

U and Np uptake on biogenic and abiotic ferrihydrite – a comparison by EXAFS spectroscopy

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The ferrous iron-oxidizing and stalk-forming bacterium *Gallionella ferruginea* was cultivated in laboratory experiments. Since this bacterium is gaining energy for its growth from the oxidation of ferrous iron, ferric iron is precipitating quickly and forming biogenic ferrihydrite. $\text{UO}_2(\text{NO}_3)_2$ and $\text{NpO}_2(\text{ClO}_4)$ was added to these samples under anaerobic conditions in the neutral pH range, adjusting a final U and Np concentration of 0.08 mM, respectively. The results showed an uptake of 91 mg U and 38 mg Np/g dry mass by the abundant surface area of the samples.

At the ROBL Beamline of the European Synchrotron Radiation Facility in Grenoble Extended X-ray absorption fine structure (EXAFS) spectroscopy at the uranium L_{III} -edge and the neptunium L_{III} -edge were carried out. The k^3 -weighted chi-spectrum and its Fourier transform magnitude of the studied biogenic ferrihydrite sample bears close resemblance to the bidentate edge-sharing inner-sphere sorption complex (^1E), which is the most prominent surface species in the absence of carbonate and the main sorption species on abiotic ferrihydrite [1]. As a second species a smaller portion of the aqueous type-B ternary uranyl-carbonato complex was determined as a result of the addition of a carbon source during the cultivation of the *Gallionella ferruginea* strain. By iterative target test factor analysis (ITFA), using the spectra of the two endmember species, we determined that the ^1E complex is in fact predominant with 95%, while the ternary uranyl-carbonato complex is present only to 5%. Based on the shell fit analysis, the distances of the coordination shells $\text{U}-\text{O}_{\text{eq}} \sim 2.34 \text{ \AA}$, $\text{U}-\text{O}_{\text{ax}} \sim 1.79 \text{ \AA}$, and $\text{U}-\text{Fe} \sim 3.44 \text{ \AA}$ are similar to those determined of abiotic ferrihydrite samples [2]. The data of the biogenic Np ferrihydrite sample were compared to Np interaction with a hematite surface and showed similar distances of the coordination shells, also indicating a bidentate edge-sharing coordination [3].

- [1] Rossberg, A. et al. (2009), *Environ. Sci. Technol.* **43**, 1400–1406. [2] Ulrich, K.-U. et al. (2006), *Geochimica et Cosmochimica Acta* **70**, 5469–5487. [3] Müller, K. et al. (2015), *Environ. Sci. Technol.*, **49**, 2560–2567.