

4.64.61

Uranyl uptake at the calcite (104) single crystal surface – a spectroscopic and microscopic study

D. BOSBACH, M.A. DENECKE, K. DARDENNE, J. ROTHE
AND T. FANGHÄNEL

Forschungszentrum Karlsruhe, Institut für Nukleare

Entsorgung (Dirk.Bosbach@ine.fzk.de;

Melissa.Denecke@ine.fzk.de; Joerg.Rothe@ine.fzk.de;

Kathy.Dardenne@ine.fzk.de;

Thomas.Fanghaenel@ine.fzk.de)

Uranyl uptake by calcite is a key-process which controls the availability and migration of U(VI) in natural environments. The local structural environment of U(VI) incorporated into the calcite crystal structure has been studied extensively [1,2].

A linear adsorption at pH 8.5 up to 10^{-3} M has been observed [3]. U(VI) uptake during calcite growth occurs preferentially at molecular steps parallel to [-441]. and [48-1]. [1]. Here, we have focused on the spectroscopic characterisation of U(VI) site specific adsorption and kinetic effects during coprecipitation on a molecular level.

Polarized dependent grazing incidence (P-GIXAFS) measurements of U(VI) sorbed onto a calcite (104) cleavage surface after equilibration with a $1.3 \cdot 10^{-4}$ M (pH 8.3) uranyl solution were performed at the HASYLAB X1 experimental station. The EXAFS indicates that the calcite sorbed uranyl species is not simply a tricarbonato species. It is sorbed at crystal Ca positions with monodentate coordination to carbonate groups and one bidentate carbonate ligand. Uranyl cations are at a near constant tilt to the (104) surface, suggesting that binding is likely on molecular steps and not parallel to the crystal surface. Our P-GIXAFS measurements suggest preferred uranyl binding to a [-441]- molecular step.

In-situ Atomic Force Microscopy (AFM) observations of growing calcite (104) crystal surfaces showed the influence of aqueous U(VI) on the dynamics of nanotopographic changes during crystal growth. Adsorbed U(VI) seems to influence the kink site dynamics along molecular growth steps. Complementary crystal growth experiments with calcite suspensions in mixed flow reactors allowed us to quantify the incorporation depending on the geochemical conditions. The partition coefficient depends on the precipitation rate and thus confirms the kinetic effects as observed on a molecular level by AFM.

References

- [1] Reeder, R.J., Nugent, M., Tait, C.D., Morris, D.E., Headl, S.M., Beck, K.M., Hess, W.P. and Lanzirrotti, A. (2001) *GCA* **65**, 3491-3503.
- [2] Kelly, S., Newville, M.G. Cheng, L. Kemner, K.M., Sutton, S.R., Fenter, P., Sturchio, N.C. and Spötl, C. (2003) *ES&T* **37**, 1284-1287.
- [3] Geipel, G., Reich, T., Brendler, V., Bernhardt, G., Nitsche, H. (1997) *J. Nucl. Mat.* **248**, 408-411.

4.64.62

Radionuclides sorption onto mineral surfaces. The role of carbonate as the linkage between uranium and iron cycling

M. GRIVÉ¹, L. DURO¹, J. DE PABLO² AND J. BRUNO¹

¹Enviros Spain, Pg. Rubí, 29-31, 08197- Valldoreix,
Barcelona, Spain (mgrive@enviros.biz)

²DEQ Universitat Politècnica de Catalunya, 08028-
Barcelona, Spain

The presence of radionuclides in soils and waters due to nuclear waste management facilities and uranium mining tailings is a problem of major environmental concern. The mobility of these radionuclides in oxic groundwaters is linked to the iron cycle and controlled by geochemical processes such as adsorption on major mineral surfaces and precipitation/dissolution. In this context, iron oxides and oxyhydroxides are of particular importance due to the fact that they are ubiquitous in nature and to their large capacity to sorb radionuclides, among them hexavalent uranium. The Fe and U cycles are also linked to the carbon one and aqueous carbonate plays a major role in the transport of radionuclides due to its high affinity to form complexes with some radionuclides, specially with uranium. On the other hand, dissolved carbonate can compete for the sorption sites of the iron oxides, promoting the dissolution of these oxides and consequently increasing the mobility of the associated radionuclides in natural systems.

The ability to develop adequate models for predicting the fate of inorganic contaminants in surface environments is highly dependent on accurate knowledge of the distribution of these constituents between the solid and solution phases and ultimately on the capability to provide molecular-level information on chemical species distributions in both of these phases. Most of the information we have about interactions of cations or anions at mineral/water interfaces comes from macroscopic measurements. In the last years, efforts to quantify observed sorption reactions at solid/liquid interfaces by means of surface complexation models have been developed. However, it is very difficult to precisely study these sorption reactions without spectroscopic evidence, mainly due to the uncertainty in the definition of the nature of the surface species formed.

We will show the outcome of the use of combined information gathered from thermodynamic and kinetic macroscopic studies with information from EXAFS spectroscopy, which gives both qualitative and quantitative information about the coordination environments and short-range order of metal ions, including metal-oxygen bond distances and coordination numbers, to characterize bonding environments of uranium onto Fe-oxide surfaces and to study the most probable mechanism of uptake of this radionuclide in carbonated solutions.