Simulation of neptunium migration as a function of clay mineralogy and redox conditions

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Motivation

Quantification of neptunium migration in the Opalinus Clay

- Neptunium, i.e. ^{237}Np, is a minor component of high-level radioactive waste with a long half-life and high radiotoxicity
- Diffusion is the transport process in argillaceous formations, characterized by low permeabilities and a high sorption capacity retarding migration
- Opalinus Clay (OPA), the preferred host rock in Switzerland and also considered as an option in Germany, is regarded as a reference formation
- Mineralogical and geochemical variations examined for two diffusion laboratory experiments to numerically study neptunium migration [1, 2]

Methods

Laboratory experiments and conceptual numerical set-up for one dimensional neptunium diffusion simulations

- Numerical simulations are performed with PHREEQC in one dimension using Fick's laws and surface complexation models to quantify diffusion and sorption processes of Np(V) by means of the distribution coefficient K_d (m^3/kg)
- 8 µM Np(V) was applied via a synthetic OPA pore water with pH 7.6 and pe 6 to two different OPA core samples with unknown mineralogical composition potentially affecting transport processes in the experiments that had the same setup [1, 2]
- Scenarios for the minimum and maximum amount (15 and 35 wt.%) of 3-layer clay minerals with highest sorption are used to quantify the impact of mineralogy, whereas an average value of 35 wt.% is chosen for the 2-layer clay minerals [3]
- Redox potentials are assumed to be controlled by pyrite within the sample and a range between source solution (pe = 6) and in-situ (pe = -3.4), undersaturation refers to kinetic effects, the pH is buffered by calcite of the system

Conclusions

Neptunium migration is mainly governed by redox conditions and less the clay mineralogy

- Redox conditions are governed by pyrite dissolution and strongly affect the migration behaviour of neptunium due to changes in its speciation, and thus significant variations of the sorption
- Clay mineral quantities have only a minor impact on neptunium migration, sorption occurs mainly on 3-layer clay minerals due to their high sorption capacity
- K_d values vary significantly by several orders of magnitude depending on the respective redox potential and therefore these conditions need to be controlled within laboratory experiments
- Np(IV) surface complexation data will be integrated for clay minerals to obtain a comprehensive understanding of neptunium sorption and migration in argillaceous formations

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References:

[1] Fröhlich, D. R. et al. (2013): Influence of humic acid on neptunium (V) sorption and diffusion in Opalinus Clay, Radiochimica Acta, 101(9), 553-560, DOI:10.1524/ract.2013.2059.

[2] Wu, T. et al. (2009): Neptunium (V) sorption and diffusion in Opalinus Clay, Environmental Science & Technology, 43(17), 6567-6571, DOI:10.1021/es9008568.

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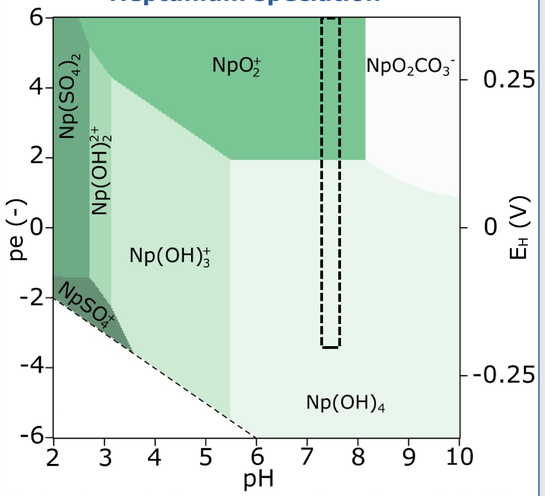
Results

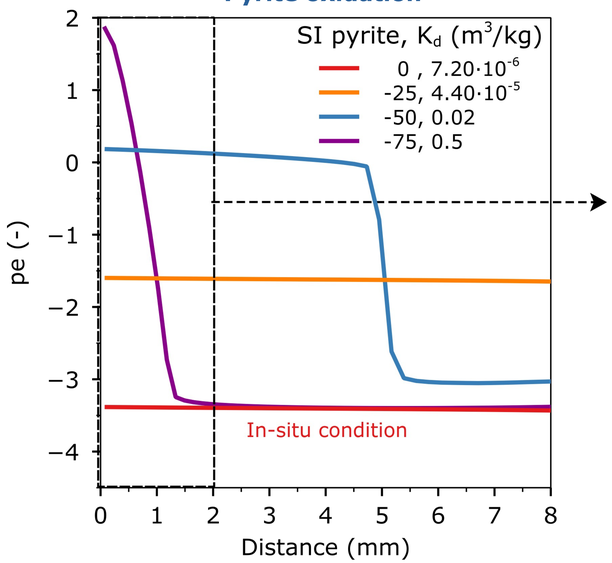
Neptunium triggers pyrite oxidation which governs the iron amount and speciation in the pore water, increased iron leads to an increased pe, sulfur is fully oxidised and calcite buffers the pH of the system

Neptunium speciation

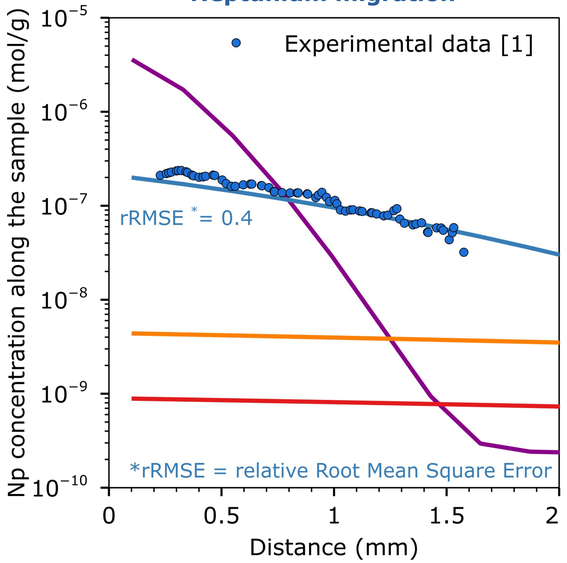


Pourbaix diagram for Np concentration of 1 nmol/L in synthetic OPA pore water. The dashed box marks the pH and pe range potentially present in the experiments (source solution with pe = 6) [1, 2] and measured in the OPA (in-situ conditions with pe = -3.4), respectively.

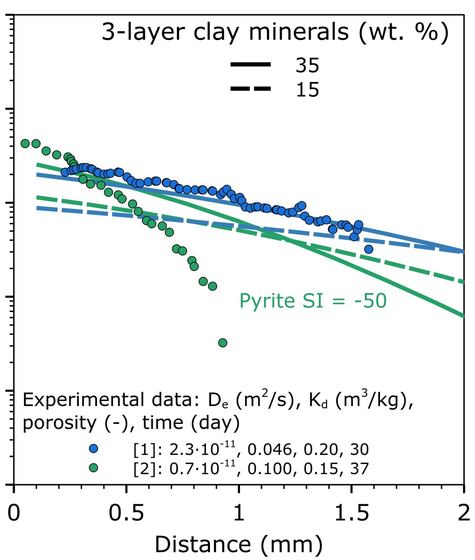
Pyrite oxidation



Neptunium migration



Mineral variations



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