Environmental Context

Groundwater remediation is mostly a costly long-term process. In-situ remediation by permeable reactive barriers is a potential solution. For pollution by halogenated hydrocarbons, nitrate, and chromium, zerovalent iron (ZVI) has been found to induce a chemical reduction. ZVI remediation technology has been extended to metal pollution, where one of the major removal mechanisms seems to be co-precipitation with the products of iron corrosion. Due to difficulties of identifying reaction products in the matrix of corrosion products, investigation methods for characterising the contaminant removal with respect to interactions between contaminant and corrosion products need to be developed.

Abstract

Zerovalent iron (ZVI) has been proposed as a reactive material in permeable in-situ walls for groundwater contaminated by metal pollutants. For such pollutants which interact with corrosion products, the determination of the actual mechanism of their removal is very important to predict the long-term stability of reactive walls. From a study of the effects of pyrite (FeS$_2$) and manganese nodules (MnO$_2$) on the uranium removal potential of a selected ZVI material, a test methodology (FeS$_2$-MnO$_2$-method) is suggested to follow the pathway of contaminant removal by ZVI materials. An interpretation of the removal potential of ZVI for uranium in presence of both additives corroborates coprecipitation with iron corrosion products as a major removal mechanism for uranium.

Key Words: contaminant, groundwater, in-situ remediation, zerovalent iron, uranium.
Introduction

Groundwater contamination is one of the most difficult and expensive environmental problems.\textsuperscript{[1, 2]} The most common technology used to remediate groundwater is the pump-and-treat technology (pump the water and treat it at the surface).\textsuperscript{[3]} Reactive permeable barriers are discussed as economically preferable alternatives.\textsuperscript{[4-7]} Permeable reactive walls have been developed for various pollutants. Operating permeable reactive walls treat (degrade or immobilize) contamination as halogenated hydrocarbons, chromium, nitrate, and radionuclides.\textsuperscript{[1, 8-10]}

A permeable reactive wall is constructed from appropriate treatment media mixed with sand (to improve permeability) and installed downgradient of a pollutant source. The mitigation effect on the pollutant has to be assured for the entire lifespan (tens of years) of the treatment system and the removed pollutant has to be kept immobile in the wall. The most commonly used reactive material is granular ZVI. ZVI walls are assumed to be active for several decades,\textsuperscript{[1, 7]} although the long-term reactivity of ZVI materials is currently under investigation.\textsuperscript{[11, 12, 13, Vikesland et al. 2003]} Even though a considerable amount of work has become available in the field of ZVI application to groundwater remediation, fundamental questions regarding the reaction mechanism remain open.\textsuperscript{[1, 7, Lin & Lo 2005]} For example, field data did not confirmed quantitative U(VI) reduction in ZVI reactive walls.\textsuperscript{[Gu et al. 2002, Matheson et al. 2002]}

The efficiency of ZVI for contaminant removal is presumed to highly depend on the properties of the metal surface because contaminant reduction reaction may mainly occur on the surface of iron.\textsuperscript{[Keum & Li 2005, Matheson & Tratnyek 1994, Weber 1996]} Although it has been recognised that the formation of iron oxide or hydroxide over the surface may decrease the reactivity of ZVI materials, available information of the effects of oxide-films on the reductive capacity of ZVI materials results largely from well-mixed batch experiments.\textsuperscript{[Huang et al. 2003, Johnson et al. 1998, Kim & Carraway 2000, Lin & Lo 2005, Ritter et al. 2002, Weber et al. 1996]} However, this experimental procedure (shaken or stirred batch experiments) may be inconsistent with groundwater environments (flow velocities 5-50 cm/day) where iron precipitates are continuously generated on ZVI surface, probably forming a reactive physical barrier to several contaminants.\textsuperscript{[Devlin et al. 1998, Devlin & Allin 2005, Mishra & Farrell 2005, Noubactep et al. 2001, 20]} Consequently, it is important to investigate the mechanism of contaminant removal by ZVI under not shaken conditions, where generated corrosion products remain on the iron surface and compete with ZVI for contaminant removal. For this purpose a contaminant such as uranium which is known for his strong interactions with iron oxides (products of iron corrosion)\textsuperscript{[34, Ho & Doern 1985, Hsi & Langmuir 1985]} is very suitable.
The suitability of ZVI for mitigating concentrations of uranium, has been discussed previously. Here, a controversial issue is the uncertainty in removal mechanisms for uranium. Considering the chemistry of uranium and iron under conditions of natural aqueous systems, it is unlikely that reduction of U(VI) species to less soluble U(IV) species is the main mitigating process. In fact, few evidence has been reported for the formation of U(IV) precipitates and the identification of reactions products suffers from strong interference of corrosion products and other inorganic precipitates. Coprecipitation of U(VI) species by iron corrosion products [amorphous and crystalline iron (oxyhydr)oxide] allows to explain the immobilisation.

The aim of this paper is to present the experimental procedure which enabled the elucidation of the mechanism of U(VI) removal from aqueous solutions by ZVI. The method consists in carefully characterizing the role of the products of iron corrosion on the mechanism of ZVI remediation using reactive materials to modify the reactivity and/or the availability of ZVI and iron corrosion products.

The experimental procedure was the following: the ZVI material and each of the two additives (FeS$_2$, MnO$_2$) were mixed and left to stay unstirred over the period of the experiment.

Some Relevant Aspects of the “Pollutant-ZVI-H$_2$O”-System

Pollutant removal by ZVI primarily depends on the chemical thermodynamics of the two redox-systems of iron: Fe$^0$–Fe$^{2+}$ (E° = -0.44 V) and Fe$^{2+}$–Fe$^{3+}$ (E° = 0.77 V). Both the aqueous solution behavior and the redox thermodynamics are of interest. In addition, reaction kinetics is a decisive factor in designing the spatial dimensions of a reactive wall. These three factors have been investigated for several pollutants. The primarily aim of using ZVI in groundwater remediation has been to exploit the negative potential of the couple Fe$^0$–Fe$^{2+}$ to degrade or immobilize several redox-labile compounds. However, ferrous iron from the Fe$^{2+}$–Fe$^{3+}$ redox couple, either in aqueous solution or adsorbed on mineral surfaces, can be part of a convenient delivery path for electrons, reducing and immobilizing organic and inorganic pollutants. Furthermore, pollutant coprecipitation with corrosion products has been demonstrated as another removal pathway. Therefore there are at least three possible immobilization pathways for several pollutants: reduction by Fe$^0$, by Fe$^{2+}$ and coprecipitation with corrosion products. To be able to optimise the functionality of a ZVI wall, the actual main removal pathway for each pollutant has to be identified. Since ZVI (Fe$^0$ and generated Fe$^{2+}$/H$_2$/H as reductants) and
corrosion products (sorbents) react simultaneously, selectively modifying the reactivity of corrosion products and iron solubility can allow a better comprehension of reaction mechanism. The pH dependence of the oxidation potential of ferrous iron is an important aspect of the thermodynamics of electron transfer in the aqueous iron system. Ferric iron undergoes appreciable hydrolysis in aqueous solutions according to the reaction: $x\text{Fe}^{3+} + y\text{H}_2\text{O} \rightleftharpoons \text{Fe}_x(\text{OH})_{3x-y}^y + y\text{H}^+$. As the solution pH is increased, the ferric state is stabilized relative to the ferrous state because of the higher affinity of $\text{Fe}^{3+}$ for the hydroxide ion relative to $\text{Fe}^{2+}$. The primary discussion for this purpose can be limited to the fate of ferrous ions ($\text{Fe}^{2+}$) generated by iron corrosion (Eq. 1, table 1). This limitation is justified by the fact that the fate of $\text{Fe}^{2+}$ determines whether and where mineral precipitates (iron hydroxides and oxides) are formed.

In a ZVI reactive wall the primary reaction is the oxidation of metallic iron to ferrous ions ($\text{Fe}^{2+}$, Eq. 1 - table 1). Depending on the groundwater solution chemistry, there is at least a four way competition for the resulting $\text{Fe}^{2+}$ (Eq. 2 to 8, table 1):

- Pathway 1: $\text{Fe}^{2+}$ can be sorbed on a mineral (e.g. oxide) surface (Eq. 2);
- Pathway 2: $\text{Fe}^{2+}$ can be complexed by organics (Eq. 3);
- Pathway 3: $\text{Fe}^{2+}$ can precipitate with $\text{CO}_3^{2-}$ as $\text{FeCO}_3$ (Eq. 4);
- Pathway 4: $\text{Fe}^{2+}$ can be oxidized by a contaminant, molecular $\text{O}_2$ or other oxidants to various iron oxides (Eq. 5–8).

Assuming for simplification that no organics are available in the barrier zone, only reaction pathways 1, 3 & 4 are relevant for further discussion. Numerous works have shown that $\text{Fe}^{2+}$ adsorbed onto mineral oxide surface (pathway 1) is a potent reductant for several contaminants.\[Charlet et al. 1998, 25\] Pathway 3 is applicable to all precipitates (e.g. $\text{CaCO}_3$, $\text{MgCO}_3$, $\text{FeCO}_3$, $\text{Fe}_3(\text{PO}_4)_2\,8\text{H}_2\text{O}$, $\text{FeS}$) that can be formed in reactive barriers and possibly inhibit the reactivity of ZVI materials. Pathway 4 yields to various corrosion products (including $\text{FeOOH}$ and $\text{Fe}_3\text{O}_4$) which are similarly capable of inhibiting the reactivity of ZVI materials. Iron corrosion products are of higher specific surface area (up to $> 40$ m$^2$/g) than ZVI ($< 5$ m$^2$/g) and are produced at the surface of ZVI\[Balasubramaniam et al. 2003\]. Therefore the accessibility of the ZVI surface for several pollutants could be limited since corrosion products may act as a sort of reactive physical barrier. Note that the affinity of iron hydroxides for metallic pollutants is greater than that of ZVI (bare surface of $\text{Fe}^\circ$).\[12\]

The presented methodology consists in following the contaminant removal process by controlling the availability of “free” corrosion products in the bulk solution ($\text{Fe}^{2+}$-ions are oxidized at the surface of $\text{MnO}_2$) and by modifying the reactivity of iron corrosion products
by shifting the pH value to values between pH4 and pH5. In this pH range sorption of metal ions onto iron hydroxides is less pronounced and the solubility of metal ions is increased.

**Experimental Section**

**Materials**

The used scrap iron was selected from 14 materials because of its reactivity after the EDTA-test. The material contains apart from iron about 3.5% C, 2% Si, 1% Mn, and 0.7% Cr. The material was crushed and the size fraction 1.0 – 2.0 mm was used without further pretreatment. To simulate real barrier conditions, natural minerals were used as additives: a pyrite from the Harz mountains (Germany) and manganese nodules from the pacific ocean (Guatemala- basin: 06°30 N, 92°54 W and 3670 m depth). Pyrite mineral (FeS$_2$: 40% Fe) was crushed and sieved. The fractions: $0.2 \leq d_1 \leq 0.315$; $0.315 \leq d_2 \leq 0.63$; and $0.63 \leq d_3 \leq 1.0$ (d$_{in}$ in mm) were used. The material served as a pH shifting reagent. Manganese nodules (MnO$_2$) were also crushed and sieved. The fractions 1.0 – 2.0 was used.

**Batch experiments**

Two types of U(VI) removal experiments were performed with 15 g/L ZVI, 25 g/L FeS$_2$/MnO$_2$ and a 20.0 mg/L (0.084 mM) U(VI) solution at laboratory temperature (about 20 °C). All experiments were performed in triplicates. The U(VI) solution was synthesized by dissolving UO$_2$(NO$_3$)$_6$H$_2$O in the tap water of the city of Freiberg (Saxony, Germany). The initial pH of the solution was 6.6. Since non-shaken experiments were involved, the tap water was chosen because it contains corrosion promoters such as chloride and carbonate ions (7.7 and 88.0 mg/L respectively).

- Shaken experiments were performed in sample bottles. In each bottle, 0.0 or 0.9 g ZVI and 0.0 or 1.25 g additive material (FeS$_2$ or MnO$_2$) were added to 60 mL U(VI) solution (zero headspace). Immediately after U(VI) addition, the bottles were sealed and vigorously shaken for 48 h. After shaken, the bottles were left for 24 hours before sampling.
- Non-shaken experiments: 0.0 or 0.3 g of ZVI and 0.0 to 0.5 g of each additive (FeS$_2$, MnO$_2$) were allowed to react in sealed sample tubes containing 20.0 mL of U(VI) solution for various experimental durations.

**Analytical Method**

Analysis for uranium was performed after reduction to U(IV) with the Arsenazo III method.$^{[31]}$ The pH value was measured by combination glass electrodes (WTW Co.,
Germany). The electrode were calibrated with five standards following a multi-point calibration protocol\cite{Meinrath & Spitzer 2000} and in agreement with the new IUPAC recommendation\cite{Buck et al. 2002} The redoxpotential measurements were corrected to give equivalency to the Standard Hydrogen Electrode (SHE). All experiments were performed in triplicate. Error bars given in figures represent the standard deviation from the triplicate runs.

Results and Discussion

The experiments were compared on the basis of the U(VI) fixation $P_U$ (in %) defined as:

$$P_U = 100\% \times (1 - \frac{C}{C_0})$$

where $C_0$ is the initial U(VI) concentration in solution, while $C$ gives the U(VI) concentration after the experiment.

To characterize U(VI) removal by ZVI while taking individual properties of the additives into account, five different experiments have been performed over a duration up to 120 d: I) ZVI alone, II) FeS$_2$ alone, III) MnO$_2$ alone, IV) ZVI + MnO$_2$, and V) ZVI + FeS$_2$ (System I, II, II, IV and V). In system V, three different particle sizes of FeS$_2$ were tested: $d_1$, $d_3$ and $d_3$ (System Va, Vb, and Vc respectively).

Suitability of non-shaken tests

The suitability of non-shaken batch tests was investigated by comparing U(VI) removal efficiency of material in vigorously-shaken and non-shaken batch experiments. The idea behind this is that shaking could alter ZVI surface in a dramatic fashion not duplicated in the subsurface.\cite{Delvin & Allin 2005, Noubactep 2003} Non-shaken batches could help to avoid experimental biases.

Figure 1 summarizes the results of U(VI) removal by the materials in the five systems. It can be seen that, in both cases (shaken and non-shaken tests), the best fixation rate is achieved when ZVI is present alone (> 80%). The efficiency is the smallest when FeS$_2$ is present alone (< 20%). Therefore, the increasing order of U(VI) removal efficiency for single material systems was FeS$_2$ < MnO$_2$ < ZVI (figure 1). This observations suggest that, if FeS$_2$ and MnO$_2$ are consider as pure U(VI) adsorbents, then their addition to ZVI should primarily increase the number of adsorption sites such that the increasing order of U(VI) removal efficiency should be: FeS$_2$ < MnO$_2$ < (ZVI + FeS$_2$) < (ZVI + MnO$_2$) < ZVI in both cases, the extent been different due to differences in the kinetics of mass transfer (shaken > non-shaken). This prevision was not confirmed by experimental results (figure 1). These results suggest that
other processes than adsorption are involved. In fact, the increasing order of U(VI) removal efficiency was:

FeS$_2$ < MnO$_2$ < (ZVI + MnO$_2$) < (ZVI + FeS$_2$) < ZVI for shaken tests, and

FeS$_2$ < (ZVI + MnO$_2$) < (ZVI + FeS$_2$) < MnO$_2$ < ZVI for non-shaken tests.

It is interesting to observe that in shaken tests, U(VI) removal efficiency by FeS$_2$ was lower than in non-shaken experiments. In fact, shaking increase the extent of pyrite oxidation, yielding to a lower pH value (2.5 to 3.5 figure 1) which increases U(VI) solubility. [Meinrath et al. 1996, Noubactep 2003] Thus U(VI) fixation by FeS$_2$ occurs essentially through adsorption.

The predicted behavior of systems with ZVI and MnO$_2$ [MnO$_2$ < (ZVI + MnO$_2$) < ZVI] was observed only in shaken experiments. In non-shaken experiments (figure 1b), U(VI) removal efficiency through MnO$_2$ alone (60 %) was more than two times higher than that of [(ZVI + MnO$_2$): 26 %]. This results can not be explained by adsorption phenomena since the reductive dissolution of MnO$_2$ yields to Mn(II)/Mn(III)/Fe(III)-species which are all U(VI) adsorbents. Furthermore, if U(VI) removal was due to direct electrons transfer by ZVI, the removal efficiency ($P_U$) should have been intensified in the presence of MnO$_2$ [$P_U$(ZVI + MnO$_2$) > $P_U$(ZVI)], since Fe$^{2+}$ consumption for MnO$_2$ reduction favors ZVI oxidation.

Two other important issues are the variation of pH and $E_{H}$ values. Table 2 shows that shaking yields to lower $E_{H}$ values and higher pH values. The lowest $E_{H}$ values was achieved in the presence of pyrite. Under given experimental conditions, the evolution of the pH value in each system is determined by two concurring factors: (1) acidity generation through FeS$_2$ oxidation or MnO$_2$ dissolution (eqs. 7 and 8, table 1), and (2) alkalinity generation through iron corrosion. If acidity generation dominates upon alkalinity generation, then the pH of the system will be lower than the initial value of 6.6; otherwise pH > 6.6. Figure 1 shows that acidity generation dominates only in systems with pyrite and that in shaken experiments with (ZVI + FeS$_2$), 95 % U(VI) removal could be achieved at pH 4.2. At this pH value (4.2), U(VI) adsorption onto iron oxides is not favorable. [Farrell et al. 1999] This result indicates that another process plays an important role in the mechanism of U(VI) removal by ZVI.

The previous discussion presents important facts that suggest that shaking experimental vessels to investigate contaminant mechanism could accelerate the removal process in such a way that important processes could be overseen. The rest of this work will focus on the effects MnO$_2$ and FeS$_2$ on U(VI) removal by ZVI in non-shaken tests. Particular attention will be directed at understanding why MnO$_2$ and FeS$_2$ addition decreases U(VI) removal efficiency by ZVI, why the presence of MnO$_2$ did not favor U(VI) removal, and why in the presence of
FeS$_2$ a considerable U(VI) removal by ZVI could be achieved at pH 4.2. For this purpose target experiments were performed for experimental duration up to 120 days.

**Effects of MnO$_2$ addition**

As discussed above, reductive dissolution of MnO$_2$ delays the availability of newly generated corrosion products (CP) by consuming Fe$^{2+}$-ions as soon as they form from Fe$^0$ oxidation. The role of newly generated CP on U(VI) removal by ZVI was investigated by performing non-shaken batch experiments with ZVI (15 g/L) and MnO$_2$ (0 to 25 g/L) for 14 and 30 days, figure 2 summarizes the results.

Figure 2 shows that the best U(VI) removal efficiency is achieved when ZVI is present alone. U(VI) removal decreases with increasing MnO$_2$ amount. After 14 days, only 25 % of U(VI) was removed for [MnO$_2$] > 7 g/L. This observation suggests that, the products of MnO$_2$ reductive dissolution (Eq. 7 and 8 - table 1) do not substantially increase U(VI) removal. Therefore, U(VI) removal starts once the available amount of MnO$_2$ is depleted. This conclusion is supported by the evolution of the system after one month (30 d). After 30 days, the extent of U(VI) removal increases considerably for all MnO$_2$ amounts. This increase of U(VI) removal efficiency was attributed to increasing availability of newly generated corrosion products which sequestrated U(VI) in their matrix while ageing. A long-term experiment with 5 g/L MnO$_2$ (and 15 g/L ZVI) showed that after about 60 days complete U(VI) removal was achieved under the same experimental conditions.$^{[20]}$

Contaminant removal from the aqueous phase in contact with ZVI proceeds by concurrent sorption and reduction.$^{[Burris et al. 1995, Kim & Carraway 2000, 20]}$ Significant contaminant sorption in “Pollutant-ZVI-H$_2$O”-Systems have been demonstrated and attributed to iron corrosion products or graphitic inclusions in ZVI materials.$^{[Burris et al. 1998, Lin & Lo 2005]}$ Furthermore, the role the products of iron corrosion has been mostly investigated on synthetic materials$^{[Farrell et al. 1999, Huang et al. 2003,]}$ or by pretreating ZVI materials by several procedures (e.g. acid-washing or H$_2$ reduction of ZVI).$^{[Lin & Lo 2005, 22]}$ However, all these experimental procedures oversee two important facts: (1) corrosion products are continuously generated at the surface of ZVI; (2) freshly generated corrosion products are very reactive (nascent iron hydroxides). The results of the use of MnO$_2$ to retard the availability of corrosion suggests that, comparing reaction rate or removal efficiency of acid-pretreated and untreated ZVI for a contaminant$^{[22, Su & Puls 1999]}$ could be seen as characterising the role of atmospheric corrosion products on ZVI reactivity. In fact, in both cases new corrosion products will be generated and coprecipitated with contaminants.
Effects of FeS$_2$ addition

Pyrite addition intended to shift the pH to the region where the extent of sorption onto corrosion products of iron is very low (acidification by FeS$_2$ oxidation). Thus, experiments have been performed with 15 g/L ZVI and 0 to 25 g/L of FeS$_2$ (0.315 ≤ $d_2$ (mm) ≤ 0.63). The results are shown in figure 2 together with those of MnO$_2$. Similarly as with MnO$_2$, U(VI) removal efficiency decreases with increasing amount of additional material. But the trend observed after 14 days was not reproduced after 30 days for [FeS$_2$] > 8 g/L. After 14 days the pH value decreases with increasing amount of FeS$_2$ and reached a value of 4.31 for [FeS$_2$] > 20 g/L. The corresponding U removal efficiency was about 41%. This value further decreased to 20 % after 30 days while the pH value decreases to 4.18. This results suggest that, a decrease of the pH value from the 8 to 4 (e.g. trough pyrite oxidation) will yield to a considerable U(VI) release from iron oxides.

To better investigate the involved processes, other experiments for longer experimental durations and different particle sizes of pyrite ($d_i$ ≤ 1 mm) were performed. The results are presented in figure 3 and table 3.

Table 3 presents the variation of the pH value as function of time in the systems “ZVI” (system I), “FeS$_2$ ($d_2$)” (system II), “[ZVI + FeS$_2$ ($d_2$)]” (system Vb), and “[ZVI + FeS$_2$ ($d_3$)]” (system Vc). The results of the pH variation can be summarized as follows: (1) in system I the pH increased from 6.6 (initial value) to 7.6 as result of ZVI corrosion; (2) in system II the pH decreased from 6.6 to 3.5 as result of pyrite dissolution; (3) in system Vb, the variation of the pH was not uniform. The global trend was that the pH first decreased from 6.6 ($t = 0$) to 3.9 ($t = 55$ d) and then increased to a value of 4.5 at the end of the experiment ($t = 119$ d); (4) the evolution of the pH in system Vc was very close to that of system I, suggesting that no significant FeS$_2$ dissolution occurred. The comparison of the pH evolution in the single systems corroborates the assumption that the pH is controlled by FeS$_2$ oxidation and ZVI corrosion. Thereafter, the pH was the lowest in system II (FeS$_2$ alone, pH = 3.5) and the highest in system I (ZVI alone, pH 7.6). In systems with material mixture, the final pH value depends on the extend of both concurring reactions. Final pH values in system Vc were higher that 7.6. This can be explained by the fact that, under the experimental conditions (non-shaken tests), the particle size of 0.63 to 1.0 mm was not reactive enough to yield acidification. Therefore, FeS$_2$ oxidation in neutral pH range [Williamson & Rimstidt 1994] intensified ZVI corrosion, yielding to a pH elevation of 0.2 unit. As discussed above, for $d_i$ < 0.63 (e.g. $d_i$ and $d_2$), FeS$_2$ dissolution decreases the pH of the system, increasing the solubility of U(VI) and reducing the adsorptive properties of the corrosion products of iron.
Figure 3 shows the effect of the three different grain diameters of pyrite ($d_1$, $d_2$, $d_3$) on the U(VI) removal from the aqueous solutions. The results can be summarized as follows: (1) U(VI) removal was the lowest in system II ["FeS$_2$ ($d_2$)"] and the highest in system II (ZVI), confirming that U(VI) adsorbs onto FeS$_2$; (2) The presence of FeS$_2$ (System Va, Vb and Vc) retards U(VI) removal to various extent. The maximal retardation been observed for FeS$_2$ ($d_2$)" (system Vb). The grain diameters of a material such as FeS$_2$ is known to be inversely proportional to the available surface area. Therefore, smaller grains have a larger surface area and exhibit a higher oxidation rate.[Strömberg & Banwart 1999] Accordingly the magnitude of the pyrite effect should have directly correlate with particle size, i.e. $d_1 > d_2 > d_3$. As discussed above, $d_3$ is not reactive enough under not shaken conditions. Under the experimental conditions (closed system), the amount of O$_2$ and Fe$^{3+}$ for FeS$_2$ oxidation[Gleisner 2005] is limited. Therefore the acidification capacity of FeS$_2$ is limited. Thus, the more reactive the particle size, the faster the exhaustion of his acidification capacity. Figure 3 and table 3 show that the acidification capacity of FeS$_2$($d_1$) was exhausted after about 40 days and U(VI) removal (coupled wit pH increase) starts. For FeS$_2$(d$_2$) with larger particle size, the exhaustion of the acidification capacity was timely delay.

Figure 3 shows that, the curves of U(VI) removal for systems Va and Vb exhibit very similar behavior. System Vb is a sort of time delay reproduction of system Va. The curve of U(VI) removal is not uniform. For the system “ZVI + FeS$_2$(d$_2$)” for instance, the initial U(VI) fixation of 32% (day 15) increases to 52 % after 25 days and then decreases to 18 % after 43 days. During this period the pH of the system decreases from 6.6 to a minimum of 3.9. Afterwards U(VI) removal increases to 94% at day 94 whereas the pH value increases to 4.4. The pH minimum corresponds to the point where the acidification capacity of FeS$_2$ is exhausted. The evolution of the pH then depends on the iron corrosion. U(VI) removal starts 40 days after the beginning of the experiment and occurs in a very narrow pH range (4.0 to 4.4). It was shown that U(VI) removal is accompanied by a decrease of aqueous iron concentration and that Fe(II) was the dominating iron species under the experimental conditions.[21]

In the pH range of observed U(VI) removal (4.0 to 4.4), iron corrosion should mostly occur without H$_2$ production,[32, 33] and U(VI) reduction trough ZVI should have been very favorable because ZVI surface is neither covered by iron corrosion products nor H$_2$ bubbles.[12] Instead of that, U(VI) removal occurred only very slowly (18 % at day 43 and 94 % at day 94) and was accompanied by a decreased of iron corrosion, suggesting that U(VI) removal is the result of U(VI) entrapment in the matrix of precipitating iron hydroxide.
**General Discussion**

Contaminant Removal in reactive walls can occur through reduction, adorption and coprecipitation. Contaminant reduction pathways involve either direct electron transfer from ZVI at the surface of the iron metal or reaction with dissolved Fe$^{2+}$ or H$_2$/H, which are products of iron corrosion. Direct reduction by either Fe$^{2+}$ or H$_2$ (H) is generally a very slow reaction, and may occur under catalytic effect of iron or oxide surfaces. A key question that remains is whether reduction occurs at the iron surface, involving either direct electron transfer by ZVI (or an electrical conductive product of iron corrosion, e.g Fe$_3$O$_4$), or in the aqueous phase by release of a water-soluble reductant. This study has shown that U(VI) is removed from the aqueous solution by its adsorption onto newly generated corrosion products, and not by chemical reduction. The sorbed U(VI) is then entrapped in the matrix of aging corrosion products: this is the process of co-precipitation. Iron corrosion products are mainly porous iron oxides through which reductants such as Fe$^{2+}$, H$_2$ or H can diffuse and induce abiotic reduction of sorbed U(VI). The result of this suggests that reported U(VI) reduction in the presence of ZVI under anoxic conditions is the result of a surface catalyzed reaction of iron(II). In a subsurface ZVI reactive wall, U(VI) can be reduced by a number of abiotic and microbially mediated processes. In particular, abiotic reduction by green rusts (mixed ferrous/ferric hydroxides) have been reported. Therefore, the success of ZVI in mitigating U(VI) in reactive walls may rely in the progressive production of Fe$^{2+}$ ions which react themselves as reductants or contribute to the formation of reductive species such as green rusts. The long term stability of U(IV) species in ZVI walls is not guaranteed because of the presence of Fe(III) species. When solubilized, Fe(III) species are capable on re-oxidating U(IV) to mobile U(VI) species.

**Generalization of the approach**

Conducting experiments with the systems “ZVI + FeS$_2$” and “ZVI + MnO$_2$” under strictly anoxic conditions ($P_{O_2} \approx 0$ atm) and various $P_{O_2}$ values can help to discuss the ZVI removal mechanism for several organic and inorganic contaminans under various possible site conditions. In “ZVI – pollutants – groundwater” systems there are three possible reductants for U(IV) and several other pollutants (e.g. chlorinated aliphatics): (i) the iron metal Fe$^0$, (ii) ferrous iron associated with iron oxide coatings, and (iii) hydrogen in the presence of an
appropriate catalyst \cite{25, 35}. From these possibilities, only the thermodynamically favorable reductive reaction by iron metal (Fe$^0$) is usually discussed although it is not sure whether the pollutants will reach the material surface, where the electron transfer is supposed to occur. By retarding the availability of corrosion products with MnO$_2$ the reaction mechanism can be better characterized.

The proposed methodology can be denoted as “FeS$_2$-MnO$_2$-method” for the investigation of the mechanism of contaminant removal by ZVI. Since each of both additives reacts with a different mechanism and has yielded to the same conclusion for uranium removal, the method consists in two different tests: “FeS$_2$-test” and “MnO$_2$-test”. The application of these tests depends on the targeted contaminant, the availability of the additives and the wished duration of the experiments. It can be emphasized that the “MnO$_2$-test” is more appropriate for organics, whereas the “FeS$_2$-test” is the best test for inorganics of more pronounced pH dependant solubility. ZVI-MnO$_2$-experiments (“MnO$_2$-test”) can be achieved within some days or weeks whereas ZVI-FeS$_2$-experiments (“FeS$_2$-test”) demand some months. Because pyrite induces changes in the pH value, modifying the solubility of inorganic contaminants and freeing ZVI surface from corrosion products in the initial phase of the experiment, the FeS$_2$-test alone can be recommended for future works on removal mechanism investigation.

**Material’s availability and pretreatment**

A possible difficulty for the application of this method is the availability of reactive additives. Pyrite is a very common mineral, and occurs in numerous localities worldwide. It is expected that geological institutes will have several samples of this mineral in their collection. Is it the case, then the a suitable sample has to be selected and various particle sizes tested to choose the most appropriated. As concerning MnO$_2$, instead of manganese nodules, well characterized manganese oxides such as birnessite,\cite{36} can be synthesized and used.

**Conclusion**

A systematic method for the characterization of the role of corrosion products on the mechanism of U(VI) removal by ZVI materials in reactive walls has been outlined. The proposed method consists in long-term, non-shaken batch experiments with and without appropriated additives for a better comprehension of the mechanism of U(VI) removal by ZVI materials (FeS$_2$-MnO$_2$-method). This experimental tool can be useful in elucidating the mechanism of other contaminants by ZVI.
This experimental tool, when properly modified can be suitable at investigating some aspects of mineral precipitation on the long term performance of ZVI reactive barrier. For example, if instead of adding MnO$_2$ to the system CaCO$_3$ (calcite) is added, then the role of carbonates ions and/or FeCO$_3$ on the contaminant removal process can be characterized.

This paper has shown that additional efforts to understand the hydrogeochemical evolution of a ZVI barrier system are required. Beside the actual removal mechanism of any metal pollutant, the long term stability of his immobilized form has to be addressed. Since uranium is surely removed under oxic conditions by a co-precipitation mechanism, it is important to be able to predict his behavior in the case changes occur in the system; e.g. iron dissolution.

The interactions between contaminant, ZVI and selected model reactive media (CaCO$_3$, FeS$_2$,...) have to be investigated also in long-term column studies to better understand the hydrochemical processes (e.g. loss of permeability) taking place in permeable reactive barrier systems. The results of such studies will help to more accurately model the long term performance of reactive barriers.

Acknowledgments

The authors would like to express their gratitude the branch of the MAZ (Metallauflbereitung Zwickau, Co) in Freiberg (Germany) who kindly purchased the used scrap iron. The work was granted by the Deutsche Forschungsgemeinschaft (DFG-GK 272).

Literature


[...] C. Noubactep, P. Volke, G. Meinrath, B. Merkel, Session 51-2, Abstract #364 in ICEM'01 Conference, **2001** (Brugges).


**Table 1:** Possible reaction pathways for ferrous ions (Fe\(^{2+}\)) from the iron corrosion in a ZVI reactive barrier and their reversibility under natural conditions. Min. is a mineral whereas Ox and Red are the oxidized and the reduced form of a pollutant.

<table>
<thead>
<tr>
<th>mechanism</th>
<th>reaction</th>
<th>reversibility</th>
<th>Eq.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe(^0) corrosion:</td>
<td>Fe(^0)(_{(s)}) ⇔ Fe(^{2+}) + 2 e(^-)</td>
<td>irreversible</td>
<td>(1)</td>
</tr>
<tr>
<td>sorption:</td>
<td>Fe(^{2+})(_{(aq)}) + Min. ⇔ (Min.-Fe(^{2+}))</td>
<td>reversible</td>
<td>(2)</td>
</tr>
<tr>
<td>sorption:</td>
<td>Fe(^{2+})(_{(aq)}) + Org. ⇔ (Org.-Fe(^{2+}))</td>
<td>reversible</td>
<td>(3)</td>
</tr>
<tr>
<td>precipitation:</td>
<td>Fe(^{2+})(_{(aq)}) + CO(_3^{2-}) ⇔ FeCO(_3)</td>
<td>reversible</td>
<td>(4)</td>
</tr>
<tr>
<td>oxidation:</td>
<td>2 Fe(^{2+})(_{(aq)}) + (\frac{1}{2}) O(_2) + 5 H(_2)O ⇔ 2 Fe(OH)(<em>3)(</em>{(s)}) + 4 H(^+)</td>
<td>reversible</td>
<td>(5)</td>
</tr>
<tr>
<td>oxidation:</td>
<td>Fe(^{2+})(<em>{(aq)}) + Ox(</em>{(aq)}) ⇒ Fe(^{3+})(<em>{(aq\ or\ s)}) + Red(</em>{(s)})</td>
<td>irreversible</td>
<td>(6)</td>
</tr>
<tr>
<td>oxidation:</td>
<td>Fe(^{2+})(_{(aq)}) + MnO(_2) + 2 H(_2)O ⇒ FeOOH + MnOOH + 2 H(^+)</td>
<td>irreversible</td>
<td>(7)</td>
</tr>
<tr>
<td>oxidation:</td>
<td>Fe(^{2+}) + MnO(_2) + 2 H(_2)O ⇒ FeOOH + MnOOH + 2 H(^+)</td>
<td>irreversible</td>
<td>(8)</td>
</tr>
</tbody>
</table>

**Table 2:** Variations of solution parameters (pH and E\(_{H}\)) with 15 g/L ZVI and 25 g/L additive material (FeS\(_2\) or MnO\(_2\)) for shaken and non-shaken batch experiments.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>System</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ZVI</td>
</tr>
<tr>
<td></td>
<td>shaken</td>
</tr>
<tr>
<td>pH</td>
<td>10.6</td>
</tr>
<tr>
<td>E(_H) (mV)</td>
<td>-96</td>
</tr>
</tbody>
</table>
Table 3: Variations of the pH value with the time in four selected systems (initial value: pH 7.2)

<table>
<thead>
<tr>
<th>t (days)</th>
<th>Reference systems</th>
<th>Systems ZVI + FeS₂</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ZVI</td>
<td>FeS₂(d₂)</td>
</tr>
<tr>
<td>15</td>
<td>7,6₂</td>
<td>3,5₃</td>
</tr>
<tr>
<td>25</td>
<td>7,5₅</td>
<td>3,₄₉</td>
</tr>
<tr>
<td>43</td>
<td>7,₆₅</td>
<td>3,₄₀</td>
</tr>
<tr>
<td>55</td>
<td>7,₅₈</td>
<td>3,₃₅</td>
</tr>
<tr>
<td>72</td>
<td>7,₅₈</td>
<td>3,₄₂</td>
</tr>
<tr>
<td>94</td>
<td>7,₅₉</td>
<td>3,₅₆</td>
</tr>
<tr>
<td>108</td>
<td>7,₆₂</td>
<td>3,₅₁</td>
</tr>
<tr>
<td>119</td>
<td>7,₅₀</td>
<td>3,₃₇</td>
</tr>
</tbody>
</table>
Figure 1

(a) shaken

V = 50 mL

$t = 3$ days

U(VI) removal

(b) non-shaken

V = 20 mL

$t = 14$ days

U(VI) removal / [%]
Figure 2

[U(VI)$_0$ = 20 mg/L
[ZVI] = 15 g/L

U(VI) removal / [%]

additive material / [g/L]
Figure 3

[U(VI)]_0 = 20 mg/l

- ▼ ZVI (reference)
- ★ ZVI + FeS\textsubscript{2} (d\textsubscript{1})
- △ ZVI + FeS\textsubscript{2} (d\textsubscript{2})
- ○ ZVI + FeS\textsubscript{2} (d\textsubscript{3})
- × FeS\textsubscript{2} (d\textsubscript{4})
Figures Captions

**Figure 1**: Percent uranium removal as a function reactive materials in shaken (a) and non-shaken (b) batch experiments. The values on the columns indicated the final pH value, the initial pH was 7.20. The experiments were conducted in triplicate. Error bars give standard deviations. [ZVI] = 69 g/L; [FeS₂] = [MnO₂] = 25 g/L

**Figure 2** Impact of manganese nodules (MnO₂) and pyrite (FeS₂) on the percent U(VI) removal from the aqueous solution as a function of material amount for 14 and 30 days. The experiments were conducted in triplicate. Error bars give standard deviations. Particle grain size; FeS₂: 0.2 ≤ d ≤ 0.315, MnO₂: 1.0 ≤ d ≤ 2.0; d (mm). The represented lines are not fitting functions, they just joint the points to facilitate visualization.

**Figure 3**: Impact of pyrite (d) on the percent U(VI) removal from the aqueous solution as a function of equilibration time. The reference system consists of ZVI alone. The values on the curves indicate the pH at selected dates, the initial pH was 7.20. The experiments were conducted in triplicate. Error bars give standard deviations. Pyrite: 0.2 ≤ d₁ ≤ 0.315; 0.315 ≤ d₂ ≤ 0.63; and 0.63 ≤ d₃ ≤ 1.0; d (mm). The represented lines are not fitting functions, they just joint the points to facilitate visualization.