Stabilisation of Pu(III)

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In earlier experiments, it was demonstrated that plutonium exists in the presence of humic substances as Pu(III) and Pu(IV) [1]. To simplify the study of the processes in which these two species might be involved under natural conditions, it is necessary to investigate the behavior of each one, individually.

A 1 M $HClO_4$ solution of Pu(III) which was obtained by electrolysis [2], was studied over a long period of time in the presence of air with respect to its redox behavior. It was found that at pH values above pH = 2, plutonium is oxidised in a relatively short time (from days to minutes depending on pH) to higher oxidation states (mostly Pu(IV) and Pu(V)). The speciation method used was the coupling of Capillary Electrophoresis to Inductively Coupled Plasma Mass Spectrometry (CE-ICP-MS), a method developed in our group [3].

The stability of Pu(III) in 0.1 M $NaClO_4$ has also been studied under an inert atmosphere (argon gas with $[O_2] \approx 1$ ppm) at pH = 5.5. It was found that Pu(III) is relatively fast oxidised to Pu(IV) and finally to Pu(V) as illustrated in Fig. 1.

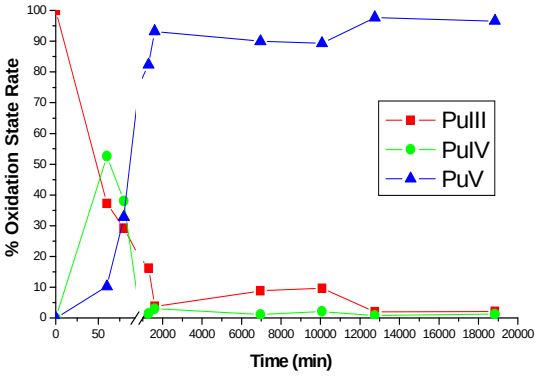

Figure 1: Oxidation of Pu(III) at pH 5.5 in an Ar atmosphere

Thus, attempts to stabilise Pu(III) in an inert gas box were performed. A solution of freshly electrolysed Pu(III) in 1 M $HClO_4$, $[Pu(III)] = 7.5*10^{-6}$ M, was contacted with Gorleben fulvic acid (GoHy – 573) (FA) at concentrations of 1.5 and 15 mg/L. It was found that a concentration of 1.5 mg/L of FA is not enough to stabilise Pu(III) whereas a concentration of 15 mg/L FA was sufficient to keep plutonium as Pu(III), see Fig. 2. However, this is not possible in the presence of oxygen.

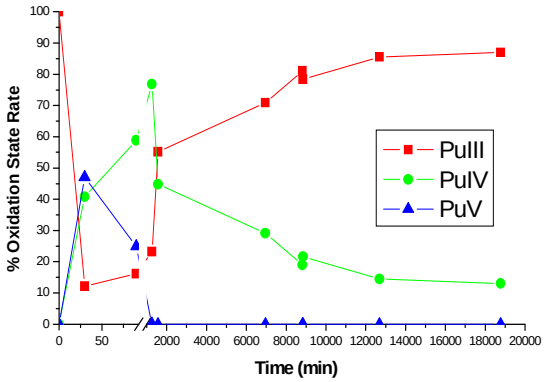

Figure 2: Stabilisation of Pu(III) with GoHy-573 fulvic acid (15 mg/L), at pH 5.5 in an Ar gas atmosphere

In order to stabilise Pu(III) in the presence of air, a solution of freshly prepared Pu(III) ($2*10^{-7}$ M) in 0.1 M $NaClO_4$, was contacted at pH = 1, 3, and 5 with NH_2OHHCl (0.025 M), ß Alanin (0.025 M), and ascorbic acid (0.02 M), respectively. For comparison, a solution containing no reducing agents was prepared. After one week, the solutions were analyzed by means of liquid-liquid extraction. It was found in all solutions that at pH = 1, plutonium remained in the oxidation state 3^+. At pH = 3 only the solution contacted with NH_2OHHCl (0.025 M) consisted of less than 9 % Pu(IV) with the remainder being Pu(III). At pH = 5 Pu(III) was oxidised to higher oxidation states in the presence of the reducing agents even with NH_2OHHCl.

The stabilisation of Pu(III) under argon atmosphere, using NH_2OHHCl (0.025 M), was also studied. It was found that Pu(III) can be stabilised under these conditions up to a pH ≈ 5.5.

References:

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