



Section 15. Innovative applications of quantum beams in material research

Laser and X-ray spectroscopic studies of uranium–calcite interface phenomenaG. Geipel^{*}, T. Reich, V. Brendler, G. Bernhard, H. Nitsche*Forschungszentrum Rossendorf e. V., Institut für Radiochemie, P.O. Box 510119, D-01314 Dresden, Germany***Abstract**

Calcite (CaCO_3) was treated with uranyl solutions of different concentrations in perchlorate medium at an initial pH of 6. X-ray photoelectron spectroscopy (XPS) measurements showed that there is no physi- or chemisorption of uranyl perchlorate molecules at the mineral surfaces and no diffusion of ClO_4^- anions into the mineral grains. We conclude this, because no chlorine atoms could be detected by XPS measurements. A significant amount of uranyl hydroxides is formed at the mineral surfaces. In addition, up to 20% of the calcium ions are exchanged by uranyl ions at the calcite surface. The inter-atomic uranium–oxygen distances of the reaction products at the mineral surface were determined using extended X-ray absorption fine structure (EXAFS) spectroscopy. In addition, the contacting solutions were studied by time-resolved laser-induced fluorescence spectroscopy (TRLFS). A new uranyl species was found in solution, which is also present in seepage waters from mine-tailing piles. © 1997 Elsevier Science B.V.

1. Introduction

The activities of the former uranium mining company WISMUT produced many mine-tailing piles in East Germany. In the mining district of Aue–Schlema–Alberoda alone, mine-tailing piles exist with a total volume of about forty million cubic meters [1].

Due to weathering processes, radionuclides are mobilized and transported through the pile. Uranium has the highest concentration of all radionuclides present in the seepage waters. Several minerals that are formed by weathering processes can act as natural ion exchangers. These materials can adsorb radionuclides from the seepage waters. For modeling the radionuclides' transport process in a tailing pile, it is necessary to know distribution ratios and loading capacities of the rock materials. Furthermore, it is important to know how the solution speciation changes as a result of the sorption process. The species in the contact solution represent the non-sorbed species and if

exchange processes occur on the surface/solution interface, the solution speciation must change.

We studied the interaction of a uranyl perchlorate solution with calcite mineral. This mineral seems to have an important influence on the behavior of uranium in natural systems, like the ones we find in the mining areas of Saxony.

2. Experimental

Sorption experiments were carried out without external pH control and under atmospheric conditions. The mineral CaCO_3 was used in form of a crystalline powder with a particle size smaller than 63 μm and a specific surface area of 6.8 m^2/g . The pH of the solution was controlled by the properties of the rock material and reached a characteristic value of about 8.0. The initial uranyl perchlorate solution (1×10^{-5} M to 1×10^{-2} M, 0.1 M NaClO_4 , pH ~ 4.0) were contacted with the rock material for 50 h [2], and then the solid and solution were separated by centrifugation (10 min; 3000 rpm). Afterwards, the samples were rinsed several times with de-ionized water and dried. A solid to solution ratio greater than 1 to 20 was

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Table 1
Preparation of calcite samples for XPS and EXAFS measurements

No.	Treatment	Ratio solution/mineral (ml/g)	Final pH	Loading (mg U/g)
A1	de-ionized water	20/1	8.21	–
A2	UO ₂ (ClO ₄) ₂ , 1 s rinse with water	100/1	8.65	12.8
A3	UO ₂ (ClO ₄) ₂ , 1 s rinse with water	500/1	8.93	66.3
A4	UO ₂ (ClO ₄) ₂ , 2 h rinse with water	500/1	8.58	56.8

used for all experiments [3]. The treatment of samples used for EXAFS- and XPS-measurements is given in Table 1.

The XPS spectra were measured at the Kurchatov Institute, Moscow, with a HP 5950A spectrometer using monochromatized Al K $\alpha_{1,2}$ (1486.6 eV) X-rays [4]. Samples A1–A4 (see Table 1) were measured before and after grinding in a mortar. The electron binding energies, E_b , given in this paper are relative to E_b of C1s electrons (285.0 eV) of the hydrocarbon layer. The uncertainties in the electron binding energy and the relative line intensity are '0.1 eV and '10%, respectively.

For the EXAFS measurements, the calcite samples were mixed with Teflon powder and pressed to pellets. The uranium L_{III} edge (17166 eV) EXAFS spectra were measured in transmission mode at the Stanford Synchrotron Radiation Laboratory (SSRL) on the beamline 2–3 using a Si(220) double-crystal monochromator. For the EXAFS data analysis we used the software package EXAFSPAK [5]. Theoretical scattering amplitudes and phases were calculated using the program FEFF [6].

The uranium-containing solutions from the sorption experiments were investigated by TRLFS in order to determine the influence of the rock material on the speciation of the non-sorbing solution uranium.

Details of the experimental setup of the TRLFS measurements were given elsewhere [7,8].

Spectrometer control and data collection were performed using a compiled program in basic. For data handling and calculations, the following software programs were used: Excel 5.0 (Microsoft, USA), Grams'386TM (Galactic, USA) and Origin 3.5 (Microcal, USA)

3. Interaction of uranium with calcite

Fig. 1 shows the measured isotherm for carbonate minerals (calcite and dolomite). The calculated maximum concentrations of sorbed uranium were found to be $8 \times$

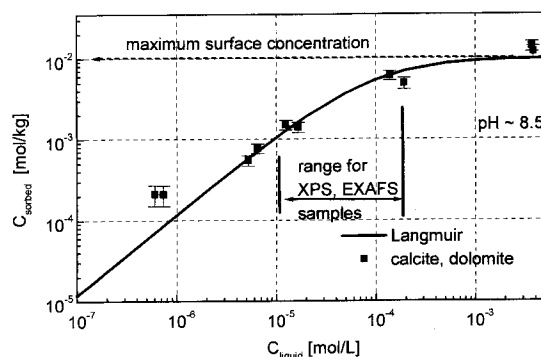


Fig. 1. Sorption isotherm and Langmuir fit for the sorption of UO₂²⁺ on calcite and dolomite.

10^{-3} mol/kg. Using the specific surface area, that was determined by BET measurements, we calculated a surface concentration of 1.2×10^{-6} mol/m².

An adsorption constant was derived from the Langmuir isotherm. This constant can be seen as a surface complex formation constant [9]. Table 2 shows the calculated values for the sorbing material calcite.

The electron binding energies of the inner shells of the different elements are the same before and after sample grinding: 381.9 eV for U4f_{7/2}, 347.1 eV for Ca2p_{3/2}, 531.6 eV for O1s, and 289.6 eV for C1s of the CO₃²⁻ group. The U4f_{7/2} line shows a satellite feature at higher binding energy of approximately 12% intensity. These characteristics of the U4f_{7/2} line confirm the formation of a uranyl species at the calcite surface [4].

The lower E_b of the U4f_{7/2} electrons for samples A2–A4 as compared to E_b for UO₂(ClO₄)₂ (382.9 eV), and its similarity to E_b in K₄UO₂(CO₃)₃ (392.1 eV) indicate the possibility that the uranyl ions enter the lattice and replace calcium ions. According to Goldschmidt's rule [10] the ionic radii can differ from each other up to 15% to

Table 2
Specific surface area, maximum surface concentration and adsorption constant of uranium on different sorbing materials

Sorbing material	Specific surface area (m ² /g)	Maximum surface concentration of uranium (mol/m ²)	Adsorption constant (ml/g)
Calcite, dolomite	6.8 ± 0.5	$(1.2 \pm 0.3) \times 10^{-6}$	1.7×10^4

Table 3
Atomic ratio U:Ca for the interaction product of uranyl perchlorate solution with calcite

Sample	A2	A3	A4
Before grinding	0.028	0.079	0.06
After grinding	0.021	0.066	0.055

allow the replacement of ions in the lattice. Ca^{2+} has an ionic radius of about 1.0 Å and the ionic radius for U^{6+} and U^{4+} is about 0.81 Å and 0.9 Å, respectively. More important is the crystal structure of the compounds. If at the surface of the calcite the rhombic aragonite ($n_{XYZ} = 1.530 \text{ \AA}; 1.682 \text{ \AA}; 1.686 \text{ \AA}$) [10] will be formed, then it is possible that schoepite ($\text{UO}_2(\text{OH})_2$), which also has a rhombic crystal structure ($n_{XY} = 1.690 \text{ \AA}; 1.735 \text{ \AA}$) [10], can enter the CaCO_3 -lattice.

In several cases the extent of this exchange at the surface is greater than 20%. However, one has to take into account that in addition to the CO_3^{2-} groups, the uranyl ions at the calcite surface can be surrounded also by OH^- groups as a result of hydrolysis [11].

As one would expect, the atomic ratio U:Ca at the calcite surface increases with the amount of adsorbed uranium (see the results for samples A2–A4 given in Table 1). After grinding the samples A2–A4, the U:Ca ratio decreases (see Table 3). Therefore, we conclude that the exchange of calcium ions by uranyl ions proceeds more actively in the surface layers of the calcite grains and no diffusion of UO_2^{2+} into the inner lattice will occur.

The EXAFS structural parameters of samples A2–A4 are the same within the experimental uncertainties. The bond length of the uranium atom to the two axial oxygen atoms of the uranyl group is $1.81 \pm 0.02 \text{ \AA}$. The equatorial oxygen shell of the uranyl group is characterized by a broad distribution of uranium–oxygen bond distances. The average inter-atomic distance is $2.34 \pm 0.02 \text{ \AA}$. Similar inter-atomic distances of 1.81 Å and 2.30 Å were reported for the axial and equatorial U–O bonds in $\text{UO}_2(\text{OH})_2$ [12]. Due to the signal-to-noise ratio we did not determine the U–Ca distance.

The obtained results agree with the main conclusions of previous studies on the interaction of $\text{UO}_2(\text{ClO}_4)_2$ with CaCO_3 [13,14]. The XPS measurements confirmed that uranyl hydroxides and carbonates are formed mostly at the CaCO_3 grain surface. No chlorine containing surface species were detected.

4. Species in the contact solution

The species in the contact solution after the sorption process were studied using TRLFS. At steady state conditions these species are in (near)-equilibrium with the sorb-

ing surface and knowledge about their composition should allow conclusions about the sorption reaction mechanism.

The time-resolved fluorescence spectra of the contact solution consist of two different types of components. In solutions with a pH between 7.5 and 8.5 after the sorption experiments, the spectra indicate the presence of two different uranium species.

The spectra of the contact solution were measured with delay times between 0.03 and 0.17 μs after the applications of the laser pulse. Fig. 2 shows the deconvolution of such a spectra into two components with lifetimes of 40 ns and 17 μs , respectively. The exponential fit for the lifetime measurements did not give any hint, that more than two species with fluorescence properties are present in the solution.

The 17 μs species could be a uranium hydrolysis product, like $\text{UO}_2(\text{OH})_2$. The emission lines (464 nm, 483 nm, 505 nm, and 526 nm) of the 40 ns species are shifted to shorter wavelengths when compared to the lines of the free uranyl ion. Compared to the fluorescence of the hydroxo species and free uranyl ion, the fluorescence intensity of this species is very small. Fluorescence spectra studies on solutions containing Ca^{2+} -ions, UO_2^{2+} -ions and CO_3^{2-} -ions show that this species is a calcium-uranyl-carbonato-complex $\text{Ca}_2[\text{UO}_2(\text{CO}_3)_3](\text{aq.})$ [7]. Uranyl carbonato complexes, except the uncharged $\text{UO}_2\text{CO}_3(\text{aq.})$ did not show any fluorescence properties [15]. Speciation calculations using the formation constant of $\log \beta_{I=0.1} = 26.3$ and the speciation modeling program EQ3NR [16] for the calciumuranyl-carbonato-complex [7] show that this species becomes the main carbonato species in the contact solution.

This species exists also in natural seepage waters. We found this species in several seepage waters and mining waters from a mining region, where these waters are in contact with calcium-containing minerals and rocks. The time-resolved fluorescence spectra are typical for these waters (Fig. 3). The mean fluorescence emission bands are same which we found in the contact solution from the

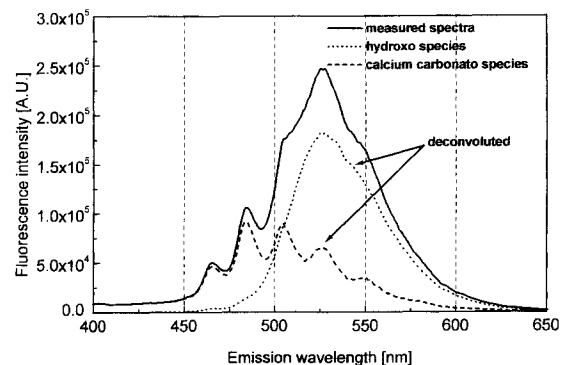


Fig. 2. Fluorescence spectra of contact solution after sorption of UO_2^{2+} on calcite (delay time 70 ns, gate width 50 ns).

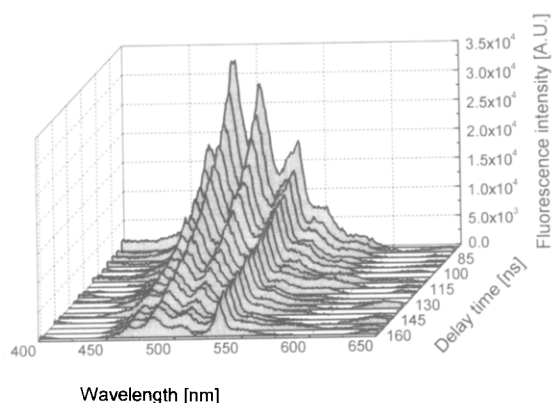


Fig. 3. Time-resolved fluorescence spectra of a seepage water (rockpile No. 66, Schlema, Germany).

sorption experiments and for the $\text{Ca}_2[\text{UO}_2(\text{CO}_3)_3]$ -mineral liebigite, are the same.

5. Summary

In natural systems the speciation of uranyl ions depends very closely on the kind of the contacted rock material, the weathering and sorption properties of this rock material. In the case of calcite and dolomite the main species in the contacting solution is $\text{Ca}_2[\text{UO}_2(\text{CO}_3)_3](\text{aq.})$. On the mineral surface exist uranyl hydroxo species together with UO_2^{2+} bound in the calcite lattice via ion exchange. Further investigations aim at the study of the formation of other uncharged uranyl species and the fluorescence properties of solid uranyl compounds and sorbates.

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P.G. Allen, J.J. Bucher, N.M. Edelstein, D.K. Shuh (Lawrence Berkeley National Laboratory, Chemical Sciences Division, MS 70A-1150, Berkeley, CA 94720, USA) are mainly involved in the EXAFS measurements.

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