

# Speciation of Tetravalent Neptunium in Fulvic Acid Solution

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Within the frame of performance assessment of nuclear waste disposal in deep geological repositories, we have studied the complexation of tetravalent Neptunium by fulvic acid. All experiments have been performed with <sup>237</sup>Np in a glove box in argon atmosphere at room temperature. Gorleben fulvic acid (GoHy-573 FA) with concentrations of 600 and 1000 mg/L were used. In first batch experiments, the fulvic acid concentration was kept constant (0.1 and 1 g/L) and the Np concentration varied from  $3 \times 10^{-9}$  to  $3 \times 10^{-4}$  M at pH 1 and 3.

To minimize the colloid formation of Np(IV) as competing reaction the experiments were performed with colloidal-free Np(III) stock solutions at pH 1 and 3. Np(III) was prepared by reducing Np(V) with liquid Zn-amalgam. After the removal of Zn-amalgam, a GoHy-573 FA solution was added to Np(III). Within 1-2 days the Np(III) is slowly oxidized to Np(IV). Immediately after the oxidation and because of the strong interaction of Np(IV) with complexing ligands, the fulvic acid complexes the Np(IV) with the consequence that the uncomplexed Np(IV) concentration is kept below its solubility limit. Thus, this method will avoid colloid formation of tetravalent neptunium even at high metal concentrations.

After 20 and 40 hours equilibration time, we characterized the solution by absorption spectroscopy in the wavelength range from 920 to 1040 nm. Here, the absorption bands for the free Np(IV) ion (at 960 nm) and of Np(IV) fulvate species (> 960 nm) appear.

At pH 1 and 1000 mg/L FA, we observed mainly the absorption band at 970 nm after 20 h, whereas after 40 h a small new peak at 978 nm arises. By decreasing the FA concentration to 600 mg/L, 3 peaks were observed at 960 nm for the uncomplexed Np(IV) and at 970 and 978 nm for some fulvate species.

At pH 3 and both FA concentrations, the peak at 978 nm besides a small absorption band at 970 nm dominates the spectrum (Figure 1). No free Np(IV) was detected at 960 nm, because of the higher actual FA concentration due to the deprotonation of carboxylic groups of the FA. However, by increasing the Np(IV) concentration, a new band near 984 nm arises. The nature of these fulvate species is so far unclear. Earlier studies by Pirlet [1] showed the same dominating absorption band at 978 nm, although the preparation and the pH value was different. In this work, Np(V)FA was reduced by dithionite to

Np(IV)FA at about pH 7. We conclude that independent of the pH value in the range between 3 and 7 only one Np(IV) fulvate species prevails.

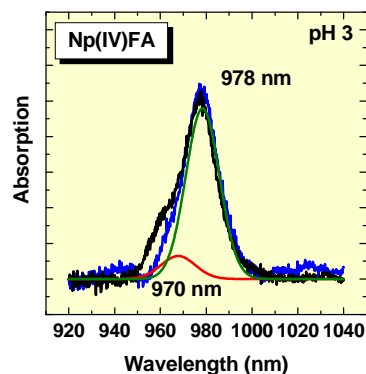


Figure 1: Absorption spectra and deconvoluted spectra of Np(IV)-FA at pH 3.

To characterize the Np(IV) in the fulvic acid, the Np(IV)FA was separated by ultrafiltration and analyzed by XPS. The resulting XPS spectra of two samples - 1 day and 14 days equilibration time - are shown in Figure 2. No significant differences could be observed.

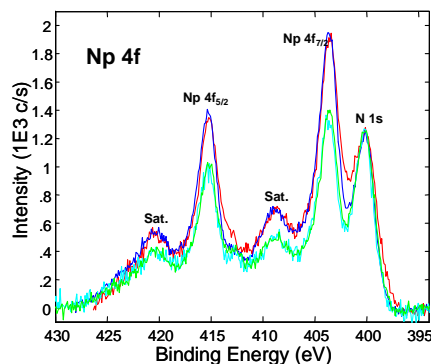


Figure 2: XPS spectra of Np(IV)-FA after a reaction time of 1 d (green) and 14 d (blue and red).

In any way, further studies on the Np(IV) fulvate complexation are necessary to enable reliable interpretations of our results and to quantify the complexation process.

## References:

[1] V. Pirlet (2003) *The investigation of the neptunium complexes formed upon interaction of high-level waste glass and Boom Clay medium*, Doctoral Thesis, University of Liege, Belgium, Faculté des Sciences.