

Pu(V) and Np(V) Reduction by Hydroquinone Enriched Humic Derivatives

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INTRODUCTION

The concept of deep underground repositories in geological formations is accepted in many countries as a final step of nuclear fuel cycle. The multi-barrier systems are designed at the repository sites and are aimed to prevent radionuclide release into the environment. Materials commonly used as engineered barriers should have high sorption properties towards radionuclides, maintain low Eh values of groundwaters and have low hydrolytic conductivity. Among proposed materials are bentonite clays, cements, etc. This study deals with the possible application of humic substances (HS) derivatives as nano-sized material for sequestration of actinides from aqueous solutions.

Natural HS are known to reduce Pu(V) and Pu(VI) to less mobile Pu(IV) and even to Pu(III). Marquardt et al.¹ established stepwise reduction of Pu(VI) to Pu(IV) and Pu(III) by humic materials from Gorleben groundwater. Similar results were obtained by Andre and Choppin². However, the ambiguous results were reported for Np(V). According to Choppin³, Np(V) is not reduced by natural HS, while Artinger et al.⁴ showed slow reduction of Np(V) by HS from Gorleben groundwater. The capability of HS to reduce Pu, Np, and other actinides offers their use as reducing agents for in situ remediation technologies. It was hypothesized that reducing performance of natural humics can be enhanced by incorporating additional hydroquinone moieties. The aim of this research was to evaluate reducing performance of leonardite humic acids and of their hydroquinone-enriched derivatives with respect to Pu(V) and Np(V).

EXPERIMENTAL PART

The quinonoid-enriched humic derivatives were obtained as described in Perminova et al.⁵ using the reaction of formaldehyde copolycondensation between parent humic material (leonardite humic acid, CHP) and hydroquinone at hydroquinone (HQ): CHP ratio of 100 mg per 1g of CHP. The obtained derivative was designated as HQ100.

The reduction of Pu(V) by humic derivatives at tracer level concentrations of plutonium ($2.3 \cdot 10^{-8}$ M) and HS concentrations of 10 mg/l was studied by solvent extraction technique². The visible-near-IR spectrophotometry⁴ was used to study reduction of Np(V) at macro-concentrations ($3.5 \cdot 10^{-5}$ M) and HS concentrations of 250 mg/l. Reduction of Pu(V) was studied using solvent extraction described by Andre and Choppin which allows tracing trivalent form². Np(V) reduction was studied by tracing of NpO_2^+ and Np(V)-humate absorbance at 980.9 and 987.5 nm respectively.

Pu(V) and Np(V) reduction was studied in plastic 20 mL vials foiled to prevent HS photolysis. In case of Np(V), all manipulations were carried out in the glove box under N_2 atmosphere. Pu(V) reduction was studied on the air. All experiments were carried out at pH of 4.5 ± 0.2 without a

background electrolyte. The oxidation states were tracked by sampling 1.5 ml aliquots for solvent extraction in case of Pu(V), and for NIR-spectrophotometry - in case of Np(V).

RESULTS AND DISCUSSION

Reduction of Pu(V) and Np(V) by HQ100 sample is presented in Figure 1. As it can be seen, only slight reduction was observed for Np(V). At the same time complete reduction of Pu(V) was observed in the presence of HQ 100 within 180 h despite the presence of air oxygen. No Pu(III) was found in the reaction mixture over total exposure time (180 h) that indicates a predominance of Pu(IV). Hence, under environmental conditions reduction of Pu(V) to Pu(III) is hardly possible and Pu immobilization could be achieved. It appears that hydroquinone groups play a major role in Pu(V) and Np(V) reduction by HS.

The obtained results demonstrate a viability of the undertaken approach to producing humic materials of the enhanced redox properties. This opens a way for broad application of the humic materials in the practice of remediation technologies.

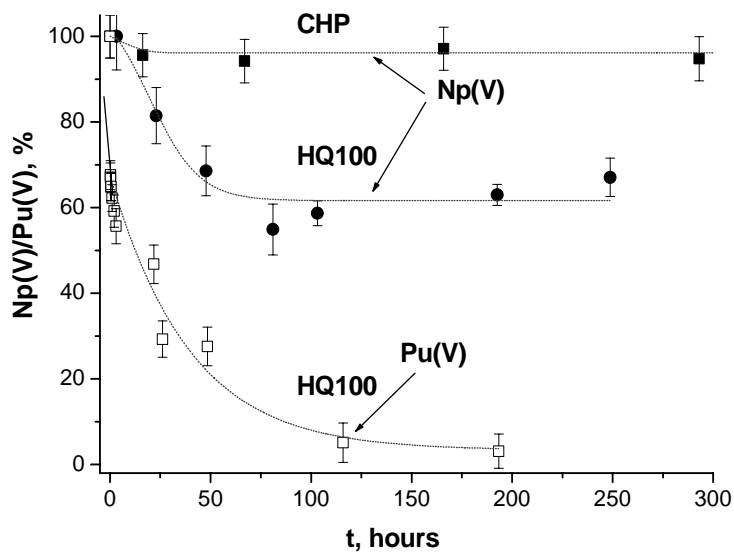


Fig. 1 Pu(V) and Np(V) reduction by CHP and HQ100; $C(\text{Pu})=2.3 \cdot 10^{-8}$ M, $C(\text{Np})=3.5 \cdot 10^{-5}$ M, $\text{pH } 4.5 \pm 0.2$, $I=0$ M

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