

Speciation of Trivalent Actinides (U, Np, Pu) in aqueous solution

N. L. Banik, C. M. Marquardt, A. Geist, B. Brendebach, M. A. Denecke, H. Geckeis

Institut für Nukleare Entsorgung, Forschungszentrum Karlsruhe, Postfach 3640, D-76021 Karlsruhe, Germany

Speciation of redox sensitive actinides like uranium (U), neptunium (Np), and plutonium (Pu) is necessary to understand their chemical and physical behaviour in experiments related to various research areas such as safety of nuclear waste disposal, environmental radiochemistry and minor actinide partitioning. These actinides (An) can co-exist in different oxidation states in organic and aqueous solution. Each of them has a different physical and chemical behaviour in the solution. However, only a few speciation studies of trivalent actinides (U, Np, Pu,) in the solution have been reported [1, 2]. Trivalent actinides like U, Pu, Np are extremely redox-sensitive against oxygen traces, therefore, the stabilisation of trivalent actinides in solution is a major task for performing experiments. In this work, we have studied different methods for preparation and stabilisation of U(III), Np(III), and Pu(III) at different pH values under anaerobic conditions.

For the production of An(III), all experiments were performed with An(III) stock solutions which were prepared by the reduction of U(VI), Np(V), Pu(VI) by electrolysis, with Zn-amalgam or Rongalit. Potentiostatic electrolysis is a generally applicable method to reduce all three actinide ions, but it has the disadvantage to be somewhat time consuming and it cannot be handled easily at a micro-scale. Therefore, we have looked for alternative methods for reduction. All experiments have been performed with ^{238}U , ^{237}Np , ^{242}Pu in a glove box with 100% argon atmosphere at room temperature. A pH range of 0 – 5.5 was investigated with trivalent actinide concentrations ranging from 2×10^{-3} to 1×10^{-4} M and three different reducing agents (hydroxylamine, acetohydroxymic acid, and Rongalit) were employed. The time dependence of formation and stabilisation of An(III) in solution at different pH values was investigated. Additionally, we have focused on the question, whether the actinide ions are complexed by the introduced redox agents, and hence, these agents can interfere reactions to be studied in future experiments.

UV-Vis and XAFS absorption spectroscopy have mainly been applied for the speciation of U(III), Np(III), and Pu(III) in organic and aqueous solution. Spectroscopic studies in aqueous solution (mainly HCl medium) were carried out at 2.0×10^{-3} – 1.0×10^{-5} M An(III) in presence of the above mentioned redox stabilisation agents. UV-Vis spectra of U(III), Np(III), Pu(III) show main characteristic absorption bands (522, 786, 601 nm respectively) suggesting that only the aquo ions of U(III), Np(III), and Pu(III) dominates at pH up to 5 and no complex formation with holding reductants could be observed. For the first time, U(III), Np(III), and Pu(III) complexation with BTP (Alkylated 2,6-

ditriazinylpyridine) in organic solution has successfully been investigated by XAFS spectroscopy. In those experiments related to minor actinide partitioning investigations, the speciation of An(III) has been studied by spectroscopic and extraction methods by varying BTP concentrations in solution and using Rongalit as holding reductant.

In this contribution we will discuss the application of the studied reducing agents for our experiments.

References:

- [1] M. Olsson, On the stability of Pu(III) at different pH under non-inert conditions, *Radiochimica Acta*, **94**, 575 (2006).
- [2] Yusob et al. Uranium (III) in aqueous solutions: preparation, properties, synthesis of solid compounds, *Radiochemistry*, **49**, 1-13 (2007).