

Kinetics of Plutonium–Aldrich Humic Acid Complexation Using the Ultrafiltration Method

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Metal-humic acid complexes are considerably influencing the migration behavior of the actinides in the environment. In earlier work, it has been shown that in Gorleben groundwater, containing humic substances, Pu(VI) is reduced within minutes to Pu(V) and further, within a few hours or days, to Pu(IV) and Pu(III) [1]. Therefore, our current work focuses on Pu(IV) complexation with Aldrich humic acid.

Pu(IV) was prepared electrochemically and the oxidation state was verified by UV-VIS spectroscopy. The time dependence of the complexation was investigated in order to find out when equilibrium of the complexation was reached. Three different plutonium metal concentrations and two humic acid concentrations were used. The experiment was performed under the experimental conditions summarized in Table 1.

Humic acid and Pu(IV) were brought into contact at pH 1.8 and the mixture was shaken continuously. After a set time period (20 h; 168 h; 672 h) aliquots of the solution were filtrated using ultrafiltration (1k Dalton pore size), and the free plutonium ion concentration was determined by liquid scintillation counting (LSC). As is shown in Figure 1, there is no significant change in the recovery of free Pu(IV) between one week and one month.

The time between one day and one week was investigated in a second experiment (Expt.2). Here, the free plutonium was determined after 20 h; 48 h; 96 h; 168 h. From the results, shown in Figure 2, one can see that it requires one week to reach equilibrium.

Table 1: Experimental conditions for the kinetics of plutonium complexation with Aldrich humic acid.

Ionic-strength	0.01M NaClO ₄
Buffer	0.01M MES
C _{HA}	0 mg/L; 1 mg/L; 10 mg/L
C _{Pu}	7.3 × 10 ⁻⁶ mol/L 7.3 × 10 ⁻⁷ mol/L 7.3 × 10 ⁻⁸ mol/L
Time	20 h; 168 h; 672 h
pH- Value	1.8
Filtration	Ultrafiltration; Pore-size 1K Dalton
Detection	Liquid Scintillation Counting (LSC)
Other Expt. Conditions	Continuously shaken; Room temperature

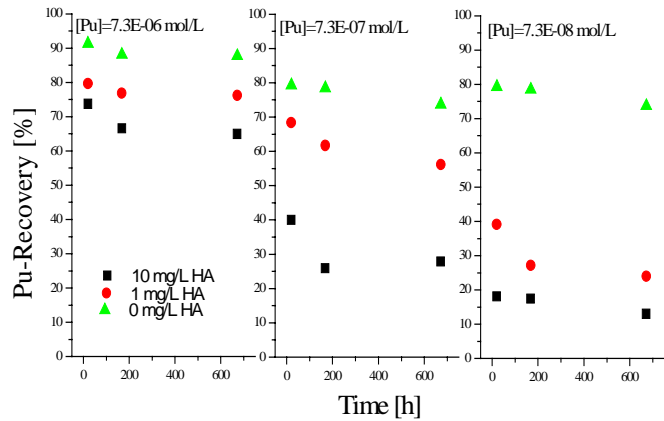


Figure 1: Time dependence of the complexation of Pu(IV) with Aldrich humic acid at pH 1.8.

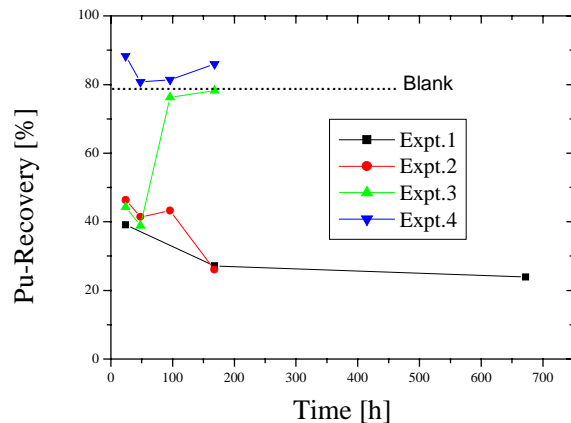


Figure 2: Kinetics of the complexation of Pu(IV) with Aldrich humic acid at varying time periods.

To exclude an interference between complexation and pH adjustment of the HA, experiments were performed where the plutonium solution and the HA solution were kept at pH 1.8 for 3 days before mixing them together. The conditions were otherwise the same as in the experiments before. The obtained results of these experiments (Expt.3, Expt.4) are shown in Figure 2. After one week the recovery of free plutonium was the same as in the blank.

References:

[1] B. Kuczewski et al.; Institut für Kernchemie, Universität Mainz, Jahresbericht 2001, C5.