Characterizing the reactivity of metallic iron in Fe\(^0\)/U\(^{VI}\)/H\(_2\)O systems by long-term column experiments

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Abstract

Aqueous iron corrosion has been identified as a powerful process for environmental remediation and safe drinking water provision. The intrinsic reactivity of conventional micro-scale metallic iron (Fe\(^0\)) has been mostly enhanced by the association of other metals (e.g. Cu, Ni, Pd) or by using nano-scale Fe\(^0\). However, the mechanisms responsible for increased reactivity are yet to be univocally elucidated. Therefore, it appears that basic knowledge on Fe\(^0\) intrinsic reactivity decreases as Fe\(^0\) technology advances. This work was performed to address the intrinsic reactivity of four selected conventional Fe\(^0\) materials in long-term column studies. Five systems were investigated. Each system was made up of two columns in series. The first column contains 5.0 g of a U-bearing rock mixed with sand. The second sand column contained 0.0 or 4.0 g of each Fe\(^0\). The extent of U fixation in the systems was used to characterize the reactivity of the Fe\(^0\) materials. Results showed a clearer differentiation among the three Fe\(^0\) materials which exhibited very closed extents of iron dissolution in 2 mM EDTA under dynamic conditions. The crucial importance of long-term column experiments to test the suitability of Fe\(^0\) for field applications is delineated. A new research trend is presented.

Keywords: Column study, Material reactivity, Natural rock, Water treatment, Zerovalent iron.
Science and technology have developed various efficient methods for safe drinking water provision, wastewater recycling, and groundwater remediation. These methods can be classified on the basis of biological, chemical, physical, and thermal principles [1]. The most current methods include adsorption, centrifugation, coagulation, crystallization, distillation, evaporation, flotation, ion exchange, oxidation, precipitation, sedimentation (and gravity separation), and reverse osmosis [1-7]. Among these methods, adsorption, ion exchange and reverse osmosis are excellent technologies, adsorption being the most affordable one [6,7].

The use of metallic iron (Fe⁰) for safe drinking water production has been discussed in the literature during the last 10 to 15 years [8-16]. Actually, detailed concepts for the application of Fe⁰ for safe drinking water production at several scales have been presented. In particular, Fe⁰ seems to be an ideal safe water production medium in emergency situations, for remote and in low-income communities [12,15]. For the realization of these concepts, a profound knowledge on Fe⁰ intrinsic reactivity under field conditions is needed. A purposeful use or modification of Fe⁰ for each application can only be based on such a profound knowledge.

The present work is a continuation of an effort which objective is to establish a reliable tool to characterize Fe⁰ intrinsic reactivity under natural near conditions. Previous works have characterized the reactivity of 18 materials using batch EDTA-test [17,18]. The batch EDTA-test was significantly disturbed by the abundance of atmospheric corrosion products and was not suitable for powdered materials [18]. On the other hand, the long-term EDTA leaching column test could not really differentiate the reactivity of seven granular materials [19]. The shortcoming of the EDTA-test is that Fe⁰ materials are characterized by the extent of Fe dissolution which is not necessarily linearly coupled to contaminant removal. Another short term batch test accounting for this shortcoming has been developed [20]. This test is based on the extend of discoloration of a methylene blue solution by Fe⁰ in the presence of a well-
characterized MnO₂ (MB-test). The MB-test suffers from the lack of a referential MnO₂ material but could be satisfactorily used for internal purposes.

Filtration on Fe⁰ beds is a deep-bed filtration. This means that contaminants are not only removed in the entrance zone or at a reaction front but in the whole bed [15,21]. Accordingly, characterizing the reactivity of Fe⁰ in column studies should not be limited to determine the time to contaminant breakthrough, but rather the reactivity of Fe⁰ in the beds. Based on this evidence, this work intentionally used small amounts of Fe⁰ and characterized the systems by the extent of U fixation in the bed (also see ref. [22]). The other peculiarity is that, not a U solution is piped into the columns, but U was leached in-situ from a natural rock by a natural spring water.

The objective of this study was to further differentiate the reactivity of Fe⁰ materials from recent works by using near natural systems. For this purpose, U was leached from a natural rock by a spring water and the intrinsic reactivity of Fe⁰ materials was characterized as the extent of fixation of leached U. Preliminary works enable the optimisation of experimental conditions. Results delineate the importance of natural near systems for the characterization of Fe⁰ materials for practical use. A new experimental trend for laboratory experiments regarding the characterization of the suitability of Fe⁰ under natural conditions is introduced.

2 Materials and methods

2.1 Solid materials

2.1.1 U-bearing rock

The used U-bearing rock was crushed and sieved at the Helmholtz-Zentrum Dresden-Rossendorf. The fraction 0.200 to 0.500 mm was used without any further pre-treatment. The rock contains around 0.6 % U and is further composed of: 74.16 % SiO₂, 0.19% TiO₂; 7.42 % Al₂O₃, 1.64 % Fe₂O₃, 0.03% MnO; 0.86 % MgO, 12.68 % CaO, 1.53 % Na₂O, 1.45 % K₂O, 0.04 % P₂O₅ and 0.18% SO₃. The composition was determined by X-ray fluorescence (XRF) analysis. The EDX analysis (results not shown) revealed that the used rock is a multi-
mineralic one containing, among others, uraninite (UO$_2$), arsenopyrite (FeSAs), and galena (PbS). Associations of U with arsenopyrite was also encountered.

2.1.2 Fe$^0$ materials

One scrap iron (ZVI1), and three commercially available Fe$^0$ materials have been tested. The main characteristics of these materials are summarized elsewhere [19]. Before being used ZVI4 was crushed and sieved; the size fraction 1.0-2.0 mm was used without any further pre-treatment. The specific surface area of the materials varies between 0.043 and 0.63 m$^2$ g$^{-1}$. These data were compiled from the literature (Tab. 1). The materials were compared solely on the basis of the extent of U removal by the same initial mass of Fe$^0$ (1.2 or 4.0 g) under similar experimental conditions. Apart from ZVI4, all other materials were used as obtained. Crushing and sieving ZVI4 aimed at working with materials of particle size relevant for field applications. The materials differ regarding their characteristics such as iron content, nature and proportion of alloying elements, and shape.

The four used materials were selected from nine materials which were recently characterized by leaching with 0.2 M EDTA in column study [19]. In turn, the tested nine materials were selected from eighteen materials after a screening in batch experiments using the EDTA-test [17,18]. Both tests could not really differentiate the reactivity of ZVI1, ZVI3 and ZVI4. The reactivity of these three materials toward U removal from a natural rock was investigated in this study. For comparison the least reactive commercial Fe$^0$ (ZVI2) was incorporated in this study.

2.1.3 Other materials

Dolomite: The used dolomite mineral was crushed, sieved and the fraction 0.63 to 1.0 mm was used. The mineralogical composition (XRF) is: SiO$_2$: 1.2%, TiO$_2$: 0.03%; Al$_2$O$_3$: 0.4%, Fe$_2$O$_3$ 0.6%, MgO: 20.24%, CaO: 30.94%, Na$_2$O: 0.04%. Dolomite is a carbonate mineral; its dissolution increases the kinetics of U leaching because of the formation of stable complex
with carbonates [23,24]. The dolomite layer was placed after of the rock layer and thus its capacity in retarding U transport is investigated.

**Apatite**: The used hydroxyapatite was a natural sample from a private collection (origin unknown). The material was crushed, sieved and the fraction 0.5 to 1.0 mm was used.

**Glass beads**: The used glass beads were from Roth (Karlsruhe, Germany). Their particle size was $0.25 < d (\text{mm}) < 0.50$. They were used as filling material. Their adsorption capacity was also tested in using three different volumes of glass beads in columns containing sand.

**Sand**: The used sand was a commercial material for aviculture ("Papagaiensand" from RUT – Lehrte/Germany). Papagaiensand was used as received without any further pre-treatment nor characterization. This sand was the operational reference non-adsorbing material.

### 2.2 Leaching solution

The leaching solution was spring water from the Lausebrunnen in Krebeck (administrative district of Göttingen). Spring water was used as proxy for natural groundwater and was supplied weekly. Its average composition (in mg/l) was: $\text{Cl}^–: 9.4$; $\text{NO}_3^–: 9.5$; $\text{SO}_4^{2–}: 70.9$; $\text{HCO}_3^–: 95.1$; $\text{Na}^+: 8.4$; $\text{K}^+: 1.0$; $\text{Mg}^{2+}: 5.7$; $\text{Ca}^{2+}: 110.1$; and an initial pH 7.8.

### 2.3 Uranium leaching and immobilization

Laboratory scale glass columns were operated in up-flow mode (Fig. 1). The influent solution was spring water (Lausebrunnen/Krebeck) and was pumped upwards from PE bottles using a peristaltic pump (Ismatec, ICP 24). Tygon tubes were used to connect inlet reservoir, pump, column and outlet. Ten glass columns (40 cm long, 2.6 cm inner diameter) were used in two series of experiments. The columns were mostly packed with sand (Fig. 1). The effective length, the bulk density and the porosity of the packed columns were not characterized as they were not necessary for the discussion of the results. The extent of U dissolution by water and the extent of its removal by selected materials were the sole targets. The experiments were performed at room temperature ($22 \pm 3 ^\circ \text{C}$) in the ISOLAB at the Department of Physical
Chemistry. In individual experiment series, a stable flow rate was maintained throughout the experiment. Samples for analysis were collected at periodic intervals.

### 2.3.1 One-column experiments

U rock and other materials (including Fe\(^0\)) were packed into the same column (Fig. 1 - left). The rock was placed at the inlet, at 5.0 cm from the bottom on a layer of sand. The other material was placed at 5.0 cm from the outlet. 10 parallel experiments were performed with 3.0 g of the rock, 1.2 g of Fe\(^0\), 6.0 g of dolomite, 6.0 g of apatite and three different depths of glass beads (5.0, 10.0 and 20.0 cm – mass not measured). The columns were fed with spring water at a constant flow rate of 19.0 mL/h. The experiments were stopped after 37 days when each column was leached by about 17.0 L of water.

### 2.3.2 Two-column experiments

Based on the results of the one-column experiments, the two-column experiments were designed to better characterize the reactivity of tested Fe\(^0\) materials (Fig. 1 - right). Five parallel experiments were performed. The same mass of the rock (5.0 g) was placed in a first column and 4.0 g of each tested Fe\(^0\) was placed in the second column. In the reference system, the second column contained only sand (no Fe\(^0\)). The experiments were stopped after 84 days when each column was leached by 24.0 L of water. The water flow rate was constant at 12.0 mL/h.

### 2.4 Analytical methods

Analysis for U was performed by inductively coupled plasma mass spectrometry (ICP-MS) at the Department of Geochemistry (University of Göttingen). All chemicals used for experiments and analysis 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 [25] and in agreement with the new IUPAC recommendation [26].
3 Results and discussion

3.1 Expression of experimental results

The mass \( (m) \) of leached U \((\text{mg})\) at any time \((t)\) is calculated from the concentration of the effluent using Eq. (1):

\[
m = P \cdot V
\]

(1)

Where \( P \) is the U concentration (in mg/L) and \( V \) the volume (L). At the end of the experiment the total amount of leached U can be calculated by addition and the extent of U leaching by spring water deduced. Knowing the percentage of U in the natural rock (0.6 %), the maximal leachable mass \((m_0)\) of uranium can be calculated. The percentage \((P)\) uranium leaching at each time is given by Eq. (2):

\[
P = 100 \times \frac{m}{m_0}
\]

(2)

At each time the amount of U leached in the reference system \((P_{\text{ref}})\) can be set to 100 and the relative leaching percent \((P_{\text{rel}})\) for all other systems deduced by Eq. (3):

\[
P^* = P_{\text{rel}} = 100 \times \frac{P}{P_{\text{ref}}}
\]

(3)

Finally, the relative percent of U removal \((P_{\text{fix}})\) by each material is given by Eq. (4):

\[
P_{\text{fix}} = 100 - P_{\text{rel}}
\]

(4)

3.2 Uranium removal in one-column experiments

Table 2 and Figure 2 summarize the results of U leaching (reference system) and removal by glass beads, apatite, dolomite and the four Fe\(^0\) materials. It can be seen from Tab. 2 that the maximal U leaching corresponds to 10.43 mg of U. This value corresponds to 29 % of the total amount of U contained in the 3.0 g U rock. It is important to note that in all systems, the effluent U concentration after 37 days was larger than 350 \(\mu\text{g}/\text{L}\) (Fig. 2). That is more than 16 times the maximum contaminant level (MCL) of the World Health Organization (WHO MCL = 20 \(\mu\text{g}/\text{L}\) [27]. This experimental fact suggests that instead of synthetic solutions, natural rocks and minerals can be leached by natural or relevant synthetic solutions and the leachates used as initial solution for decontamination experiments. The double advantage of this
approach is: (i) the leaching process of contaminant from natural phases can be accurately investigated/characterized, and (ii) contaminant removal is investigated with concentration nearer to the real world as with all possible synthetic solutions. Note that the used rock was a multi-mineralic one, making the leachates multi-contaminant systems. Presently, however, multi-contaminant systems have received less attention in the Fe remediation community [28].

Fig. 2a shows clearly that the process of contaminant removal under natural near conditions is complex. There is no uniform trend for the evolution of U concentration. The elevated U release at the beginning of the experiment (up to day 12) could be attributed to the presence of fines and very reactive site at the surface. Based on relative steady state after day 20 it was decided at day 30 to stop the reaction. However, prolonged sojourn in the laboratory (“restricted access area”) was not possible from day 27 to 37 due to technical problems. Accordingly, the experiments were stopped at day 27 and the peak at day 37 is due to a 10-days-stagnation which resulted in increased U leaching.

Table 2 shows no U removal in the systems with 5 cm and 10 cm glass beads. This both systems are very comparable to the reference system showing that the results were reproducible. The 6 % U removal in the column with 20 cm glass beads can be attributed to U precipitation in the glass beads-layer at the beginning of the experiment as the solution are necessarily over-saturated [24]. In fact, given the small size of glass beads, precipitation of U as U(VI) phases (e.g. as schoepite UO$_3$.2H$_2$O) is very likely. Table 2 also shows that used apatite and dolomite are not suitable for U removal. The suitability of apatite for U removal is well documented [29-31].

Fig. 2b shows the cumulative mass of uranium in selected systems representative for all investigated systems. It can be seen that the curves have the same allure and are very closed to each other. Remember that experiments aimed at differentiating materials ZVI1, ZVI3 and ZVI4 for their intrinsic reactivity using less reactive ZVI2 as negative reference. P* values
from Tab. 2 confirmed that ZVI2 is less reactive than the three other materials while a slight
differentiation between (ZVI1, ZVI3) and ZVI4 was possible. These results are not
satisfactorily. Accordingly, the system was modified to exploit the huge potential of this
experimental tool. The water flow velocity was reduced from 19 to 12 mL/h, the Fe\(^0\) mass
was increased from 1.2 to 4.0 g and the mass of U rock was increased from 3.0 to 5.0 g.
Additionally, the Fe\(^0\) and rock were packed in different columns (Fig. 1) and the experimental
duration was lengthened.

3.3 Uranium removal in two-column experiments

Table 3 and Figure 3 summarize the results of U leaching (reference system) and removal by
four Fe\(^0\) materials in the two-column experiment mode. It is clear from Fig. 3 a and b, that a
differentiation of ZVI1 and ZVI3 is not possible. ZVI4 is clearly the most reactive material.
This observation is confirmed by P\(_{\text{fix}}\) values from Tab. 3 (83.4 % U removal). Accordingly the
order of increasing reactivity for the Fe\(^0\) materials is: ZVI2 < ZVI1 ≅ ZVI3 < ZVI4. It should
be noted that in this experimental procedure, the U concentration was still higher than 20 \(\mu\)g/L
(WHO MCL value) after 70 days. On the contrary, in Fe\(^0\) systems the U concentrations were
lower than 15 \(\mu\)g/L after 55 days (see Fig. 4). This observation corroborates the suitability of
long term column experiment with natural rocks and minerals for more reliable data. In such
experiments, the natural material could be initially washed with the used water to eliminate
fines at the surface and avoid the artificial peak at the beginning of the experiment.
Alternatively, the first pore volumes (e.g. 10 or 20) can be discarded and the Fe\(^0\)
characterization starts when the initial peak is over.
As a rule of thumb it can be considered that any natural rock or mineral from which relevant
contaminants could be leached for a long time (e.g. 2 months) at concentrations larger to the
MCL value is suitable for this type of experiment. To optimise the experimental conditions,
the material particle size and the used amount should be carefully tested. Testing a large
number of materials under such conditions could enable the establishment of a data base
which could be used to bridge the huge gap between short term laboratory experiments and
long-term processes on the field.

3.3 Discussion

Since the discovery of Fe⁰ materials as water treatment medium [32] several groups of Fe-
based materials have been tested for their suitability for field application [17,33-42].
However, apart from Reardon [33,39] and Noubactep et al. [17,18] all Fe⁰ characterization
attempts were based on the extent of the removal of selected contaminants by the materials.
Given that large variability of experimental conditions [18,22,35], available results are not
really comparable. Furthermore, there is still no single standard test (or proposition therefore)
for the characterization of the intrinsic reactivity of used materials. This situation is not
acceptable, efforts should be directed at developing such tests. The objective being to generate
the chain of knowledge on which the promising technology of using Fe⁰ for water treatment
will be further developed.

The next point will be to characterize materials and group them for individual purposes. For
example, Fe⁰ for drinking water, Fe⁰ for wastewater, Fe⁰ for carbonate-rich groundwater, or
Fe⁰ for MnO₂-containing soils. The objective should not be to select the most reactive
material but the material that is appropriate for a given objective (site-specific). For example a
material suitable for carbonate-rich groundwater could be too reactive for a MnO₂-containing
soil because the reactivity is sustained by MnO₂ [43-45]. Similarly, plating a Fe⁰ could be
superfluous or even disadvantageous at certain sites. In other words, plating Fe⁰ to generate
bimetallic systems or even composites should be justified by field requirements. For this
purpose a better material characterization is needed.

After the development of a two simple tests for the characterization of intrinsic Fe⁰ reactivity
using a diluted EDTA solution [17-19], the present study has used a natural near system to
further differentiate the reactivity of Fe⁰. It is shown that the proper characterization of the
reactivity of Fe⁰ materials is necessarily time consuming. In fact the 30 day-experiment was
not really conclusive. A clear conclusion could only be given after the 84 day-experiments. It should be recalled that the 62 day-column-experiment with EDTA [19] was not sufficient to differentiate the reactivity of Fe\(^0\) tested here. It appears that an attitude change is necessary to overcome the current impasse characterized by the intensive production of non comparable data.

It has already been reiterated that all current data for the characterization of Fe\(^0\) materials (surface area, elemental composition, surface charge, surface roughness, surface state…) are not sufficient to evaluate/predict the intrinsic reactivity of Fe\(^0\) materials [18]. Only a purposeful characterization of available materials will enable the manufacture of new efficient materials. On this path, efforts should be directed at obtaining particularly corrosive materials which are necessarily composite containing for instance over-proportional proportions of corrosive alloying element like S or Mn. It is likely, that such material with electrochemical cells in the whole body will be more reactive in the long term than bimetallic or multi-metallic coatings. The fundamental suitability of Fe\(^0\) composites for water treatment and their superiority over conventional Fe\(^0\) materials has been demonstrated by Hussam et al. [9,46].

These authors replaced conventional iron shavings/fillings by a porous composite iron material and could transform a highly efficient but not sustainable system (3-Kolshi filter) into a highly functional and sustainable system (SONO filter) [46].

4 Concluding remarks

The future of Fe\(^0\) as water treatment material, and thus the fate for the Fe\(^0\) remediation technology as a whole, depends on the ability of researchers to traceably define/characterize used materials. Since used materials considerably affect the success of the systems, there is a dire need to optimize material characterization. This basic operation has the advantage of minimizing system failures at the origin.

This work has presented a possible way for the characterization of Fe\(^0\) intrinsic reactivity in long-term column studies using natural near conditions. A beneficial side-effect of the
presented concept is the investigation of the process of contaminant release from natural rocks
and minerals and the investigation of contaminant in multi-contaminant systems at
concentrations close to those encountered in nature. Using such systems will ease the bridging
on the huge gap between short term laboratory experiments and field observations [47].
Finally, a full commitment of Fe⁰ remediation operators with independent researchers is
needed to enable applied research to develop relevant scientific models and management
schemes based on sound laboratory results from long-term experiments.

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Cited references


Table 1. Elemental composition and specific surface area (SSA) of iron materials used in this study. n.d. = not determined. Modified from ref. [19]. The materials are range in increasing order of the carbon content to ease comparison with previous work.

<table>
<thead>
<tr>
<th>ZVI</th>
<th>Element (%)</th>
<th>SSA (m²/g)</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>C</td>
<td>Si</td>
</tr>
<tr>
<td>ZVI4</td>
<td>1.96</td>
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</tr>
<tr>
<td>ZVI2</td>
<td>3.39</td>
<td>0.41</td>
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<tr>
<td>ZVI1</td>
<td>3.52</td>
<td>2.12</td>
</tr>
<tr>
<td>ZVI3</td>
<td>3.13</td>
<td>2.17</td>
</tr>
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</table>
Table 2: Extent of uranium fixation by apatite, dolomite, and Fe$^0$ materials in one-column experiments. It can be seen that the column containing 20 cm of glass beads (Glass beads 3) could significantly removed U. The extent of U removal by Fe$^0$ varies from 10.0 to 16.0 %. 3 g of U-mineral was used and each column was flooded by a volume $V_T$ of spring water. $m_f$ is the leached mass of U, $P$ is the percent leaching relative to the total amount of U in the mineral and $P^*$ is the relative percent of U leaching. The sand column is the reference system.

<table>
<thead>
<tr>
<th>System</th>
<th>Material</th>
<th>$V_T$ (L)</th>
<th>$m_f$ (mg)</th>
<th>$P$ (%)</th>
<th>$P^*$ (%)</th>
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<tbody>
<tr>
<td>Ref.</td>
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<td>17.32</td>
<td>10.43</td>
<td>29.0</td>
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<td>11.32</td>
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<tr>
<td>Glass beads 2</td>
<td>10 cm</td>
<td>17.48</td>
<td>10.56</td>
<td>29.3</td>
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<td>18.25</td>
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<td>26.7</td>
<td>92.3</td>
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<tr>
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<td>16.96</td>
<td>9.05</td>
<td>25.1</td>
<td>86.8</td>
</tr>
<tr>
<td>ZVI2</td>
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<td>17.40</td>
<td>9.39</td>
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<td>90.0</td>
</tr>
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<td>8.77</td>
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</tr>
<tr>
<td>ZVI3</td>
<td>1.2</td>
<td>18.10</td>
<td>9.01</td>
<td>25.0</td>
<td>86.4</td>
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Table 3: Extent of uranium fixation by Fe\(^0\) materials in two-column experiments. The extent of U removal by Fe\(^0\) varies from 37.3 to 83.4%. 5 g of U-mineral was used and each column was flooded by a volume \(V_T\) of natural water. \(m_f\) is the leached mass of U, \(P\) is the percent leaching relative to the total amount of U in the mineral and \(P^*\) is the relative percent of U leaching. The sand column is the reference system. 4.0 g of Fe\(^0\) was used in each system.

<table>
<thead>
<tr>
<th>System</th>
<th>(V_T) (L)</th>
<th>(m_f) (mg)</th>
<th>(P_U) (%)</th>
<th>(P^*) (%)</th>
<th>(P_{fix}) (%)</th>
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<tr>
<td>Ref.</td>
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<td>30.7</td>
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<tr>
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<td>11.9</td>
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<td>19.2</td>
<td>62.7</td>
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<tr>
<td>ZVI3</td>
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<td>11.8</td>
<td>38.5</td>
<td>61.5</td>
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<td>ZVI4</td>
<td>24.1</td>
<td>3.06</td>
<td>5.1</td>
<td>16.6</td>
<td>83.4</td>
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</table>
Figure 1:

Figure 1° (left)

[Diagram of a vertical column filled with layers of sand, other material, and uranium rock (3 g), with an inflow at the bottom and a sample at the bottom right.]
Figure 1b (right)
Figure 2

(a) Reference, glass bead, dolomite, apatite, metallic iron

(b) Reference, glass bead, dolomite, apatite, metallic iron
Figure 3:
Figure 4

[Graph showing the elapse of uranium in micrograms per liter over days for different conditions labeled as Reference, ZVI1, ZVI2, ZVI3, and ZVI4. The WHO MCL line is also visible.]
**Figure Captions**

**Figure 1:**
Schematic diagram of the experimental design: one-column (left) and two-column experiments (right). For the one-column experiments used materials were Fe\(^{0}\) (1.2 g), dolomite (6.0 g), apatite (6.0 g) and glass beads (5.0, 10.0 and 20.0 cm).

**Figure 2:**
Representative trend of uranium release from the one-column systems for 37 days by tested materials: (a) variation of the extent of U release with time, and (b) cumulative uranium release (μg). The lines are not fitting functions, they simply connect points to facilitate visualization.

**Figure 3:**
Extent of uranium release from the two-column-systems for 84 days by tested Fe\(^{0}\) materials: (a) variation of the extent of U release with time, and (b) cumulative uranium release (μg). The lines are not fitting functions, they simply connect points to facilitate visualization.

**Figure 4:**
Comparison of the evolution of the residual U concentration in the five systems of the two-column experiment with the WHO MCL (20 μg/L). It is shown that up to day 75 the U concentration of the effluent from the reference system was too high. Up to this date, lower U concentration in other system is attributed to the reactivity of Fe\(^{0}\) materials. The lines are not fitting functions, they simply connect points to facilitate visualization.