

Determination of the reduction behavior of plutonium(VI) by Gorleben fulvic acid using CE-ICP-MS

S. Bürger[#], N. L. Banik, R. A. Buda, J. V. Kratz, N. Trautmann

Institut für Kernchemie, Johannes Gutenberg-Universität Mainz, D-55099 Mainz, Germany

present address: Chemical & Isotope Mass Spectrometry Group, Oak Ridge National Laboratory, TN, USA

Plutonium can coexist in aqueous solutions in four different oxidation states, Pu(III) to Pu(VI), and the chemical behavior of the plutonium aquo ions, like complexation, sorption, and colloid formation, depends strongly on the chemical species. In contact with humic and fulvic acids, ubiquitous humic substances, the oxidation state or the composition of oxidation states of plutonium can be changed due to the redox ability of the humic and fulvic acids. The understanding of the physical and chemical processes responsible for the mobilization or im-mobilization of plutonium enables to predict the migration of plutonium and thus advances the long term safety assessments of nuclear waste repositories or facilitates the developing of new remediation strategies for contaminated sites.

For the speciation of the plutonium oxidation states in aqueous solutions, the online coupling of capillary electrophoresis (CE) with inductively coupled plasma mass spectrometry (ICP-MS) has been developed [1]. Depending on the radius / electrical charge ratio, the oxidation states III, IV, V, and VI of plutonium are separated by CE, based on the different migration times through the capillary and are detected by ICP-MS. The detection limit is 20 ppb, i.e. $10^9 - 10^{10}$ atoms ($10^{-12} - 10^{-13}$ g) for one oxidation state [2].

Figure 1 presents the reduction of Pu(VI) ($2.5 \cdot 10^{-6}$ mol/L) in contact with Gorleben fulvic acid (Gohy-FA 573, 0.5 mg/L) at ionic strength $I \approx 1$ mol/L determined by CE-ICP-MS at different pH values. The reduction of Pu(VI) shows an approximately linear behavior (in half-logarithmic scaling) and a significant dependence on the pH value, similar to its behavior in humic acids (HA) reported in the literature. The enhanced reduction of Pu(VI) by increasing the pH may be explained by the increased fraction of dissociated groups of the FA. Therefore, the speed of reduction increases by increasing the pH. At neutral pH, a complete reduction of Pu(VI) by Gohy-FA within one day can be observed. Consistently, a fast reduction of Pu(VI) by humic substances is reported for Gorleben groundwater in [4].

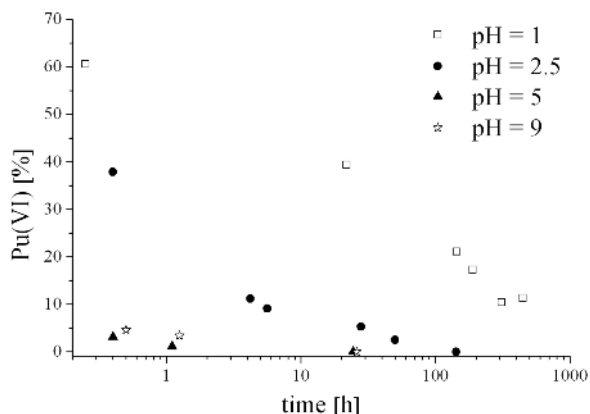


Figure 1: Reduction of Pu(VI) ($2.5 \cdot 10^{-6}$ mol/L) in contact with Gorleben fulvic acid (0.5 mg/L) at $I \approx 1$ mol/L and at different pH values

The experiments demonstrate that in a geogenic system with an adequate amount of fulvic acid (here Gorleben fulvic acid) a fast reduction, compared to the time scale of nuclear waste storage, of aqueous Pu(VI) to Pu(IV) and Pu(III) [2] occurs. This would lead to an enhanced immobilization of the aqueous plutonium due to the strong sorption of Pu(IV) onto stationary mineral surfaces [3] in comparison to Pu(V) and Pu(VI). The sorption counteracts the complexation of plutonium with humic substances or the formation of colloidal particles, which leads to a mobilization due to the facile migration of humic substances and colloidal particles in aquatic systems. To enhance the understanding of the mechanisms responsible for the mobilization vs. immobilization of plutonium and, thus, the possible migration of plutonium from a nuclear waste repository or contaminated site towards the biosphere, is an important task for the future.

Literature:

- [1] Kuczewski, B. et al., *Analytical Chemistry* **75**, 6769-6774 (2003)
- [2] Bürger, S. et al., *Radiochimica Acta*, **submitted**
- [3] Banik, N. L. et al., *Annual Report*, this issue
- [4] Marquardt, C. M. et al., *Radiochimica Acta* **92**, 617-623 (2004)