Release of coprecipitated uranium from iron oxides

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HYPERLINKThe removal of uranium (VI) from zerovalent iron permeable reactive barriers and wetlands can be explained by its association with iron oxides. The long term stability of immobilized U is yet to be addressed. The present study investigates the remobilization of U(VI) from iron oxides via diverse reaction pathways (acidification, reduction, complex formation). Prior, uranium coprecipitation experiments were conducted under various conditions. The addition of various amounts of a pH-shifting agents (pyrite), an iron complexing agent (EDTA) or iron (III) reduction agent ($TiCl_3$) yielded in uranium remobilization, concentrations above the US EPA allowed maximum contaminant level (MCL = 30 μg/l). This study demonstrates that U(VI) release in nature strongly depends on the conditions and the mechanism of its fixation by geological materials.

Introduction

Iron oxides, ubiquitous in soils and sediments, are known to play an important role in the mobility (retardation and transport) of many organic and inorganic contaminants in natural environments. The retention property is primarily due to the large surface area, the strong adsorptive properties and the high adsorptive capacity for both cationic and anionic species.[1,2]

Iron (hydr)oxides readily eliminated inorganic contaminants from the aqueous phase via different competing mechanisms: adsorption, coprecipitation, and reduction on green rust.[3] The extent of coprecipitation depends on the bio-geochemical conditions, in particular on the reactivity of iron oxides and the contact time of the contaminant with them. Generally, it can be assumed that the coprecipitation is favored when the iron(III) concentration is high and the contaminant concentration is low.[2,4–8] In this case, the contaminant is adsorbed first onto amorphous ferrihydrite [e.g., $Fe(OH)_3$] and coprecipitated with it as it is aged.[9–11] Depending on the geometrical characteristics of the contaminant relative to iron, stoichiometrical coprecipitates can be formed [e.g., $FeAsO_4 \cdot xH_2O$, $Fe_{1-x}Cr_x(OH)_3$]. Whether the associated contaminant is primarily structurally incorporated or surface-adsorbed is important for the long term stability of the fixed contaminant.

Several active and passive remediation strategies aim at immobilizing long-term contaminants. Among the passive strategies in which contaminant retention by interactions with iron oxides are important, wetlands, permeable reactive barriers and natural attenuation can be listed.[2,12] Under relevant natural conditions the interactions between iron oxides, organic components, and microorganisms will increase the contaminant

removal. For example, ZUYI et al.[13] showed an elevated U(VI) sorption by iron oxides in the presence of fulvic acids. The important impact of microorganisms for the contaminant retention has been demonstrated for example by BEHRENDS and CAPPELLEN[14] and NICO et al.[15] These authors have shown that *Shewanella putrefaciens* can induce the reduction of U(VI) to U(IV). However, the long term optimization of microbiological processes under natural conditions is yet to be properly investigated. Biological processes are not experimentally addressed in this study.

A zerovalent iron (Fe^0, ZVI) permeable reactive barrier is a typical case where the ratio Fe : contaminant is high to favor coprecipitation. Table 1 summarizes some relevant processes governing the fate of iron.

Iron corrosion [Eq. (1) in Table 1] produces ferrous iron (Fe^{2+}) that can be further oxidized to ferrihydrite [Eq. (2), $Fe(OH)_3$] which is an excellent trace metal (e.g., As, Cr, U) adsorbent. Ferrous and ferric ions from Eqs (1) and (2) can react to build green rust [Eq. (3)] which is known for its reductive capacity.[16] Ferrihydrite from Eq. (2) then aged and transformed into several iron oxides [Eq. (4)] entrapping the contaminant in their mass (coprecipitation). These processes are probable in wetlands with elevated iron(III) concentration and relative low pH values.[5]

Several processes are capable of releasing coprecipitated metal ions from iron oxides back into solution. These processes are of special interest concerning the mobility of contaminants in natural systems. Some relevant remobilization processes are listed in Table 1,[17,18] they include: (1) acidic oxide dissolution [Eqs (5) and (6)], (2) oxide dissolution by complex formation [Eq. (7)], and (3) abiotic (or biotic) reductive dissolution of oxides [Eq. (8)]. The understanding of these individual processes is crucial to the comprehension of the mobility of metal ions in the geosphere and, therefore, the prediction of long term

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stability of (inorganic) contaminants associated with iron oxides.

Table 1. Some relevant reactions for the elucidation of the mechanism of coprecipitated U(VI) release from iron oxides

Process	Reaction equation		Eq. No.
Iron corrosion	Fe^0	$\Leftrightarrow Fe^{2+} + 2\,e^-$	(1)
$Fe(OH)_3$ formation	$2\,Fe^{2+} + 1/2\,O_2 + 5\,H_2O$	$\Leftrightarrow 2\,Fe(OH)_3 + 4\,H^+$	(2)
GR formation	$(1-x)Fe^{2+} + xFe^{3+} + (2+x)OH^-$	$\Leftrightarrow [Fe^{2+}_{1-x}Fe^{3+}_x(OH)_2]^x[x\,OH^-]$	(3)
$Fe(OH)_3$ aging	$Fe(OH)_3$	$\Leftrightarrow FeOOH, (Fe_3O_4, Fe_2O_3)$	(4)
Acidic dissolution	$Fe(OH)_3 + 3\,H^+$	$\Leftrightarrow Fe^{3+} + 3\,H_2O$	(5)
	$FeOOH + 3\,H^+$	$\Leftrightarrow Fe^{3+} + 2\,H_2O$	(6)
Complexive dissolution	$FeOOH + EDTA + 3\,H^+$	$\Leftrightarrow Fe(EDTA)^{3+} + 2\,H_2O$	(7)
Reductive dissolution	$FeOOH + Ti^{3+} + H^+$	$\Leftrightarrow Fe^{2+} + 2\,OH^- + Ti^{4+}$	(8)

GR: Green rust.

The remobilization of metals by synthetic anthropogenic chelating agents such as ethylenediaminetetraacetic acid (EDTA) and nitrilotriacetic acid (NTA) has been addressed because of their potential for increasing solubilization and remobilization of heavy metals from aquatic sediments or from aquifer materials during infiltration from river water to groundwater.[18] The metal (re)mobilization by acidification has been mostly discussed in the context of acid mine drainage (AMD).[19] The investigation of reductive transformation of iron oxides and their impact on trace metal mobility and remediation is currently under investigation.[20,21]

The geochemical conditions of the "U(VI)-iron oxides" system can be summarized as follows: low pH destabilizes iron oxides; chelates (e.g. EDTA) decrease U(VI) sorption and dissolve iron oxides; iron hydroxides are dissolved at low redox potential (E_H) but U(VI) reduction is favored, and high carbonate levels provide favorable conditions for uranium mobilization.[5] To date, the association of U(VI) with iron oxides has mostly been investigated with the objective to understand its environmental retardation process,[1,10] or to develop efficient decontamination processes for contaminated steels.[9] Since it was demonstrated that the U(VI) retention in reactive barriers is not necessarily the result of a "reductive precipitation"[12,20,22] there is a high need for the understanding of the fate of U(VI) as iron oxides undergo transformations, in particular dissolution.

The present study aims at investigating the influence of fundamental mechanisms of iron oxide transformations on the U(VI) removal from corrosion products. For this purpose, iron complexation by EDTA, acidification by pyrite and reductive dissolution by Ti(III) were tested and their effects on the remobilization of coprecipitated U(VI) from iron corrosions products were recorded. Experimental results were discussed for their implications on the long-term efficiency of two passive remediation techniques: permeable reactive barriers and wetlands.

Experimental

Materials

The used ZVI is a scrap iron from MAZ (Metallaufbereitung Zwickau, Co.). Its elemental conditions were 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 1.0–2.0 mm fraction was used without any further pretreatment. ZVI is used as U(VI) reducing agent.

Pyrite was crushed and sieved. Five different particle sizes (d_i, mm) of pyrite were used: $0.063 < d_1 < 0.125$; $0.125 < d_2 < 0.250$; $0.250 < d_3 < 0.315$; $0.315 < d_4 < 0.63$; $0.63 < d_5 < 1.0$. The elemental composition was 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 agent, diminishing the sorptive reactivity of corrosion products, enhancing the solubility of U(VI), promoting the coprecipitation of U(VI) with iron corrosion products in long term experiments.[11]

Fixation experiments, desorption with Na_2CO_3

The experimental procedure for the fixation experiments, the desorption by 0.1M Na_2CO_3 and the analytical method were described elsewhere in detail.[11,12] Fixation studies consisted of different not shaken experiments for given duration with 5 g/l ZVI, and 15 g/l FeS_2: ZVI and additives were allowed to react in sealed sample tubes containing 20.0 ml of an uranium solution (20 mg/l or 0.084mM) 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. The contact vessels were allowed to equilibrate in darkness to avoid photochemical side reactions, the initial pH was ~7.2. Desorption experiments were conducted in a 0.1M Na_2CO_3 solution for about 14 hours. The experiments were performed in triplicate. The mean values are presented.

The experiments were conducted in closed assay tubes under non-controlled O_2 (and CO_2) pressure. It is certain that P_{O_2} was less than the atmospheric pressure. It can be assumed that U(VI) removal mainly occurred under very low O_2 partial pressure, because iron corrosion (and pyrite dissolution) is O_2 consuming. Note that strictly anoxic conditions are not expected in the majority of ZVI reactive walls, since the technology is yet applicable for rather shallow plumes: 15–22 m (50–70 feet deep; US EPA 1998).[23] Therefore, working at low oxygen level ($P_{O_2} < P_{O_2,atm}$ and $P_{O_2} \neq 0$) is a good simulation for groundwater situations at several sites.

Remobilization experiments with pyrite, EDTA, HCl and TiCl₃

Previous fixation experiments were conducted for one, two or three months with ZVI (15 g/l) alone or the system "ZVI + FeS_2 (d_2)", containing 25 g/l FeS_2. The remobilization occurred for a given duration or as a function of time through the addition of defined amounts of additives: pyrite (1 g or 50 g/l), EDTA (10mM) and $TiCl_3$ (1.25%). The selection of these reactants was motivated by previous results[11,12] and literature data from HERON et al.[24] and FORD.[25] The aim was to achieve different dissolution samples of corrosion products.

Analytical method

Analysis for U was performed by inductively coupled plasma mass spectrometry (ICP-MS) at the Institute of Geosciences of the University of Jena. All chemicals used were of analytical grade. The pH value was measured by combination glass electrodes (WTW Co., Germany). The electrodes were calibrated with five standards following a multi-point calibration protocol[26] and in agreement with the new IUPAC recommendation.[27] All experiments were performed in triplicate. Error bars given in figures represent the standard deviation from triplicate runs.

Results

The experiments were compared on the basis of the final U(VI) concentration (C in µg/l), the total fixation P_{tot} (in %) defined by:

$$P_{tot} = 100\% (1 - (C/C_0)) \qquad (9)$$

where C_0 is the initial concentration of uranium in solution, while C gives the uranium concentration after the experiment. The percent recovery, P_{rev}, of uranium after the end of the experiment (recovery with 0.1M Na_2CO_3, 0.01M EDTA, $TiCl_3$, or pyrite (d_i)) was calculated by:

$$P_{rev} = 100\% \frac{C_0(V_0 - V_1)}{V_0(C_0 - C)} \qquad (10)$$

where V_0 gives the initial volume, and V_1 the volume after removing solution for uranium analysis at the end of the fixation experiment.

Uranium fixation and remobilization with 0.1M Na₂CO₃

Figure 1 shows a typical kinetic curve for the uranium total fixation and reversible fixation with 0.1M Na_2CO_3 under the experimental conditions of this study. It can be seen that after three weeks the total fixation of aqueous uranium was almost completely achieved ($P_{tot} > 99\%$), whereas the reversibility of the uptake as achieved with 0.1M Na_2CO_3 was less than 10% (P_{rev}) after one month. Based on this observation, a minimal fixation duration of one month was selected for further experiments aiming at investigating the uranium release from iron oxides by processes likely to occur in nature. In one experiment the coprecipitation was promoted by the addition of pyrite (FeS_2, d_2) and an experimental duration of three months. As discussed elsewhere,[12] Na_2CO_3 is not able to dissolve nor to transform iron oxide. On the other hand, the use of 0.1M Na_2CO_3 as remobilizing agent has been shown to be inadequate since its employment yields to elevated Na^+ concentration at high pH values and therefore to a likely formation of sodium uranates such as Na_2UO_4. Uranates formation induces an underestimation of the reversibility of U removal since U in uranates is supposed to be irreversibly fixed onto iron oxides.[27] This study investigates some plausible scenarios likely to occur in nature to gain a realistic idea on the reversibility of coprecipitated uranium both in wetlands and reactive barriers.
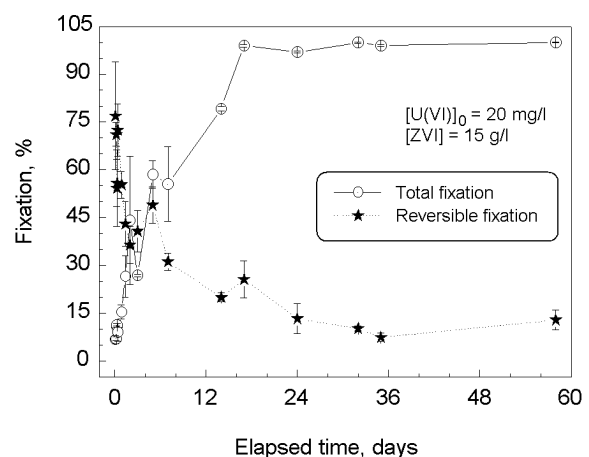

Fig. 1. Evolution of total and reversible uranium(VI) fixation from aqueous solution by scrap iron (ZVI) as a function of time. The recovery experiments were conducted in 0.1M Na_2CO_3. Error bars give standard deviations (triplicate experiments). The lines are not fitting functions, they simply join the data points to facilitate visualization

Effects of various factors on the mobilization of coprecipitated uranium

There are two major possible pathways that can induce the release of coprecipitated uranium: (1) local change of the solution chemistry; changes in pH or E_H for example by infiltration of waters from acidic or reduced zones. Alternatively this change can be the result of the weathering of available minerals (e.g., FeS_2). (2) dissolutive transformation of iron oxides (e.g., complex formation by infiltrating chelating agents, biotic and abiotic iron oxide reduction).

To gain an impression on the fate of the coprecipitated uranium as corrosion products are transformed in the environment, calculated amounts of target additives were added to reaction vessels after two months of uranium fixation to achieve the given final concentration of the transformation agents. Mobilization agents were pyrite (d_3, d_4), 0.1M Na_2CO_3 as reference desorption agents for laboratory investigations, 10mM EDTA as an environmentally relevant complexing agent, and 1.25% $TiCl_3$ as iron oxide reducer. Note that EDTA can increase the dissolved concentration of U(VI) by two processes: by remobilization of adsorbed or precipitated U(VI) and by dissolution of iron oxides.

Figure 2 summarizes the results of U(VI) recovering (P_{rec}) by the enumerated agents for an experimental duration of 14 hours. The U(VI) removal efficiency varied from 0.3% to 40% depending on the treatment agent. As shown in Fig. 2, the two different particle sizes of the used pyrite gave the same recovery efficiency of about 0.3% (the lowest). The recovery efficiency by EDTA was about one half of that of Na_2CO_3 (1.3%) for the experimental duration. However, it can be expected that the recovery efficiency for EDTA will increase with the time since the complexation kinetics by EDTA depends on the crystallization grade of iron oxides.[18] Finally the recovery efficiency for the system including $TiCl_3$ was about 40% for the 14 hours. It should be emphasized that, although the reduction of all Fe(III) contained in the available amount of corrosion products in each vessel is completed, a total recovery of U(VI) can not be expected since U(VI) also adsorbs onto Fe(II) colloids.[12]

The above experiments show that partial or total dissolution of iron oxides in wetlands or reactive barriers will be associated with a release of sequestrated U(VI) into the environment. Note that the experiment with $TiCl_3$ solely shows the fate of the coprecipitated U(VI) qualitatively, as iron oxides are reduced. A quantitative characterization is almost impossible under the experimental conditions of this work because of the complicated interactions between U(VI) and Fe(II) and Fe(III) with increasing pH.[12] However, new concepts have to be developed to characterize the fate of coprecipitated U(VI) in the environment as physical,

chemical or biological transformations of corrosion products occur.

Effect of local acidification

The effect of local acidification was studied by two sets of experiments. The first used various particle sizes of pyrite (d_1 to d_5) and both fixation and recovery experiments were conducted for 30 days (Fig. 3). The second set used a pyrite particle size d_5 (0.63<d (mm) <1.0), the fixation experiment was conducted for 30 days and the recovery experiment was conducted for 0 to 50 days (Fig. 4).
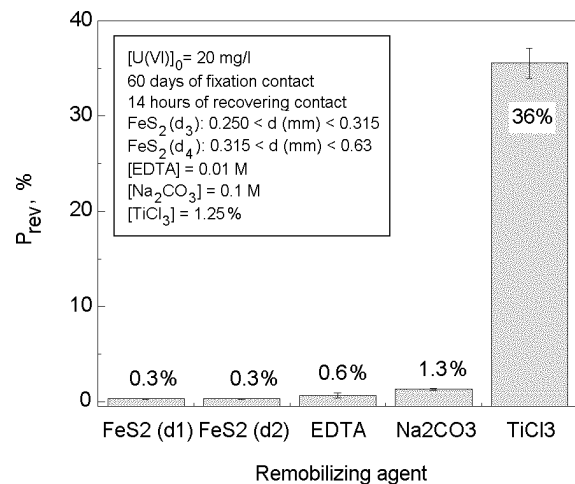

Fig. 2. Percent recovery P_{rev} of uranium from ZVI and corrosion products by different remobilizing agents for 14 hours. P_{rev} = 0.3% corresponds to a concentration of 60 μg/l (>30 μg/l, MCL of the US EPA). Error bars provide standard deviations (triplicate experiments)
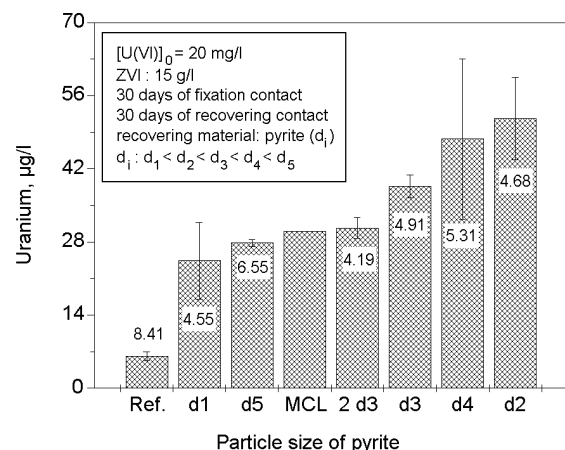

Fig. 3. Uranium remobilization (ppb or μg/l) from ZVI and corrosion products by different particle sizes of 25 g/l pyrite (d_i). One experiment (2 d_3) was conducted with a double amount of pyrite d_3 (50 g/l). The reference consisted in an accompanying experiment without pyrite addition (P_{tot} = 99.97%). MCL = 30 μg/l is the maximum contaminant level of the US EPA. The values on the bars indicated the final pH. Error bars provide standard deviations (triplicate experiments)
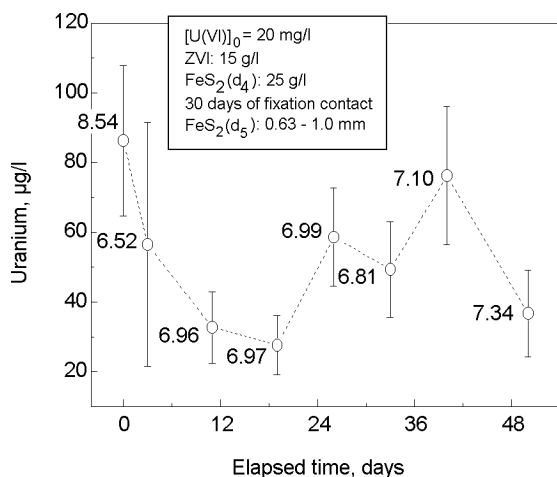
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Fig. 4. Uranium remobilization (ppb or $\mu g/l$) from ZVI and corrosion products by 25 g/l pyrite (d_5) as function of time. The experimental point at $t = 0$ (pH 8.54) represents the solution at the end of the fixation experiment (no pyrite addition; $P_{tot} = 99.4\%$). The values on the curve indicated the pH. Error bars provide standard deviations (triplicate experiments). The lines are not fitting functions, they simply join the data points to facilitate visualization

Figure 3 shows that the addition of pyrite either induces the uranium release or delays its uptake. Towards the end of the experiment, the U(VI) concentration in the reference system (ZVI alone, 60 days fixation) was 6.1 µg/l and, together with that in the systems with FeS$_2$ (d_1) and FeS$_2$ (d_5), was below the US EPA maximum contaminant level (MCL = 30 µg/l). In all other systems (FeS$_2$: $2d_3$, d_3, d_4, d_2) the uranium concentration was above the MCL. This suggests that a local acidification can release coprecipitated U(VI) in wetlands and permeable barriers. From the variation of the pH value with the particle size (Fig. 3) it is apparent that, the smaller the particles (d_1 being the smallest), the lower the pH value. This implies that reactivity increases with decreasing particle size in accordance with other observations in the literature.[29] This tendency is not confirmed by the order of efficiency of U(VI) release: $d_1 < d_5 < 2\ d_3 < d_3 < d_4 < d_2$. These results are not surprising since the impact of pyrite is twofold and conflicting: acidifying the solution (therefore, promoting U(VI) release) as discussed and adsorbing uranium (lowering U(VI) concentration). The results for both systems with FeS$_2$ (d_3) illustrates this clearly. In fact, the "FeS$_2$ (d_3)" system with 25 g/l pyrite induced a smaller pH decrease than "FeS$_2$ ($2\ d_3$)" with 50 g/l pyrite. The U(VI) release was lower in the system with 50 g/l pyrite due to the adsorption onto the pyrite material. The behavior of the system for 25 g/l pyrite (d_5) was further investigated for 50 days (Fig. 4).

Figure 4 shows that the variation of pH with time was not uniform. The pH first decreased as a result of the addition of pyrite (FeS$_2$ dissolution) from an initial value of 8.54 to a minimum of 6.52 after 3 days and again increased to 7.34 at the end of the experiment (day

50). The evolution of the uranium concentration was not synchronous. The uranium concentration decreased in all cases as a result of pyrite addition. The decrease was initially uniform from the beginning up to day 19, then a progressive increase occurred until day 40 and the concentration decreased again to the end value (37 µg/l>MCL). It should be noted that the variation of the pH value was not noticeable, a smaller particle size of pyrite (e.g., d_2 or d_3) would have permitted a better discussion of the processes. Nevertheless, the competing processes (fixation through adsorption and mobilization through acidification) governing the U(VI) release could be addressed. The large variation within the triplicates (error bars on Fig. 4) provide an impression of the likely complexity of the involved processes.

Effects of reductive transformation of iron oxides

Investigating the reductive transformation of iron oxides and their impact on trace metal (e.g. As^{5+}, Cr^{6+}, U^{6+}) mobility in the environment receives an increasing interest since the major uptake mechanism of several contaminants by Fe^0 materials is not their chemical reduction.[2,20,30] It is apparent from Fig. 2 that from the coprecipitated uranium (30 days with ZVI), approximately 40% could be resolubilized within 14 hours in the presence of 1.25% TiCl$_3$. To further investigate this finding another fixation experiment was conducted for three months in the presence of 25 g/l FeS$_2$ (d_2) (system "ZVI+FeS$_2$ (d_2)"). The uranium release was recorded as a function of time (for 57 hours). Figure 5 shows that the uranium release initially increased rapidly with time (first 12 hours) and then reached a plateau (hour 12 to 36). After that the release rate tended to decrease. The error bars show that the standard deviation (s) of the triplicates was very large within the first six hours and at the end of the experiment ($s > 4\%$). Maximum remobilization efficiency in this experiment (27%) was less than the 40% in the absence of pyrite (14 hour experiment with 30 day fixation). As discussed elsewhere,[11,20] the U(VI) uptake was delayed in the system with pyrite (ZVI+FeS$_2$), yielding to a progressive U(VI) coprecipitation with aging iron oxides around pH 4. This result clearly indicates that the particular moment at which U(VI) is associated with native iron oxide (reactivity, crystallization degree) is essential for the stability of the coprecipitated U(VI). Future investigations will have to address this aspect.

Discussion and conclusions

The widespread evidence for various degrees of irreversible uptake of contaminants by soils and soil minerals has been reported.[4,7,8,9,17] Recent results in the context of groundwater remediation with so called

passive techniques have demonstrated the importance of irreversible contaminant removal by iron oxides.[2,11,12,30] However, the existing transport codes do not typically account for irreversible contaminant uptake by the rock/soil matrix.[5]

Our work demonstrates that the remobilization of U(VI) from iron oxides is determined by three factors: (1) the age and the crystallinity of iron oxide, (2) the contact time of the contaminant with iron oxides, and (3) kinetics of the coprecipitation reaction. Typically, if U(VI) is adsorbed onto aged corrosion products, the fixation mechanism is ion-exchange and the reaction is almost completely reversible. Sorption onto amorphous iron hydroxides [$Fe(OH)_3$] is often observed to be irreversible over time spans exceeding years.[5] This irreversibility is promoted if amorphous $Fe(OH)_3$ is generated and allowed to age in the presence of U(VI); in this way, U(VI) is entrapped in the matrix of aging $Fe(OH)_3$: that is the process of coprecipitation.[6,11] Therefore, U(VI) can only be released if the oxide is destroyed (dissolutive transformations).

The rate and extent of U(VI) dissolution in the individual systems depend on its association with the oxide. ENG et al.[9] reported that U(VI) present as oxyhydroxide or polyuranate species undergoes rapid dissolution followed by a slow dissolution of iron, while inner-sphere complexation of U(VI) with iron resulted in concomitant dissolution of U(VI) and Fe. A thorough understanding of the association of uranium with iron oxides at the molecular level is useful for the prediction of the long term stability of coprecipitated U(VI) in passive decontamination processes.
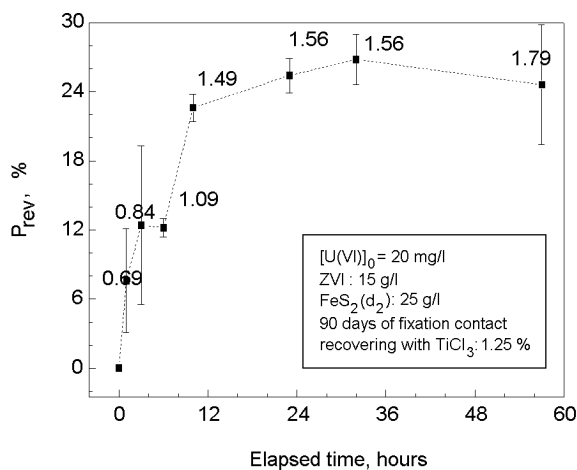
Some scenarios of oxide dissolution are presented in this study. The acidic dissolution through pyrite weathering and the dissolution through complex formation are surely possible in an aquifer. The reductive dissolution, as investigated in this study ($TiCl_3$ at low pH, Fig. 5), is solely of qualitative importance. Better results can be obtained with selected reducing agents, efficient at neutral pH values (e.g. 0.008M Ti^{3+} in 0.05M EDTA at pH 6).[23] It can be expected that in nature enzymatic oxide reduction will play a more important role than abiotic reduction.

To access the long term stability of coprecipitated U(VI) in any specific case, a fundamental understanding of the likely range of groundwater compositions over time and their effect on iron oxides in the future is needed. Among the factors to be considered the following are very important: (1) weathering of soil minerals, (2) atmospheric inputs, and (3) biological activity.

Finally, since drastic changes in the compositions of natural waters are more an exception than the rule,[5] it can be considered that the factors favoring U(VI) coprecipitation (in wetlands or reactive barriers) will be maintained far into the future. However, continuous surveillance and monitoring of the groundwater is needed in order to detect and evaluate eventual U(VI) release from the barrier zone. Moreover, alternatives for a satisfactorily U(VI) mitigation downstream from the barrier have to be envisaged.

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Fig. 5. Uranium remobilization from ZVI and corrosion products by 1.25% $TiCl_3$ as function of time. The fixation experiment was conducted for three months with 15 g/l ZVI and in the presence of 25 g/l pyrite (d_2) in order to favor U(VI) coprecipitation. The values on the curve indicated the pH. Error bars provide standard deviations (triplicate experiments). The lines are not fitting functions, they simply join the data points to facilitate visualization

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