Complexation of Pu(III) by Aldrich Humic Acid

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Among the actinides, plutonium delivers the major contribution to the radiotoxicity of spent nuclear fuel over long time storage. It can coexist under natural conditions in four oxidation states, from Pu(III) to Pu(VI), but it is expected that Pu(III) and Pu(IV) are the dominant oxidation states [1].

The kinetics of the complexation of Pu(III) with Aldrich humic acid (AHA) was studied at pH = 2.5, 3, 3.5, and 4 with (Pu(III)) = $1.1 * 10^{-6}$ M and (AHA) = 0, 2.5, 10, and 25 mg/L.
Pu(III) was obtained by electrolysis, and the oxidation state was verified by UV-VIS spectrometry. The oxidation state was stabilised in all the experiments with 0.025 M NH_2OHHCl [2].
After the contact of Pu(III) with AHA, a buffer was added to stabilise the pH, then the solutions were continuously shaken and the concentration of the free metal ions was periodically determined by ultrafiltration (filter pore-size 1 kDalton) and subsequent Liquid Scintillation Counting (LSC). It was found that the complexation is rather fast, one day being enough for the process to be completed as illustrated by the recovery of the free Pu(III) in Fig. 1.
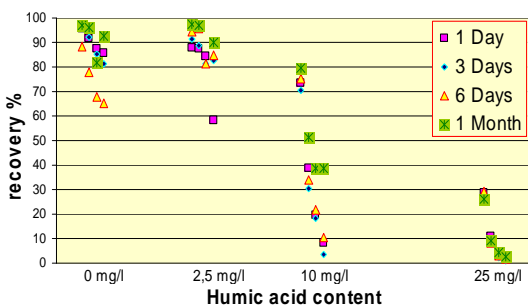

Figure 1: The complexation of Pu(III) by AHA at different concentrations as a function of the contact time

The interaction of Pu(III) with AHA was studied in order to determine the complexation constants. Several solutions of 1 M $HClO_4$ with different concentrations of ^{239}Pu(III) were contacted with AHA at concentrations varying between 0 and 55 mg/L. The pH values were between 3 and 4. The choice of pH was motivated as follows: at a value lower than pH = 3, AHA can form precipitates [3] and at values above pH = 4.5 it is uncertain whether the plutonium solution is still in the form of Pu(III) [2].
The conditions for the experiments are summarised in the Table 1.

Table 1: Experimental conditions for the determination of the complexation constants of Pu(III) with AHA

Exp.	[Pu(III)) M	(AHA) mg/L	pH	Atmosphere
1	1 E-06	0 - 55	3	air
2	1 E-06	0 - 55	4	air
3	2.5 E-06 - 1 E-08	25	3	air
4	2.5 E-06 - 1 E-08	25	4	air
5	1 E-06	0 - 55	3	argon
6	1 E-06	0 - 55	4	argon
7	1.5 E-06 - 1 E-08	25	3	argon
8	2.5 E-06 - 1 E-08	25	4	argon

The method of ultrafiltration with subsequent LSC detection was applied. The complexation of Pu(III) is described by the charge neutralization model [4]. It was found in the different experiments that at pH = 3 the loading capacity (LC) of AHA with Pu(III) was 4.5% and at pH = 4 LC = 10.2%. With these values for LC, the complexation constant was calculated as $log\text{ß}_{LC} = 6.2 - 6.8$ L/mol. No significant differences were found between the values for $log\text{ß}_{LC}$ obtained under normal atmosphere and the ones obtained under argon atmosphere.

For comparison, similar experiments were performed with Am(III). The constants found for the complexation of Am(III) with AHA are in good agreement with the data published in literature [4], and the complexation constants of Pu(III) by AHA.

References:

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