Mechanism of Uranium Fixation by Zero Valent Iron: The Importance of Co-precipitation

C. Noubactep (1,3), G. Meinrath (1,2), P. Volke (1), H.-J. Peter (1), P. Dietrich (1), B. Merkel (1)

[1] Departement for Geology, TU BAF, Gustav Zeuner Straße 12, 09596 Freiberg
[2] RER Consultants, Schießstattweg 3a, D-94032 Passau, Germany
[3] Department for Geology, FSU Jena; Burgweg 11; D-07749 Germany

Abstract. The co-precipitation of U (VI) with iron corrosion products from aqueous solutions by zero valent iron was investigated. The evidence of co-precipitation was demonstrated by conducting experiments with well characterized scrap iron, pyrite and a mixture of both materials with experimental durations of up to four months. Results indicate that under anoxic conditions only less than one tenth of the immobilized U(VI) was associated with the surface of scrap iron, whereas the remaining amount is entrapped in aging corrosion products.

Introduction

Uranium mining activities are sources of contamination for surface and ground waters of worldwide concern (e.g. Meinrath et al. 2002, Morrison et al. 2001). Efficient, applicable and affordable techniques are necessary to mitigate the health risk by eliminating or reducing removal of uranium from the mine waters and contaminated ground waters.

Zero valent iron (ZVI) has been discussed in the literature as a uranium-removing reagent in permeable reactive walls. To be effective in the long term, any remediation technique for uranium must target both mobile aqueous U(VI)-species and U(VI)-precipitates that may be long term sources. Therefore, the remediation with ZVI that possibly reduces mobile U(VI) aqueous species to less soluble U(IV) precipitates is very promising. Furthermore ZVI can maintain reducing conditions in the subsurface, under which beside Fe^0 other electron donors (e.g. organics) may also contribute to the U(VI) reduction.

The results of previous investigations on the U removal mechanism by ZVI are not univocal. Reductive precipitation and adsorption onto iron corrosion products have been shown to govern the U uptake (Cantrell et al. 1995, Farrell et al. 1999, Fiedor et al. 1998, Qiu et al. 2000). It is believed that under anoxic conditions the U removal will mostly occur through a slow reductive precipitation, whereas the removal will occur through rapid adsorption onto iron corrosion products under oxic conditions. Investigations that came to the conclusion that reductive precipitation is the principal removal mechanism have been conducted under conditions that are very far from the nature (Gu et al. 1998, Abdelouas et al. 1999); i.e. the reaction vessels were shaken for several days or weeks, the initial U solution were over-saturated with respect to the solubility of schoepite, the solid-to-solution ratios of ZVI were very large, up to 200 g/L (Noubactep et al. 2001a and 2002).

Some evidence for co-precipitation in U removal from aqueous solution by ZVI has been shown recently by means of controlling the availability and the reactivity of corrosion products (Noubactep et al. 2001a). Controlling the reactivity of ZVI was achieved by using a pyrite mineral. This mineral is able to lower the pH and to reduce uranium sorption onto corrosion products. Supposedly, pyrite did not exhibit any fixation capacity itself. However, pyrite and other sulfide minerals have been discussed in the literature as potential reductants of U in low-temperature geo-chemical systems (< 50°C) (Liger et al. 1999 and references therein). Wersin et al. (1994) have indicated that the reductant for the uranium reduction "is Fe(II) rather than S(-II)". No specific U(IV) minerals could be identified; the conclusions are based on X-ray photoelectron spectroscopy (XPS) observations. This technique however detects only dissolved species (U(IV) or/and U(VI)).

The present study aims on a better characterization of the primary process responsible for the uranium removal from aqueous solution by ZVI. Particular attention was directed at determining the extent to which uranium is associated to the added materials (ZVI and FeS_2) and in-situ generated corrosion products under varying solution chemistry (essentially pH value, iron concentration and speciation).

Theoretical Background

Uranium uptake by ZVI is supposedly based on the electrochemical corrosion of iron resulting in reductive precipitation of U(VI) according to Eq.1 in table 1. This reaction is not the most favorable under natural geochemical conditions (Noubactep et al. 2001b). Competing reactions by local sediment constituents such as MnO_2 may oxidize iron to various hydrous Fe(II) phases, and further to various secondary minerals; e.g. $Fe(OH)_3$, Fe_3O_4, Fe_2O_3, FeOOH (e.g. Ritter et al. 2002).

If, e.g., dissolved Fe(III) is present, UO_2 (resulted from Eq.1) can be re-oxidized according to Eq.2; yielding to increased dissolved Fe(II) and U(VI) concentrations. In the presence of pyrite, there will be a competition for Fe(III) (cf. Eq. 3). Hence, Fe(III) is not available to oxidize UO_2, and U(VI) concentration will remain low. On the other hand, pyrite can reduce U(VI) yielding to UO_2 precipitation according to Eq. 4. Furthermore if any source of Fe(II) exists, the acidification possibility under oxic conditions is increased according to Eq. 5 (Bain et al. 2001).

Table 1. Some relevant reactions for the uranium behavior under experimental conditions. The log K values are from Bain et al. (2001).

Reaction equation			log K	Eq.
$UO_2^{2+} + Fe°$	⇔	$UO_{2\,(s)} + Fe^{2+}$	-	(1)
$UO_{2\,(s)} + 2\,Fe^{3+}$	⇔	$UO_2^{2+} + 2\,Fe^{2+}$	11.96	(2)
$FeS_2 + 14\,Fe^{3+} + 8\,H_2O$	⇔	$15\,Fe^{2+} + SO_4^{2-} + 16\,H^+$	16.78	(3)
$FeS_2 + 7\,UO_2^{2+} + 8\,H_2O$	⇔	$7\,UO_2 + 2\,SO_4^{2-} + 16\,H^+$	-20.91	(4)
$2\,Fe^{2+} + ½\,O_2 + 5\,H_2O$	⇔	$2\,Fe(OH)_3 + 4\,H^+$	7.20	(5)

In the presence of ZVI (covered by corrosion products) and pyrite, all the above mentioned reactions (Eq. 1 to 5) are possible. The U(VI) uptake should be governed principally by reductive precipitation. If the reaction vessel is closed, the acidification reaction due to Eq. (5) or the pyrite oxidation through air oxygen will be limited. Then, the removal of U(VI) from the aqueous solution can be due to reductive precipitation by ZVI (Eq. 1) and/or FeS_2 (Eq. 4); sorption on the surface of ZVI, FeS_2 and onto iron corrosion products (iron oxides).

Reductive precipitation trough ZVI will be more favorable when the surface of the material is not covered by corrosion products (especially around pH 4) and the sorption onto corrosion products (iron oxides) will occur favorably at pH > 5 (e.g. Farell et al. 1999). Thus, combining ZVI and FeS_2 into closed vessels is a suitable way to investigate the mechanism of U(VI) uptake by both materials; in particular to understand the mechanism of U(VI) uptake by ZVI. It is expected that various experimental durations will yield various final pH values permitting the characterization of the influence of corrosions products on the removal process.

Experimental Section

Batch experiments without shaking were conducted. The batches consisted in constant amounts of ZVI and a pyrite mineral (FeS_2), respectively. Equilibration times varied from two weeks to four months. A further series of experiment with a mixture of both materials were conducted. Thus, the extend of U fixation by ZVI, FeS_2 and in situ generated iron corrosion products was characterized.

Initial uranium concentration was 20 mg/L (0.084 mM) with a solid:solution ratio of 15 g/L for scrap iron and 0 to 25 g/L for the additives, respectively. The ZVI is a scrap iron from MAZ (Metallaufbereitung Zwickau, Co.) termed internally “Sorte 69”. Its elemental composition is given as C: 3.52%; Si: 2.12%; Mn: 0.93%; Cr: 0.66%. The material was fractionated by sieving; the fraction 1.6 - 2.5 mm has been used. The sieved ZVI was used without any further pretreatment. The pyrite mineral was crushed and sieved. The fraction 0.315 to 0.63 mm is used.

Elemental composition is: Fe: 40%; S: 31.4%; Si: 6.7%; Cl: 0.5%; C: 0.15% and Ca <0.01%.

Unless indicated otherwise, 0.3 g of ZVI and 0.5 g of FeS_2 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 (16 ml graded) were filled to the total volume to reduce the head space in the reaction vessels. All experiments were conducted with the tap water of the city of Freiberg (Saxonia, Germany) of composition (in mg/L) Cl^-: 7.5; NO_3^-: 17.5; SO_4^{2-}: 42; HCO_3^-: 42; Na^+: 7.1; K^+: 1.6; Mg^{2+}: 6.8 and Ca^{2+}: 37.1 (resulting HCO_3^- to U molar ratio: ~8). Initial pH was ~7.2. After equilibration, the supernatant solutions were separated for uranium and iron analysis, pH and E_H measurements.

The contact vessels were turned over-head at the beginning of the experiment and allowed to equilibrate in darkness to avoid photochemical side reactions. The uranium solution were prepared from $UO_2(NO_3)_2 \cdot 6\ H_2O$ in tap water. The samples were filtered through filter paper. Analysis for uranium was performed after reduction to U(IV) with the Asernazo III method (Meinrath et al. 1999 and references therein). Uranium concentrations were determined by a HACH UV-Vis spectrophotometer at a wavelength of 665 nm using cuvettes with 1 cm light path. All chemicals were analytical grade. The pH value and the redox potential were measured by combination glass electrodes (WTW Co., Germany). Electrodes were calibrated with nine standards following a multi-point calibration protocol (Meinrath and Spitzer 2000) in agreement with the new IUPAC recommendation (Buck et al. 2001). Redox potentials are reported relative to the Standard Hydrogen Electrode (SHE). Each experiment was performed in triplicate and averaged results are presented.

Results and Discussion

After the determination of the residual uranium concentration (C) the corresponding total fixation was calculated according to the following equation:

$$P_{tot} = [1 - (C/C_0)] \times 100\%$$

where C_0 is the initial concentration of uranium in solution. To characterize the U(VI) uptake from aqueous solution while taking individual properties of the iron materials into account, three different experiments have been performed over a duration up to 4 months with 15 g/L ZVI and 25 g/L FeS_2: I) ZVI alone, II) FeS_2 alone and III) ZVI + FeS_2 (system I, II and III).

Figure 1 summarizes the results of uranium fixation and table 2 gives the variation of the pH value with the experimental duration in the three systems. Fig. 1 shows the best fixation rate being achieved when ZVI is present alone (> 80%). The efficiency is smallest when FeS_2 is present alone (< 20%). These observations suggest either that the fixation capacity of pyrite for U(VI) is very limited (sorption) or the kinetic of the reductive precipitation by FeS_2 is very slow. The second hypothesis is less probable since the initial fixation rate of 21% (after 14 days, pH 3.5) further decreases to 16% at the end of the experiment (120 days, pH 3.4). Thus the uranium fixation by pyrite for $3.4 < pH < 3.6$ (table 2) occurs through adsorption. As concerning the system with ZVI alone, it has been shown that the co-precipitation of sorbed U(VI) with corrosions products is the main mechanism of U(VI) removal in the neutral pH-range (Noubactep et al. 2001a).

Table 2. Variations of the pH value with the time in the three systems (initial value: pH ~7.2)

System I: ZVI		System II: FeS_2		SystIII: (ZVI + FeS_2)	
t (days)	pH	t (days)	pH	t (days)	pH
13	7.6_2	15	3.5_3	15	4.1_5
23	7.5_5	25	3.4_9	25	4.3_2
41	7.6_3	43	3.4_0	43	3.9_5
53	7.5_8	55	3.3_5	55	3.9_4
70	7.5_8	72	3.4_2	72	4.1_2
92	7.5_9	94	3.5_6	94	4.4_1
106	7.6_2	108	3.5_1	108	4.4_5
117	7.5_0	119	3.3_7	119	4.4_9

Investigation of the behaviour of system III (ZVI + FeS_2) shows a fixation rate increasing considerably in a very close pH range: from 18% at pH ~3.9 (day 43) to 94% at pH ~4.4 (day 94, table 2 and Fig. 1). It should be pointed out that if reductive precipitation were the dominant removal mechanism, the reduction reaction would be more efficient and rapid around pH 4, where the iron corrosion mostly occurs with or without H_2-production depending on the availability of oxygen and the corrosion products mainly remain in the bulk solution, keeping the metal surface free for further reaction. Figure 1 shows the fixation rate for this system first decreasing to a minimum (18%) and subsequent progressive increase to more than 90% after three months. An interpretation of this observation will be given later. The evolution of the pH of this system is depicted on the experimental points. The fact that all final pH values remain below 5 (pH_{max} = ~4.5) suggests a slow reductive precipitation to be responsible for uranium removal in system III. To understand the evolution of this system, it is important to consider also the behaviour of the iron concentration. In system I the final pH was almost constant to an average value of ~7.6, the same observation was made for the system III (final pH: ~3.5).

Beside the pH values, the iron and uranium concentrations, the E_H-values and the iron speciation were measured in system III, where variations were expected owing to the evolved possible reactions (Eq.1 to 5). Table 3 summarizes the results. Because of the limited volume of samples the solution parameters (pH and E_H) were measured once for each triplicate and after 24 hours.

Table 3 shows a decreasing E_H value with increasing experimental duration. This observation is consistent with the fact both iron corrosion and pyrite oxidation consumes oxygen and care for reducing conditions. This is also confirmed with the predominance of Fe(II) (> 50%) for experimental duration < 100 days, although air oxygen would have oxidized a considerable part since the experiments were conducted under laboratory conditions. Figure 2 depicts the variation of iron concentrations in the three systems.

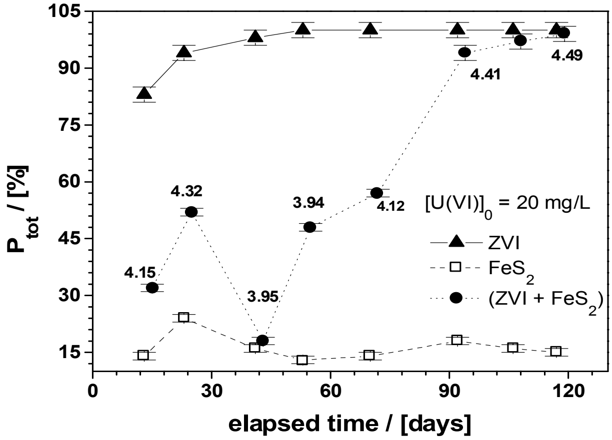

Fig. 1. Uranium fixation by zero valent iron (ZVI: 15 g/L), a pyrite mineral (FeS_2: 25 g/L) and the mixture of both materials (ZVI + FeS_2) as a function of the time. The reported numbers on the plot (ZVI + FeS_2) are the corresponding final pH values. The lines are given to facilitate visualization.

Table 3. Variations of the uranium fixation rate and solution parameters with 15 g/L ZVI and 25 g/L FeS_2 for different experimental durations. $P_{Fe(II)}$ is the percentage of Fe(II) in the bulk solution and $P_{uranium}$ represent the total fixed amount of uranium.

Time (days)	pH	$E_{H(SHE)}$ (mV)	[Fe(II)] (mg/L)	[Fe]tot (mg/L)	$P_{Fe(II)}$ (%)	$P_{uranium}$ (%)
15	4.15	85	35.5	58.5	60.7	32
25	4.32	51	38.5	65.0	59.2	52
43	3.95	88	50.5	96.0	52.6	18
55	3.94	77	58.5	104.5	56.0	48
72	4.12	62	53.5	100.5	53.2	57
94	4.41	11	50.0	93.5	53.5	94
108	4.45	8	40.0	92.0	43.5	97
119	4.49	21	39.5	90.0	43.9	99

In system I (pH ~7.5), the iron concentrations remain below 1 mg/L. In system II & III the iron concentrations were essentially higher (up to 100 mg/L or 1.9 mM).

For experimental duration >60 days a concentration decrease was observed in system III. This iron concentration decrease coincides with the decrease of the uranium concentration between pH ~3.9 (18%) and pH ~4.4 (94 %). Co-precipitation is confirmed. Thus the uranium uptake accompanies the precipitation of iron oxides, the sorbed U(VI) is entrapped in the mass of aging corrosion products and is not available for desorption with commonly used carbonated reagents: CO_3^{2-}; HCO_3^- (Gu et al. 1998, Liger et al. 1999). The exact precipitation process is not known, probably several parallel reactions occur, yielding to $Fe(OH)_3$, FeOOH, Fe_3O_4 (Ritter et al. 2002).

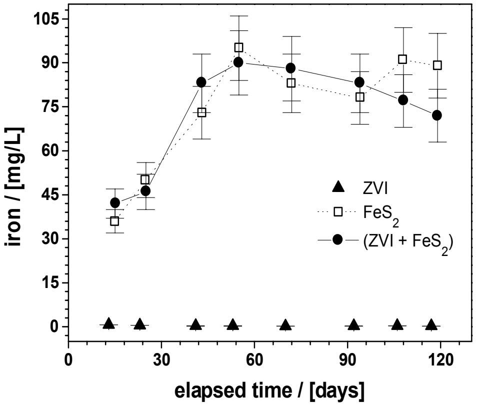

Fig. 2. Variation of the iron concentration in the experimental systems with the time. The represented lines are not fitting functions, they just joint the point to facilitate visualization. The big errors in system II & III resulted from the strong dilution (1/100).

Hence the commonly reported reduction of U(VI) by pyrite and other Fe(II) bearing materials (Charlet et al. 1998, Liger et al. 1999, Wersin et al. 1994) is probably the results of a co-precipitation of U(VI) sorbed onto newly formed Fe-oxides. Noubactep et al. (2001b) have shown that the reversibility of adsorption as measured by desorption with carbonate solutions depends on the age of corrosion products. Freshly formed corrosion products sorb U(VI) by incorporating it in their structure while aging. On the contrary U(VI) sorbed onto surfaces will be readily released in carbonated solutions. The reported U(VI) reduction of by pyrite and other Fe(II) bearing materials will occur by the same mechanism when Fe(II) species are oxidized. Figure 3 compares the total fixation rate for uranium as a function of the final pH value for the three systems. It can be seen that:

- in system I (ZVI) the pH increased from 7.2 to ca. 7.6 and $P_{tot} > 94$ %;
- in system II (FeS_2) the pH decreased and remained < 4 and $P_{tot} < 33\%$;
- in system III (ZVI + FeS_2) the pH evolution (3.95 < pH < 4.49) wasn't monotone and P_{tot} varied considerably; from 18 to 99%.

It is important to note that fixation rate evolution as function the pH value in system III is practically a straight line parallel to the y-axis, indicating that a chemical process at nearly constant pH accompanies the uranium fixation. As discussed above the process is iron oxide precipitation. To gain insight in this phenomenon and better understand the evolution of the fixation curve for system I (Fig. 1) other experiments were conducted with 15 g/L ZVI and varying amount of FeS_2 for 2 and 4 weeks.

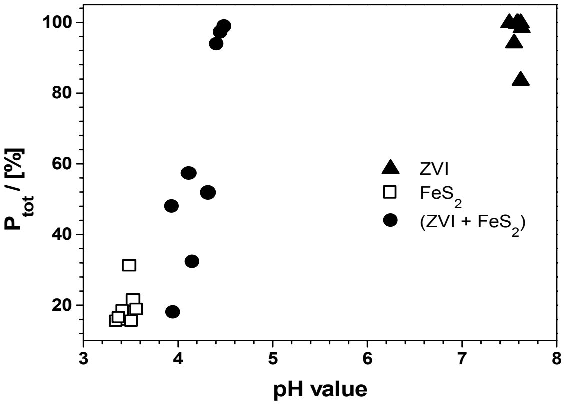

Fig. 3. Comparison of the total fixation rate as function of the final pH value for the three experimental systems.

The results show a decrease of the fixation rate (Noubactep 2002) with the amount of pyrite (decreasing pH). For low pyrite doses (< 10 g/L), the fixation rate increases for a longer reaction duration (4 weeks). This is attributed to the predominance of iron corrosion on the pyrite dissolution. The final pH values were > 4.6. For larger pyrite doses (> 10 g/L) on the contrary, the iron corrosion was not able to consume the acidity produced by the pyrite dissolution and the final pH value was < 4.20. Adsorbed uranium (after two weeks) was partly released into the solution. Thus an explanation of the behaviour of the curve for system III in figure 1 can be given. It is obvious that U(VI) first adsorbs onto ZVI, FeS_2 and iron corrosion products. During the first stage of the experiment, pyrite dissolution predominates over iron corrosion and determines the pH of the system. At this stage pH decreases, the iron concentration increases and the fixation rate decreases. Between day 25 and day 43 the minimum is attained due to a lack of oxygen for further pyrite oxidation. The evolution of the system is determined by anaerobic iron corrosion with production of H_2 (gas bubbles were observed in the reaction tubes), the pH increased progressively and eventually reached a value of ~4.5 (120 days). Thus the primary mechanism of uranium fixation by zero valent iron even under anoxic conditions is the co-precipitation with corrosion products.

As discussed above the fixation of uranium by ZVI is strongly dependent on the pH value. For example, the total amount of uranium fixed in the experiment with (ZVI + FeS_2) and FeS_2 alone are identical after 43 days. This observation suggests that the uranium fixation by ZVI itself in this pH range (3.40 - 3.95) is negligible. To better understand this observation, another experience was conducted with the same amount of FeS_2 (25 g/L) and 0, 3, 8 and 15 g/L ZVI for 1 month. The corresponding fixation rates were: 18, 20, 20 and 28 % respectively, and the pH value varies from 3.6 to 4.2. The maximal efficiency difference was 8% when the ZVI dose was quintupled (3 to 15 g/L). These Results confirmed the hypothesis that uranium reduction didn't play any important role in the mechanism of the U(VI) fixation by ZVI. On the other hand the efficiency difference between 0 and 15 g/L ZVI was 10 %, indicating that maximal 10 % of the fixed uranium is associated with the ZVI surface (not necessarily reduced).

Conclusions

U removal from the aqueous solution by ZVI in the pH range 3.8 to 7.6 is mostly due to the co-precipitation of adsorbed U(VI) with aging iron corrosion products. This mechanism is predominant both under oxic (system I: ZVI alone) and anoxic conditions (system III: ZVI and FeS_2).

Pyrite and other iron (II) bearing minerals also fix U(VI) by co-precipitation with newly formed iron (II, III) oxides, even under anoxic conditions. Thus Fe(III) and Fe(II, III) oxides are formed. Co-precipitates with U(VI) enclosing uranium into their matrix, making them unavailable for any resolubilization so far these iron oxides remain stable. In-situ iron oxide barriers will evidently have a limited remediation capacity. In contrast, the use of ZVI has the advantage of continuous production of fresh and very active corrosion products that may incorporate U(VI) into their structure while aging. However both the limited volume of pore spaces in the reactive barrier (for further corrosion products, whose volumes are at least 2.3 times larger than that of Fe in the ZVI-material) and the potential inhibition of the electrochemical dissolution of ZVI through corrosion products have been recognized but not yet solved (Noubactep 2002).

References

Abdelouas A.; Lutze W.; Nutall H.E., and Gong W. (1999): Réduction de l'U(VI) par le fer métallique: application à la dépollution des eaux. C. R. Acad. Sci. Paris, Sciences de la terre et des planètes / Earth & Planetary Sciences. 328, 315-319.

Bain J.G., Mayer K.U., Blowes D.W., Frind E. O., Molson J.W.H., Kahnt R. and Jenk U. (2001): Modelling the closure-related geochemical evolution of groundwater at a former uranium mine. J. Cont. Hydrol., 52, 109-135.

Buck R.P, Rondinini S., Covington A.K., Baucke F.G.K., Brett C.M.A, Camoes M.F., Milton M.J.T., Mussini T., Naumann R., Pratt K.W., Spitzer P., and Wilson G.S. (Draft, 6 July 2001): The measurement of pH - definition, standards and procedures. Report of the working party on pH (34 pages).

Cantrell K.J., Kaplan D.I., and Wietsma T.W. (1995): Zero-valent iron for the in situ remediation of selected metals in groundwater. Jour. of Hazard. Mat. 42, 201-212.

Charlet L., Liger E., and Gerasimo P. (1998): Decontamination of TCE- and U-rich waters by granular iron: role of sorbed Fe (II). Journal Environ. Eng.,124 (1) , 25-30.

Farrell J., Bostick W.D, Jarabeck R.J., and Fiedor J.N. (1999): Uranium removal from ground water using zero valent iron media. Ground water 34, 618-624.

Fiedor J.N., Bostick W. D. Jarabek R.J and Farrel J. (1998): Understanding the mechanism, of uranium removal from groundwater by zero-valent iron using X-ray photoelectron spectroscopy. Environ. Sci. Technol., 32, 1466-1473.

Gu B., Liang Liyuan, Dickey M.J., Yin X. and Dai S. (1998): Reductive precipitation of uranium (VI) by zero-valent iron. Environ. Sci. Technol., 32, 3366-3373.

Liger E., Charlet L. & Van Cappellen (1999): Surface catalysis of uranium(VI) reduction by iron (II). Geochim. Cosmochim. Acta 63, 2939-2955.

Meinrath A., Schneider P. and Meinrath G. (2002): Uranium ores and depleted uranium in the environment - With a reference to the biosphere from the Erzgebirge/Sax´chsen, Germany. J. Environ. Radioactivity (in press)

Meinrath G. and Spitzer P. (2000): Uncertainties in determination of pH. Mikrochim. Acta 135: 155 - 168

Meinrath G., Volke P., Helling C., Dudel, E.G. and Merkel P. (1999): Determination and interpretation of environmental water samples contaminated by uranium mining activities. Fresenius J Anal Chem. 364: 191 - 202

Morrison J.S, Metzler, R. D. and Carpenter, E. C. (2001): Uranium precipitation in a permeable reactive barrier by progressive irreversible dissolution of zerovalent iron. Environ. Sci. & Technol., 35, 385-390.

Noubactep C. (2002): Untersuchungen zur passiven in-situ-Immobilisierung von U(VI) aus Wasser. Ph.D. Thesis, TU Bergakademie Freiberg.

Noubactep C. Meinrath G., Volke P.; Peter H.-J., Dietrich P. and B. Merkel (2001a): Understanding the mechanism of the uranium mitigation by zero valent iron in effluents. . Wiss. Mitt. Institut für Geologie der TU Bergakademie Freiberg, Band 18, pp.37-44. ISSN 1433-1284.

Noubactep C., Meinrath G., Dietrich P. and B. Merkel B (2002) Mitigating of uranium in ground water: prospects and limitations; Environ. Sci. & Technol. (submitted)

Noubactep C., P. Volke; G. Meinrath and B. Merkel (2001b): Mitigation of uranium in effluents by zero valent iron: the role of iron corrosion products; paper presented at the ICEM'01 Conference, September 30 - October 4, 2001, in Brugge Belgium. published on CD-ROM, December, 2001

Qiu S.R., Lai H.-F., Roberson M.J., Hunt M.L., Amrhein C., Giancarlo L.C., Flynn G.W., and Yarmoff (2000): Removal of contaminants from aqueous solution by reaction with iron surfaces. Langmuir 16, 2230-2236.

Ritter K, Odziemkowski and Gillham R.W. (2002): An in situ study of the role of surface films on granular iron in the permeable iron wall technology. J. Cont. Hydrol., 55, 87-111.

Wersin P., Hochella Jr. M.F., Per Person, Redden G., Leckie J.O. and Harris W.D. (1994): Interaction between aqueous uranium (VI) and sulfide minerals: spectroscopic evidence for sorption and reduction. Geochim. Cosmochim. Acta 58, 2829-2843.