ELSEVIER

Journal of Alloys and Compounds 271–273 (1998) 201–205

Journal of ALLOYS AND COMPOUNDS

Uranium speciation in waters of different uranium mining areas

G. Bernhard*, G. Geipel, V. Brendler, H. Nitsche

Forschungszentrum Rossendorf e.V., Institute of Radiochemistry, P.O. Box 510 119, D-01413 Dresden, Germany

Abstract

The uranium speciation in three uranium mining-related waters from Saxony/Germany was experimentally determined by laser spectroscopy. The obtained species distributions were successfully compared with modeling predictions for the different U(VI) species that were calculated with the modeling software EQ3/6 using the NEA data base [1,2]. Three different solution complexes characterize the uranium speciation in the investigated waters:

1. In carbonate- and calcium-containing mine water from Schlema at pH 7.1, $Ca_2UO_2(CO_3)_3$ (aq.);
2. In carbonate-containing and calcium-poor tailing water from Helmsdorf at pH 9.8, $UO_2(CO_3)_3^{4-}$;
3. In sulfate-rich mine water from Königstein at pH 2.6, UO_2SO_4 (aq.). © 1998 Elsevier Science S.A.

Keywords: Uranium; Speciation; Natural aquatic system; Time-resolved laser-induced fluorescence spectroscopy; Complexation

1. Introduction

Between 1945 and 1990, WISMUT, the former mining company, mined about 220,000 tons of uranium in eastern Germany, especially in Saxony and Thuringia. These intensive mining and milling activities have created substantial residues such as numerous mine tailing piles, mine shafts and mill tailings from the uranium ore processing. Uranium and its decay products can be released from these residues and transported by water into the environment. A knowledge of uranium speciation in these waters is essential for predicting radionuclide migration and for installing effective water purification technology. Furthermore, comprehensive and accurate knowledge of the speciation of uranium and its decay products is required to aid decisions for restoration strategies of the contaminated sites. The Organisation for Economic Cooperation and Development (OECD) and the Nuclear Energy Agency (NEA) has published a comprehensive and peer-reviewed data base. However, due to a lack of experimental data, it still contains some thermodynamic data with rather large uncertainties. Indeed, some of the proposed species are derived as a result of data fitting with no other independent experimental verification such as spectroscopy. The much simpler laboratory systems often contain significantly less constituents than environmental aqueous systems and may therefore not completely represent the speciation in natural systems. Such unknown species can only be identified if thermodynamic information is obtained from real systems. In an earlier study, we have identified a calcium uranyl carbonate species in a mine tailing seepage water that was not listed in the NEA data base because of the reasons discussed above [3]. Therefore, it was the goal of this study to experimentally determine uranium speciation in different mining-related waters and compare the findings with modeling results to detect possible discrepancies and limitations of the NEA uranium data base.

We used time-resolved laser-induced fluorescence spectroscopy (TRLFS) and laser-induced photoacoustic spectroscopy (LIPAS) [4] to measure the uranium speciation. These methods are nonintrusive and therefore do not change the chemical composition of the investigated waters. This is very important, because any change of the system under study may also change the speciation. Furthermore, we measured the change of uranium speciation in the tailing water sample as a function of the pH and the calcium content.

2. Experimental details

2.1. Quantitative analysis

Water samples from different mining areas were analyzed for elemental content by inductively coupled plasma mass-spectrometry (ICP-MS) and atom absorption spectroscopy (AAS). The samples were collected under oxi-

---

*Corresponding author. Tel.: 00 49 351 2 60 3280; fax: 00 49 351 2 60 3553; e-mail: G.Bernhard@fz-rossendorf.de

PII: S0925-8388(98)00054-1

dizing conditions and were filtered through a 1-nm cellulose acetate filter (AMICON, Beverly, MA, USA) before measurement. The anions were determined by ion chromatography.

2.2. Laser spectroscopic measurement

A Nd-YAG-MOPO laser system (Spectra Physics, Mountain View, CA, USA) was used as the light source. The two barium borate crystals of the MOPO system can be rotated in the laser beam generating a tunable laser output needed for LIPAS. For TRLFS of uranyl complexes, the excitation wavelength of 266 nm with a measured laser energy of 2.5–2.7 mJ was used. All functions of the laser spectrometer are computer controlled. A detailed description of the equipment and spectra calculations is given elsewhere [5].

3. Results

3.1. Analytical data

Table 1 summarizes the concentrations of major ions of three mining related waters in Saxony in Germany. Two from uranium mines in Schlema and Königstein, and one mill tailing water from Helmsdorf. The pH was measured on site during sampling and did not differ from the pH determined later in the laboratory. The Königstein mining water contains relatively high amounts of total organic carbon (TOC), carbonate/hydrogen carbonate, sulfate, calcium, and magnesium ions. The pH was determined as 7.13, and the uranium concentration was 0.021 mmol l^{-1}. In the Königstein mine, uranium was directly leached underground with diluted sulfuric acid. Therefore, the resulting mine water is very acidic having a pH of 2.6, and only sulfate is present as major anion. The uranium concentration is 0.073 mmol l^{-1}. As a result of the uranium processing, the Helmsdorf mill tailing water is relatively concentrated in sulfate, hydrogen carbonate/carbonate and chloride ions. It has a pH of 9.76. This water also contains substantial amounts of phosphate, arsenate, and TOC. The uranium concentration is 0.025 mmol l^{-1}. According to the chemical composition of these original waters, a different uranium speciation can be expected.

Table 1
Chemical Analysis of different mining related waters

Component	Concentration (mmol l^{-1})		
	Mine water Schlema	Mine water Königstein	Tailing water Helmsdorf
Ca	6.9	5.9	0.3
Mg	11.6	0.7	0.9
Na	20.6	6.1	166.3
K	1.0	0.04	0.9
U	0.021	0.073	0.025
SO_4^{2-}	20.7	23.9	35.6
$CO_2/HCO_3^-/CO_3^{2-}$	3.9	<0.02	10.3
PO_4^{3-}	<0.02	<0.02	0.29
AsO_4^{3-}	0.03	0.01	0.52
Cl^-	3.3	3.8	25.8
TOC(mg l^{-1})	62.0	3.5	132.0
pH	7.13	2.6	9.76

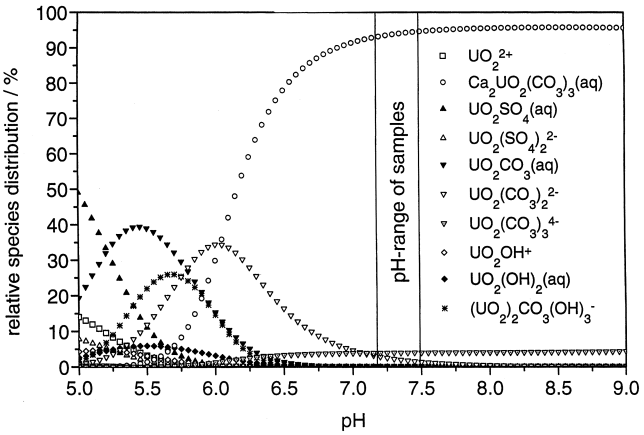

Fig. 1. Mine water from Schlema—calculated uranium speciation.

3.2. Thermodynamic modeling of the waters

The chemical behavior of uranium (VI) in natural aquatic systems is mainly influenced by the pH, the redox potential, and the presence of various complexing agents. The distribution of U(VI) complexes was calculated with the speciation software EQ3/6 using the NEA data base [1,2]. Because the filtered sample solutions were clear and appeared homogeneous and did not show any precipitate, we assumed that they were not supersaturated with minerals. We included in the speciation calculations the recently determined calcium uranyl carbonate complex, $Ca_2UO_2(CO_3)_3$ (aq.) [3]. The modeling results are shown in Figs. 1–3. The speciation diagram of the mine water from Schlema is depicted in Fig. 1. In the natural pH

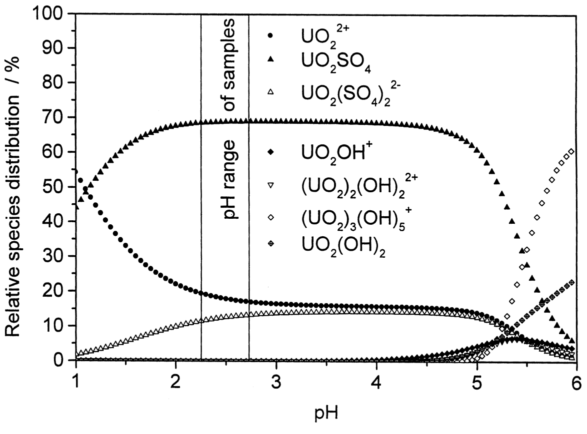

Fig. 2. Mine water from Königstein—calculated uranium speciation.

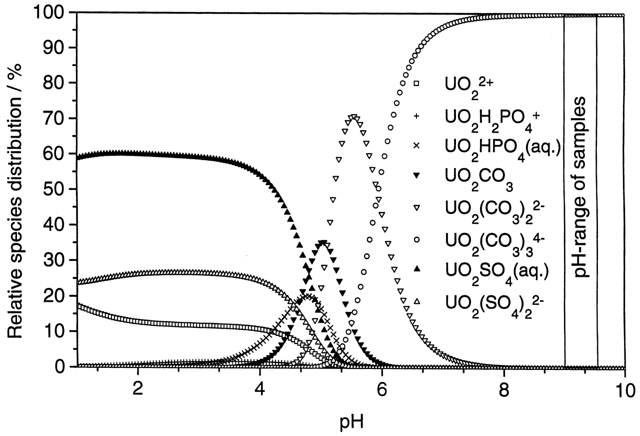

Fig. 3. Tailing water from Helmsdorf—calculated uranium speciation.

range, the calcium uranyl carbonate complex is the main species in the mine water of the Schlema region. The uranium speciation of the Königstein mine water shown in Fig. 2 is quite different. There, uranyl sulfate complexes, $UO_2SO_4/UO_2(SO_4)_2^{2-}$, and UO_2^{2+} are the major species. In the Helmsdorf tailing water, uranyl carbonate complexes, mainly $UO_2(CO_3)_3^{4-}$ and $UO_2(CO_3)_2^{2-}$, are the main solution species as shown in Fig. 3. The calcium content is presumably too low to form the calcium uranyl carbonate complex predicted in the Schlema mine water.

3.3. Spectroscopic determination of uranium speciation

To validate the thermodynamic calculations, the different mining related waters were measured by TRLFS. Uranium speciation can be detected by the characteristic lifetimes and the fluorescence wavelengths of the different complexes. Table 2 shows the wavelengths of the main fluorescence bands and the lifetimes for the different waters and for model uranyl complexes. The TRLFS

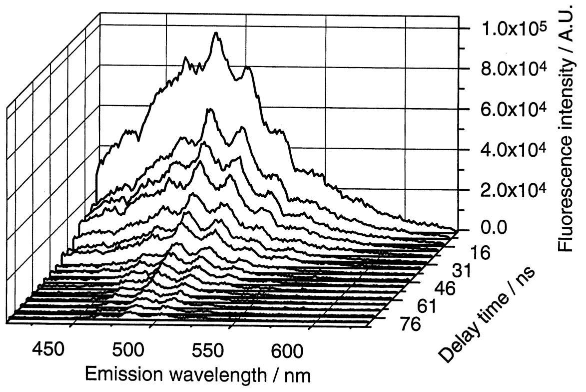

Fig. 4. TRLFS spectrum of mine water from Schlema.

spectrum in Fig. 4 shows the mine water from Schlema. A very short lifetime component is present in this water which indicates the possible presence of organic material [6]. By comparing the fluorescence bands and the lifetimes mine water from Schlema with the data for the calcium uranyl carbonate complex, $Ca_2UO_2(CO_3)_3$ (aq.) [3], both listed in Table 2, we conclude that this is also the main species in these waters. The somewhat smaller lifetime of 25±2 ns in the mine water, compared to 43±12 ns in the model complex solution, is possibly due to chloride fluorescence quenching. The spectra, shown in Fig. 5, and the fluorescence lifetime of the Königstein mine water are different from the Schlema waters. The emission band wavelengths are characteristic for uranium sulfate complexes. The lifetimes of the sulfate complexes found in the original water, also listed in Table 2, are substantially smaller than in the system containing only sulfate and uranyl ions [5]. This is presumably due to chloride fluorescence quenching. This is also the reason that the free uranyl ion is not detectable in this water although the free uranyl ion was predicted by speciation calculation (Fig. 2). The Helmsdorf tailing water sample showed no

Table 2
Spectroscopic data of mining related waters and model complexes

Solution	Main fluorescence bands (nm)	Lifetime (ns) ±3σ
Mine water Schlema	466, 485, 505, 525	25±2
Mine water Königstein	477, 494, 515, 540	540±90, 1300±700
Tailing water Helmsdorf		
at original pH 9.76	No uranium fluorescence	12±1, organic compound
acidified to pH 1.5	479, 495, 516, 540	350±17, 3350±335
after addition of		
12.2 mmol calcium	467, 485, 505, 525	40±5
Model complexes [3,5]		
$Ca_2UO_2(CO_3)_3$ (aq.)	465, 484, 504, 524	43±12
$UO_2(CO_3)_3^{4-}$	No uranium fluorescence	
UO_2SO_4 (aq.)	477, 493, 514, 538	4300±400
$UO_2(SO_4)_2^{2-}$	477, 493, 514, 538	11 000±1000
UO_2^{2+}	472, 488, 510, 533	1600±200
$UO_2H_2PO_4^+$	477, 495, 517, 541	14 000±1300
UO_2HPO_4(aq)	477, 495, 517, 541	14 000±1300
UO_2OH^+	481, 497, 518, 541	32 000±2500

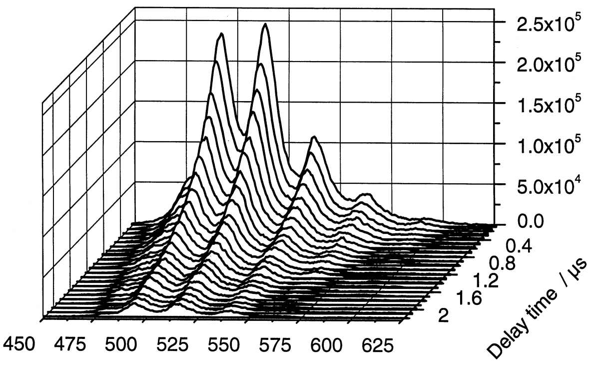

Fig. 5. TRLFS spectrum of mine water from Königstein.

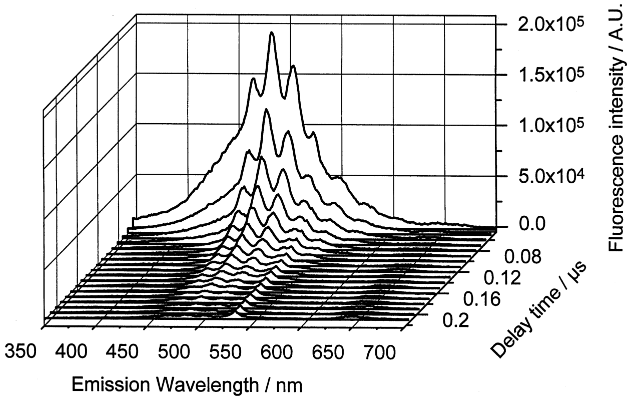

Fig. 7. TRLFS spectrum of tailing water from Helmsdorf, calcium (12.2 mmol l^{-1}) added, pH 8.0.

uranium fluorescence (Fig. 6). Only a very broad fluorescence band was observed with a very short lifetime that is typical for organic matter [6]. As we reported earlier [3], the dimeric and trimeric uranyl carbonate complexes show no uranium fluorescence. Based on this information and first photoacoustic measurements which detected the uranyl carbonate complexes [7], we conclude that uranyl carbonate complexation is prevalent in the unaltered tailing water.

To study the influence of pH alteration and changing calcium content on the uranium speciation in the water samples, TRLFS spectra were recorded after adding calcium and/or altering the pH. Fig. 7 shows the spectra of Helmsdorf tailing water after the addition of 12.2 mmol l^{-1} calcium and changing the pH from 9.76 to 8.0. Because the spectra show the same fluorescence maxima and lifetime as the calcium uranyl carbonate complex solution, we can conclude that the $Ca_2UO_2(CO_3)_3$ (aq.) complex is formed in this solution. When the Helmsdorf tailing water was adjusted to pH 1.5 by adding perchloric acid and no calcium was added, the spectra shown in Fig. 8 was recorded. The fluorescence maxima are identical to the ones recorded in the mine water of Königstein and to the uranyl sulfate model systems. The bands are identical for the first and second uranyl sulfate complexes. The determined lifetimes, however, are different in each system because chloride fluorescence quenching occurs due to the varying amount of chloride in each solution.

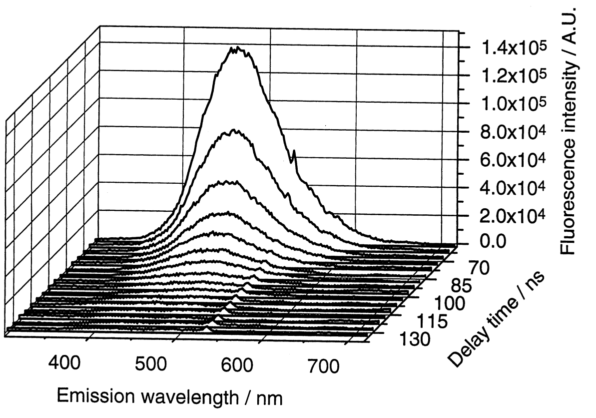

Fig. 6. TRLFS spectrum of tailing water from Helmsdorf, original pH 9.76.

4. Conclusion

Laser spectroscopy is an appropriate technique for a direct measurement of uranium speciation in mining related waters. We have shown that modeling calculations using the EQ3/6 software and NEA uranium data base and including the thermodynamic value for the $Ca_2UO_2(CO_3)_3$ (aq.) complex describe very well the thermodynamic speciation of uranium in mining related waters. According to the obtained TRLFS data and thermodynamic calculations we found that the following three different solution complexes characterize the uranium speciation in the investigated waters:

In carbonate- and calcium-containing mine water from Schlema at pH 7.1, $Ca_2UO_2(CO_3)_3$ (aq.), in carbonate-containing and calcium-poor tailing water from Helmsdorf at pH 9.8, $UO_2(CO_3)_3^{4-}$, and in sulfate-rich mine water from Königstein at pH 2.6, UO_2SO_4 (aq.).

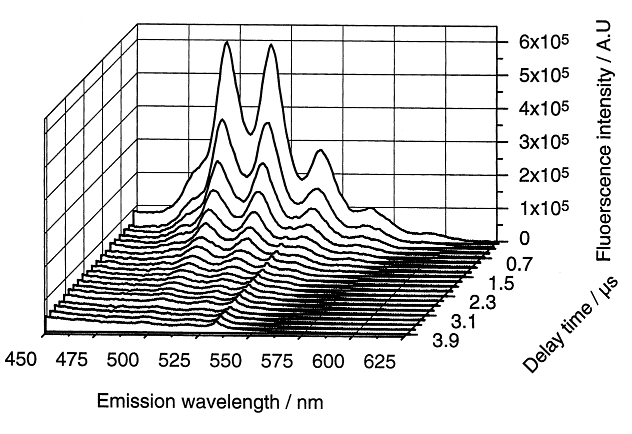

Fig. 8. TRLFS spectrum of tailing water from Helmsdorf, pH 1.5.

Acknowledgements

The authors would like to thank Dr. K. Krogner and Dr. W. Wiesener, Department of Analytics, Forschungszentrum Rossendorf e.V., for the AAS and ICP-MS measurements.

References

[1] T.J. Wolery, EQ3/6, A software package for the geochemical modeling of aqueous systems, UCRL-MA-110662 Part I, Lawrence Livermore National Laboratory, CA, USA, 1992.

[2] I. Grenthe, J. Fuger, R.J. Lemire, A.B. Muller, C. Nguyen-Trung, H. Wanner, Chemical Thermodynamics of Uranium, 1st ed., Elsevier, Amsterdam, 1992.

[3] G. Bernhard, G. Geipel, V. Brendler, H. Nitsche, Radiochim. Acta 74 (1996) 87.

[4] D.L. Andrews, Lasers in Chemistry, Springer-Verlag Berlin, 1990, pp. 84–102.

[5] G. Geipel, A. Brachmann, V. Brendler, G. Bernhard, H. Nitsche, Radiochim. Acta 75 (1996) 199.

[6] M.U. Kumke, H.-G. Löhmannsröben, T. Roch, J. Fluoresc. 5 (1995) 139.

[7] G. Geipel, G. Bernhard, V. Brendler, H. Nitsche, Radiochim. Acta. (1998), accepted.