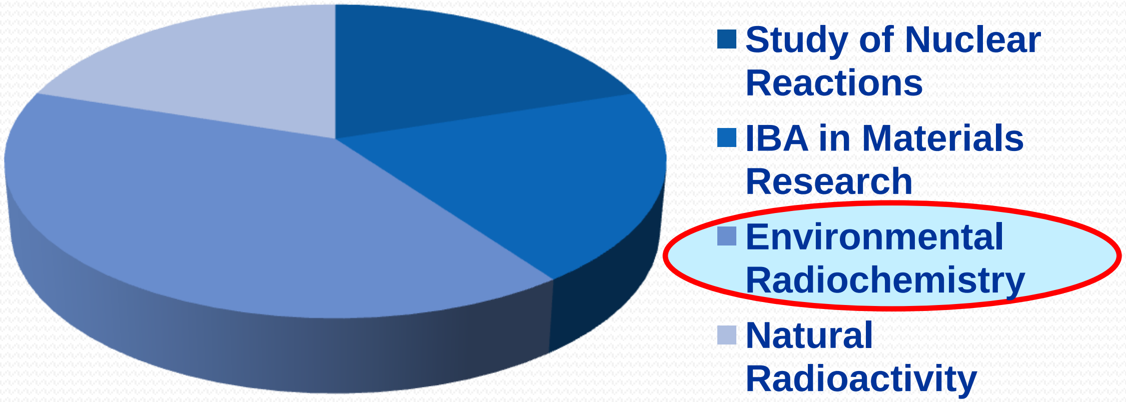
Environmental radiochemistry of actinides: A short presentation of the recent activities at the Chemistry Department of the Aristotle University of Thessaloniki.

Panagiotis Misaelides and Fotini Noli
Department of Chemistry – A.U.Th.

Distribution of the recent research activity at the Radiochemical Laboratory



Relevant publications 2012 – 2014

Application of ion beam analysis techniques for the investigation of the oxidation and corrosion resistance of low-energy high-flux nitrogen-implanted stainless steel.
F. Noli, P. Misaelides, E. Pavlidou, A. Lagoyannis, **Nucl. Instr. Meth. B 270**(2012)1

Plasma-based nitriding and oxidizing of CoCrMo: investigation of structural and corrosion characteristics for biomedical applications.
Fotini Noli, Jean-Paul Rivière, Luc Pichon, Orhan Ozturk, Michel Drouet, 12th Intern. Workshop on Plasma-based Ion Implantation and Deposition (PBII&D 2013)**,**Poitiers-FRANCE, July, 1 – 5, 2013

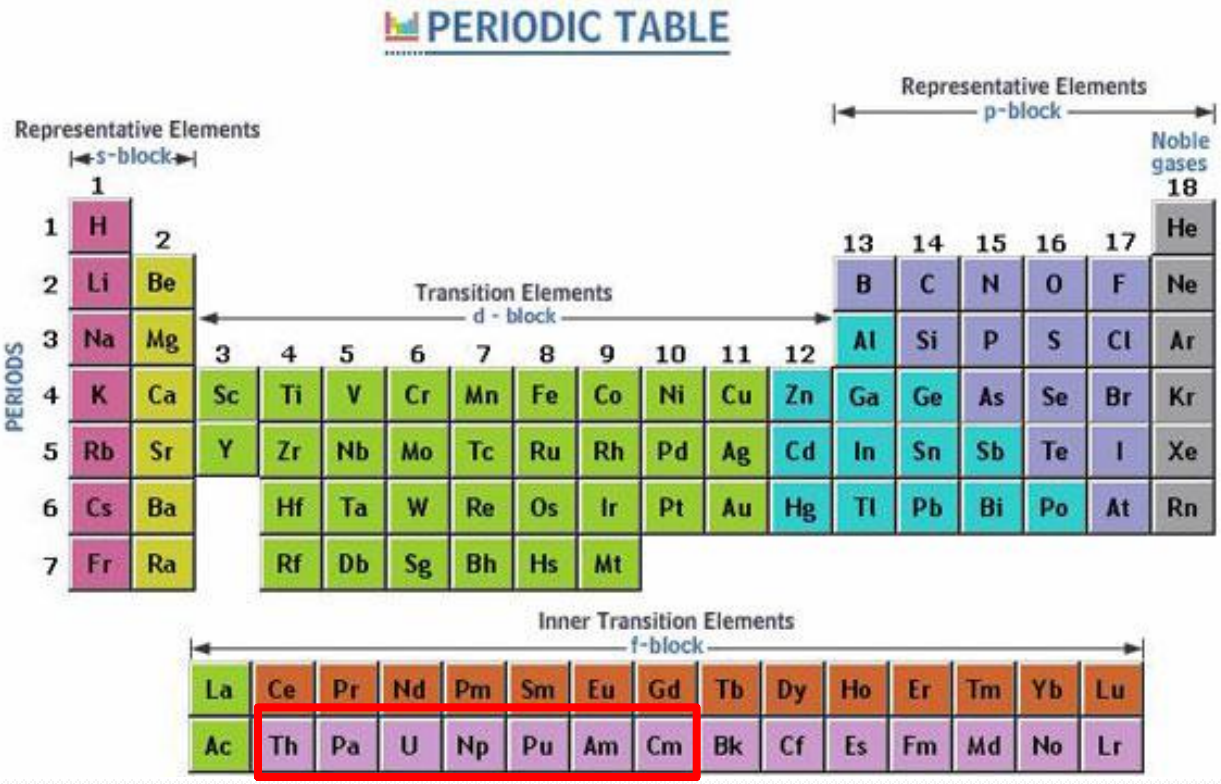
Application of NRA and RBS for the investigation of the corrosion process on CoCrMo biomaterial
F. Noli, P. Misaelides, A. Hatzidimitriou, E. Pavlidou, A. Lagoyannis
Abstracts of the 11th European Conference on Accelerators in Applied Reasearch and Technology, Namur, Belgium, 2013, p. 101.

Determination and Evaluation of the Differential Cross-Sections of the ^{2}H(d,p) Reaction at Energies and Detection Angles Suitable for NRA (Nuclear Reaction Analysis).
V. Paneta, M. Axiotis, P. Gastis, A. Gurbich, M. Kokkoris, A. Kontos, A. Lagoyannis,M. Meyer, P. Misaelides, G. Perdikakis, R. Vlastou, ***International Nuclear Physics Conference INPC2013: 2-7 June 2013, Firenze, Italy.***

Study of the ^{24}Mg(d,p$_{0,1,2}$) reactions at energies and angles relevant to NRA.
V. Paneta, X. Aslanoglou, M. Axiotis, P. Gastis, M. Kokkoris, A. Lagoyannis, P. Misaelides, N. Patronis, R. Vlastou, **Nucl. Instr. Meth. B 319 (2014) 34–38**

Use of combination of accelerator-based ion-beam analysis techniques to the investigation of the corrosion behavior of CoCrMo alloy.
F. Noli, P. Misaelides, A. Lagoyannis, L. Pichon, O. Ozturk, **Nucl. Instr. Meth. B (In press-** Available online 10 February 2014).

Study of the environmental behavior of actinides



PERIODIC TABLE

Representative Elements
s-block

Transition Elements
d - block

Representative Elements
p-block

Noble gases

PERIODS

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	H																	He
2	Li	Be											B	C	N	O	F	Ne
3	Na	Mg											Al	Si	P	S	Cl	Ar
4	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
5	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
6	Cs	Ba		Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
7	Fr	Ra		Rf	Db	Sg	Bh	Hs	Mt									

Inner Transition Elements
f-block

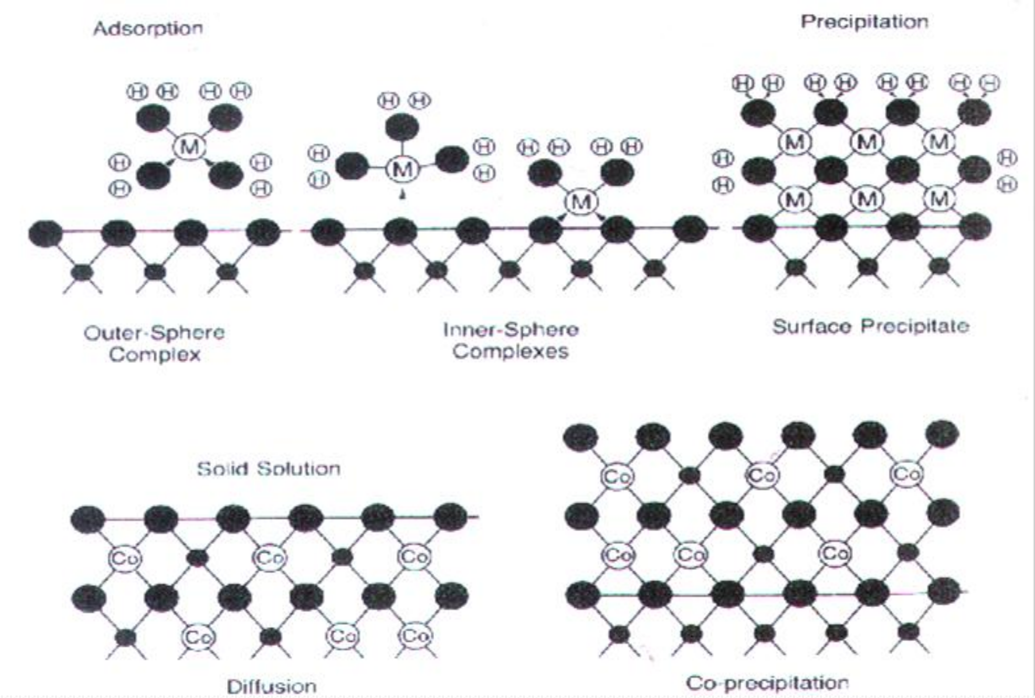
La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

The presence of actinides in the environment is not only due to natural reasons but also to human activities closely related with the production and use of fertilizers, the nuclear and conventional energy production, the development and testing of nuclear weapons.

The transport of actinides in the biosphere mainly takes place through aquatic pathways and their mobility strongly depends on the geologic environment, the temperature and pressure profiles, the pH of the local waters, the redox potential (Eh) and concentration of inorganic (e.g. carbonates) or organic (e.g. humic acids) ligands. The interaction of their dissolved species with the highly sorptive geological materials also influences their migration behavior.

Unfortunately, only few studies concerning the geochemical behavior of actinides can be performed in-situ and therefore laboratory experiments are necessary to elucidate their environmental behavior. Laboratory experiments are also necessary in order to evaluate the effectiveness of these materials as actinides decontamination agents, as backfill and sealing materials in nuclear repositories and as permeable reactive barriers for cleaning of waters.

The chemical processes taking place include sorption through different mechanisms (e.g. adsorption/ surface sorption, absorption/ion exchange, surface precipitation), complexation (mainly with carbonate anions) as well as formation of colloidal- and pseudocolloidal systems.



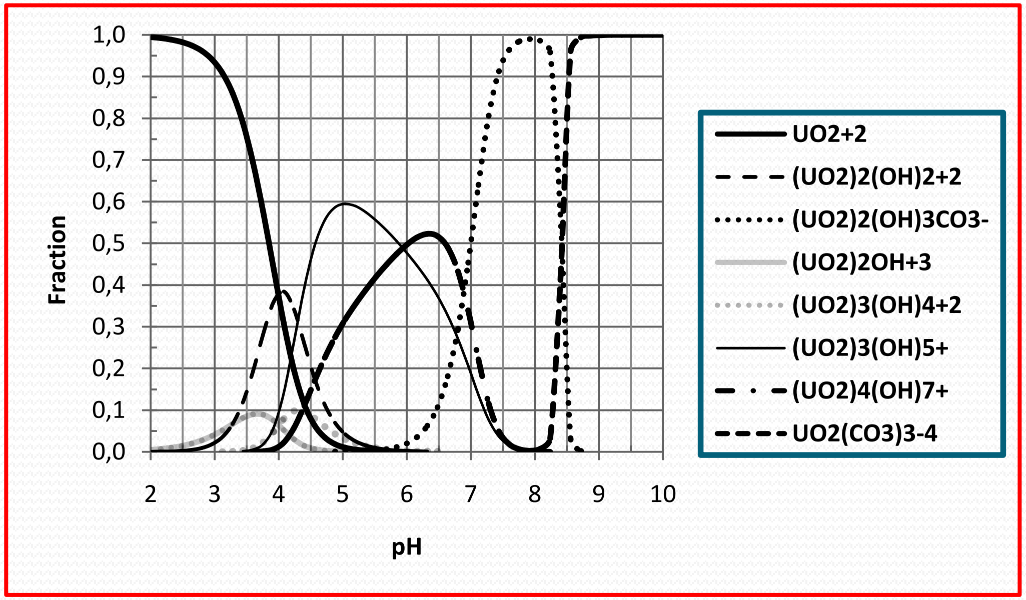
The Environmental Chemistry of the Actinides

The actinide elements exhibit many oxidation states and show a complex environmental chemistry.

ACTINIDES		
Symbol	*Z*	*Oxidation states*
Ac	89	3
Th	90	3, 4
Pa	91	4, 5
U	92	3, 4, 5, 6
Np	93	3, 4, 5, 6, 7
Pu	94	3, 4, 5, 6, 7
Am	95	2, 3, 4, 5, 6
Cm	96	2, 3, 4
Bk	97	2, 3, 4
Cf	98	2, 3, 4
Es	99	2, 3
Fm	100	2, 3
Md	101	1, 2, 3
No	102	2, 3
Lr	103	3

The hydrolysis of the actinides plays the determining role in the interaction processes.

In general, the solid/liquid distribution coefficients (R_d) measured in a given solution /sorbent system (mostly not taking into account the underlying molecular reaction mechanism), the use of adsorption isotherms and their modelling using semi-empirical equations as well as the surface-complexation modelling are the most frequently used tools for the retention performance assessment calculations.



Fraction diagram of U(VI)-species in aqueous solutions of varying pH in equilibrium with atmospheric CO_2 ($\log P_{CO2}$ = -3.5) for total $(UO_2)^{+2}$ concentration 10.0 mM. Only aqueous species are shown in the diagram.

The objective of these studies:

The study of the interactions of aqueous solutions of actinides (U, Th, Np, Eu) with natural sorbents (mainly raw and modified natural zeolites and clay minerals) in order to get information about their environmental behavior and the possibility to inhibit their migration in the biosphere.

Experiments with other radioactive species (e.g., Tc-, Cs-, Ba-, I-isotopes) as well as hazardous heavy metals were also performed. In addition to the zeolites and clay minerals a number of other sorbents (e.g., Zero-valence Fe, polymeric resins, metal phosphates, coal-fired power station ash, modified diatomites) were also used in experimental work.

The applied techniques:

For the measurement of the uptake capacity: Nuclear spectroscopic techniques (gamma-and alpha spectroscopy), liquid scintillation counting, ICP-MS, AAS, UV-Vis.

For the characterization of the materials: SEM/EDS, XRD, XRFA, XPS, TG/DTA, BET

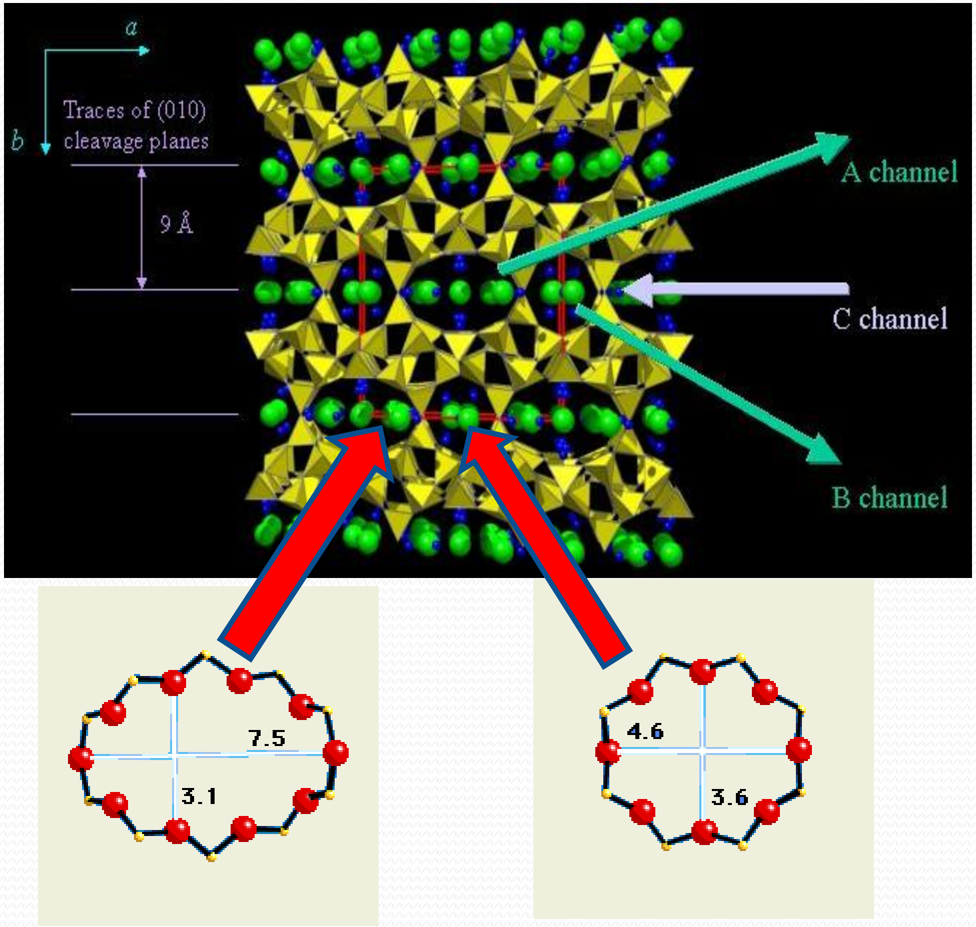
THE ZEOLITES

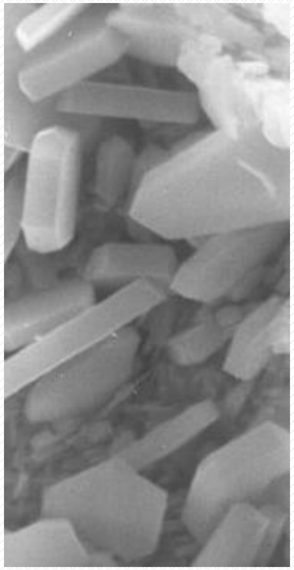
The zeolites are crystalline natural or synthetic alumino-silicates with structure consisting of ordered [SiO_4] and [AlO_4] tetrahedra linked by corner-oxygen sharing.

Due to the presence of Al-containing tetrahedra, the zeolites exhibit a negatively charged framework, which is counter-balanced by exchangable cations.

The presence of these exchangeable cations also explains the enhanced sorption properties of the zeolites.

Example: HEU-type Zeolite

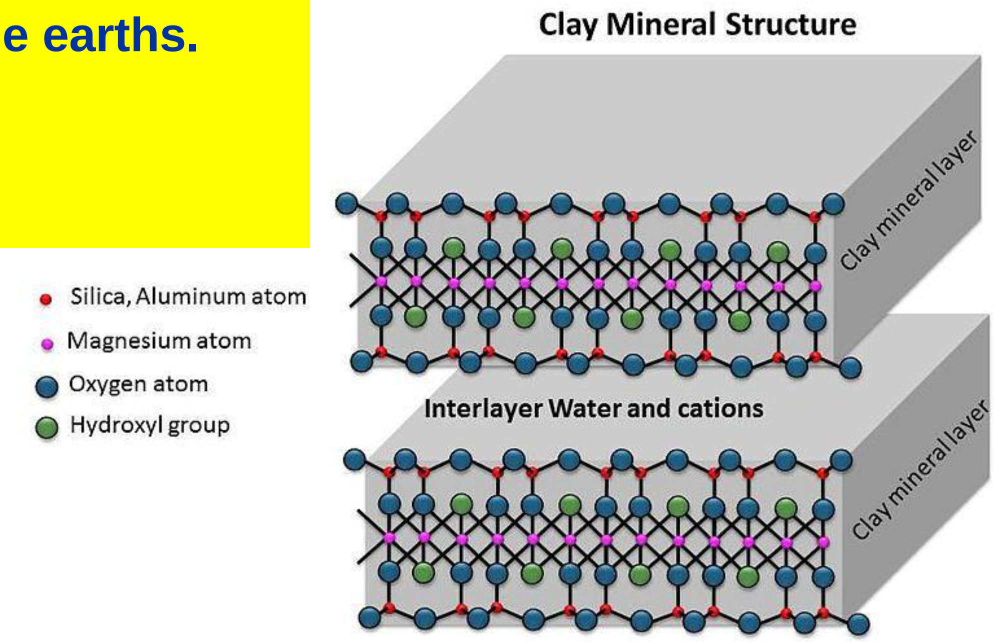




Clinoptilolite ($(\mathrm{CICII}_{0.5})_6[\mathrm{Al}_6\mathrm{Si}_{30}\mathrm{O}_{72}]. 20\ \mathrm{H_2O}$)

THE CLAY MINERALS

Clay minerals are hydrous aluminum phylosilicates with variable amounts of Fe, Mg, alkali metals and alkaline earths.



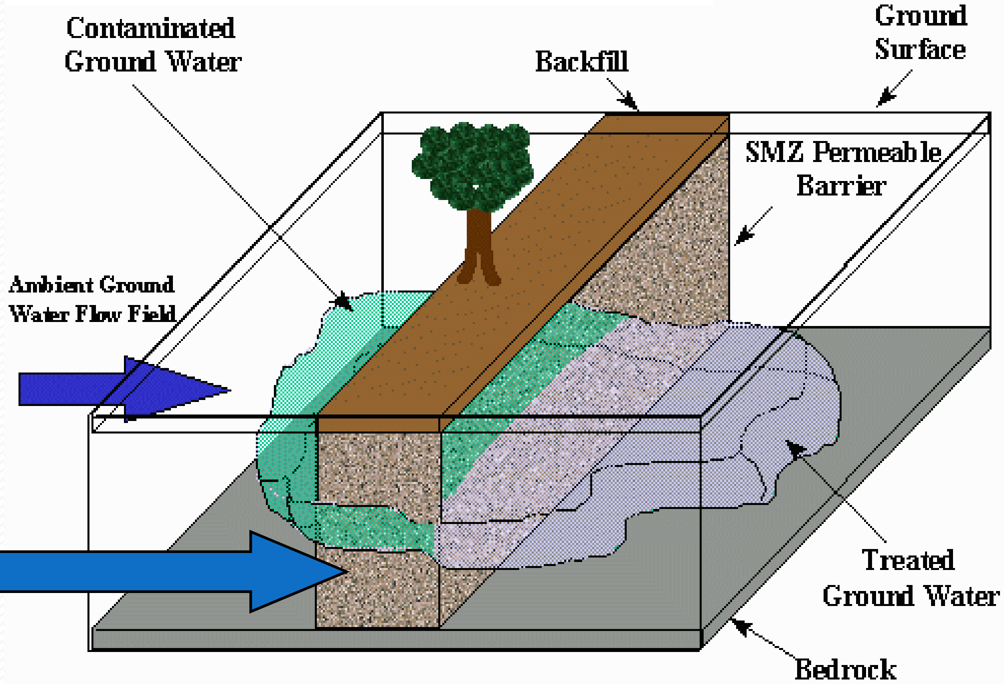
Clays and zeolites find application as

as **backfill and sealing materials** in underground repositories retarding the migration of fission products and actinides in the environment

as **engineered barriers** for the cleaning of waters and

as **decontamination agents** for soils and water basins.

Locations rich in natural zeolites and clays were also proposed and studied as potential repositories for HLW.

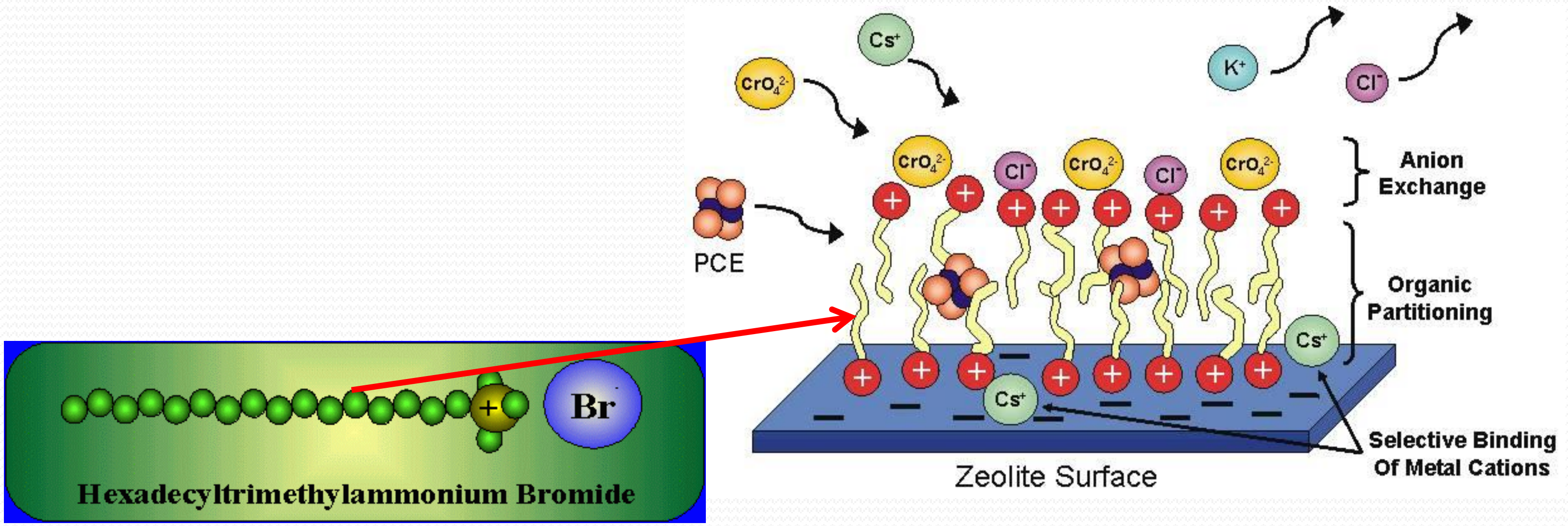


Yucca Mountains, Nevada

As expected, the zeolites and clays, because of their negatively charged framework, can only remove cationic species from solutions

BUT

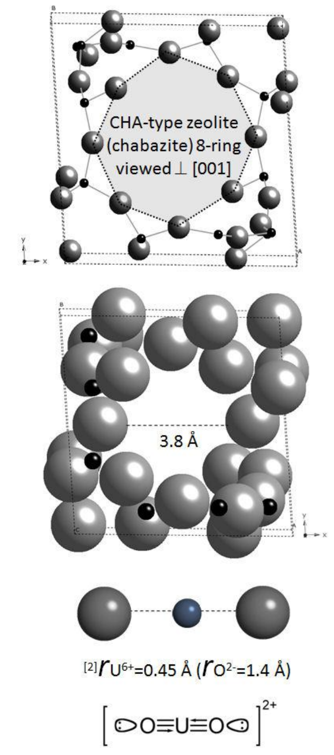
the modification of their surface by quaternary amines can also provide them with anion and non-polar species sorption ability.

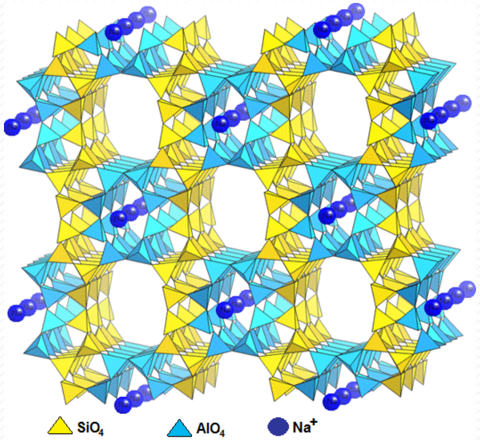


Just a few examples of our work

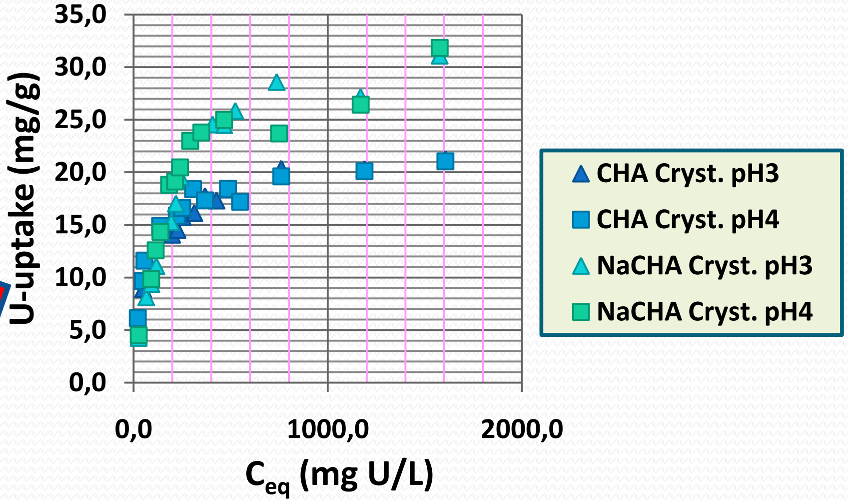
U + Chabazite (CHA)

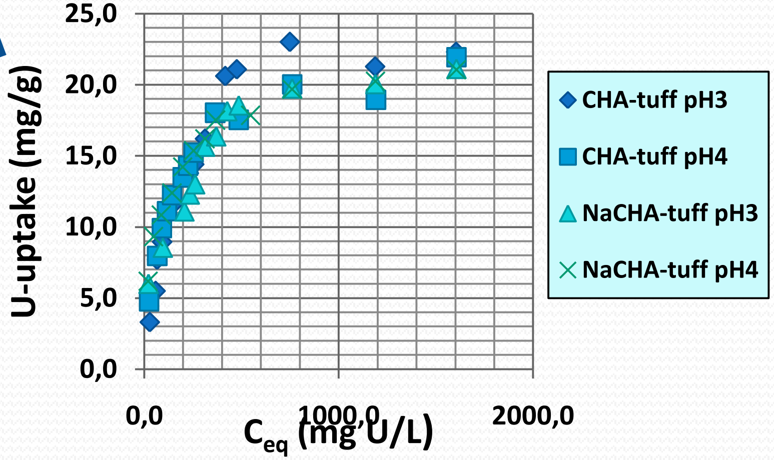
Interaction of U^{VI}_{aq} with CHA-type zeolitic materials.
(J. Warchol et al., Micropor. Mesopor. Mater. 153(2012)63)

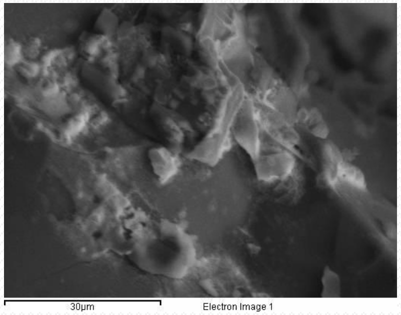


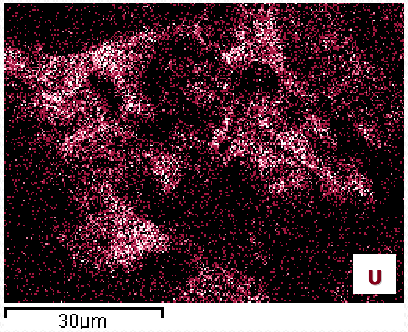


U + CHA crystals
U + CHA tuff





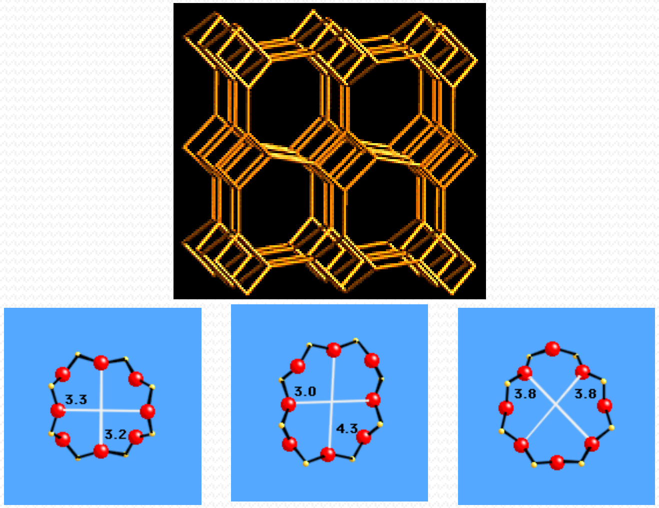




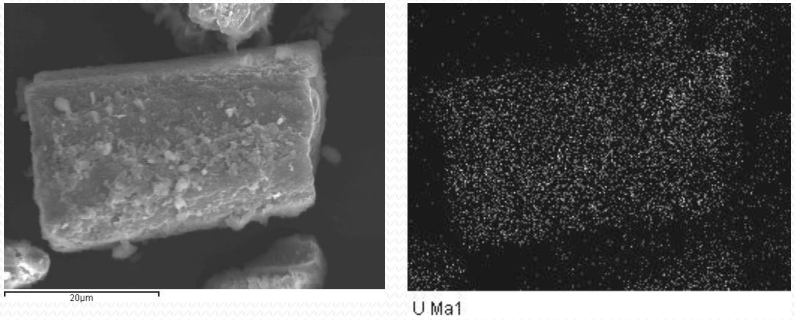
U + raw and HDTMA - modified Phillipsite (PHI) tuff

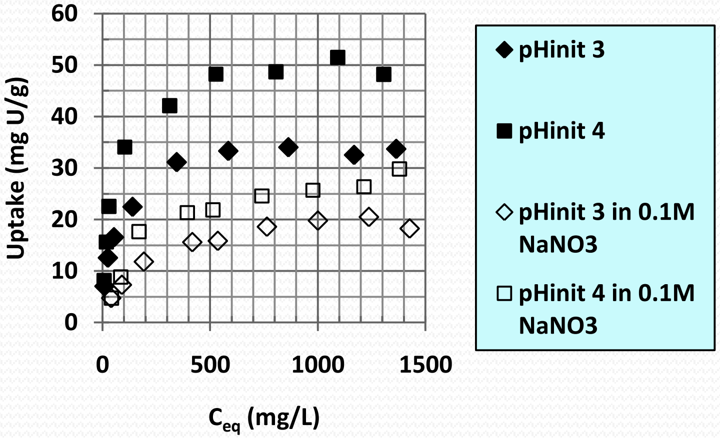
Interaction of uranium aqueous solutions with raw- and HDTMA-modified phillipsite - bearing tuff.

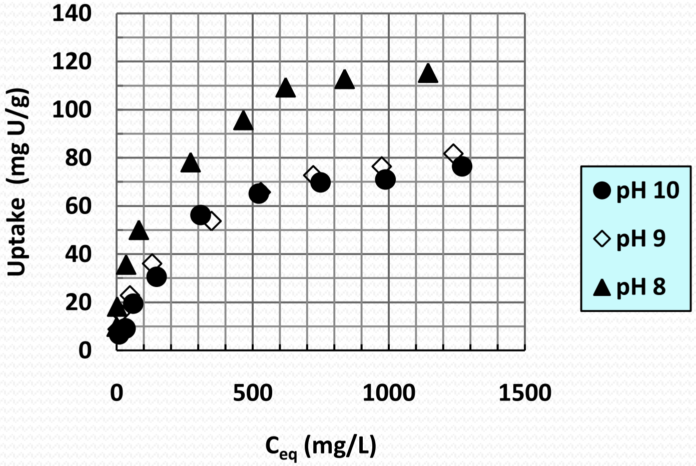
A. Bampaiti, P. Misaelides, F. Noli (in press)

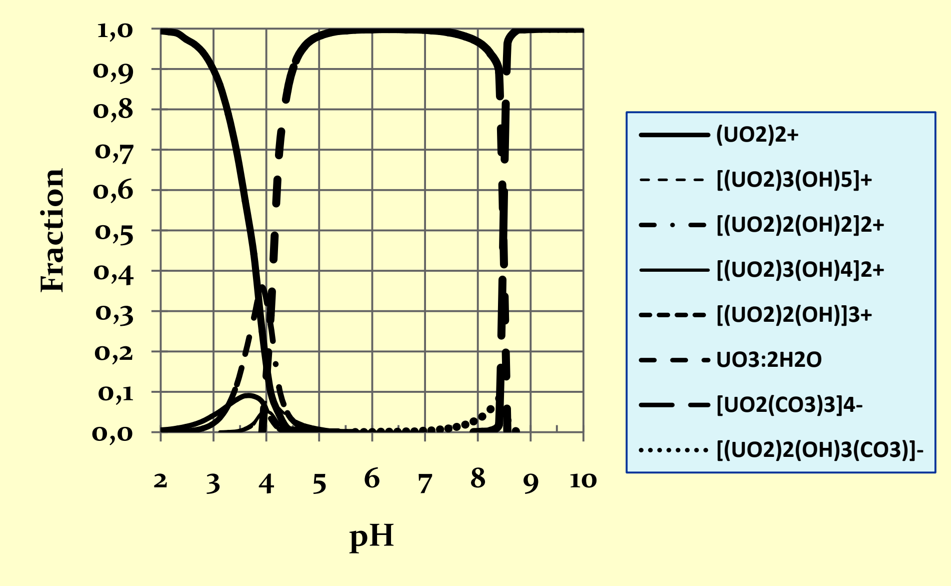


$(K^{+}{}_{2},Ca^{2+},Na^{+}{}_{2})_{3}Al_{6}Si_{10}O_{32}\cdot 12H_{2}O$

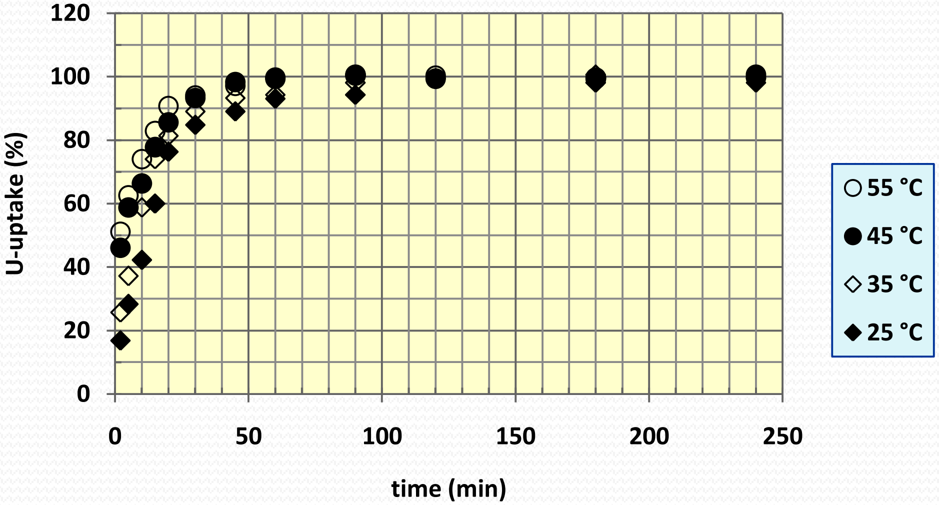




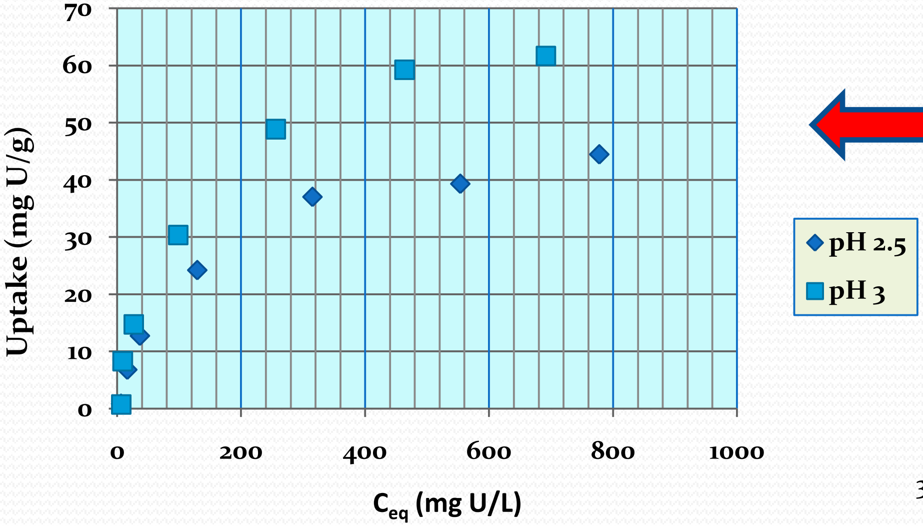




The Uranium uptake is relatively fast.

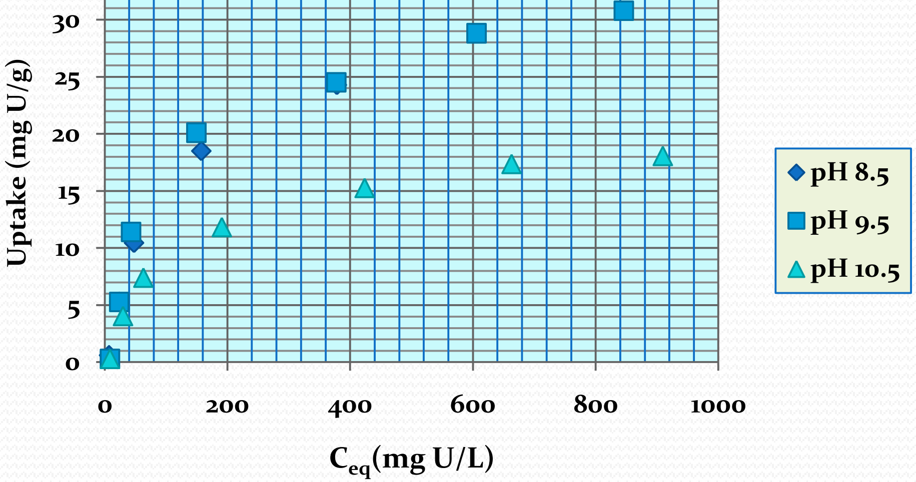


Uranium + raw- and HDTMA-modified bentonite from Kimolos island, Greece



Raw Bentonite

HDTMA-modified Bentonite



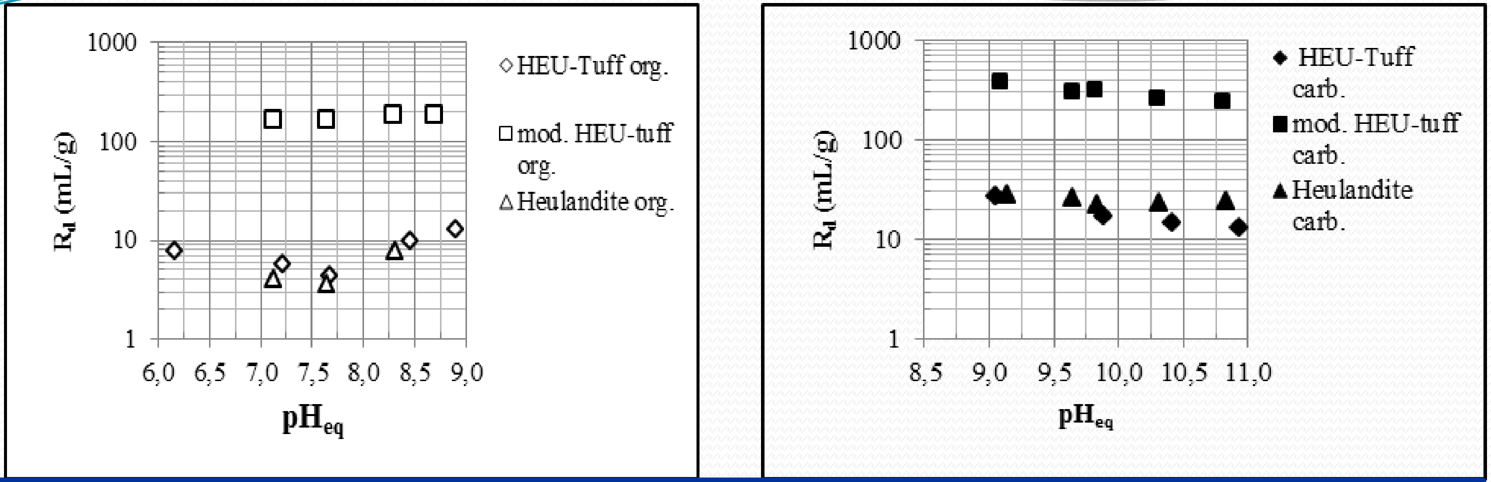
Neptunium removal from carbonate solutions by a Greek HDTMA-modified HEU-type zeolite containing tuff.

P. Misaelides, D. Fellhauer, X. Gaona, M. Altmaier and H. Geckeis, Contribution to the ZEOLITE2014 Conference (Belgrade, June 2014)

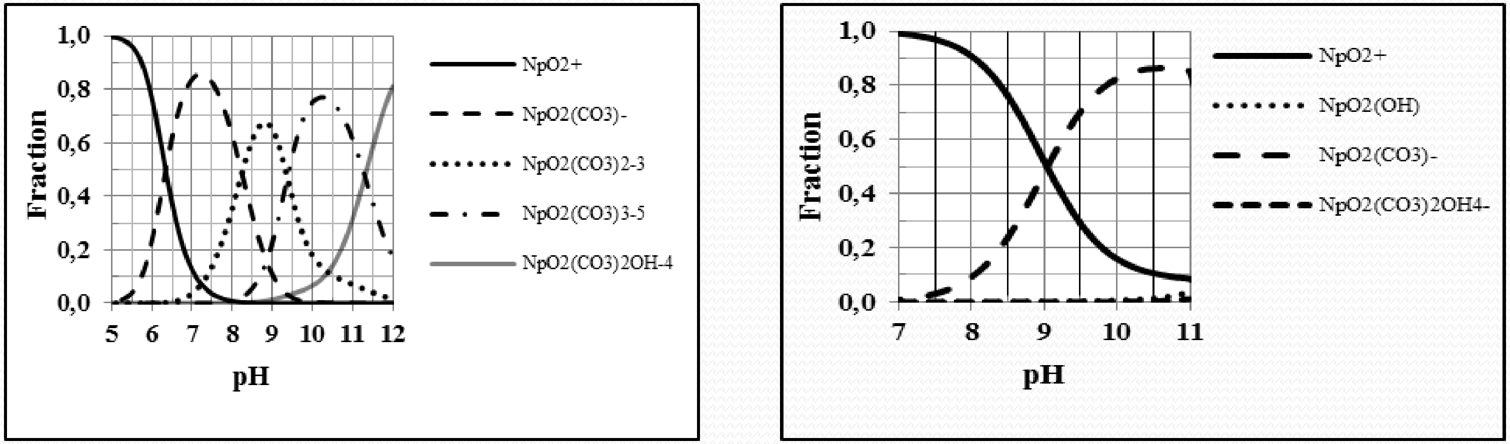
Under sub-oxic and oxidizing redox conditions, neptunium is mainly found in its +V redox state. Due to the low effective charge of the neptunyl cation (NpO_2^+, Z_{eff} ~2.3), Np(V) shows weak hydrolysis, high solubility and weak sorption. These properties facilitate its mobility in the environment, which can be further enhanced in the presence of carbonate.

The neptunium sorption experiments were performed under inert atmosphere (Ar) glove-boxes using ^{237}Np(V) solutions of $2.6 \cdot 10^{-5}$ M concentration.

In order to cover the region of pH 6 -11, two series of experiments were performed, one using solutions of 0.25 M total carbonate concentration prepared with Na_2CO_3/$NaHCO_3$ buffers and the other of $3 \cdot 10^{-4}$ M carbonate concentration . In the second case MES, PIPES, HEPES and TRIS buffer solutions were used for the adjustment of the pH. The determination of ^{237}Np ($t_{1/2} = 2.144 \cdot 10^6$ years) in the solutions was performed by liquid scintillation (Wallac/ Perkin-Elmer QUANTULUS).



Sorption coefficients for the Np(V)-removal from carbonate solutions (left: $3{\cdot}10^{-4}$ M and right: 0.25 M total carbonate concentration) by raw- and HDTMA-modified Petrota tuff and heulandite.



Fraction diagrams of Np(V)-species in solutions of varying pH in the presence of 0.30 mM (left) and 250 mM (right) carbonate. Total Np(V) concentration: 10 µM.

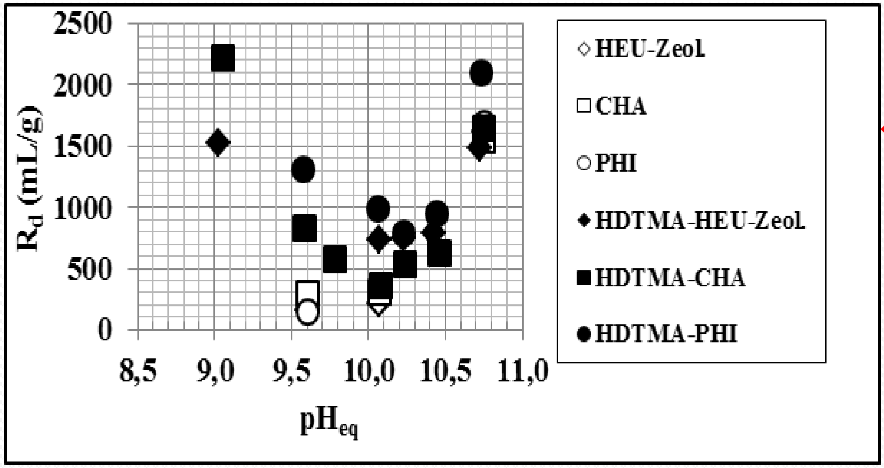
Thorium removal from carbonate solutions by HDTMA-modified HEU-type zeolite-, chabazite- and phillipsite-bearing tuffs.

P. Misaelides, X. Gaona, M. Altmaier and H. Geckeis, Contribution to the ZEOLITE2014 Conference (Belgrade, June 2014)

Thorium is a primordial radioactive element. Its most stable isotope, ^{232}Th, has a half-life of $1.41 \cdot 10^{10}$ years. The most stable redox state of Th 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 $Th_x(OH)_y^{(4x-y)}$. The number of hydroxyl ligands depends on the Th concentration and strongly rises with increasing pH. In carbonate containing solutions, Th forms a series of carbonato- and 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 $Th(OH)_4(CO_3)_2^{-}$). The formation of these species is strongly dependent on the pH and carbonate concentration.

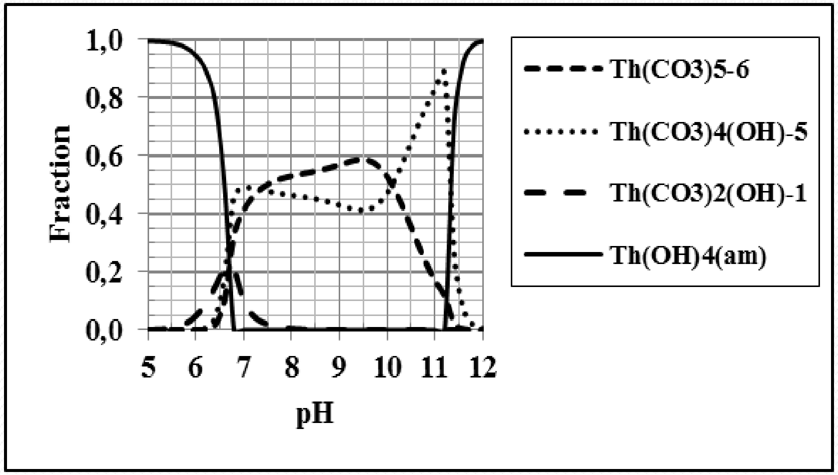
The sorption experiments were performed using 9.7×10^{-5} M $^{232}Th(IV)$ in carbonate solutions between pH 9.0and 10.8 ($Na_2CO_3/NaHCO_3$ buffering; total carbonate concentration 0.25 M). The solid to liquid ratio was 10 $g \cdot L^{-1}$ and the contact time 48 hours. The Th-determination was performed by ICP-MS (Perkin-Elmer, Elan 6100).

Th sorption coefficients (R_d = $[Th]_s$ / $[Th]_{aq}$) for the zeolitic materials are given in Figure 1. A very high sorption was observed for the modified tuffs at pH 9 where the predominance of highly charged anions ($Th(CO_3)_5^{6-}$ and $ThOH(CO_3)_4^{5-}$, see Figure 2) promotes the strong uptake by the HDTMA-modified materials. The decrease of R_d with increasing pH values can be explained by the increase of $[CO_3^{2-}]$ in solution and the consequent competition for the sorption sites of the modified tuffs. The increase in sorption observed at pH > 10.5 is attributed to the precipitation of the $Th(OH)_4$(am) solid phase.



Sorption coefficients for the Th(IV)-removal from carbonate solutions by the raw- and HDTMA-modified HEU-type zeolite-, chabazite- (CHA) and phillipsite- (PHI) tuffs (Th conc.: 9.7 10^{-5} M; carbonate conc.: 250 mM).

Fraction diagrams of Th calculated for 5<pH<12 and $[CO_3^{2-}]_{tot}$ = 0.25 M and $[Th]_{tot}$ = 10^{-4} M. Calculations performed using the code MEDUSA and the OECD-NEA Thermochemical Databank for T = 25 °C.



SOME RECENT RELEVANT PUBLICATONS (2012-2014):

Uranium removal from aqueous solutions by raw and modified thermal power plant ash.

G. Buema, F. Noli, P. Misaelides, D. M. Sutiman, I. Cretescu, M. Harja, J. Radioanal. Nucl. Chem. 299(2014)381

Interaction of uranium aqueous solutions with raw- and HDTMA-modified phillipsite - bearing tuff.

A. Bampaiti, P. Misaelides, F. Noli (2014, in press)

Removal of uranium anionic species from aqueous solutions by polyethylenimine–epichlorohydrin resins.

S. Sarri, P. Misaelides, D. Zamboulis, L. Papadopoulou, J. Warchoł, J. Radioanal. Nucl. Chem. 295(2013)1731

Interaction of U^{VI}aq with CHA-type zeolitic materials.

J. Warchoł, M. Matłok, P. Misaelides, F. Noli, D. Zamboulis, A. Godelitsas, *Micropor. Mesopor. Mater. 153 (2012) 63*

Thorium removal from carbonate solutions by HDTMA-modified HEU-type zeolite-, chabazite- and phillipsite-bearing tuffs.

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Neptunium removal from carbonate solutions by a Greek HDTMA-modified HEU-type zeolite containing tuff.

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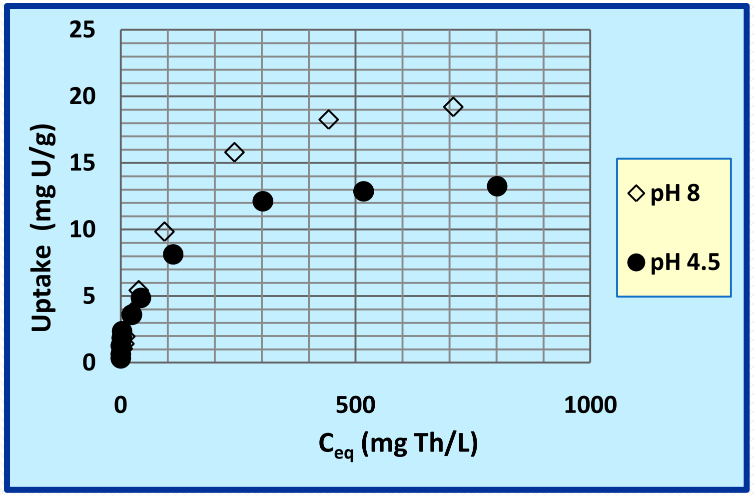
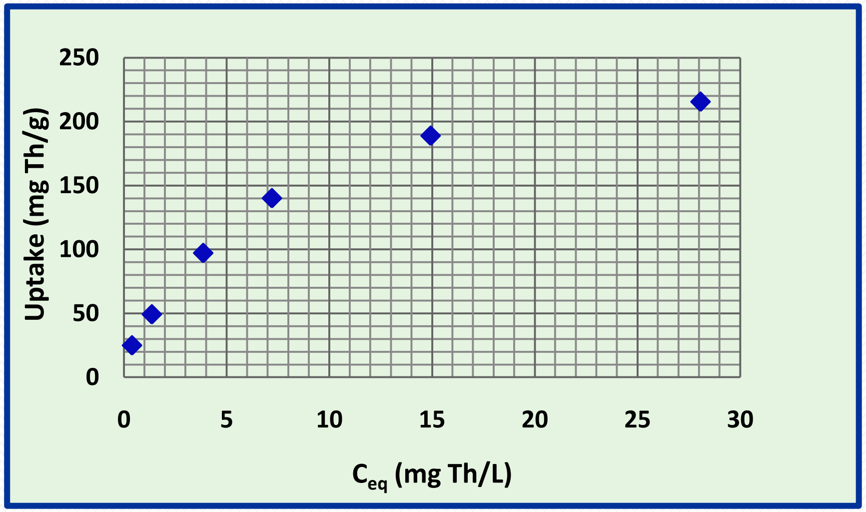
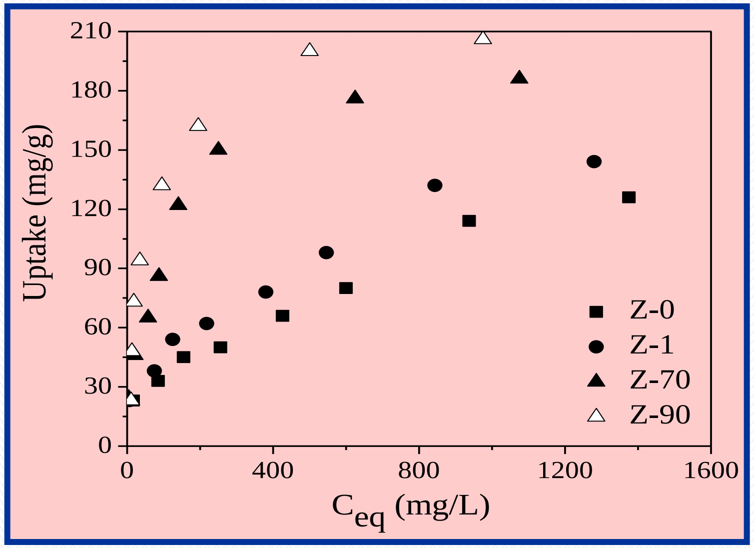
Uranium removal by zero-valence iron



Thorium removal by ZnO nanoparticles





Uranium removal by raw- and NaOH-treated coal power station ash.

Z-0 untreated ash
Z-1 ultrasound treated
Z-70 5M NaOH treated (70 °C)
Z-90 5M NaOH treated (0 °C)

Thank you very much for your attention!