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

Noubactep C. (a) *, Sonnefeld J. (b) & Sauter M. (a)

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

(b) Institute of Physical Chemistry Friedrich-Schiller University of Jena; Lessingstrasse 10; D - 07743 Jena

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

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

Abstract

Understanding how uranium (U) 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 (UO_2-rock) in different waters under test conditions relevant to U transport from mine wastes (tailings). For this purpose, not shaken batch experiments were conducted with a constant amount of an UO_2-rock and different types of water (deionised, tap and mineral water). For comparison parallel experiments were conducted with 0.1 M Na_2CO_3 and 0.1 M H_2SO_4. Further dissolution experiments using UO_2-rock together with dolomite and pyrite were conducted. The results indicate that carbonate addition (soluble or in-situ generated) enhanced U solubilization, whereas pyrite addition essentially slowed the initial U solubilization. It is shown that SiO_2 and other rock constituents may contribute to retard U transport.

Key Words: uranium, oxic conditions, carbonates, iron oxides.

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 (Catchpole & Kirchner 1995, McMurty & Elton 1985, Nyer et al. 1996).

Uranium (U) has been reported to be leached from rocks and to be present in water in concentrations up to 10 μgL^{-1} (Brits & Smit 1977, Merkel & Sperling 1998). Uranium content of land waters in excess to 1 μgL^{-1} is regarded as an anomaly (Sadeghi et al. 2003). On the other hand, laboratory solubility experiments with synthetic schoepite (pure phase) showed that about 1000 μgL^{-1} U can be dissolved at neutral pH values (Noubactep 2003). 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 heterogeneous materials. For example, concentrations of complexing surface sites may be difficult to estimate from measurable characteristics of the natural materials (e.g. Logue et al. 2004, Grauer 1997). 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 (e.g. Meinrath & May 2002). Therefore it is necessary to closely investigate the processes that influence the U dissolution and transport under conditions similar to oxic mine wastes.

For modelling 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 (Elless & Lee 1998, Grauer 1997). To corroborate this assumption, modellers used to choose less soluble minerals as solubility controlling phases (Grauer 1997). In this way, "residual discrepancies" are usually attributed to co-precipitation mostly with iron oxides and to complex interactions with supposedly available humic substances (Langmuir 1978). However, recent works reported considerable U sorption onto sand (quartz), which is commonly considered as non-reactive material (Read et al. 1993, Noubactep 2003, Logue et al. 2004). For example, when investigating the retention capacity of non-ferric sandstone core materials, Read et al. (1993) illustrated the strong affinity of aqueous U species for natural surfaces under strongly oxidising conditions. Noubactep (2003) 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 (Nyer et al. 1996). 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 modelling purposes.

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, [HCO_3^-] and presence of Fe(III)-species).

Background

In natural U deposits and U tailings the dissolution process typically involves oxidation and destabilization of U(IV) minerals such as uraninite (UO_{2+x}) and coffinite ($USiO_4$:nH_2O) resulting in high concentrations of U(VI) aqueous species (Langmuir 1978). In these environments U concentrations of up to more than 10,000 μgL^{-1} have been reported depending on the geochemical conditions (Jerden Jr. & Sinha 2003, Junghans & Helling 1998, Langmuir 1997, Miekeley et al.1992). For example, Jerden & Sinha (2003) reported that groundwaters with U concentrations of up to 575,000 μgL^{-1} (575 ppm, average value) could be reduced to values as low as 15 μgL^{-1} in phosphate rich environments 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 (Langmuir 1978, Merkel & Sperling 1998, Sowder et al. 2001). This process is in turn strongly influenced by the carbonate concentration (HCO_3^-, P_{CO2}) which lowers sorption onto inorganic minerals (Fe/Mn-oxides) and organic substances (Clark et al. 1997, Kalin et al. 2005, Meinrath 1998, Wazne et al. 2003).

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 0.5 M are commonly used: sodium carbonate (Na_2CO_3), sodium bicarbonate ($NaHCO_3$), ammonium carbonate ($(NH_4)_2CO_3$), nitric acid (HNO_3), sulphuric acid (H_2SO_4) … (Sowder et al. 2001, Duff et al. 1997, Fredrickson et al. 2000, Kaplan & Serkiz 2001, Mason et al. 1997, Noubactep et al. 2003). 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 (e.g. Gadelle et al. 2001, Peters 1978). These conditions are somewhat far from natural conditions ($4.5 \leq pH \leq 9.5$) where U is leached by natural water which is generally mineralised 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 modelling of the mechanisms of U transport in the subsurface (Bain et al. 2001, De Windt et al. 2003, Meinrath et al. 1999), 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 (deionised, tap and mineral waters) 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 0.1 Na_2CO_3 and a CO_2-riched mineral water.

Experimental Section

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 multimineralic 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 different waters were used. Table 2 summarises the carbonate contents and simulated effects. Two known leaching solutions (sodium carbonate and sulphuric acid, both 0.1 M) were used for comparison.

Uranium release experiments

Three different types of experiments were conducted:

Not homogenised 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; NO_3^-: 10.0; SO_4^{2-}: 37.5; HCO_3^-: 88.5; Na^+: 7.0; K^+: 1.2; Mg^{2+}: 7.5; Ca^{2+}: 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 0.1 N Na_2CO_3 and 0.1 N H_2SO_4.

Air homogenised batch experiments: These experiments were conducted in special reaction vessels (Noubactep 2003) allowing the system to be homogenised by a humid current of air supplied by a small aquarist pump. The goal was to homogenise 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 the 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, Na_2CO_3 or H_2SO_4) 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 analysed 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 analysed by ICP-EOS, ICP-MS and spectrophotometry (ArsenazoIII-method) and the relative error was less that 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 protocol (Meinrath & Spitzer 2000) and in agreement with the new IUPAC recommendation (Buck et al. 2002). 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 procedure (Brunauer et al. 1938) with a cross sectional area of 20.5 $Å^2$ for Kr. Prior to measurements, the samples were degassed at 300°C for 1 hour.

A part from column experiments, all experiments were performed in triplicate. Error bars given in 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 (Malmström et al. 1996, Reiche 1950). 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 more "reactive fraction" and four different sub-fractions have been used for this batch experiments (not homogenised). Table 3 and figure 1 summarise the results.

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 0.1 N Na_2CO_3 (table 3). For the systems with tap water (TW) and 0.1 N H_2SO_4, the reactivity sequence was $d_1 > d_2 \cong d_3 > d_4$ (figure 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 0.1 N 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 (McMurty & Elton 1985; Nyer et al. 1996, Mackay and Cherry 1989). In real life other minerals and organic substances will further complicate the situation by reducing the leaching capacity of the water. The water chemistry, particularly the carbonate content (HCO_3^- or P_{CO2}) 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 (Peters 1978). To access the reactivity of materials for U retention or removal in the laboratory, many operational leaching solutions have been defined (Duff et al. 1997, Fredrickson et al. 2000, Gadelle et al. 2001, Kaplan & Serkiz 2001, Liu et al. 2004). 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 where compared with that of 0.1 N Na_2CO_3 and 0.1 N H_2SO_4. Table 4 and figure 2 show the results.

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 $pH_i > 7$, 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 comparison of the $[CO_3^{2-}]$ to [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 investigate the effect of reactive material on U release consisted in mixing the rock and an additive in the so-called “air homogenised batch experiments”. Table 5 shows the variation of the pH and E_H values and figure 3 summarises the results of the variation of the U concentration.

Table 5 shows that:

- 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;

- 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 (Bain et al. 2001, Williamson & Rimstidt 1994) that normally increases the solubility of U (Noubactep et al. 2002). Under the experimental conditions (neutral pH, oxic) however dissolved Fe^{2+} ions from pyrite lead upon oxidation by dissolved oxygen to $Fe(OH)_{3(am)}$ precipitates that are excellent sorbents for U (Ho & Miller 1986, Jambor & Dutrizac 1998). 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. 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. (1996, 2001) 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 ($Ca_2[UO_2(CO_3)_3].10H_2O$). 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 modelled is the local evolution of the system at non-equilibrium (or before an equilibrium state is established). Such situations are for example (Spiessl 2004):

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 homogenised 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 the tap water (1:1 dilution). In the systems with additives 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 figure 3 in that the rock particle sizes were smaller (d_1, table 1). It is therefore not surprising that the initial concentrations here are higher than the final concentrations of figure 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 re-adjusting the pH value to 4 after each sampling operation, the results are shown in Figure 3.

It is apparent from Figure 3 that the adjustment of the pH value at 4 increases considerably the initial leaching rate of U (2768 μg/L after 0.4 day) but only at the beginning of the experiment (first day, figure 3a); further pH-fixation leads to a decrease of the U concentration to values lower than 1100 μg/L even after the pH fixation was stopped at day 34 (marked in Fig. 3b).

This observation is probably due to the formation of co-precipitation products of U, Ca (Morrison & Spangler 1992).

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 emphasised 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 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 system I, II and III were 43, 72 and 12 % respectively, showing that the U concentration in 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 $Fe(OH)_{3(am)}$) 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. Co-precipitation 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 (Langmuir 1978, Langmuir 1997, Ho & Miller 1986).

Column experiments

Two types of 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 where 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. Figure 5 and 6 summarise the results.

Figure 5 confirms the leaching capacity of the tested solutions as observed in batch experiments: H_2SO_4 >> MW > Na_2CO_3 > TW > 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 µg/L (EPA threshold value 30 µg/L). These result illustrates 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 deionised 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.

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. Homogenised batch experiments have shown that the influence of dolomite dissolution is significant only after two weeks (figure 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 summarised as follows:

- 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%;
- the systems with higher particle sizes (d_4 and d_5) and H_2SO_4 exhibited leaching goals (P_U) higher than 100% ($m^1_U < 0$). This justifies the definition of an operative relative leaching percent (P_{H2SO4}). Beside the inhomogeneity of rock samples, the well known difficulty of completely dissolving rocks for elemental analysis are two possible justifications for this observation.
- 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 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 a n-value of 284 whereas the MW (d_2)-system with a P_U = 35.2 % has a n-value of only 25. This result is apparently contradictory but become 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 effect (Sontheimer et al. 1988) 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.

Conclusion

In this study the leaching process of U from a natural rock was characterised 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:

- From the tested natural near solutions, the carbonate rich mineral water (MW) was the most effective one for leaching U from the rock.
- The U release from the rock increases with the carbonate concentration as long as the rock dissolution is not competing with the U co-precipitation at elevated pH values;
- The presence of any mineral (including SiO_2) retards the U transport; the strong retarding influence of $Fe(OH)_{3\ (am)}$ has been confirmed in experiments with pyrite.
- The mobilisation 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, 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 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 minimise uncertainties due to various complex processes.

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Table 1: Used particle sizes of the U-bearing rock and corresponding specific surface area. S_1(m^2/g) is the specific surface area for a different rock with around 1.2 % U (n.d. = not determined).

Size range (mm)	0.063 - 0.125	0.250 - 0.315	0.315 - 0.630	0.630 - 1.0	1.6 - 2.0
S (m^2/g)	4.66	3.53	n.d.	n.d.	n.d.
S_1 (m^2/g)	2.03	0.64	2.06	1.81	n.d.
Code	d_1	d_2	d_3	d_4	d_5

Table 2: HCO_3-content and simulated conditions of the used waters (n.d. = not determined).

Water (reagent)	**Code**	**[HCO_3^-] (mg/L)**	**simulated conditions**	**Example**
Deionised	DW	n.d.	HCO_3-poor water	rain water
Tap	TW	89	current groundwater	infiltrating rainwater
Mineral	MW	1854	HCO_3-rich water	a HCO_3-rich GW

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

	Reagent and percent (%) leaching					
	TW		**Na_2CO_3**		**H_2SO_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

Table 4: Variation of the pH value and U leaching efficiency as a function of the leaching solution for two weeks. pH_i = initial pH value; pH_f = final pH value; and P_U = percentage of leached U. [Si] is the silicon release from a pure SiO_2 phase for 72 hours in the corresponding solutions.

Reagent	**pH_i**	**pH_f**	D**pH**	**[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	-

Table 5: Variation of the pH and E_H values in the air homogenised batch experiments. The E_H values were corrected to give equivalency to the Standard Hydrogen Electrode.

	Reference (rock)		**Rock + dolomite**		**Rock + pyrite**	
time (day)	**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

Table 6: Comparison of the U leaching rate from various column experiments. m_U is the total leach amount (initial amount: 23.2 mg); m^1_U is the remaining amount in the rock, v is the leached amount of the 10th week which is consider as constant for further irrigations and "n" in the number of irrigations necessary to leach m^1_U. d_i is the particle size of the used rock as defined in table 1. P_{H2SO4} is the relative percent leaching assuming 100% leaching efficiency in H_2SO_4 for a given d_i, and P_U is the absolute percent leaching related to the initial U in 1 g of rock.

System	m_U **(mg)**	$\mathbf{P_{H2SO4}}$ **(%)**	$\mathbf{P_U}$ **(%)**	$\mathbf{m^1_U}$ **(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	-

Figure 1

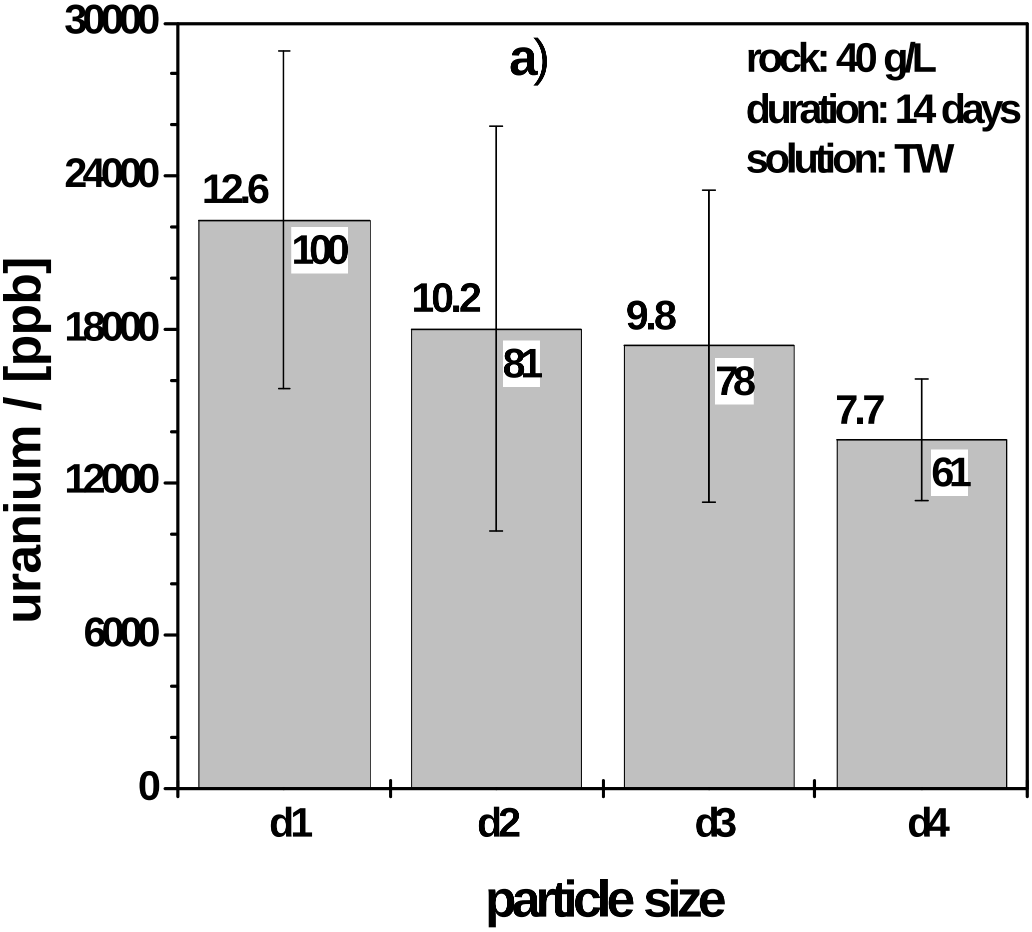

a)
rock: 40 g/L
duration: 14 days
solution: TW
uranium / [ppb]
30000
24000
18000
12000
6000
0
12.6
100
10.2
81
9.8
78
7.7
61
d1
d2
d3
d4
particle size

Figure 2

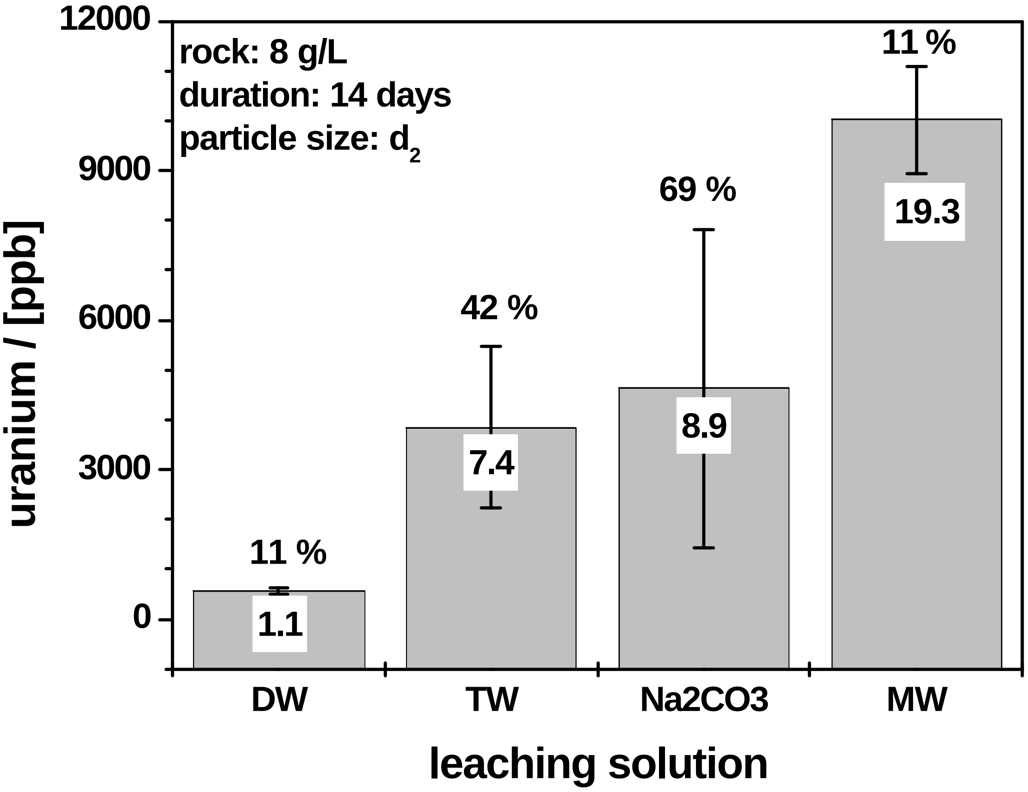
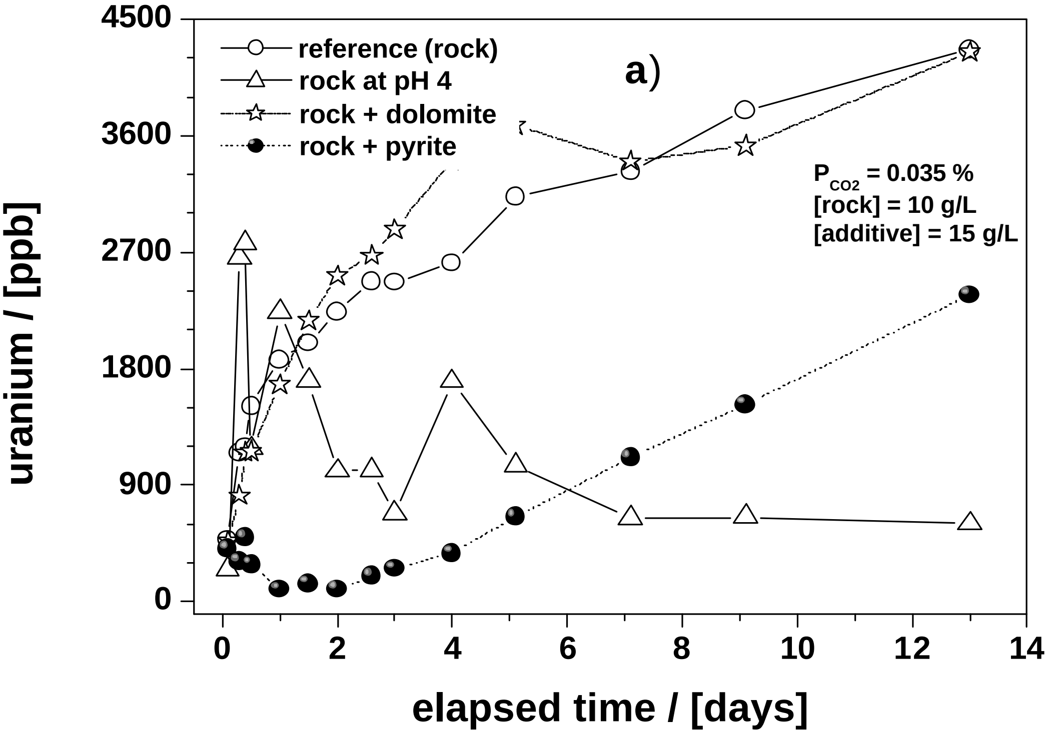

rock: 8 g/L
duration: 14 days
particle size: d_2
uranium / [ppb]
12000
9000
6000
3000
0
11 %
42 %
69 %
11 %
1.1
7.4
8.9
19.3
DW
TW
Na2CO3
MW
leaching solution

Figure 3


a)
reference (rock)
rock at pH 4
rock + dolomite
rock + pyrite
P_{CO2} = 0.035 %
[rock] = 10 g/L
[additive] = 15 g/L
uranium / [ppb]
4500
3600
2700
1800
900
0
0
2
4
6
8
10
12
14
elapsed time / [days]

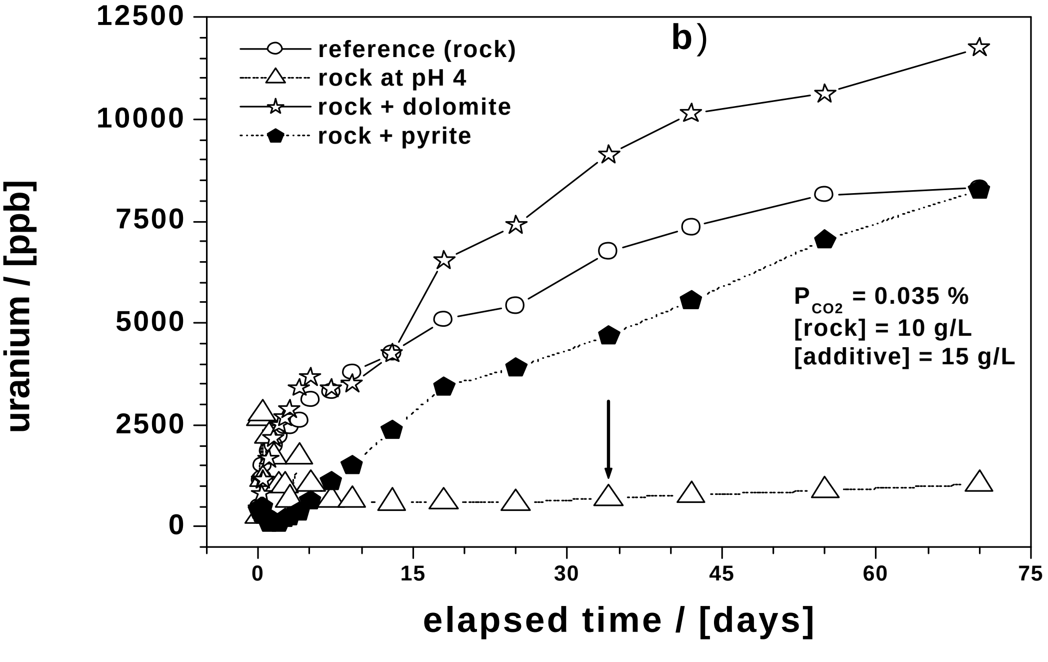

b)
reference (rock)
rock at pH 4
rock + dolomite
rock + pyrite
P_{CO2} = 0.035 %
[rock] = 10 g/L
[additive] = 15 g/L
uranium / [ppb]
12500
10000
7500
5000
2500
0
0
15
30
45
60
75
elapsed time / [days]

Figure 4

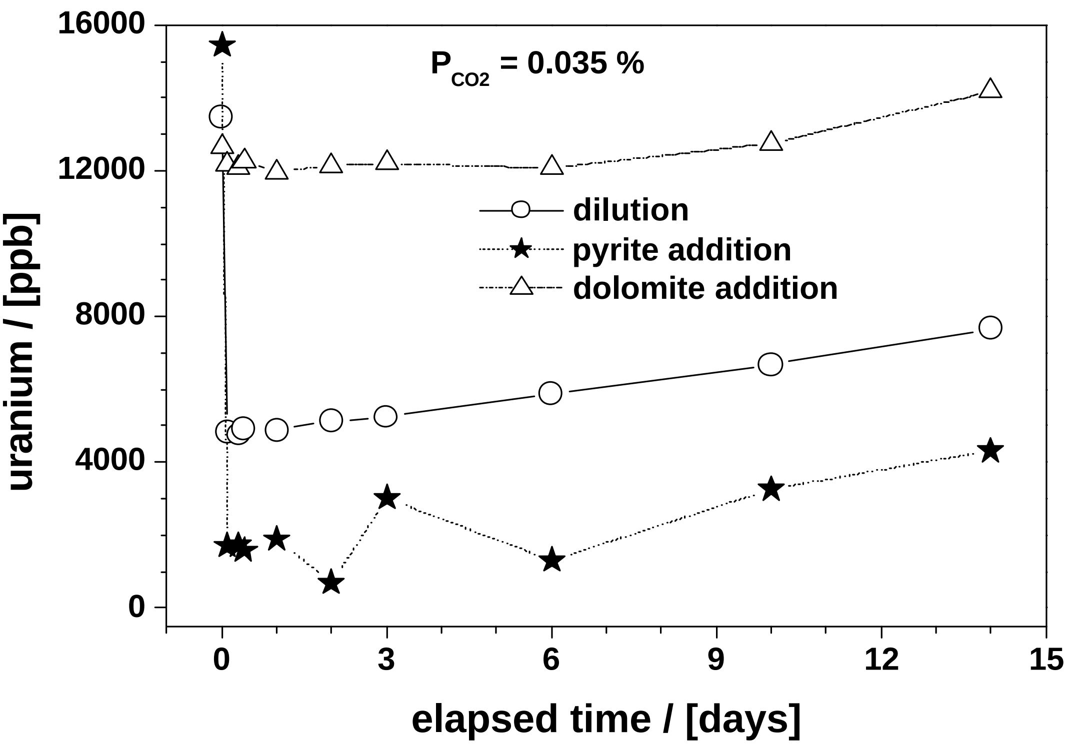

P_{CO2} = 0.035 %
dilution
pyrite addition
dolomite addition
uranium / [ppb]
16000
12000
8000
4000
0
0
3
6
9
12
15
elapsed time / [days]

Figure 5

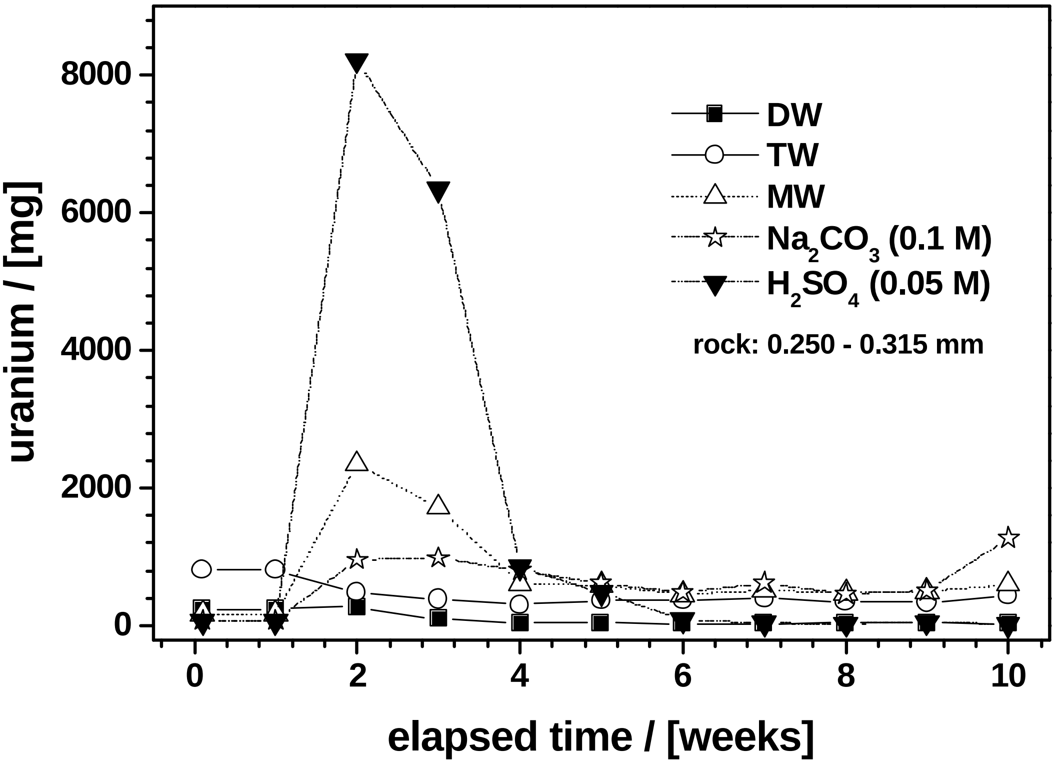
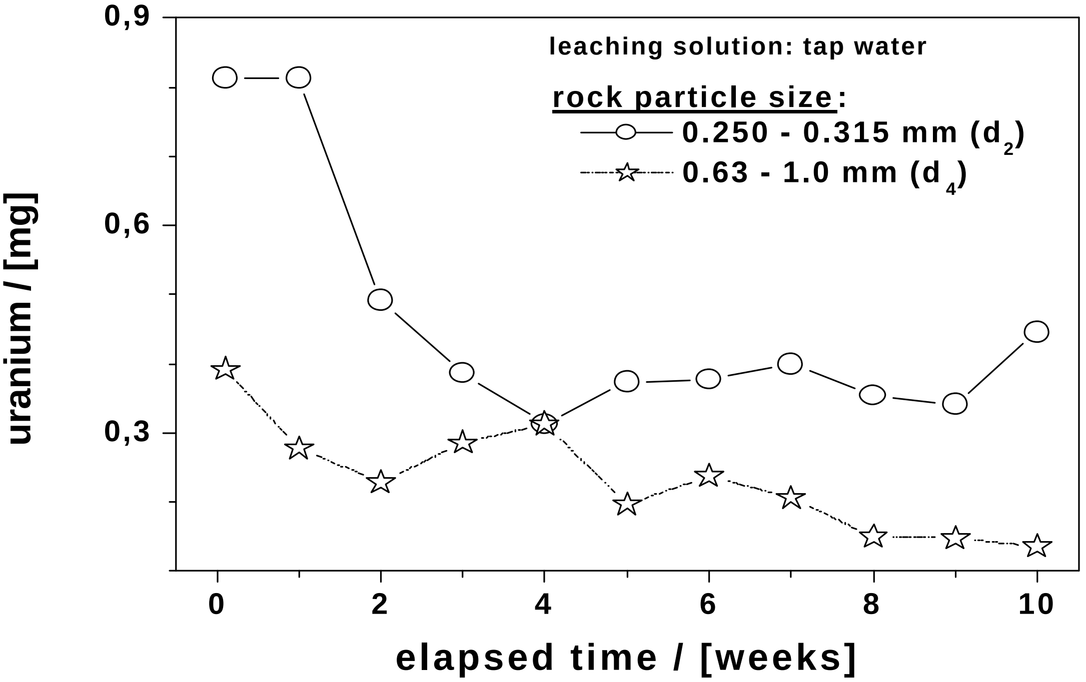

uranium / [mg]
8000
6000
4000
2000
0
0
2
4
6
8
10
elapsed time / [weeks]
DW
TW
MW
Na_2CO_3 (0.1 M)
H_2SO_4 (0.05 M)
rock: 0.250 - 0.315 mm

Figure 6


leaching solution: tap water
rock particle size:
0.250 - 0.315 mm (d_2)
0.63 - 1.0 mm (d_4)
uranium / [mg]
0,9
0,6
0,3
0
2
4
6
8
10
elapsed time / [weeks]

Figures Captions

Figure 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.

Figure 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 (0.1 M).

Figure 3: Evolution of the total U concentration as a function of time in air homogenized batch experiments. a) initial phase (13 days) and b) entire experiment (70 days). “rock at pH 4” represents an experiment in which the pH of the system was repeatedly adjusted to a value of approx. 4 with 0.2 M HCl. This adjustment was stopped at day 34 as indicated by an arrow. P_{CO2} is the atmospheric partial pressure of CO_2 (open system).

Figure 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.

Figure 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.

Figure 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.