Sorption of Tetravalent Actinides on Kaolinite

N. L. Banik, R. A. Buda, S. Bürger[#], H. Hummrich, J. V. Kratz, N. Trautmann
Institut für Kernchemie, Johannes Gutenberg-Universität, Mainz, Germany
Present address: *Chemical & Isotope Mass Spectrometry Group, Oak Ridge National Laboratory, and USA*

Tetravalent transuranic elements like plutonium are among the radionuclides of greatest concern in the field of safety assessment of underground radioactive waste repositories. The sorption of tri, tetra, and pentavalent actinides (Am, Th, Np) on silica were investigated [1]. The investigation of the sorption of the tetravalent actinides, An(IV), on minerals, e.g. kaolinite, are not yet well studied. Therefore, we have studied the sorption behavior of tetravalent Pu and Th on kaolinite. Very strong sorption of tetravalent actinides on kaolinite is expected due to their higher hydrolysis and solubility constant [2].

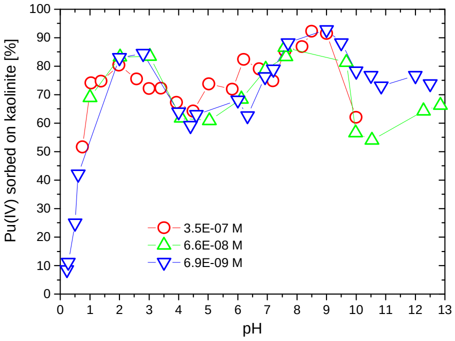

Figure 1: Sorption of Pu(IV) on kaolinite in presence of CO_2 at different plutonium concentrations

The sorption of tetravalent Pu and Th on kaolinite was investigated as a function of pH. The sorption studies were performed by batch experiments under aerobic and anaerobic conditions. A pH range of 0-12 was carried with Pu(IV) concentrations of 3.5E-07 M – 6.9E-09 M, and a Th(IV) concentration of 6.6×10^{-13} M using a solid phase concentration of 4 g/L. For the experiment, 0.1 M $NaClO_4$ was applied as an electrolyte and the contact time of the actinides with kaolinite was 5 days.
The batch experiments were conducted in absence and presence of CO_2/O_2. The sorption of tetravalent plutonium on kaolinite for varying plutonium concentrations is shown in Figure 1. A sorption edge below pH 1 and maximum sorption around pH 9 have been found. For intermediate pH values 4-6, a lower sorption was found which was a little bit unexpected. To understand the minimum in the sorption around pH values 4-6, the oxidation state of Pu in solution (after sorption onto kaolinite) was determined by liquid-liquid extraction. It has been observed that around pH 4, Pu(V) is the dominant species in solution. It seems that initially added Pu(IV) in contact with kaolinite at pH values 4-6 is oxidized to Pu(V) in the solution which might be an explanation for the lower sorption in this pH range. At pH 9 in presence of CO_2, the sorption of Pu(IV) is decreasing as can be seen in Figure 1 due to the formation of plutonium carbonate species.

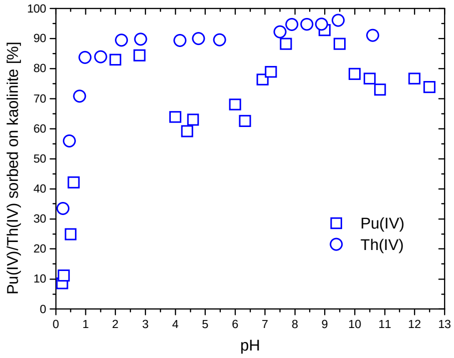

Figure 2: Sorption behavior of tetravalent actinides [Pu(IV) and Th(IV)] on kaolinite, [KGa-1b] = 4 g/L, contact time = 5 days

For comparison the sorption behavior of the oxidation state analog thorium has been investigated (Figure 2). There is no minimum in the sorption curve in the pH range 4-6 for Th(IV) as it was found for Pu(IV).
After the study of the binary systems Pu(IV)-kaolinite and Th(IV)-kaolinite, the ternary system An(IV)-kaolinite-humic substances will be investigated in order to understand the migration behavior of An(IV) in the aquifer close to a radioactive waste repository.

References:

[1] Righetto. L. et al., Environmental Science & Technology, **25**, 1913-1919 (1991)
[2] Neck. V. et al., Radiochim. Acta, **89**, 01-16 (2001)