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Immobilization of uranium and arsenic by injectible iron and hydrogen stimulated autotrophic sulphate reduction

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Abstract

The main object of the study was the development of a long-term efficient and inexpensive in-situ immobilization technology for uranium (U) and arsenic (As) in smaller and decentralized groundwater discharges from abandoned mining processing sites. Therefore, corrosion of grey cast iron (gcFe) and nano-scale iron particles (naFe) as well as hydrogen stimulated autotrophic sulphate reduction (aSR) were investigated. Two column experiments with sulphate reducing bacterias (SRB) (biotic gcFe , biotic naFe) and one abiotic gcFe-column experiment were performed. In the biotic naFe column, no particle translocation was observed and a temporary but intensive naFe corrosion indicated by a decrease in E_h, a pH increase and H_2 evolution. Decreasing sulphate concentrations and ^{34}S enrichment in the column effluent indicated aSR. Fe(II) retention could be explained by siderite and consequently FeS precipitation by geochemical modeling (PhreeqC). U and As were completely immobilised within the biotic naFe column. In the biotic gcFe column, particle entrapment in open pore spaces resulted in a heterogeneous distribution of Fe-enriched zones and an increase in permeability due to preferential flow. However, Fe(II) concentrations in the effluent indicated a constant and lasting gcFe corrosion. An efficient immobilization was found for As, but not for U.

Keywords: Uranium; Arsenic; In-situ; Immobilization; Iron corrosion; Sulphate reduction

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1. Introduction

Intensive uranium ore mining until the mid-seventies resulted in many abandoned mine processing sites in Eastern Germany. Hydraulic connections between sites and shallow aquifers resulted in numerous, smaller and decentralized groundwater discharges contaminated with heavy metals, arsenic and radionuclides including uranium. Their concentrations frequently exceed thresholds for remediation of groundwater from abandoned mine processing sites (Schneider et al., 2001). For Germany, the thresholds are 0.3 mg U/L (SSK, 1992) and 0.02–0.06 mg As/L (LAWA, 2000). However, more strict groundwater standards for arsenic (0.01 mg/L) and uranium (0.03 mg/L) were given by (US-EPA, 2000) for drinking water regulations. In order to prevent an ongoing contamination of ground- and surface water, many abandoned mine processing sites need remediation. Classical 'pump-and-treat' combined with conventional water treatment technologies is common remediation practice, but this is a cost intensive approach, because it leaves concentrated hazardous waste residues

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for disposal (Neitzel et al., 2000). Development of long-term efficient and inexpensive in-situ treatment methods has therefore become a research topic of major importance and interest.

During the last decade, zero valent iron (ZVI) was often used within permeable reactive barriers (PRB), amongst others for in-situ containment of U. The activity of SRB in PRB's was described by (Gu et al., 1999) previously. A relatively new approach for in-situ remediation is the specific stimulation of biotic iron sulphide formation in order to provide additional contaminant immobilization reactions. However, the application of PRB is limited to shallow aquifers (up to 22 m below surface, Simpkin, 2003). Construction of a PRB requires an expensive excavation, which makes thus technology rather inefficient for smaller, decentralized groundwater contaminations. A potential alternative to PRB is the creation of reactive zones (RZ) by deep injection of iron particle suspensions perpendicular to the groundwater flow direction (i.e. using the direct-push-method). This technology requires injection of colloidal sized metallic iron (usually $\ll 100$ µm in diameter, depending on the pore size of the aquifer) with small quantities (≤ 1 wt.% of aquifer materials) (Simpkin, 2003) to maintain the movement of the iron particles in the pore space without clogging. Due to the small quantities of the metallic iron applied, reducing conditions and contaminant removal capacity of RZ are not as high as in the conventional PRB approach, where 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 the depth achievable by the drilling equipment used. This innovative technology therefore seems to be more economic at sites with smaller, decentralized groundwater discharges.

In this study, the precipitation of iron sulphide minerals by anaerobic iron corrosion and biological sulphate reduction in reactive zones is tested as a potential method for in-situ immobilization of arsenic and uranium. Iron sulphide minerals co-precipitate arsenic very effectively (Morse and Arakaki, 1993). Their capacity for sorption with consequent reductive precipitation of uranium was described previously (Wersin et al., 1994; Moyes et al., 2000; Livens et al., 2004). H_2, generated by the anaerobic iron corrosion, may accumulate at the iron surfaces. Autotrophic sulphate reducing bacteria consume the hydrogen to produce sulphide and this reaction promotes the corrosion process further. The produced sulphide precipitates with ferrous iron as patches of iron sulphide at anodic areas of the iron surfaces. This process also promotes corrosion, since iron sulphide does not precipitate on the iron surface as a uniform, passivating film (Ehrlich, 1997).

To minimize costs and technical effort of field applications, maximum time intervals between iron injections were proposed in the immobilization concept. For this reason and an efficient autotrophic iron sulphide production (Eqs. (1) and (2)), periodical additions of H_2 (and CO_2) between the iron injections were required. Because of the more homogeneous distribution and efficient storage of gases as compared to conventional liquid and solid carbon sources, the stimulation of sulphate reduction by gaseous H_2 (and CO_2) is an attractive option for in-situ treatment. Storage, resolution and their hydraulic impacts of reactive gases on aquifers are topics of ongoing research. Successful pilot studies and field tests were described by (Engelmann et al., 2004) and (Giese et al., 2004). The use of reactive gases can be realised by mixing with inert gas (Luckner, 2001), i.e. to ensure H_2 explosion protection limit of 4 vol.%.

$$Fe^0 + 2H_20 \rightarrow Fe^{2+} + H_2 + 2OH^- \tag{1}$$

$$Fe^{2+} + SO_4^{2-} + 4H_2 \rightarrow FeS + 4H_2O \tag{2}$$

This study will present the verification of the introduced U and As immobilization concept under flow conditions using column tests. Their concept and test design were based on the optimal immobilization reactions (batch tests) and injection tests for iron particles and gaseous H_2/CO_2 (column tests). These experiments were described previously (Burghardt, 2006).

2. Materials and methods

2.1. Reactive iron materials

Zero-valent iron materials (ZVI) used in PRB technologies (US-EPA, 1998) tend to develop surface passivation by forming precipitation due to their high purity (Friedrich and Knappik, 2001). Impure, particulate grey cast iron (gcFe) was therefore selected for the column tests where impurities like carbides counteract an early passivation and promote iron corrosion. The gcFe was obtained from the Maier Metallpulver GmbH Rheinfelden (Germany), and a mean particle size of <30 µm was selected by gas classification (Laser diffraction instrument, Co. Helios). Injectible nano-scale iron (naFe) was selected as a promising new alternative for groundwater remediation because of great surface area, which should significantly improve U and As immobilization (Vance, 2003). The naFe used in this study (Toda Kogyo GmbH, Japan) is colloidal in size with a mean grain size of