

ACTINIDE SORPTION BY Fe- AND Mn-CONTAINING OXIDES

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Abstract

The sorption of plutonium and neptunium by synthesized and well-characterized goethite (α -FeOOH), maghemite (γ -Fe₂O₃) and amorphous manganese oxide (δ -MnO₂) was investigated. Pu(V), Np(V) and Pu(IV) as initial oxidation states were used in sorption experiment. Actinide sorption dependences on pH, ionic strength and total metal concentration were studied. The type of surface complexation (inner- or outer-sphere) was determined.

Plutonium and neptunium speciation in solution and on the solid phases was studied using liquid extraction by TTA and HDEHP and X-ray photoelectron spectroscopy (XPS). Disproportionation of Pu(V) upon sorption by α -FeOOH occurred due to high concentration gradient appears near the surface in double-electrical layer. While Pu(V) and Np(V) sorption by γ -Fe₂O₃ were not accompanied by any redox reactions. In case of Pu(V) and Pu(IV) sorption by δ -MnO₂ the disproportionation and oxidation to Pu(V) and Pu(VI) occur respectively. While Np(V) did not change its oxidation state upon sorption.

It was found from FITEQL modeling that plutonium and neptunium form inner-sphere monodentate surface complexes with surface hydroxyl groups. It was found that in case of Np (that does not undergo any redox transformations) the complexation strength varies in the following sequence: $\log\beta_{\delta\text{-MnO}_2} > \log\beta_{\alpha\text{-FeOOH}} > \log\beta_{\gamma\text{-Fe}_2\text{O}_3}$

Introduction

Sorption and migration ability of actinides in geological formations should be clarified for the safety assessment of radioactive waste disposal. Actinide behavior on water-mineral interface is an important factor that controls actinide migration in the environment. Sorption by minerals and colloids is considerably influenced by their phase composition (1,2,3). The molecular level understanding of sorption is required to quantify environmental behavior of actinides. This includes the establishment of sorption mechanisms, actinide speciation and calculation of stability constants of surface complexes. This work is aimed to compare different minerals in their ability to sorb actinides. In the present work, the sorption of Pu(V), Np(V) and Pu(IV) on synthetic goethite (α -FeOOH), maghemite (γ -Fe₂O₃) and amorphous manganese oxide (δ -MnO₂) was investigated in the pH range from 2 to 10.

Materials and methods

Mineral synthesis and characterization

Goethite was prepared by the addition of 200 ml of 2.5 M KOH to 50 g of Fe(NO₃)₃·9H₂O (MERK) in 825 ml of double-distilled water (DDW) to give a final pH near 12 (4). Pyrex glass vessels were used, and no precautions were taken to prevent silicate contamination, which is possible at high pH. Goethite precipitates were dialyzed in cellulose tubing using DDW

changed twice daily until NO_3^- concentrations were $<10^{-4}$ M. Finally, goethite sample was washed by acetone and dried at 40°C for 48 hours.

The maghemite was synthesized by the method described by Parks and DeBruyn (5). 100 g of high pure $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ was added to one liter of DDW and precipitate was boiled during 18 days. The solution was discarded after centrifugation and washed several times with DDW. The solid phase was dried at 40°C .

Hydrous manganese dioxide was synthesized according to the method described by Murray (6). The potassium permanganate was dissolved in DDW by addition of sodium hydroxide to neutralize acid that was evolved in the reaction. The equivalent amount of MnCl_2 was added and continuous mixing was applied. The precipitate was washed repeatedly with DDW and then stored as aqueous suspension.

The characterization of samples included powder XRD, SEM, surface BET analysis, potentiometric titration. The X-ray pattern indicates the low degree of crystallinity. The MnO_2 sample was quite non-uniform in its morphology. X-ray diffraction of goethite and maghemite confirmed the respective mineral phases and no impurities were detected. The specific surface area of all matrixes was determined by N_2 gas adsorption at 77°K using the standard BET procedure. The potentiometric titration was performed to determine surface protonation constants. The main characteristics of sorbents used are presented in *Table 1*.

Table 1. Characterization of mineral phases

	$\alpha\text{-FeOOH}$	$\gamma\text{-Fe}_2\text{O}_3$	$\delta\text{-MnO}_2$
Total specific surface area	41.7 m^2/g	20.4 m^2/g	182 m^2/g
Specific micropore surface area	7.23 m^2/g	9.8 m^2/g	32.9 m^2/g
Granular size	$\sim 0.3 \mu\text{m}$	$\sim 0.44 \mu\text{m}$	-
Site density	2.31 nm^{-2}	7.56 nm^{-2}	80 nm^{-2}
pKa ₁	-7.8	-7.9	-1.2
pKa ₂	9.8	9.9	4.2

1. $=\text{Fe-OH} + \text{H}^+ \leftrightarrow =\text{FeOH}_2^+$; 2. $=\text{Fe-OH} \leftrightarrow =\text{Fe-O}^- + \text{H}^+$

Experimental protocol for An(IV,V) sorption experiments

To prepare solution with different actinide concentrations Pu-238, Pu-239, Pu-242 and Np-237 were used. The sorption experiments were performed in NaClO_4 solutions under N_2 atmosphere (in order to prevent carbonate complexation).

The kinetics of Np(V), Pu(V) and Pu(IV) sorption by $\alpha\text{-FeOOH}$, $\gamma\text{-Fe}_2\text{O}_3$ and $\delta\text{-MnO}_2$ was studied at a goethite mass concentration of 15 m^2/l , maghemite concentration of 7.6 m^2/l and manganese dioxide mass concentration of 40.8 m^2/l .

Experiments with $\alpha\text{-FeOOH}$ were conducted using $^{237}\text{Np(V)}$ ($5.6 \cdot 10^{-8}$ M), $^{242}\text{Pu(V)}$ ($1.8 \cdot 10^{-8}$ M) and $^{238}\text{Pu(IV)}$ ($1.25 \cdot 10^{-11}$, $1.8 \cdot 10^{-10}$ M) in 0.1 M NaClO_4 in pH range from 2 to 10. The contact time was 24 hours that was enough to reach the equilibrium.

The actinide sorption onto $\delta\text{-MnO}_2$ was conducted using $^{237}\text{Np(V)}$ ($1.5 \cdot 10^{-7}$ M), $^{242}\text{Pu(V)}$ ($1.8 \cdot 10^{-8}$ M) and $^{238}\text{Pu(IV)}$ ($5.9 \cdot 10^{-12}$ M) solutions in 0.1 M NaClO_4 at pH range from 2 to 8 in wide range of contact time.

Actinide sorption by $\gamma\text{-Fe}_2\text{O}_3$ was studied using $^{237}\text{Np(V)}$ ($3.8 \cdot 10^{-9}$ M), $^{238}\text{Pu(IV)}$ ($6.43 \cdot 10^{-12}$ M) and $^{242}\text{Pu(V)}$ ($1.8 \cdot 10^{-8}$ M) in 0.1 M NaClO_4 at pH range from 2 to 7. As in case of sorption on $\delta\text{-MnO}_2$ the wide range of contact time was used.

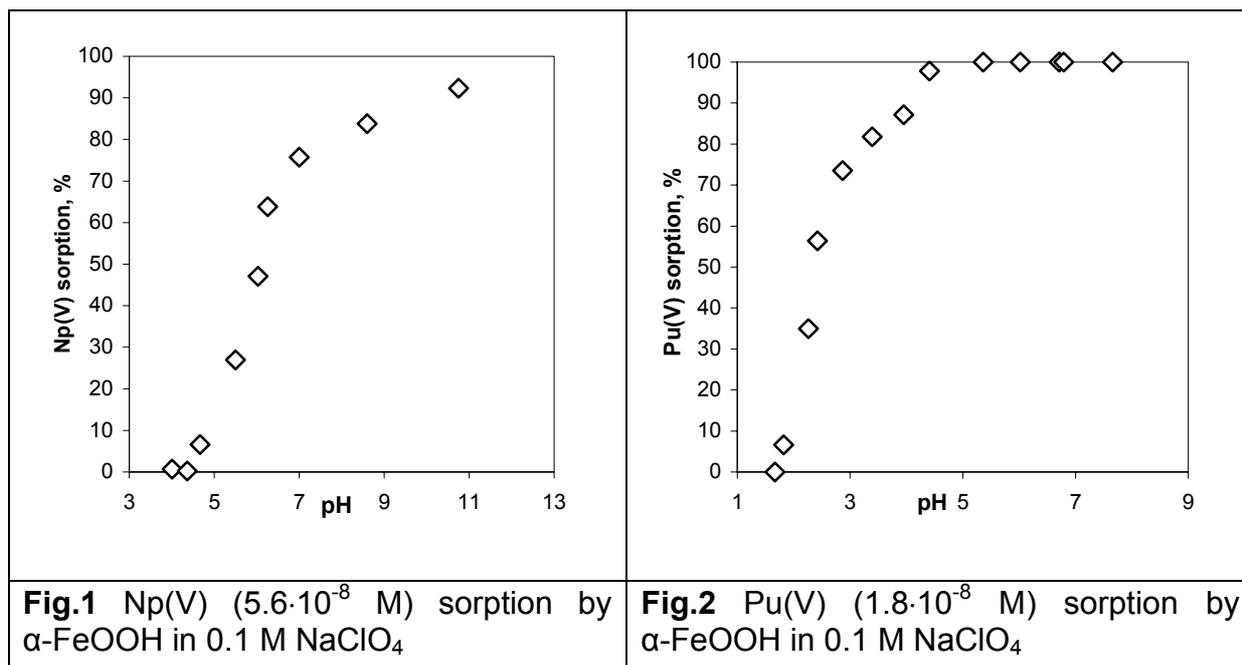
Actinide redox speciation

The actinide redox speciation either in solution or on solids was studied using solvent extraction by TTA and HDEHP (7). For solid phases extraction was performed after complete desorption of actinides by acidifying to pH about 1.5. The XPS was performed to study actinide redox forms for the samples with macroconcentrations of actinides.

Results and discussions

Sorption of Pu(IV,V) and Np(V) by α -FeOOH

The dependences of Np(V) and Pu(V) sorption on pH are presented in **Fig.1** and **Fig.2**. Since Np(V) is a chemical analogue to Pu(V) the sorption curves should be similar. However, the sorption curves were different.



Possibly, redox reaction is taking place upon sorption in case of Pu(V). According to redox speciation of Pu only pentavalent form is found in solution, while on the surface only 10% correspond to Pu(V). The disproportionation of Pu(V) to Pu(IV) and Pu(VI) takes place due to high concentration gradient appeared near the surface. According to the solvent extraction and XPS analysis Np remained in pentavalent form upon sorption.

Sorption of Pu(IV,V) and Np(V) by δ -MnO₂

The sorbed amount of NpO₂⁺ and PuO₂⁺ is shown as a function of pH in **Fig.3** and **Fig.4** respectively. As in case of sorption by goethite the shape of sorption curves for Pu(V) and Np(V) are different. According to solvent extraction data (*Table 2*) Pu(V) disproportionated upon sorption. In case of Pu(IV) sorption by δ -MnO₂ oxidation to Pu(VI) and Pu(V) was occurred.

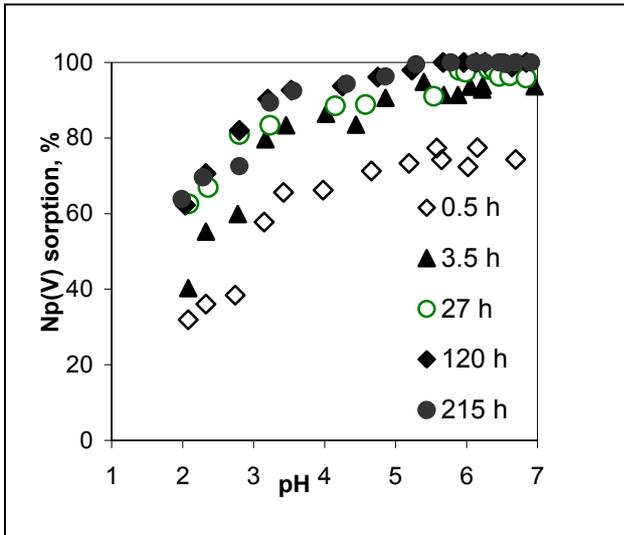


Fig. 3 Np(V) ($1.5 \cdot 10^{-7}$ M) sorption by δ -MnO₂ in 0.1 M NaClO₄.

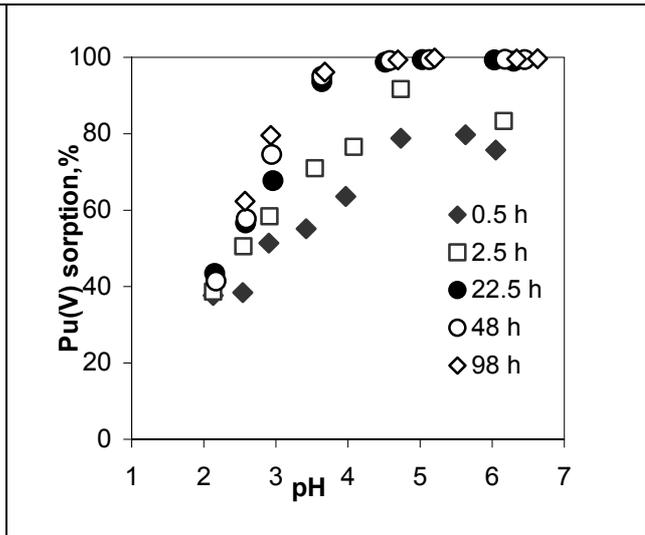


Fig. 4. Pu(V) ($1.8 \cdot 10^{-8}$ M) sorption by δ -MnO₂ in 0.1 M NaClO₄

Table 2. Pu speciation on δ -MnO₂ determined by solvent extraction (initially Pu(V))

pH	Pu(IV)	Pu(V)	Pu(VI)
3.73±0.03	50±5%	<5%	45±5%
4.93±0.03	38±4%	<5%	58±5%
5.50±0.05	53±5%	<5%	43±5%

Sorption of Pu(IV, V) and Np(V) by γ -Fe₂O₃

There were no redox reactions in case Pu(V) and Np(V) sorption by maghemite observed either in solution or on the solids. The sorption curves at different contact time for Pu(IV) and Np(V) are shown in **Fig. 5** and **Fig. 6**.

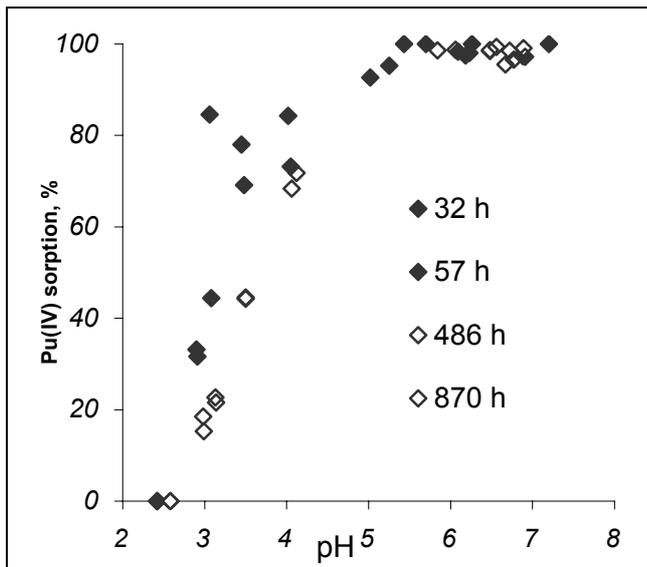


Fig. 5 Pu(IV) ($6.43 \cdot 10^{-12}$ M) sorption by γ -Fe₂O₃

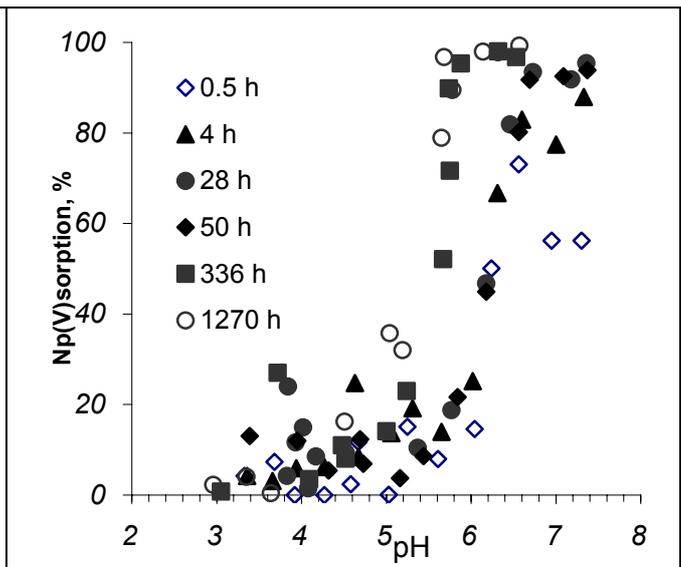


Fig. 6 Np(V) ($2.74 \cdot 10^{-7}$ M) sorption by γ -Fe₂O₃

FITEQL modeling

FITEQL modeling was performed for the studied system (8). It was established that the surface complexes are of monodentate inner-sphere character. The stability constants for surface complexes are: $\log K_{\alpha\text{-FeOOH}}(\sim\text{FeONpO}_2) = -1.14$; $\log K_{\gamma\text{-Fe}_2\text{O}_3}(\sim\text{FeONpO}_2) = -2.49$; $\log K_{\delta\text{-MnO}_2}(\sim\text{MnONpO}_2) = 0.25$; $\log K_{\alpha\text{-FeOOH}}(\sim\text{FeOPu}^{3+}) = 2.64$; $\log K_{\alpha\text{-FeOOH}}(\sim\text{FeOPu}(\text{OH})^{2+}) = -1.93$; $\log K_{\alpha\text{-FeOOH}}(\sim\text{FeOPu}(\text{OH})_2^+) = -5.87$; $\log K_{\alpha\text{-FeOOH}}(\sim\text{FeOPu}(\text{OH})_3) = -11.9$.

Conclusions

The differences in sorption mechanisms of Np(V), Pu(V) and Pu(IV), on well-characterized synthetical samples were established: Pu(V) sorption by $\delta\text{-MnO}_2$ and $\alpha\text{-FeOOH}$ followed by redox reactions, while Np(V) remains its oxidation state. It was found that no valence changes take place either in case of Pu(V) or Pu(IV) sorption by $\gamma\text{-Fe}_2\text{O}_3$. In case of Pu(IV) sorption by $\delta\text{-MnO}_2$ plutonium oxidized to Pu(V) and Pu(VI) upon sorption.

Stability constants for surface complexes of Np(V), Pu(V) and Pu(IV) were calculated using of FITEQL software. The strength of Np(V) bonding for sorbent synthesized was estimated as following consequence: $\delta\text{-MnO}_2 > \alpha\text{-FeOOH} > \gamma\text{-Fe}_2\text{O}_3$.

Acknowledgments

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