Characterizing Uranium Solubilization Under Natural Near Oxic Conditions

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Abstract. A 782 d solubilization study using not shaken batch experiments and involving one uranium-bearing rock and three natural carbonate minerals was conducted to characterize uranium (U) leaching under oxic conditions. Results showed that aqueous U concentration increased continuously with a solubilization rate of 0.16 $\mu gm^{-2}h^{-1}$ for the first 564 d (1.5 y). After 1.5 y, U concentration reached a maximum value (saturation) and decreased afterwards. The saturation concentration of 54 mgL^{-1} (mean value) was influenced to various extent by the presence of carbonate minerals. Dissolution/precipitation, adsorption or ion exchange processes appear to control U solubilization.

Introduction

Contamination of soils and groundwater with uranium (U) has been observed at several former mining sites worldwide, posing hazards to human health (e.g. Jerden and Singa 2003, Junghans and Helling 1998). U has a very long half-live (4.5 10^9 years) and can circulate in the environment for millions of years. Therefore, a thorough clean-up of contaminated sites should be performed immediately once pollution occurs. U retention in the soil matrix through processes such as sorption or ion exchange cannot reduce the potential adverse effects of this long-lived radionuclide (e.g. Langmuir 1997, Lee et al. 2005; Naftz et al. 2002). Therefore, methods have been developed which could enable complete U extraction from soil

and groundwater and its eventual subsequent appropriate treatment (e.g. Lee et al. 2005). One of the most favourite methods consists in immobilizing U in permeable reactive barriers (PRB). U immobilization in PRB can be biotic and/or abiotic (Naftz et al. 2002).

Regardless from the nature of U immobilizing processes in a PRB, the pollutant has to be solubilized (e.g. from tailing materials) and transported to the barrier. U solubilization from soils and mine tailings and its subsequent transport to the PRB is the result of interactions in the local system "natural water–geomaterials" (Felmy et al. 2002, Froment et al. 2002). The kinetics of U solubilization at each site will depend on the interactions between local geochemistry and infiltrating natural water. However, available data on U solubilization are mostly gained from leaching experiments performed on synthetic samples with technical solutions; so called lixiviants: $(NH_4)_2CO_3$, Na_2CO_3, $NaHCO_3$, H_2SO_4… (Elles and Lee 1998, Kaplan and Serkiz 2001, Noubactep et al. 2005).

The main reactions taking place between water and mineral phases in the subsurface fall into four main categories: dissolution/precipitation reactions, exchange reactions, acid-base reactions, and redox reactions (Elles and Lee 1998, Wilson 2004). Together with sorption/desorption processes, these interactions control contaminant mobilization/retardation in the environment. Discussing whether sorption/desorption processes or mineral dissolution/precipitation controls the levels of soluble U in nature has been an interesting research area (e.g. Elles and Lee 1998). Highly natural sorptive materials of concern include organic matter and Al/Fe/Mn/Ti oxyhydroxides. In the absence of sorptive materials, dissolution/precipitation reactions, exchange reactions, acid-base reactions, and redox reactions are expected to control U solubilization. The overall kinetics of U(VI) dissolution is relative rapid compared that of U(IV) oxidation. Therefore, it is expected that acid-base and dissolution/precipitation reactions will dominate interactions between water and minerals under oxic conditions.

Short term shaken laboratory batch experiments are commonly performed when investigating U solubilization from environmental samples (Carroll et al. 1998, Eless and Lee 1998, Felmy et al. 2002, Kaplan and Serkiz 2001). Alternatively, long term non stirred batch experiments involving solution replacement are conducted (e.g. Froment et al. 2002). Such experimental conditions are not appropriate for all environmental scenarios. For instance, if groundwater inflow in a subsurface area is faster than the outflow, a quasi-stagnation will be observed. In such regions, groundwater residence time can be long enough to be simulated by not shaken batch experiments.

The widespread approach to characterize the environmental behavior of trace metals and radionuclides consists in performing well-controlled laboratory experiments with synthetic model substances and then use the results to better understand more complex natural systems (Carroll et al. 1998, Malmström et al. 2000). Therefore, an important gap exists between laboratory experiments and field observations (Malmström et al. 2000). It can be expected that performing laboratory experiments with natural samples could help to bridge this gap (Noubactep 2003).

The objective of this study was to characterize U solubilization from a multimineralic rock under quasi-stagnating oxic conditions. For this purpose not shaken batch experiments were conducted with tap water and a fixed amount of an U-bearing rock (8 gL^{-1}) and three carbonate bearing additives (calcite, dolomite and vaterite – 8 to 48 gL^{-1}) for experimental duration of up to two years (782 days). While U-bearing rock was used to mimic tailing materials, the three natural additives of different solubility have been added in order to characterize the effect of CO$_3^{2-}$-bearing minerals on U solubilization. Carbonate mineral weathering by tap water could provide elevated CO$_3^{2-}$ concentrations as encounter in nature as result of microbial activity. It is expected that association of aqueous U with CO$_3^{2-}$ to form soluble aquo-complexes such as Ca$_2$[UO$_2$(CO$_3$)$_3$]·10H$_2$O (Bernhard et al. 2001) will enhance aqueous U solubility and promote rock dissolution.

Experimental Section

Batch experiments without shaking were conducted. The batches consisted in mixtures of constant amounts of an U-bearing rock (8 gL^{-1}) and a carbonate mineral (calcite, dolomite, vaterite), respectively. Equilibration times varied from 14 to 782 days. A further experiment without carbonate mineral (rock alone) was conducted. Thus, the extent of U solubilization by tap water (simulant for seepage water – Noubactep 2003) as influenced by carbonate minerals was characterized.

Uranium solubilization was initiated by adding 13.0 mL of a tap water to 0.1 g of the U-bearing rock and 0.1 g of each additive in glass essay tubes at laboratory temperature (about 21° C). The used tap water of the city of Jena (Thuringia, Germany) has a composition (in mgL^{-1}) of Cl$^-$: 15.72; NO$_3^-$: 10.0; SO$_4^{2-}$: 72.1; HCO$_3^-$: 270; Na$^+$: 8.72; K$^+$: 5.28; Mg^{2+}: 29.3 and Ca^{2+}: 80.9. Initial pH was 7.4. At selected dates, 0.05 to 0.25 mL of the supernatant solution was retrieved at the top of each tube for U analysis. The aqueous U concentration was recorded as a function of time.

The used U-bearing rock was crushed and sieved. The fraction 0.250 to 0.315 mm was used without any further pre-treatment. The rock contains around 2.3 % U and is further composed of: 81.25 % SiO$_2$, 0.14% TiO$_2$; 7.36 % Al$_2$O$_3$, 1 % Fe$_2$O$_3$, 0.01% MnO; 0.48 % MgO, 0.67 % CaO, 1.19 % Na$_2$O, 1.48 % K$_2$O, 0.36 % P$_2$O$_5$ and 0.01% SO$_3$.

Calcite (pK$_{sp}$ = 8.48; SiO$_2$: 0.3 %, MgO: 1.02 %, CaO: 55.1 %), dolomite (pK$_{sp}$ = 17.09; SiO$_2$: 1.2 %, MgO: 20.3 %, CaO: 31.0 %) and vaterite (pK$_{sp}$ = 8.34; SiO$_2$: 0.5 %, MgO: 1.12%, CaO: 55.0 %) minerals were crushed, sieved and the fraction 0.63 to 1.0 mm was used. It is expected that their dissolution will increase the kinetic and the extent of U solubilization. Calcite and dolomite were selected because of their natural abundance (Elfil and Roques 2004, Sherman and Barak 2000). Although vaterite is almost rare in the nature, it was used in this study because it has some features such as high specific surface area and high solubility compared with calcite (Su and Wu 2004).

Dissolved U concentrations were measured with inductively coupled plasma mass spectrometry (ICP-MS, PQ3-S, ThermoElemental) because of its higher sensitivity and fast analysis speed. The quality of the analyses was checked using synthetic standards. The instrumental precision, determined as $\pm$ 1 standard deviation for three runs on the same sample and was better than 5%.

The pH value was measured by combination glass electrodes (WTW Co., Germany). All experiments were performed in triplicate. Error bars given in figures represent the standard deviation from the triplicate runs.

In all experiments, dissolved U was normalized to rock surface area (3.53 m^2g^{-1}), solution volume (using 0.013 L for all runs) and rock concentration (7.69 gL^{-1}). Rock dissolution rates ($\mu gUm^{-2}h^{-1}$) were determined from the slopes of linear regressions of normalized U concentration released versus time including the point (0,0). The calculated uncertainty of the slopes ranged from 2.1 to 14.2%.

SEM analyses: Crushed grains of the rock sample were C-coated and examined by scanning electron microscopy (SEM) and mineral phases were identified by semi-quantitative energy dispersive X-ray analysis (EDX) using a LEO1530 Gemini microscope equipped with an OXFORD Inca analytical system. The accelerating voltage was 25 kV, probe current ca 150 nA, counting time 60 sec.

Results and Discussion

SEM Observations

Qualitative SEM–EDX examinations of a rock sample provided direct information on rock composition that complemented information obtained from X-ray fluorescence analyses (experimental section). The EDX analysis revealed that the used U-bearing rock is a multimineralic rock containing among others uraninite (UO_2), arsenopyrite (FeAsS,), and galena (PbS). Associations of U with arsenopyrite was also encountered. The gangue mainly consists of alkali-feldspars and quartz.

Uranium solubilization

After the determination of the aqueous U concentration (C = mean value of a triplicate) at any time, the corresponding standard deviation (σ) was calculated and the relative error ($P_r = 100 * \sigma/C$; in %) was deduced. At the end of the experiment pH values (7.8 to 8.4 for the eight systems) and aqueous concentrations of selected elements were determined. To characterize U solubilization from the multimineralic rock while taking individual properties of CO_3-bearing rocks into account, four different experiments have been performed over a duration up to 782 d (2.14 y) with 8 gL^{-1} U rock and 0 or 8 gL^{-1} additive: I) rock alone, II) rock + vaterite, III) rock + calcite, and IV) rock + dolomite (system I, II, III and IV). Additional experiments were conducted in system III with 16, 32 and 48 gL^{-1} calcite

[systems IIIa, IIIb and IIIc] and in system IV with 48 gL^{-1} dolomite [system IVc] to access the influence of CO_3^{2-}-mineral amount on U solubilization.

Kinetics of U solubilization

Fig. 1 summarizes the variation of the U concentration (C in μgL^{-1}) and the relative error (P_r in %) within the triplicates as a function of time for U-bearing rock in tap water (system I). It can be seen that C increases continually with the time from the start of the experiment (t = 0) to a maximum at t = 564 d, afterwards C slowly decreases throughout the end of the experiment (day 782). For t $\leq$ 564 d, the rate of U solubilization (μgm^{-2}h^{-1}) was defined as the slope of the straight line C = a * t. The obtained rate of U solubilization (a = 0.16 μgm^{-2}h^{-1}) was very comparable to that of amorphous silica reported by Xu and Pruess (2000). This value is by far smaller than 0.78 μgm^{-2}h^{-1} obtained under atmospheric conditions in air homogenized batch experiments (Noubactep et al. 2005). The difference is easily explained by the slowness of diffusive processes in the present work.

The plot of the variation of the relative error (P_r) shows a maximum (41%) at the beginning of the experiment (t = 14 d). This value continuously decreases to a minimum of 4 % at t = 564 d, afterwards P_r increases to 20 % at the end of the experiment (t = 782 d). The maximum value of C (C_{max}; U saturation) coincides with the minimum value of P_r suggesting that, around t = 564 d, the system is closed to a steady state ("pseudo-equilibrium"). The measured C_{max} (54 mgL^{-1}) is comparable to reported values at some contaminated sites (Jerden and Sinha 2003, Junghans and Helling 1998), validating the capacity of the experimental procedure (not shaken closed batch systems) to simulate certain field conditions. While performing similar experiments at atmospheric pressure (P_{CO2} = 0.035 %), Noubactep et al. (2005) reported an U concentration of 8.3 mgL^{-1} at pseudo-equilibrium (pH 7.8). This value is obviously larger than that predicted by the solubility of schoepite (10^{-5} M or 2.4 mgL^{-1}, Noubactep 2003), but thermodynamic equilibria are rare in nature (Meinrath and May 2002). Therefore the present experiments can be helpful to explain some observations in the real nature.

The evolution of C results from several complex processes: U leaching from rock, U sorption onto rock by-minerals (e.g. Al_2O_3, SiO_2), U precipitation from the aqueous phase (e.g. $UO_3.2H_2O$). It can be emphasized that, during the first phase of the experiment (0 $\leq$ t(d) $\leq$ 564) U releasing processes are dominating. At t > 564 d, U precipitation dominates since U concentration decreases. The characterization of individual processes (adsorption, complexation, precipitation…) responsible for the evolution of C under the experimental conditions of this work is not possible. However, the objective of this study is not to accurately define the systems in which the materials (U-bearing rock and CO_3-minerals) are involved, but rather to characterize the effect of the minerals on U solubilization qualitatively. Therefore, the evolution of other systems (system II, III and IV) will be compared to that of the reference system (system I) while characterizing system evolution by the rate of U solubilization and the trend in the variation of both C and P_r.
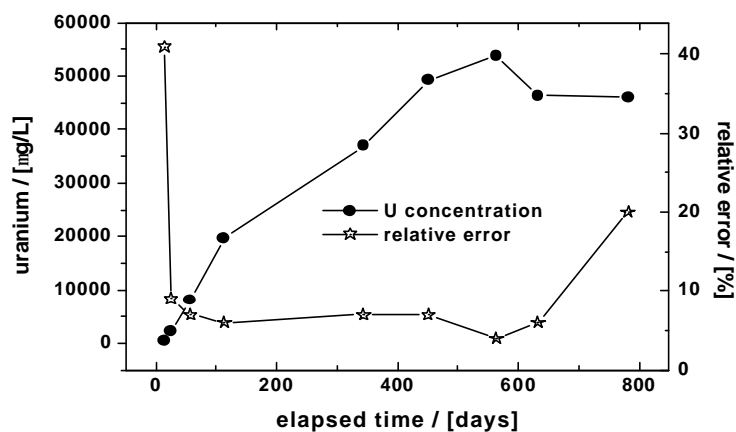
Fig.1: Variation of the uranium concentration (μg/L) and the relative error (%) within the triplicates as a function of time for the reference system (U-bearing rock in tap water).

Table 1. Variation of the relative error (%) in the individual systems as function of the time.

t	system							
(days)	I	II	III	IV	IIIa	IIIb	IIIc	IVc
14	41	106	14	21	20	24	26	13
25	9	71	9	43	30	11	45	43
57	7	39	6	23	21	9	9	15
113	6	3	5	8	8	11	5	6
344	7	10	2	13	6	11	2	9
451	7	14	2	12	5	13	2	8
564	4	8	2	8	4	5	7	11
633	6	12	3	11	5	11	3	9
782	21	11	1	11	7	11	1	9

Effect of the nature of carbonate minerals

Fig. 2 (a and b) summarizes the results of the U solubilization in systems I, II, III and IV and table 1 gives the variation of the relative error with the experimental duration in all the systems. From figure 2a it can be seen that the best U solubilization rate for the first 250 days is achieved when vaterite is present (system II), attesting that U solubilization is affected by the presence of CO_3^{2-}-minerals. Apart from vaterite, all other minerals reveal lower U solubilization during the first 100 days of the experiment (Fig 2a). This observation suggests either that: (1) U solu-

bilization is inhibited by the presence of certain CO_3^{2-}-minerals, (2) solubilized U is adsorbed on rock materials until its sorption capacity is exhausted, or (3) the amount CO_3^{2-}-ions from mineral dissolution is insufficient to solubilize adsorbed U from rock materials.

The first hypothesis is an absurdity since vaterite and calcite are of almost of the same chemical composition. Therefore, it can be assumed that once U is leached from the rock, it is sorbed to rock by-materials until sufficient CO_3^{2-}-ions are generated to form soluble U complexes. Thus vaterite with the highest solubility could enhance U solubilization already in the early stage of the experiment. For other minerals this enhancing effect was delayed due to their lower solubility.
The solubilization efficiency is the lowest when calcite is present (system III); this observation is confirmed by the values of the rate of U solubilzation (Tab. 2). For longer experimental durations (up to 564 days, figure 2b), system III still exhibits the smallest U solubilization rate whereas system II and IV (vaterite and dolomite) significantly increase U solubilization comparatively to the reference system. The solubilization enhancement was the highest in the presence of dolomite (system IV). These observations can not be explained by the relative solubility of the mineral, since dolomite is by far less soluble than calcite and vaterite. It should be kept in mind that solubility products are defined for pure phases. The evolution of the relative error (P_r, table 1) shows that the mineral dissolution is a complex process. In fact, system II exhibits the largest variation of P_r-values in the initial phase (up to 105 %) which then rapidly decreases to 3 % after 113 days. Apart from system IV (dolomite) for which the P_r-value was not maximal at the beginning of the experiment (14 days) all other additives presented the same evolution of P_r as the reference system with the difference that no minimum was attained but rather a relative constant value at the end of the experiment (t > 300 d). The fact that the curve of P_r-value did not reach a minimum as for system I illustrates the complexity of the processes determining C under experimental conditions. Since CO_3^{2-}-mineral dissolution was not at equilibrium it can be emphasized that C decrease results from precipitation (e.g. $UO_2.2H_2O$, UO_2CO_3), co-precipitation (e.g. $CaUO_2(CO_3)_2$) and U incorporation into the structure of CO_3^{2-}-minerals.

Effect of the amount of carbonate minerals

To further investigate the impact of CO_3^{2-}-minerals on U solubilzation and particularly the possibility of U incorporation into the structure of CO_3^{2-}-minerals (e.g. Reeder et al. 2000) larger amount of calcite and dolomite were tested in systems III (IIIa, IIIb, IIIc) and IV (IVc). If the impact of U incorporation into the structure of calcite and dolomite is important, then U concentration in systems IIIc and IVc (48 g.L^{-1} additive) will be significantly lower than in system III and IV (8 g.L^{-1} additive) at any time. The results for system III showed that during the whole experiment, system III (8 g.L^{-1} calcite) exhibits the lowest U solubilization whereas the evolution of systems with other calcite amounts (16, 32 and 48 g.L^{-1}) was very close to that of the reference system. Therefore, for calcite higher mineral amount enhances U solubilization. For dolomite (system IV), U solubilization was higher in system IV (8 g.L^{-1}) than system IVc (48 g.L^{-1}) from the start of the experiment

to t = 400 d, afterwards the inverse occurs. These observations suggest that U incorporation into mineral structure is more likely to occur in dolomite that in calcite. In both cases, P_r-value variation was minimal in the system with the highest mineral amount (IIIc and IVc).
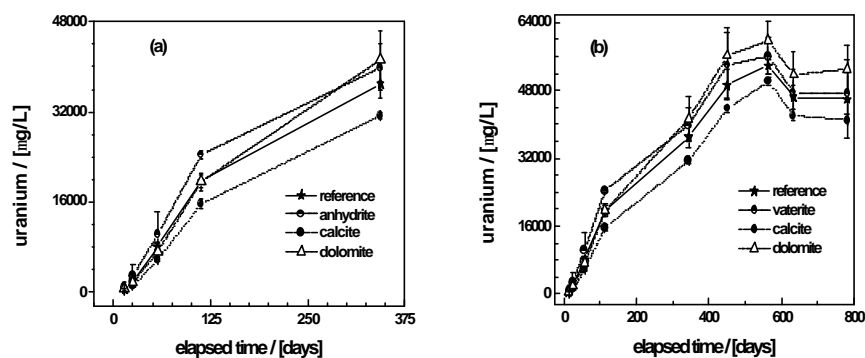
Fig.2: Comparison of U(VI) solubilization as influenced by used carbonate minerals for 344 days (a) and 782 days (b). For clarity, only the plots for the reference system (system I) and the systems with 8 g/L additives (system II, III & IV, see text) are presented. The experiments were conducted in triplicates. Error bars give standard deviations. The lines are represented to facilitate visualization.

Table 2: Co, Ni, Pb, Sb, Sr and U concentrations as measured in different systems at the end of the experiment (782 d). a ($\mu gm^{-2}h^{-1}$) is the rate of U solubilization. The absolute element concentration ([X] in $\mu g/L$) of system I is given in the first line and serves as reference for the definition of the relative concentration. The elements are ranged in the order of increasing relative concentration for system II from the left to the right.

System	a $\mu gm^{-2}h^{-1}$	^{121}Sb	^{238}U	^{208}Pb	^{88}Sr	^{60}Ni	^{60}Co
[X](μgL^{-1})		28	55.000	116	360	0.55	0.09
I	0.16	100	100	100	100	100	100
II	0.17	52	105	172	215	565	980
III	0.14	59	92	128	99	105	138
IV	0.18	69	114	131	107	108	77
IIIa	0.16	57	103	129	101	161	187
IIIb	0.17	61	105	183	108	186	552
IIIc	0.17	59	106	114	103	111	192
IVc	0.17	46	110	132	107	187	220

Solubilization of other elements

In order to gain an insight on the solubilization behaviour of other components of the multimineralic rock, the concentration of nine (9) elements was determined at the end of the experiment (t = 782 d): Co, Ni, Cu, Zn, Rb, Sr, Sb, Ba and Pb. Table 5 presents the results for five selected elements together with that of U. The absolute concentration (C - mean value of triplicates) of each element in the reference system is given. For other systems the relative concentrations are given. The relative concentration (P_r' in %) is defined as $100 * C/C_{ref}$. Such that for system I (reference) P_r' = 100 %; P_r' > 100 % when a CO_3^{2-}-mineral enhances element solubilization and P_r' < 100 % when a mineral inhibits element solubilization.

From table 5 it can be seen that, apart from Sb, CO_3^{2-}-minerals enhance solubilization of all other elements. The extent of the solubilization modification varies from 46 % for Sb in system IVc to 980 % for Co in system II (calcite). It would have been interesting to follow the evolution of several of these elements with time. To characterize target mixed contamination scenarios, one or more metal-bearing rocks can be mixed similar as in this study for solubilization studies.

Conclusions

The mixture of U- and CO_3^{2-}-bearing minerals has revealed that adsorption, solution/precipitation and U incorporation in mineral structures are determinant in discussing U solubilization. In nature, the situation will be complicated by organic ligands derived from decomposing organic matter or from the direct activities of soil microbes or plant roots (e.g. Wilson 2004). In closed areas in the environment U concentration can reach very high values. The extent of U transport from such areas into the environment for instance after a rainfall or any other water supplying event depends on site specific geochemical conditions. When sufficient amount of organic matter and/or Al/Fe/Mn/Ti oxyhydroxides is present, U transport can be significantly retarded, if groundwater flow is slow enough to allow adsorption equilibrium. Otherwise U can be transported to distances up to hundreds of kilometers in relatively short times (Lee et al. 2005). Field and laboratory studies suggest that both dissolution/precipitation of U-bearing minerals and adsorption/desorption reactions are the most important processes in the attenuation or release of U (e.g. Elless and Lee 1998). However, attempts have been made to deduce the nature of mineral phases from U concentrations via thermodynamic arguments. This work has shown that under stagnant conditions metastable states can persist over months. Therefore any attempt to determine solubility limiting phases from field U concentration is uncertain (Fanghänel & Neck 2002).

The results of the present study indicate that investigating the dissolution from multimineralic rocks can be a powerful tool to characterize multi-contaminant systems. Further testing of mineral-water systems under various experimental conditions is asked for, to verify capacity of such systems to describe natural processes.

Acknowledgments

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