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In-situ Treatment of Radioactive Mine Water using Reactive Materials – Results of Laboratory and Field Experiments in Uranium Ore Mines in Germany*

Flooding of uranium mines causes a release of considerable amounts of uranium, radium-226 and arsenic into rivers and aquifers. Thus treatment is necessary in some cases. In order to evaluate alternative water treatment methods for mine water a research project was carried out by means of both lab experiments and small scale field tests in abundant mines of the Ore Mountains in East Germany. At two test sites columns filled with Fe⁰, Fe/Mn containing waste sludge and peat were installed for the duration of one year to investigate geochemical reactions and the fixation processes of relevant radionuclides and arsenic. While Fe⁰ is changing the geochemical conditions from oxidizing to reducing milieu, peat and Fe/Mn-sludge have a significant sorption capacity. In addition iron hydroxides coprecipitate residual contaminants. The fixation capacity of peat was found to be exhausted within half a year. The Fe/Mn-sludge adsorbed 60 % of radium and 70 % of arsenic. The best results for uranium elimination of about 96 % were obtained by means of Fe⁰.

In-situ-Behandlung von radioaktiven Bergbauwässern mit reaktiven Materialien – Ergebnisse von Labor- und Feldversuchen in deutschen Uranbergwerken

Bei der Flutung von Bergwerken sind die Metall- und Radionuklidgehalte der Wässer deutlich erhöht und müssen vielfach vor dem Eintritt in die Vorfluter behandelt werden. Als Alternative zu konventionellen Wasserreinigungsverfahren wurden neben Laborversuchen in Bergwerken im sächsischen Erzgebirge über ein Jahr Feldversuche mit reaktiven Materialien zur Eliminierung der Schadstoffe aus Flutungswässern durchgeführt. Als Materialien wurden Fe⁰, Fe/Mn haltiger Klärschlamm und Torf ausgewählt. Während die Fixierung des Urans mittels Fe⁰ auf einer geochemischen Milieuwandlung und Aus- bzw. Mitfällung an Eisenhydroxiden basiert, wird bei den übrigen Materialien die hohe Sorptionskapazität ausgenutzt. Wie die Ergebnisse zeigen, ist Fe⁰ gut für die alternative Behandlung von Flutungswässern geeignet. Die Sorptionskapazität von Torf war nach einem halben Jahr erschöpft. Mit Hilfe der Fe/Mn-Verbindungen wurden im Mittel 60 % Radium und 70 % Arsen eliminiert. Die höchste Effektivität für Uran-Spezies zeigten Eisenspäne mit einer Eliminierungsrate von bis zu 96 %.

Keywords: Mine Water Treatment, Mine Flooding, Zero-valent Iron, Geochemical Barrier, Radionuclide Fixation

Schlagwörter: Wasserbehandlung, Grubenflutung, Nullwertiges Eisen, Geochemische Barriere, Radionuklidimmobilisierung

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1 Introduction

After reunification of East and West Germany remediation of abandoned mining sites in Eastern Germany is one of the environmental problems. During and after mine flooding considerable amounts of uranium, radium-226 and arsenic are contaminating aquifers and rivers. Common pump and treat techniques may be used to immobilize the metal and radionuclide content, however, being an expensive mitigation problem for many years and even decades. In 1998 the Ministry of Environment and Agriculture of Saxony funded a research project to evaluate alternative water treatment methods for these contaminated mine waters [1]. The treatment methods should be applicable with a minimum of energy, manpower and without the need of permanent renewal of chemicals. Appropriate passive treatment techniques are reactive walls and successive alkalinity producing systems (SAPS) [2–4].

Element concentrations of mine water after closing down and stop of pumping are controlled by a variety of geochemical and geotechnical processes. Depending on the relevance of these processes, contaminant contents can increase or be reduced. Mobilisation of metals and radionuclides is caused by leaching of aquifer material and oxidation of minerals. Contaminants can be transported both as ions and bound to colloids. A natural decrease of concentrations over time may be caused by sorption and mineral precipitation.

In order to immobilize radionuclides and arsenic different chemical processes can be used: sorption on reactive surfaces, a reducing geochemical milieu and coprecipitation with e.g. iron-hydroxides. The aim of the study was to find a way to reduce mobile U(VI) to immobile U(IV). The idea was to use reactive materials, which can be easily deposited in the shafts during flooding. The following studies were investigated in detail:

- geochemical modeling of reactions with suitable reactive materials,
- column tests using reactive materials,
- underground field tests using Fe⁰-, Fe/Mn-sludge and peat,
- investigation of input and output of radionuclides and arsenic,
- evaluation of the immobilisation rates for uranium, radium and arsenic.

In order to investigate the immobilisation of metals and radionuclides main topic of the study was the in-situ application of the treatment system. Due to the geochemical milieu, which is needed for the forming of long term stable uranium minerals, special investigations were prepared for the evaluation of the geochemical behaviour of uranium under varying geochemical conditions. According to the contamination potential present in the mines, parameters for the prognosis of the long term behaviour of the contaminants uranium, radium-226, lead-210 and arsenic had to be defined, additionally.

2 Column and field experiments – methods and materials

2.1 Column Investigations

In order to identify suitable materials for the field experiments batch tests and small scale column experiments were performed. These experiments included fixation and remobilization (desorption) tests for uranium and arsenic using reactive materials and percolating water with pH ranging from 2.1 to 6.6. The fixation experiments were performed by batch tests using 32 types of reactive materials (organic and inorganic adsorbents, zeolithes, phosphate rocks, dolomite, and reductive precipitants) selected on the basis of literature data [5].

The different materials were treated with drinking water spiked with 2·10⁻⁴ M uranium acetate solution. Sulfuric acid and sodium hydroxide were added to control the pH value. In contrast to common shaking, samples were turned over three times in 14 days. After decantation and filtration uranium was analyzed by arsenazo-III-method [6, 7]. On the basis of the obtained results, another type of experiments was performed using glass columns of 24 mm diameter and 400 mm length. Four laboratory-column experiments using the following different reactive media have been completed:

- iron (scrap), zero valent iron (Fe⁰)
- iron and brown coal
- brown coal
- Fe/Mn- water works sludge

The columns were filled with 10% (wt) of zero valent iron or 50% of other reactive materials mixed with quartz sand. One column contained just sand as a blank comparison. Uranium solution was added from the bottom over a period of 3 months with flow rates varying from 0.016 to 0.16 mL/min.

A rapid porosity loss was obtained for brown coal due to clogging effects yielding to a decrease of the flow rate to zero after only 107 pore volumes exchanged for the column with brown coal and sand and after 607 pore volumes in that with brown coal, steel (type 69) and sand. Thus for field application it is highly recommended to use brown coal mixed with quartz sand or gravel of larger particle size.

2.2 Field investigations

As a result from the column investigations the reactive materials Fe⁰, Fe/Mn-sludge and peat were selected for field investigations in abandoned mines of the Ore Mountains. The underground reactive test fields were installed in two old shafts in the Ore Mountains in Eastern Germany (near the villages Niederschlag and Johanngeorgenstadt, figure 1). The silver and uranium mining area of “Shaft 216” is situated in Niederschlag near Oberwiesenthal. The ore and uranium

mining "Glückauf-Schäft" Johanngeorgenstadt is situated near the Czech border. The shafts were carried down from 18 th to 20 th century. Nowadays they are closed and flooded. The test fields were installed in the free flowing mine waters on the bottom of the cross-cut level. Two sites were selected according to typical water contamination problems: the arsenic rich Glückauf Shaft Johanngeorgenstadt and the uranium rich Niederschlag mine.

Both underground test fields were equipped with three separate reactor columns of 100 mm diameter, 1000 mm length and 3.9 L volume made of plexiglass. The flow rate was adjustable from 1 mL/min to 1 L/min. Fe⁰ and peat were filled in the reactor columns, Fe/Mn-sludge was mixed with sand (maximum grain size 2 mm). A percolation rate of 0.07 L/min to 0.19 L/min was used depending on the structure and density of the reactive material. A horizontal percolation was used in the test fields of Johanngeorgenstadt, while in Niederschlag a vertical percolation was practicable.

The zero valent iron used in the reaction columns was scrap material of the Metallaufbereitung Zwickau GmbH (Germany) containing traces of carbon (3.3 %), silicon (2.11 %), manganese (0.53 %), sulfur (0.097 %) and chromium (0.072 %). The material had a grain size of 2 - 50 mm. Fe/Mn-compounds were water works sludge, i.e. residues of the drinking water treatment of the water works Torgau (Germany). The peat material used was commercial peat type (Ehfi).

The hydrochemical analyses of percolation waters were performed using following methods: cations - atomic adsorption spectroscopy, anions - ion chromatography and heavy metals including uranium ICP-MS (uranium detection limit: 0.1 µg/L). For the detection of radium activity emanometry method was used (detection limit: 10 mBq/L). The inflowing water and the effluent water of the reactor columns were analysed for pH, electrical conductivity, redox potential, major ions, metals and radionuclides, initially on a weekly and later on a monthly time scale. After completion of the field tests the particles were investigated by scanning electron microscope to characterise solid reaction products.

3 Results

3.1 Results of the laboratory experiments

A break through was observed for Fe/Mn-sludge after 570 pore volumes. No breakthrough was observed in the column filled with zero valent iron even after 1200 pore volumes (total duration of the experiment). These results are summarized in Figure 2.

In addition the reactive materials were left for three months in the columns and then tested for uranium desorption with deionized water for two days and in 0,1 M Na₂CO₃ for 24 hours. By this about 6% of the fixed uranium could be recovered from columns containing zero valent iron taking into consideration that reductive precipitation is the major process of uranium removal from aqueous solutions [8]. It has to be mentioned that during the desorption experiment (3 days), no big effort was done to eliminate oxygen gas, thus a part of the recovered uranium could have been reoxidized due to oxic conditions. On the contrary, about 50% of the fixed uranium was recovered from the column containing Fe/Mn-sludge showing that desorption is much more likely to be responsible for the remobilization in this case.

3.2 Characterization of the flooding waters

The flooding water of the field experiments can be classified as Ca(HCO₃)₂-water, as well including sulfate in Johanngeorgenstadt. The conductivity of these aerobic water was about 360 µS/cm and pH value was around seven. The flooding water of Johanngeorgenstadt is characterized by an average arsenic content of 100 µg/L and an average radium-226 activity of 240 mBq/L caused by uranium ore deposit. The average uranium concentration of 0.011 mg/L in Johanngeorgenstadt is low. To evaluate the speciation of uranium and arsenic in the mine water depending on varying pH values a PHREEQC-modeling [9] was performed (Figures 3 and 4) using the database NAGPSI_1.DAT [10]. Geochemical

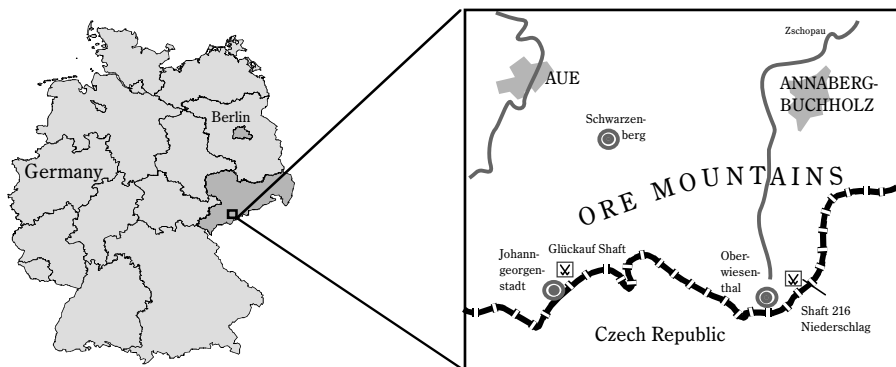


Figure 1: Map showing the location of the underground test fields Shaft 216 Niederschlag and Glückauf Shaft Johanngeorgenstadt in the Ore Mountains, Germany.

Übersichtskarte der untertägigen Versuchsstandorte im Schacht 216 in Niederschlag und Glückauf-Schacht Johanngeorgenstadt im Erzgebirge, Deutschland.

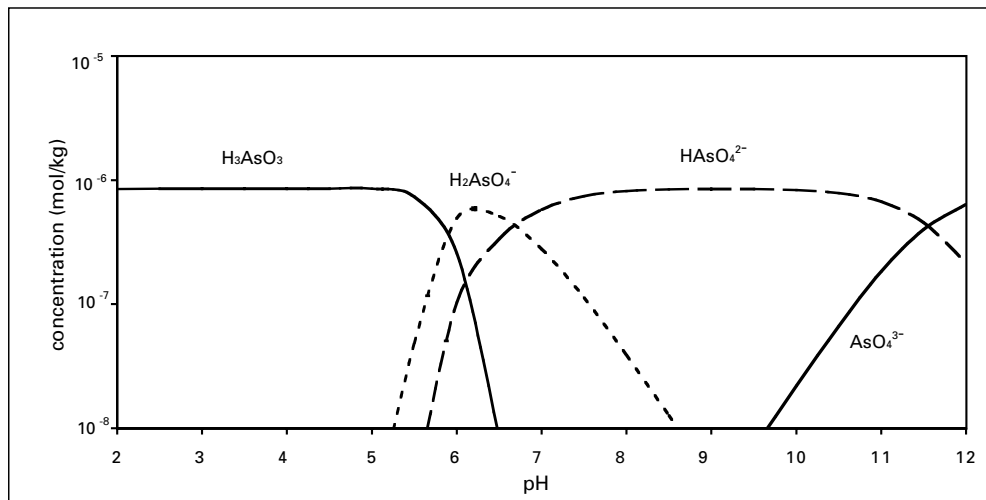


Figure 2: Dissolved arsenic species in the flooding water of the Glückauf Shaft in Johanngeorgenstadt as function of the pH value.

Gelöste Arsenspezies als Funktion des pH-Wertes im Flutungswasser des Glückauf-Schachtes Johanngeorgenstadt.

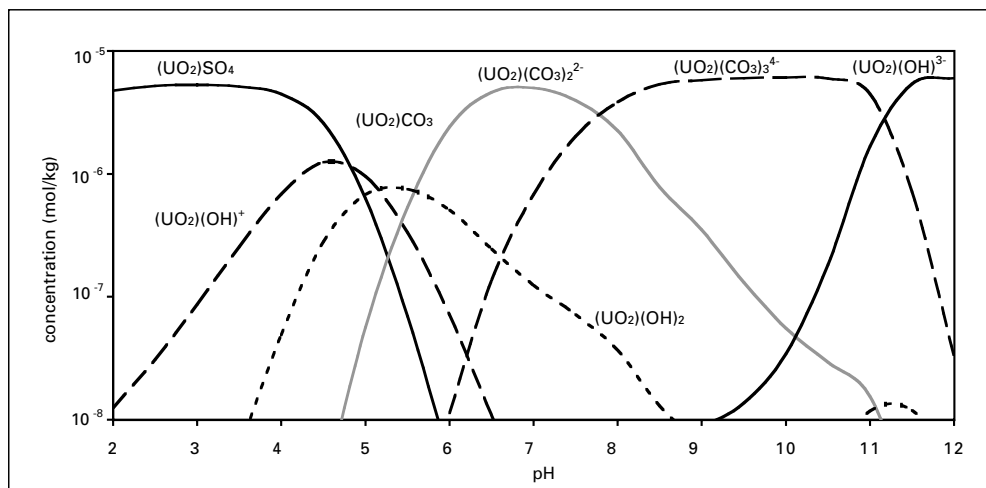


Figure 3: Dissolved uranium species in the flooding water of Shaft 216 in Niederschlag as function of the pH value.

Gelöste Uranspezies als Funktion des pH-Wertes im Flutungswasser des Schachtes 216 in Niederschlag.

modeling included equilibrium and mixing calculations, while sorption due to the small data base before starting the experiments could not be taken into account.

The average uranium content in the mine water of shaft 216 in Niederschlag was higher than in Johanngeorgenstadt reaching values of 1.9 mg/L. It is characterized by an average arsenic content of 6.5 $\mu\text{g/L}$ and an average radium-226 activity of 180 mBq/L. The water contains oxygen ranging from 2.5 to 4.5 mg/L. The iron and manganese concentrations at Johanngeorgenstadt were about 2.46 and 1.27 mg/L, respectively. Iron and manganese hydroxides may precipitate and cause clogging effects affecting both the hydraulic conductivity and the chemical reactivity of the materials.

3.3 Prognosis of the chemical behaviour of the reactive materials

In order to predict chemical reactions being in contact with reactive material PHREEQC-modeling [9] was performed. Figure 5 shows results for the use of Fe^0 . Due to the high reduction potential of Fe^0 reacting with water the redox milieu will reach negative values ($E_{\text{H}} = -410 \text{ mV}$ to -600 mV). These redox values are not found in natural groundwaters.

Due to the oxidation of Fe^0 to Fe^{2+} a reduction of mobile uranium(VI) to highly insoluble uranium(IV) is possible depending on the available anions for complex binding [11, 12]. The mechanism of uranium removal considering these two

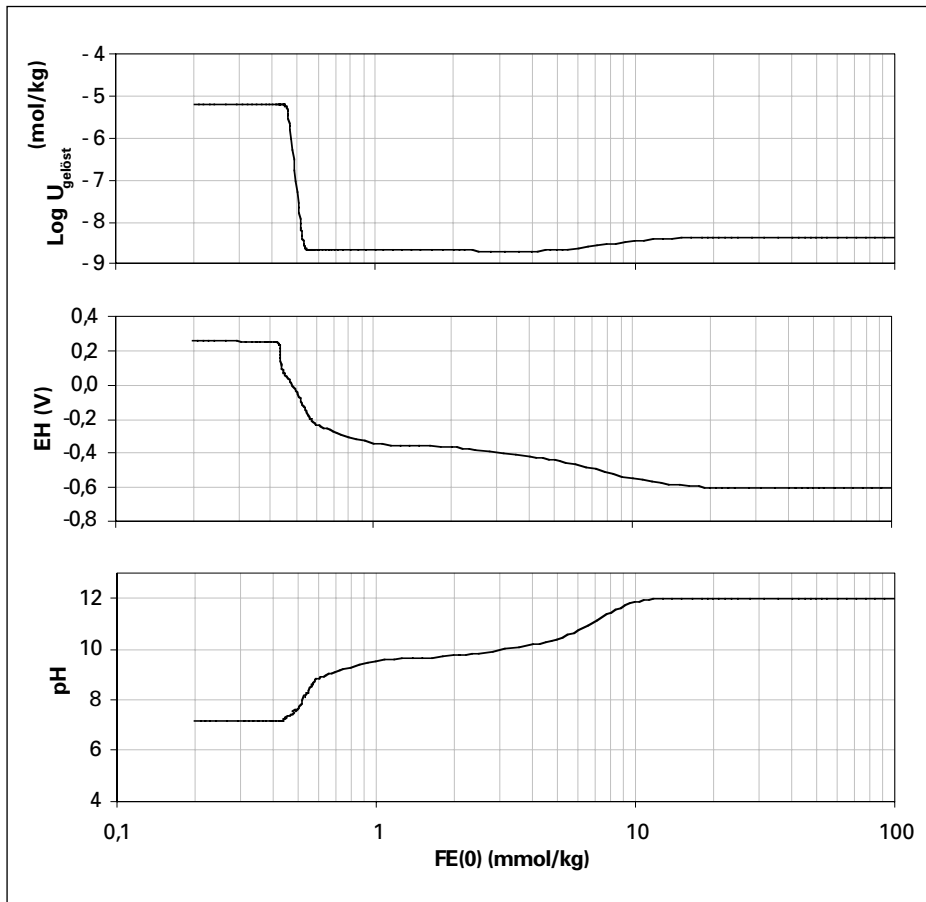


Figure 4: Plot of the theoretical uranium concentration in the flooding water of Shaft 216 in Niederschlag as function of EH value and pH value according to the amount of Fe^0 as reactive material (results of a PHREEQC-modeling).

Darstellung der theoretischen Urankonzentration in Abhängigkeit von der Menge an zugegebenem Fe^0 als reaktives Material im Flutungswasser des Schachtes 216 in Niederschlag als Funktion des Redoxpotentials EH und des pH-Wertes (Ergebnisse einer PHREEQC-Modellierung).

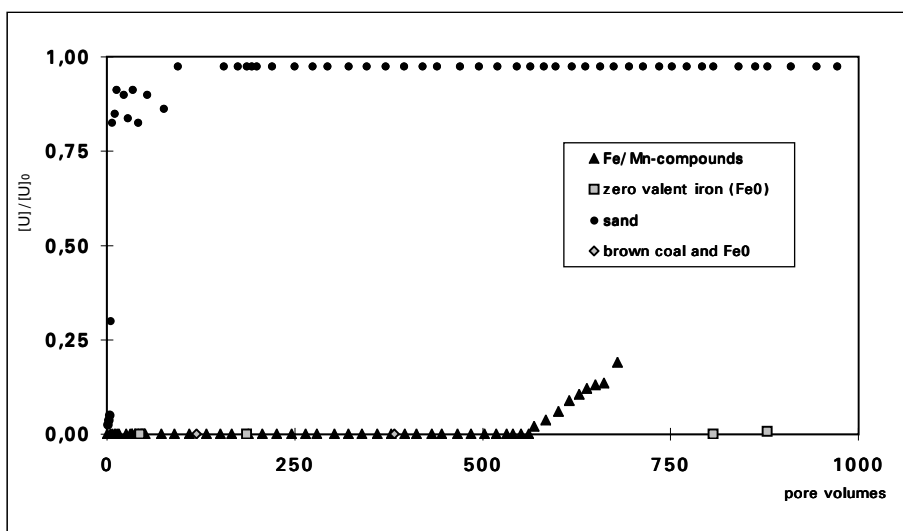


Figure 5: Results of column tests with three different reactive media and sand.

Ergebnisse der Säulenversuche mit drei verschiedenen reaktiven Materialien und Sand.

different reactive processes is discussed in detail in [8, 13]. In one mechanism, Fe^0 causes the oxidation state to decrease, resulting in reduction of dissolved uranium (VI) to immobile uranium(IV) [13]. Uranium(IV) is transferred from aqueous phase to low-solubility minerals, such as uraninite (UO_2). In the other mechanism, ferric oxyhydroxides adsorb the dissolved uranium(VI) [13]. This adsorption had been described to be a precipitation on the iron surface [13].

Geochemical modeling of the chemical behaviour of arsenic in the mine water using Fe^0 as reactive material shows that arsenic removal is not controlled by redox reactions, but adsorption [14, 15]. Therefore experiments using the high adsorption capacity of reactive surfaces of peat and Fe/Mn-sludge were performed.

3.4 Results of the field experiments

Elimination of contaminants was observed about two weeks after the beginning of the field experiments (Figures 6 and 7). The pH values of effluent water from columns containing Fe^0 increased due to the hydrolysis of iron. The increase of the pH-values of effluent water from Fe/Mn-sludge may be related to a complex process of hydrolysis and organic reactions caused by small amounts of organic matter in the Fe/Mn-sludge.

The treated water from the reactor columns showed electric conductivities between 100 and 300 $\mu\text{S}/\text{cm}$. The concentrations of U, As and Pb in the treated water of the columns were low (0.001 – 0.1 mg/L). Radium activity of the treated water was

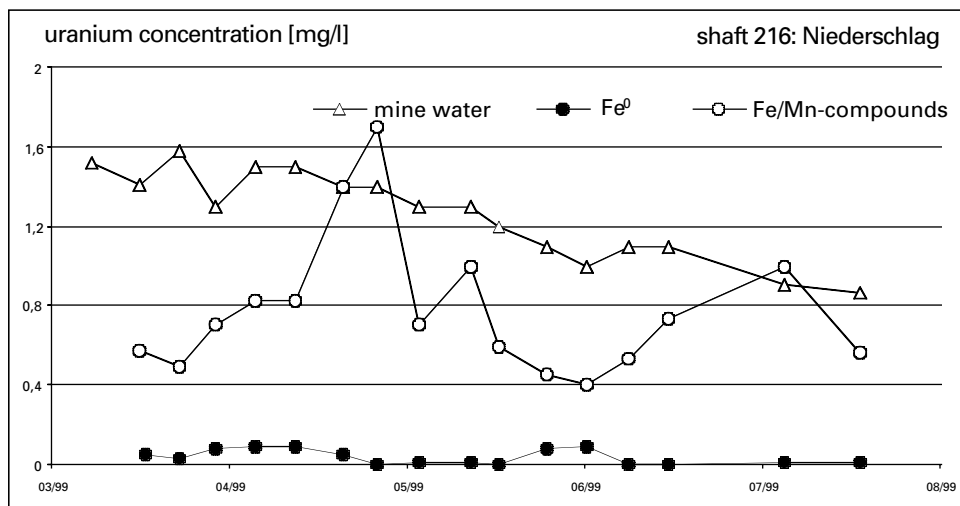


Figure 6: Plot of the uranium concentrations of untreated mine water and water from the Fe^0 and Fe/Mn reactor columns in the Shaft 216 in Niederschlag.

Darstellung der Urankonzentration in unbehandeltem Flutungswasser sowie in den Auslaufwässern der Reaktorsäulen mit Fe^0 und Fe/Mn-Schlämmen.

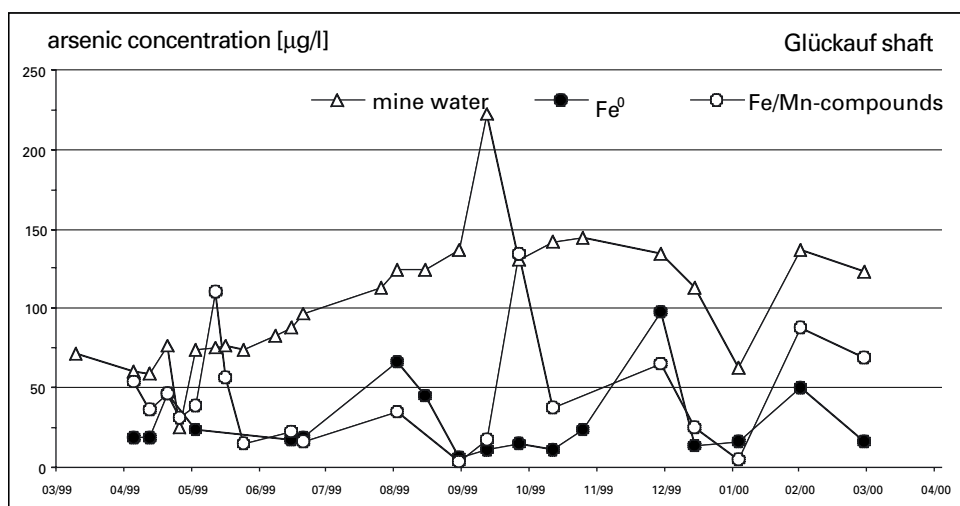


Figure 7: Plot of the arsenic concentrations of untreated mine water and treated water in the Glück-auf Shaft Johanngeorgenstadt.

Darstellung der Arsenkonzentration in unbehandeltem und behandeltem Flutungswasser im Glück-auf-Schacht Johanngeorgenstadt.

Table 1: Immobilisation rates in [%] of contaminants in the percolation water of the investigated flooding water.

Immobilisierungsraten in % für die betrachteten Kontaminaten im behandelten Auslaufwasser der untersuchten Flutungsgewässer.

parameter	Niederschlag		Johanngeorgenstadt	
	Fe/Mn-compounds	Fe ⁰	Fe/Mn-compounds	Fe ⁰
Uranium	38 %	96 %	70 %	80 %
Radium-226	73 %	50 %	52 %	43 %
Lead	57 %	77 %	53 %	65 %
Arsenic	85 %	84 %	55 %	70 %
Sulfate	0 %	52 %	13 %	3 %
Nitrate	1 %	55 %	25 %	56 %

Table 2: Mass balance of uranium, arsenic and radium-226.

Massenbilanzierung für Uran, Arsen und Radium-226.

Test field and configuration	Input of contaminants per year (average values)			Amount of eliminated contaminants		
	U [g]	As [g]	Ra-226 [Bq]	U [g]	As [g]	Ra-226 [Bq]
JGS: 1,5 kg WW	1.24	11.13	27 100	0.87	6.23	13 550
JGS: 4,15 kg Fe ⁰	0.75	6.73	16 400	0.64	4.85	6 900
NS: 1,7 kg WW	102.4	0.51	14 200	32.8	0.42	10 200
NS: 4,35 kg Fe ⁰	47.8	0.24	6 600	45.0	0.20	3 300

NS: Niederschlag WW: Fe/Mn-compounds JGS: Johanngeorgenstadt Fe⁰: zero-valent iron

about 50 mBq/L for Fe⁰ and 100 mBq/L for Fe/Mn-sludge. The sorption capacity of peat for radionuclides and Arsenic was exhausted after half a year. At several times the arsenic and uranium output of the reactor columns containing peat was higher than the input.

The Fe/Mn-sludge adsorbed 60 % of radium and 70 % of arsenic. The uranium elimination capacity of the Fe/Mn-sludge was about 50 %, which is 40 % less than that of the Fe⁰-compounds (Table 1). The high elimination rate of uranium by Fe⁰ of about 96 % was observed for the whole duration of the experiment.

The mass balance of the eliminated contaminants was calculated for uranium, arsenic and radium-226 (Table 2). In the mine water of Shaft 216 in Niederschlag 45.0 g of uranium were removed compared to an uranium input of 47.8 g.

3.5 Chemical and mineralogical characterization of the reaction products

After the experiments had been completed samples of the reactive material were investigated by means of scanning electron microscope to evaluate secondary minerals formed during the field tests. (Figure 8). UO₂ and ThO₂-particles were found in Fe⁰-material and Fe/Mn-compounds in a grain size ranging from 2 µm to 20 µm. Precipitates of manganese carbonate containing uranium oxide were found in the centre of the Fe/Mn-sludge column. The Fe⁰-material was covered by precipitates of calcium carbonate containing uranium oxide. Precipitates formed in the Fe⁰ reactor column showed a finer grain structure than in the reactor columns containing Fe/Mn-sludge.

Geochemical modeling by means of PREEQC was performed to check which uranium mineral phases might be present as

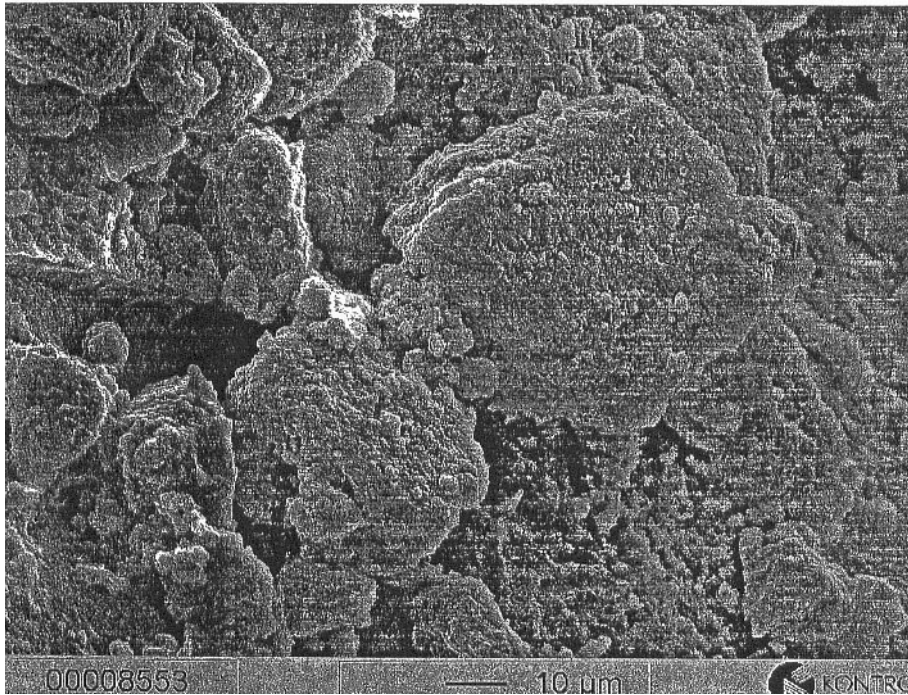


Figure 8: Plot of the scanning electron microscope picture of the surfaces of the Fe⁰ reactor filling material of Shaft 216 Niederschlag.

Fotografie der Oberflächen der Partikel des Fe⁰-Reaktor-säulenfüllmaterials im Schacht 216 in Niederschlag unter dem Rasterelektronenmikroskop.

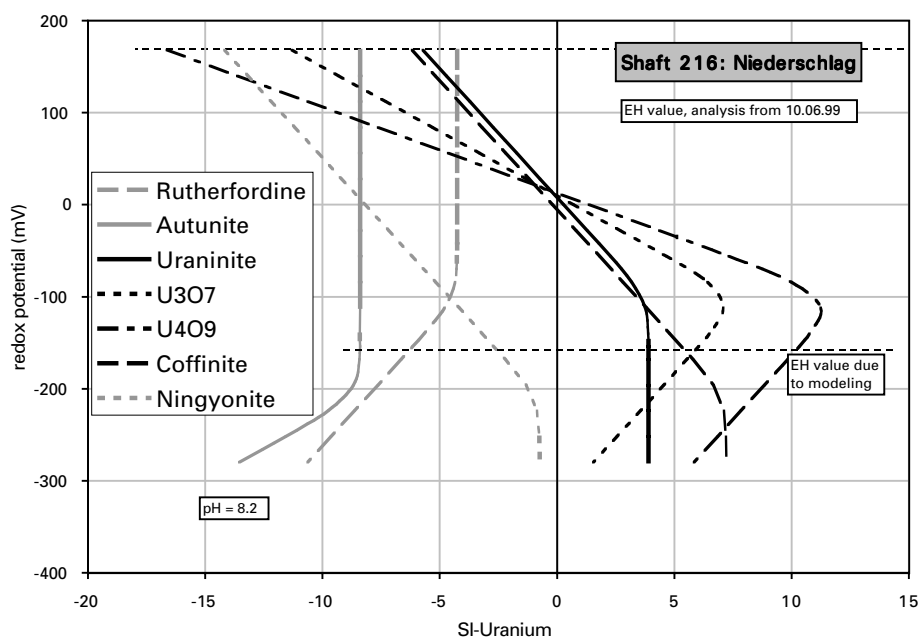


Figure 9: Plot of SI of Uranium mineral phases versus redox potential from the Fe⁰ reactor of Shaft 216 Niederschlag (SI: saturation index, results of PHREEQC modeling).

Grafische Darstellung der Uranmineralphasen in Abhängigkeit vom Redoxpotential in der Fe⁰-Reaktorsäule im Schacht 216 in Niederschlag (SI: Sättigungsindex, Ergebnisse einer PHREEQC-Modellierung).

a function of decreasing redox potential (Figure 9). Uraninite, coffinite and the oxidic species U_3O_7 and U_4O_7 show positive saturation indices (SI) indicating possible precipitation.

Whether these minerals are precipitated or not may depend on the kinetics of the reactions which were not taken into account in this type of geochemical modeling.

4 Conclusions

Results of the field experiments show that Fe^0 is a suitable material for the alternative water treatment of contaminated mine water. The reduction of mobile uranium(VI) to immobile uranium(IV) combined with coprecipitation on iron hydroxides causes up to 96 % decrease of uranium in the mine water of Niederschlag. At the Johanngeorgenstadt site 80 % of the uranium was eliminated by the use of Fe^0 . As well arsenic and radium-226 can be eliminated by the use of Fe^0 . The elimination rates of arsenic are ranging from 55 % in Johanngeorgenstadt to 84 % in Niederschlag. Using peat is not recommended since break through occurred very soon. Fe/Mn-sludge is a suitable material for the elimination of radium-226 and arsenic due to its adsorption capacity and the building of iron and manganese hydroxides on the surfaces. Elimination rates of radium-226 range from 52 % in Johanngeorgenstadt to 73 % in Niederschlag. Elimination of arsenic ranges from 55 % in Johanngeorgenstadt to 85 % in Niederschlag. The use of reactive materials for the treatment of mine water will minimise the water treatment costs compared to the costs of conventional treatment methods.

To use of reactive materials for the remediation of contaminated mine water on a technological scale it is necessary to predict the composition of the contaminant output for any time of groundwater recovery process. Calculating a mass balance of the mine water and the necessary amount of reactive materials will help to avoid a break through of the contaminants for the required time scale. Since it is unknown if the reduced uranium(IV) species on iron surfaces are reoxidized to uranium(VI) species over time [8], the long-term stability of the reaction products is topic of further investigations. The results of the mineralogical investigations indicate the forming of insoluble coprecipitation byproducts, which are supposed to be stable also in case of rechanging the geochemical conditions for example by consumption of the reactive material. In order to investigate this problem, lab experiments are in preparation, currently.

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