

Redox behavior of Plutonium and Neptunium in aqueous solution containing humic substances or Hydroquinone

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The migration of redox sensitive actinides in the geological environment of a nuclear repository is strongly governed by their oxidation state. Previous studies showed that plutonium occurs mainly as Pu(III), and Pu(IV) in humic substance containing groundwater [1]. Neptunium mainly exists as tetravalent ion in such a groundwater [2]. Due to complexity of natural groundwater, we've started to study the behavior of both actinides in aqueous solutions of known and simple composition with only one reducing agent. It is assumed that humic substances play an important role in the reduction process of metal ions in groundwaters, and therefore, investigations have been performed with fulvic acid (FA) and humic acids (HA). In addition various types of hydroquinones have been used as model for the reducing entities of humic substances. Here, the hydroquinone (HQ) and the 9,10-anthraquinone-2,6-disulfonic acid (AH2DS) with an E^0 of 0.6992 V and 0.228 V [3], respectively, were chosen to cover a broad range of normal redox potentials (E^0). The normal potential of fulvic acids lies in between both values and is estimated to be about 0.5 V [4]. The objective of this work is to compare results from these studies, and to describe them by a thermodynamic equilibrium model. We specifically attempt to answer the question whether or not the behavior of actinides in humic-rich groundwater can be quantified by the application of thermodynamic equilibrium constants for the purpose of safety analysis of nuclear waste disposal.

Our Pu experiments were started with Pu-242, mostly Pu(VI) with small residues of pentavalent Pu (Pu(V)), to ensure colloid free start solution. Pu-242 was used to avoid radiolysis effects during the experiment. Colloid formation is expected with reduction of Pu(V, VI) to Pu(IV) at the relatively high Pu concentrations required for spectroscopic studies. To estimate the extent of colloid formation, a concomitant experiment with Pu-238 at tracer concentrations was performed. The final Pu concentrations were typically $1\text{-}2\cdot 10^{-4}$ M and about $1\cdot 10^{-9}$ M, respectively. The Neptunium experiments have been done with the long-lived Np-237. The concentrations were typically $2\cdot 10^{-5}$ M of Np(V).

The FA concentrations were 4 – 200 mg/L ($2.7\cdot 10^{-5}$ – $1.7\cdot 10^{-3}$ eq/L proton exchange capacity). The hydroquinone were used at various concentrations of $1\cdot 10^{-4}$ - $3\cdot 10^{-3}$ eq/L. The pH of solutions varied between pH 1 and 7. All experiments were performed in a glove box under Ar atmosphere (O_2 content < 20 ppm). UV-Vis-NIR absorption spectroscopy was applied

to characterise solutions at definite time intervals. For the Pu-238 experiment at tracer concentrations liquid-liquid extraction with PMBP and HDEHP was applied for the determination of oxidation states.

The results showed that Pu(V) and (VI) are not stable in all aqueous solutions containing HQ, AH2DS or FA. Pu in such solutions is converted totally to Pu(IV) within 20 days. The tetravalent state is the main oxidation state in FA at pH 3 - 7 and in HQ at pH 5 – 7 (relevant for natural aquifers). But reduction of Pu(IV) to Pu(III) was also observed in the same pH range. Np(V) was reduced to Np(IV) in AH2DS, and HS solutions, but not in HQ solution.

Eh was monitored in all experiments and those data were compared with calculated pe values. For pe calculations it was assumed that dissolved Pu(III) and Np(V)-species were in equilibrium with colloidal Pu(OH)₄, and Np(OH)₄, respectively. For Pu the calculation shows that Pu(III) can be stabilized in presence of FA at higher pH values. According to thermodynamic estimations for the Np(V)/Np(IV) redox couple there is a limiting value for the redox potential of -32 ± 41 mV. For all investigated AH2DS systems Eh lies below this value. Therefore, prediction of Np(V) reduction is in good agreement with experimental data. Pu and Np redox reaction mechanisms in aqueous solution containing humic substances or hydroquinone will be outlined in detail within this presentation. The predictive description of actinide reactions in the vicinity of a nuclear waste repository by application of a thermodynamic equilibrium approach is discussed.

References

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This work is partly supported by the European Commission within the Integrated Project FUNMIG: Project Number FP6-516514 and a DAAD fellowship.