

Uranium release from a natural rock under near-natural oxidizing conditions

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(Received August 29, 2005)

Understanding how uranium moves through the soil and groundwater is essential to determine the effectiveness of cleanup technologies. Uranium release and transport in the subsurface under oxic conditions have been reported to be mostly dependent on sorption onto Fe/Mn-oxide and complex interactions with organic substances. Available information in the literature, however, presents evidence of U retardation by natural sands. The aim of this investigation was to characterize U dissolution from a uraninite-containing rock (UO₂-rock) in different waters under test conditions relevant to U transport from mine tailings. For this purpose, not shaken batch experiments were conducted with a constant amount of an UO₂-rock and different types of water (deionised, tap and mineral water). For comparison parallel experiments were conducted with 0.1M Na₂CO₃ and 0.1M H₂SO₄. Further dissolution experiments using UO₂-rock together with dolomite and pyrite were conducted. The results indicate that carbonate addition enhanced U solubilization, whereas pyrite addition essentially slowed the initial U solubilization. It is shown that SiO₂ and other rock constituents retard U transport.

Introduction

The understanding of the processes influencing chemical weathering of minerals and the release of various inorganic contaminants in the hydrosphere is of worldwide concern. Particularly, the property of natural waters to dissolve target contaminants requires thorough investigation to enable realistic estimations of the suitable lifespan of in situ reactive barriers since the contaminants are to be leached by local waters to the barrier.^{1–3}

Uranium has been reported to be leached from rocks and to be present in water in concentrations up to 10 µg·l⁻¹.^{4,5} Uranium content of land waters in excess to 1 µg·l⁻¹ is regarded as an anomaly.⁶ On the other hand, laboratory solubility experiments with synthetic schoepite (pure phase) showed that about 1000 µg·l⁻¹ U can be dissolved at neutral pH values,⁷ schoepite been the most soluble U(VI) solid phase. This gap between field observations and laboratory data gained on pure mineral phases shows that low U contents in natural waters cannot be explained by the solubility of pure schoepite under the same conditions. In fact, there are major difficulties in using reference materials to describe heterogeneous materials. For example, concentrations of complexing surface sites may be difficult to estimate from measurable characteristics of the natural materials.^{8,9} Additionally, a rock–water system is almost never in equilibrium. Some kind of steady state can be achieved but in nature processes are not usually in equilibrium.¹⁰ Therefore, it is necessary to closely investigate the processes that influence the U dissolution and transport under conditions similar to oxic mine wastes.

For modeling purposes, it is generally assumed that the solubility of U-bearing minerals is the critical factor in controlling U leaching from soils rather than sorption/desorption processes.^{8,11} To corroborate this assumption, modelers choose less soluble minerals as solubility controlling phases.⁸ In this way, “residual discrepancies” are usually attributed to co-precipitation mostly with iron oxides and to complex interactions with supposedly available humic substances.¹² However, recent works reported considerable U sorption onto sand (quartz), which is commonly considered as non-reactive material.^{7,9,13} For example, when investigating the retention capacity of non-ferric sandstone core materials, READ et al.¹³ illustrated the strong affinity of aqueous U species for natural surfaces under strongly oxidizing conditions. NOUBACTEP⁷ used a sand column as reference in sand/iron experiments and reported considerable U retention in the reference column. Therefore, it is necessary to closely investigate the processes that influence U release and transport in the subsurface, particularly under conditions more close to natural situations but in the absence of Fe/Mn-oxides and organic substances.

The potential of natural waters to leach U from rocks or mining wastes has not been investigated. This issue needs to be addressed for an accurate prediction of the suitable lifespan of a reactive barrier (irrespective of the barrier material) downstream of U tailings since the contaminant is progressively leached by natural waters.³ For this purpose, it is suitable to obtain and characterize simulated realistic steady states in the laboratory and to use them together with solubility constants (strictly defined for pure phases) for modeling purposes.

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The present study aims at a better characterization of the primary processes responsible for the U release from a well characterized rock in natural near oxidizing systems excluding organic substances (known for sorptive and reductive properties) and only including two known active species (dolomite, pyrite) or supposedly inactive quartz sand. Particular attention was directed at quantifying the extent of U release into the aqueous phase under varying solution chemistry (essentially pH value, carbonate concentration, $[\text{HCO}_3^-]$ and presence of Fe(III)-species).

Background

In U tailings the dissolution process typically involves oxidation and destabilization of U(IV) minerals such as uraninite (UO_{2+x}) and coffinite ($\text{USiO}_4 \cdot n\text{H}_2\text{O}$) resulting in high concentrations of U(VI) aqueous species.¹² In these environments, U concentrations of up to more than $10,000 \mu\text{g}\cdot\text{l}^{-1}$ have been reported depending on the geochemical conditions.^{14–17} For example, JERDEN and SINHA¹⁴ reported that groundwaters with U concentrations of up to $575,000 \mu\text{g}\cdot\text{l}^{-1}$ (575 ppm, average value) could be reduced to values as low as $15 \mu\text{g}\cdot\text{l}^{-1}$ in phosphate rich environment through the formation of low soluble U(VI) phosphate minerals.

Apart from phosphate rich environments the transport of oxidized U [U(VI)-species] in natural waters (neutral pH range) is believed to be primarily controlled by sorption processes onto different minerals.^{5,12,18} This process is in turn strongly influenced by the carbonate concentration (HCO_3^- , PCO_2) which lowers sorption onto inorganic minerals (Fe/Mn-oxides) and organic substances.^{19–22}

When testing the effectiveness of U retention (e.g., sorption capacity, retention mechanism) by various materials, different technical (carbonate and acidic) leaching solutions in concentration varying from 0.1 to 0.5M are commonly used: sodium carbonate (Na_2CO_3), sodium bicarbonate (NaHCO_3), ammonium carbonate $[(\text{NH}_4)_2\text{CO}_3]$, nitric acid (HNO_3), sulphuric acid (H_2SO_4), etc.^{18,23–27} These solutions aim at desorbing U in an excess of carbonate at elevated pH (≥ 9) or an excess of sulphate or nitrate at low pH commonly employed in the soil remediation, respectively, in the mining industry.^{28,29} These conditions are somewhat far from natural conditions ($6.5 \leq \text{pH} \leq 9.5$) where U is leached by natural water which is generally mineralized rain water with elevated CO_2 -pressure. Therefore, leaching experiments in more realistic conditions are required to better understand the processes of U release.

Although a lot of research is aimed at the investigation and/or modeling of the mechanisms of U transport in the subsurface,^{30–32} experimental results based on realistic laboratory scenarios are scarce. This study aims at the characterization of the influence of carbonate ions and the effect of in situ generated iron-species on the U release from a natural rock under near-natural conditions. Different near-natural waters of varying carbonate concentrations [deionized (DW) tap (TW) and mineral waters (MW)] were used in batch and column experiments and the results are compared with those obtained from near-technical conditions (H_2SO_4 and Na_2CO_3). Particular attention is directed at the comparison of results of U release in 0.1M Na_2CO_3 and a CO_2 -riched mineral water.

Experimental

Solid materials

The chemical composition of the rock used in this study was determined by X-ray fluorescence (XRF). The rock contains around 2.3% U and is composed of: 81.25% SiO_2 , 0.14% TiO_2 , 7.36% Al_2O_3 , 1% Fe_2O_3 , 0.01% MnO , 0.48% MgO , 0.67% CaO , 1.19% Na_2O , 1.48% K_2O , 0.36% P_2O_5 and 0.01% SO_3 . The EDX analysis (results not shown) revealed that the used U-bearing rock is a multiminerale rock containing, among others, uraninite (UO_2), arsenopyrite (FeSAs), and galena (PbS). Associations of U with arsenopyrite was also encountered. The material was crushed and fractionated by sieving. Table 1 shows the different fractions that were used in this study without any further pre-treatment.

Pyrite mineral was crushed and sieved and the fraction 0.315 mm to 0.63 mm was used. The elemental composition is: Fe: 40%, S: 31.4%, Si: 6.7%, Cl: 0.5%, C: 0.15% and Ca <0.01%. The material served as a pH shifting reagent as well as an iron oxide producer.

Dolomite mineral was crushed, sieved and the fraction 0.63 to 1.0 mm was used. The mineralogical composition is: SiO_2 : 1.2%, TiO_2 : 0.03%, Al_2O_3 : 0.4%, Fe_2O_3 : 0.6%, MgO : 20.24%, CaO : 30.94%, Na_2O : 0.04%. Dolomite is a carbonate mineral and it is expected, that its dissolution and complex formation will increase the kinetics of U release.

Solutions

To mimic natural conditions various waters were used. Table 2 summarizes the carbonate contents and simulated effects. Two known leaching solutions (sodium carbonate and sulphuric acid, both 0.1M) were used for comparison.

Table 1. Used particle sizes of the U-bearing rock and corresponding specific surface area

Specific surface area, m ² /g	Size range, mm				
	0.063–0.125	0.250–0.315	0.315–0.630	0.630–1.0	1.6–2.0
<i>S</i>	4.66	3.53	n.d.	n.d.	n.d.
<i>S</i> ₁	2.03	0.64	2.06	1.81	n.d.
Code	<i>d</i> ₁	<i>d</i> ₂	<i>d</i> ₃	<i>d</i> ₄	<i>d</i> ₅

*S*₁ (m²/g) is the specific surface area for a different rock with around 1.2% U.

n.d.: Not determined.

Table 2. HCO₃⁻-content and simulated conditions of the used waters

Water (reagent)	Code	[HCO ₃ ⁻], mg/l	Simulated conditions	Example
Deionized	DW	n.d.	HCO ₃ ⁻ -poor water	Rain water
Tap	TW	89	Current groundwater	Infiltrating rainwater
Mineral	MW	1854	HCO ₃ ⁻ -rich water	HCO ₃ ⁻ -rich GW

n.d.: Not determined.

Uranium release experiments

Three different types of experiments were conducted:

Not homogenized batch experiments: Unless indicated otherwise, 0.1 g of the U-bearing rock and 0.1 g of the additive (pyrite or dolomite) were allowed to react in sealed sample tubes containing 13.0 ml of the tap water (reference leaching solution) at laboratory temperature (about 22 °C). The tubes had a total volume between 13.2 ml and 14.1 ml and a graduation to 10 ml. The tubes were filled to a total volume to reduce the head space. The solid:solution ratios were 8 g/l both for the U-bearing rock and the additive. For comparison, a further set of experiments was conducted with the U-bearing rock alone. The tap water of the city of Göttingen (Lower Saxonia, Germany) has a composition (in mg/l) of Cl⁻: 7.7; NO₃⁻: 10.0; SO₄²⁻: 37.5; HCO₃⁻: 88.5; Na⁺: 7.0; K⁺: 1.2; Mg²⁺: 7.5; Ca²⁺: 36; and an initial pH 8.3. After equilibration, 0.5 ml of the supernatant solution was retrieved at the top of each tube for U analysis. To compare the leaching capacity of the tested waters (Table 2) some experiments were conducted with 40 g/l of the U-bearing rock and different leaching solutions including 0.1N Na₂CO₃ and 0.1N H₂SO₄.

Air homogenized batch experiments: These experiments were conducted in special reaction vessels⁷ allowing the system to be homogenized by a humid current of air supplied by a small aquarist pump. The goal was to homogenize the experimental systems at atmospheric pressure without breaking down the materials. 10 g/l of the U-bearing rock and 0 or 7.5 g/l of the additive (pyrite or dolomite) were allowed to react in sealed vessels containing 100 ml of tap water at laboratory temperature (about 22 °C). At given dates 1.5 ml of the solution was retrieved for U analysis and

the same volume of tap water was added to the system. The pH value and the redox potential were recorded at selected dates.

Column experiments: Conventional chromatographic columns of 26 mm internal diameter and 300 mm length were packed in their lower part with a mixture of sand and U-bearing rock (1 g of the *d*₂-fraction, see Table 1) or sand, U-bearing rock (1 g) and an additive (1.5 g of pyrite or dolomite). In all systems the remaining space above the material column varies between 90 and 100 ml. Selected leaching solutions (DW, TW, MW, Na₂CO₃ or H₂SO₄) were allowed to equilibrate with the column content before being filtered through the material mixture after one week. The experiment was conducted for 10 weeks. Each eluted volume was measured and analyzed for U and pH.

Analytical method

Analysis for U was performed by inductively coupled plasma mass spectrometry (ICP-MS) at the Institute of Geosciences, University of Jena. All chemicals used for experiments and analysis were of analytical grade. Despite large dilution factors (up to factor 400), ICP-MS gives satisfactory results for the concentration range of this study. Two representative samples were analyzed by ICP-EOS, ICP-MS and spectrophotometry (Arsenazo III-method) and the relative error was less than 12% and the standard deviation was larger or equal to the absolute deviation.

The pH value was measured by combination glass electrodes (WTW Co., Germany). The electrodes were calibrated with five standards following a multi-point calibration protocol³³ and in agreement with the new IUPAC recommendation.³⁴ The redox potential measurements were corrected to give equivalency to the

Standard Hydrogen Electrode (SHE). Krypton adsorption isotherms at 77 K were measured with Autosorb-1 instrument (Quantachrome). The specific surface area was calculated using the standard multipoint BET procedure³⁵ with a cross sectional area of 20.5 Å² for Kr. Prior to the measurements, the samples were degassed at 300 °C for 1 hour.

Apart from column experiments, all experiments were performed in triplicate. Error bars given in the figures represent the standard deviation from the triplicate runs.

Results and discussion

After the determination of the aqueous U concentration at a given date, the corresponding amount of leached U (mg or %) was calculated for an adequate discussion. In some cases, the U concentration (in µg/l) was sufficient.

Effect of the particle size

Particle size is an important aspect of mineral dissolution.^{36,37} As a result of mechanical weathering (e.g., pressure release, freezing water, thermal expansion and contraction, biological action, salt crystal growth), rocks and minerals are broken down into smaller pieces. It can be assumed that a range of particle sizes will have varying dissolution rates. The current assumption is the smaller the particle size the quicker the dissolution (chemical weathering by water and air). The <2 mm fractions of the studied U-bearing rock (Table 1) can be considered as the most “reactive fraction” and four different sub-fractions have been used for this batch experiments (not homogenized). Table 3 and Fig. 1 summarize the results.

Table 3. Absolute (P_U) and relative (P_{rel}) variation of the percent U release rate in different leaching solutions as a function of the particle size

Code	Reagent and percent of leaching					
	TW		Na ₂ CO ₃		H ₂ SO ₄	
	P_{rel}	P_U	P_{rel}	P_U	P_{rel}	P_U
d_1	100	13	100	17	100	43
d_2	81	10	53	9	68	29
d_3	78	10	40	7	70	30
d_4	61	8	28	5	47	20

The maximal leaching capacity (100%) in each case has been attributed to the smallest particle size (d_1). Data have been gained in not homogenized batch experiments with 40 g/l U-bearing rock.

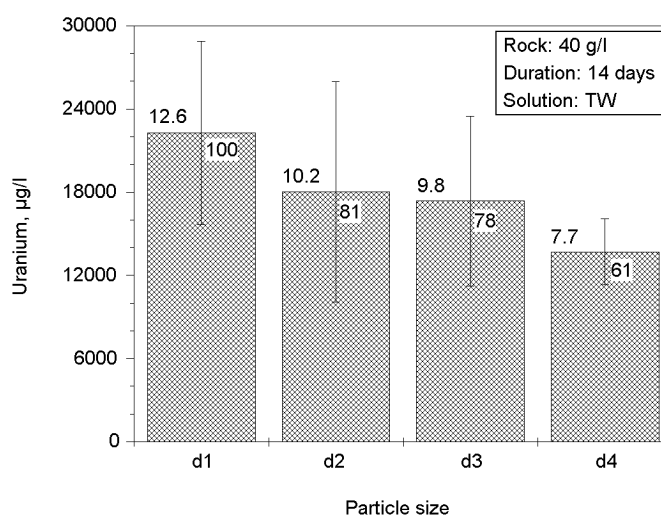


Fig. 1. Total U concentration as a function of particle size for tap water as leaching solution. The experiments were conducted in triplicate. Error bars give standard deviations. The values in the bars represent the leaching percentage assuming 100% leaching for the smallest particle size and the values above the give leaching percentage referred to the total U amount in the rock

According to the assumption above, the sequence of reactivity is $d_1 > d_2 > d_3 > d_4$; this is strictly true only for the experiment in 0.1N Na_2CO_3 (Table 3). For the systems with tap water (TW) and 0.1N H_2SO_4 , the reactivity sequence was $d_1 > d_2 \approx d_3 > d_4$ (Fig. 1). Table 1 shows an abnormality in the evolution of the specific surface area of another U bearing rock, suggesting that other effects (e.g., mineralogical effects) influence the dissolution of the mineral in that range of particle size. Further investigations were not possible due to the limited amount of the sample. Table 3 also shows that in all the cases less than 50% of the total U content could be leached from the rock in a single batch experiment even with a reagent as strong as 0.1N H_2SO_4 (43%). The leaching rate with the tap water which can be assumed to be very close to most natural ground waters varies between 8 and 13%, confirming the reported effectiveness difficulty of the pump-and-treat technology.^{2,3,38} In real life other minerals and organic

substances will further complicate the situation by reducing the leaching capacity of the water. Water chemistry, particularly the carbonate content (HCO_3^- or PCO_2) will also play an important role.

Effect of the leaching solution: carbonate content

The processes that enable U to be dissolved and leached from the ore body are known and used in the mining industry as solution mining.²⁹ To access the reactivity of materials for U retention or removal in the laboratory, many operational leaching solutions have been defined.^{23–25,28,39} All these solutions are more aggressive than natural waters. To check the ability of natural waters to leach U from the studied rock, parallel experiments were conducted with different waters (as defined in Table 2) and the results were compared with that of 0.1N Na_2CO_3 and 0.1N H_2SO_4 . Table 4 and Fig. 2 show the results.

Table 4. Variation of the pH value and U leaching efficiency as a function of the leaching solution for two weeks

Reagent	pH _i	pH _f	ΔpH	[U], ppb	P _U , %	[Si], mM/l
DW	5.86	7.82	1.96	583	0.3	0.12
TW	8.43	7.77	-0.66	3854	2.0	2.09
Na_2CO_3	11.47	11.2	-0.27	4634	2.2	10.15
MW	6.87	6.92	0.05	10028	5.0	–
H_2SO_4	1.09	1.24	0.15	51843	23.9	–

pH_i: Initial pH value.

pH_f: Final pH value.

P_U: Percentage of leached U.

[Si] is the silicon release from a pure SiO_2 phase for 72 hours in the corresponding solutions.

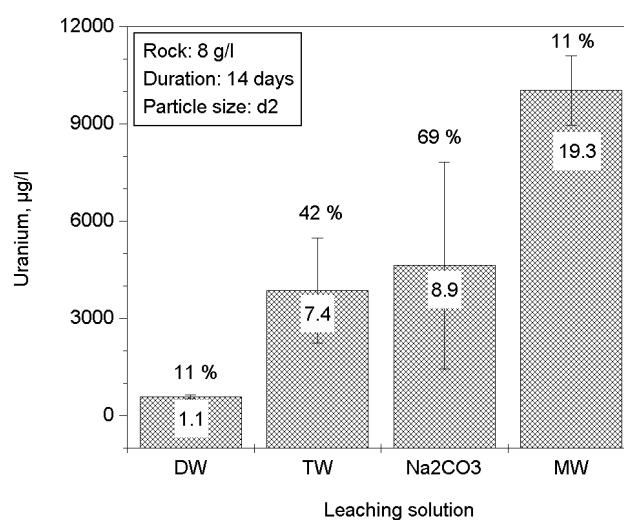


Fig. 2. Total U concentration as a function of the leaching solution for a rock particle size of 0.250–0.315 mm (d_2). The experiments were conducted in triplicate. Error bars give standard deviations (values in %). The values in the bars represent the relative leaching percentage assuming 100% leaching in H_2SO_4 (0.1M)

The results in Table 4 can be summarized as follows:

(1) The dissolution of the U-bearing rock induced a minor increase in pH value when the initial value (pH_i) was lower than 7 and a minor decrease for $\text{pH}_i > 7$, suggesting that the rock dissolution will not have any major influence on the pH, this observation is confirmed by the mineralogical composition of the rock, that consists of 81.3% of SiO_2 .

(2) In natural waters the U leaching efficiency varies between 0.3% and 5% whereas the leaching efficiency for Na_2CO_3 and H_2SO_4 were 2.2% and 24%, respectively (Fig. 2).

It is interesting to note that the U leaching efficiency in mineral water (MW; pH_i 6.87) is greater than in Na_2CO_3 (pH_i 11.47), although the comparison of the $[\text{CO}_3^{2-}]$ to $[\text{U}]$ molar ratios of both systems indicated that there are four times more carbonate ions available for U complexation in the system with Na_2CO_3 than in the system with MW. This result can be justified by the trend of U to build co-precipitates at higher pH values, hence a part of dissolved U may co-precipitate for example as sodium uranates (Na_2UO_4). This hypothesis is supported by the Si release in three different solutions (Table 4). At elevated pH value (Na_2CO_3) the U-bearing rock (81.25% SiO_2) dissolves more easily.

Considering the better reproducibility of the results in the mineral water (11% compared to 69% standard deviation; Fig. 2) selected CO_2 -saturated (therefore, HCO_3^- -rich) waters can be suggested as an alternative to technical carbonate solutions for leaching experiments for environmental purposes. The leaching efficiency in H_2SO_4 is by far the largest but no conclusions for natural conditions can be drawn from those types of experiments. Therefore, the H_2SO_4 -leaching were used as the maximal removable amount of U under the given

experimental conditions and as reference for the definition of the relative leaching percentage (Fig. 2).

Effect of the additive materials

Another way to qualitatively characterize the effect of reactive material on U release consisted in mixing the rock and an additive in the so-called "air homogenized batch experiments". Table 5 shows the variation of the pH and E_H values and Fig. 3 summarizes the results of the variation of the U concentration.

Table 5 shows that:

(1) The pH of the reference system and the system with dolomite was constant at a value of about 8.3 during the whole experiment whereas the system with pyrite shows a lower pH (initial value 6.38) that progressively increases to a final value of 8.00 after 70 days. It can be emphasized that the pH will reach the equilibrium value of 8.3 for longer experimental duration.

(2) The redox potential (E_H) shows the same trend and a final value of about 430 mV was obtained in all systems.

The decrease of the pH is due to pyrite oxidation^{30,40} that normally increases the solubility of U.⁴¹ Under the experimental conditions (neutral pH, oxic), however, dissolved Fe^{2+} ions from pyrite lead upon oxidation by dissolved oxygen to $\text{Fe}(\text{OH})_{3(\text{am})}$ precipitates that are excellent sorbents for U.^{42,43} This fact explains the low U concentration in the initial phase of the experiment (Fig. 3a). After this initial phase (4–5 days), the U concentration progressively increased, indicating that the acidification capacity of the pyrite is consumed and the pH of the system progressively increased.

Table 5. Variation of the pH and E_H values in the air homogenized batch experiments

Time, day	Reference (rock)		Rock + dolomite		Rock + pyrite	
	pH	E_H , mV	pH	E_H , mV	pH	E_H , mV
0.1	8.33	366	8.31	441	6.38	324
0.3	8.32	401	8.28	422	6.37	374
0.5	8.29	441	8.27	428	7.71	381
1	8.31	324	8.32	426	7.54	466
2	8.22	445	8.25	439	7.51	461
4	8.31	433	8.31	442	7.76	453
9	8.33	427	8.33	442	7.97	446
18	8.30	422	8.30	434	7.93	445
34	8.33	428	8.33	443	7.99	465
42	8.31	416	8.29	425	7.96	428
70	8.28	427	8.25	432	8.00	433

The E_H values were corrected to give equivalency to the Standard Hydrogen Electrode.

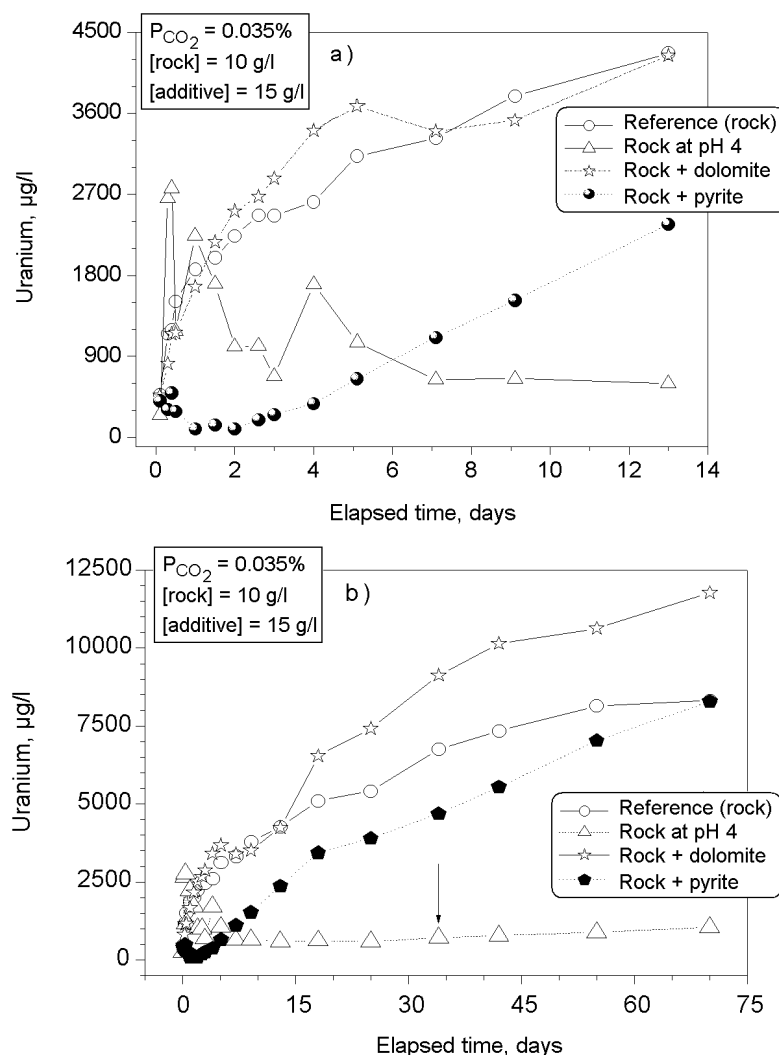


Fig. 3. Evolution of the total U concentration as a function of time in air homogenized batch experiments; initial phase (13 days) (a) and entire experiment (70 days) (b); “rock at pH 4” represents an experiment in which the pH of the system was repeatedly adjusted to a value of approx. 4 with 0.2M HCl. This adjustment was stopped at day 34 as indicated by an arrow. P_{CO_2} is the atmospheric partial pressure of CO_2 (open system)

The continuous increase of the U concentration suggests that the sorptive capacity of in situ produced $Fe(OH)_{3(am)}$ and that of pyrite by-mineral are consumed while the U-bearing rock continues to release U into the solution as the pH increases. This suggestion is supported by the comparison between the reference system and the system with dolomite that showed a very similar evolution in the initial phase (Fig. 3a) and a net difference above 14 days, while the system with dolomite shows higher U release efficiency (Fig. 3b) due to increased carbonate concentrations. BERNHARD et al.^{44,45} showed that under similar natural conditions (pH 8.1), the aqueous U speciation of a seepage water was dominated by a soluble aquo-complex of di-calcium uranyl carbonate ($Ca_2[UO_2(CO_3)_3] \cdot 10H_2O$). At the end of the experiment (day 70) the reference system and the system with pyrite showed almost the same leaching

efficiency, suggesting that a steady state was achieved. The discussion of the experiment “rock at pH 4” is given later in the text.

Effect of locally induced variations

An important aspect of contaminant transport that is often neglected when transport processes are modeled is the local evolution of the system at non-equilibrium (or before an equilibrium state is established). Such situations are for example: (1) bulk dilution (mixture of infiltrating non-contaminated water with water of a contaminated zone); (2) soil contamination (contaminated water enters a region of non contaminated soil), and (3) a zone directly downstream of an acid producing area (the recharging acid water can be assumed to be of constant pH).

To simulate the two first cases, the following modifications were performed in experiments carried out in a similar way to the above described air homogenized experiments (“reference”, “rock + dolomite” and “rock + pyrite”, Fig. 3) at day 70: 50 ml of the solution was retrieved from the reference system and replaced by 50 ml of tap water (1:1 dilution). In the systems with additives of 2 g of the corresponding material (resulting total additive amount: 3.5 g or 35 g/l) was added to the bulk solution in the vessel. It is important to note that these experiments differed from those presented in Fig. 3 in that the rock particle sizes were smaller (d_1 , Table 1). Therefore, it is not surprising that the initial concentrations here are higher than the final concentrations of Fig. 3. The evolution of the systems were recorded for two weeks (U, pH). Figure 4 shows the evolution of the U concentration in the three systems.

The third modification was simulated by conducting an experiment parallel to those described above but readjusting the pH value to 4 after each sampling operation, the results are shown in Fig. 3.

It is apparent from Fig. 3 that the adjustment of the pH value at 4 increases considerably the initial leaching rate of U (2,768 $\mu\text{g/l}$ after 0.4 day) but only at the beginning of the experiment (first day, Fig. 3a); further pH-fixation leads to a decrease of the U concentration to values lower than 1,100 $\mu\text{g/l}$ even after the pH fixation was stopped at day 34 (marked in Fig. 3b). This observation is probably due to the formation of coprecipitation products of U, Ca.⁴⁶

Figure 4 shows that the dilution (System I) diminished the U concentration by approximately 64%. The addition of pyrite (System II) and dolomite (System III) induced a decrease of U concentration of 89% and 4%, respectively. In all cases the U concentration increases continuously until the experiment was stopped after 14 days. It can be emphasized that the U concentration will rise to the initial value (before perturbation) for a longer experimental duration. The fact that the U concentration decreases in all systems (even in the presence of dolomite) shows that the sorption onto mineral is not always negligible, even in the presence of carbonate species. At the end of the experiment, the percent concentration decrease (relative to the start at day 70) in the Systems I, II and III were 43%, 72% and 12%, respectively, showing that the U concentration in the System III is above the value at day 70, whereas the concentration increase in the other systems occurs only very slowly. The processes in System II (pH decrease, formation of $\text{Fe}(\text{OH})_{3(\text{am})}$) have already been discussed. The decrease of the U concentration to more than 50% (64%) as result of a 1:1

dilution in System I is difficult to explain, since the U concentration increases only to 43% of its initial value even after 14 days equilibration. Coprecipitation of U with Ca^{2+} ions contained in tap water, flocculation with Al-species from the rock and sorption onto the reactor vessel are possible reasons for this decrease. The minor and very short decrease of the U concentration in System III, confirms the fact that the presence of dissolved carbonate species inhibits U sorption.^{12,16,42}

Column experiments

Two types of column experiments were conducted. The first aimed at simulating the repeated leaching of a mineral by the same solution as it probably occurs in nature in a soil profile (saturated zone). These experiments were conducted as described in the Experimental section. A variation consisted of charging the column with a layer of pyrite or dolomite above the U-bearing rock layer, while separating the two layers with ca. 5 cm of quartz, the material mixtures were then leached with tap water once a week for 10 weeks (Table 6). The second type of experiments aimed at the relationship between the kinetics of U release and the particle size. Figures 5 and 6 summarize the results.

Figure 5 confirms the leaching capacity of the tested solutions as observed in batch experiments: $\text{H}_2\text{SO}_4 \gg \text{MW} > \text{Na}_2\text{CO}_3 > \text{TW} > \text{DW}$. It also shows that a steady state was achieved only after 5 runs and that even at the end of the experiment (10 runs), the residual U concentration of the effluents were higher than 260 $\mu\text{g/l}$ (EPA threshold value 30 $\mu\text{g/l}$). These results confirmed the difficulty of “sweeping” the contaminant from the soil with groundwater with a pump-and-treat technology (as discussed above) and also the difficulty of predicting the life-time of a reactive barrier. In fact, under the above experimental conditions the leaching efficiency at the end was 5%, 22%, and 35% of the total amount of U for DW, TW and MW, respectively.

Assuming steady state at the end of the experiment, the number of flushings needed to achieve a complete leaching of the remaining U from the rock was estimated as 25 for the mineral water (MW), 41 for tap water (TW), and 722 for deionized water (DW). Depending on the climatic conditions at individual sites, the estimated flushing efficiencies can take up to several decades to be achieved. It should be kept in mind, that these results are only valid for the particle size used. Natural systems, however, are characterized by large heterogeneities. Figure 6 shows that the assumed steady state concentration will be different for another range of particle sizes.

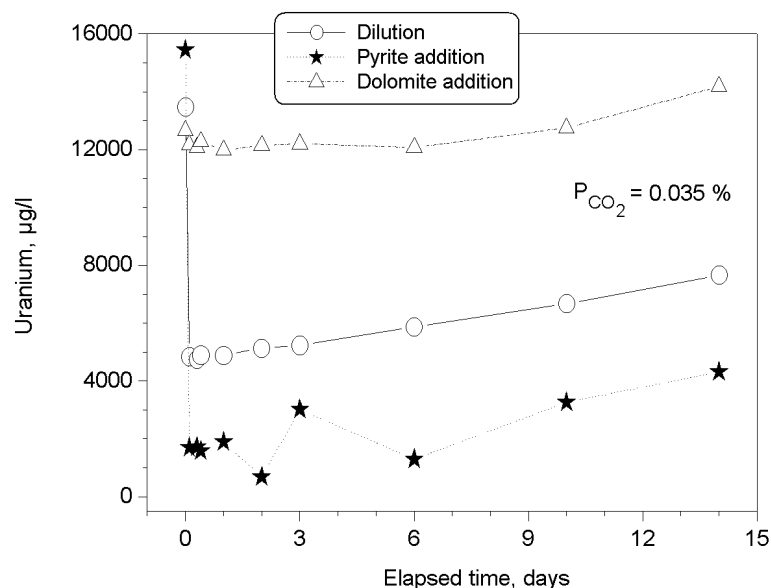


Fig. 4. Variation of the U concentration as reaction of the system to dilution and addition of additive (20 g/l) as a function of the time in air homogenized batch experiments. The initial time ($t=0$) corresponds to the end of an equilibration time of 70 days

Table 6. Comparison of the U leaching rate from various column experiments

System	m_U , mg	$P_{H_2SO_4}$, %	P_U , %	m_U^1 , mg	v , mg/week	n
DW (d_2)	1.13	6.9	4.9	22.03	0.031	722
pyrite (d_4)	2.39	5.6	10.3	20.77	0.122	170
dolomite (d_4)	2.52	6.0	10.9	20.64	0.13	159
TW (d_4)	2.57	6.1	11.1	20.59	0.136	151
TW (d_2)	5.11	31.4	22.1	18.05	0.446	41
Na_2CO_3 (d_2)	6.89	42.3	29.8	16.27	0.514	32
MW (d_2)	8.18	50.2	35.3	14.98	0.602	25
H_2SO_4 (d_2)	16.28	100.0	70.3	6.88	0.024	284
H_2SO_4 (d_4)	41.82	100.0	180.6	-18.66	0.061	–
H_2SO_4 (d_5)	42.30	100.0	182.6	-19.13	0.348	–

m_U : Total leach amount (initial amount: 23.2 mg).

m_U^1 : Remaining amount in the rock.

v : Leached amount of the 10th week which is considered as constant for further irrigations.

n : Number of irrigations necessary to leach m_U^1 .

d_i : Particle size of the used rock as defined in Table 1.

$P_{H_2SO_4}$: Relative percent leaching assuming 100% leaching efficiency in H_2SO_4 for a given d_i .

P_U : Absolute percent leaching related to the initial U in 1 g of rock.

The experiments with dolomite and pyrite (Table 6) generally supported the observations from the batch study: no major change due to the presence of dolomite and a retardation in the presence of pyrite. In the batch experiment, however, a clearly higher U release due to the presence of dolomite was observed in comparison to the reference system. In column experiments this difference was not obvious. This can be explained by both U sorption onto sand particles and the slow kinetics of dolomite dissolution in tap water since the equilibration time was only one week. Homogenized batch experiments have shown that the influence of dolomite dissolution is significant only after two weeks (Fig. 3). In the field, elevated carbonate concentrations

originate both from mineral dissolution and biological processes.

Table 6 shows the systems classified from the top to the bottom in order of increasing U leaching efficiency. The observed leaching efficiency of batch experiments is confirmed for each range of particle size (d_2 and d_4). These results can be summarized as follows:

(1) The systems with natural waters showed leaching efficiency of up to 35% (after 10 flushings). In both types of batch experiments the maximum achieved leaching efficiency was 5%.

(2) The systems with higher particle sizes (d_4 and d_5) and H_2SO_4 exhibited leaching goals (P_U) higher than 100% ($m_U^1 < 0$). This justifies the definition of an

operative relative leaching percent ($P_{H_2SO_4}$). Beside the inhomogeneity of rock samples, the well known difficulty of completely dissolving rocks for elemental analysis are two possible justifications for this observation.

(3) To achieve a complete leaching of U from the rock, the flushing will have to be performed at least 25 times (n values, see Table 6).

In summary, these results show the difficulty to predict the leaching rate of U under natural conditions. When considering n -values between the systems, it can be seen that the " H_2SO_4 (d_2)"-system with a $P_U = 70.3\%$ has an n -value of 284 whereas the MW (d_2)-system with a $P_U = 35.2\%$ has an n -value of only 25. This result is apparently contradictory but becomes comprehensible

when one considers the v -values. This is mathematically correct since the smaller the v -value the larger the n -value. Physically, this can be explained by the fact that a real steady state is achieved for the " H_2SO_4 (d_2)"-system whereas the MW (d_2)-system will only slowly attain such a stage. This observation corresponds to the well known tailings effect⁴⁷ and is responsible for the non-effectiveness of pump-and-treat systems in groundwater remediation for U contaminates sites. It also shows how difficult it will be to predict the suitable service life of reactive barriers, since in natural systems the heterogeneity of the subsurface together with the variability of the geochemical conditions (presence of U sorbents, solution chemistry, ...) will further complicate any accurate prediction.

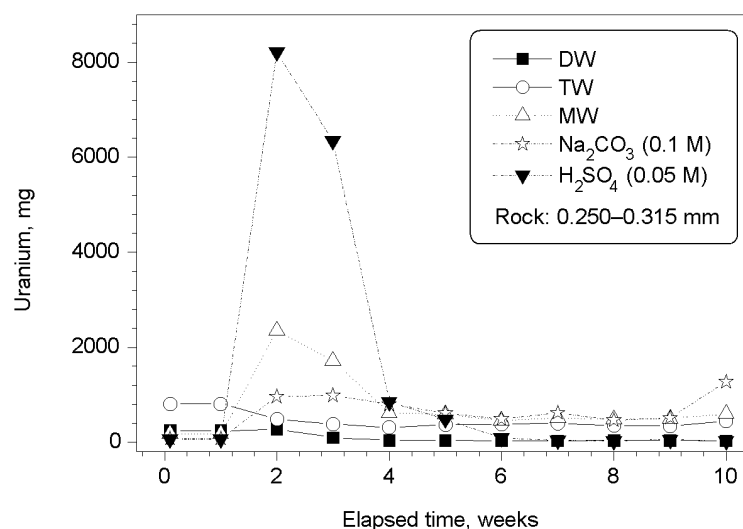


Fig. 5. Variation of the leaching rate of U from the rock as a function of time in various leaching solutions. A steady state is achieved after about 5 weeks

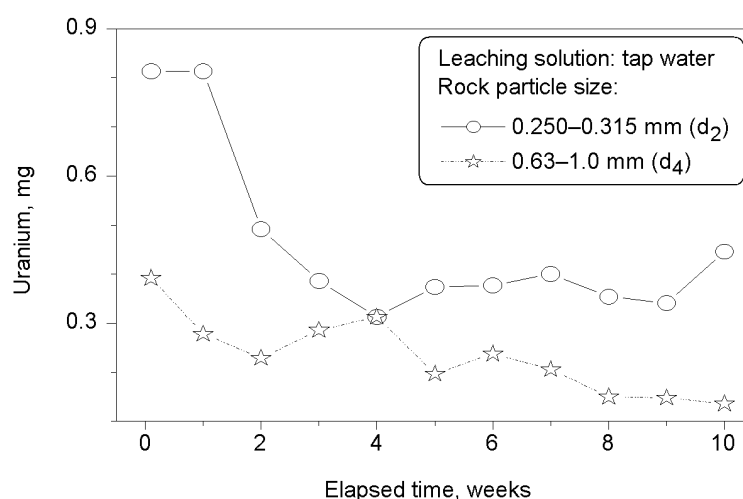


Fig. 6. Variation of the leaching rate of U from the rock as function of the particle size in tap water. In each case a steady state was achieved after about 8 weeks

Conclusions

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The leaching process of U from a natural rock was characterized by three different types of experiments. Known active species (carbonate) were added as solute to the rock in batch experiments on one hand, and on the other hand, the U bearing rock was mixed in batch experiments with an active mineral (dolomite or pyrite) or were packed into a column the active mineral been upwards from the U-bearing rock. The results show that:

(1) From the tested natural near solutions, the carbonate rich mineral water (MW) was the most effective one for leaching U from the rock.

(2) The U release from the rock increases with the carbonate concentration as long as the rock dissolution is not competing with the U coprecipitation at elevated pH values.

(3) The presence of any mineral (including SiO_2) retards the U transport. Strong retarding influence of $\text{Fe}(\text{OH})_{3(\text{am})}$ has been confirmed in experiments with pyrite.

(4) The mobilization rate will rapidly decrease with time, yielding a tailing effect that will complicate any prediction effort if the residual contamination level is above a threshold value.

Another important result of this investigation is that well characterized over-saturated CO_2 solutions are better alternatives to conventional carbonate solutions for the assessment of the leaching ability of U from environmental samples. In this study a commercially available mineral water was used.

Among the list of natural processes believed to inhibit migration of U, sorption onto Fe/Mn-oxide and other so-called active organic and inorganic substances have been assumed to be the most important ones. This study has shown that the understanding the retarding influence of by-minerals both of the U rocks and the active inorganic substances can help to develop better strategies for understanding/predicting the transport of U and thus managing the contaminated sites and nuclear waste repositories.

Since weathering is controlled by the climate (temperature, precipitation), rock properties (surface area, permeability and mineralogy), contact time, and microbiological processes it is necessary to thoroughly assess the geochemical situation of a site (U content of the mineral or tailings, by-mineral, organic substances) in order to accurately predict the migration rate of the contaminant to the barrier zone. An effort should be taken to keep the short possible pathway from the contaminant source zone to the reactive barrier to minimize uncertainties due to various complex processes.

The authors express their gratitude to Dr. Dirk MERTEN of the Institute Geoscience of the University of Jena for the ICP uranium analyses. Mr. Dipl.-Min. Holger DIENEMANN of the Institute of General Ecology and Environmental Protection of Tharandt (University of Technology Dresden) contributed with discussion and suggestions to the quality of this work. The work was supported by the German Science Foundation (Deutsche Forschungsgemeinschaft; DFG-SA 501/15-1).

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