Neptunium Sorption onto Hematite and Goethite in Presence of Different Humic Acids

A.B. Khasanova*, St.N. Kalmykov*, I.V. Perminova*, S.B. Clark[†]

[*] Lomonosov Moscow State University, Chemistry Department, Moscow, 119992, Russia
[†]Washington State University, Chemistry Department, Pullman, WA 99164-4630, USA

INTRODUCTION

Organic and mineral colloids may enhance the mobility of pollutants in subsurface environment, including actinides. The effect of humic substances in actinide-mineral interaction is essential for modeling of actinide behavior in the far-field conditions of nuclear wastes repository sites. The goal of this work is to study the effect of humic acids (HA) with different content of hydroquinone groups on Np(V) sorption by goethite (α-FeOOH) and hematite (α-Fe_2O_3) colloids in the broad pH range.

EXPERIMENTAL

Samples of hematite and goethite were synthesized according to Penners and Koopal[1] and Atkinson et al.[2] accordingly. Their physical characteristics were obtained using XRD, SEM, potentiometric titration and BET surface analysis.

The hydroquinone-enriched derivative of HA was synthesized according to Perminova et al.[3] using the reaction of formaldehyde copolycondensation between parent humic material (leonardite humic acid, CHP) and hydroquinone. The derivative was obtained for monomer : CHP ratio of 100 mg per 1 g and marked as HQ-100.

The batch sorption and kinetic experiments were studied in 50-ml polypropylene tubes in $NaClO_4$ solution in a glove-box in N_2-atmosphrere and in the absence of UV-light.

Micro- and ultrafiltrations were used for solid/liquid separation. The redox speciation of Np(V) and Pu(V), formation of actinide-humate complexes and determination of HA concentration in the solution were studied by solvent extraction[4], Vis-NIR spectrophotometry and X-ray photoelectron spectroscopy.

RESULTS AND CONCUSIONS

The batch kinetic experiments indicated that the steady state equilibrium of Np(V) sorption in binary goethite / Np and hematite / Np systems was achieved for 3 days while in case if HA are present it took more than one

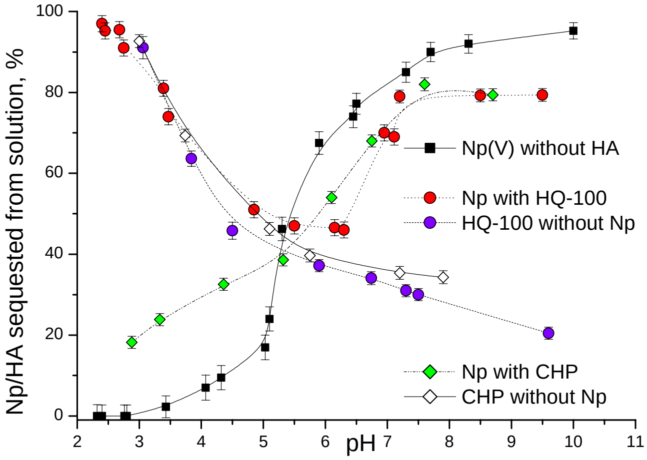

Fig 1: The pH dependences of Np(V) sorption by α-FeOOH (c=0.22 g/l) in the presence of HQ-100 (44 ppm) or CHP (43 ppm); c(Np)=$5.8 \cdot 10^{-7}$ M.

month to reach steady state equilibrium.

The sorption of Np(V) onto goethite in binary and ternary systems is presented in Fig. 1 for CHP and HQ-100. The presence of hydroquinone-enriched HQ-100 sample enhanced Np(V) sorption at the pH < 6 with slight effect in case of CHP sample (Fig. 1). The explanation of these effects is due to the reduction of Np(V) by Np(IV) by HQ-100 at low pH values that is not the case for CHP sample. The distribution of Np fits the distribution of HQ-100 at low pH values in case of goethite that is demonstrated in Fig. 2. It was established that the sequestration of Np at low pH values upon interaction with quinone enriched HA was observed only in case of goethite colloids and not in case of hematite colloids.

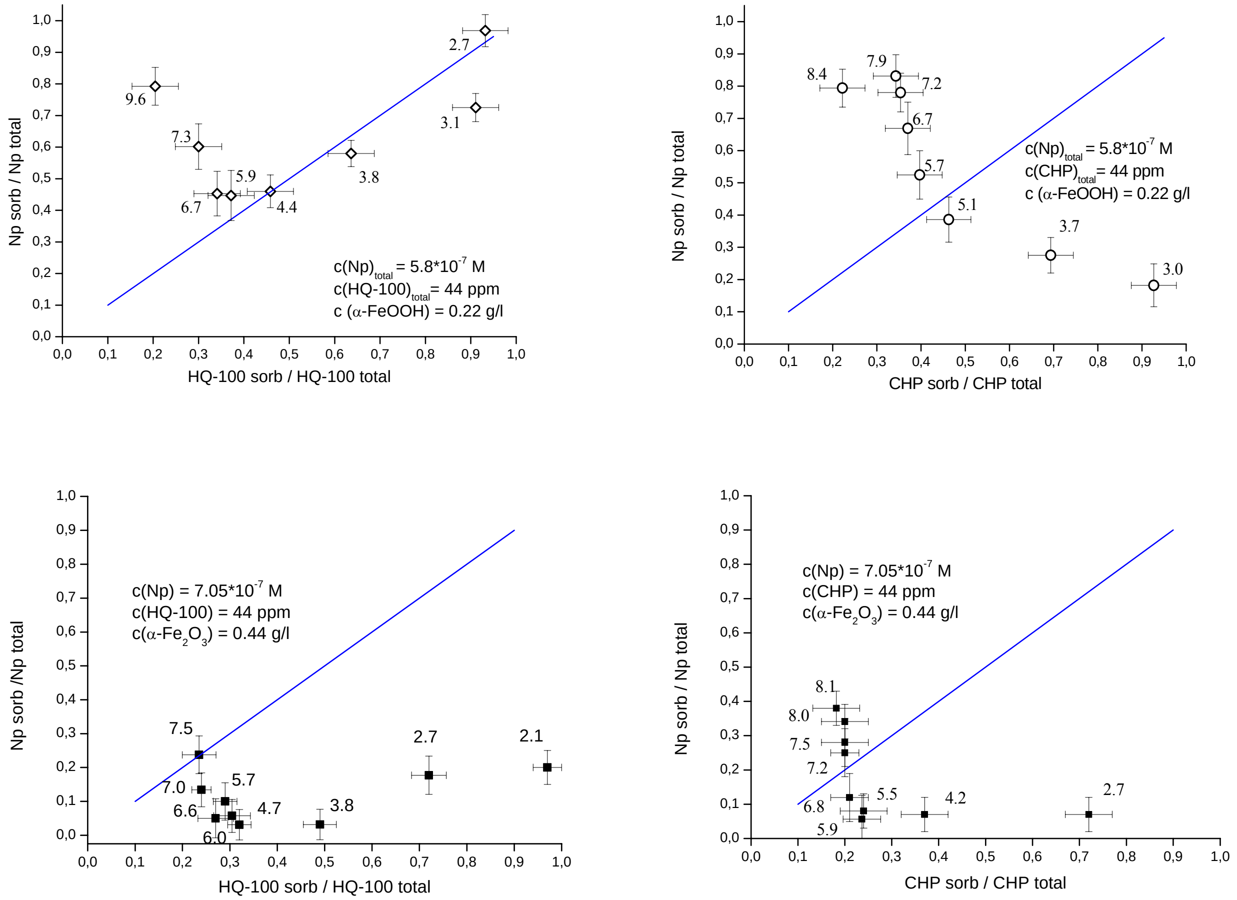

Fig 2: The correlation of Np sorbed / Np total concentrations to HA sorbed / HA total concentrations for studied ternary systems at different pH values.

This work was supported by US DOE (RUC2-20008-MO04) and by RFBR (grant 05-03-33028).

1 N.H.G. Penners, L. K. Koopal, J.Coll.Surf. **19,** (1986).
2 R.J. Atkinson, A.M. Posner, J.P. Quirk, J. Phys. Chem. **71(3),** (1967).
3 I.V. Perminova, A.N. Kovalenko, *et al.*, Environ. Sci. Technol. **39(21)**, (2005).