basis for an effective in-situ immobilisation of arsenic and uranium. To do this, we combined microbial sulphate reduction with anaerobic corrosion of grey cast iron powder and nano-scale iron colloids, respectively. While nano scale iron showed an extremely high, but temporary reactivity, a lasting iron corrosion and environmental reduction was observed for grey cast iron powder. By adding methanol or H_2/CO_2 respectively, heterotrophic and autotrophic sulphate reduction as well as iron sulphide precipitation were stimulated and therewith reducing conditions were maintained. In the tests, iron sulphide was shown to coprecipitate arsenic and to catalyse reductive uranium precipitation, which was indicated by X-Ray photoelectron spectroscopy (XPS). However, scanning electron microscopy (SEM) with an energy-dispersive X-Ray (EDX) measurement pointed out, that most uranium was fixed directly to the surface of the grey cast iron particles.

For in-situ immobilisation, a suitable treatment zone technology must be developed. Using high injection pressure and volume flow after an initial hydraulic or pneumatic fracturing of the sediment we attained good results for nano-scale iron colloids and grey cast iron powder injection. In both cases injection range exceeded the test-barrel radius (0,74 in.) and generated amounts of 0,5 - 3 g Fe/kg sediment. No hydraulic conductivity loss was observed.

1   Introduction

Motivation   The intensive uranium ore mining which took place until the mid-seventies has resulted in many abandoned mine processing sites in East Germany which need to be restored. Residues have been dumped in waste disposal sites and tailings-lakes without aquifer sealing. Thus, groundwater run-off exceeds uranium and arsenic legal limit values. To prevent pollution of adjacent aquifers, in-situ immobilisation of uranium and arsenic has to be developed downstream of waste disposal sites and tailings-lakes. The objectives of the study are both investigations of the geochemical and microbial immobilisation for arsenic and uranium as well as developing the technical basis for an iron particle injection.

   Geochemical and microbial basis   We use anaerobic iron corrosion for initial environmental reduction as well as for ferrous iron and hydrogen supplies (Equation 1). For an in-situ application, it is necessary to focus on choice and verification of long-term reactive iron materials. We selected a grey cast iron powder, because impurities like carbides counter surface passivation therefore encouraging iron corrosion [Friedrich and Knappik, 2001]. The development of nano-scale iron colloids by ARCADIS revealed another interesting possibility for pollutant immobilisation in our research [Vance, 2002]. In order to keep reducing conditions and to produce sulphide, microbial sulphate reduction is stimulated by adding methanol or hydrogen and carbon dioxide. Eq. (2a) and (2b) show heterotrophic and autotrophic sulphate reduction. Under appropriate environmental conditions the produced sulphide precipitates with ferrous iron to form amorphous iron sulphide (Eq. 3). It is known that iron sulphides co-precipitate arsenic very well [Morse et al., 1987]. The capacity of iron sulphides for sorption and the consequent reductive precipitation of uranium is presently under investigation [Fiedor et al., 1998], [Wersin et al., 1994]. Eq.(4) and (5a), (5b) show the reaction patterns for pollutant immobilisation.

$$Fe^0 + 2\,H_2O \rightarrow Fe^{2+} + H_2 + 2\ OH^- \quad (1)$$

$$SO_4^{2-} + H^+ + 4/3\,CH_3\text{-}OH \rightarrow HS^- + 4/3\,CO_2 + 8/3\,H_2O \quad (2a)$$

$$SO_4^{2-} + H^+ + 4\,H_2 \rightarrow HS^- + 4\,H_2O \quad (2b)$$

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

$$Fe^{2+} + 0{,}9HS^- + 0{,}1H_3AsO_3 \rightarrow FeAs_{0,1}S_{0,9} + 0{,}6\,H^+ + 0{,}3\,H_2O \quad (4)$$

$$FeS + UO_2^{2+} \rightarrow FeS{=}UO_2^{2+} \quad (5a)$$

$$FeS{=}UO_2^{2+} + 2e^- \rightarrow FeS + UO_{2(s)} \quad (5b)$$

Technical basis   For in-situ immobilisation of arsenic and uranium, a zero valent iron (ZVI) treatment zone technology is intended. This technology consists of the installation of a line of overlapping ZVI injection points perpendicular to the groundwater flow direction. Pilot tests with effective abiotic reduction of chlorinated solvents using ZVI treatment zone technology were described in several US-papers [Liskowitz et al., 1999], [Schuring et al., 1999], [Simpkin, 2003]. In contrast to permeable reactive barriers (PRBs), no excavation and therefore no damage to the cover sealing of waste disposal sites is required. Furthermore PRBs are limited in depth (circa 21 m), a ZVI treatment zone is only limited to the depth of the drilling equipment.

2   Materials and Methods

Batch design   Geochemical and microbial immobilisation processes of uranium and arsenic were studied in anaerobic batch tests for 100 days at 12°C. Sediment and groundwater were gathered from the abandoned mine processing site in Lengenfeld, East Germany. The sediment consisted of weathered granite gravel, which was mixed in a ratio of 1:3 with silica sand. The groundwater contained about 5 mg/L organic carbon, 70 mg/L inorganic carbon, 300 mg sulphate and less than 1 mg/L oxygen. The pH was neutral and the redox potential was approximately +300 mV. Uranium (20-30 mg U/L as uranylnitrate) and arsenic (10-20 mg As/L as natriumarsenite) were enriched as well as cast iron powder (3 g/L, particle size 20-63 μm) and nano-scale iron colloids (about 30 mg/L, 0,1μm colloid size) respectively. Sulphate reducing bacteria from the native groundwater were cultured in separate microcosms under ideal conditions, then added to the tests. Then, heterotrophic and autotrophic sulphate reduction was stimulated with methanol (200 mg/L) and regular H_2/CO_2 gassing (1:1), respectively. Parallel, batch tests without sediment were carried out for mineralogical analyses of iron precipitates.

Batch analyses   During the batch tests, sampling of the aqueous phase were carried out at regular intervals using plastic syringes. In addition to pH and redox, carbon was analysed by TOC-Analyser, elements were measured by ICP-OES, anions were analysed by IC and ferrous iron was measured by a photometer. Sulphide was quantified by an amperometric H_2S-microsensor. According to the test, pollutant binding forms and iron sulphide concentrations were analysed under strictly anaerobic conditions by means of sequential sediment extractions and acid volatile sulphur (AVS)digestions. Via sequential extraction with pH-graded inorganic salt

solutions cations were differentiated to six binding fractions; (1) exchangeable, (2) carbonatic and specific adsorbed, (3) organic and specific adsorbed or bound to amorphous iron hydroxides, (4) bound to weakly crystalline iron hydroxides, (5) bound to crystalline iron hydroxides as well as (6) sulphidic or residual bound [Krumnöhler, 1995]. Using the iron precipitates from the batch tests without sediment, X-Ray diffraction (XRD) analyses, SEM micrographs with EDX measurements as well as X-Ray photoelectron spectroscopy (XPS) analyses were carried out to identify newly formed minerals and the amounts of arsenic and uranium bound to the precipitates. Precipitates were dried via acetone and vacuum filtration in a nitrogen atmosphere.

Injection test design   A downstream perforated injection lance was placed in the centre of a closed barrel (height 0.6 m , diameter 0.45 m) filled with silica sand. Injection lance diameter and perforated zone was 0.05 m, respectively. The non-perforated zone of the lance was sealed with a packer. In order to avoid upward streaming, horizontal caulking plastic disks were set in the barrel around the lance. Preceding the iron particle injection preferential flow paths had to be created through hydraulic [Hocking and Ospina, 1999] or pneumatic fracturing [Liskowitz et al., 1999], [Schuring et al., 1999]. For this purpose water (15 minutes for nano-scale iron colloids injection) or gas (5 minutes for grey cast iron injection) were injected through the lance with high pressure (about 3-4 bar) and volume flow (about 50 L/h). Subsequently, 120 L and 200 L iron particle suspension (0,25 g nano scale iron/L or 0,1 g cast iron/L < 20 μm) were delivered through the lance by means of a peristaltic pump with flow rates from 40 to 50 L/h, respectively. To maintain the suspension of the iron particles, that was stirred in the storage tank and circulated through the lance with a pump.

Injection test analyses   Following the injection test, sediment samples were collected around the lance and subsequently leached in acified distilled water with a pH of 1. Ferrous iron, released within six minutes, was measured by ferrous-iron-strips and converted to sediment mass (g Fe/kg sediment) by means of a calibration curve. Therefore, six known amounts of cast iron powder and nano scale iron were eluted for six minutes in acified distilled water with a pH of 1, respectively. A '6 minutes-corrosion-factor' was derived from the ratio of ferrous iron released to total iron amount. Within this time, 50 % nano scale iron and about 20 % grey cast iron (< 20 μm) corroded. Column tests were conducted to assess the hydraulic conductivity loss of the treated sediment.

3   Results and Discussion

Batch tests   A lasting environmental change and ferrous iron release was observed in the test with cast iron powder addition. Both heterotrophic and autotrophic sulphate reduction resulted in amorphous iron sulphide precipitation. Using acid volatile sulphur digestions at the end of the test 0.05 wt% and 0.04 wt% iron sulphide were detected respectively. According to a 14- day- lag time, heterotrophic sulphate reduction set in with a rate of 0.1 mmol/L*d. Autotrophic sulphate reduction started after 35 days and averaged 0.05 mmol/L*d. Remarkably, the rate of iron corrosion in the latter test (0.13 mmol/L*d) was nearly double that with methanol addition for heterotrophic sulphate reduction (0.06 mmol/L*d). Due to CO_2 gassing iron corrosion was promoted because HCO_3 is able to break through corrosion layers around iron particles [Gu et al., 1999]. Figure 1 presents trends of arsenic, uranium and sulphate concentrations as well as redox change for the tests with anaerobic grey cast iron (3 g/L) corrosion and heterotrophic sulphate reduction stimulated through methanol addition. Figure 2 presents the same for the parallel attempt with autotrophic sulphate reduction stimulated by gassing with hydrogen and carbon dioxide.
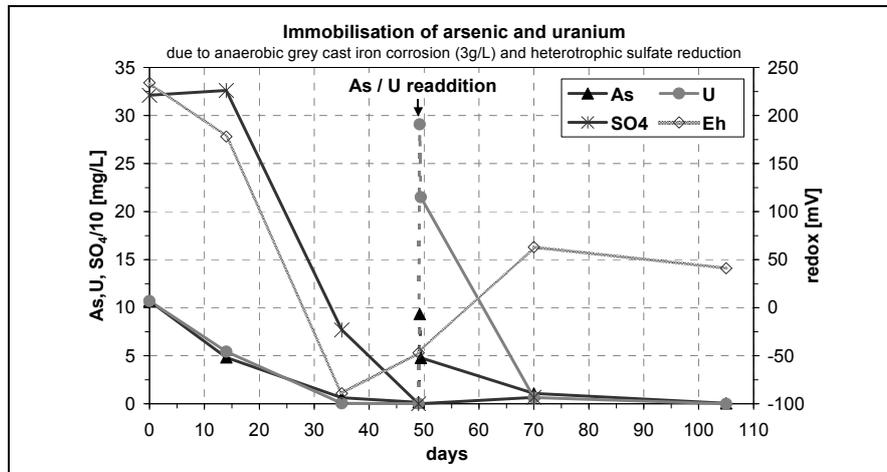

Immobilisation of arsenic and uranium
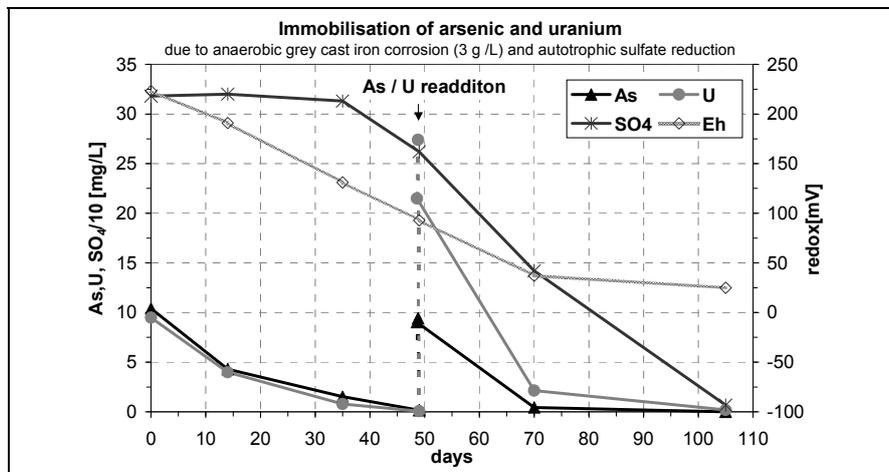due to anaerobic grey cast iron corrosion (3g/L) and heterotrophic sulfate reduction

Fig. 1.   trends of arsenic, uranium, sulphate and redox due to anaerobic grey cast iron corrosion and heterotrophic sulphate reduction

In both tests uranium and arsenic were completely immobilised. While most uranium was immobilised by surface complexation, probably directly on the surface of grey cast iron particles, arsenic bound predominantly to newly formed amorphous iron hydroxides and co-precipitated with amor-

phous iron sulphide after sulphate reduction was initiated. These findings were attained from a SEM-EDX analysis as well as sequential sediment extractions. Furthermore, a XPS analysis and geochemical modelling (phreeqC 2.7) indicated reductive precipitation of Uranium (VI) to amorphous uraninite in minor parts. These may have been catalysed by cast iron and iron sulphide surfaces. XRD measurements did not indicate newly formed, crystalline minerals. As shown in the diagrams, readded uranium and arsenic were immobilised too, and the retention capacity of reactive phases had not yet been exhausted.

Fig. 2. trends of arsenic, uranium, sulphate and redox due to anaerobic grey cast iron corrosion and autotrophic sulfphate reduction

In contrast to the tests with cast iron powder, the addition of nano-scale iron colloids resulted in a temporary, intensive environmental change. Nano-scale iron colloids were completely corroded within a few hours, long before sulphate reduction could set in. After a lag of 14 days heterotrophic sulphate reduction occurred at a rate of 0.08 mmol/L*d, autotrophic sulphate reduction was first observed after a 50 day-lag with only 0.01 mmol/L*d. Significant amounts of aqueous sulphide were measured, indicating the lack of ferrous iron for iron sulphide precipitation. After re-addition of arsenic, it was immediately precipitated as arsenic-sulphide. The sequential sediment extractions indicated for arsenic mainly a sorption to newly formed amorphous iron hydroxides and also a co-precipitation with (iron) sulphides in minor parts. Most of uranium was immobilised by sorption to older, poorly crystalline iron hydroxides from the sediment. The SEM-EDX micrograph of the precipitate from the batch test with het-

erotrophic sulphate reduction (without sediment) shows extremely high contents of uranium (Fig.5), whose homogeneous distribution indicated an independent, but amorphous uranium-phase. Uranium, arsenic, sulphate and redox trends for the nano scale iron tests are shown in Fig. 3 (heterotrophic sulphate reduction) and Fig. 4 (slight autotrophic sulphate reduction).
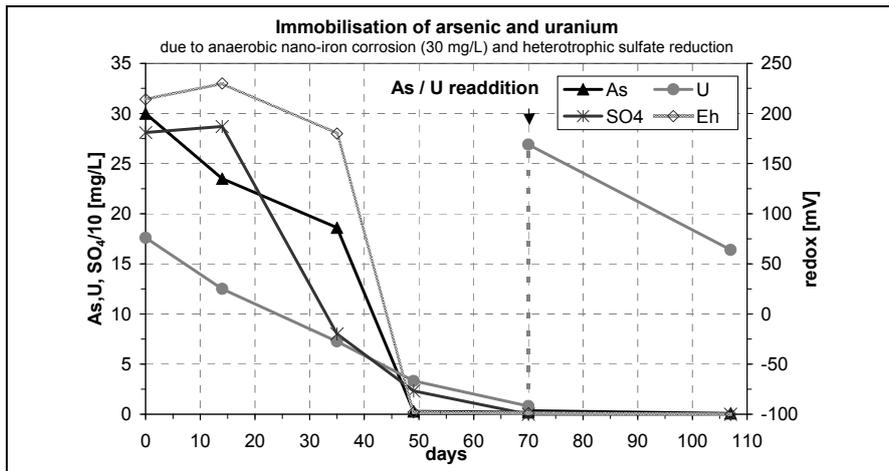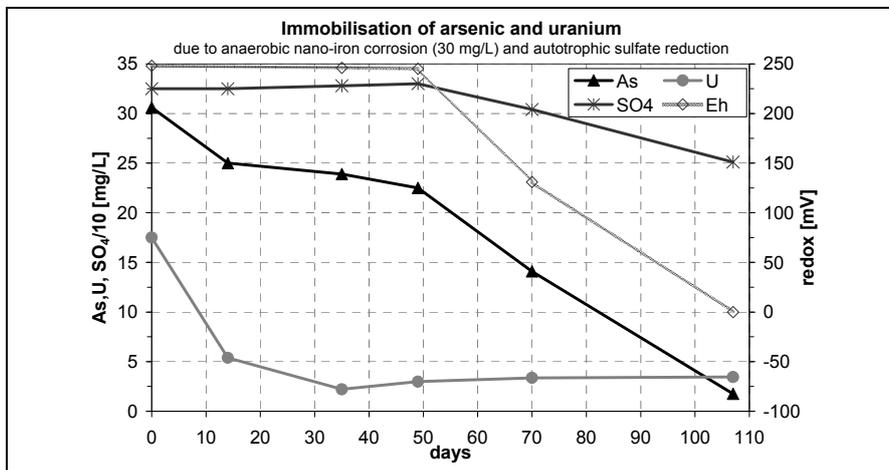

Fig. 3. trends of arsenic, uranium, sulphate and redox due to anaerobic nano iron corrosion and heterotrophic sulphate reduction

Fig. 4. trends of arsenic, uranium, sulphate and redox due to anaerobic nano iron corrosion and autotrophic sulphate reduction
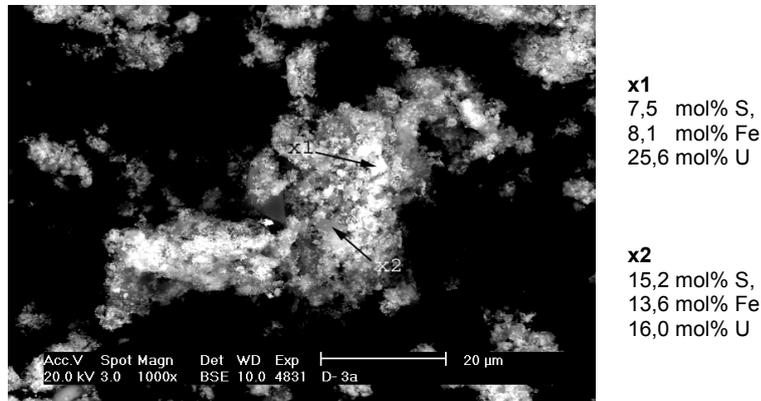
x1
7,5 mol% S,
8,1 mol% Fe
25,6 mol% U

x2
15,2 mol% S,
13,6 mol% Fe
16,0 mol% U

Fig. 5. SEM micrograph and EDX analysis of iron precipitate from an attempt with nano scale iron and heterotrophic sulphate reduction

Injection tests Using high injection pressure and volume flow after an initial fracturing of the soil we attained good results for nano-scale iron colloids and grey cast iron powder injection. The blackening of the barrel outlet of both the nano scale iron and grey cast iron injection indicated an iron break through and therewith injection ranges, which exceeded the barrel radius (0,74 in.). Fig. 6 and Fig. 7 present clearly black coloured soil in the injection areas. Total amounts of 0,5 -3 g Fe/kg soil were determined by means of the '6-minutes-corrosion-factor'. The treated sediment showed no hydraulic conductivity loss due to the low iron content and the initial hydraulic or pneumatic fracturing.
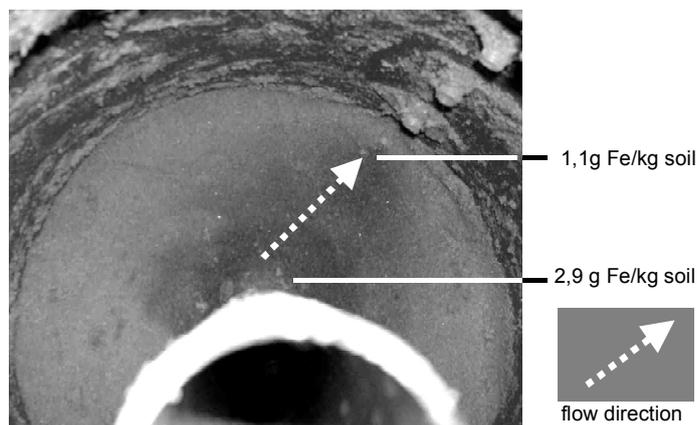

1,1g Fe/kg soil

2,9 g Fe/kg soil

flow direction

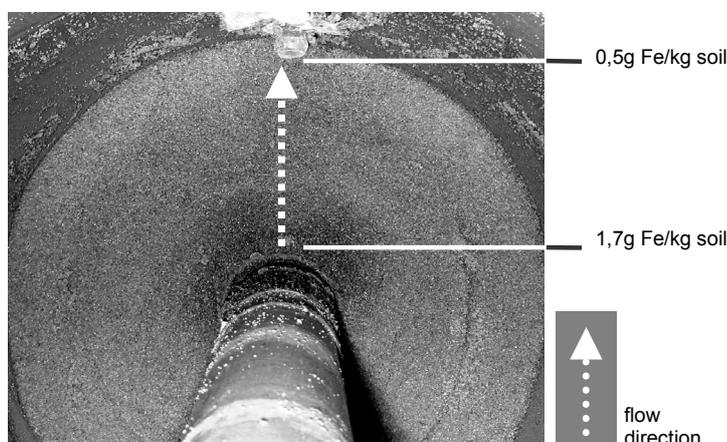**Fig. 6.** iron propagation in the nano scale iron injection test

Fig. 7. iron propagation in the grey cast iron injection test

4 Conclusion

The injection of grey cast iron powder and subsequent, continuous H_2/CO_2 gassing was the best combination tested for in-situ treatment of arsenic and uranium. Both the stimulating force of CO_2 on iron corrosion and autotrophic sulphate reduction and the microbial consumption of H_2 produced by iron corrosion promote a lasting and effective iron corrosion and environmental reduction. Through the stimulation of autotrophic sulphate reduction reducing conditions were maintained and amorphous iron sulphide precipitation took place. The latter was able to co-precipitate arsenic and to catalyse reductive uranium precipitation. However, in our tests most uranium was attached directly to grey cast iron particles. Due to its high and only temporary reactivity, nano scale iron appears inapplicable for a lasting in-situ immobilisation technology. Using high injection pressure ($\approx$ 3-4 bar) and volume flow ($\approx$ 50 L/h) as well as an initial hydraulic or pneumatic fracturing we attained good results for nano-scale iron colloids and grey cast iron powder injection. In both cases injection range exceeded the test-barrel radius (0.22 m) and generated amounts of 0,5 to 3 g Fe/kg sediment. No hydraulic conductivity loss was observed. Recently, column tests were started to evaluate long-term reactivity of injectible iron particle amounts. Our study showed the need for further research into autotrophic sulphate reduction and its effective contribution on arsenic and uranium immobilisation under flow conditions. Larger scale tests in order to verify injection range of the favoured injection technology are under way.

Acknowledgments

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