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Mechanism of Uranium Removal from the Aqueous Solution by Elemental Iron

Noubactep C.,*[(a)] Schöner A.,[(b)] Meinrath G.[(c, d)]

[(a)] Centre of Geosciences - Applied Geology; Goldschmidtstrasse 3, D - 37077 Göttingen;

[(b)] Institute of Geosciences, Friedrich-Schiller-University Jena; Burgweg 11, D - 07749 Jena;

[(c)] Technical University Mining Academy Freiberg, Institute of Geology, G.-Zeuner-Str. 12, D - 09596 Freiberg;

[(d)] RER Consultants, Schießstattweg 3a, D - 94032 Passau.

(*) corresponding author: cnoubac@gwdg.de;

Tel. +49 551 39 3191, Fax: +49 551 399379

Abstract

The effectiveness of elemental iron (Fe^0) to remove uranium (U) from the aqueous phase has been demonstrated. While the mitigation effect is sure, discrepancies in the removal mechanism have been reported. The objective of this study was to investigate the mechanism of U(VI) removal from aqueous phases by Fe^0. For this purpose a systematic sequence of bulk experiments was conducted to characterize the effects of the availability and the abundance of corrosion products on U(VI) removal. Results indicated that U(VI) removal reactions did not primary occur at the surface of the metallic iron. It is determined that U(VI) co-precipitation with aging corrosion products is a plausible explanation for the irreversible fixation under experimental conditions. Results of XRD analyses did no show any U phases, whereas SEM-EDX analyses showed that U tended to associate with rusted areas on the surface of Fe^0. Recovering U with different leaching solutions varied upon the dissolution capacity of the individual solutions for corrosion products, showing that the irreversibility of the removal

depends on the stability of the corrosion products. U(VI) co-precipitation as removal mechanism enables a better discussion of reported discrepancies.

Key Words: co-precipitation, elemental iron, mechanism, removal, uranium.

1. Introduction

Groundwater at some contaminated sites has uranium-contents up to 50 mg/L.[1-3] This value is more than 1600 times larger than the US EPA threshold value of 30 µg/L. Therefore efficient, applicable and affordable techniques are necessary to mitigate the health risk by eliminating or reducing the removal of U from the mine water and contaminated groundwater. Elemental iron (Fe^0), widely termed in the literature on permeable reactive barriers as zerovalent iron, has been discussed as an U-removing reagent.[4,5] To be effective in the long term, any remediation technique for U must target both mobile aqueous U(VI)-species and U(VI)-precipitates that may be long term sources. Therefore, remediation with Fe^0 that possibly reduces mobile U(VI) aqueous species to less soluble U(IV) precipitates is very promising.[6] Furthermore, elemental iron could maintain reducing conditions in the subsurface, under which other electron donors besides Fe^0 (e.g. organics) may also contribute to U(VI) reduction.

Several U(VI) reduction methods for groundwater remediation have been proposed including application of Fe^0,[4,6,7] application of mixed ferrous/ferric iron hydroxides,[8-12] and bioreduction.[13,14,15]

Information regarding the mechanism of U(VI) removal by Fe^0 is confusing and even conflicting.[16-18] For example Cantrell et al.[4] used thermodynamic calculations to predict reduction of U(VI) to U(IV) not only as a possible, but also as eventual dominant reaction pathway. This conclusion was experimentally supported by Abdelouas et al.,[19] Farrell et al.,[7] Gu et al.[6] Based on the paper of Gu et al.[6] a clear trend for “reductive precipitation of

U(VI) by Fe^0" can be observed in the recent literature.[18,20-24] However, the initial experimental conditions of these authors were not adequate for appropriate conclusions.[16,25] Moreover, available field data are not consistent with quantitative U(VI) reduction by Fe^0.[20, 26] On the other hand, Morrison et al.[22] stated that no U(IV)-phases were reported, whereas Abdelouas et al.[19] reported the identification of poorly crystallized $UO_{2(s)}$. Note that Cui & Spahiu [27] reported U(VI) reduction to $UO_{2(s)}$ on the top of green rust (a corrosion product), whereas from the works of Behrends and Van Cappellen[11], Charlet et al.[8], Jeon et al.[12], and Liger et al.[9] it is evident that Fe^0 may serve as a source of Fe(II) for an abiotic U removal process involving structural Fe(II) [$Fe^{2+}_{(s)}$] at the surface corrosion products.

In contrast, Qiu et al.[28] experimentally observed no reduction of U(VI) to U(IV) under anoxic conditions. This result was supported by Bostick et al.[29] and Fiedor et al.[30] Fiedor et al.[30] explained the absence of reduction with the fact that the purging mixture to maintain anoxic conditions contained CO_2. This CO_2 (dissolved HCO_3^- or CO_3^{2-}) forms stable complexes with U(VI) and favors its remaining in the bulk solutions. On the other hand, Qiu et al.[28] carefully characterized the reacted iron surface with scanning tunneling microscopy and X-ray photoelectron spectroscopy and concluded that "under certain conditions, Fe^0 can remove contaminants effectively without reduction". Note that Qiu et al.[28] also noticed that an extremely thick U(VI) film was formed in the absence of CO_2, when the reaction took place in a N_2-purged solution. The importance of CO_2-availability for the removal of U(VI) by Fe^0 was not further investigated and indicates that sorption may play an important role in this removal process, because CO_2-availability could avoid U(VI) accumulation at the surface of Fe^0.

In a reactive barrier, U(VI) removal will be the result of a competition between at least three possible processes: (1) U(VI) reduction by Fe^0 and certain corrosion products [including structural Fe(II) and green rust]; (2) U(VI) adsorption onto in situ generated iron corrosion products; and (3) U(VI) incorporation in the structure of ageing corrosion products (co-

precipitation). Therefore, it is very difficult to resolve the effect of specific redox reactions on U(VI) removal from the effects of other processes. Fortunately, a systematic sequence of bulk reactions can quench one process or the other. For example acidification to values < pH 5 will minimize adsorption and co-precipitation. Under these conditions, U(VI) removal should mostly result from Fe^0 reduction. Similarly, controlled dissolution of corrosion products after U(VI) removal may give some insights on the mechanism of its retention. Therefore, a variety of reactions (sorption, desorption, acidic or reductive dissolution, and iron oxide dissolution through complex formation) can be undertaken to improve the understanding of the interactions of U(VI) with Fe^0 in the aqueous solution.

The objectives of this study were to elucidate the mechanism of U(VI) removal from aqueous solution by Fe^0 in three steps:

- by characterizing the role of Fe^0 in U(VI) removal from an aqueous solution;
- by characterizing the effect of availability and reactivity of iron corrosion products on U(VI) removal;
- by conducting remobilization experiments with different leaching solutions.

For this purpose, batch experiments were carried out without mixing (stirring or agitating) the solutions with a constant amount of a well-characterized Fe^0 and fixed amounts of two known natural U adsorbents: pyrite mineral, FeS_2 (in two different fractions: d_1 and d_2) and manganese nodules, MnO_2. Leaching experiments were conducted with sodium carbonate (0.1 M), EDTA (0.01 M), hydrochloric acid (0.2 M) and $TiCl_3$ (1.25 %). The initial U(VI) concentration was 0.084 mM (20 mg/L) and the solid:solution ratio was 5 g/L for Fe^0 and MnO_2 and 15 g/L for FeS_2 respectively.

2. Theoretical Background on the applied methodology

The uncertainty on uranium removal mechanism by Fe^0 (adsorption, co-precipitation or reduction) is a controversial issue for the scientific community.[16,20,21,26] Initially, it was

believed that U(VI) would be removed by reductive precipitation.[4,6] The reduced form of U is less soluble and would provide the longest and safest long-term immobilization. However, published studies suggested that a significant portion of the U removed by Fe^0 would remain in the oxidized form.[7,16,20,26,28,30-32] At present, these evidently contradictory results have not been discussed.

Table 1 summarizes the possible involved mechanisms for the U removal. Among the listed mechanisms, the formation of uranyl-hydroxy compounds such as schoepite ($UO_3.2H_2O$) has not been discussed, even though many studies have used over-saturated U(VI)-solutions with respect to schoepite.[16] This is particularly important in the neutral pH range when the U concentration is above 10^{-5} M and a pH-shift can occur during the reaction. Reductive precipitation is the most suitable reaction pathway and has been considered for some years as a primary reaction mechanism. Surface catalysed U(VI) reduction by structural Fe(II) [$Fe^{2+}_{(s)}$] has also been reported (Eq. iv, ref. 8, 9, 11 and 12).

Table 2 summarizes some relevant reactions for the elucidation of the mechanism of U(VI) fixation by Fe^0 in this work. U(VI) removal is supposedly based on electrochemical corrosion of iron resulting in "reductive precipitation" of U(VI) according to Eq. 1 (Eq. iii in table 1). U(VI) can be reduced to U(IV) by structural Fe(II) (Eq. 2). Iron corrosion also produces molecular hydrogen (H_2) which is capable of chemically reducing U(VI) (Eq. 3). Therefore, establishing a reductive atmosphere by adding molecular H_2 (gas) is to be avoided when investigating possible reduction of U(VI) to U(IV). Thermodynamically, H_2 is capable of chemically reducing U(VI) to U(IV) and since it is a gas, the reduction can occur even if U(VI) is sorbed onto the Fe^0 surface (non-electrochemical mechanism). In the present study, no attempt has been made to control more parameters than in previous works.[16] The detailed conditions in a reactive barrier based on Fe^0 will certainly vary over its lifetime. In particular, it can not be expected that strictly anoxic conditions will prevail in the majority of reactive walls because they are installed at depths not greater than 15 - 22 m (50 - 70 feet deep).[34]

In the presence of an oxidant (molecular O_2 or MnO_2), Fe^{2+} formed from Eq. 1 will be oxidized to Fe^{3+}. If dissolved Fe^{3+} is present, UO_2 (resulting from Eq. 1, 2 or 3) can be re-oxidized according to Eq. 4, yielding dissolved Fe^{2+} and U(VI). This potential re-oxidation of UO_2 by Fe^{3+}[35] is often ignored in the reactive barrier literature.[16] Since the solubility of Fe^{3+} is very low in the neutral pH range, it will precipitate as $Fe(OH)_3$ and other secondary minerals (Eqs 5 & 6). In the presence of pyrite, there will be a competition (between pyrite and UO_2) for Fe^{3+}, see Eq. 7 (cf. Eq. 4). Hence, Fe^{3+} is not available to oxidize UO_2, and U(VI) concentration remains low. On the other hand, pyrite can reduce U(VI) yielding UO_2 precipitation according to Eq. 8.

Equation 9 illustrates the effect of manganese nodules (MnO_2) as Fe^{2+}-scavenger and potential accelerator of Fe^0 corrosion. If this is the case, and the mechanism of U(VI) removal by Fe^0 is “reductive precipitation”, U(VI) removal will be accelerated by the presence of MnO_2 (assumption 1). Equation 10 shows that Ti^{3+} is capable of inducing reductive dissolution of iron oxide and Eq. 11 shows that EDTA can dissolve iron oxides by complexing Fe^{3+} ions. In both cases it is essential that, if U is retained (at least in part) by adsorption onto iron oxides, their dissolution will release U in the aqueous solution (assumption 2). Finally as illustrated by Eqs 5 & 7, the addition of pyrite to a system can induce a pH decrease (H^+ production), which is known to increase U solubility (Eq. i in table 1).

In the presence of Fe^0 (covered by corrosion products) and pyrite, reactions 1 to 8 are possible. U(VI) removal should be governed principally by reductive precipitation. If the reaction vessel is closed, the acidification reaction due to Eq. 5 or pyrite oxidation through molecular O_2 will be limited. The removal of U(VI) from the aqueous solution can be due to each of the mechanisms from table 1: (a) U(VI) reduction by Fe^0, structural Fe(II) and/or FeS_2 (Eqs 1, 2 and 8); (b) sorption onto the surface of Fe^0, FeS_2 or onto iron corrosion products, and (c) formation of uranyl-hydroxy compounds.

Reductive precipitation through Fe^0 is more favored when the surface of the material is not covered by corrosion products (especially around pH 4) and sorption onto iron corrosion products (iron oxides) occurs favorably at pH > 5 (assumption 3). Thus, combining Fe^0 and limited amounts of FeS_2 into closed vessels is a suitable way to investigate the mechanism of U(VI) removal by both materials. It is expected that various experimental durations will yield various final pH values, thereby permitting the characterization of the impact of corrosion products on the removal process, especially their reactivity.

Similarly, combining Fe^0 and limited amounts of MnO_2 into closed vessels is a suitable way to investigate the influence of the availability of corrosion products on the process of U(VI) removal by Fe^0. Finally, adding HCl-, Ti^{3+}- and/or EDTA-solutions (or FeS_2-grains to induce a pH-shift) to a system consisting of U(VI) and Fe^0, which have reacted for a suitable period, is a suitable way to investigate the role of acidic, complexive, or reductive dissolution of iron oxides on the fate of fixed uranium, and therefore to deduce the mechanism of their initial fixation.

3. Experimental Section

3.1 Materials

The used scrap iron was selected from 13 materials because of its reactivity after the EDTA-test.[36,37] The material contained 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. Fe^0 was used as U(VI) reducing agent.

Manganese nodules from the deep sea were crushed and sieved. An average particle size of 1.5 mm was used comprising the following elemental composition: 41.8 % Mn, 2.40 % Fe, 2.41 % Si, 0.74 % Ni, 0.22 % Zn, 1.39 % Ca, and 0.36 % Cu. The target active component is MnO_2. MnO_2 is a Fe^{2+}-scavenger, supporting iron corrosion and retarding the availability of “free” corrosion products in the bulk.

Pyrite was crushed and sieved. The fractions 0.2-0.315 mm (d_1) and 0.315-0.63 mm (d_2) were used. The elemental composition 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 reagent, modifying the reactivity of corrosion products and the solubility of U(VI), hence inhibiting the precipitation of iron oxides at the surface of Fe^0.

Water works sludge (WWS) is typically a mixture of iron and manganese oxides, the detailed composition depending on the composition of the treated water. WWS from the Torgau water treatment plant (Saxonia, Germany) with a low content of 1.09 % Mn (43.9 % Fe, 6.2 % Ca, 5.42 % Si) was used as U(VI) adsorbent simulating aged corrosions products.

The used apatite was crushed and sieved, an average particle size of 1.5 mm was used with the following elemental composition: 26.7 % P, 36.8 % Ca, 0.83 % Fe, 0.72 % Si, and 0.13 % S. Apatite (a phosphate mineral) was used to remove dissolved U(VI) by adsorption or/and by the formation of low soluble phases.[38,39]

3.2 Fixation Experiments, Desorption with Na_2CO_3 and Analytical Method

The experimental procedure for the fixation experiments, the desorption by 0.1M Na_2CO_3 and the analytical method is described in detail elsewhere,[16] and will not be repeated here. Unless indicated otherwise, fixation studies consisted in three different non-shaken experiments with 5 g/L Fe^0, 5 g/L MnO_2 and 15 g/L FeS_2: I) Fe^0 alone (reference system); II) Fe^0 + MnO_2; and III) Fe^0 + FeS_2 (termed as systems I, II and III). Fe^0 and additives were allowed to react in sealed sample tubes containing 20.0 mL of an U(VI) solution (20 mg/L or 0.084 mM) at laboratory temperature (about 22° C). The experimental duration varied from 14 to 150 days. The tubes (16 mL graded) were filled to the total volume (20 mL) 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 ~6.6. Desorption experiments were conducted in a 0.1 M Na_2CO_3 solution for 14 h. Analysis for U was performed after reduction

to U(IV) with the ArsenazoIII method (detection limit: 25 µg/L).[40,41] Analysis for dissolved ferrous iron and total iron was determined using FerroVer iron reagent (HACH DR/2000 Spectrophotometer Handbook, Loveland, CO). The experiments were performed in triplicates. The mean values are presented in the figures.

The experiments were conducted in closed essay tubes under non-controlled O_2 (and CO_2) pressure. It is certain that P_{O2} was less than the atmospheric pressure. It can be assumed that U(VI) removal mainly occurred under very low O_2 partial pressure, since iron corrosion (and pyrite dissolution) is O_2 consuming.[42] Since strictly anoxic conditions are not expected in the majority of Fe^0 reactive walls,[34] working at low oxygen level ($P_{O2} < P_{O2,atm}$ and $P_{O2} \neq 0$) is probably a good simulation for groundwater situations at several sites.

3.3 Remobilization Experiments with pyrite, EDTA, HCl, $TiCl_3$ and Ti-EDTA

Prior fixation experiments were conducted for two months; then uranium remobilization occurred for 14 hours through addition of defined amounts of additives: pyrite (1g, two different particle sizes), EDTA (0.01 M), HCl (0.2 M), $TiCl_3$ (1.25 %) and a mixture of EDTA (0.01 M) and $TiCl_3$ (1.25 %). The selection of these reactants and their concentrations were motivated by literature data from Ford[43] and Heron et al.[44]

3.4 X-Ray diffraction and SEM analyses

The corrosion products of Fe^0 were identified by X-ray diffraction (XRD) analyses. Samples were prepared by retrieving iron fillings with a magnetic bar and filtering the suspended particles from the mixture of Fe^0 and U(VI) solution under laboratory conditions. The samples were then dried under laboratory conditions and pulverized for XRD analyses at the Institute of Physical Chemistry of the University of Freiberg. Under these experimental conditions, partial transformations of iron (oxyhydr)oxides and reoxidation of U(IV) by air oxygen are possible.[45]

Coupons of the same Fe^0 material (> 2.5 mm) were pre-washed for 14 hours in 0.2 M HCl and allowed to react in the identical way as the fillings. Scanning electron microscope (SEM) and Energy Dispersive Spectroscopy (EDS) of the coupons were conducted to examine the distribution of iron corrosion products and U coatings on Fe^0 at the Institute of Geology of the University of Freiberg.

4. Results and Discussion

The experiments were compared on the basis of the total fixation P_{tot} (in %) defined by Eq. 13

$$P_{tot} = 100\ \% * (1 - (C/C_0)) \qquad (13)$$

where C_0 is the initial concentration of uranium in solution, while C gives the uranium concentration after the experiment. The percent recovery, P_{rec}, of uranium after finishing the experiment (recovery with 0.1 M Na_2CO_3, 0.1 M HCl, 0.01 M EDTA, $TiCl_3$, TiEDTA or FeS_2) is calculated by Eq. (14)

$$P_{rec} = 100\% \frac{C_0(V_0 - V_1)}{V_0(C_0 - C)} \qquad (14)$$

where V_0 gives the initial volume, and V_1 the volume after removing about 13 mL for uranium analysis.

4.1 Evidence of progressive U(VI) removal in the presence of Fe^0

Figure 1 compares three fixation curves of U(VI) removal from aqueous solution by WWS, apatite and Fe^0. While physical adsorption is the major mechanism responsible for uranium removal by WWS, both adsorption and precipitation can remove U(VI) in experiments with apatite (chemical precipitation) and Fe^0 ("reductive precipitation"). As shown on Fig. 1, adsorption onto WWS (aged corrosion products) and adsorption or chemical precipitation by apatite (a PO_4^{3-} bearing mineral) are relatively rapid and are achieved within the three first days of contact. U(VI) removal through Fe^0 was also effective but slow and still continued

even after 50 days. Since the reaction vessels were not shaken, U(VI) removal by Fe^0 can be the result of U(VI) adsorption onto progressively generated corrosion products or the result of a slow electrochemical reduction through Fe^0. Shaking the reaction vessels would have yielded a rapid production of corrosion products and their removal from the Fe^0 surface, keeping the surface free for eventual "reductive precipitation".[46] However, it is the aim of this study to characterize the role of corrosion products present at the surface of Fe^0 as it will be the case in subsurface reactive walls.[37]

The major conclusion from Fig. 1 is qualitative: aged corrosion products can rapidly remove U(VI) from the aqueous solution; this reaction has been recognized for years.[47-49] U(VI) sorbed onto aged corrosion products can be readily recovered (desorption) in a 0.1 M Na_2CO_3 solution.[16,50] The observed progressive U(VI) removal using Fe^0 over a long period validates the efficiency of the chosen experimental conditions (non-shaken batch experiments) to elucidate the mechanism of U(VI) removal from aqueous solutions by Fe^0. The experiments described consecutively target better characterization of progressive U(VI) removal by Fe^0.

4.2 Effect of the presence of MnO_2 and FeS_2 on U(VI) removal by Fe^0

A popular hypothesis to rationalize irreversible fixation of U(VI) by Fe^0 is the U(VI) reduction to less soluble U(IV) species or "reductive precipitation".[6,7,21,24] Shortcomings in the applied experimental procedures have been discussed. In particular, starting pH and total initial U concentration indicate that precipitation phenomena may have spoiled the reported results.[16] Furthermore, the authors have conducted shaken batch experiments for periods varying from few hours to few days. A reactive barrier is however expected to work for decades. It is therefore important to conduct laboratory experiments for longer times (here up to 150 days) to better characterize the interaction between U(VI), Fe^0 and corrosion products. In the present study and related works,[16,50,51] two natural materials (MnO_2 and FeS_2) were

employed to modify the behavior of the reference system consisting of U(VI) and Fe^0 in tap water of the city of Freiberg (Saxony, Germany).

The results of U fixation and recovery in 0.1 M Na_2CO_3 were given by Noubactep et al.[16] Two main observations were made from the fixation experiments: (1) the best fixation rate is achieved when Fe^0 is present alone (system I) and the least efficient was system III (Fe^0 + FeS_2); (2) system II (Fe^0 + MnO_2) is a delayed reproduction of system I (Fe^0 alone).

The first observation suggests that the dominant mechanism of the U(VI) removal from the aqueous phase is not "reductive precipitation" because neither assumption 1 (favor U(VI) reduction through MnO_2 addition) nor assumption 3 (favor U(VI) reduction through FeS_2 addition) is verified. The second observation suggests that the availability of "free" corrosion products influences the efficiency of U(VI) removal by Fe^0. This hypothesis was confirmed by varying the amount of MnO_2.[50] The results showed that the larger the amount of MnO_2, the lesser the U(VI) fixation efficiency for the same experimental duration. The major conclusion from fixation experiments is that the presence and the amount of corrosion products influence U(VI) removal by Fe^0.

To investigate the effect of reactivity of the corrosion products on the removal process, the pH was varied by varying the contact time with pyrite (system III), attending various dissolution/oxidation rates. The result shows that U(VI) removal was considerably retarded (starting 40 days after the beginning of the experiment) and that the fixation efficiency first decreased with decreasing pH. Then U(VI) removal increased rapidly between day 40 and day 90 practically at constant pH. The final pH was below 5; therefore a quantitative adsorption onto the surface of iron corrosion products was not likely. A thoroughly discussion of this experiment is given elsewhere.[51] It was shown that U(VI) removal is accompanied by a decrease of iron concentration. This result is supported by the pH dependency of iron speciation. Fe^{2+} species are more soluble than Fe^{3+} species, which undergo appreciable hydrolysis in aqueous solutions to form $Fe_x(OH)_y^{(3x-y)}$. As the solution pH increases, the ferric

state is stabilized relative to the ferrous state because of the higher affinity of Fe^{3+} for the hydroxide ion relative to Fe^{2+}.[52] U(VI) is then entrapped in the mass of these precipitating hydroxides according to the schematic reaction:

$$n\ Fe_x(OH)_y^{(3x-y)} + UO_2^{2+} \Rightarrow UO_2[Fe_x(OH)_y^{(3x-y)}]_n^{2+}$$

Beside the pH values, the iron and U concentrations, the Eh values and the iron speciation were measured in system III, where variations were expected owing to the evolved possible reactions (Eqs 1 to 4 and Eqs 7, 8 - Tab. 2). Because of the limited volume of samples the solution parameters (pH and Eh) were measured once for each triplicate 24 hours after the end of the fixation experiment. The results showed a decreasing Eh value with increasing experimental duration.[51] This observation is consistent with the fact that both iron corrosion and pyrite oxidation consume oxygen and care for low O_2 level. This observation was also confirmed by the iron speciation. In fact, the solutions still contained more that 50 % ferrous iron (Fe^{2+}) even though the speciation was not performed immediately at the end of the experiment and no attempt was made to protect the vessels from air oxygen. Therefore, air oxygen would have oxidized a considerable part of Fe^{2+} during this time (24 h).

To access the reversibility of the U fixation, desorption experiments were conducted with 0.1 M Na_2CO_3.[16] The results showed that P_{rec} was comparatively high during the first 25 days for system I and system II. Afterwards, P_{rec} decreased steadily and was almost zero for both systems after 125 days. In system III (Fe^0 + FeS_2), the fixation was nearly irreversible during the whole experiment. This is not surprising because U(VI) removal is accompanied by iron precipitation. U(VI) was therefore enclosed in the matrix of precipitating iron oxides and was not available for desorption with Na_2CO_3. The co-precipitation reaction of U(VI) with iron oxides was well described in another context by Dodge et al.[53], Duff et al.[54], and Eng et al.[55] The extent of U(VI) co-precipitation by corrosion products of carbon steel was thoroughly characterized by another research group.[53,55] These authors also report about a differential recovery efficiency of surface-sorbed and co-precipitated U(VI). Particularly, for

maghemite, magnetite and goethite, U(VI) species were associated as oxyhydroxide species and were readily dissolved in concentrated HCl solution, but for lepidocrocite and ferrihydrite U(VI) species formed a bidentate complex with iron, which resisted acidic dissolution.[53] Both U(VI) and U(IV) are soluble in Na_2CO_3.[56] Hence, this observation can only be explained by formation of amorphous aged iron corrosion products enclosing U since corrosion products are not soluble in carbonate solution. Therefore, it was concluded that the U(VI) removal was the result of the co-precipitation of U(VI) with aging corrosion products.

4.3 Arguments for U(VI) co-precipitation with aging corrosion products

Reported experiments for elucidating the mechanism of U(VI) removal by Fe^0 have been mostly conducted under shaken or stirred conditions. These experimental tools are sometimes suitable for adsorption experiments, in which no reaction between tested materials and water is expected, respectively as long as the tested material is not broken down (into small pieces) during the experiment.[57,58] In the case of Fe^0, however, aqueous iron corrosion is well known and documented for more than one century.[59-62] Therefore, shaking the reaction vessels causes intensive iron corrosion, thereby producing more corrosion products.[63] On the other hand, shaking continuously frees corrosion products from the iron surface, potentially making the surface available for U(VI) reduction.

The possible U(VI) reduction through shaking is a probable reason for the identification of "poorly crystallized $UO_{2(s)}$" reported by Abdelouas et al.[19] It is not surprising that all other authors could not identify any uranium phases.[22] About 5 % of the initial amount of Fe^0 was consumed under the experimental conditions of this work, which yielded to a Fe:U molar ratio of 154 in the mass of corrosion products (Tab. 3). That is 0.65 % weight of not crystalline U(VI) entrapped in the mass of (partly amorphous) iron oxides, therefore non-detectable by X-ray diffraction for example. Because other authors have used larger amounts of Fe^0 (solid to solution ratios up to 200 g/L) under shaken or stirred conditions, it can be assumed that

more corrosion products were formed to entrap U(VI). Table 3 shows that under the experimental conditions of Abdelouas et al.[22], 0.06 to 45 % U (molar Fe:U = 554 to 1662) can be present in the mass of corrosion products when the Fe^0 consumption varies from 5 to 15 %. For the same Fe^0 consumptions, the percent U in the mass of corrosion products varies from 7.5 to 18.6 % under the experimental conditions of Gu et al.[6] This result shows that in both cases, sufficient amounts of corrosion products were present to entrap U(VI) in their matrix, making them inaccessible for desorption with Na_2CO_3. Note that although Gu et al.[6] used Scanning Electron Microscopy (SEM), Energy Dispersive X-Ray Spectroscopy (EDX), and X-ray Fluorescence Spectroscopy (XFS) analyses to study the "reductive precipitation and coating of U on Fe^0 surface" they could not identify any U(IV) phase. Furthermore, their XFS analysis was limited at showing that supposedly U(IV) remained at the surface of Fe^0. As discussed above, U(VI) can be either accumulated at the surface of Fe^0, precipitated for instance as schoepite ($UO_3.2H_2O$), or entrapped in the mass of corrosion products. Speciation data on U(VI) removal from groundwater in Fe^0 permeable reactive barriers at several sites support the formation of partially oxidized U deposited on Fe^0 media. Matheson et al.[26] reported approximately equal amounts of U(IV) (~55 %) and U(VI) (~45 %) in anoxic samples from Y-12 Plant in Oak Ridge (Tennessee) and ~80 % U(VI) in oxic samples. At Bodo Canyon Site (Durango, Colorado) uranium was present nearly exclusively as U(VI). Table 4 presents uranium speciation in four field Fe^0 reactive barriers (ref. 5) after service life of up to three years. These results clearly show that under actual field service conditions U(VI) reduction through Fe^0 is not quantitative, even though, beside reduction through structural Fe(II), microbial activity might have contributed to U(VI) reduction.[64,65]

Another important fact in favor of U(VI) co-precipitation with aging corrosion products is given by Morrison et al.[22], who conducted laboratory column experiments under anoxic conditions and could not accurately model their results according to reductive precipitation or U(VI) adsorption onto Fe(III) oxides. They stated that "while a reductive precipitation

mechanism is not inconsistent with the results of the laboratory column experiment, the decrease in Eh in the bulk is suspect. Other mechanisms of U removal such as adsorption on ferrous hydroxide or incorporation into mineral structures of ferrous hydroxide or magnetite are also possible". Note that they came to this statement because they used experimental conditions under which sorption onto iron oxides was inhibited (higher pH, higher dissolved carbon). In fact, regardless from the nature of corrosion products (oxic or anoxic conditions) the present work has shown that the accessibility of the surface of Fe^0 for U(VI) is almost impossible since corrosion products with higher affinity to U(VI) are formed on the surface of Fe^0. Even though these corrosion products are porous, it is not expected that adsorbed U(VI) will quantitatively diffuse to the surface of Fe^0. Ciu & Saphiu[27] reported that green rust on Fe^0 was more efficient than Fe^0 for U(VI) removal. This experimental result is supported by the Eh value for the solid state redox system [Fe(II)–Fe(III)] from White and Paterson (–0.34 to –0.65 V),[66] possibly making structural Fe(II) a more stronger reducing agent than Fe^0 [E° for the redox system Fe(0)–Fe(II): –0.44 V].

Abdelouas et al.[19] also used a solution of ETDA to avoid the formation of corrosion products and demonstrated the reductive precipitation as mechanism of U(VI) removal by Fe^0. At the same time they did not mention the capacity of EDTA to form complexes with U(VI) and to accelerate iron corrosion. Iron corrosions yields to a complex mixture in which U(VI) will surely be entrapped without having any ability to reach the surface of Fe^0 since U(VI) solubility may increase by EDTA complexation (e.g. ref. 67).

Further arguments for U(VI) co-precipitation with aging corrosion products were given from investigations of U(VI) removal from contaminated carbon steel surfaces.[53,55] The surface of steel coupons was exposed to uranyl nitrate [$UO_2(NO_3)_2$] solution. This operation led to the formation of a lightly corroded surface that was investigated using various spectroscopic techniques including X-ray Photoelectron Spectroscopy (XPS) and Scanning Electron Microscopy / Energy Dispersive Spectroscopy (SEM/EDS). The results showed that: (1)

U(VI) tends to associate with lepidocrocite [FeO(OH)] and hydroxyl-rich areas on the surface of actively corroding steel; (2) U(VI) is well distributed within the upper micron of the corrosion layer and, (3) U(VI) is occluded by corrosion products as indicated by XPS. Similar to the present study, occluded U(VI) was not efficiently removed from the surface by a citric acid/hydrogen peroxide cleaning method, which successfully extracted U in lightly corroded areas.[55]

The investigation of the stability of U(VI) enclosed in the matrix of corrosion products is of major importance. EDTA will play a key role in this effort (assumption 2).

4.4 Impact of iron oxide transformations on remediation efficiency

It is important to investigate the impact of possible transformations of iron oxides on the remediation efficiency (long term stability of co-precipited uranium). The main possible transformation is dissolution (reductive, acidic, Eqs 10 and 12 in Tab. 1, or microbial). In nature, complexation of iron may also yield to U(VI) release (Eq. 11, Tab. 1).

To gain an impression on the fate of fixed U(VI) as corrosion products are transformed in the environment, a fixation experiment with 15 g/L Fe^0 and 20 mg/L U(VI) was conducted for 60 days in tap water of the city of Jena (Thuringia, Germany); the achieved total fixation was > 99 %. Afterwards, calculated amounts of target solution were added to the vessels to achieve the final concentration of the transformation agents. In two sets of experiments the remobilization agent was pyrite of two different particle sizes (pyrite 1: 0.2-0.315 mm and pyrite 2: 0.315-0.63 mm). The modification with pyrite aimed at simulating a local transformation that can lower the pH, increasing the solubility of U.[25,51] The other modification agents were: (a) 0.1 M Na_2CO_3 as reference desorption agent for laboratory investigations; (b) 0.01 M EDTA as an environmental relevant complexing agent; (c) 0.2 M HCl as strong iron oxide digester (acidic dissolution); (d) 1.25 % $TiCl_3$ as iron oxide reducer; (e) and a mixture of 0.01 M EDTA + 1.25 % $TiCl_3$.

Figure 2 summarizes the results of U(VI) recovering (P_{rec}) by the enumerated agents for an experimental duration of 14 hours. As shown in Fig. 2, the two different particle sizes of the employed pyrite gave the same recovery rate of about 0.3 % (the lowest) whereas the immobilization rate for 0.2 M HCl was the highest (almost 100 %), suggesting that destroying iron corrosion products will yield to U(VI) release into the environment. The recovery efficiency by EDTA was about one half of that of Na_2CO_3 (1.3 %) for the experimental duration (14 h). However, it can be expected that the recovery efficiency for EDTA will increase with time since the kinetics and the extent of complexive dissolution depend on the crystallization grade of iron oxides. Therefore assumption 2 [favor of U(VI) release through EDTA] is verified confirming that reductive precipitation is not the major pathway of the U(VI) removal by Fe^0. Finally, the recovery efficiency for both systems including $TiCl_3$ was about 40 % for the 14 hours. It should be emphasized that, even if the reduction of all Fe(III) contained in the available amount of corrosion products in each vessel is completed, the total recovery of U(VI) can not be expected since U(VI) also adsorbs onto Fe(II) colloids (ref. 16 and references therein).

This experiment shows that partial or total dissolution of some corrosion products in a reactive barrier will be associated with a release of sequestrated U(VI) into the environment. These experiments solely show qualitatively the fate of co-precipitated U(VI), as iron corrosion products are transformed. 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.[16] However, intelligent concepts have to be developed to characterize the fate of co-precipitated U(VI) in the environment as physical, chemical or biological transformations of corrosion products occur.

4.5 Identification of reaction products

The reaction products were identified by XRD and SEM/EDX.

X-ray diffraction spectra of corrosion products showed the presence of lepidocrocite, goethite, magnetite and/or maghemite and no single U phase.[25] Amorphous compounds will not be seen in a XRD spectrum. Therefore, U species (IV or VI) present in the matrix of corrosion products may mostly be amorphous.

Scanning electron microscopy images of Fe^0 coupon surface showed iron oxyhydroxides (termed as FeO in Tab. 5) on the surface, which is probably a layer of corrosion products. This external layer may physically shield other U containing corrosion product layers.[53,55] Fig. 3 and Tab. 5 show that U is not uniformly distributed at the coupon surface. Rather, U tends to accumulate in corroded regions of the Fe^0 surface (P_3 on Fig. 3). This observation is justified by the discussed larger affinity of corrosion products for U and corroborates U(VI) co-precipitation with iron corrosion products as a major removal mechanism. Thus, U containing regions are probably rusted regions of initial accelerated corrosion. Eng et al.[55] observed by means of FTIR spectroscopy, that the uranyl ion is associated with iron corrosion products throughout the corrosion product layer formed on steel coupons. Their X-ray photoelectron spectroscopy results indicated a clear U(VI) incorporation within layers of corrosion products. This co-precipitation was more evident when a thin native oxide layer was generated in situ in the presence of U.

5. Conclusions

The interactions between U(VI), Fe^0 and corrosion products in bulk U(VI)/ Fe^0/additive-systems were characterized under reaction conditions pertinent to natural aquatic environments. The results provide no evidence for quantitative U(VI) reduction by Fe^0 over the entire range of reaction conditions ($4 < pH < 8$). Rather, U(VI) removal by Fe^0 is mostly caused by co-precipitation of adsorbed U(VI) with aging corrosion products. This concept is consistent with many experimental observations, for instance under conditions as retarding the availability of “free” corrosion products, respectively controlling their amount by MnO_2

and modifying their reactivity by FeS_2. Even under anoxic conditions, generated corrosion products have greater affinity for U than the bare Fe^0 surface. Furthermore, these corrosion products are produced on the surface of Fe^0. Therefore, it is very probable that the success of Fe^0 in mitigating U(VI) in groundwater relies on a continuous generation of corrosion products which immobilize U(VI) by entrapping it in their matrix while aging. Field speciation data by Matheson et al.[26] are consistent with U(VI) co-precipitation with iron corrosion products as major removal mechanism.

It is commonly assumed, that contaminant removal in Fe^0 reactive barriers occurs principally under anoxic condition since molecular oxygen is consumed by iron corrosion in the barrier entrance zone.[42,68] The present work has shown that generated corrosion products (aged or nascent) are capable of fixing U(VI). Thus, U(VI) can only migrate across the entrance zone (pre-treatment zone[68]) if the adsorptive capacity of actual available corrosion products is exhausted. Therefore, in an operative barrier both adsorption onto aged corrosion products and co-precipitation with nascent iron oxides occur. Corrosion products form an active physical barrier avoiding the accessibility of the bare surface of Fe^0 materials to U(VI). This assertion is supported by experimental evidences from Huang and Zhang[69] who showed that dissolved oxygen is mostly consumed by Fe^{2+} rather than the surface of metallic iron (Fe^0). Therefore, reported U(VI) reduction in Fe^0 barriers may mostly result from structural Fe(II) reaction,[8,9,27] and/or microbial activity.[64,65]

With this study, the potential of bulk reactions with selected additives for providing mechanistic information on aqueous contaminant removal has been demonstrated. This applicable technique can be very useful to obtain qualitative information on Fe^0 removal mechanisms for several contaminants; particularly for other radionuclides, metals and some organics which are known to interact with iron oxide.[47,70,71] It is difficult from a practical standpoint to obtain quantitative information on processes or mechanisms because of the complex nature of corrosion products and the proportion of U species in their matrix. It can be

emphasized that co-precipitation or surface catalyzed reduction will govern the primary contaminant removal whenever strong interactions of the contaminant with corrosion products can be awaited. Selecting Fe^0 for remediation of such contaminants is simplified because reactivity is a unique function of the material dissolution (iron corrosion), and not of the specific interaction of the contaminant with the material.

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Figures Captions

Figure 1: Comparison of the kinetics of uranium removal with water works sludge (WWS), apatite and elemental iron (Fe^0). All experiments were applied in triplicate, error bars give standard deviations. The used particle size of the material was 1.6-2.0 mm. The used apatite contains around 36 % P and was not further characterized. The represented lines are not fitting functions, they just joint the points to facilitate visualization.

Figure 2: Percent recovery P_{rec} of uranium from Fe^0 and corrosion products by different agents for 14 hours. All experiments were applied in triplicate. P_{rec} = 0.3 % corresponds to a concentration of 60 µg/L (> 30 µg/L, MCL of the US EPA). Error bars give standard deviations. The percent recovery is given in/on the bars.

Figure 3: Scanning electron microscopy image of Fe^0 coupon after three months reaction time with 20 mg/L U(VI). The mineralogical composition of selected points (P1, P2 and P3) is shown in Tab. 5.

Table 1: Possible reaction pathways for U removal from the aqueous phase by Fe^0 under the experimental conditions and their reversibility under natural conditions.

Mechanism	**Reaction**	**Reversibility**	**Eq.**
Precipitation:	$UO_2^{2+}{}_{(aq)} + 2\ OH^- \Leftrightarrow UO_3.2H_2O_{(s)}$	Reversible	(i)
Sorption:	$UO_2^{2+} + S_{(sorption\ site)} \Leftrightarrow S\text{-}UO_2^{2+}$	Reversible	(ii)
Fe^0 Reduction:	$Fe^0 + UO_2^{2+}{}_{(aq)} \Rightarrow UO_{2\ (s)} + Fe^{2+}$	Irreversible	(iii)
$Fe^{2+}{}_{(s)}$ Reduction:	$UO_2^{2+} + 2\ Fe^{2+}{}_{(s)} \Rightarrow UO_2 + 2\ Fe^{3+}{}_{(s)}$	Irreversible	(iv)

Table 2: Some relevant reactions for the elucidation of the mechanism of U(VI) fixation by Fe^0.

Reaction equation			**logK**	**Eq.**
$UO_2^{2+} + Fe^0$	$\Leftrightarrow$	$UO_{2\ (s)} + Fe^{2+}$	-	(1)
$UO_2^{2+}{}_{(aq\ or\ s)} + 2\ Fe^{2+}{}_{(s)}$	$\Leftrightarrow$	$UO_{2\ (s)} + 2\ Fe^{3+}{}_{(s)}$	-	(2)
$UO_2^{2+} + H_{2\ (g)}$	$\Leftrightarrow$	$UO_{2\ (s)} + 2\ H^+$	-	(3)
$UO_{2\ (s)} + 2\ Fe^{3+}{}_{(aq)}$	$\Leftrightarrow$	$UO_2^{2+}{}_{(aq\ or\ s)} + 2\ Fe^{2+}{}_{(aq)}$	11.96*	(4)
$2\ Fe^{2+} + ½\ O_2 + 5\ H_2O$	$\Leftrightarrow$	$2\ Fe(OH)_3 + 4\ H^+$	7.20*	(5)
$Fe(OH)_3$	$\Leftrightarrow$	α-, β-FeOOH, Fe_3O_4, Fe_2O_3	-	(6)
$FeS_2 + 14\ Fe^{3+}{}_{(aq)} + 8\ H_2O$	$\Leftrightarrow$	$15\ Fe^{2+} + 2\ SO_4^{2-} + 16\ H^+$	16.78*	(7)
$FeS_2 + 7\ UO_2^{2+} + 8\ H_2O$	$\Leftrightarrow$	$Fe^{2+} + 7\ UO_{2\ (s)} + 2\ SO_4^{2-} + 16\ H^+$	-20.91*	(8)
$Fe^{2+}{}_{(aq)} + MnO_2 + 2\ H_2O$	$\Leftrightarrow$	$FeOOH + MnOOH + 2\ H^+$	-	(9)
$FeOOH + Ti^{3+} + H^+$	$\Leftrightarrow$	$Fe^{2+} + 2\ OH^- + Ti^{4+}$	-	(10)
$FeOOH + EDTA + 3\ H^+$	$\Leftrightarrow$	$Fe(EDTA)^{3+} + 2\ H_2O$	-	(11)
$FeOOH + 3\ H^+$	$\Leftrightarrow$	$Fe^{3+} + 2\ H_2O$	-	(12)

* From Bain et al.[29]

Table 3: Comparison of the molar Fe:U ratios $(Fe:U)_x$ in the mass of corrosion products under the experimental conditions of two references and those of this work. In $(Fe:U)_x$, x represents the percent consumption of the initial amount of Fe^0 (5 % in this work).

Reference	**pH_0**	**Fe^0 (g/L)**	**$[U]_0$ (mg/L)**	**V_0 (mL)**	**$(Fe:U)_5$**	**$(Fe:U)_{10}$**	**$(Fe:U)_{15}$**
Gu et al. (1998)	5.00	200	10000	10	4.1	8.2	12.4
Abdelouas et al. (1999)	7.00	25	9.3	40	554	1108	1662
	-	25	4285	40	1.2	2.4	3.6
this work	7.20	15	20	20	154	-	-

Table 4: Published uranium speciation data from field Fe^0 reactive barriers (from ref. 5).

Site location	service life	uranium speciation	reference
Y-12 Plant Oak Ridge; Tennessee	~3 years	mostly U(VI)	Gu et al. 2002
Y-12 Plant Oak Ridge; Tennessee	1.2 years	~55 % U(IV) ~45 % U(VI)	Matheson et al. 2002
Bodo Canyon Site; Durango - Colorado	3 years	~100 %. U(VI)	Matheson et al. 2002
Former Mill Site; Manticello Utah	3 years	U(IV) and U(VI)	Morrison et al. 2002

Table 5: Mineralogical distribution of reaction products on the surface of Fe^0 coupon as observed at three selected points (Fig. 5) by means of energy-dispersive X-ray (EDX).

Sample	Al_2O_3	SiO_2	Cr_2O_3	MnO	FeO	MgO	CaO	U
P_1	0.09	4.45	0.20	0.48	94.48	0.09	0.04	0.00
P_2	0.02	1.99	0.09	1.46	96.11	0.16	0.16	0.00
P_3	0.24	3.44	0.00	0.36	95.73	0.00	0.02	0.20

Figure 1

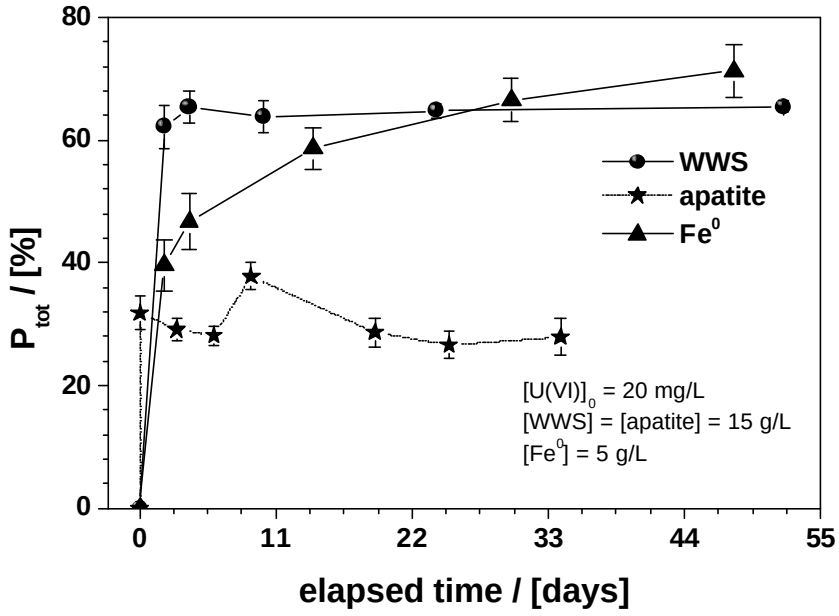
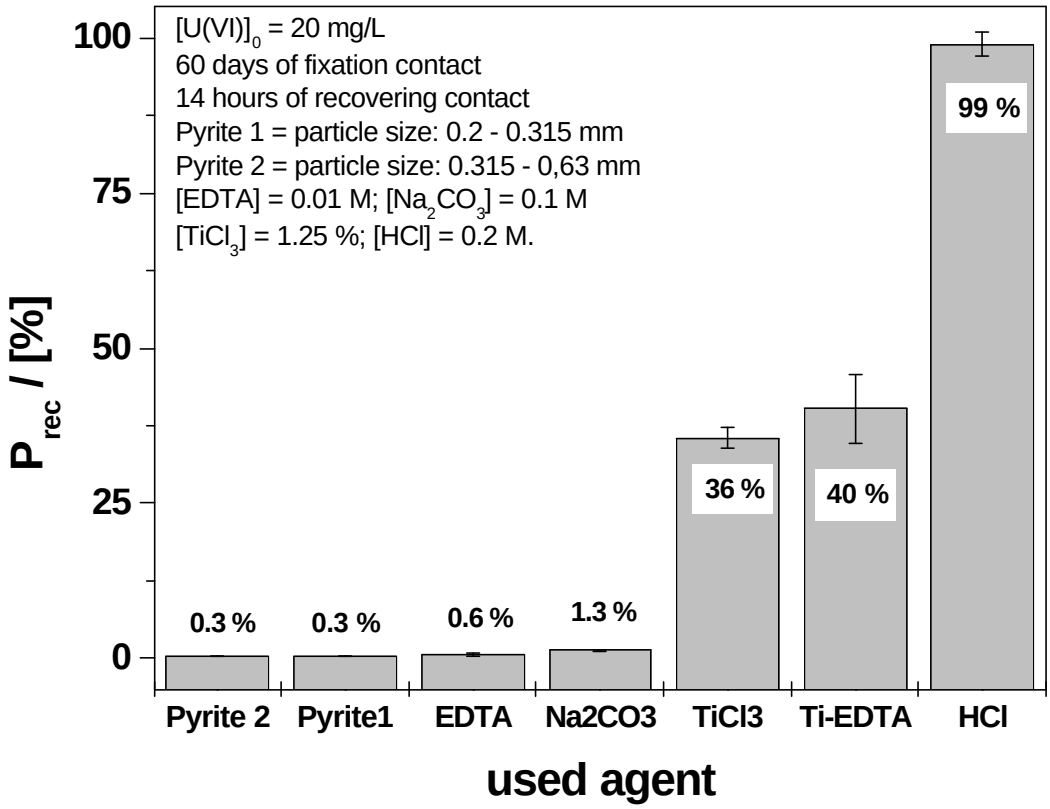

80
60
40
20
0
0
11
22
33
44
55
P tot / [%]
elapsed time / [days]
WWS
apatite
Fe0
[U(VI)]0 = 20 mg/L
[WWS] = [apatite] = 15 g/L
[Fe0] = 5 g/L

Figure 2


[U(VI)]0 = 20 mg/L
60 days of fixation contact
14 hours of recovering contact
Pyrite 1 = particle size: 0.2 - 0.315 mm
Pyrite 2 = particle size: 0.315 - 0,63 mm
[EDTA] = 0.01 M; [Na2CO3] = 0.1 M
[TiCl3] = 1.25 %; [HCl] = 0.2 M.
P rec / [%]
100
75
50
25
0
0.3 %
0.3 %
0.6 %
1.3 %
36 %
40 %
99 %
Pyrite 2
Pyrite1
EDTA
Na2CO3
TiCl3
Ti-EDTA
HCl
used agent

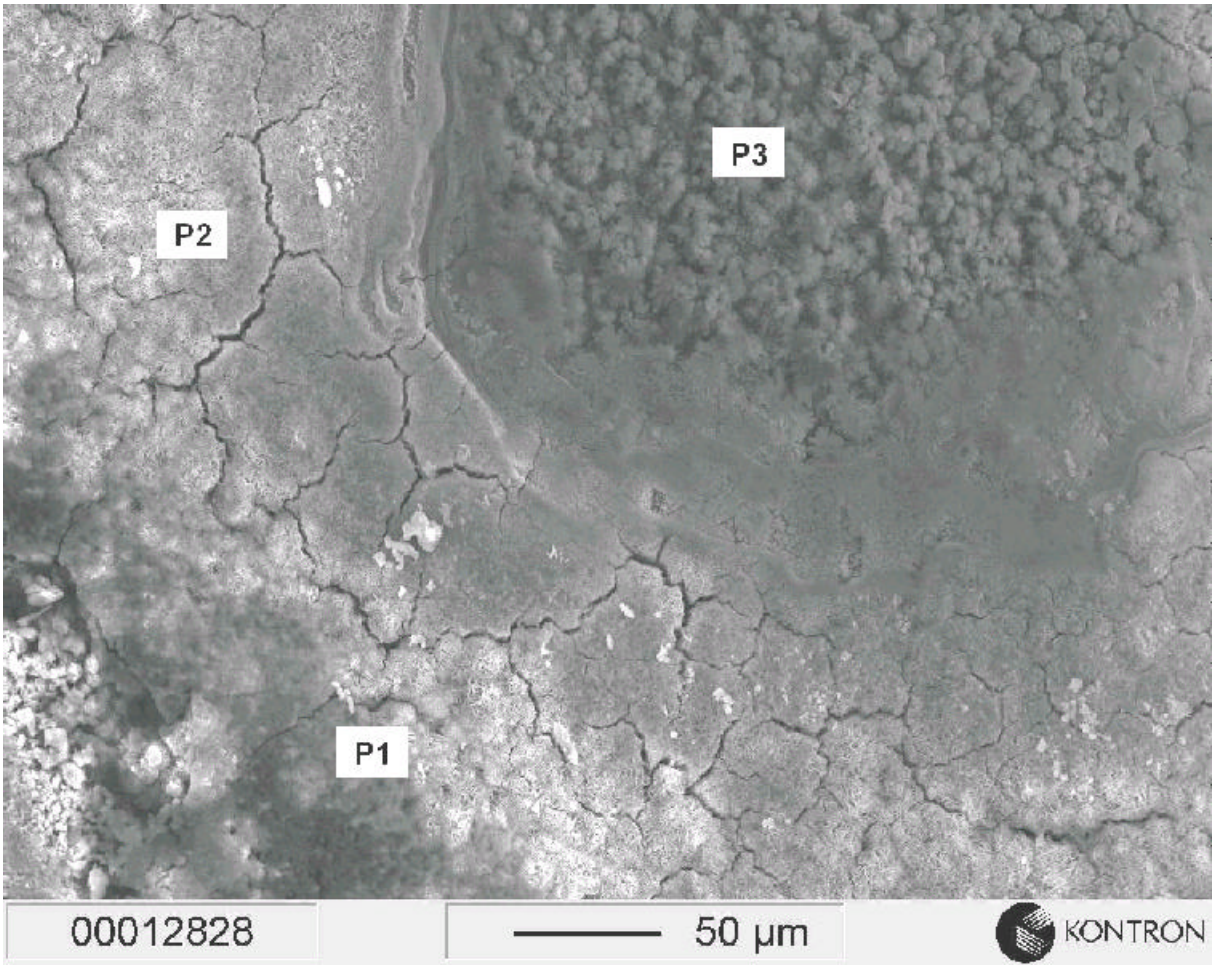



Figure 3