

## Interaction of Pu with Humic Substances

R. A. Buda, N. L. Banik, S. Bürger, B. Kuczewski, J. V. Kratz, N. Trautmann

Institut für Kernchemie, Johannes Gutenberg-Universität Mainz, Germany

For the risk assessment of plutonium being released into the environment in different ways, very precise knowledge on its interaction with natural groundwater is necessary. As this contains humic substances which form complexes with metal ions, complexed plutonium may be transported over long distances. Humic substances are natural polyelectrolytes with non-uniform structural and chemical characteristics. Mainly carboxylic and phenolic groups are responsible for the complexation behaviour of humic substances. The irregular nature of humic substances results in different approaches to explain their complexation with metal cations. However, all models agree in the view that pH and ionic strength are main factors which influence the complexation reaction of metal ions with humic substances [1].

The redox behaviour of plutonium in contact with fulvic acid was investigated. A mixture of all four oxidation states of plutonium, Pu(III) 5,1%; Pu(IV) 39,2%; Pu(V) 22,1%; Pu(VI) 33,6% at pH  $\approx$  0,  $C_{Pu} \approx 60 \mu\text{mol/l}$ , was brought in contact with GoHy fulvic acid under atmospheric conditions (final solution pH  $\approx$  1). The redox behaviour was determined by CE-ICP-MS.

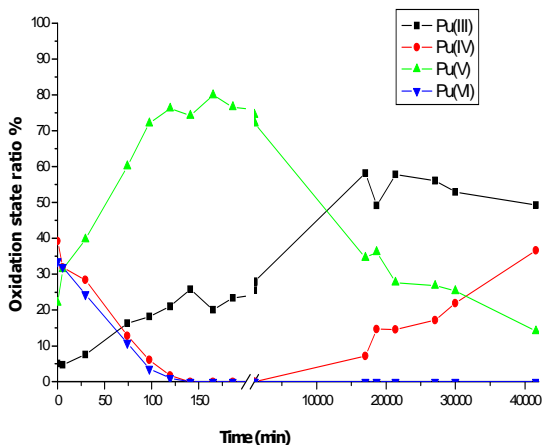


Fig.1 Redox behaviour of plutonium in contact with GoHy fulvic acid

Fig.1 shows that, after a long interaction time (28 days), the predominant oxidation states in solution are Pu(III) and Pu(IV). It must be mentioned that Fig.1 refers strictly to the free ions of plutonium in solution. There is no

knowledge about the behaviour of the complexed and colloidal plutonium in solution. Furthermore, the behaviour of Pu(III) in contact with Aldrich humic acid was investigated.

The determination of the oxidation state of the used Pu stock solution was performed by applying UV/VIS-spectrometry and CE-ICP-MS. The Pu(III) solution in different concentrations ( $10^{-6}$  M,  $10^{-7}$  M,  $10^{-8}$  M), was brought in contact with Aldrich humic acid (0 – 25 mg/L) at pH = 5,5. Afterwards, the solutions were ultrafiltered (filter pore size 1 kDalton), and the content of free plutonium in the filtrate was detected, using liquid scintillation counting (LSC). It was found that plutonium is complexed by Aldrich humic acid and reaches equilibrium in the course of one week. However, a strong adsorption process of plutonium by the contact surfaces was observed, yielding data with large uncertainties.

Therefore, the process of adsorption of Pu(III) by vessels and filters was investigated. The ultrafilter material, as well as the vials similar to the ones used in the earlier experiment, were brought in contact with Pu(III) at pH = 3, 4, and 5. The content of plutonium in solution was determined by LSC. The percentage of plutonium recovery after one day of contact showed that there was no plutonium adsorption on the vial walls. Instead there was a very strong adsorption on the filter material (60 – 70 % of plutonium adsorbed). Other trivalent ions like Am(III) and Cm(III) show no such effect. Unfortunately, no method that is sensitive enough, to determine the oxidation state of the plutonium in these solutions at these concentrations is available at this time. If an oxidation of Pu(III) to Pu(IV) would occur, this could make the observed strong adsorption plausible. As a consequence, the subsequent experiments will be performed in an inert gas atmosphere in order to maintain the plutonium ions in the Pu(III) state.

Furthermore, other methods will be used [2] in order to determine the complexation constant of Pu(III) with humic and fulvic acids over a pH range of 3 to 7.

### References:

- [1] Ziechmann, H.: *Huminstoffe*. Verlag Chemie, Weinheim, 1980.
- [2] B. Kuczewski et al.; Institut für Kernchemie, Universität, Mainz, Jahresbericht 2004.