Radionuclide migration in a single fracture from Äspö, Sweden: Experiments and reactive transport modeling

F. Huber[1], P. Trinchero[2], J. Molinero[2] & Th. Schäfer[1]

[1]Karlsruhe Institut für Technologie, Institute for Nuclear Waste Disposal (KIT-INE)
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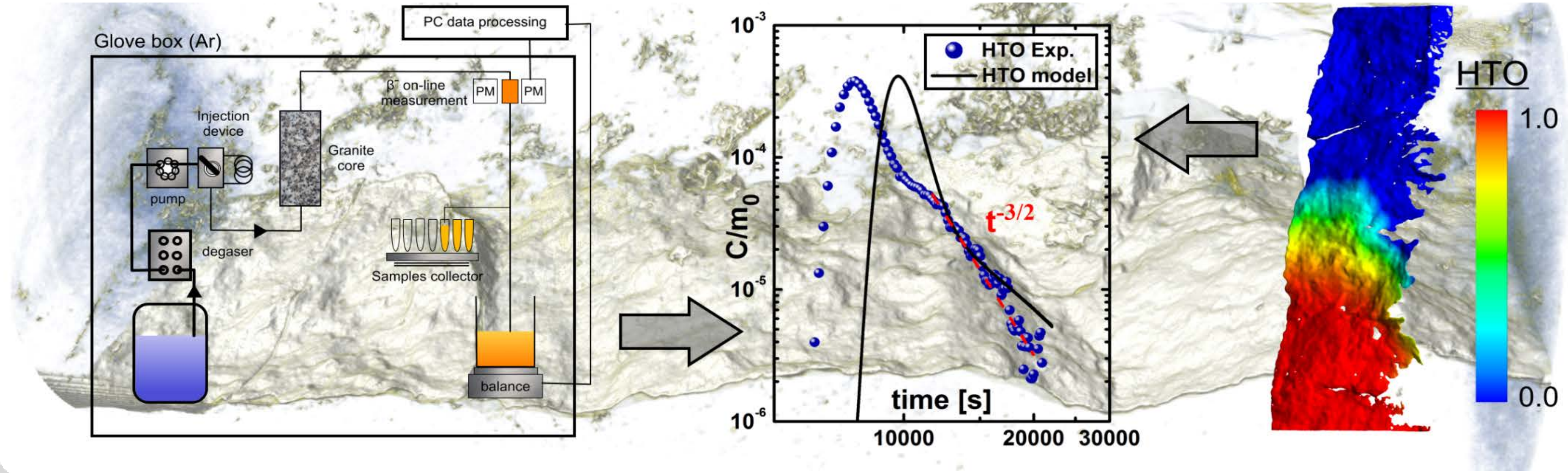


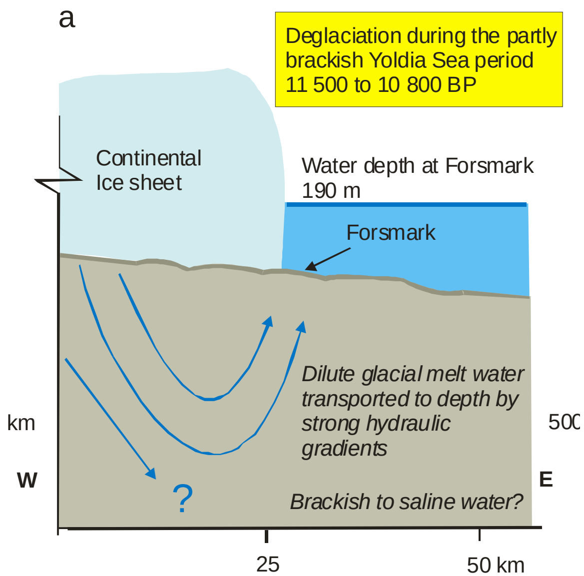
Outline

- Introduction
- Core characterization
- Migration experiments
  - Setup
  - Geochemical conditions
  - Results
- Modeling
  - 3D flow
  - Reactive transport modeling
    - FASTREACT
      - Plan A
      - Plan B
        - First results
- Summary & Conclusions
- Outlook

Introduction

- One of the reference scenarios in the Swedish safety case is the infiltration of glacial melt water (low ionic strength, oxidizing Eh, high pH) down to repository depth
- Geochemical perturbation influence and alter migration behavior of released radionuclides
- Ground water may lead to erosion of buffer material and formation of bentonite colloids which migrate into the far field (==> **colloid facilitated RN transport**)

➡ Study the influence of glacial melt water conditions on RN migration by means of batch and **migration experiments and modeling** on a fractured diorite drill core from Äspö, Sweden.

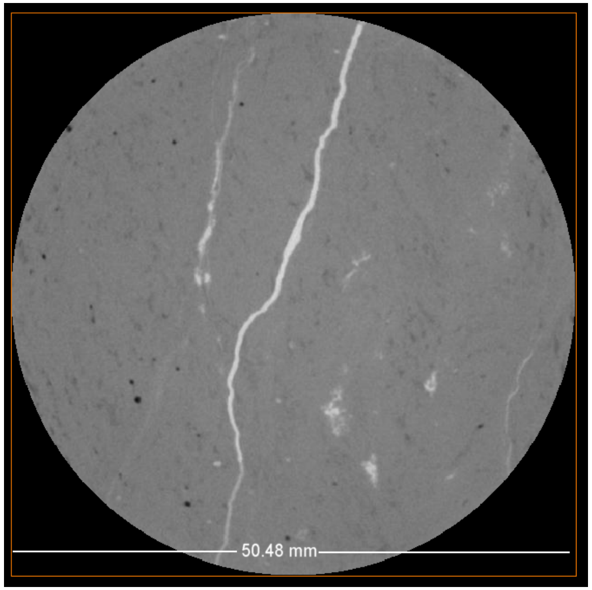


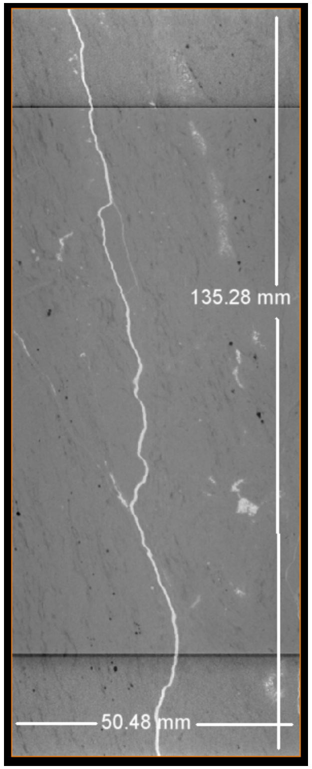
Core characterisation by computed tomography (CT)

F. Enzmann / Inst. f. Geowissenschaften

slices through 3D raw CT data in 8bit gray scale

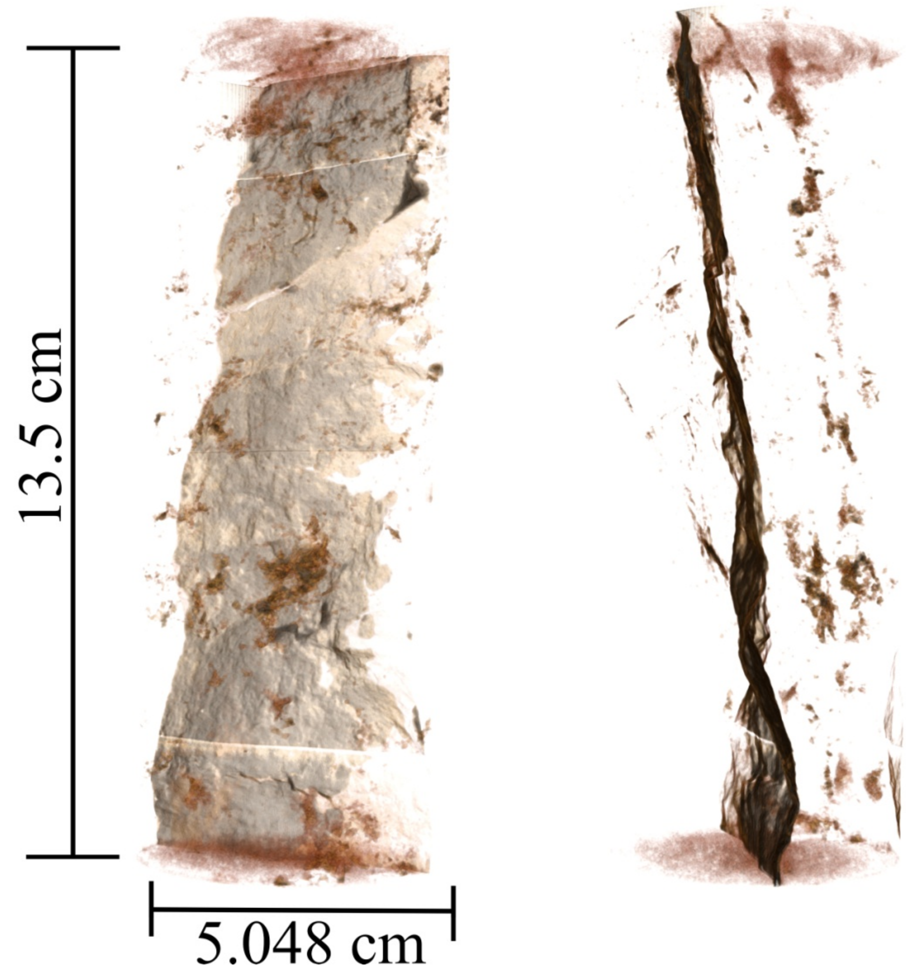
- data dimension: 631 x 631 x 1691 voxel @ 80 µm resolution
- 1691 slices in z-direction





Core characterisation by computed tomography (CT)

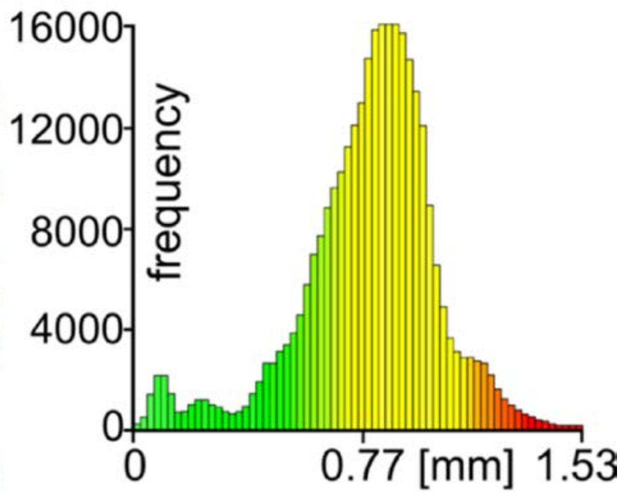
porosity distribution



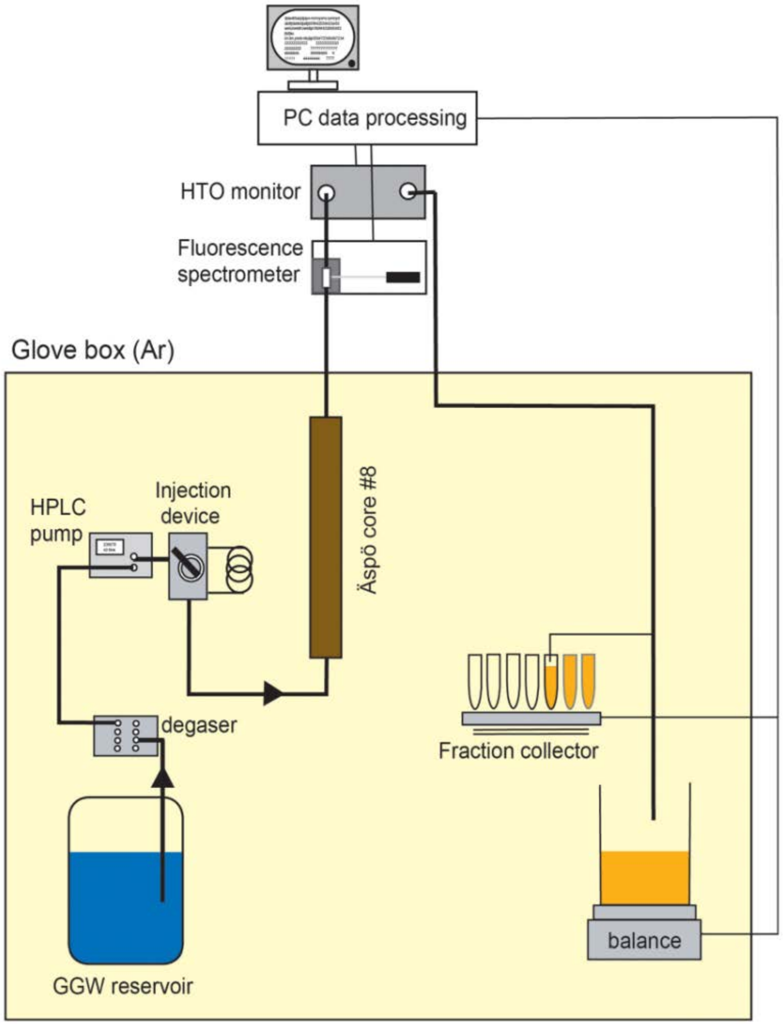
Core characterisation by computed tomography (CT)

aperture distribution

Min aperture [mm]: 0.0
Max aperture [mm]: 1.531
Mean aperture [mm]: 0.4503
Std. deviation [mm]: 0.1385
Variance: 0.0192
Surface area [m^2]: 0.0165
Volume [ml]: 2.70



Experimental setup



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Experimental conditions

Grimsel ground water

	Grimsel GW (MI shearzone) initial
Contact time	12.2.08*
pH	9.67
$Eh_{(SHE)}$	n.d.
$[Mg^{2+}]$	12.6 µg L^{-1}
$[Ca^{2+}]$	5.3 mg L^{-1}
$[Fe^{2+,3+}]$	<DL
$[Mn^{2+}]$	<DL
$[Sr^{2+}]$	182 µg L^{-1}
$[Cs^{+}]$	0.79 µg L^{-1}
$[La^{3+}]$	<DL
[U]	0.028 µg L^{-1}
[Th]	0.00136 µg L^{-1}
$[Al^{3+}]$	42.9 µg L^{-1}
$[Na^{+}]$	14.7 mg L^{-1}
$[Cl^{-}]$	6.7 mg L^{-1}
[Si]	5.6 mg L^{-1}
$[SO_4^{2-}]$	5.8 mg L^{-1}
$[F^{-}]$	6.3 mg L^{-1}
$[Br^{-}]$	n.d.
$[NO_3^{2-}]$	<DL
$[HCO^{3-}]$	3.0 mg L^{-1}

* Sampling date; n.d.: not determined

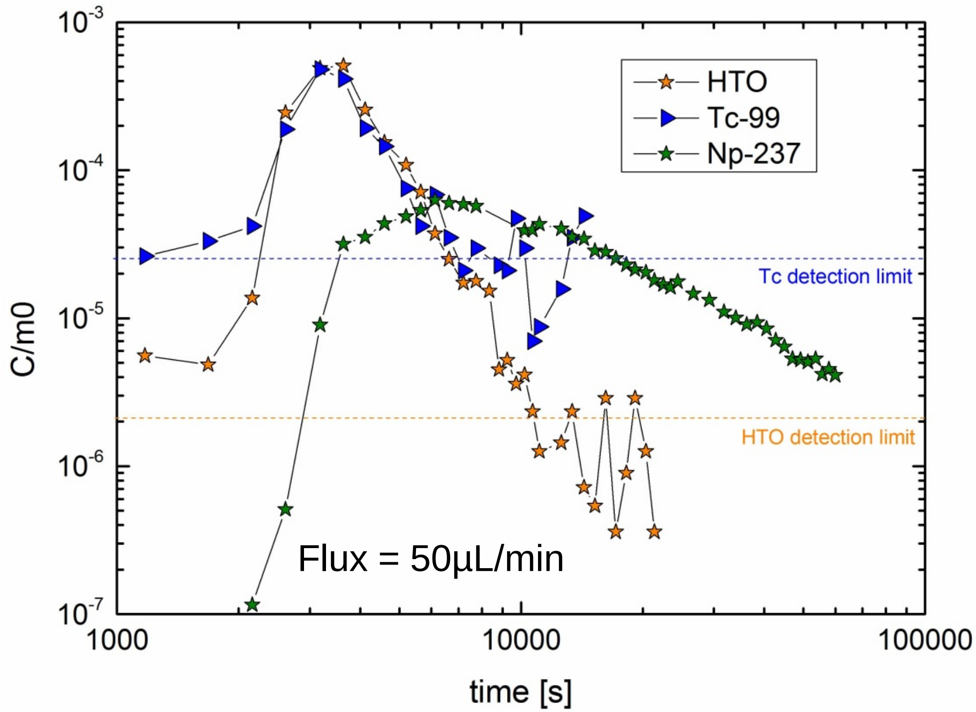
RN cocktail

Grimsel ground water
pH 9.7; I = ~1 mmol/L
Eh = +150 - +200mV
[Febex colloids]: 25.56 mg/L
Conservative tracer: HTO
[Radionuclides]:
$^{243}Am(III)$: 8.0*10^{-9} mol/L
$^{242}Pu(III)$: 1.3*10^{-8} mol/L
$^{232}Th(IV)$: 7.3*10^{-9} mol/L
$^{237}Np(V)$: 1.3*10^{-6} mol/L
$^{233}U(VI)$: 4.3*10^{-7} mol/L
$^{99}Tc(VII)$: 1.0*10^{-8} mol/L

=> Favorable conditions for colloidal transport

RN migration experiments

No colloidal breakthrough



R_p=peak elution time

R_f = retardation factor

$R_f=R_p[RN]/R_p[HTO]$

	Injected mass (mol)	Colloid associated (%)	Recovery (%)	R_p (min)	R_f (-)
HTO	-	0	98	61	1
Al	$9.0 \cdot 10^{-5}$	-	0.9	-	-
Tc-99	$1.5 \cdot 10^{-11}$	0.9	79	53	0.87
Th-232	$1.7 \cdot 10^{-11}$	99.7	2.1	-	-
U-233	$8.0 \cdot 10^{-10}$	1.6	0.2	-	-
Np-237	$1.8 \cdot 10^{-9}$	0.1	76	102	1.8
Pu-242	$3.0 \cdot 10^{-11}$	84.1	3.9	-	-
Am-243	$8.0 \cdot 10^{-9}$	94.8	0.01	-	-

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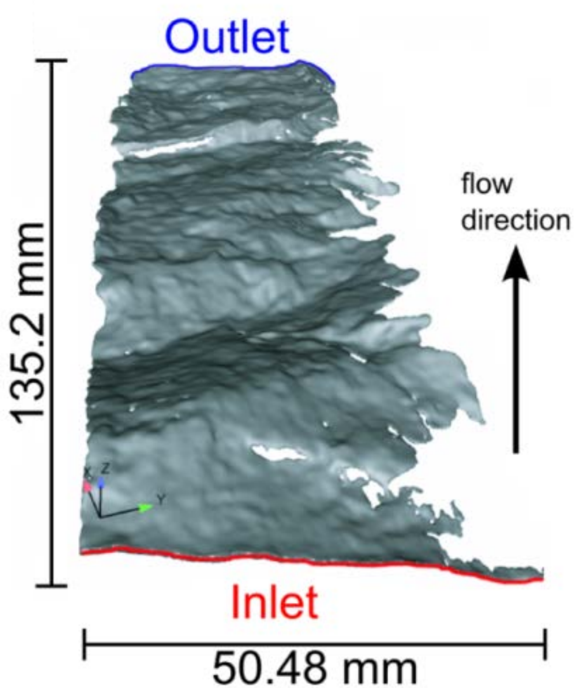
Computational Fluid Dynamics (CFD) simulations

3D model



~10.5 Mio. elements (≈ 3.54 Mio. nodes)

CFD Solver Setup

- **Flow:**
  - incompressible, laminar, steady-state
  - pressure inlets and pressure outlets
  - Navier-Stokes simulations (CFD code: ANSYS Fluent)
- **Transient mass transport:**
  - Diffusion coefficient HTO = 2.5e-9 m^2/s
  - step input ($C = 0$ for $t < 0$; $C = 1$ for $t > 0$)
  - no-slip conditions on fracture walls (= impermeable)

➔ *No matrix diffusion*

Computational Fluid Dynamics (CFD) simulations

3D model

Outlet

135.2 mm

~10.5 Mio. elements
(≈ 3.54 Mio. nodes)

CFD Solver Setup

➢ **Flow:**

walls (= impermeable)

➔ ***No matrix diffusion***

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Natural micro-scale heterogeneity induced solute and nanoparticle retardation in fractured crystalline rock

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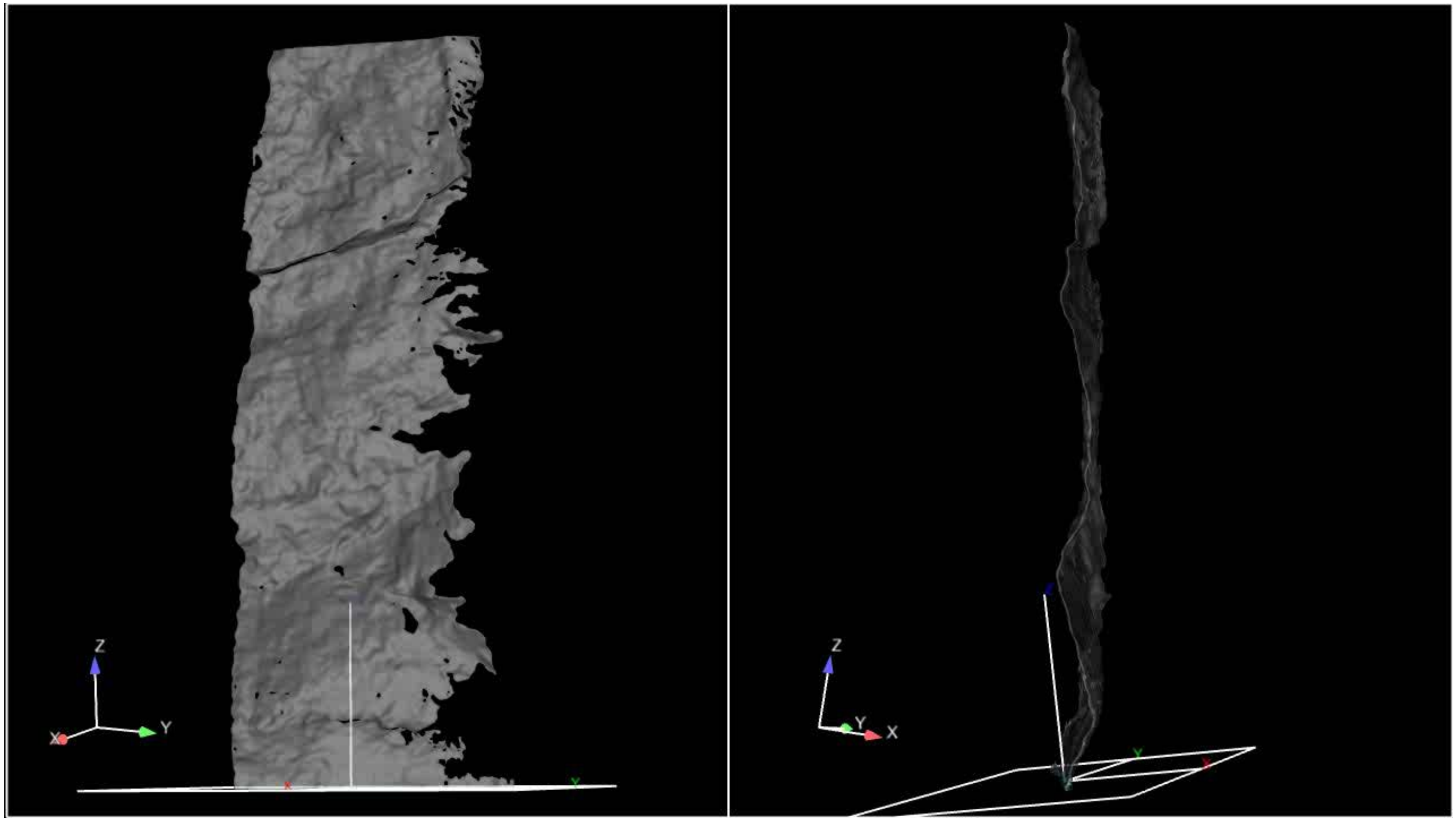
[b] Institute of Geological Sciences, Department of Earth Sciences, Freie Universität Berlin, 14195 Berlin, Germany
[c] University of Mainz, Institute for Geosciences, 55099 Mainz, Germany
[d] Institute of Micro Process Engineering (IMVT), Karlsruhe Institute of Technology (KIT), P.O. Box 3640, 76021 Karlsruhe, Germany
[e] Department of Geosciences, Institute of Environmental Assessment and Water Research (IDAEA-CSIC), C/Jordi Girona, 18, 08034 Barcelona, Spain

3D flow simulation

Flow field



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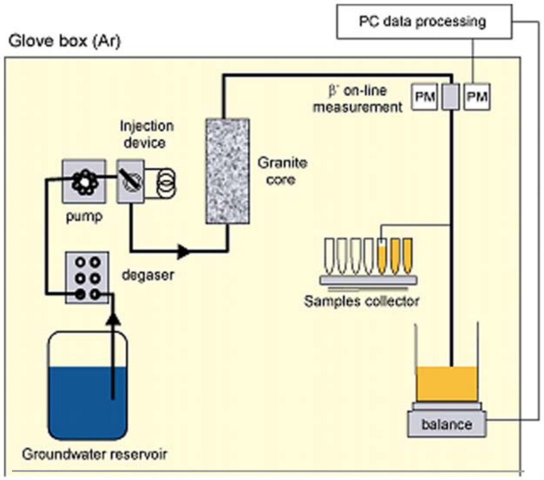
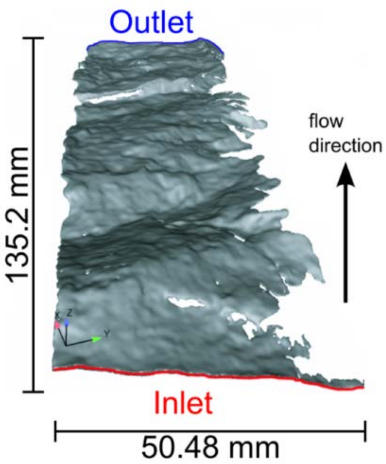
Starting point for reactive transport modeling

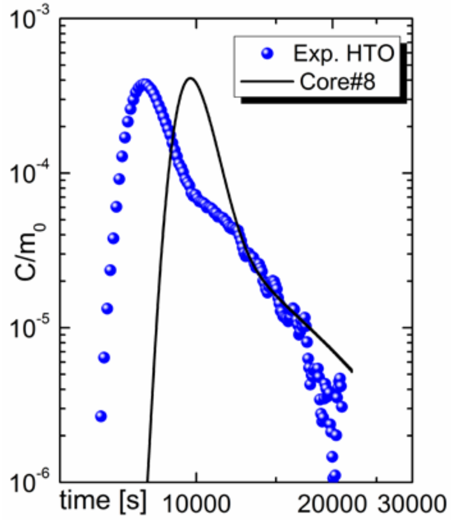
Migration experiments



Core #8

µCT & CFD





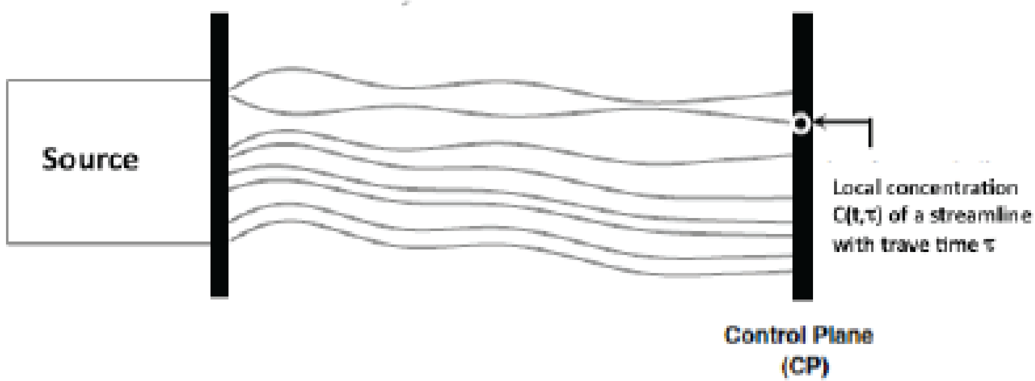
HTO, Tc & Np BTCs

3D flow model

Reactive transport modelling

FASTREACT

- Lagrangian-based framework on basis of Stochastic-Convective (SC) models[1] to efficiently solve multicomponent reactive transport
- Complex 3D problems reduced to a set of 1D models (streamtubes)
- Can be coupled to an arbitrarily geochemical code (**PhreeqC**, etc…)
- Travel time distribution of particles (streamtubes) and a reference reactive transport simulation needed



- Assuming no mass exchange (dispersion, diffusion) between single streamlines, they can be treated independently (advection dominated)
- Tracer breakthrough curves can be described by convolution between inflow concentration and probability density functions of the arrival times of the independent streamlines

1) Shapiro and Cvetkovic (1988), WRR 24(10), 1711-1718

Reactive transport modelling

Approach Plan “A”

3D flow field

↓

Particle tracking

↓

Particle travel time distribution

↓

BTC HTO_{EXP} ⇔ BTC_{PTT}

↓

~~PhreeqC~~

↓

~~FASTREACT~~

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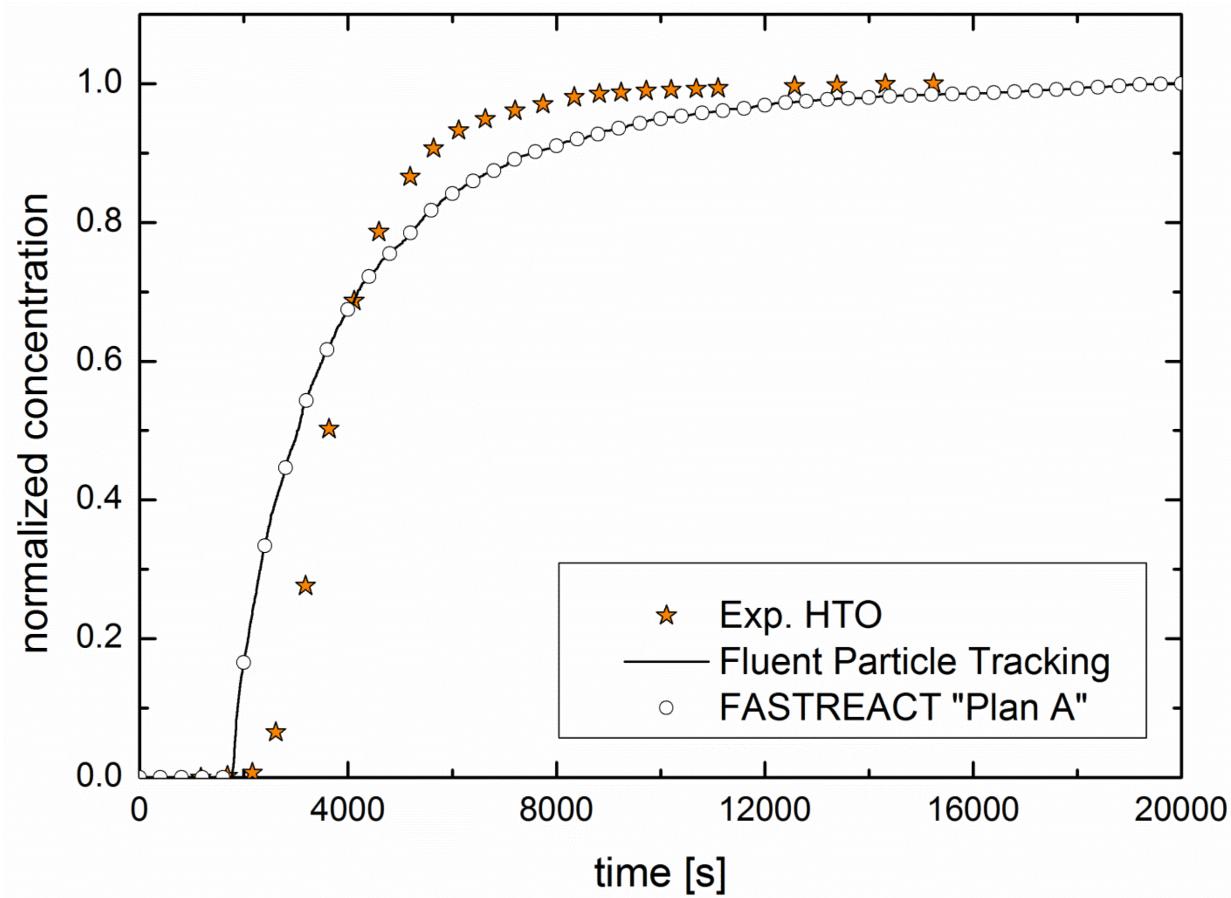
Reactive transport modelling

Plan “A”



Reactive transport modelling

Approach Plan "B"

Fit probability density function (pdf) to exp. HTO BTC

↓

FASTREACT „calibrated“ with pdf to model HTO BTC

↓

Derive Kd from exp. Np BTC

↓

simulate Kd with PhreeqC “batch” (geochemistry) file for NpO_2^+ sorption

↓

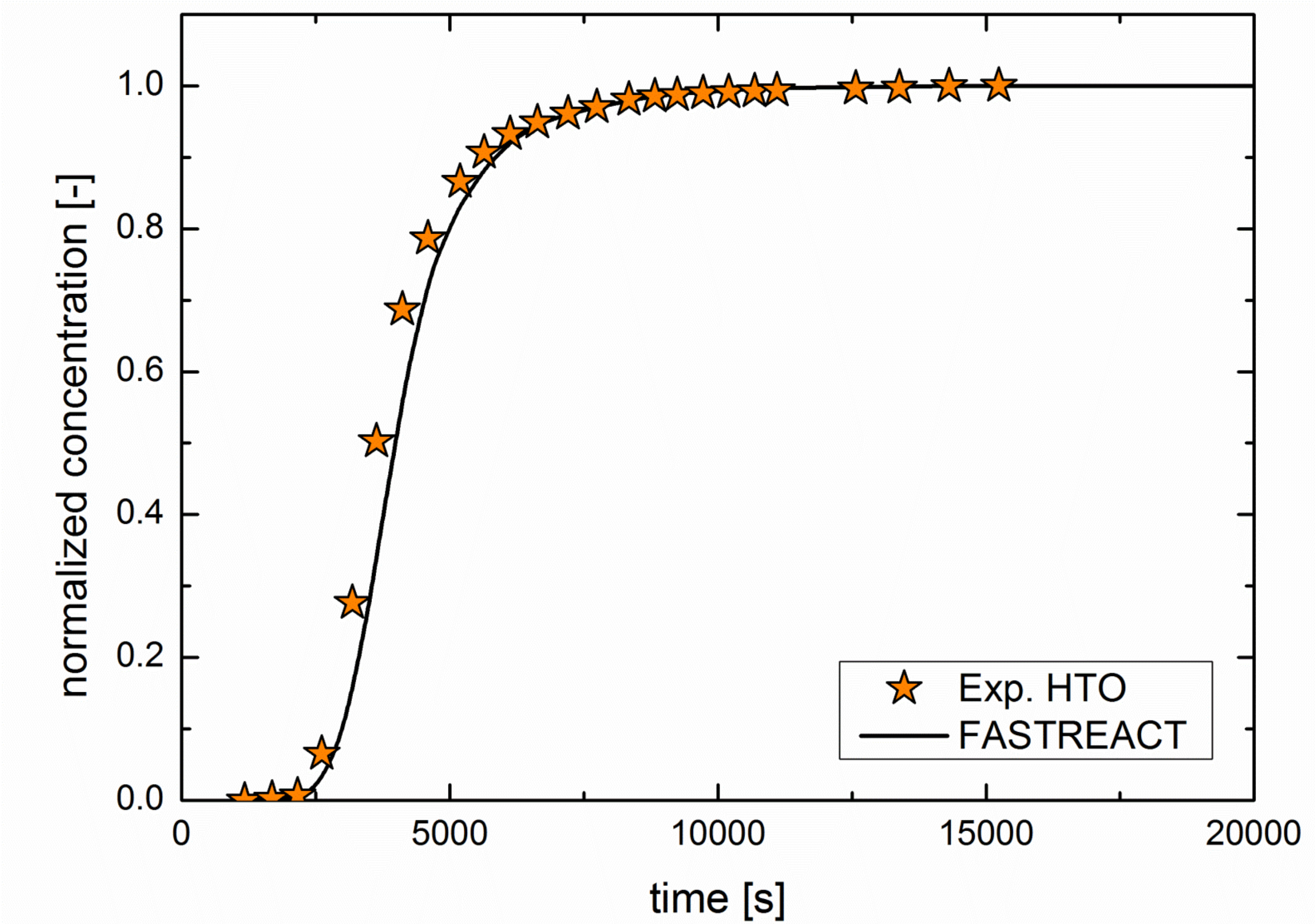
FASTREACT Np transport

↓

Coupling of PEST to FASTREACT to obtain „best-fit“ and vary parameters automatically

Reactive transport modelling

Plan “B”



Reactive transport modelling

Plan B – Conceptual geochemical model

Assumptions:

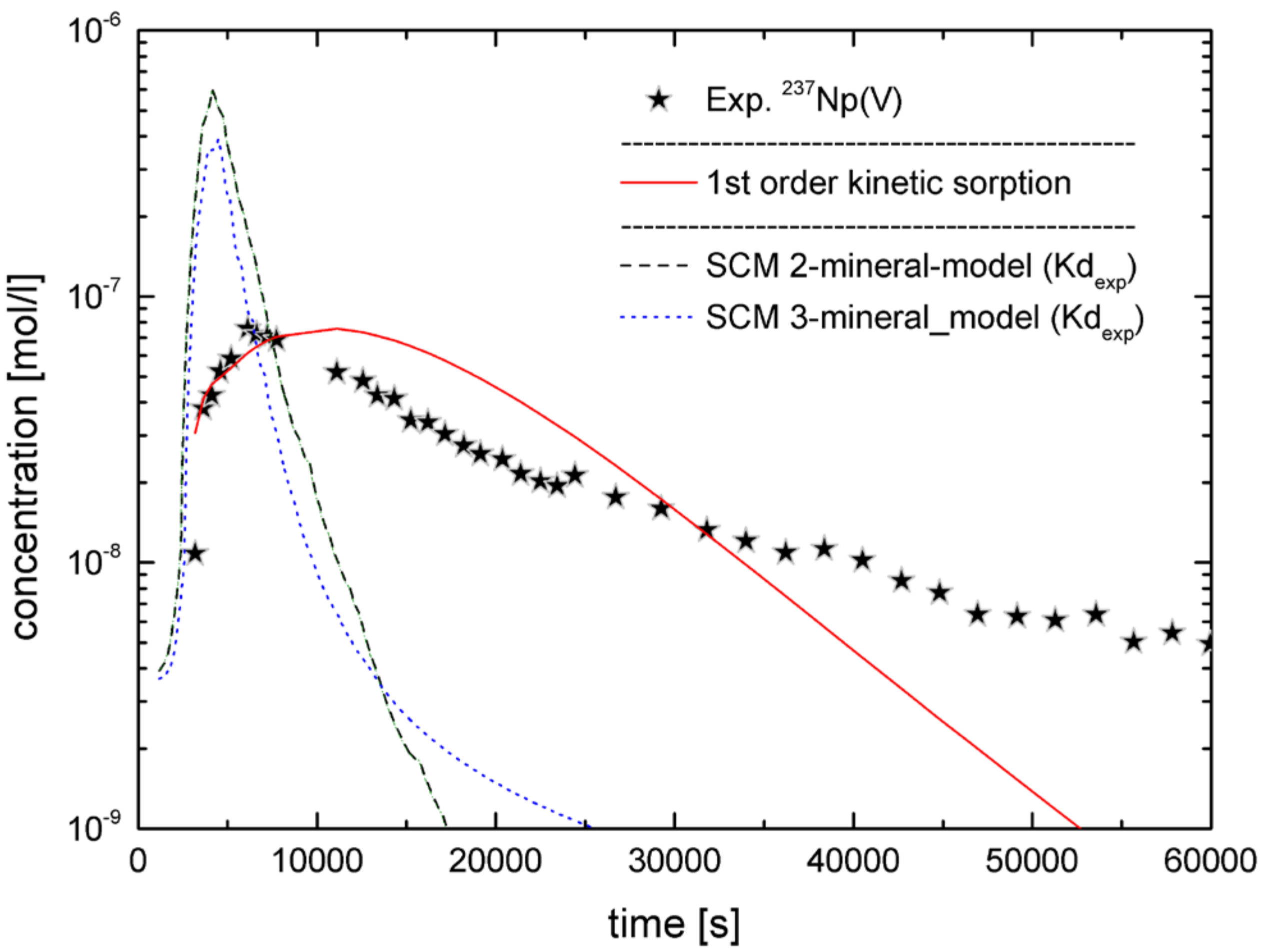
- Grimsel ground water conditions
- Speciation dominated by Np(V) (= no reduction to Np(IV))
- Sorption of Np(V) is dominating retardation process
- (Blind) predictions using SCM models available in literature[1]

  for Np(V) sorption onto ferrihydrite , biotite & kaolinite
- Only fitting parameter is (reactive) surface area = total number of sites

1) Wang et al. (2001), Ind. Eng. Chem. Res. 40, 4428-4443

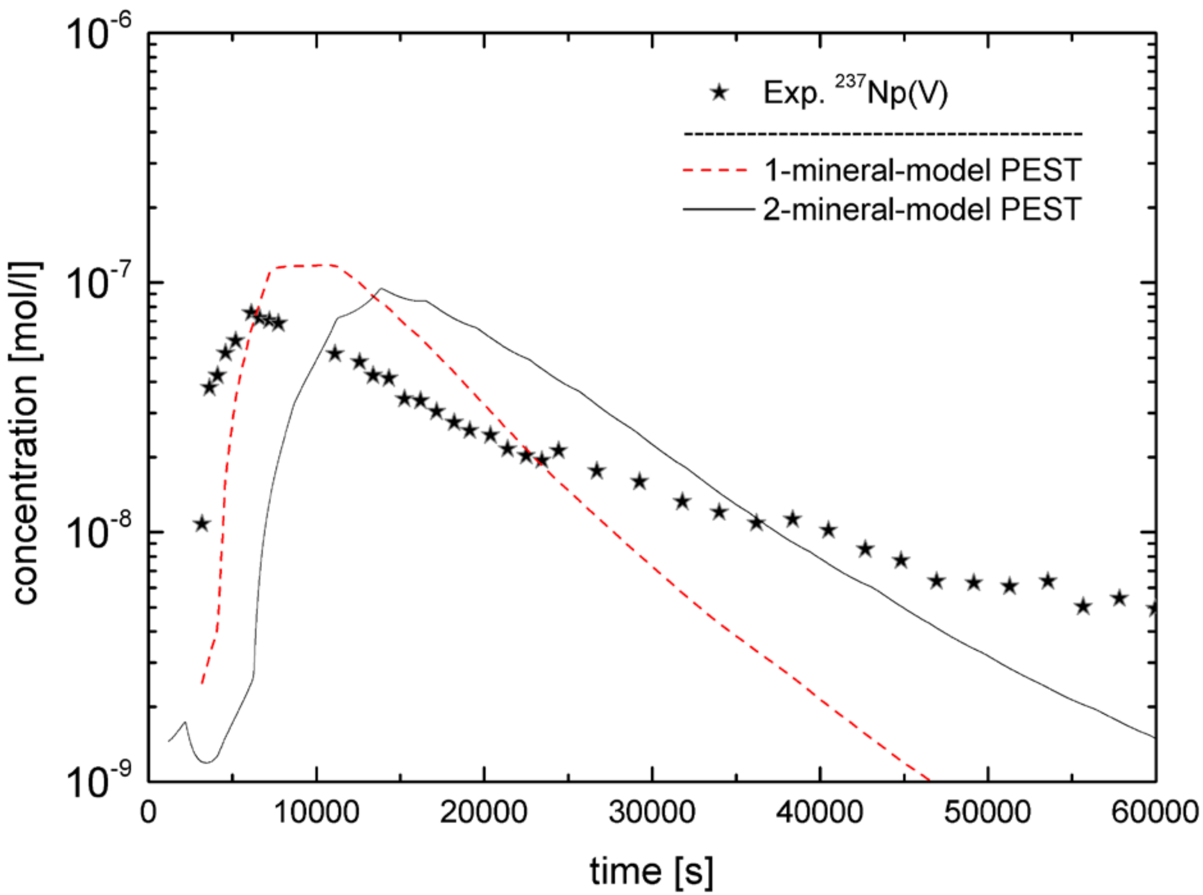
Reactive transport modelling

Plan B – First results



Reactive transport modelling

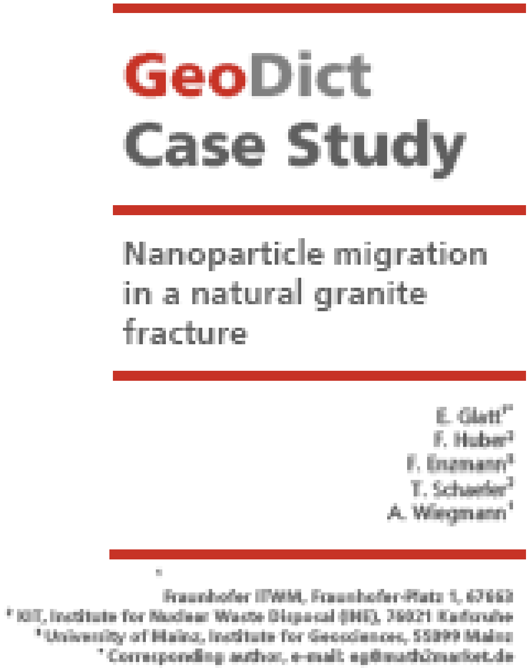
Plan B – First results



Summary & Conclusion

- No breakthrough of bentonite colloids and associated RN although favorable conditions prevail
- Tc behaves like the conservative tracer HTO
- Experimental Np BTC shows pronounced tailing due to interaction with fracture surface via (most likely) sorption processes (no Np reduction observed)
- First application of the framework FASTREACT coupled to PhreeqC and PEST to experimental data
- “Kd-SCM approach” fails in describing exp. Np breakthrough curve
- Fitting of (reactive) surface area provides significantly better results
- More systematic parameter studies are underway:
  - e.g. varying ratio of mineral surfaces
  - …

Outlook



-Developed by the Fraunhofer Institute in Kaiserslautern, Germany

- Collaboration with F. Enzmann (University of Mainz)

Application of GeoDict to model nanoparticle/colloidal transport in µCT derived geometries

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AMPHOS 21
SCIENTIFIC AND STRATEGIC ENVIRONMENTAL CONSULTING

COMSOL Multiphysics® coupled to PhreeqC

Acknowledgement

Funding:

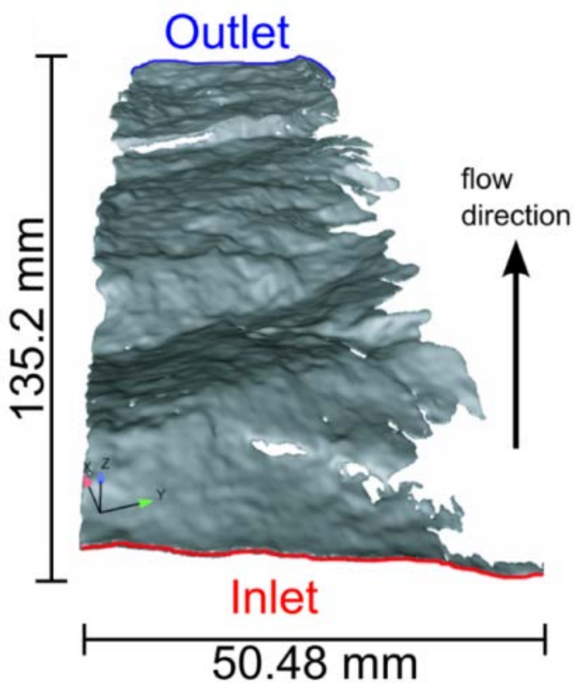
- Federal Ministry of Economics and Technology (BMWi) under the joint FZK-INE, GRS research project "**KOLLORADO & KOLLORADO 2**"
- **SKB/KTH "Colloid project"**
- European Atomic Energy Community Seventh Framework Program [FP7/2007-2013] under Grant Agreement No.212287, **Collaborative Project RECOSY**.
- BELBar ☺

Amphos21

- Marek Pekala
- Cristina Domènech
- Elisenda Colàs
- David Garcia
- Albert Nardi
- ...

Computational Fluid Dynamics (CFD) simulations

3D model



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(≈ 3.54 Mio. nodes)

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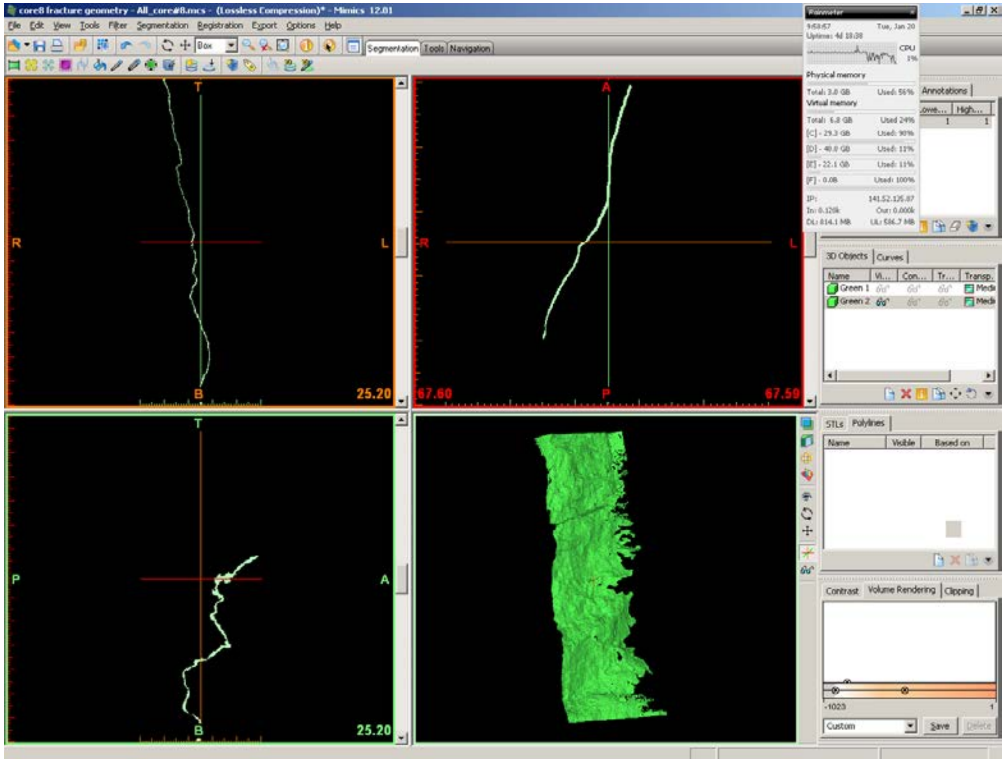
  - no-slip conditions on fracture walls (= impermeable)

➔ *No matrix diffusion*

µCT data processing / mesh generation



- ➢ Import of µCT data (DICOM) in Mimics©
- ➢ Segmentation on basis of threshold grey-values to extract fracture planes
- ➢ Calculation of triangulated 3D fracture surface geometry
- ➢ Export of 3D geometry as STL file for further meshing procedure

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OUTLINE

APPROACH

MIGRATION EXPERIMENTS

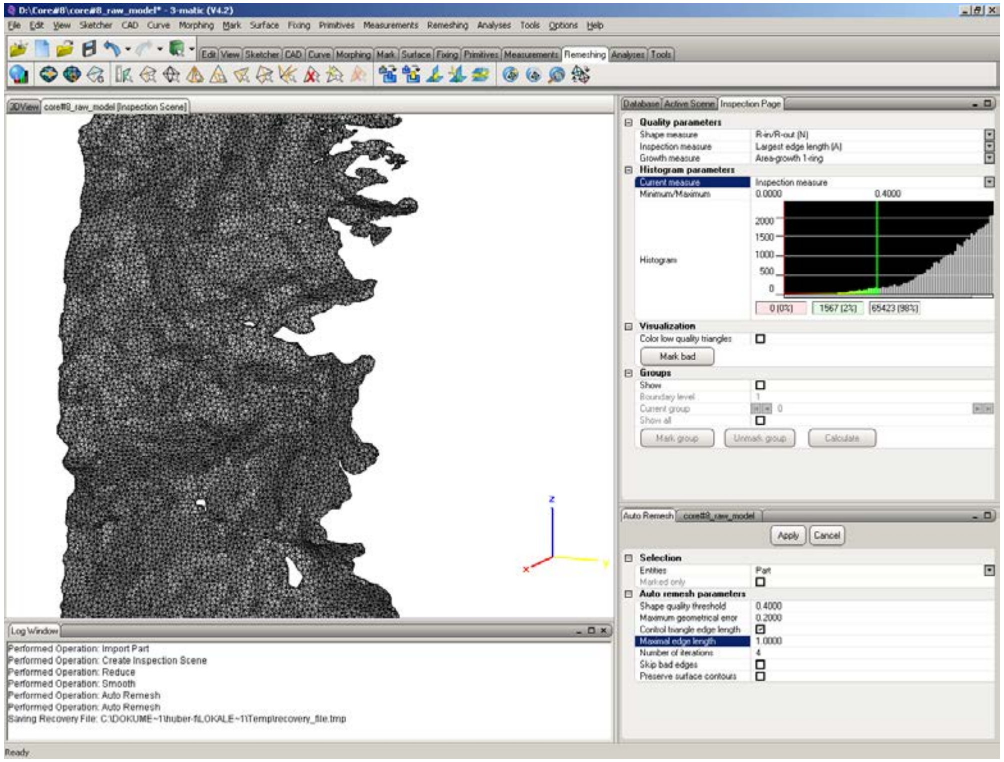
MODELING

- µCT Characterization
- Mesh Generation
- Solver Setup
- Flow Simulations
- Transport Simulations

CONCLUSIONS

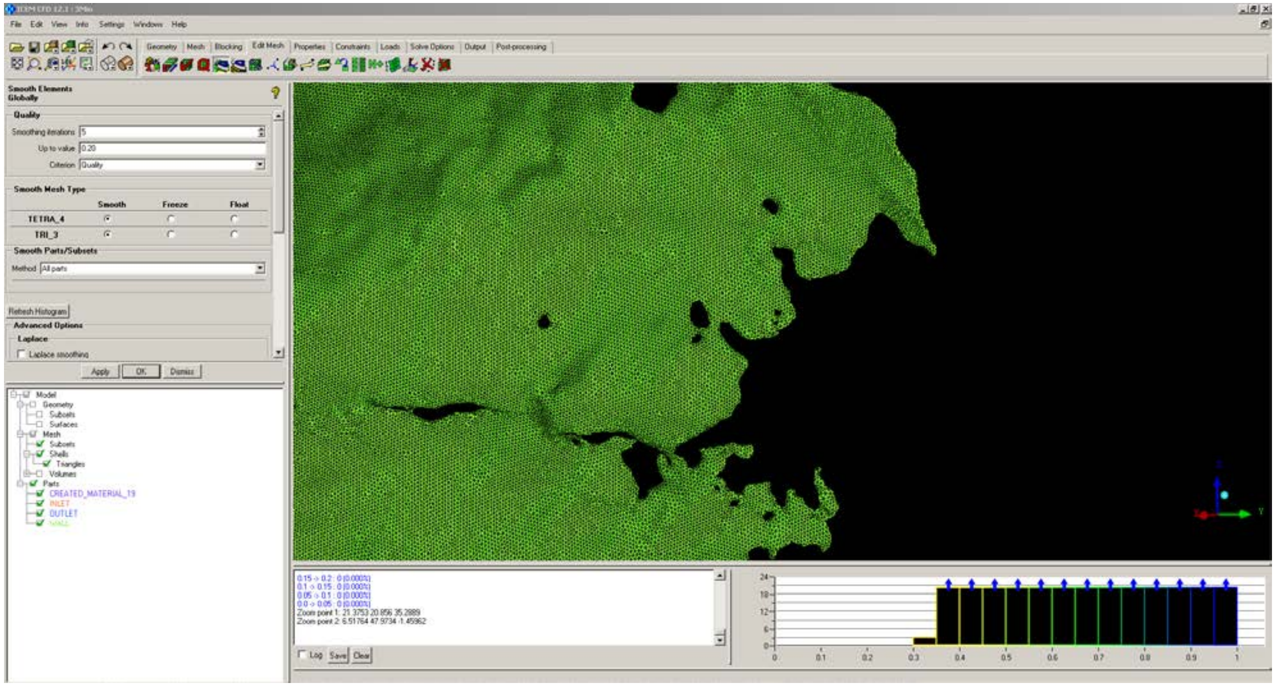
OUTLOOK

µCT data processing / mesh generation



- Import of STL file in 3matic© (RP)
- Surface remeshing on basis of user defined specifications
- Repair and fixing of generated surface mesh (duplicated and/or overlapping elements, „poor“ elements)
- Export of surface mesh as NASTRAN file

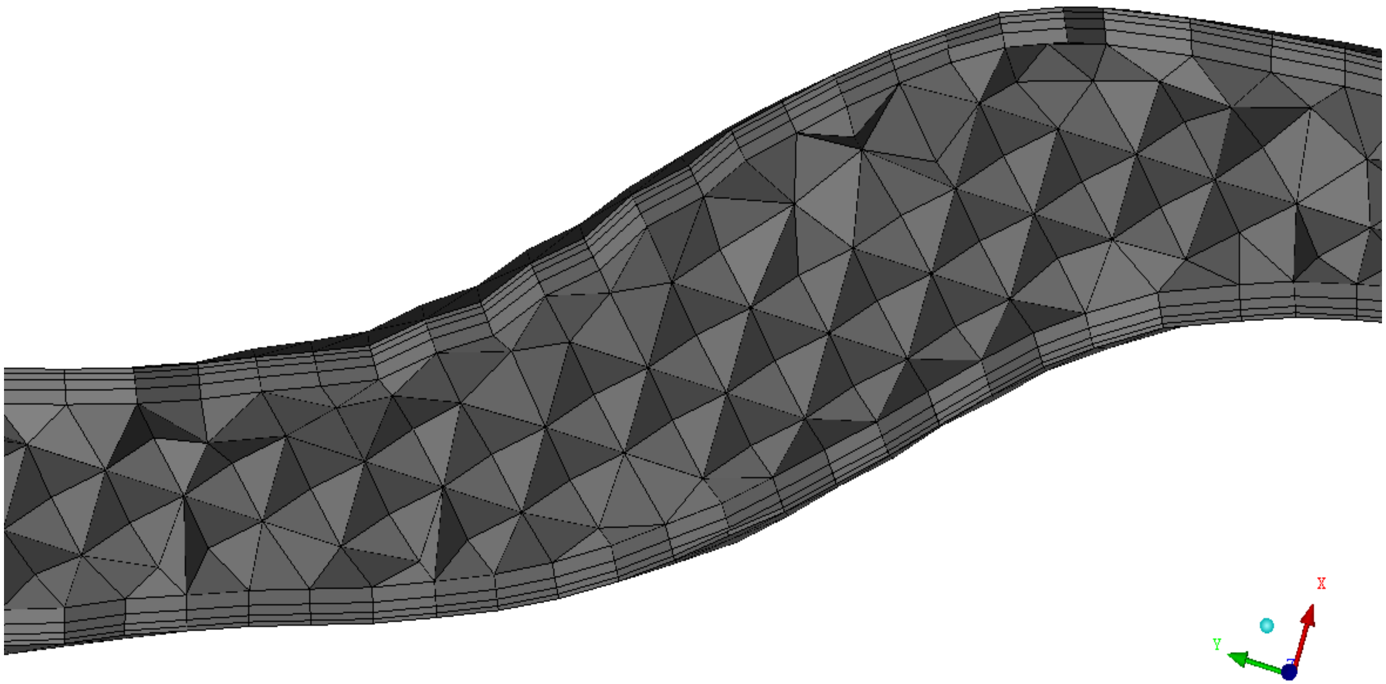
µCT data processing / mesh generation



- ➢ Import of NASTRAN file in ICEM CFD ©
- ➢ Further refinement of surface mesh
- ➢ Generation of mixed (tetras and prisms volume mesh (+ fixing)
- ➢ Export as Fluent © mesh

µCT data processing / mesh generation

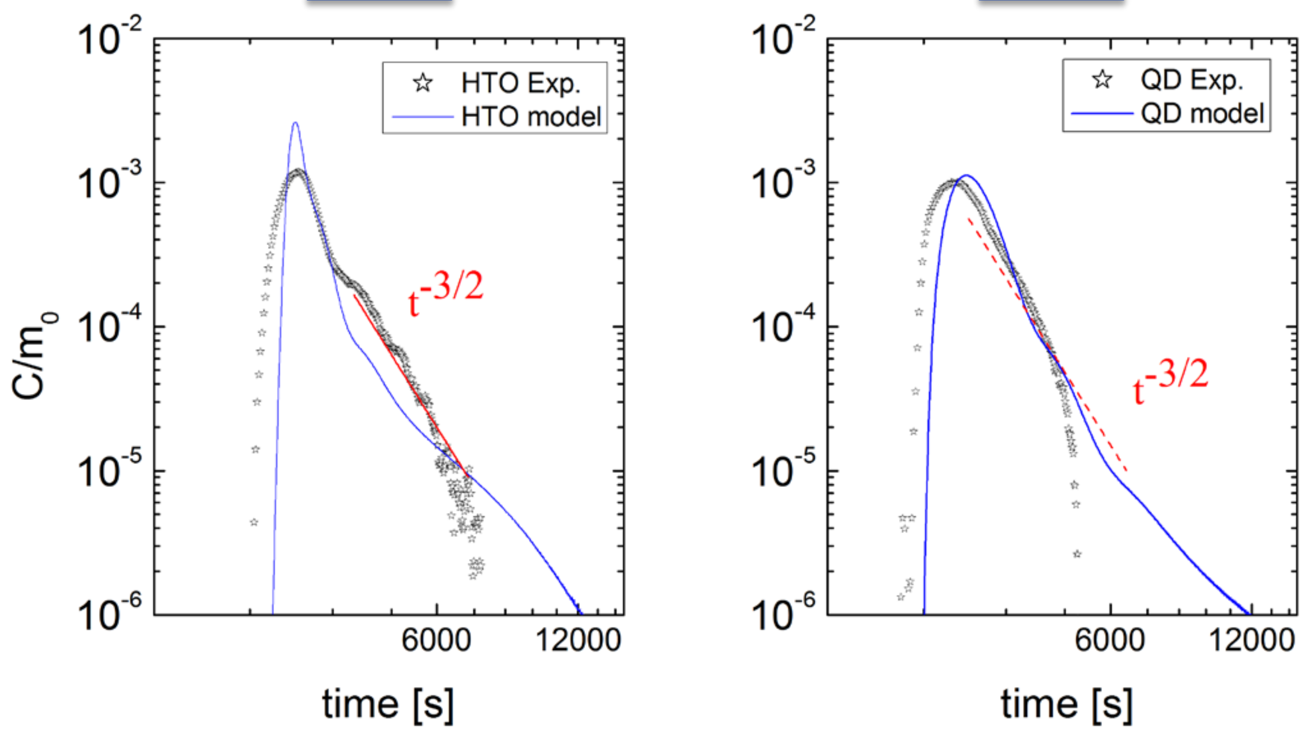
mixed volume mesh (tetras with 4 boundary prism layers)



arbitrary cut plane || to z

Experiments vs. 3D transport simulations

HTO | QD



- ➢ complex flow field leads to pronounced tailing in the BTCs
- ➢ experimental and simulated BTCs characterized by pronounced tailings
- ➢ tailing in the simulated BTCs solely due to fracture geometry
- ➢ exp. HTO BTCs may be influenced by matrix diffusion; QD BTCs not
- ➢ fracture geometry / hydrodanymic leads to enhanced residence times (retardation)

3D transport simulation

Flux [µl/min]	66.8	14.2
Re [-]	0.026	0.006
Pe HTO[-]	10	2
Pe QD [-]	607	135
max. velocity magnitude [m/s]	1.3×10^{-3}	2.9×10^{-4}
volume averaged velocity magn. [m/s]	5.67×10^{-5}	1.26×10^{-5}
R_p (Peak max. exp. HTO) [min]	51	129
R_p (Peak max. exp. QD) [min]	48	128
R_p (Peak max. model. HTO) [min]	50	161
R_p (Peak max. model. QD) [min]	49	159
R_f exp. [-]	0.94	0.99
R_f model [-]	0.98	0.99
Recovery HTO	96%	99%
Recovery QD	88%	68%
R_p = peak elution time; R_f = retardation factor ($R_f = R_p[QD]/ R_p[HTO]$)		

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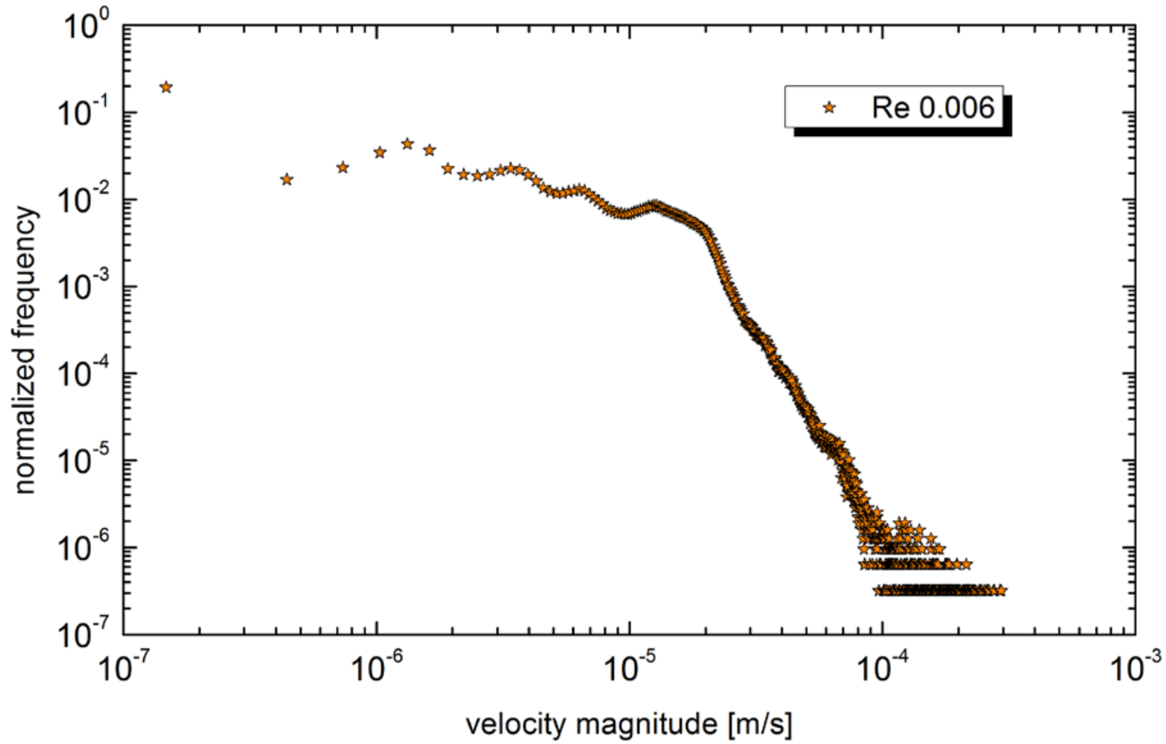
Outlook



Velocity distribution → Residence time variation → Different RN desorption → Prediction of RN breakthrough

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OUTLINE

APPROACH

MIGRATION EXPERIMENTS

MODELING

- µCT Characterization
- Mesh Generation
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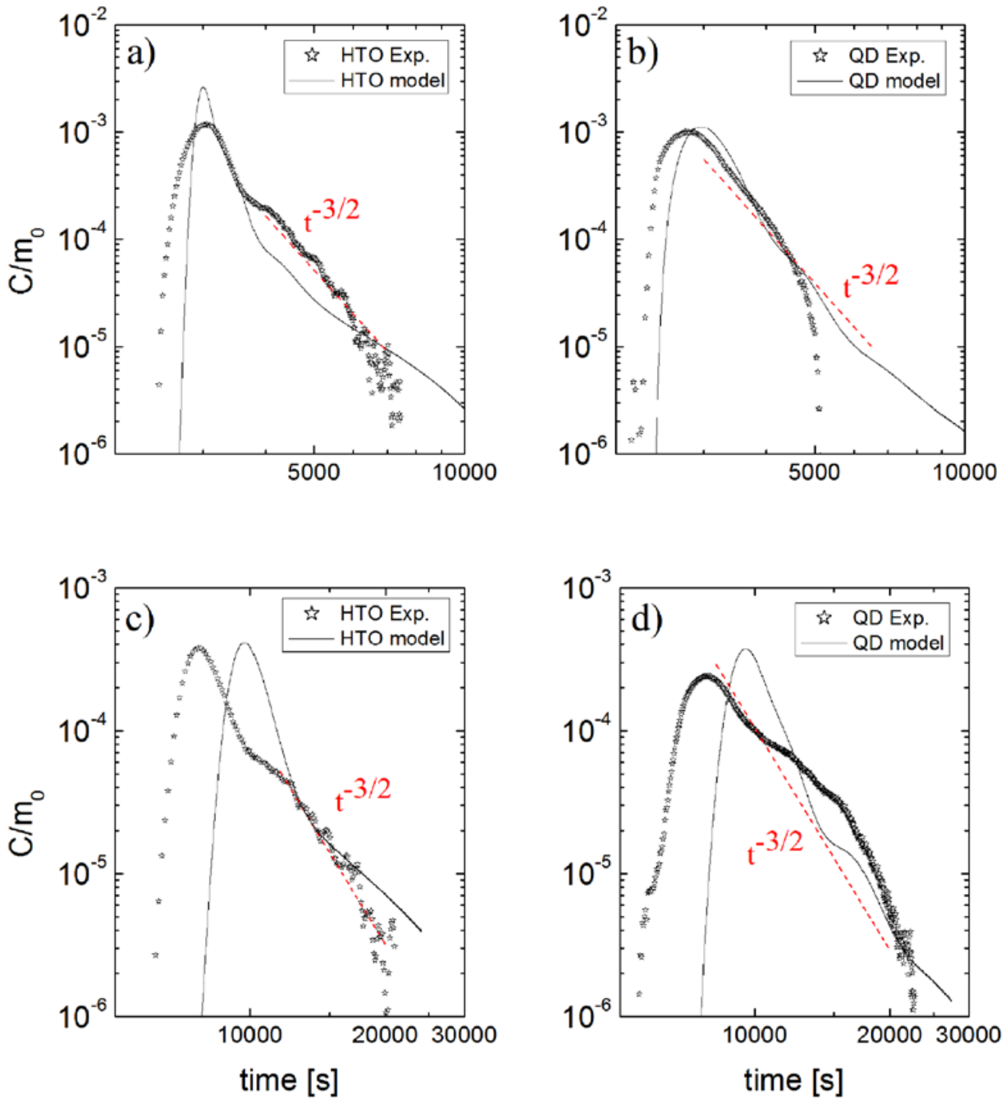
- Flow Simulations
- Transport Simulations

CONCLUSIONS

OUTLOOK

3D Transportsimulation



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Reactive transport modelling

Plan B – Kd

WATER RESOURCES RESEARCH, VOL. 32, NO. 7, PAGES 1943–1954, JULY 1996

Influence of specific surface area on transport of sorbing solutes in fractures: An experimental analysis

Christoph Wels[1] and Leslie Smith
Geological Engineering Program, Department of Earth and Ocean Sciences, University of British Columbia, Vancouver, British Columbia, Canada

T. T. Vandergraaf
Whiteshell Laboratories, Atomic Energy of Canada Limited, Pinawa, Manitoba, Canada

where D_e is the effective diffusion coefficient for the matrix, defined by *Neretnieks* [1980] as ($D_e = \varepsilon_p \tau D_m$), and R_a is the surface retardation factor, defined as

$$R_a = 1 + a_w K_a \quad (2)$$

a_w = flow wetted surface area (ratio of fracture surface to fracture volume)

known from CT data: **0.0165 m²/2.7e-6 m³ = 4306**

Ra or **Rf** from migration experiment: **1.8**

→ Ka or Kd = 1.85e-4 m^3/m^2 = 0.185 l/m^2

OUTLINE

INTRODUCTION

CORE CHARACTERIZATION

MIGRATION EXPERIMENTS

MODELING

- 3D flow field

- FASTREACT

- Plan "A"

- Plan "B"

OUTLOOK

Reactive transport modelling

Plan B – SCMs (DLM) for NpO_2^+ onto HFO, biotite & kaolinite

4428 *Ind. Eng. Chem. Res.* **2001,** *40,* 4428–4443

SEPARATIONS

Thermodynamic Modeling of the Adsorption of Radionuclides on Selected Minerals. I: Cations

Peiming Wang* and Andrzej Anderko

OLI Systems, Inc., 108 American Road, Morris Plains, New Jersey 07950

David R. Turner

Table 4. Summary of Parameters Used for the Determination of Binding Constants for the Sorption of Np(V) on Various Minerals[a]

solid	A_{sp} (m^2/g)	m/V (g/L)	C_{NR} (M)	I (M)	P_{CO_2} (atm)	log K_+[b]	log K_-[b]	log K_1[c]	log K_2[c]	log K_3[c]	log K_4[c]	log K_5[c]	ref
ferrihydrite ($Fe_2O_3{\cdot}H2O$)	600	0.89	4.7×10^{-12}	0.1	$10^{-3.5}$ ($NaNO_3$)	7.29	−8.93	–	−2.72 (0.03)	–	–	–	9
biotite[g] (Si/Al=3)	7.5	1.0	6.0×10^{-6}	0.1 ($NaNO_3$)	none	8.33	−9.73	–	–	−11.50 (0.04)	–	–	13
						–	−7.20	–	−4.17 (0.03)	–	–	–	

[a] A site density of 2.31 sites/nm² … Turner and Sassman.[34] [c] Binding constants K_1–K_5 correspond to the … ≡XOH–M^{z+}; K_2, ≡XOH⁰ + M^{z+} = ≡XO–$M^{(z-1)+}$ + H^+; K_3, ≡XOH⁰ + … = ≡XO–$M(OH)_2^{(z-3)+}$ + $3H^+$; K_5, 2(≡XOH⁰) + M^{z+} = $(≡XO)_2$–$M^{(z-2)+}$ … H/M = tris(hydroxymethyl)amino-

$NpO_2^+ + H_2O = NpO_2OH^0 + H^+$	−8.90
$NpO_2^+ + 2H_2O = NpO_2(OH)_2^- + 2H^+$	−23.0[b]
$NpO_2^+ + CO_3^{-2} = NpO_2CO_3^-$	4.6
$NpO_2^+ + 2CO_3^{-2} = NpO_2(CO_3)_2^{-3}$	7.0
$NpO_2^+ + 3CO_3^{-2} = NpO_2(CO_3)_3^{-5}$	8.5

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