PSI Center for Nuclear Engineering and Sciences

BGE BUNDESGESELLSCHAFT FÜR ENDLAGERUNG

HZDR HELMHOLTZ ZENTRUM DRESDEN ROSSENDORF

A Reference Database of Radionuclide Sorption to Support the Safety Assessment of Deep Geological Repositories

SORDA

Marinich, O., Miron, G.D., Bok, F., Zechel, S., Brendler, V., Marques Fernandes, M. Baeyens, B.

SafeND 2025: The third BASE research symposium, 17 September 2025

Contents

- Motivation
- Background in sorption modelling of clays at the Laboratory for waste management (PSI LES)
- Details of sorption modelling workflow
- Sorption modelling examples and alternative approaches
- Outlook

Motivation

- **Safety assessment** of geological repository requires **accurate modelling** for investigating long-term behavior of radionuclides under variable conditions that cannot be directly reproduced in field or laboratory studies
- Creating a quality-assured reference sorption database for **dose-relevant radionuclides** for **key minerals** representative of German natural barriers became a central objective of the **SOREDA project**

Cs	Sr	Ra	Ni	Am	Cm	Sn	Th	Np				Pu				U			Tc		I			Se		
I	II	II	II	III	III	IV	IV	III	IV	V	VI	III	IV	V	VI	IV	V	VI	IV	VII	-I	0	V	-II	IV	VI

Kaolinite, Illite, Montmorillonite, Calcite, Dolomite

↓

LES-PSI

Quartz, Ferrihydrite, Goethite, Hematite, Magnetite, Pyrite

↓

HZDR

Background in sorption modelling of clays at PSI LES

2-Site Protolysis Non-Electrostatic Surface Complexation and Cation Exchange (2SPNE SC/CE) model

Baeyens, B., Bradbury, M.H., 1997. J. Contam. Hydrol.; Bradbury, M.H., Baeyens, B., 1997. J. Contam. Hydrol.; Bradbury, M.H., Baeyens, B., 2009 (Part I and II). Geochim. Cosmochim. Acta)

Generalised **C**aesium **S**orption **(GCS)** model

Bradbury, M.H., Baeyens, B., 2000. J. Contam. Hydrol.

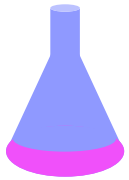
SIT model of aqueous solution

+

TDB 2020

Hummel & Thoenen, 2023

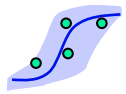
+



~ 4000 batch experiments

> 30 years of experiments at **PSI LES**

+



Uncertainty quantification

→

ClaySor 2023 sorption model package + STDB 2023

GEMS, GWB and Phreeqc formats: https://doi.org/10.5281/zenodo.15095062

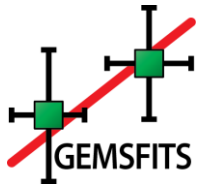
Marinich et.al. 2025 (Appl. Geochem.); NTB 23–05

Validated

Marques Fernandes et al. 2024 NTB 23-01

Tools:

Equilibrium modelling

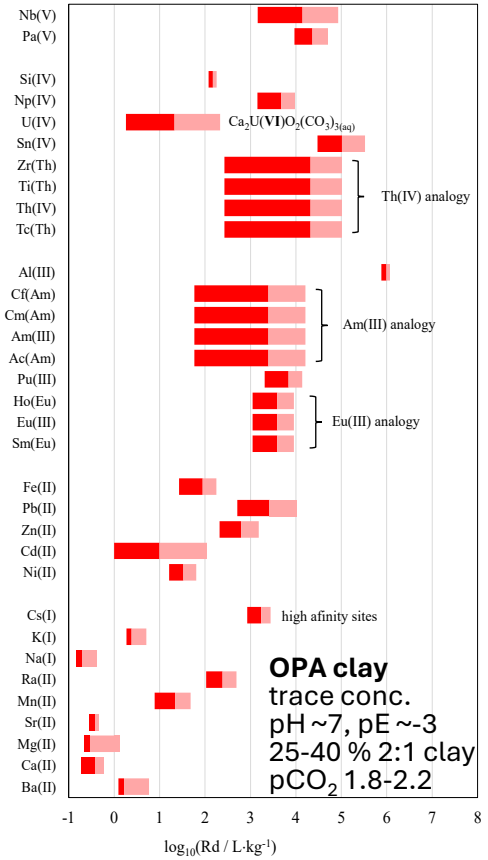


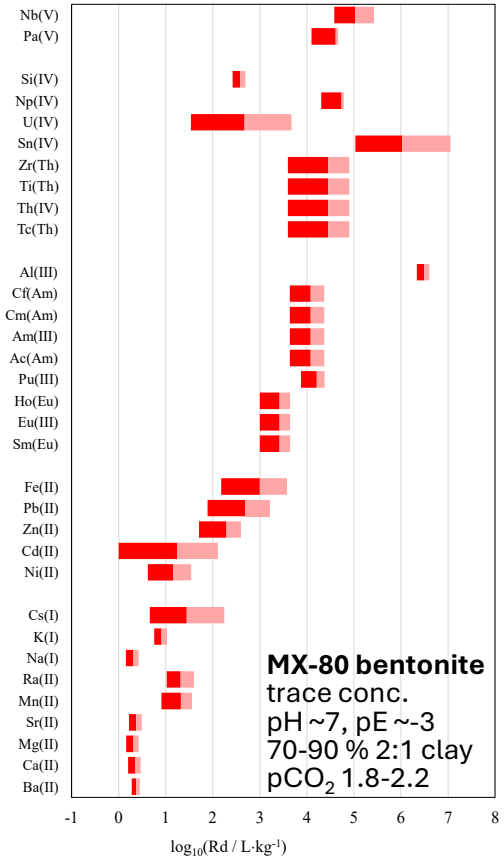
Parameter optimization

UpsaGEMS **Python code +** Uncertainpy toolbox *(Tennøe et. al. 2018)*

Rd uncertainty propagation

Application of sorption modeling results to the safety assessment of the Swiss deep geological repository





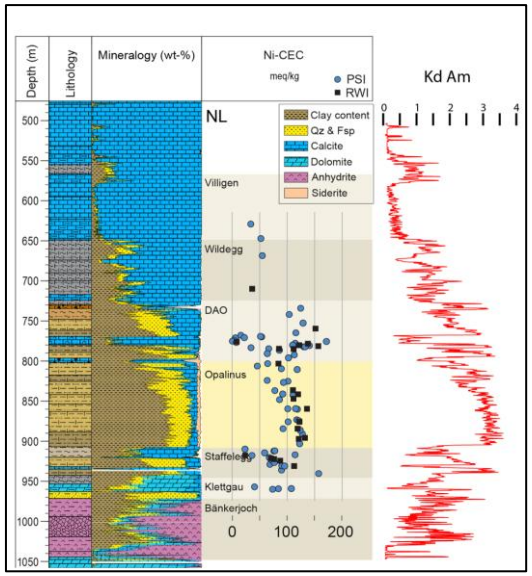
Ranges of upper and lower Rd values, depending on:

- **uncertainty**
- variation in **clay content**
- variation in **PW composition**

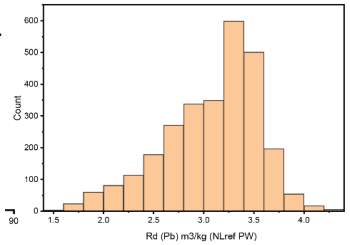
"Non-sorbing":
Mo, C, Cl, I, Ag, Hg, Cu, Pd, Po

In **SOREDA**, sorption of **I** is to be parametrized!

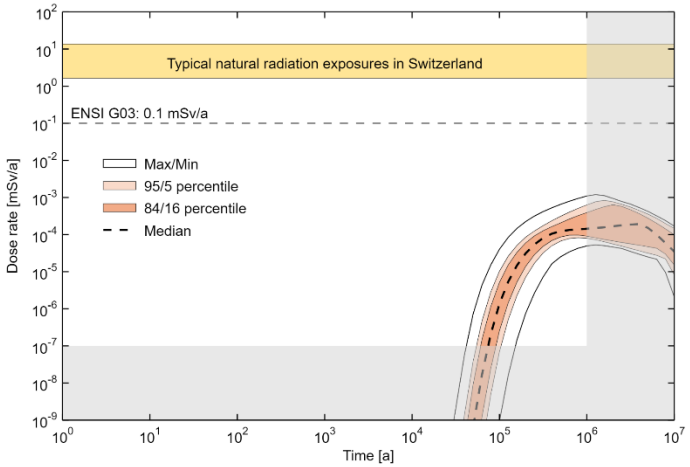
Upscaling: calculated **K_d profiles**



Statistical analysis



Probabilistic analysis: **dose** curves and bandwidths



Post-Closure Safety Report (NTB 24-10)

Details of sorption modelling workflow

example of clays

Data search and analysis

Papers, reports

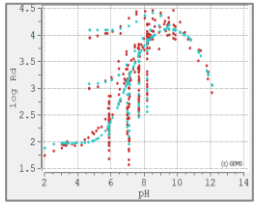
Sorption DB

Raw data

Data preprocessing and formatting

DS-01 iso_gemsfits.csv
DS-02 iso_gemsfits.csv
DS-03 edge_gemsfits.csv
DS-04 edge_gemsfits.csv
DS-05 edge_gemsfits.csv
DS-06 edge_gemsfits.csv
DS-07 edge_gemsfits.csv
DS-08 edge_gemsfits.csv

Fitting routine



GEMSFITS

Fits ok*?

No

Defining sorption species; chemical system setup

Spectr. data

GEMS SELEKTOR

Yes

Optimized $G°_{298}$ sorp. species

Transformed into selectivity coefficients and surface complexation **constants** expressed in STDB as **logK**

Monte Carlo simulations

~ 1000 steps

GEMSFITS

The unc. at 95% confidence level:

$$Un_{G^\circ_{298}} \approx 1.96 \times \sigma$$

STDB in tabular and GEMS/PHREEQC/GWB formats

Surface complex formation reaction	$^{s}G°_{298}$, kJ·mol^{-1}	$\log_{10}{}^{s}K$
≡SOH + Cd^{2+} ⇔ ≡SOCd^{+} + H^{+}	-320.22	0.93*
≡SOH + Co^{2+} ⇔ ≡SOCo^{+} + H^{+}	-299.51 ± 0.65	1.18 ± 0.11
≡SOH + Co^{2+} + H_2O ⇔ ≡SOCoOH^{0} + $2H^{+}$	-488.55 ± 3.21	-7.25 ± 0.56
≡SOH + Fe^{2+} ⇔ ≡SOFe^{+} + H^{+}	-335.21	1.28*
≡SOH + Mn^{2+} ⇔ ≡SOMn^{+} + H^{+}	-471.02 ± 0.53	0.98 ± 0.09
≡SOH + Ni^{2+} ⇔ ≡SONi^{+} + H^{+}	-286.65 ± 0.24	0.65 ± 0.04
≡SOH + Ni^{2+} + H_2O ⇔ ≡SONiOH^{0} + $2H^{+}$	-474.90 ± 0.86	-7.92 ± 0.15
≡SOH + Pb^{2+} ⇔ ≡SOPb^{+} + H^{+}	-277.95 ± 1.26	2.90 ± 0.22
≡SOH + Pb^{2+} + H_2O ⇔ ≡SOPbOH^{0} + $2H^{+}$	-469.42 ± 1.37	-5.11 ± 0.24
≡SOH + Zn^{2+} ⇔ ≡SOZn^{+} + H^{+}		
≡SOH + Zn^{2+} + H_2O ⇔ ≡SOZnOH^{0} + $2H^{+}$		

Sorption Thermodynamic Database

GEMS SELEKTOR

The Geochemist's WORKBENCH

* The quality of fit is evaluated visually

Experimental data selection

Sorption experimental data sources

- Open published data
- In-house unpublished data
- Lawrence Livermore National Laboratory (LLNL) sorption database
- Japan Atomic Energy Agency sorption database

Over **12000** batch sorption experiments were used for modelling

If no specific data available ?

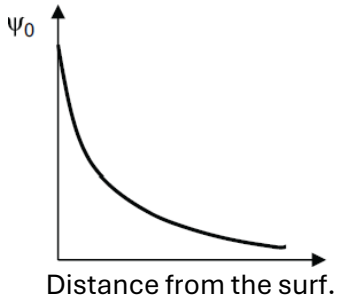
- Linear Free Energy Relationships (LFER)
- Chemical analogue
- Mineral analogue

Data selection criteria

- Clear mineral composition – no significant amounts of admixtures; Preferably purified homo-ionic clay composition
- Background electrolyte is used: no zero ionic strength (IS) solutions; IS < 0.5 M
- Simple solution composition – preferably NaCl, $NaClO_4$; complex porewater compositions were considered only when necessary
- Clear oxidation state of the element – experiments with mixed oxidation states were ignored
- CO_2-free atmosphere for the sensitive elements (valences 3 and higher). Open atm. was considered if only carbonate source was added to equilibrate solution with atm. pCO_2 (e.g. $NaHCO_3$) or dissolved inorganic carbon content was specified
- The element's precipitation was not expected (not excessive loading)

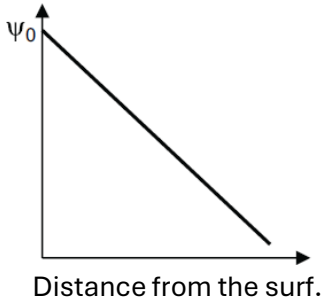
Comparison and selection of sorption models

Diffuse double layer model (DDL)



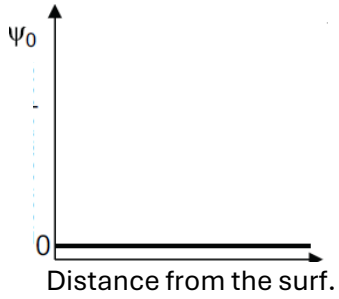
- Surface charge is balanced by a diffuse layer of counter-ions
- Less accurate for layered minerals
- **Best suited for** simple oxides such as **quartz and iron oxyhydroxides**

Constant capacitance model (CC)



- A fixed capacitance between surface and solution is assumed
- Simple, however, requires more parameters than DDL
- Is widely used for **carbonates**

Non-electrostatic model (NE)



- Sorption treated empirically without explicit surface electrostatics
- Predictive within calibration range
- Most **convenient for clays** due to surface heterogeneity and interlayer effects
- Sorption of wide range of metals on 2:1 clays was successfully described by the 2SP**NE** SC/CE model (*TSDB for montmorillonite and illite by Baeyens & Bradbury – NTB 17-13, NTB17-14; extended in Marinich et al. 2025 in Appl. Geochem.*)

Implementation of different surface complexation models in geochemistry codes

Code	Oberflächenkomplexierungsmodelle					
	NE	CC	DDL	BS	TL	CD-MUSIC
PHREEQC	✓	(✓)	✓	✗	✗	✓
Geochemist's Workbench	(✓)	(✓)	✓	✗	✓	✓
TOUGHREACT	✓	✓	✓	✗	✗	✗
GEMS	✓	✓	✓	✓	✓	✓
ChemApp	(✗)	(✗)	(✗)	(✗)	(✗)	(✗)
EQ3/6	✗	✗	✗	✗	✗	✗

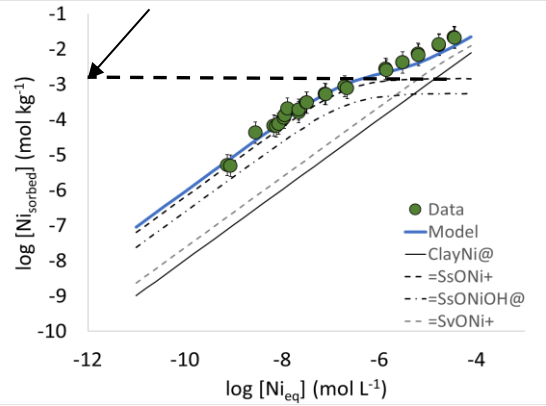
✓ : implemented, (✓): not formally implemented, but usable through adjustments in the code-specific parameter files, (✗): not implemented, but can be programmed in the code during modelling, ✗ : not implemented

Procedure for determining fixed parameters of the 2SPNE SC/CE model

example of clays

- 2SPNE SC/CE model: the sorption occurs through electrostatic binding at **planar sites** (CE – cation exchange) and pH-dependent inner-sphere **surface complexation** (SC) at amphoteric surface hydroxyl groups (≡SOH)
- SC takes place at three edge site types: **strong** sites (≡S^{S}OH) and **two types of weak** sites (≡S^{W1}OH and ≡S^{W2}OH), with **fixed site capacities** and **protolysis constants**

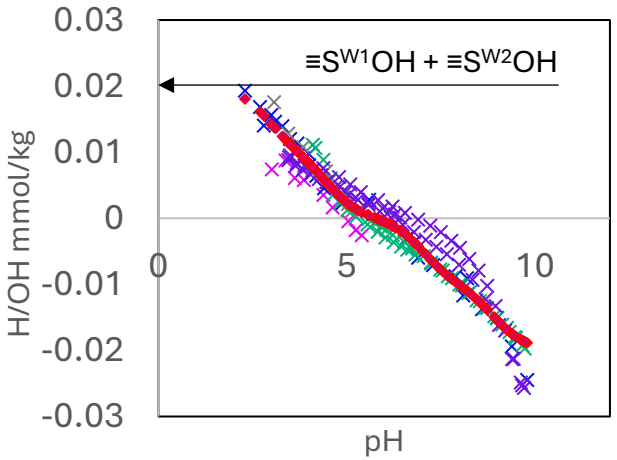
Strong edge sites capacity:
linear part of sorption isotherm



Ni sorption isotherm
on montmorillonite
(experimental data Baeyens, B., Bradbury, M.H., 1997. J. Contam. Hydrol.)

The strong edge site capacity for both illite and montmorillonite was constrained as
2 x 10^{-3} mol kg^{-1}

Weak edge sites capacity: acid-base titration data



Kaolinite titration data and model

- *Schroth et al. 1997 KGa-1*
- *Baeyens (unpub.)*
- *Heidman et al. 2005*
- *Schroth et al. 1997 KGa-2*
- *Tombácz & Szekeres 2006*
- *model*

- The weak edge site capacity (≡S^{W1}OH + ≡S^{W2}OH) of kaolinite is **~ 4 times** lower than that of illite and montmorillonite
- There were no sufficient evidence to justify **strong edge sites** inclusion into the model

Planar sites capacity = cation exchange capacity (CEC)
Accepted capacity for planar sites: **0.02** mol kg-1 as for KGa-1-b (the Clay Min. Society)

Fixed parameters of 2SPNE SC/CE model for illite, kaolinite, and montmorillonite

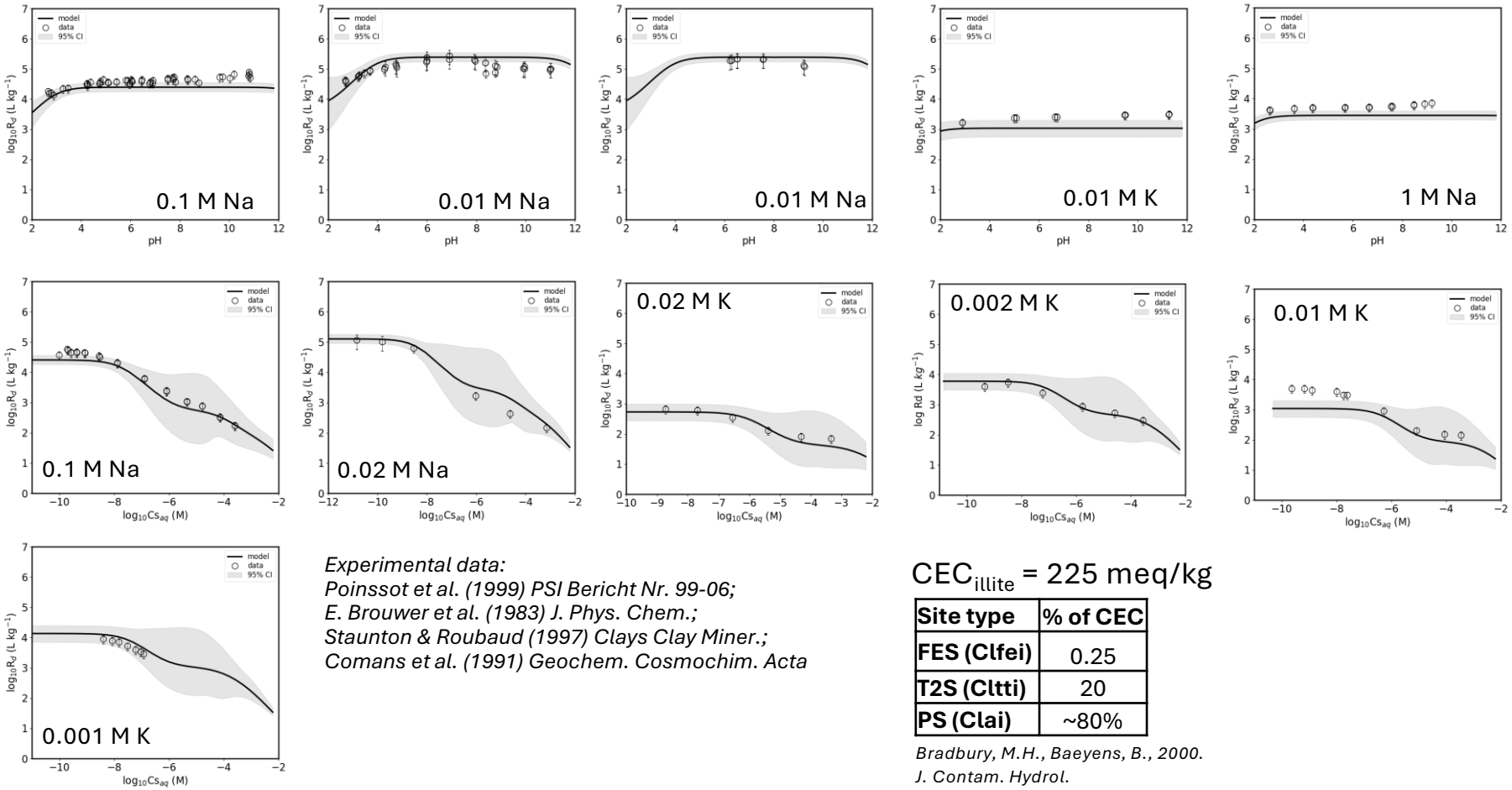
Site type	Na^+-montmorillonite		Na^+-illite		Na+-kaolinite	
Planar exchange sites	**Capacity (mol/kg)**					
nClay-Na + $M^{n+} \leftrightarrow$ Clay-M + nNa^+	8.7×10^{-1}		2.25×10^{-1}		2.0×10^{-2}	
Amphoteric edge sites						
$\equiv S^{S}OH$	2.0×10^{-3}		2.0×10^{-3}		---	
$\equiv S^{W1}OH$	4.0×10^{-2}		4.0×10^{-2}		1.0×10^{-2}	
$\equiv S^{W2}OH$	4.0×10^{-2}		4.0×10^{-2}		1.0×10^{-2}	
	logK					
Protolysis reactions	$\equiv S^{S/W1}OH$	$\equiv S^{W2}OH$	$\equiv S^{S/W1}OH$	$\equiv S^{W2}OH$	$\equiv S^{W1}OH$	$\equiv S^{W2}OH$
$\equiv SOH + H^+ \leftrightarrow \equiv SOH_2^+$	3.75*	5.93*	3.91*	8.85*	2.91	7.04
$\equiv SOH \leftrightarrow \equiv SO^- + H^+$	-8.68*	-10.55*	-5.88*	-10.43*	-4.51	-8.91

- The protolysis constants for both illite and montmorillonite were **re-evaluated*** in comparison with those previously established for the 2SPNE SC/CE model (*Baeyens, B., Bradbury, M.H., 1997. J. Contam. Hydrol.; Bradbury, M.H., Baeyens, B., 1997. J. Contam. Hydrol.; Bradbury, M.H., Baeyens, B., 2009 (Part I and II). Geochim. Cosmochim. Acta)*
- The protolysis constants for kaolinite were evaluated in this work

Sorption modelling based on experimental data

example of clays

- Modelling of Cs(I) sorption on illite



Experimental data:
Poinssot et al. (1999) PSI Bericht Nr. 99-06;
E. Brouwer et al. (1983) J. Phys. Chem.;
Staunton & Roubaud (1997) Clays Clay Miner.;
Comans et al. (1991) Geochem. Cosmochim. Acta

Selectivity coefficients for Cs(I) on illite derived from **experimental data**

Reaction	logK	err
ClaiCs@	1.49	0.74
ClfeiCs@	6.64	0.05
CltiCs@	3.03	0.85

CEC_{illite} = 225 meq/kg

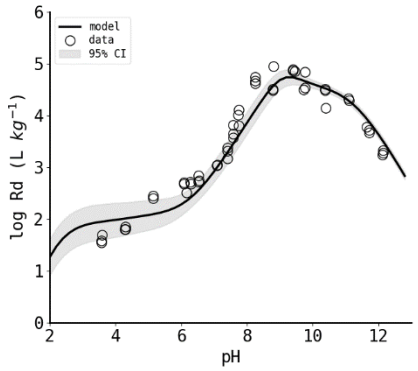
Site type	% of CEC
FES (Clfei)	0.25
T2S (Cltti)	20
PS (Clai)	~80%

Bradbury, M.H., Baeyens, B., 2000. J. Contam. Hydrol.

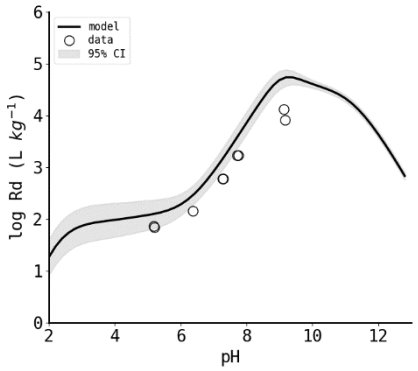
Sorption modelling based on experimental data

example of clays

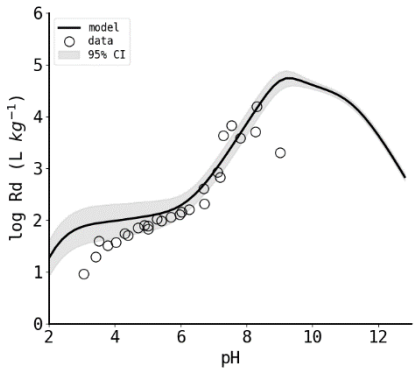
- Modelling of Ni(II) sorption on kaolinite



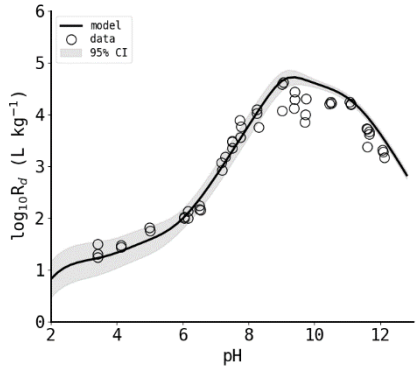
0.01 M NaClO4; exp. data: unpub. data by B.Baeyens



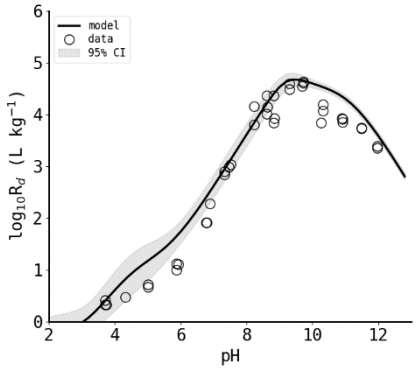
0.01 M NaNO3; exp. data Ervanne et al., 2013, Posiva working report 2013-31



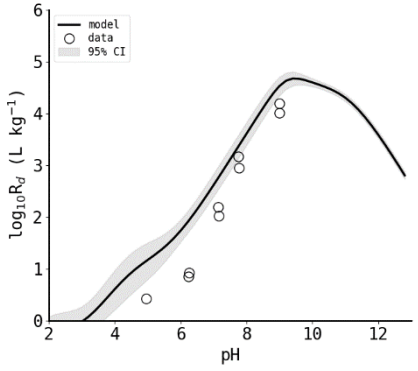
0.01 M NaNO3; exp. data Gu & Evans, 2008, Geochim. Cosmochim. Acta



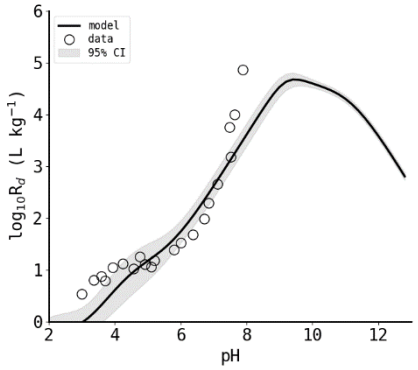
0.023 M NaClO4; exp. data: unpub. data by B.Baeyens



0.1 M NaClO4; exp. data: unpub. data by B.Baeyens



0.1 M NaNO3; exp. data Ervanne et al., 2013, Posiva working report 2013-31



0.1 M NaNO3; exp. data Gu & Evans, 2008, Geochim. Cosmochim. Acta

Surface complexation constants for Ni(II) on kaolinite derived from **experimental data**

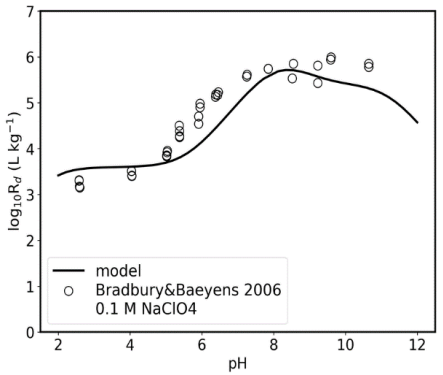
Reaction	logK	err
2ClakNa@ + Ni+2 = Clak2Ni@ + 2Na+	-0.25	0.18
=kSvOH@ + Ni+2 + 2H2O = =kSvONi(OH)2- + 3H+	-16.25	0.07
=kSvOH@ + Ni+2 = =kSvONi+ + H+	-0.94	0.24
=kSvOH@ + Ni+2 + H2O = =kSvONi(OH)@+ 2H+	-6.50	0.12

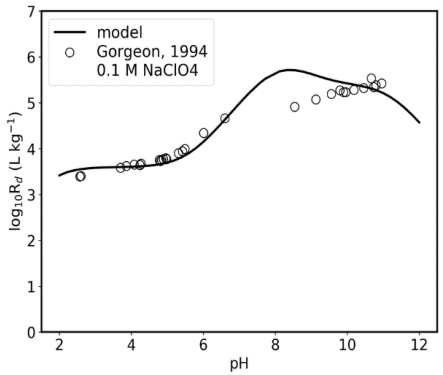
Sorption modelling based on experimental data

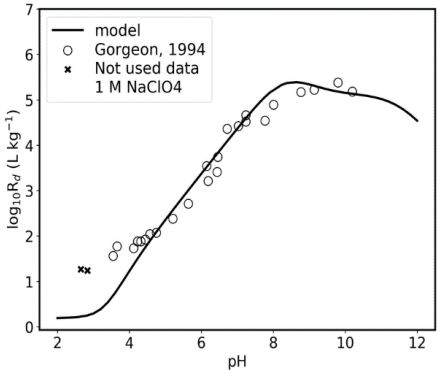
example of clays

- Modelling of Am(III) sorption on montmorillonite

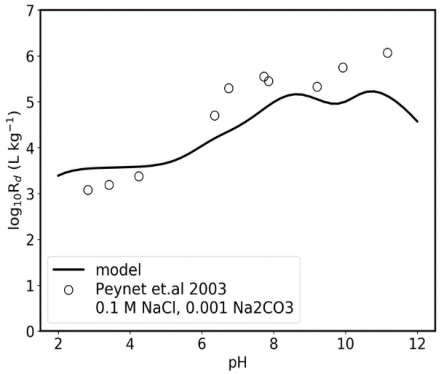
No carbonates in the systems

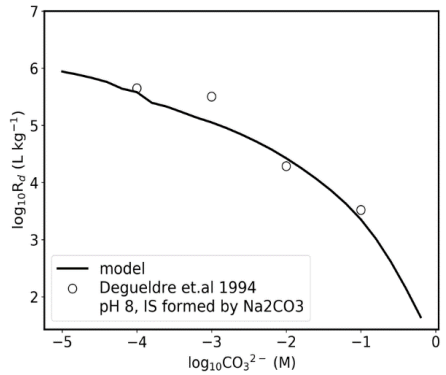






Carbonate-containing systems





Surface complexation constants for Am(III) on montmorillonite derived from **experimental data**

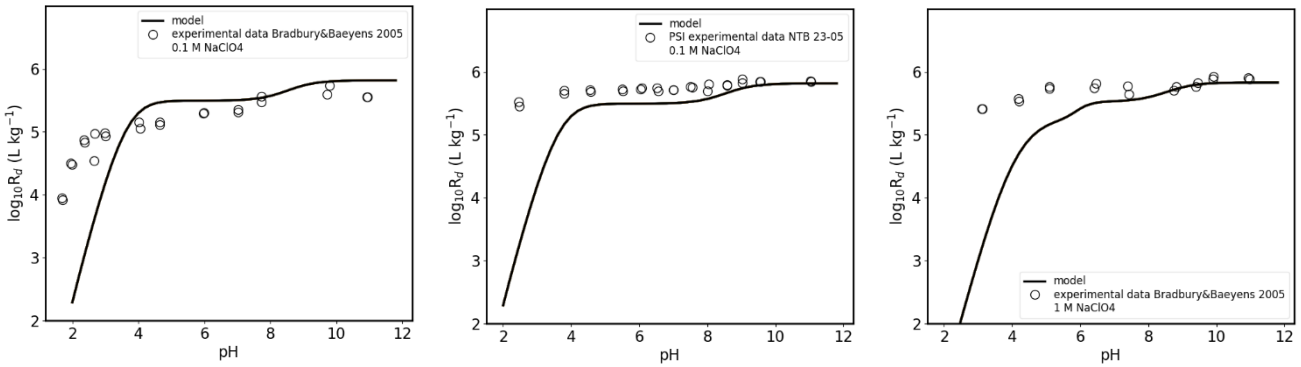
Reaction	logK
3ClayNa@ + Am+3 = ClayAm@ + 3Na+	1.32
=SsOH@ + Am+3 + 2H2O = =SsOAm(OH)2@ + 3H+	-15.56
=SsOH@ + Am+3 = =SsOAm+2 + H+	1.68
=SsOH@ + Am+3 + CO3-2 = =SsOAmCO3@ + H+	7.86
=SsOH@ + Am+3 + H2O = =SsOAmOH+ + 2H+	-6.32
=SvOH@ + Am+3 + 2H2O = =SvOAm(OH)2@ + 3H+	-18.36
=SvOH@ + Am+3 = =SvOAm+2 + H+	-1.12
=SvOH@ + Am+3 + CO3-2 = =SvOAmCO3@ + H+	5.06
=SvOH@ + Am+3 + H2O = =SvOAmOH+ + 2H+	-9.12

Sorption modelling based on experimental data

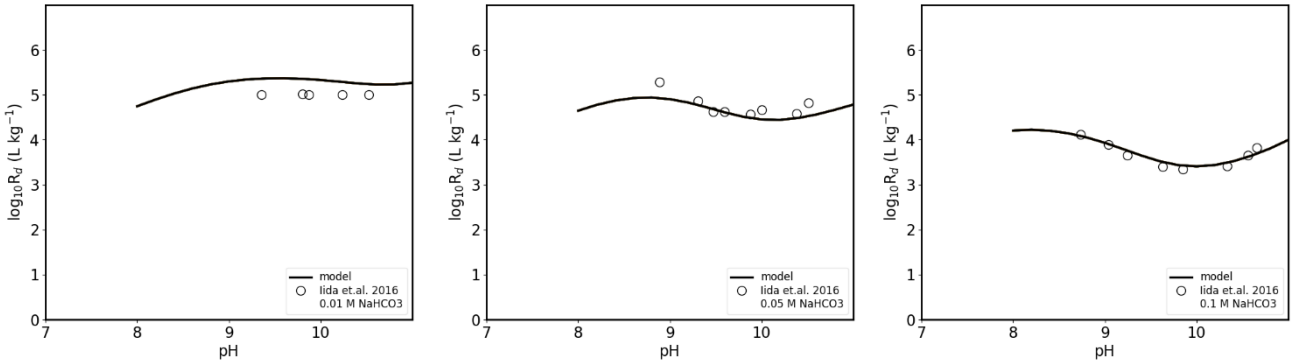
example of clays

- Modelling of Th(IV) sorption on montmorillonite

No carbonates in the systems



Carbonate-containing systems



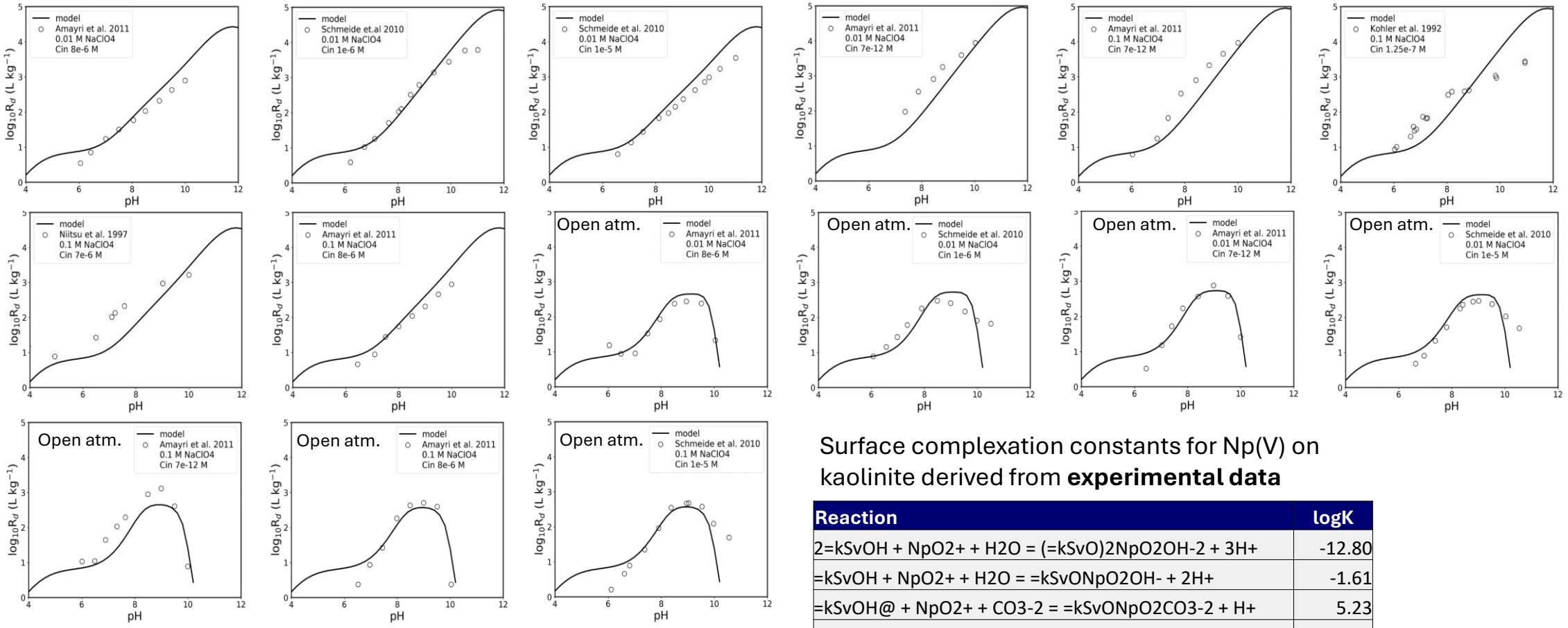
Surface complexation constants for Th(IV) on montmorillonite derived from **experimental data**

Reaction	logK
=SsOH@ + Th+4 + 3H2O = =SsOTh(OH)3 + 4H+	-9.22
=SsOH@ + Th+4 + 4H2O = =SsOTh(OH)4- + 5H+	-17.58
=SsOH@ + Th+4 = =SsOTh+3 + H+	6.75
=SsOH@ + Th+4 + H2O = =SsOThOH+2 + 2H+	2.40
=SsOH@ + Th+4 + 2OH- + 2CO3-2 = =SsOTh(OH)2(CO3)2-3 + H+	36.65
=SvOH@ + Th+4 + 3H2O = =SvOTh(OH)3 + 4H+	-12.02
=SvOH@ + Th+4 + 4H2O = =SvOTh(OH)4- + 5H+	-20.38
=SvOH@ + Th+4 = =SvOTh+3 + H+	3.95
=SvOH@ + Th+4 + H2O = =SvOThOH+2 + 2H+	-0.40
=SvOH@ + Th+4 + 2OH- + 2CO3-2 = =SvOTh(OH)2(CO3)2-3 + H+	33.85

Sorption modelling based on experimental data

example of clays

- Modelling of Np(V) sorption on kaolinite



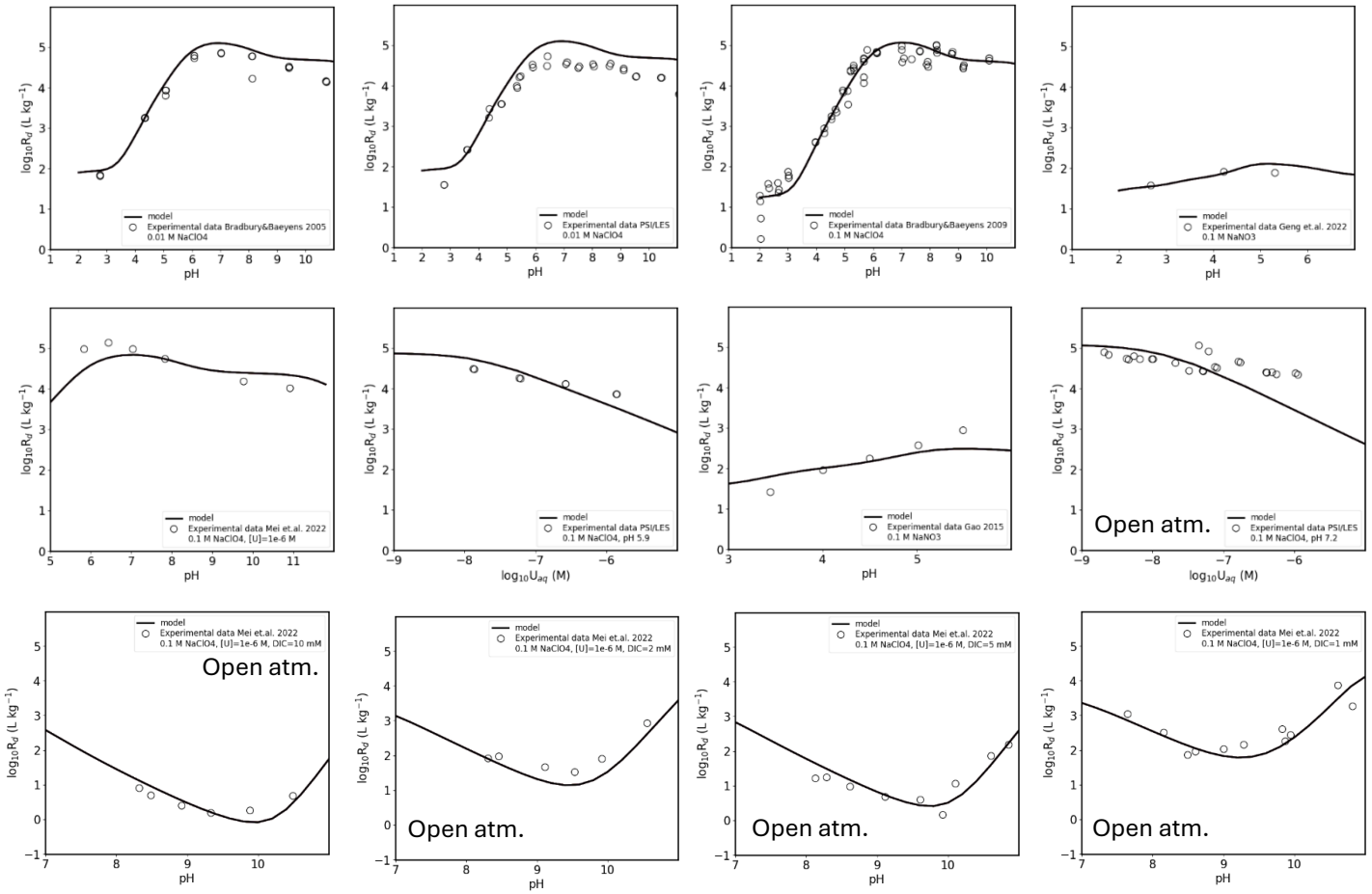
Surface complexation constants for Np(V) on kaolinite derived from **experimental data**

Reaction	logK
2=kSvOH + NpO2+ + H2O = (=kSvO)2NpO2OH-2 + 3H+	-12.80
=kSvOH + NpO2+ + H2O = =kSvONpO2OH- + 2H+	-1.61
=kSvOH@ + NpO2+ + CO3-2 = =kSvONpO2CO3-2 + H+	5.23
=kSvOH@ + NpO2+ + 2CO3-2 = =kSvONpO2(CO3)2-4 + H+	7.55

Sorption modelling based on experimental data

example of clays

- Modelling of U(VI) sorption on illite



Selectivity coefficient wrt. Na^+ and surface complexation constants for U(VI) on illite derived from **experimental data**

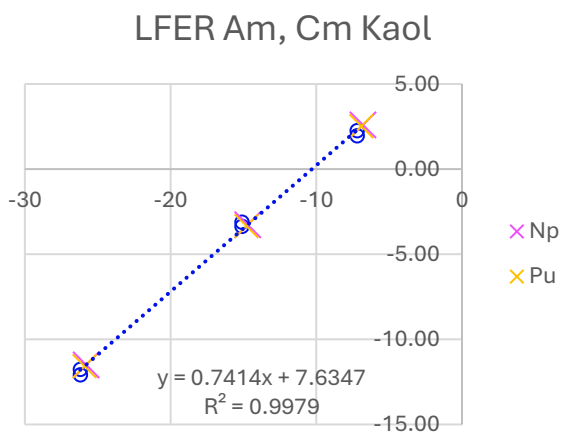
Reaction	logK
2ClaiNa@ + UO2+2 = ClaiUO2@ + 2Na+	0.43
=iSsOH@ + UO2+2 + 2CO3-2 = =iSsOUO2(CO3)2-3 + H+	17.42
=iSsOH@ + UO2+2 + 2H2O = =iSsOUO2(OH)2- + 3H+	-10.23
=iSsOH@ + UO2+2 + 3H2O = =iSsOUO2(OH)3-2 + 4H+	-18.69
=iSsOH@ + UO2+2 = =iSsOUO2+ + H+	1.87
=iSsOH@ + UO2+2 + CO3-2 = =iSsOUO2CO3- + H+	9.68
=iSsOH@ + UO2+2 + H2O = =iSsOUO2(OH)@ + 2H+	-3.18
=iSvOH@ + UO2+2 + 2CO3-2 = =iSvOUO2(CO3)2-3 + H+	14.62
=iSvOH@ + UO2+2 + 2H2O = =iSvOUO2(OH)2- + 3H+	-13.03
=iSvOH@ + UO2+2 + 3H2O = =iSvOUO2(OH)3-2 + 4H+	-21.49
=iSvOH@ + UO2+2 = =iSvOUO2+ + H+	-0.93
=iSvOH@ + UO2+2 + CO3-2 = =iSvOUO2CO3- + H+	6.88
=iSvOH@ + UO2+2 + H2O = =iSvOUO2(OH)@+ 2H+	-5.98

Sorption modelling based on the linear free energy relationship (LFER) approach

example of clays

LFER – common approach, when no sufficient thermodynamic data are available. Here, it is applied to describe the relationship **between** the stability constants of **aqueous** and **surface complexes**

aq. complex	logβ0	surf. complex	logK
Am(OH)3@	-26.2	=kSvOAm(OH)2@	-12.08
AmOH+2	-7.2	=kSvOAm+2	1.96
Am(OH)2+	-15.1	=kSvOAmOH+	-3.37
Cm(OH)3@	-26.2	=kSvOCm(OH)2@	-11.76
CmOH+2	-7.2	=kSvOCm+2	2.27
Cm(OH)2+	-15.1	=kSvOCmOH+	-3.12
PuOH+2	-6.9	=kSvOPu+2	?
Pu(OH)2+	-14.8	=kSvOPuOH+	?
Pu(OH)3@	-25.9	=kSvOPu(OH)2@	?
NpOH+2	-6.8	=kSvONp+2	?
Np(OH)2+	-14.7	=kSvONpOH+	?
Np(OH)3@	-25.8	=kSvONp(OH)2@	?

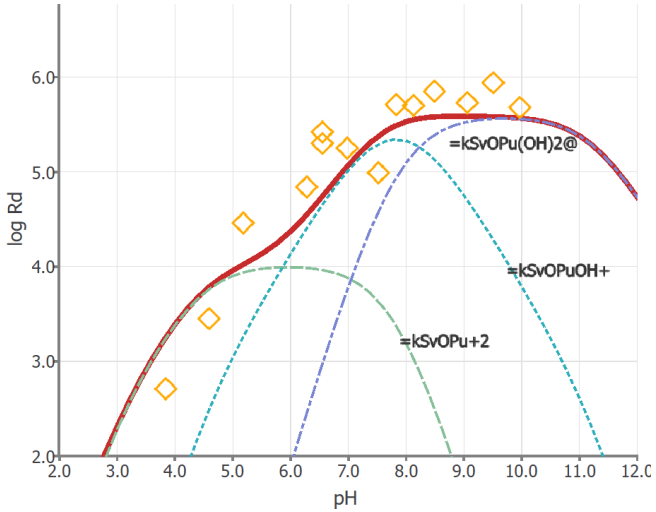


- Filling gaps in the thermodynamic sorption database is essential to avoid large errors in safety assessment calculations
- LFER is a robust approach when experimental data are lacking
- High-quality experimental data are needed to validate LFER-based models

LFER-based surface complexation constants for Np(III) and Pu(III) on kaolinite

Reaction	logK
=kSvOH@ + Np+3 + 2H2O = =kSvONp(OH)2@ + 3H+	-11.49
=kSvOH@ + Np+3 = =kSvONp+2 + H+	2.59
=kSvOH@ + Np+3 + H2O = =kSvONpOH+ + 2H+	-3.26

Reaction	logK
=kSvOH@ + Pu+3 + 2H2O = =kSvOPu(OH)2@ + 3H+	-11.57
=kSvOH@ + Pu+3 = =kSvOPu+2 + H+	2.52
=kSvOH@ + Pu+3 + H2O = =kSvOPuOH+ + 2H+	-3.34

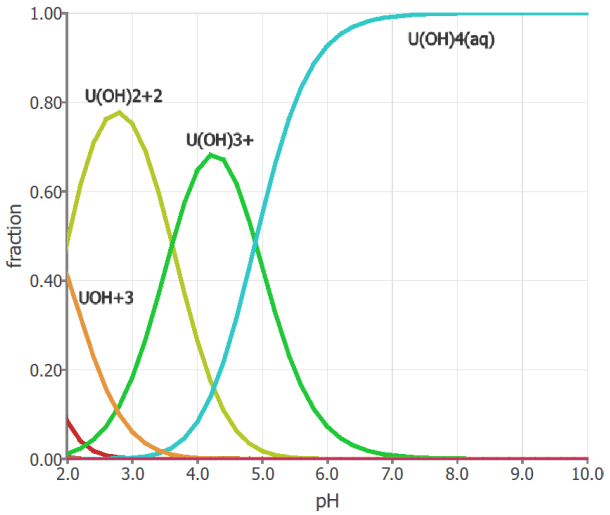


LFER-based model of Pu(III) sorption on kaolinite compared with analogue Cm(III) experimental data *(Samadfam et al., 2010, Radiochim. Acta)*

Analogy-based sorption modelling

example of clays

- LFER is not effective for tetravalent elements because **no corresponding aqueous stability constant** exists to derive the surface complex constant with the generic formula (**=kSvOMe(OH)$_4^-$**), which covers the biggest pH range in experimental pH edge datasets of Pu(IV) and Th(IV)
- Instead LFER, **Pu(IV)** data are used as an **analogue for U(IV) modelling**



U(IV) aqueous speciation *(TDB 2020 Hummel & Thoenen NTB 21-03)*

A hydrolyzed species of a metal Me with valency (*z*Me):

$$\mathrm{Me(OH)_x^{z_{Me}-x}}$$

A surface complex on an amphoteric surface hydroxyl group:

$$\equiv \mathrm{S^S OMe(OH)_y^{z_{Me}-(y+1)}}$$

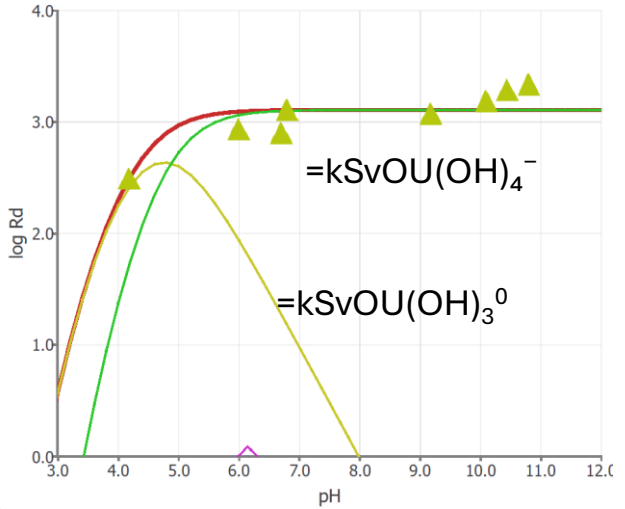
In LFER approach, the surface hydroxyl group ≡SOH is considered analogous to one hydroxyl ion, therefore x and y are related as:

$$x = y + 1$$

Thus, the aqueous complex corresponding to the surface complex ≡kSvOMe(OH)$_4^-$ would be **Me(OH)$_5^{2-}$**, which **is not included in thermodynamic databases** (if it exists at all)

Analogy-based surface complexation constants for **U(IV)** on kaolinite

Reaction	logK
=kSvOH@ + U+4 + 3H2O = =kSvOU(OH)3@ + 4H+	4.56
=kSvOH@ + U+4 + 4H2O = =kSvOU(OH)4- + 5H+	-0.31



Analogy-based model of **U(IV)** sorption on kaolinite compared with analogue **Pu(IV)** *(experimental data Banik et al., 2007, Radiochim. Acta)*

Outlook

- Improving the sorption model for **complex cases**, such as the sorption of polyvalent elements in the presence of atmospheric CO_2
- Testing the model using a bottom-up approach based on sorption data obtained from **real rocks** (Opalinus Clay) and **porewater**
- Parametrizing the sorption model for other elements, incl. **major ions and chemotoxic** elements
- Investigating **competitive sorption** effects of various metals
- Effect of **organic ligands** on radionuclide sorption
- Effect of **temperature** on radionuclide sorption
- Improving **uncertainty** analysis

Thank you for your attention!

Questions? Suggestions?

or mailto: olha.marinich@psi.ch

My grateful thanks to

- Dr. George-Dan Miron
- Dr. Maria Marques Fernandes
- Dr. Dmitrii Kulik
- Dr. Bart Baeyens
- Prof. Dr. Sergey Churakov
- HZDR team: Dr. Frank Bok, Dr. Susanne Zechel, Dr. Vinzenz Brendler - for accepting me on board for this project and collaboration
- BGE BUNDESGESELLSCHAFT FÜR ENDLAGERUNG for the project funding