Actinde(IV) colloids at near-neutral pH due to reaction with dissolved silicic acid

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Outline

- The BELBaR project as the background
- What are actinide(IV)-silica colloids?
- Conceivable geochemical implications

Colloids hitherto in the focus of BELBaR

- Bentonite errosion results in the formation of relatively stable clay mineral colloids
- Radionuclides may adsorb onto these clay mineral colloids

→ Colloid-facilitated transport of radionuclides

→ Radionuclides that are often regarded as immobile such as tetravalent actinides may become mobile

What are actinide(IV)-silica colloids?

Generation of actinide(IV)-silica colloids in the laboratory

- Starting point: solutions of actinide(IV) carbonate complexes →

- Uranium: Electrochemical reduction of U(VI) carbonate complexes to U(IV) carbonate complexes
- Neptunium: Elecrochemical reduction of Np(V) in HNO_3 to Np(III). Electrochemical oxidation of Np(III) to Np(IV) in HNO_3. Formation of Np(IV) carbonate complexes by adding the acidic solution to 1.0 M $NaHCO_3$
- Thorium: Dissolution of Th(IV) in $HClO_4$. Adding of solid $NaHCO_3$

Generation of actinide(IV)-silica colloids in the laboratory

- Destruction of the actinide(IV) carbonate complexes results in the formation of actinide(IV) nanoparticles →

- Dilution with pure water: Precipitate of actinide(IV) oxyhydroxide
- Dilution with water containing silicic acid: Waterborne actinide(IV)-silica colloids of surprisingly high concentration at near-neutral pH

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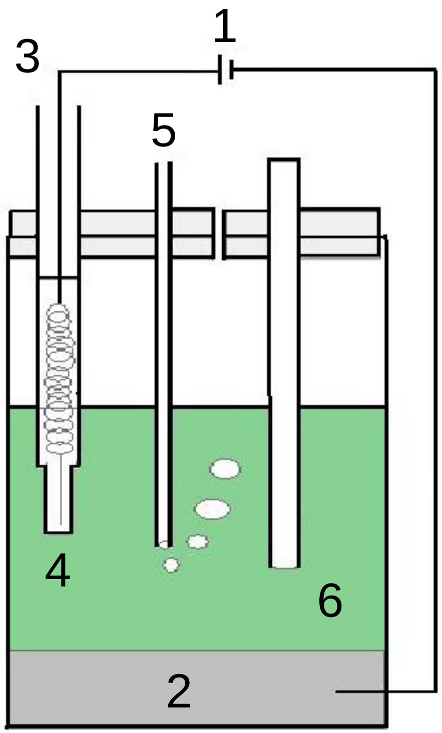
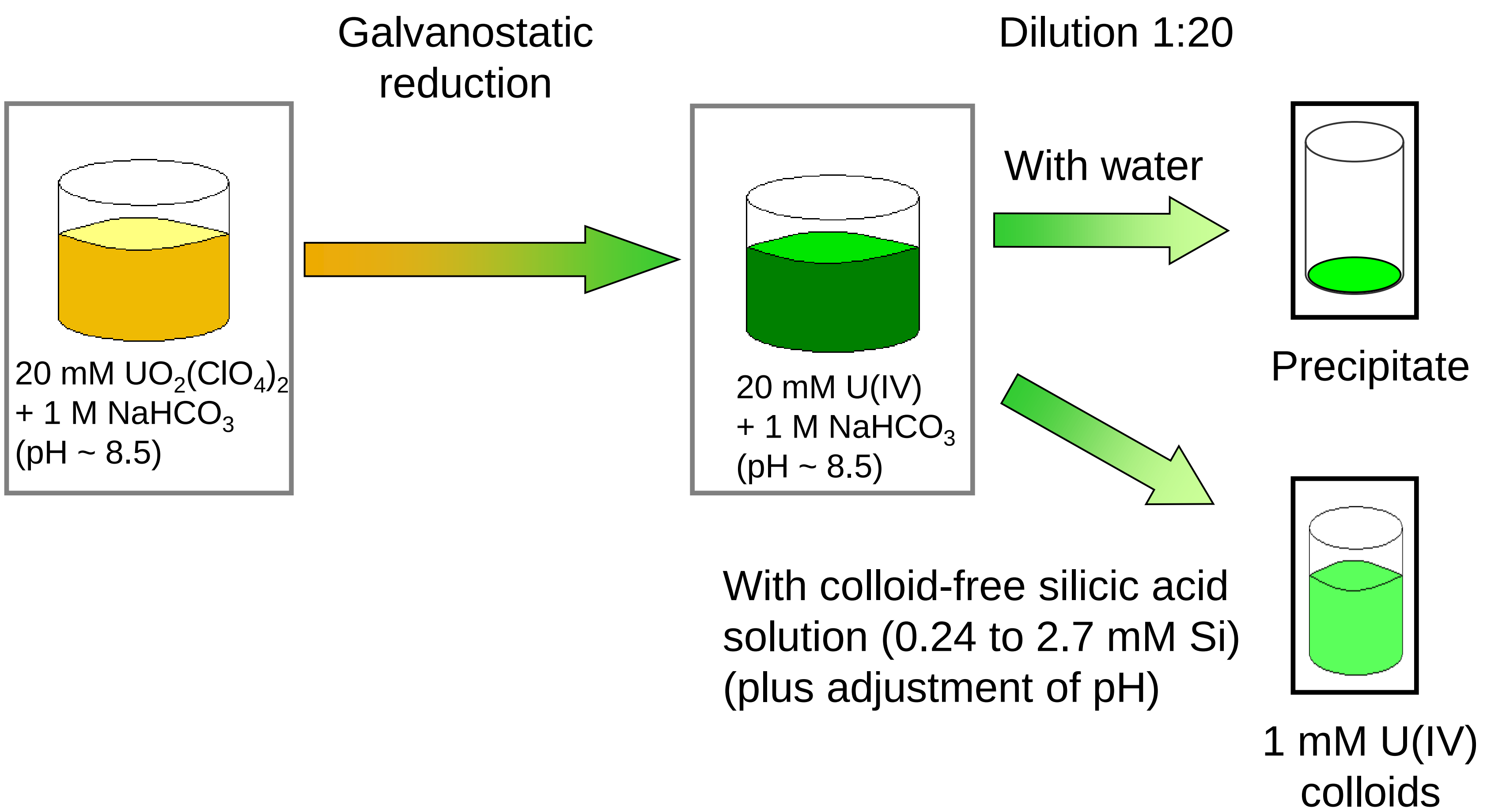
Generation of U(IV)



1 Power supply
2 Anode (Hg)
3 Cathode (Pt wire)
4 Diaphragm
5 Nitrogen
6 Solution of U

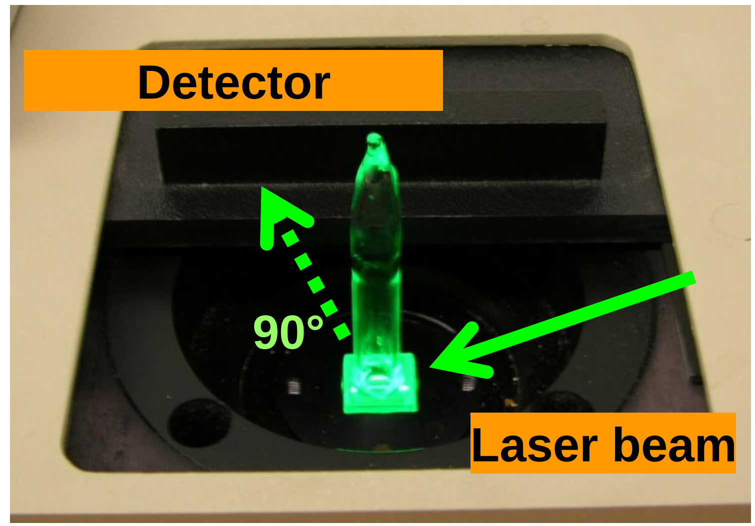
According to Ikeda-Ohno A et al. *Inorg. Chem.* **48** (2009) 7201

Generation of U(IV)-silica colloids



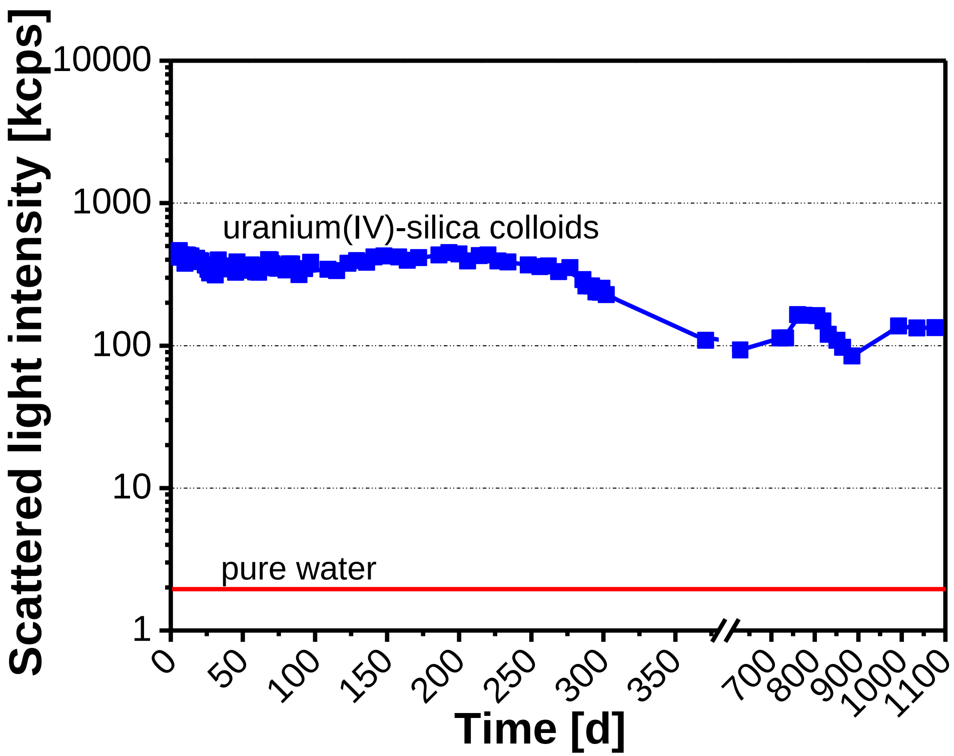
U(IV)-silica colloids: Tyndall effect

Colloidal stability by light scattering:



- Cuvette sealed by melting in inert gas
- Measuring the intensity of the light scattered by the nanoparticles
- Sedimented particles are not „seen“ by the detector

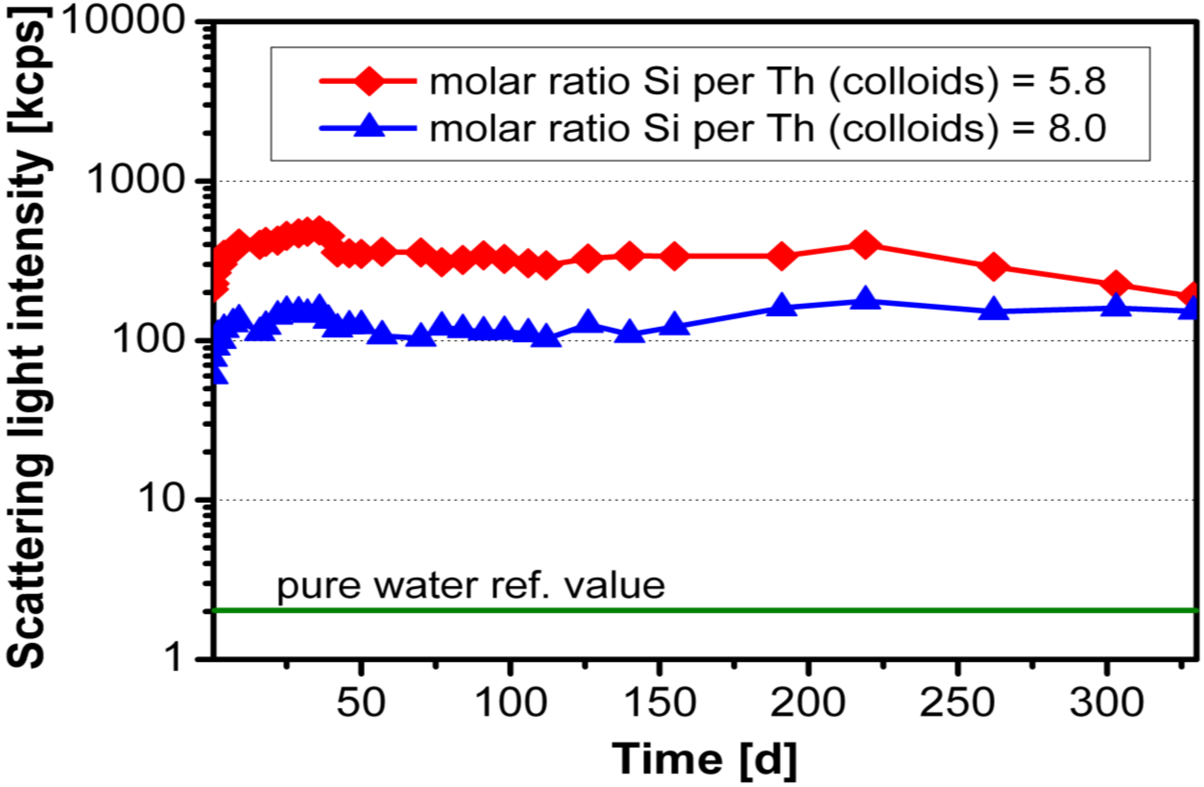
U(IV)-silica colloids: Long-term Stability by light scattering



High scattered light intensity indicates that U(IV)-silica colloids are stable over years!

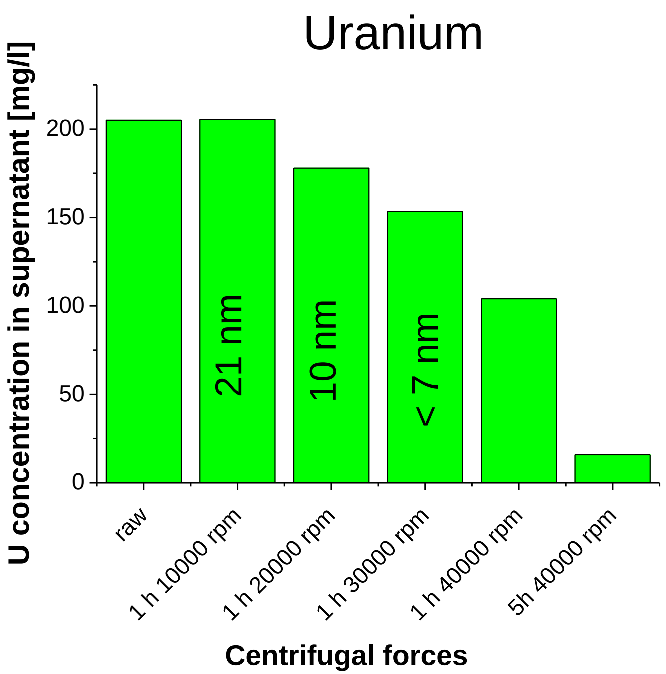
U = 9.0 × 10^{-4} M, Si = 2.2 × 10^{-3} M, pH = 6.9

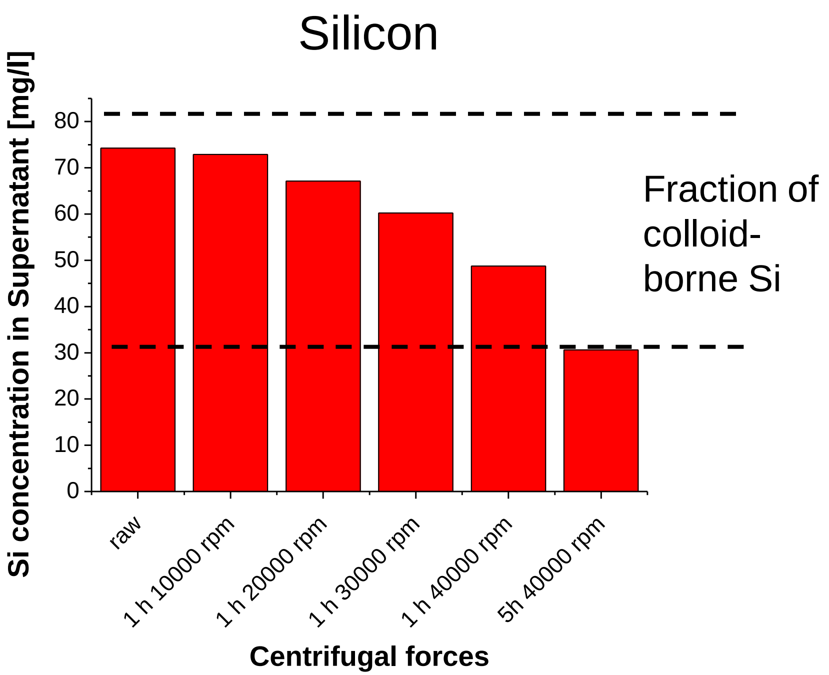
Th(IV)-silica colloids: Long-term Stability by light scattering



[Th] = 1 mM, pH ~ 7

U(IV)-silica colloids: Particle size by ultracentrifugation





U = 8.6×10^{-4} M, Si = 2.7×10^{-3} M, pH = 7.8

Particle diameter: < 20 nm

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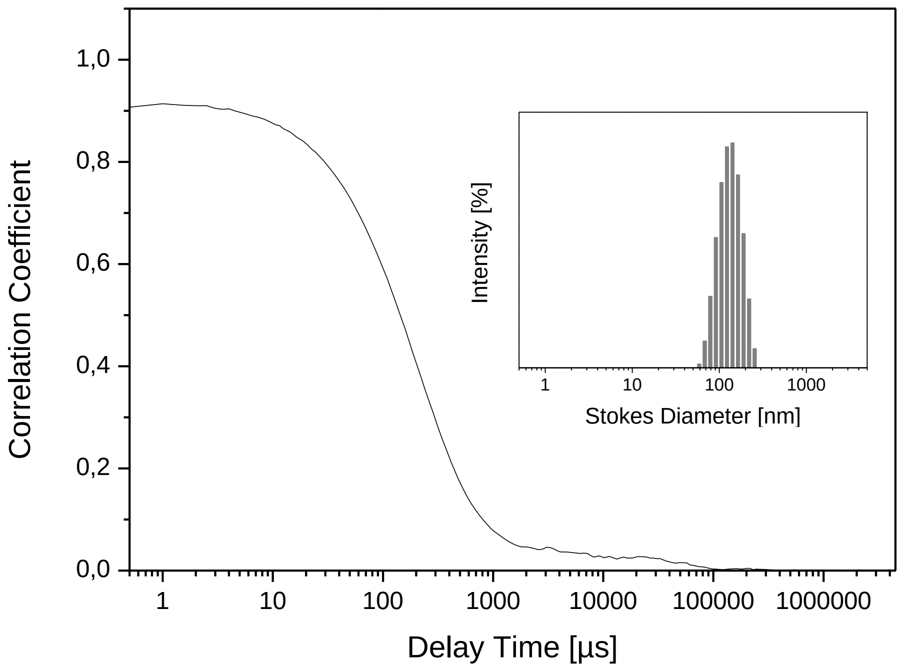
„Mononuclear wall“ of silicic acid

- Below $2 \cdot 10^{-3}$ M silicic acid occurs in a mononuclear form (“mononuclear wall”)
- Above this “wall” → fractions of polysilicic acid

  (Stumm, W., Huper, H., Champlin, L., *Environ. Sci. Technol.* **1** (1967) 221-227)
- Affinity of metal ions to polysilicic acid is much higher than affinity to monosilicic acid

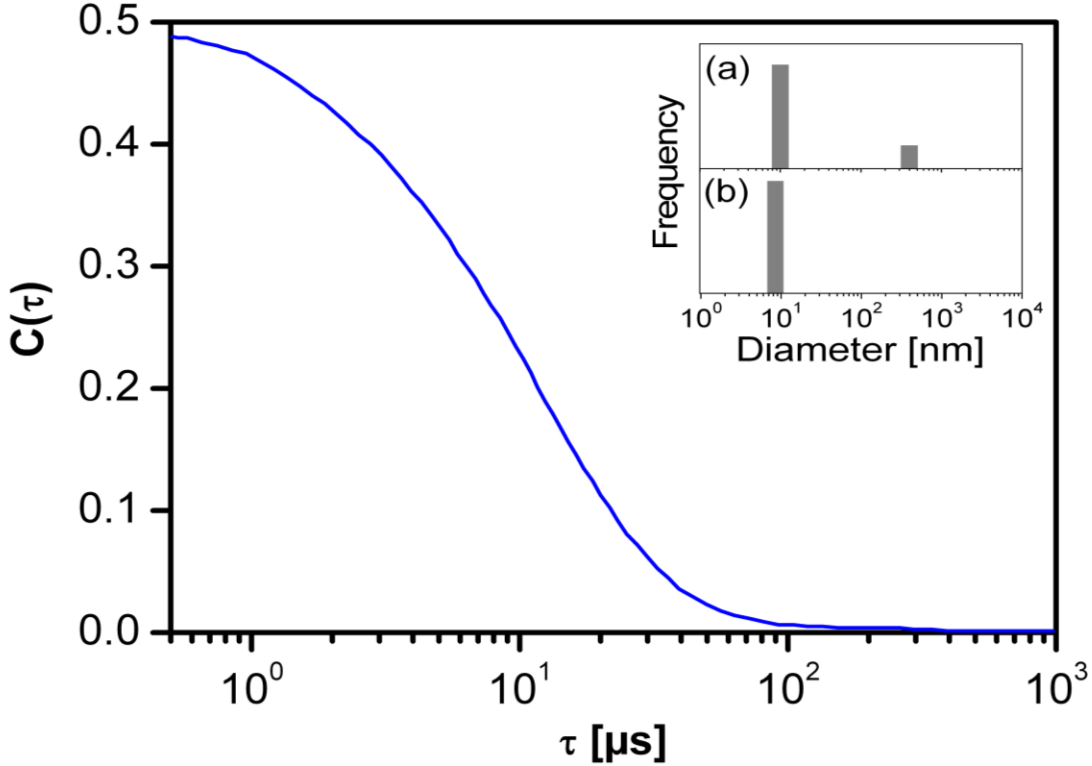
→ Formation of actinide(IV)-silica colloids below the “mononuclear wall” of silicic acid differs from that above the “mononuclear wall”

Np(IV)-silica colloids below the “mononuclear wall” of silicic acid: Particle size about 150 nm (PCS)



Np(IV) = 2.5×10^{-4} M, Si(IV) = 1.5×10^{-3} M

Np(IV)-silica colloids above the "mononuclear wall" of silicic acid: Particle size about 10 nm

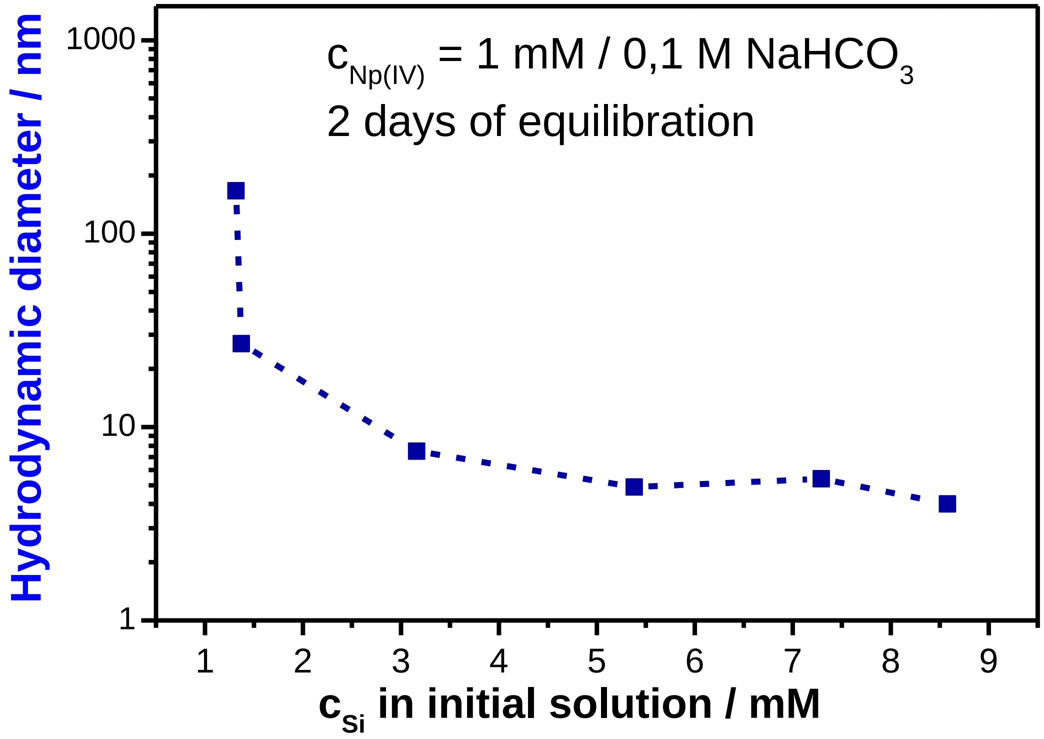


(a) Light-intensity weighted particle size distribution

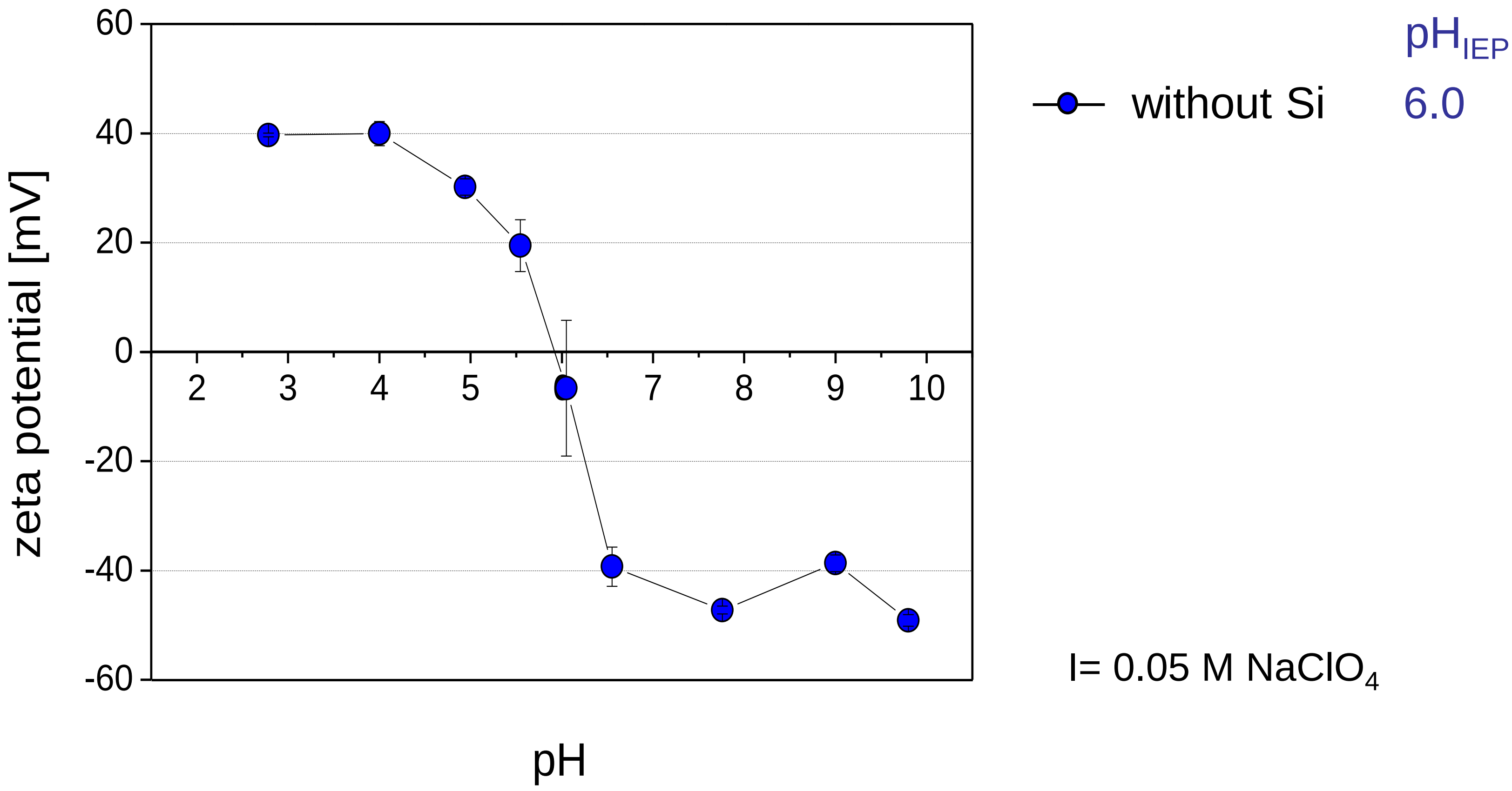
(b) Number weighted particle size distribution

Np(IV) = 10^{-3} M, Si(IV) = 8.6×10^{-3} M

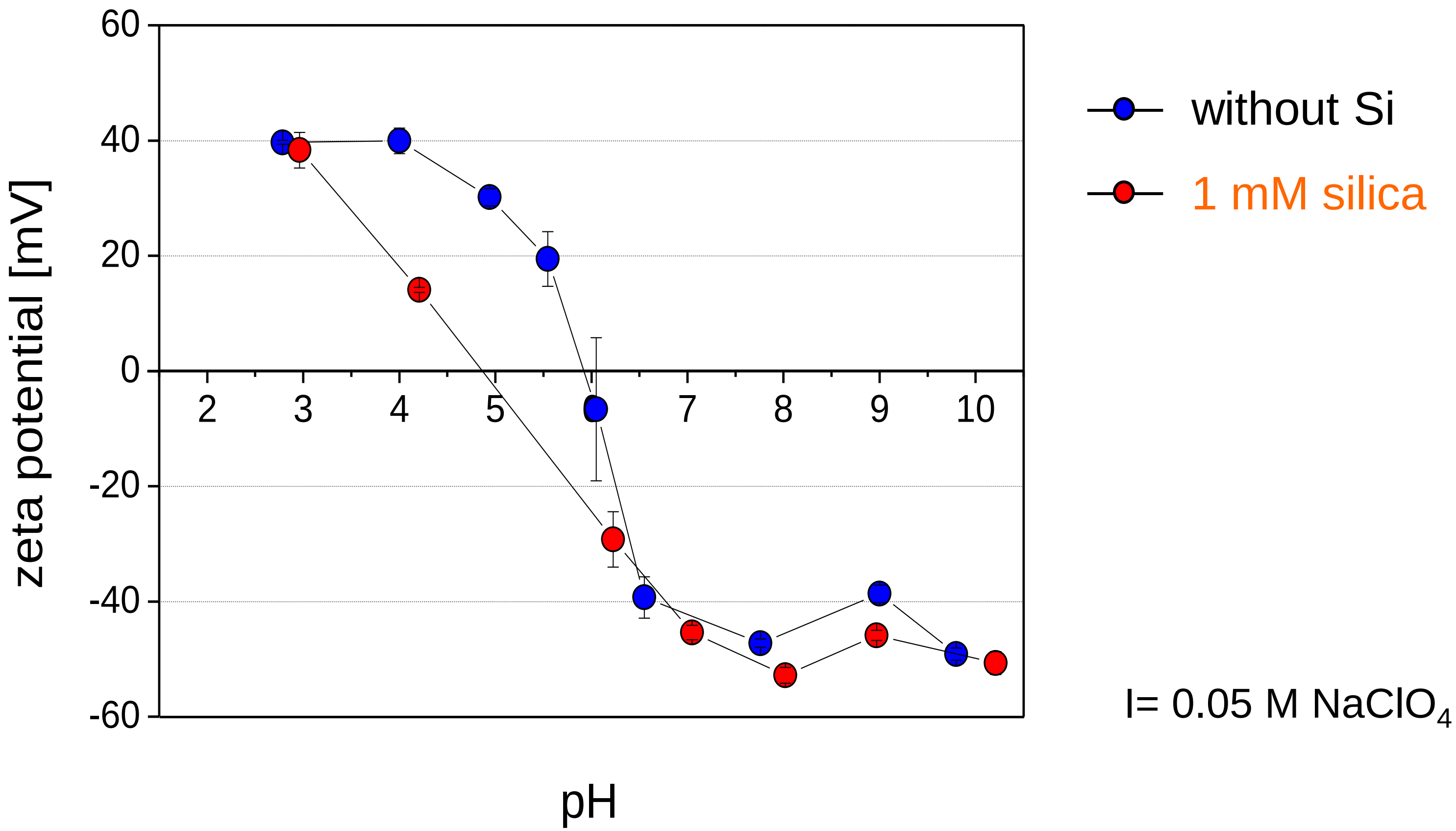
Dependence of PCS particle size of Np(IV)-silica colloids on the silicic acid concentration



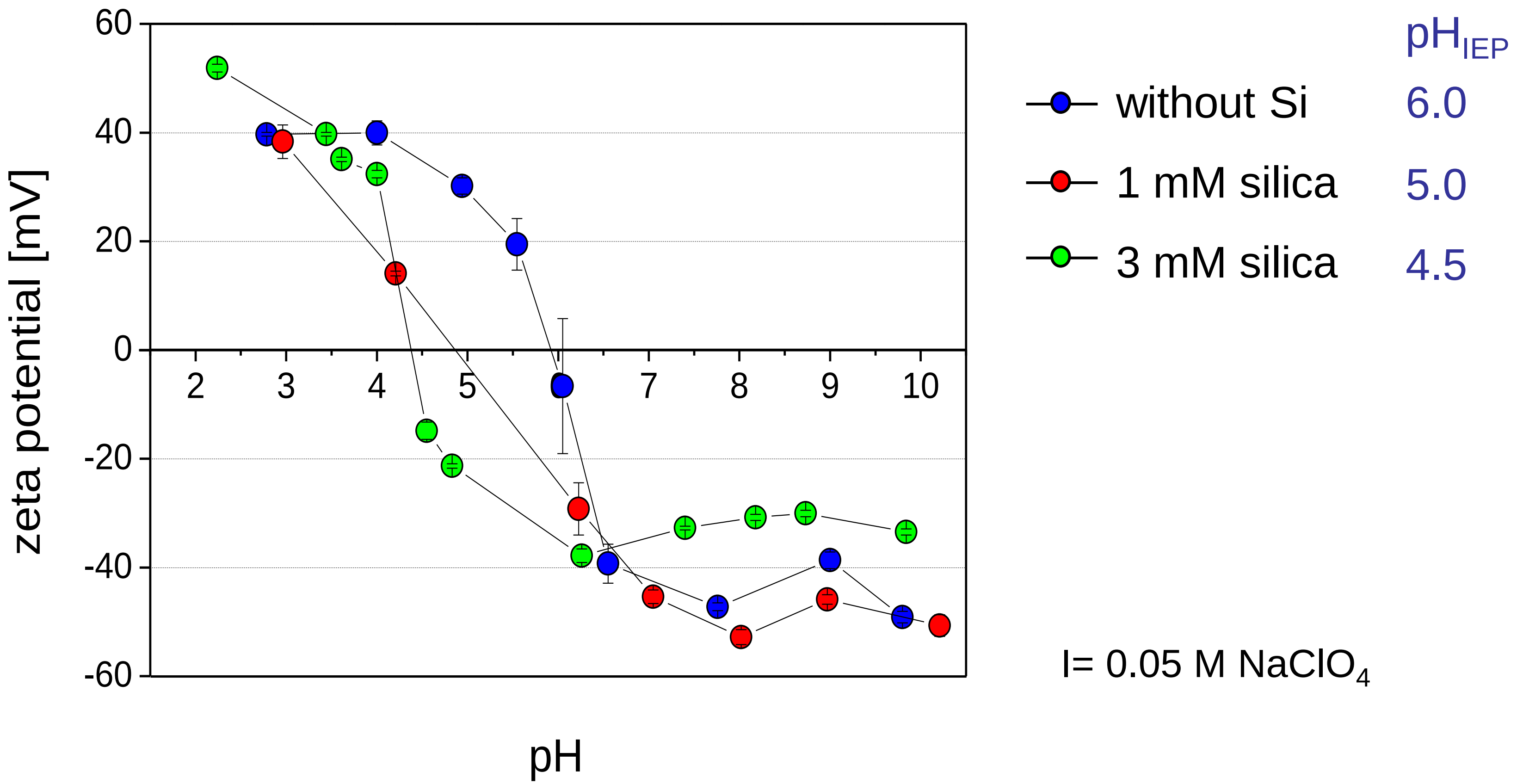
U(IV)-silica colloids: Zeta potential by Laser Doppler velocimetry



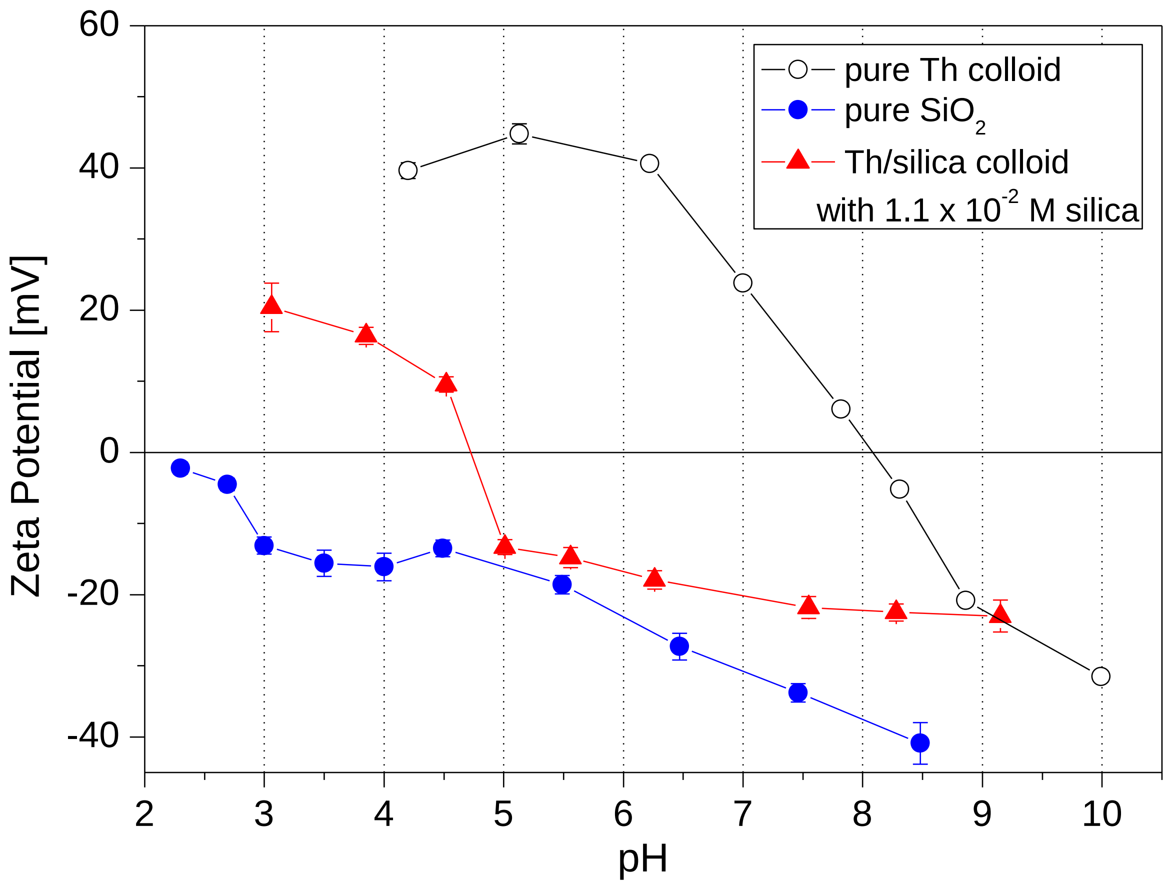
U(IV)-silica colloids: Zeta potential by Laser Doppler velocimetry



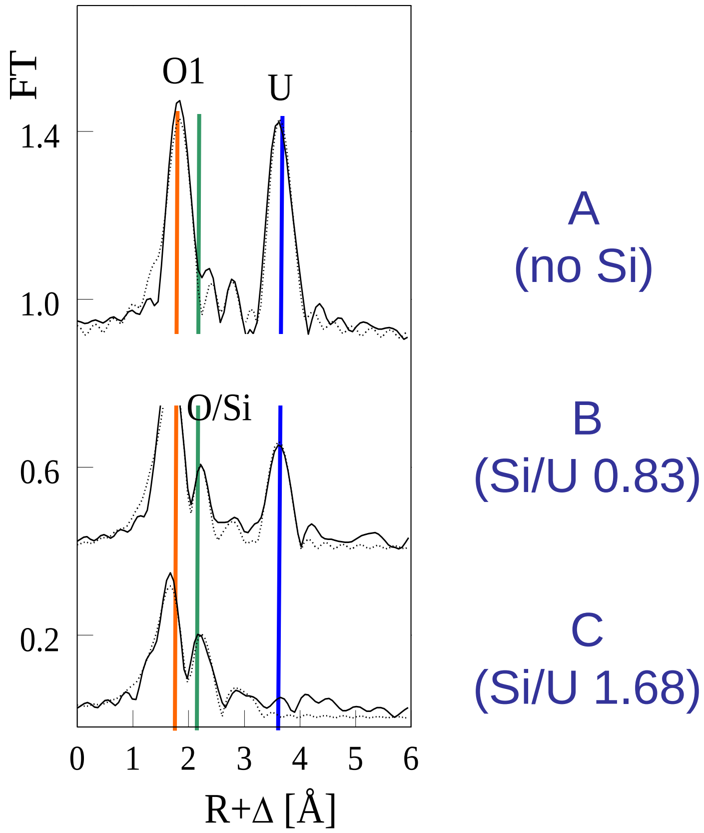
U(IV)-silica colloids: Zeta potential by Laser Doppler velocimetry



Th(IV)-silica colloids: Zeta potential by Laser Doppler velocimetry



U(IV)-silica colloids: Uranium binding by EXAFS spectroscopy (ROBL, ESRF Grenoble)



Fourier transforms (FTs) of EXAFS spectra

With increasing Si content:

distance U-O1 is shortend

U-U scattering is reduced

O/Si scattering is increased

- U-O-U bonds are partly replaced by U-O-Si bonds
- Structure similar to coffinite ($USiO_4$), but much less ordered

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Properties of the Actinide(IV)-silica colloids

- Tetravalent actindes could be stabilized in colloid-borne form at concentrations of up to 10^{-3} M. The colloids remain in suspension over years
- The colloids contain silica which stabilizes them
- The colloids form from two *dissolved* components; pre-existing colloids like bentonite colloids do not play a part

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Properties of the Actinide(IV)-silica colloids

- The prevailing particle size is <20 nm
- Silica increases the negative charge of the An(IV) particles in the near-neutral pH range (electrostatic repulsion). Shift of the isoelectric point toward lower pH values. Furthermore: Non-DLVO forces
- Internal structure of the particles: An-O-Si bonds increasingly replace the An-O-An bonds of the actinide oxyhydroxide structure

Questions

- Is there dissolved silicic acid in the near field of a nuclear waste repository?

  Yes. Ingressing groundwater; corrosion of glass, cement, bentonite, grout silica

- Can the formation of An(IV)-silica colloids be ruled out?

  No. Several mechanisms are conceivable

- Would An(IV)-silica colloids be colloidally stable (resistant to coagulation) under near-field conditions?

  They might be stable. Under laboratory conditions they could be stable over years

Questions

- Can the transport of An(IV)-silica colloids through the engineered barrier system (EBS) be ruled out?
  No. Macromolecules of 30 kDa (lignosulfate) were able to diffuse through the pores of bentonite (Wold and Erik-sen 2003)
- Can the transport of An(IV)-silica colloids in the far-field be ruled out?

  No. Colloidal radionuclide transport has been shown in column and in field experiments
- Would An(IV)-silica colloids be chemically stable (resistant to disintegration) when they leave the near-field of a repository?

  This question is largely unanswered

- Further research is needed to elucidate the potential role of actinide(IV)-silica colloids in environmental scenarios

Thank you very much!

Publications

Uranium(IV)

Dreissig I, Weiss S, Hennig C, Berhard G, Zänker H: Formation of uranium(IV)-silica colloids at near-neutral pH. *Geochim. Cosmochim. Acta* **75** (2011) 352-367

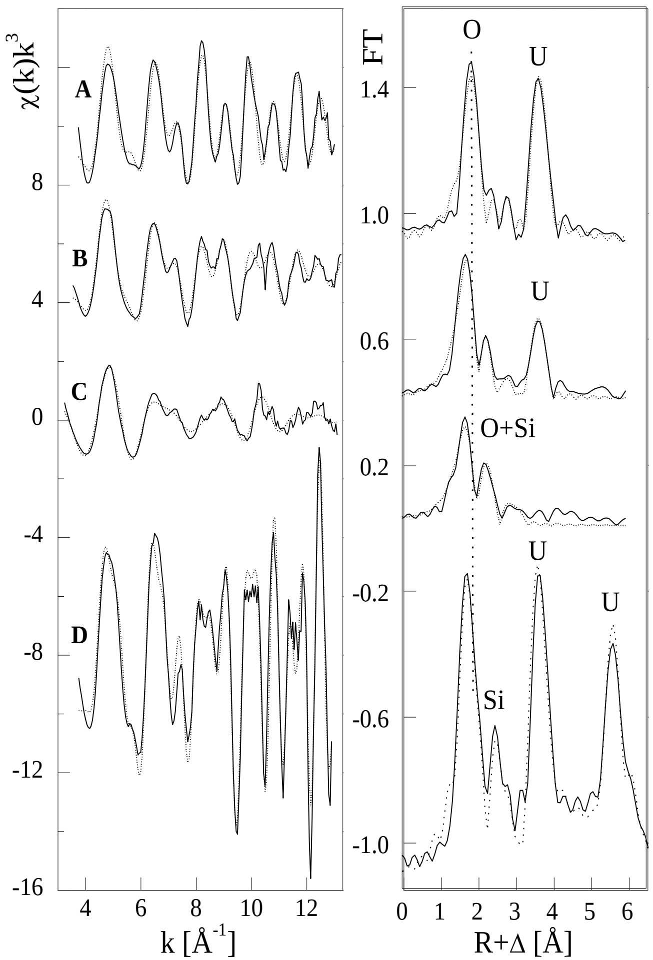
Thorium(IV)

Hennig C, Weiss S, Banerjee D, Brendler E, Honkimäki V, Cuello G, Ikeda-Ohno A, Scheinost AC, Zänker H: Solid state properties and colloidal stability of thorium(IV)-silica nanoparticles. *Geochim. Cosmochim. Acta* **103** (2013) 197-212

Neptunium(IV)

Husar R, Weiss S, Zänker H, Bernhard G: Investigations into the formation of neptunium(IV)-silica colloids. Migration 2013. Brighton, Book of Abstracts, p. 384

U(IV)-silica colloids: EXAFS



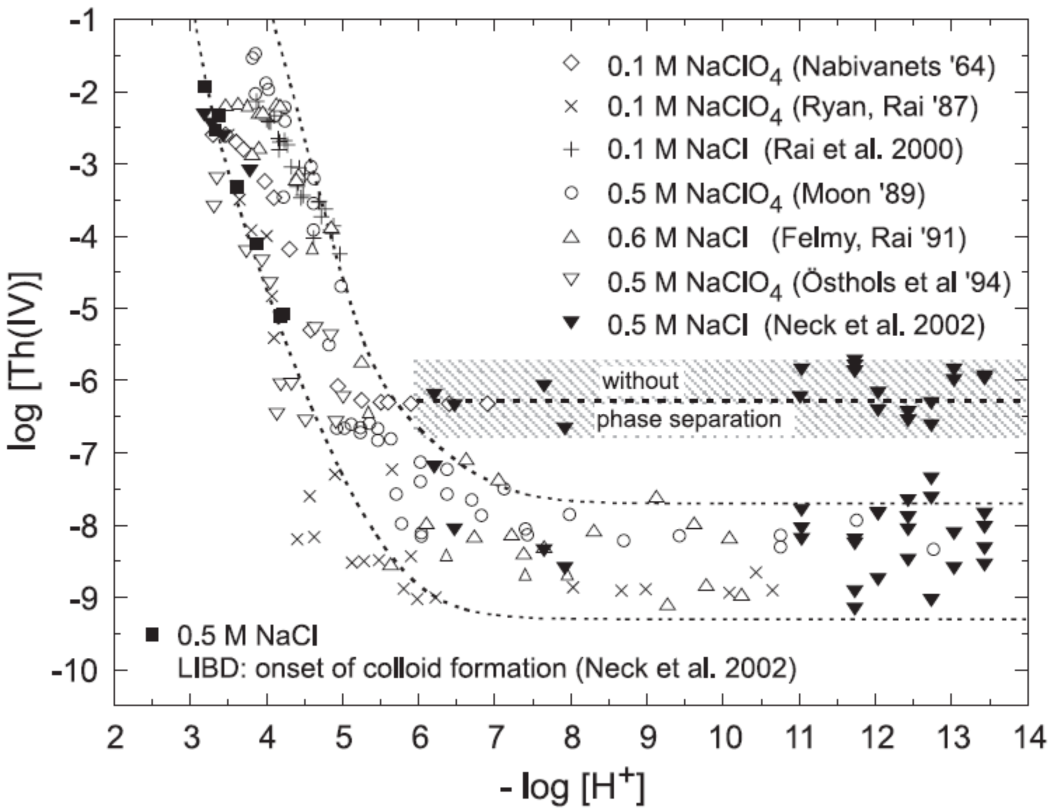
<u>Probe A:</u>
Referenz ohne Silikat
$UO_n(OH)_{4-2n} \times mH_2O$

<u>Probe B:</u>
Kolloide (ausgefällt)
Molares Si/U Verhältnis im Feststoff = 0,83

<u>Probe C:</u>
Kolloide (ausgefällt)
Molares Si/U Verhältnis im Feststoff = 1:1,68

<u>Probe D:</u>
Coffinit (synthetisch)

Hitherto laboratory experiments concerning An(IV) colloids



If colloid removal is omitted, total actinide concentrations, $[An(IV)]_{tot}$, higher by a factor of about 100 are found.

← An(IV) oxyhydroxide colloids

Altmaier, M. et al.; *Radiochim. Acta* (2004) **92**, 537

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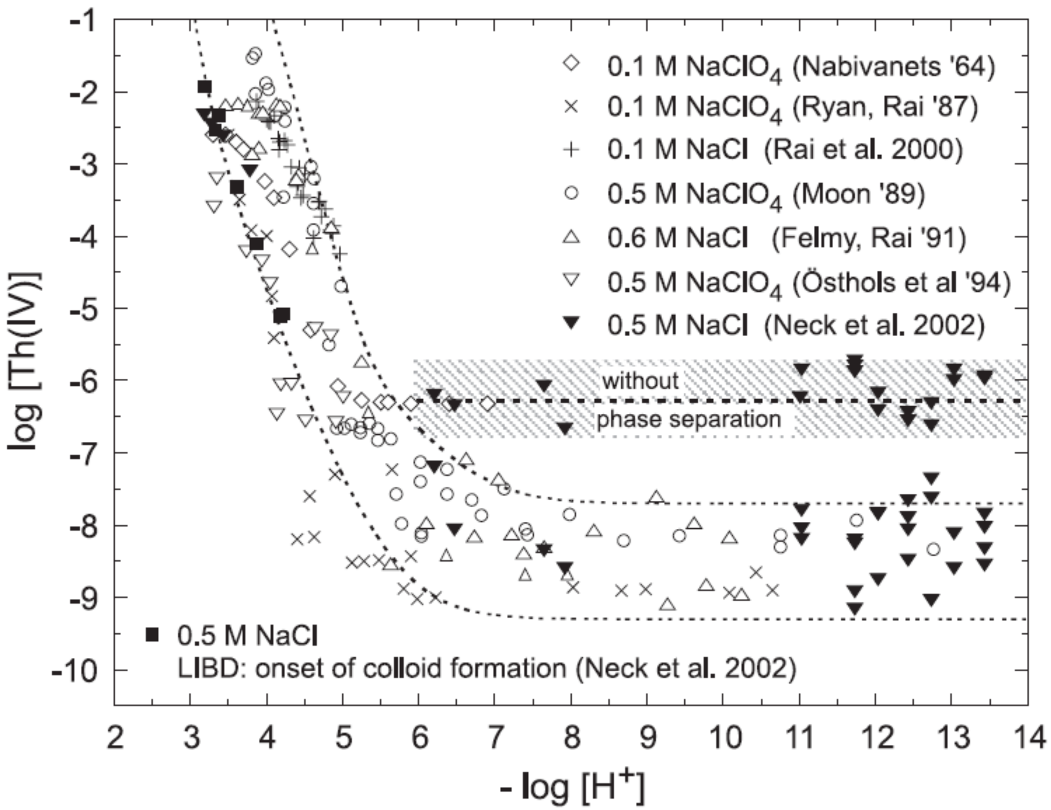
Laboratory experiments as to An(IV) colloids



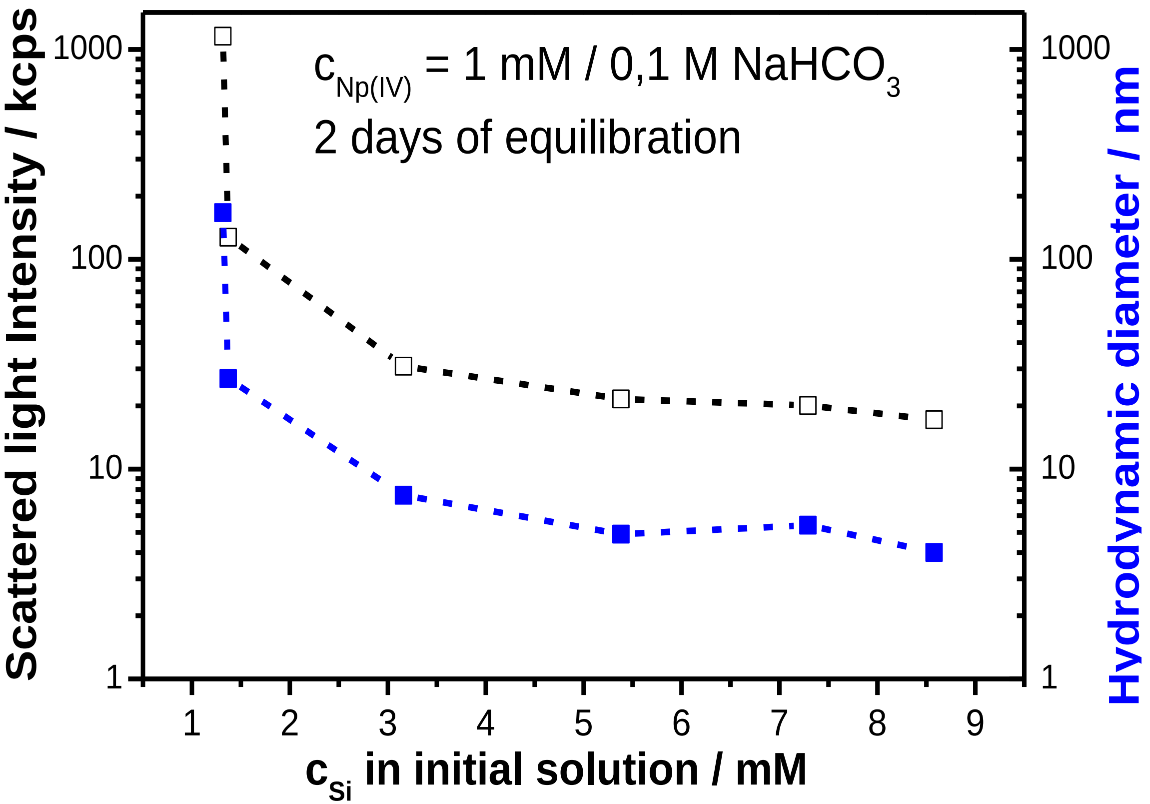
← Th(IV)- silica colloids: 10^{-3} M

Th(IV)-oxyhydroxide colloids: 10^{-6} M

Thermodyn. Solubility: 10^{-8} M

Altmaier, M. et al.; *Radiochim. Acta* (2004) **92**, 537

Dependence of SLI and particle size of Np(IV)-silica particles on the silicic acid concentration



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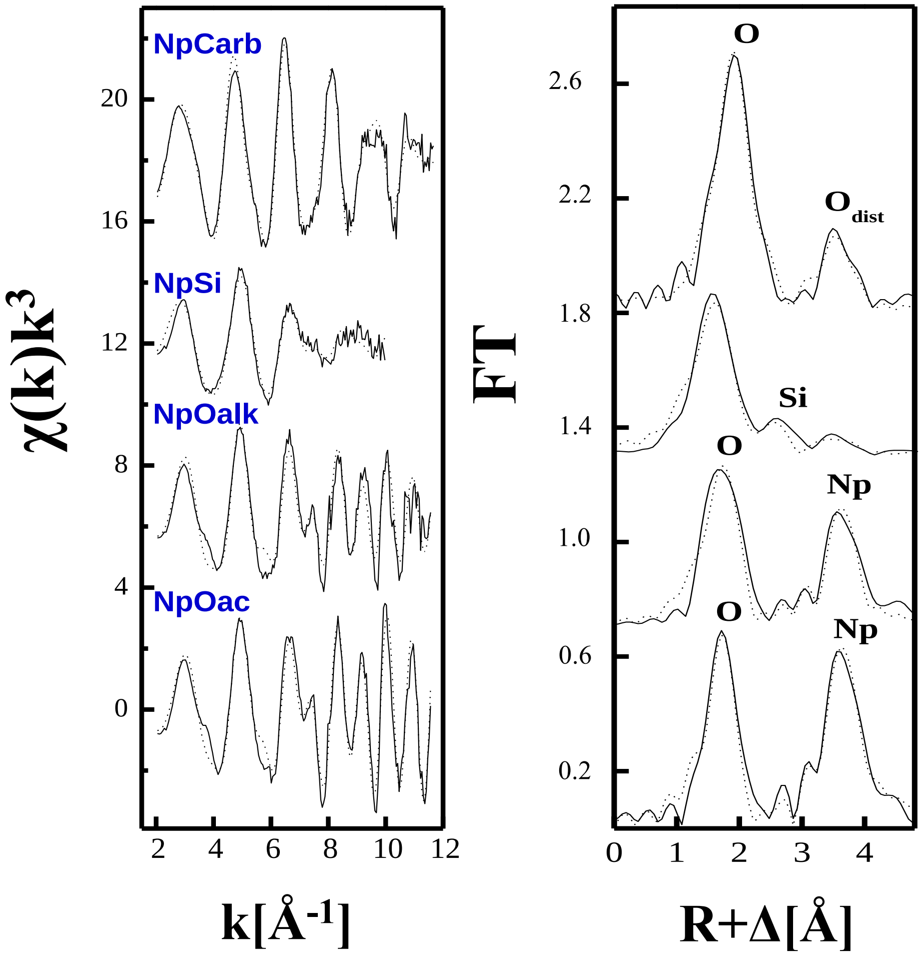
Np EXAFS



NpCarb
NpSi
NpOalk
NpOac
20
16
12
8
4
0
2
4
6
8
10
12
χ(k)k³
k[Å⁻¹]
O
O dist
Si
O
Np
O
Np
2.6
2.2
1.8
1.4
1.0
0.6
0.2
0
1
2
3
4
FT
R+Δ[Å]

Ideas for a work plan

- Formation of Pu(IV)-silica colloids is to be tested
- Mechanisms of An(IV)-silica nanoparticle formation are to be studied (ESI-MS, EXAFS, HEXS, ^{29}Si NMR)
- Quantification of DLVO and non-DLVO contributions to the stabilization (aggregation kinetics, influence of ionic strength and pH on stability)
- Passage (diffusion) of An(IV)-silica colloids through compacted bentonite (cf. C. Joseph et al.)
- Chemical persistency of An(IV)-silica colloids after leaving the near-field
- Passage (convection) of An(IV)-silica colloids through columns packed with crushed rock

Ideas for a work plan

- Deposition of actinide(IV)-silica colloids on host rock mineral surfaces by RAXR, CTR and AFM (cf. M. Schmidt et al.)
- If useful and helpful, field experiment at the Grimsel Test Site (GTS)