

Mitigating Uranium in Groundwater: Prospects and Limitations

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Removal of uranium(VI) by zerovalent iron has been suggested as a feasible pathway to control uranium contaminations in seepage waters. Available information in the literature however presents discrepant evidence on the process responsible for the mitigation effect. On basis of an E_H –pH diagram of uranium and iron, it is outlined that these discrepancies may be explained by the aqueous chemistry of uranium and iron. Additional effects contributing to the complexity of the system are given. Solubilization experiments using scrap iron together with water works sludge, MnO_2 , and pyrite indicate that U(VI) is immobilized by iron corrosion products after about 50 days.

Introduction

This study was motivated by recent reports on the application of zerovalent iron (ZVI) to the removal of uranium from aqueous solutions (1–8). The methodology to remove certain contaminants such as chlorinated hydrocarbons, chromate, or nitrate from groundwaters downstream of a plume by reactive barriers holding ZVI as reactive material is well-known (i.e., refs 9–11). Hence, ZVI has some favorable prospects in mitigating hazards from uranium contaminations by an economically attractive technology.

Such a technology is urgently needed in areas where several decades of uranium mining in densely populated area have created environmental, health, and economic long-term risks. In the German Bundesland Sachsen (Saxonia), the strategically important uranium resources (uranium was discovered here in 1789 by M. Klaproth) were exploited between 1945 and 1991 by the Soviet, later Soviet-German, stock company WISMUT. In total 1200 million tons of ores and rock have been moved, 1000 million tons have been deposited in waste stock piles and tailing ponds, and 200 million tons have been transported to treatment and processing plants. In total 231000 tons of uranium have been produced. The scars left from these activities are still widely visible. The dimensions of the sites and the required likely time scale of necessary surveillance render conventional pump-and-treat techniques almost void. Hence, removal of uranium by a reactive wall system holding scrap iron promises an environmentally and economically beneficent alternative.

However, available reports on uranium removal by ZVI are not univocal.

Some Relevant Aspects of the U–Fe–H₂O–CO₂ System

Removal of uranium by ZVI depends on the chemical thermodynamics of the two redox-sensitive systems iron and uranium. In the present situation, both the aqueous solution behavior and the redox thermodynamics are of primary interest. In addition, reaction kinetics is a decisive factor in designing the spatial dimensions of a reactive wall. These three factors have been investigated in previous studies from which controversial results have been reported. On one hand, Gu et al. (5) claim about 96% of the uranium removal due to reduction by ZVI. Similarly Abdelouas et al. (7) characterize the formation of poorly crystalline $UO_{2-x} \cdot nH_2O$ by transmission electron microscopy from solutions holding 10^{-6} to 4×10^{-5} mol of U(VI) at pH 4–9 together with granular iron. Sorption effects were claimed to be insignificant. Other authors, however, find sorption by Fe corrosion products as the main removal effect, with reduction being a side effect (3, 4), only observable at extremely reducing conditions (6), or being completely absent (8). In all cases, U(VI) has been removed from the solutions.

In Figure 1, an E_H –pH diagram of uranium is given together with some relevant boundary redox potentials of the $Fe^0/Fe(II)$ couple and the $Fe(II)/Fe(III)$ couple for ionic strength 0.1 M $NaClO_4$ medium and 0.03% CO_2 partial pressure. While the uranium redox diagram is discussed in detail elsewhere (13), some comments on the $Fe(II)/Fe(III)$ solution chemistry must be given. Despite the relevance of iron species in aqueous solution to environmental and biological processes (i.e., refs 14 and 15), the hydrolysis of $Fe(III)$ is by no means well understood (16–18). Especially data for $Fe(OH)_2^+$ and $Fe(OH)_3^0$ solution species are scarce. Evidence for amphoteric behavior of $Fe(III)$ is inconclusive (19). Thus, the diagram combines two systems with considerable uncertainties together. In the case of the U(IV)/U(V) and U(V)/U(VI) boundaries, no attempt is made in the E_H –pH diagram to eliminate the existing gaps in our knowledge. Instead two extreme cases, (a) formation of $U(OH)_4^0$ species alone (the stability field of U(V) is limited to area I) and (b) formation of uranium(IV) carbonate species with some high values (the stability field of U(V) is extended, including both areas I and II), are given. The discrepancy between the large stability fields calculated for U(V) under both assumptions and the extreme difficulties to observe U(V) in the laboratory is obvious. In the case of iron, the data from the JESS database have been used (19). Advantages of the JESS database are its public availability and its well-documented efforts to achieve consistency (20)—as far as this is possible to be achieved at present. Including speciation, the position(s) of the $Fe^0/Fe(II)$ boundary indicates that metallic iron (Fe^0) reduces U(VI), but it also indicates that $Fe(III)$ reoxidizes U(IV). While the former effect is often mentioned, the potential reoxidation by $Fe(III)$ is often ignored. Moreover, the reduction of U(VI) by different $Fe(II)$ minerals (pyrite, green rust, ...) is repeatedly reported and is claimed to be thermodynamically favorable (21–24).

Notwithstanding the existing limitations in using thermodynamic data for prediction in aquatic chemistry (16, 25–27), Figure 1 indicates a complex behavior in the U–Fe–H₂O–CO₂ system. Further complexity is introduced by kinetic constraints. The reduction of U(VI) shows a large overpotential due to the fact that two formal metal–oxygen triple bonds must be broken (28). The linear UO_2^{2+} entity is furthermore kinetically extremely inert (29).

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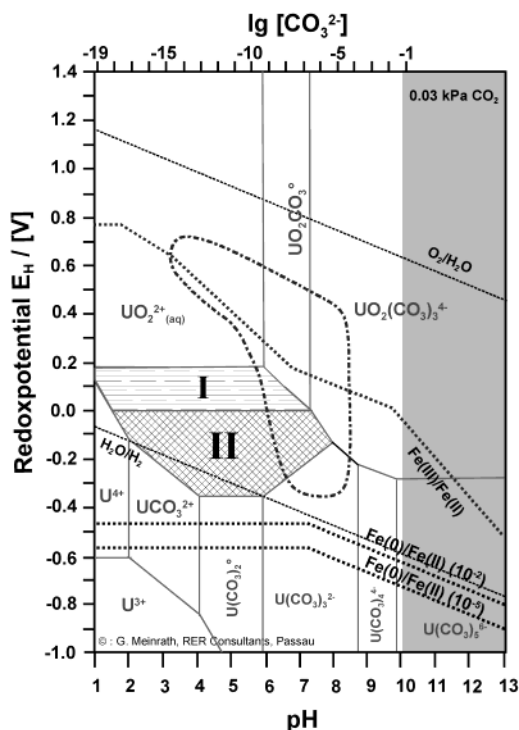


FIGURE 1. Comparison of E_h -pH boundaries of uranium species with relevant boundaries of the $Fe^{0}/Fe(II)$ and $Fe(II)/Fe(III)$ couples. The shaded right-hand section is physically not accessible under given conditions. Area I gives the stability field of U(V) if $U(OH)_4$ is assumed as the stable U(IV) species (minimal stability field), while in the presence of uranium(IV) carbonate species with the highest reported formation constants the combined fields I + II represent the calculated stability field for U(V) (maximum stability field). The boomerang-shaped field represents the E_h -pH range of natural aqueous systems (12).

Both uranium and iron show photosensitivity (30, 31). While $Fe(III)$ does not quench photochemically excited U(VI), $Fe(II)$ is an efficient quencher, being oxidized to $Fe(III)$ (32–34). Halide ions and organic materials likewise quench excited U(VI) under formation of radicals (33, 35).

Corrosion of ZVI produces various compounds, often poorly characterizable (6, 36). The efficient sorption of uranyl(VI) by iron oxides is well-known (37–41).

Hence, the variability in the outcomes of studies on uranium removal by ZVI is not surprising. The U-Fe-H₂O-CO₂ system is sensitive to several parameters that are only partly under the control of the experimenter, i.e., CO₂ partial pressure and structure, composition, and reactivity of the iron corrosion products or the detailed uranium speciation in solution.

In the present study, no attempt has been made to control more parameters than in previous work. The detailed conditions in a reactive barrier based on ZVI will certainly vary over its lifetime. In part it is of minor interest whether uranium is removed by reduction, sorption, or a combined effect; so far the immobilized uranium can be kept away from the groundwater for a long period of time. It is expected that generally U(IV) is less mobile than U(VI). However, there are also effects that redissolve U(IV) species, i.e., higher carbonate concentrations forming soluble uranium(IV) carbonate species. It must be expected that the CO₂ partial pressure below the surface may be higher than the atmospheric partial pressure (12, 42). Our interest focused on the effects of additional soil components, i.e., MnO₂, on the mitigation property of ZVI. To avoid photochemical effects, experimental solutions were kept in darkness. While the ZVI itself was a comparatively pure scrap iron, water works sludge

(WWS) has been added with the ZVI to the reaction vessels. WWS is a variable mixture of different iron oxides with some manganese content produced by an uncontrolled precipitation process in water works. Since natural iron oxides are similar mixtures (16), the use of WWS simulates natural conditions closer than any well-defined iron oxide. In the field, the variability of the conditions will prevent the formation of well-defined and almost pure iron solid phases, contrary to the easily formed synthetic iron oxides obtained under controlled laboratory conditions.

Experimental Section

Materials. The used ZVI is a scrap iron from MAZ (Metallaufbereitung Zwickau, Co.) termed “S69”. Its elemental conditions are determined as 3.52% C, 2.12% Si, 0.93% Mn, 0.66% Cr, and 92.77% Fe. The materials were fractionated by sieving. The fraction 1.6–2.5 mm was used without any further pretreatment.

WWS is typically a mixture of iron and manganese oxides. The detailed composition depends on the composition of the treated water. WWS from the Torgau (Saxonia, Germany) water treatment plant with a low content of 1.09% Mn (43.9% Fe, 6.2% Ca, 5.42% Si) was used.

Manganese nodules from the deep sea were crushed and sieved. An average particle size of 1.5 mm was used having the following elemental composition: 41.8% Mn, 2.40% Fe, 2.41% Si, 0.74% Ni, 0.22% Zn, 1.39% Ca, and 0.36% Cu (43). The target active component is MnO₂, which occurs naturally, for example, as birnessite (44).

Pyrite mineral was crushed and sieved. The fractions 0.2–0.315 mm (d_1) and 0.315–0.63 mm (d_2) were used. The elemental composition is 40% Fe, 31.4% S, 6.7% Si, 0.5% Cl, 0.15% C, and <0.01% Ca. The material served as a pH shifting reagent. It is assumed that the crushed pyrite has no significant adsorptive properties in the investigated pH range.

Fixation and Remobilization Experiments. Unless indicated otherwise, 0.3 g of ZVI and 0.1 g of WWS were allowed to react in sealed sample tubes containing 20.0 mL of a uranium solution (20 mg/L or 0.084 mM) at laboratory temperature (about 20 °C). The tubes had a total volume between 20.4 and 21.1 mL and a graduation to 16 mL. The tubes were filled to a total volume to reduce the headspace. The solid:solution ratios were 5 g/L for WWS and MnO₂, 15 g/L for ZVI, and 25 g/L for FeS₂, respectively. For comparison, a further set of experiments was conducted with ZVI alone. All experiments were conducted with the tap water of the city of Freiberg (Saxonia, Germany) of composition (mg/L) Cl[−], 7.5; NO₃[−], 17.5; SO₄^{2−}, 42; HCO₃[−], 42; Na⁺, 7.1; K⁺, 1.6; Mg²⁺, 6.8; and Ca²⁺, 37.1. The initial pH was about 7.2. After equilibration, about 13 mL of the supernatant solution was filtered for uranium analysis. The filtration occurred through a small pore size paper filter for fine precipitate filtration of the type FILTRAK. The remaining volume with the iron corrosion products and fixed uranium were filled with 10 mL of water, and 10 mL of a 0.2 M Na₂CO₃ solution (final concentration of Na₂CO₃, 0.1 M) was added. The uranium was allowed to desorb for about 14 h. The contact vessels were not agitated but turned upside down at the beginning of each reaction phase and allowed to react in darkness.

Analytical Method. The samples were filtered through FILTRAK filter paper. Analysis for uranium was performed after reduction to U(IV) with the Asernazo III method (ref 12 and references therein). Uranium concentrations were determined by a HACH UV-vis spectrophotometer at a wavelength of 665 nm using 1 cm glass cells. All chemicals and reagents used for experiments and analysis were of analytical grade. The pH value and the redox potential were measured by combination glass electrodes (WTW Co., Germany). The electrodes were calibrated with at least five standards following a multipoint calibration protocol (45)

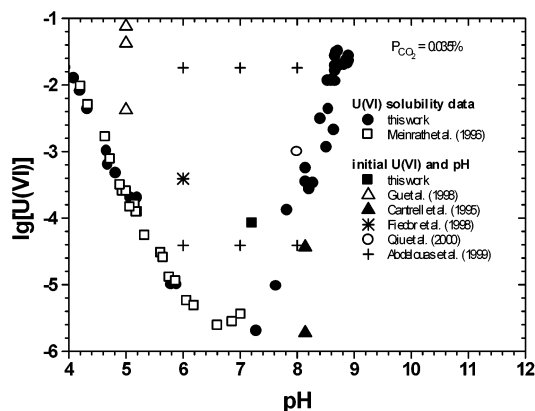


FIGURE 2. Comparison of U(VI) solubilities in 0.1 M perchlorate medium from this study with literature data. In addition, initial solution parameters from this work and given in several studies on U(VI) reduction by ZVI are included.

and in agreement with the new IUPAC recommendation (46). The redox potential measurements were corrected to give equivalency to the standard hydrogen electrode (SHE). Each experiment was performed in triplicate. Error bars given in the figures represent the standard deviation from the triplicate runs.

Results and Discussion

Four different experiments were performed: reaction of U(VI) with (I) ZVI, (II) ZVI + WWS, (III) ZVI + MnO_2 , and (IV) ZVI + FeS_2 , the latter being conducted with two different particle fractions (d_1 and d_2). The experiments were compared on the basis of the total fixation P_{tot} (%) defined by eq 1, where

$$P_{\text{tot}} = 100 \times (1 - (C/C_0)) \quad (1)$$

C_0 is the initial concentration of uranium in solution, while C gives the uranium concentration after the experiment. The percent desorption, P_{rev} , of uranium after the experiment was finished (desorption with 0.1 M Na_2CO_3) is calculated by eq 2, where V_0 gives the initial volume and V_1 the volume after removing about 13 mL for uranium analysis.

$$P_{\text{rev}} = 100 \times \frac{C_0(V_0 - V_1)}{V_0(C_0 - C)} \quad (2)$$

Figure 2 compares the experimental conditions to the solubility curve of $\text{UO}_3 \cdot 2\text{H}_2\text{O}$ obtained by separate experimentation in 0.1 M NaClO_4 solution. Calculations show that, under the experimental conditions of this work, about 90% of the initial amount of uranium can precipitate as schoepite ($\text{UO}_3 \cdot 2\text{H}_2\text{O}$). Figure 3 shows that, after about 140 days, almost 98% of the uranium has been removed from the solution. It is, therefore, obvious that the removal was mainly caused by precipitation.

The experimental U(VI) solubility data obtained within this study were compared to available data from the literature (47). The analysis of the solid phase was done by X-ray diffraction and IR spectroscopy. The results agreed with previous reports (48) and are not repeated here. The agreement between the two solubilities also validates the analytical method for uranium determination. The solid phase below pH 7 is $\text{UO}_3 \cdot 2\text{H}_2\text{O}(\text{s})$; above pH 7 there is an amorphous phase, possibly $\text{Na}_2\text{UO}_3 \cdot x\text{H}_2\text{O}$ (49). Since the solubility of U(VI) is about $4 \times 10^{-6} \text{ mol L}^{-1}$ at pH 7.2, while the initial concentration in the experiments is $8.5 \times 10^{-5} \text{ mol L}^{-1}$, the observed total fixation $P_{\text{tot}} \approx 98\%$ is merely due to precipitation. Also indicated in Figure 2 are the starting concentrations given in different reports on ZVI uranium

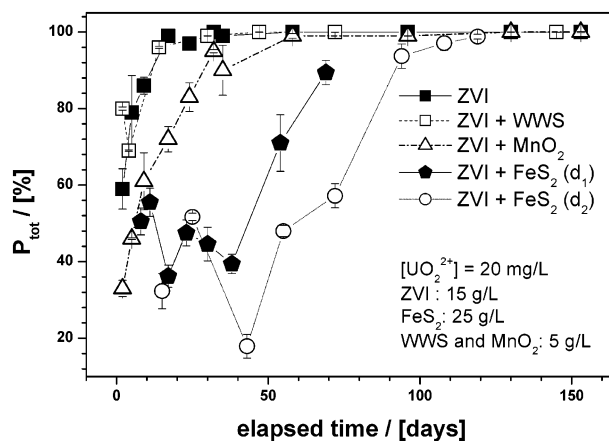


FIGURE 3. Percent total fixation P_{tot} as a function of equilibration time for four different solution compositions. Two sets of experiments with solutions holding FeS_2 were conducted. They differ in the particle size applied (see the text). The experiments were conducted in triplicate. Error bars give standard deviations.

TABLE 1. Variation of the Solution Chemistry (pH, E_H , and Iron Concentration) and the Percent Total Fixation (P_{tot}) and Desorption (P_{rev}) of Uranium as Functions of Equilibration Time for 15 g/L ZVI and 25 g/L FeS_2 ($0.315 < d$ (mm) < 0.63)

time (days)	pH	E_H (mV)	[Fe] (mg/L)	P_{tot} (%)	P_{rev} (%)
15	4.15	85	42.0	32	0
25	4.32	51	46.0	52	0
43	3.95	88	83.0	18	0
55	3.94	77	89.5	48	0
72	4.12	62	88.0	57	0
94	4.41	11	83.0	94	2
108	4.45	8	77.0	97	3
119	4.49	21	72.0	99	4

removal. It is obvious that in several cases the solutions have been considerably oversaturated with the consequence of U(VI) removal by precipitation. Precipitation of $\text{UO}_3 \cdot 2\text{H}_2\text{O}$ is a fast process. Figure 3 shows the precipitation process as a function of the time elapsed after the start of the experiment. The differences in the first three experiments are mostly due to measurement uncertainty and slight differences in pH. On the contrary, FeS_2 seems to be able to retard U(VI) precipitation. This observation is reproducible as shown with two different particle sizes of materials resulting in different uptake kinetics. The variation of the pH value in the experiment with the larger particle fraction ($0.315-0.63$) was measured (Table 1) and shows that the pH was shifted from 7.20 (initial value) to 3.94–4.49.

Table 1 shows that the pH first decreases with time as a result of FeS_2 dissolution until a value of 3.94 after 55 days and then increases progressively as iron corrosion proceeds. From the start of the experiment until day 55, the total uranium uptake decreases and reaches a minimum of 18%. This evolution is attributed to the progressive release of sorbed uranium as the pH decreases. The minimum characterizes the maximum acidic capacity of the added amount of pyrite (FeS_2) under the experimental conditions (unstirred batch experiments). At this point, the concentration of iron is maximal (90 mg/L or 1.60 mM) and decreases continuously with increasing pH. Above pH 4.12 (day 70) the percent uranium uptake increased quite suddenly from 40% to above 90% (cf. Table 1), indicating that uranium removal is the result of coprecipitation with iron corrosion products. Figure 3 shows the same trend for the experiment with $0.2-0.315 \text{ mm FeS}_2$ (50, 51).

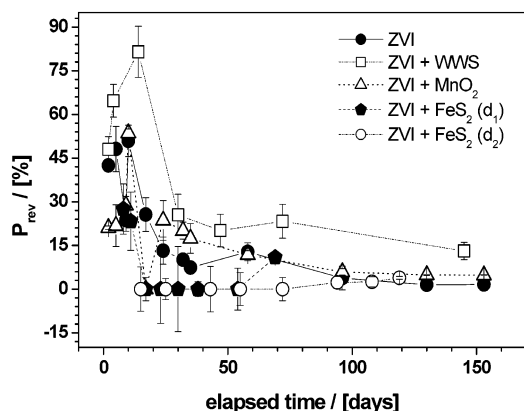


FIGURE 4. Percent desorption P_{rev} of uranium from ZVI and corrosion products as a function of equilibration time. The solutions holding FeS_2 showed considerable pH shifts, and the experiments were finished after 70 days. All experiments were done in triplicate. Error bars give standard deviations.

The response of the four systems to dissolution in a 0.1 M Na_2CO_3 solution is given in Figure 4. P_{rev} is comparatively high in the first 25 days. Afterward, P_{rev} decreases steadily and becomes almost irreversible for the ZVI and the ZVI + MnO_2 system after 125 days. Both U(VI) and U(IV) are soluble in concentrated Na_2CO_3 . Hence, this observation can only be explained by formation of amorphous aged iron corrosion products enclosing the uranium because Fe(III) is not soluble in carbonate solution.

Both WWS and MnO_2 were chosen to better simulate natural conditions (being natural themselves). In fact, efforts to investigate the adsorptive properties of these minerals have usually been conducted with synthetic birnessite (MnO_2) after the McKenzie method (52) or synthetic iron oxides, for example, α -goethite, after the Atkinson method (53). In this manner experiments are conducted with almost pure and relative well-defined products, which are to some extent far from those encountered in nature. It has been reported that corrosion products have a very variable composition, and are not reproducible (54). Thus, working with water works sludge is a better approximation to such a complex mixture.

Conclusion

Whether or not reduction plays a role in removing uranium by ZVI is still unclear (8). Previous work available in the literature has shown that reduction is not a necessary process. The E_H -pH diagram (cf. Figure 1) also suggests that special conditions must prevail to achieve reduction. The uncertainties in the uranium aqueous solution chemistry still are too large for calculating the precise behavior of a system as complex as the U-Fe- H_2O - CO_2 system. In a field reactive barrier, additional factors such as microbiology (55, 56), varying plume composition, and pH will affect the performance of a ZVI. These effects are difficult to simulate in the laboratory.

The present study has given two interesting aspects. First, ZVI alone is the most efficient material in preventing solubilization of precipitated uranium(VI). The additional presence of aged corrosion products (simulated by addition of water works sludge) even seems to favor the remobilization of fixed uranium. Apparently uranium must be present at the time the iron corrosion products form. Retardation is achieved by aging of the uranium-contaminated iron corrosion products. Second, MnO_2 and FeS_2 do not favor the U(VI) retardation.

The performance of a ZVI reactive barrier certainly can only be assessed by a field study. Before such a study can be undertaken, further laboratory experiments at initial U(VI)

concentrations below the solubility limit of U(VI) seem necessary. In the present study, U(VI) was immobilized onto the ZVI surface by precipitation. Thus, the ZVI material was given enough time to coat uranium precipitates. In a field study, however, both U(VI) concentrations and residence times will be less compared to those of the present laboratory experiments.

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