Thorium(IV) and neptunium(V) uptake from carbonate containing aqueous solutions by HDTMA-modified natural zeolites

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Abstract The ^{232}Th-uptake ($[Th(IV)]° = 9.7 \times 10^{-5}$ M) from carbonate solutions ($[CO_3^{2}]_{tot} = 0.25$ M, $9.0 < pH_c < 10.8$) by raw and HDTMA-modified HEU-type zeolitic-, chabazitic- and phillipsitic-tuffs was investigated. The strong uptake by the HDTMA-tuffs at $pH_c \approx 9$ was assigned to the $Th(CO_3)_5^{6-}$ and $ThOH(CO_3)_4^{5-}$ predominance. The sorption coefficients (R_d) decreased with increasing pH_c indicating carbonate competition. Enhanced R_d values for $pH_c > 10.5$ are likely due to ThO_2(am)-precipitation. The ^{237}Np-uptake ($[Np(V)]° = 2.6 \times 10^{-5}$ M) from carbonate solutions ($[CO_3^{2}]_{tot} = 0.25$ and 3.0×10^{-4} M) by raw and HDTMA-modified HEU-type zeolitic tuff and pulverized pure heulandite crystals was studied under Ar-atmosphere at $6 < pH_c < 11$. The R_d values for both elements indicated the modified tuffs potential to remove tetravalent- and pentavalent actinides from environmental matrices.

Keywords Thorium(IV) sorption · Neptunium(V) sorption · HDTMA-modified tuffs · Carbonate solutions

Introduction

Both thorium and neptunium are toxic and radiotoxic elements and their involvement in various geochemical and biogeochemical cycles can endanger the human health [1, 2]. Their transport in the geosphere takes place through aquatic pathways and their mobility strongly depends on the geologic environment (site-specific minerals), the temperature profiles, the pH of the local waters, the redox potential (E_h), total ionic strength and concentration of inorganic (e.g. carbonates) or organic (e.g. humic acids) ligands [3 5]. Therefore the study of their separation from aqueous media is of extreme importance.

Thorium is a primordial radioactive element. Its most stable isotope, ^{232}Th, has a half-life of 1.41×10^{10} years. Several other thorium isotopes with mass numbers $A = 227$ ($T_{1/2} = 19$ days), 228 ($T_{1/2} = 1.9$ years), 230 ($T_{1/2} = 80{,}000$ years), 231 ($T_{1/2} = 26$ h) and 234 ($T_{1/2} = 24$ days) occur in the environment as members of the natural radioactive families and decay chains. However, the presence of thorium in the environment is not only due to natural reasons but also to human activities closely related with the power production (both nuclear and conventional), the production and use of fertilizers, as well as the development and testing of nuclear weapons.

In all natural systems the stable Th oxidation state is +IV, which shows a strong tendency to hydrolyze above pH = 2 forming both mononuclear (e.g., $ThOH^{3+}$, $Th(OH)_2^{2+}$ and $Th(OH)_3^{+}$) and oligomeric species of the general type $Th_x(OH)_y^{(4x-y)}$. In carbonate containing solutions, Th forms a series of carbonato- and mixed hydroxy-carbonato complexes of the general type $Th(OH)_y(CO_3)_z^{4-y-2z}$ (e.g. $Th(CO_3)_5^{6-}$, $ThOH(CO_3)_4^{5-}$, $Th(OH)_2(CO_3)_2^{2-}$ and $Th(OH)_4(CO_3)^{2-}$) [6, 7]. The formation and thermodynamic

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stability of these species is strongly dependent on the pH and the carbonate concentration.

The vast majority of neptunium is formed as a by-product of the neutron irradiation of uranium in nuclear reactors. Its most stable isotope is ^{237}Np ($T_{1/2}$ = 2.14 × 10^6 years). The neptunium behavior in aquifer systems and its interaction with natural materials are subjects of great interest because of their environmental relevance in context with the nuclear waste disposal.

Under sub-oxic and oxidizing redox conditions, neptunium is expected to be present in its +V oxidation state. Due to the low effective charge of the neptunyl cation ($NpO_2{}^+$, Z_{eff} ∼2.3 [8]), Np(V) shows weak hydrolysis, high solubility and weak sorption. These properties facilitate its mobility in the environment, which can be further enhanced in the presence of carbonate ions [9 12]. The carbonate complexation of $NpO_2{}^+$ leads to the formation of the binary anionic species $NpO_2CO_3{}^-$, $NpO_2(CO_3)_2^{3-}$ and $NpO_2(CO_3)_3^{5-}$. The formation of several ternary Np(V) OH CO_3 species under hyperalkaline pH conditions has also been described in the literature, although only thermodynamic data for the complexes $NpO_2(CO_3)_2OH^{4-}$ and $(NpO_2)_2CO_3(OH)_3^-$ were selected in the Nuclear Energy Agency Thermochemical Database (NEA TDB) [9, 13].

Several methods have been proposed for the removal of Th(IV) and Np(V) from waters and wastewaters including solvent extraction, ion-exchange and adsorption by, among others, natural and synthetic zeolites, clays, biosorbents and carbons [14].

The zeolitic tuffs are important natural sorbents frequently used as decontamination agents for soils and water basins, backfill and sealing materials in repositories and as permeable reactive barriers for cleaning of ground-waters [15]. The zeolites, because of their negatively charged surface, exhibit high efficiency in sorbing cationic species. The modification of their surface mainly using quaternary amines (e.g., HDTMA, ODTMA, *N*-cetylpyridinium) can provide them with the additional ability to sorb anions, non-polar organic species and pathogens from aqueous media. Their original cation sorption capacity is also partly retained [16].

The work performed on the thorium(IV) removal by natural zeolites is not especially extensive. Most of the work concerns the thorium uptake by HEU-type zeolites [4, 17 29]. This type of zeolites is the most abundant on Earth. Crystals of HEU-type zeolites constitute, along with clays, the geological formations of locations considered in the past for potential nuclear waste repositories (e.g., Yucca Mountain, Nevada, USA [30]). The works concerning other natural zeolite types (mordenite [18, 23], phillipsite [31], chabazite [31, 32], green tuff [33], erionite [34], analcime [35]) are limited.

Studies concerning the interaction of neptunium aqueous solutions with natural zeolitic materials were mostly performed within the frame of the investigations of Yucca Mountain (Nevada, USA) as potential geologic nuclear waste repository [36 40] and the environmental conditions at the Nevada Test Site [41]. The effect of water alkalinity and the presence of carbonates in the solutions on the Np(V) sorption were also investigated [37, 42]. In the case of solutions undersaturated with respect to atmospheric CO_2, the sorption continuously increased with increasing pH. Under equilibrium with atmospheric CO_2, the Np(V) sorption is significant in the pH range (7 9.5), while inhibited at higher pH values where negatively charged neptunyl-carbonate complexes are the predominant species [37]. A publication concerning the interaction of Mexican natural erionite with ^{239}Np was also found in the literature [43].

To our knowledge, regardless of the appearance of a number of publications on the sorption of Th(IV)- and Np(V) cations by zeolitic materials, the removal of anionic carbonate- and mixed hydroxy-carbonate complexes of Th(IV) and Np(V) by surfactant-modified natural zeolites has not yet been extensively studied. The only publication found in the case of neptunium deals with the Np(V) sorption by hexadecyl-trimethyl-ammonium (HDTMA)-modified clinoptilolite-bearing zeolitic material as a function of pH in the presence of NaCl and atmospheric CO_2 [44]. The authors of this publication observed, at pH >6, little enhancement of the Np(V) sorption onto the specific surfactant-modified natural zeolite. They also reported that the presence of chloride anions in the solution reduced the effectivity of the sorbent.

The objective of the present work was to investigate the ability of hexadecyl-trimethyl-ammonium (HDTMA)-modified zeolitic materials to remove thorium and neptunium from alkaline carbonate-rich aqueous solutions.

Experimental

The zeolitic materials

The HEU-type zeolitic material used for the sorption experiments was from Petrota (Thrace, Greece) and supplied by GEO-VET N. Alexandridis & Co. Its mineralogical composition was 86% (Ca, K) HEU-type zeolite, 4% micas + clays, 5% feldspars and 5% SiO_2-phases. Its total cation exchange capacity (CEC) was 1.87 mmol/g [45], whereas its external cation exchange capacity, determined using HDTMA-Br solutions, was found to be 0.185 mmol/g.

The modified form of the tuff was prepared by treating 5 g of the material with 25 mL of 60 mM hexadecyl-trimethylammonium bromide (HDTMA-Br) aqueous solution at 60 °C for 24 h [46].

For comparison purposes, in the case of thorium sorption, experiments using raw and HDTMA-modified chabazite- and phillipsite bearing tuffs were also performed under the same conditions.

The chabazitic tuff (Vesuvio area, Italy) was supplied by G. Apostolico & C. Tanagro [47]. According to recent unpublished XRD investigation the utilized sample had zeolite content of 52% (27% chabazite and 25% phillipsite), 1% clay-minerals and 4% micas. The ammonium uptake ability of the material was found to be 214 meq/100 g determined by the ammonium acetate saturation method [48].

The phillipsite bearing tuff (Marano region, Naples, Italy) was supplied by Italiana Zeoliti S.R.L under the commercial name PHIL-75. The XRD examination of the later material, which indicated, except phillipsite (46%), the presence of small amounts of chabazite (ca. 5%) and clay minerals, in general agrees with the mineralogical composition of the tuffs from the Marano region [49, 50].

The particle size of all materials used for the experimental work was <1.0 mm.

In the case neptunium sorption experiments pulverized pure heulandite crystals from Poona (India) were also used as sorbent [51].

The presence of the quaternary amino-groups on the surface of the modified zeolitic materials was verified by the appearance of the 402.3 eV binding energy of the N1s electron in the X-ray photoelectron spectra measured at KIT-INE using a PHI 5600 spectrometer.

The pH measurements

The hydrogen ion concentration ($pH_c = -\log[H^+]$) was measured using combination pH electrodes (type ROSS, Orion) calibrated against standard pH buffers (pH = 1 12, Merck). The values of $pH_c = pH_{exp} + A_c$ were calculated from the operational “measured” pH_{exp} using empirical correlation factors (A_c), which include both the liquid junction potential and the activity coefficient of H^+. Because of the lack of data determined for carbonate solutions, for the calculation of the A_c values reported in the literature for NaCl solutions were utilized [52].

Thorium sorption experiments

The experiments were performed in polypropylene centrifuge tubes (Nalgene) using 9.7×10^{-5} M ^{232}Th(IV) in carbonate solutions of pH_c 9.0 10.8 ($Na_2CO_3/NaHCO_3$ buffering; total carbonate concentration 0.25 M). The solid to liquid ratio was 10 g/L and the contact time 48 h. At the end of the contact time the ^{232}Th was determined, after 10 kD ultrafiltration using Nanosep® centrifugal vials (Pall Corporation), in the liquid phase, $[Th]_{aq}$, by ICP-MS (Perkin-Elmer, Elan 6100). The concentration of ^{232}Th in the sorbent $[Th]_s$ was calculated on the basis of the data obtained for the liquid phase.

Neptunium sorption experiments

Neptunium sorption experiments were performed under argon atmosphere (glove box). For the batch experiments, 35 µL of a well-defined, oxidation state pure 3.7×10^{-3} M ^{237}Np(V) stock solution were spiked to 5 mL of the HEU-type zeolite suspensions (initial concentration of $[Np(V)]^\circ = 2.6 \times 10^{-5}$ M in the samples). In order to cover the region of pH 6 11 two series of experiments were performed, one using $Na_2CO_3/NaHCO_3$ buffer solutions (total carbonate concentration 0.25 M) and the other one using MES (2-(*N*-morpholino)ethanesulfonic acid), PIPES (piperazine-*N*,*N*′-bis(2-ethanesulfonic acid), HEPES [(4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid] and TRIS (tris(hydroxymethyl)aminomethane) buffers (carbonate concentration 3×10^{-4} M). The concentration of the buffers in the samples was around 10 mM. The ^{237}Np in the solutions, $[Np]_{aq}$ was determined, after 10 kD ultrafiltration using Nanosep® centrifugal vials (Pall Corporation), by liquid scintillation counting of its alpha activity. The ^{237}Np alpha activity was performed after automatic α/β discrimination of the β-counts of the ^{233}Pa daughter nuclide using a Wallac/Perkin-Elmer QUANTULUS equipment and Ultima Gold XR scintillation cocktail (Perkin-Elmer). The ^{237}Np concentration in the sorbent, $[Np]_s$ was then calculated using these data.

Speciation calculations

Speciation thorium and neptunium calculations were performed using the code MEDUSA [53] and the data obtained from OECD-NEA Thermochemical Database for T = 25 °C [9, 54]. The ionic strength corrections were made using the extended Debye-Hückel approach.

Results and discussion

Thorium(IV) sorption experiments

The Th-sorption coefficients ($R_d = [Th]_s/[Th]_{aq}$) for the zeolitic materials are given in Fig. 1. A very high sorption was observed for the modified tuffs at $pH_c = 9$ where the predominance of highly charged anions of the type $Th(CO_3)_5^{6-}$ and $Th(CO_3)_4(OH)^{5-}$ (Fig. 2) can promote the strong uptake by the HDTMA-modified material. The decrease of R_d with increasing pH_c values can be explained by the increase of $[CO_3{}^{2-}]$ in solution and the consequentially increased competition for the sorption sites of

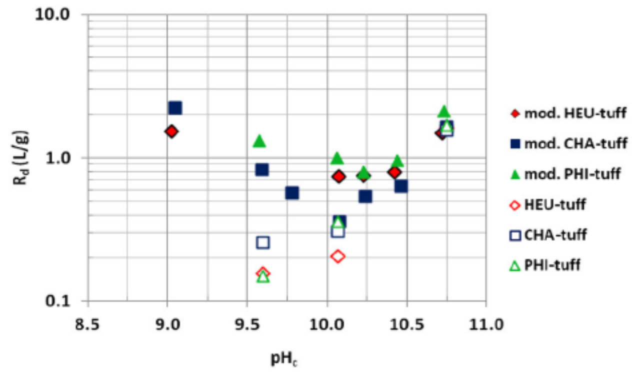

Fig. 1 Sorption coefficients for the Th(IV) uptake from carbonate solutions by the raw and HDTMA modified zeolitic materials (HEU type zeolitic tuff (HEU tuff, mod. HEU tuff), chabazitic tuff (CHA tuff, mod. CHA tuff) and phillipsitic tuff (PHI tuff, mod. PHI tuff)) as a function of the hydrogen ion concentration (pH_c) ($[Th(IV)]^\circ$ 9.7×10^{-5} M; $[CO_3^{2-}]_{tot}$ 0.250 M)

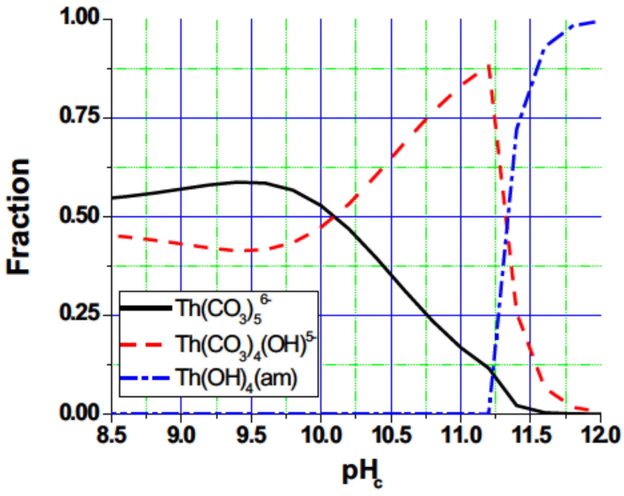

Fig. 2 Fraction diagrams of the most abundant Th(IV) species calculated for $8.5 < pH_c < 12.0$, $[CO_3^{2-}]_{tot}$ 0.250 M and $[Th]_{tot}$ 10^{-4} M

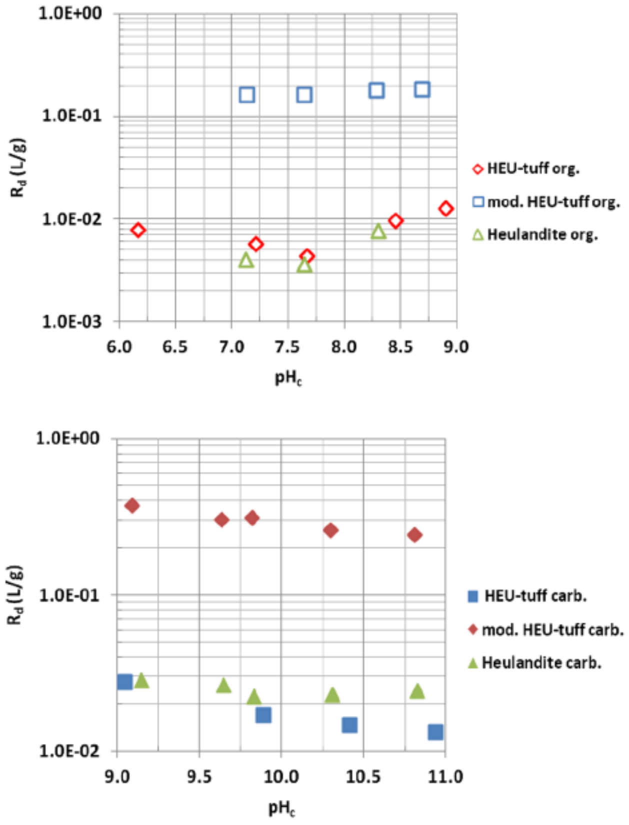

Fig. 3 Sorption coefficients for the Np(V) uptake from carbonate solutions ($[CO_3^{2-}]$ 3×10^{-4} M (*upper*) and 0.25 M (*lower*)) by raw and HDTMA modified HEU type zeolite bearing tuff (HEU tuff, mod. HEU tuff) and pulverized pure heulandite crystals (Heulandite) under organic (org.) and $NaHCO_3/Na_2CO_3$ (carb.) buffering

the modified tuffs. The increase in R_d at $pH_c > 10.5$ could be attributed to the precipitation of a $Th(OH)_4$(am) solid phase calculated to be oversaturated under the given conditions. This hypothesis is further confirmed by the similar R_d values obtained with the unmodified materials (Fig. 1). These results highlight the potential of the investigated HDTMA-modified zeolitic material evaluated for specific environmental applications.

Neptunium(V) sorption experiments

The Np-sorption coefficients [$(R_d = [Np]_s/[Np]_{aq})$] determined in the present study for the investigated materials are given in Fig. 3. A significantly higher uptake (20 50 times increase) was observed for the HDTMA-modified HEU-tuff. For all materials assayed, the uptake showed a maximum at pH_c ~9, while being slightly lower at near-neutral and hyper-alkaline pH_c conditions.

These observations can be interpreted in direct relation to the aqueous speciation of Np(V) (Fig. 4) and the carbonate concentration within this pH_c-range.

Hence, NpO_2^+ and $NpO_2CO_3^-$ species coexist at $pH_c = 6$ 9 and lower carbonate concentrations (pH_c fixed by organic buffers), whereas highly charged anions prevail at $9 \leq pH_c \leq 11$ and $[CO_3]_{tot} = 0.25$ M (pH_c fixed by the HCO_3^-/CO_3^{2-} equilibrium). The latter species are expectedly prone to a stronger uptake by the modified tuff, in agreement with the observations in the Th(IV) studies. The fraction of CO_3^{2-} increases (in detriment of HCO_3^-) with increasing pH_c, thus potentially competing with Np(V) species for the sorption sites of the material and consequently slightly decreasing R_d. The total Np(V)-uptake from solution of high carbonate concentration ($Na_2CO_3/NaHCO_3$-buffered solutions) by the HDTMA-modified tuff varies between 0.24 and 0.35 mg g^{-1}, whereas the corresponding values for the raw tuff varies between 0.07 and 0.14 mg g^{-1}. These values, although not especially high, represent a significant decrease of neptunium concentration

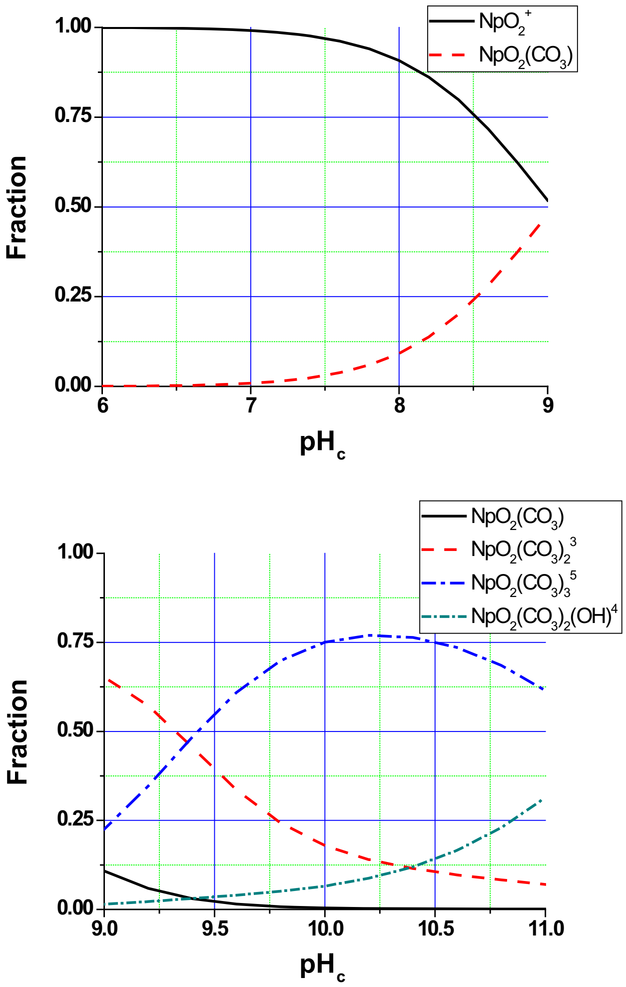

Fig. 4 Fraction diagrams of Np(V) species in solutions of 10 μM total Np(V) concentration and varying pH$_c$ in presence of [CO_3^{2-}]   0.30 mM (*upper*) and 250 mM (*lower*)

in solution with respect to the upper solubility limit expected for Np(V) under these conditions (oxidizing, high carbonate concentration) and thus confirm the potential of this material for specific environmental applications.

Conclusions

All investigated HDTMA-modified zeolitic materials showed considerable Th- and Np-sorption ability from rather concentrated (0.25 M) carbonate solutions.

The affinity of the materials towards thorium sorption was higher than the corresponding one for neptunium under comparable experimental conditions. The relatively high thorium uptake observed for $9 < pH_c < 10.5$ is likely due to the sorption of highly charged anions ($Th(CO_3)_5^{6-}$ and $ThOH(CO_3)_4^{5-}$), predominant under the experimental conditions in solution by the HDTMA-modified tuffs. The decrease of the R_d values up to $pH_c = 10.5$ can be explained by the increasing [CO_3^{2-}] in solution with increasing pH$_c$ and the consequentially enhanced competition of carbonate for the sorption sites of anions on the modified tuffs.

The R_d values for the Np(V)-sorption, although not especially high, represent a significant decrease of neptunium(V) concentration in carbonate containing solutions and confirm the potential of the HDTMA-modified HEU-type zeolitic material for specific environmental applications.

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