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# Neptunium redox behavior and sorption onto goethite and hematite in the presence of humic acids with different hydroquinone content

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## Abstract

The effect of humic acids (HA) on neptunium redox behavior and sorption onto hematite, α-$Fe_2O_3$, and goethite, α-FeOOH, colloids was established in batch sorption experiments that were carried out in broad pH interval. The sorption isotherms were provided for two samples of HA: commercial sample of leonardite humic acid and its hydroquinone-enriched derivative obtained using formaldehyde copolycondensation. The distribution of Np fitted the distribution of hydroquinone-enriched HA at low pH values in case of both solids while the influence of parent HA on Np sorption was negligible. This is due to Np(V) reduction upon interaction with hydroquinone-enriched derivative having higher reducing capacity compared to the parent HA. The order of components addition was found to be significant for Np retention.

*Keywords:* Neptunium; Humic acids; Surfaces and interfaces

## 1. Introduction

Molecular level description of actinide sorption to mineral surfaces is important for modeling of their behavior in the far-field conditions of nuclear waste repository sites. Humic substances (HS) are natural polyelectolytes that are ubiquitous in the environment and exhibit high structural heterogeneity that define their complexation with cation, sorption and adhesion onto different surfaces and also redox properties. The presence of HS may influence actinides speciation as was shown in several previous studies [1–4]. Due to their colloidal nature, HS may increase actinide subsurface migration as it was observed in work of Artinger et al. for Np [2]. Humics are known to form surface coatings on mineral surfaces that modify their properties and effect metal sorption onto them [5,6]. Moreover, iron oxides, in particular, goethite and hematite, may commonly found in potential geological repository for radioactive wastes both as component of host rocks and container corrosion products. Previously published papers [7–10] described enhanced metal sorption onto iron oxides at acidic pH values in the presence of organic ligands. The influence of components molar ratio was shown to be significant for actinide sorption in ternary systems [4,8]. The effect of the order of component addition was reported in the recent paper published by Reiller et al. [4]. Thorium retention by hematite was hindered when humics and hematite were pre-equilibrated and this effect depended upon the ratio of hematite surface sites and humics. When HS were added after hematite-Th(IV) equilibration, the decrease of thorium retention was established at pH < 7 and slight influence of decrease of hematite surface sites/humics ratio was observed to Th(IV) retention at pH > 6.4. In contrast to tetravalent thorium, Np(V) could be reduced to Np(IV) upon the interaction with humics that may affect its sorption onto mineral surface [2,11]. This work deals with the effect of different HS on neptunium retention by goethite and hematite colloids through the reduction of Np(V) at low pH values.

## 2. Experimental

### 2.1. Materials

Hematite and goethite colloids were synthesized according to Penners and Koopal [12] and Atkinson et al. [13], correspondingly. The absence of any crystal admixtures was proved by X-ray diffraction (XRD) using diffractometer FR-552 (Enraf Nonius). The samples were characterized by scanning and transmission

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Table 1
Characteristics of synthesized iron oxides

| Characteristic | α-FeOOH | α-$Fe_2O_3$ |
|---|---|---|
| Total specific surface area ($m^2/g$) | 41.7 | 6.4 |
| Specific micropore surface area ($m^2/g$) | 7.23 | 3.02 |
| Site concentration (μmol/g) | 205 | 45 |
| pH (PZC) | 8.8 | 9.2 |

electron microscopy, potentiometric titration and BET surface analysis as presented in Table 1. The goethite consisted of acicular particles with lengths of about 300–400 nm while the particles of hematite were of spherical morphology with average diameter of 300 nm.

The hydroquinone-enriched derivative of humic acids (HA) was synthesized according to Perminova et al. [14] using the reaction of formaldehyde copolycondensation between parent leonardite humic acid (CHP, Powhumus, Humintech Ltd., Düsseldorf) and hydroquinone. The derivative was obtained for monomer: CHP ratio of 100 mg/1 g and designated as HQ-100. The total acidity was determined by titration methods using $Ca(OAc)_2$ and $Ba(OH)_2$ [14] while redox capacity was obtained by reaction with $K_3Fe(CN)_6$ as oxidizing agent [15] as presented in Table 2. HA samples were characterized by elemental analyses (C, H, N) and $^{13}$C NMR (Bruker Aspect 3000) [14]. Concentration of HA in the solution was monitored by spectrophotometry using the previously prepared different standards of HA (CARY 50, Varian, USA). According to Gu et al. [16] the interaction of different fragments of HA (hydrophobic versus hydrophilic) with Fe-oxides may cause HA fractionation. Therefore, spectrophotometry gives only an estimation of HA concentration in solution after sorption. For concentration determination, the absorbance at 465 nm was traced.

The working solution of $^{237}$Np was prepared by separation of daughter $^{233}$Pa from stock neptunium nitrate solution by solvent extraction technique using 0.5 M 2-thenoyltrifluoroacetone (TTA, “Lancaster”, UK) in cyclohexane. The absence of other α-emitting isotopes was controlled by α-spectrometry (Model 7401, Canberra Ind., USA). The initial Np redox speciation was checked spectrophotometrically (Shimadzu UV-3100) and its concentration was determined by liquid scintillation spectrometry (TriCarb 2700TR, Canberra Ind., USA).

All chemicals were of analytical grade and all solutions were prepared using $N_2$(g) purged deionized water (Milli-Q).

### 2.2. Sorption experiment

Batch sorption and kinetic experiments were carried out under $N_2$-atmosphere in a glove-box in the darkness at 25 ± 1 °C. In order to avoid neptunium sorption onto walls the polypropylene tubes were used and tested before use.

Experiments were conducted in binary (e.g. Np(V)/mineral colloids or mineral colloids/HA) and ternary (Np(V)/mineral colloids/HA) component systems using different order of component addition. The aliquots of goethite or hematite suspensions were added to 45 mL of 0.1 M $NaClO_4$ solution in 50 mL polypropylene tubes and left overnight at vigorous shaking. Depending on the order of reagent addition, HA or Np(V) aliquots were added to these suspensions. Neptunium was added to hematite or goethite suspensions to make total concentration of $(6.4 \pm 0.6)10^{-7}$ M. The desired pH values were adjusted using $HClO_4$ and NaOH–$CO_2$ free solutions. The pH measurements were done using combined electrode “METTLER TOLEDO In Lab. 409”.

After the sorption equilibrium was achieved an aliquot of Np(V) or HA was added as a third component and the suspension was shaken. The pHs of the samples were adjusted at the desired value. The centrifugation at 4000 rpm and microfiltration (170 nm) were used for solid/liquid separation. The separate experiments at different pH values were done to examine Np(V) sorption onto filter material and were found to be negligible. Neptunium sorption in the presence of solid phases was determined as the difference between total initial concentration in solution and current solution concentration at each time.

Table 2
Some properties of humic acids

| Sample | Carboxyl group concentration (mmol/g) | Phenolic group concentration (mmol/g) | Redox capacity (mmol/g) |
|---|---|---|---|
| CHP | 3.8 | 1.0 | 0.6 |
| HQ-100 | 3.5 | 3.3 | 1.3 |

For redox speciation of Np sorbed onto solid phases the solutions were acidified to pH 1.5 by $HClO_4$ and Np was completely desorbed within 5 min. The speciation of Np(V) was determined by parallel solvent extraction techniques using 0.5 M 2-thenoyltrifluoroacetone (TTA, “Lancaster”, UK) in cyclohexane and 0.5 M bis-(ethylhexyl)-phosphoric acid (HDEHP, “MERCK-Schuchardt”, Germany) in heptane [17] and X-ray photoelectron spectroscopy (MK II VG Sientific using Al *K*α radiation at 14,866 eV) [18].

## 3. Result and discussion

### 3.1. Np(V) sorption onto goethite/hematite

Fig. 1 shows the results of neptunium sorption onto both solid phases. The batch kinetic experiments indicated that the steady state equilibrium of Np(V) sorption in binary goethite/Np and hematite/Np systems was achieved within 3 days. It was established that Np(V) sorption by α-$Fe_2O_3$ and α-FeOOH is described by two-steps process: rapid sorption on external surface of the colloids and the slow diffusion to internal micropores. These results are consistent with previously reported data [19,20].

Preliminary experiments have shown a negligibly small effect of ionic strength on Np(V) sorption at pH 2–9 for both solids that is an indication of inner-sphere complex formation with surface hydroxyl groups of solid phases. It was established that Np(V) sorption depends on solid/solution ratio as shown for Np–hematite system in Fig. 1.The solvent extraction technique was used to separate Np(IV)/Np(V) and indicated no redox reaction occur in binary Np(V)-solid phase systems. These results were confirmed by X-ray photoelectron spectroscopy (XPS) for Np(V) taken at about $1 \times 10^{-5}$ M. The XPS-experiment was discussed in details in paper by Teterin et al. [18].

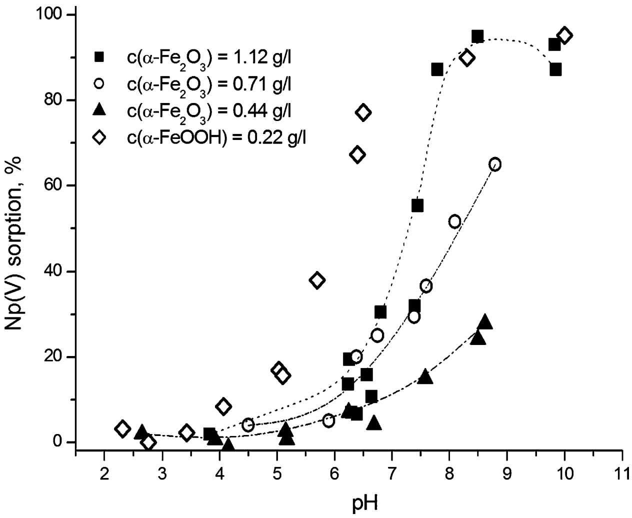

Fig. 1. The pH dependence of Np(V) sorption onto α-FeOOH and α-$Fe_2O_3$; $I = 0.1$ M, $C_{tot}(Np) = 6 \times 10^{-7}$ M.

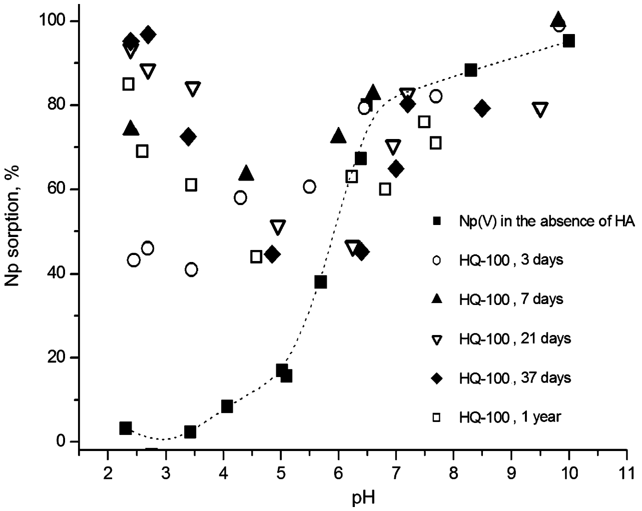

Fig. 2. The pH dependences of Np sorption onto α-FeOOH ($C = 0.22$ g/L) in the presence of HQ-100 (44 ppm); $C_{tot}(Np) = 5.8 \times 10^{-7}$ M.

### 3.2. Neptunium behavior in ternary Np/mineral colloids/HA suspension

#### 3.2.1. HA addition to the pre-equilibrated Np-solid phase suspension

The evolution of Np sorption onto goethite in the presence of HQ-100 is presented in Fig. 2. It was established that sorption equilibrium after the addition of HA is not reached in 3 days as in case of binary Np-goethite system. The difference in Np retention after more than 7 days of equilibration is possibly within the uncertainty.

The influence of different HA samples on Np retention onto goethite is presented in Fig. 3. The equilibrium distribution of Np in ternary systems containing either parent HA (CHP) or its hydroquinone-enriched derivative (HQ-100) at the total humics concentration of 45 ppm are presented for the comparison. The addition of HQ-100 sample to binary pre-equilibrated system enhanced Np(V) sorption at pH < 6 with small effect in case of CHP sample. The distribution of Np at low pH agreed with HA sorption onto goethite (not shown in Fig. 3). It was also established that enhanced Np sorption at low pH values occurred at HA total concentration higher than 20 ppm. Lenhart and Honeyman [8] found similar effects for U(VI) sorption onto hematite in the presence of Suwannee river HA. They established that addition of HA enhances U(VI) sorption at low pH values compared to the HA-free system whereas sorption is slightly decreased at alkaline pH values. This can be explained by actinide complexation by HA sorbed onto hematite at low pH. The stability constants of hexa-, tetra- and trivalent actinides humates are several orders of magnitude higher than corresponding values for pentavalent actinides. According to the values reported by different authors [21–23], the logarithms of stability constants for tetravalent actinide humates vary between 6.6 and 12.9 for $\log \beta_1$ and between 11.5 and 18.0 for $\log \beta_2$ (for dissociation degree $\alpha = 0.5$). The values of $\log \beta$ for Np(V) humates for CHP was found to be $2.26 \pm 0.16$ at pH 4.5 [24]. At low pH values, both humics form surface coatings on the goethite surface, however, only for HQ-100 the reduction of Np(V) to Np(IV) occurred. The difference in Np retention onto solid phases for two studied HA samples is explained by the difference in their reduction capacities. The hydroquinone-enriched HA sample, HQ-100, had redox capacity twofold higher than the parent HA, CHP (Table 2). The slow reduction of Np(V) in solution at low pH values by different hydroquinone-enriched HA was reported in our previous studies [24]. The retention of Np(V) onto goethite in ternary system at neutral and alkaline pH is systematically lower than in case of binary system. At these pH values both HA samples did not form surface coatings on goethite surface, as their sorption was very low. The effect of depletion of Np sorption at pH > 6 in ternary system is due to Np(V) complexation in solution with either CHP or HQ-100. It is known Np(V) humate complex is significant only at pH > 6 and did not exceed 45% at pH 10.5 [11].

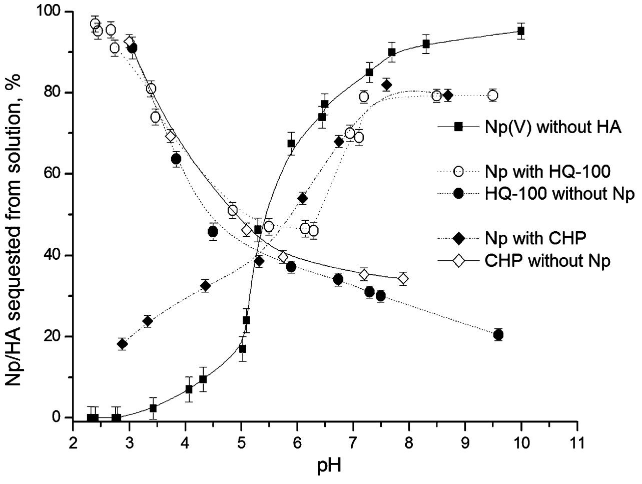

Fig. 3. The pH dependences of Np sorption onto α-FeOOH in the presence of HQ-100 (44 ppm) or CHP (43 ppm); $C(\alpha\text{-FeOOH}) = 0.22$ g/L, $C_{tot}(Np) = 5.8 \times 10^{-7}$ M.

The same types of effects were established for ternary Np–CHP–hematite and Np–HQ-100–hematite suspensions. The presence of 45 ppm of HQ-100 significantly increased retention of Np at low pH values with small effect of CHP as demonstrated in Fig. 4. It was also found that increase in Np retention at low pH is observed only for total HQ-100 concentration not less than 20 ppm.

#### 3.2.2. Np addition to pre-equilibrated HA–goethite suspension

The pH isotherms of Np retention to the pre-equilibrated HA–goethite phases are presented in Fig. 5. Significantly smaller effect of HQ-100 on Np retention at low pH values was observed in case if Np was added to pre-equilibrated HA-goethite suspension. The sorption of Np was only about 18% in case if it was added to HA-goethite suspension compared to more than 50% in case of reverse reagent addition at pH range from 4.5 to 6. The same difference in Np retention was found for ternary systems with CHP. This could be explained by competition between HA sites and goethite surface sites for Np complexation. Reiller et al. [4] postulated that this competition for Th(IV) is strongly in favor of HA in the acidic and neutral pH range,

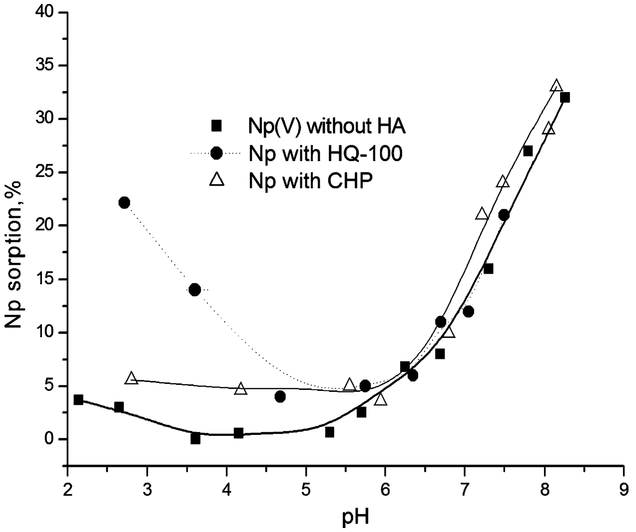

Fig. 4. The pH dependence of Np sorption by α-$Fe_2O_3$ in the presence of CHP (43 ppm) and HQ-100 (44 ppm); $C(\alpha\text{-}Fe_2O_3) = 0.44$ g/L; $I = 0.1$ M; $C_{tot}(Np) = 7.05 \times 10^{-7}$ M.

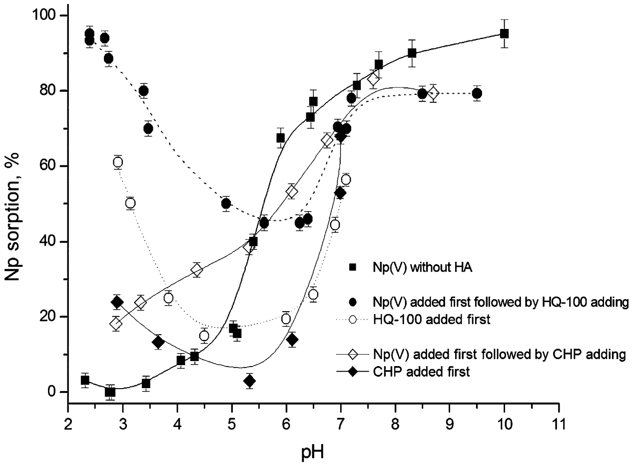

Fig. 5. The pH dependence of Np sorption onto α-FeOOH in the presence of CHP (43 ppm) or HQ-100 (44 ppm); $C(\alpha\text{-}FeOOH) = 0.22$ g/L; $I = 0.1$ M; $C_{tot}(Np) = 5.8 \times 10^{-7}$ M.

whereas at pH > 8, the complexation by hematite surface sites increases.

## 4. Conclusions

The neptunium sorption onto goethite and hematite surfaces was strongly affected by the addition of humic acids. The increase of Np retention onto these minerals at low pH values in case of hydroquinone-enriched HA due to reduction of Np(V) to Np(IV). Significantly smaller effect of HA on Np retention at low pH values in case when Np was added to pre-equilibrated HA-goethite suspension that is explained by competition between HA sorption onto goethite and neptunium–humate complexation.

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## References

[1] C.M. Marquardt, A. Seibert, R. Artinger, M.A. Denecke, B. Kuczewski, D. Schild, Th. Fanghanel, Radiochim. Acta 92 (2004) 617–623.
[2] R. Artinger, C.M. Marquardt, J.I. Kim, A. Seibert, N. Trautmann, J.V. Kratz, Radiochim. Acta 88 (2000) 609–612.
[3] C. Andre, G.R. Choppin, Radiochim. Acta 88 (2000) 613–616.
[4] P. Reiller, F. Casanova, V. Moulin, Environ. Sci. Technol. 39 (2005) 1641–1648.
[5] J. Davis, Geochim. Cosmochim. Acta 48 (4) (1984) 679–691.
[6] Y. Takahashi, Y. Minai, S. Ambe, Y. Makide, F. Ambe, Geochim. Cosmochim. Acta 63 (6) (1999) 815–836.
[7] T.E. Payne, J. Davis, T.D. Waite, Radiochim. Acta 74 (1996) 239–243.
[8] J.J. Lenhart, B.D. Honeyman, Geochim. Cosmochim. Acta 63 (19/20) (1999) 2891–2901.
[9] M.A. Ali, D.A. Dzomback, Geochim. Cosmochim. Acta 60 (1996) 291–304.
[10] Z.Y. Tao, T.W. Chu, J.Z. Du, X.X. Dai, Y.J. Gu, Appl. Geochem. 15 (2000) 133–139.
[11] P. Zeh, J.I. Kim, C.M. Marquardt, R. Artinger, Radiochim. Acta 87 (1999) 23–28.
[12] N.H.G. Penners, L.K. Koopal, Coll. Surf. 19 (1986) 337–349.
[13] R.J. Atkinson, A.M. Posner, J.P. Quirk, J. Phys. Chem. 71 (3) (1967) 550–558.
[14] I.V. Perminova, A.N. Kovalenko, et al., Environ. Sci. Technol. 39 (21) (2005) 8518–8524.
[15] A. Matthiessen, Vom Vasser 84 (1995) 229–234.
[16] B. Gu, J. Schmitt, Zh. Chen, L. Liang, J.F. McCarthy, Geochim. Cosmochim. Acta 59 (2) (1995) 219–229.
[17] A. Morgenstern, G.R. Choppin, Radiochim. Acta 90 (2002) 69–79.
[18] Yu.A. Teterin, S.N. Kalmykov, A.P. Novikov, Yu.A. Sapozhnikov, L.Dj. Vukcevic, A.Yu. Teterin, K.I. Maslakov, I.O. Utkin, A.B. Khasanova, N.S. Shcherbina, Radiochemistry 46 (6) (2004) 545–552.
[19] M. Kohler, B.D. Honeyman, J.O. Leckie, Radiochim. Acta 85 (1999) 33–48.
[20] K. Nakata, S. Nagasaki, S. Tanaka, Y. Sakamoto, T. Tanaka, H. Ogawa, Radiochim. Acta 88 (2000) 453–457.
[21] G.R. Choppin, Role of humics in actinide behavior in ecosystems, in: G.R. Choppin, M.Kh. Khankhasayev (Eds.), Chemical Separation Technologies and Related Methods of Nuclear Waste Management, Academic Publishers, Kluwer, 1999, pp. 247–260.
[22] P. Reiller, V. Moulin, F. Casanova, C. Dautel, Radiochim. Acta 91 (9) (2003) 513–524.
[23] K.L. Nash, G.R. Choppin, J. Inorg. Nucl. Chem. 42 (1980) 1045–1050.
[24] N.S. Shcherbina, St.N. Kalmykov, I.V. Perminova, R. Haire, Environ. Sci. Tech. Submitted for publication.