### 4.64.P05

# Investigations of uranyl sorption onto gibbsite

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#### Introduction

The application of surface complexation models (SCM) towards real-world problems requires not only a reliable parameter database but also information about the chemical structure of surface species and the crystallographic location of binding sites. This study focused on the sorption behavior the uranyl cation  $UO_2^{2+}$  on aluminol and silanol groups in model substances for clays, namely gibbsite:  $\gamma$ -Al(OH)<sub>3</sub>.

#### **Experimental Details**

Batch sorption experiments were carried out at an ionic strength of 0.1 M NaClO<sub>4</sub> and at different pH values with a stepping of 0.5 from 3.5 to 9.5 under air. After a contact time of 2 days in the overhead shaker gibbsite was separated by centrifugation and the uranium contend in the separated solution was measured by ICP-MS. The concentration of uranium adsorbed on gibbsite was calculated in accounting for uranium sorbed on the container wall. The sorption curve indicates a maximum sorption between pH 5.5 and 7.5.

For the spectroscopic investigations with TRLIF (Timeresolved laser-induced fluorescence) the gibbsite from the batch experiments was re-suspended in a solution with pH and ionic strength being identical to the original solution. So it was guaranteed, that the fluorescence signals were only caused from uranium sorbed on the gibbsite, and not from uranium in solution.

After a second centrifugation the solution was also measured to ensure the absence of dissolved uranyl species.

#### **Results and Conclusions**

The TRLIF spectra, excluding the wavelength range between 525 and 540 nm influenced by the laser dispersion peak, were integrated and then fitted to a sum of exponential decay terms. The best approximation for the fluorescence decay gave a bi-exponential decay function

decay gave a bi-exponential decay function  $y = y_0 + A_1 e^{-(x-x_0)/t_1} + A_2 e^{-(x-x_0)/t_2}$  yielding two fluorescence decay times:  $t_1$  in a range between 200 and 450 ns (this indicates the formation of UO<sub>2</sub>(OH)<sub>3</sub><sup>+</sup>) and  $t_2$ between 3200 and 7900 ns (indicates for UO<sub>2</sub>(OH)<sub>2</sub>).

The peak maxima (at approximately 498, 521, 543 and 557 nm) differ slightly at varying pH, but do not show systematic shifts. The uranium surface species are therefore assumed to be similar throughout the investigated pH range. They should have identical numbers of hydroxyl groups in their first coordination sphere and differ only in the respective water content. This is valid both for the short lived and the long lived species.

## 4.64.P06

# Lead isotopes as a tool for understanding the lead mobility in smelter-impacted soils

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The impact of base metal smelting on soil contamination is a well-known phenomenon on numerous metallurgical sites [1,2]. Four forest/tilled soil profiles were sampled according to the distance from the lead smelter in Příbram (Czech Republic), prevailing wind direction, geological background and soil type. Bulk Pb concentrations were measured using a Varian 200HT FAAS. The Pb isotopic composition (<sup>206</sup>Pb/<sup>207</sup>Pb and <sup>208</sup>Pb/<sup>206</sup>Pb) in smelter-impacted soils was measured using a quadrupole based ICP-MS (VG Elemental PlasmaQuad 3). The results were compared with the Pb isotopic composition of bedrocks, galena (PbS) from the metalliferous veins of the Příbram mining districts and waste materials from Pb metallurgy, such as smelting slags and airpollution-control (APC) residues [2].

The isotopic composition of soils confirms the predominant role of metallurgy on the general pollution in the area. The highly contaminated forest soils from the vicinity of the smelter contain up to 35 300 mg Pb kg<sup>-1</sup>. Total Pb concentrations were approximately 10 times lower in tilled soil due to intensive ploughing and annual crop off-take. The isotopic composition of surface and subsurface soil horizons were close to that of car battery processing (<sup>206</sup>Pb/<sup>207</sup>Pb up to 1.177). The mineral horizons of soils just above the bedrock of the mining area showed an isotopic composition close to that of primary Pb smelting residues and galena (<sup>206</sup>Pb/<sup>207</sup>Pb around 1.164 - 1.165). In less contaminated soils with bedrock isotopic value significantly different from that of smelting (<sup>206</sup>Pb/<sup>207</sup>Pb is 1.22), the binary mixing model was applied in order to estimate the percentage contribution of different sources [2]. This calculation showed that the smelterinduced pollution had penetrated even to the mineral C soil horizons, indicating a significant vertical mobility of Pb contaminant within the soil profile. The calculated downward penetration rate of Pb in soils ranged from 0.3 to 0.36 cm  $y^{-1}$ .

#### References

- Rieuwerts J.S., Farago M., Cikrt M., Bencko V. (1999) Water Air Soil Pollut. 122, 203-229.
- [2] Ettler V., Mihaljevič M., and Komárek M. (2003) Anal. Bioanal. Chem. 378, 311-317.