Migration of Contaminants in Fractured-Porous Media in the Presence of Colloids: Effects of Kinetic Interactions

Tatiana Reiche(1), Ulrich Noseck(1), Thorsten Schäfer(2)

(1)Gesellschaft fuer Anlagen- und Reaktorsicherheit (GRS) mbH

(2)Karlsruher Institut für Technologie (KIT-INE)

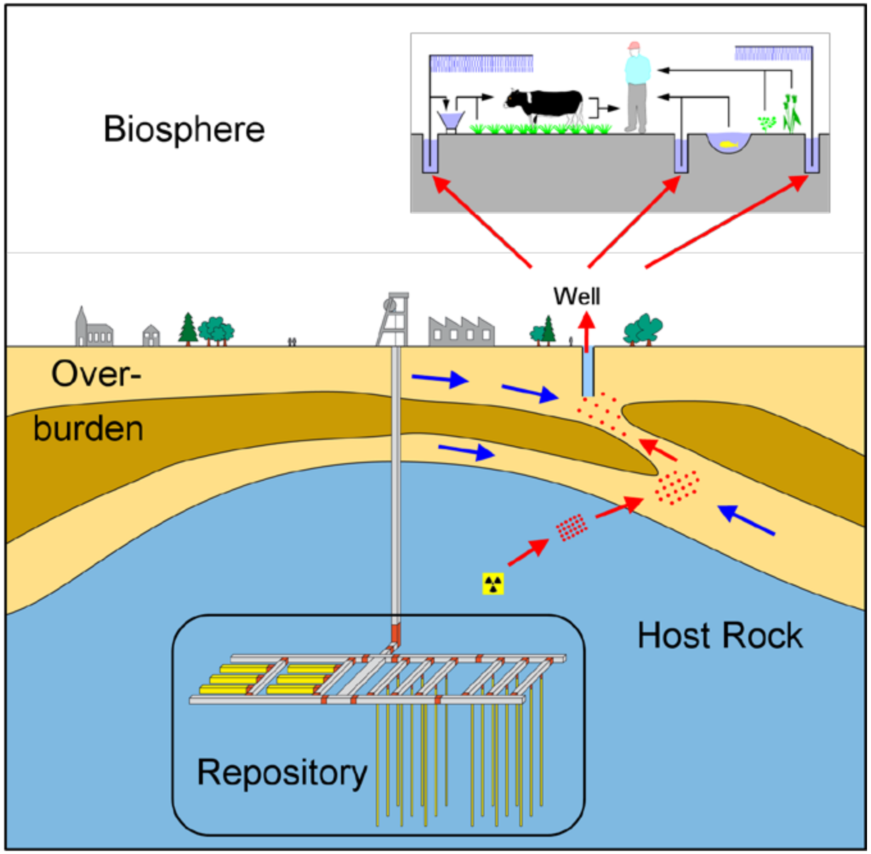
October 3, 2014

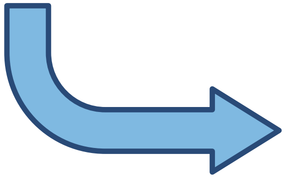
NM2PorousMedia 14, Dubrovnik, Croatia, 29 Sep. – 3 Oct. 2014

Introduction

Numerical long-term performance assessment for a deep underground repository for radioactive waste

- Water intrusion cannot be excluded
- Canister corrosion and contaminant mobilization
- Fluid flow inside the underground facility, release to the geosphere
- Radionuclide (RN) transport through the far field by the groundwater
- Radioactive exposure of man





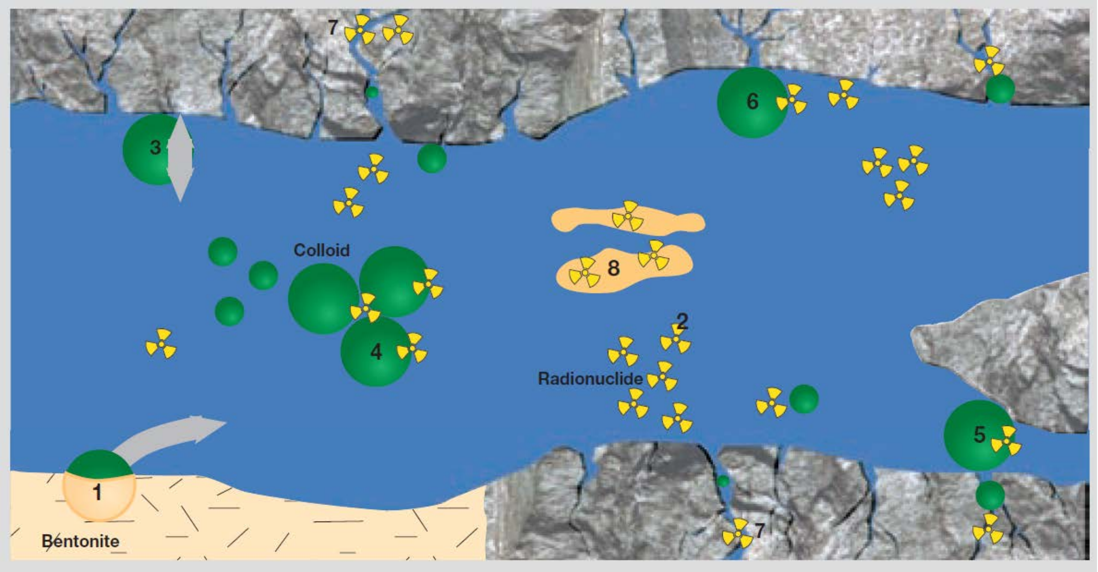
GRS-developed software tool: **RepoTREND**

- near field: NaTREND
- far field: GeoTREND:
  - POSA, FRAME, COFRAME
- biosphere: BioTREND

The role of colloids for radionuclide (RN) transport

Colloids:

- Particles with diameters between 1 nm and 1000 nm
- Interaction with fracture surface: filtration / remobilization
- Surface abilities dominate compared to the bulks properties → enormous sorption capacity
- Because of their large size
  - colloids might not diffuse into the rock matrix
  - linger in the middle of the fracture → the average colloid velocity higher than the average fluid velocity $u_c > u$



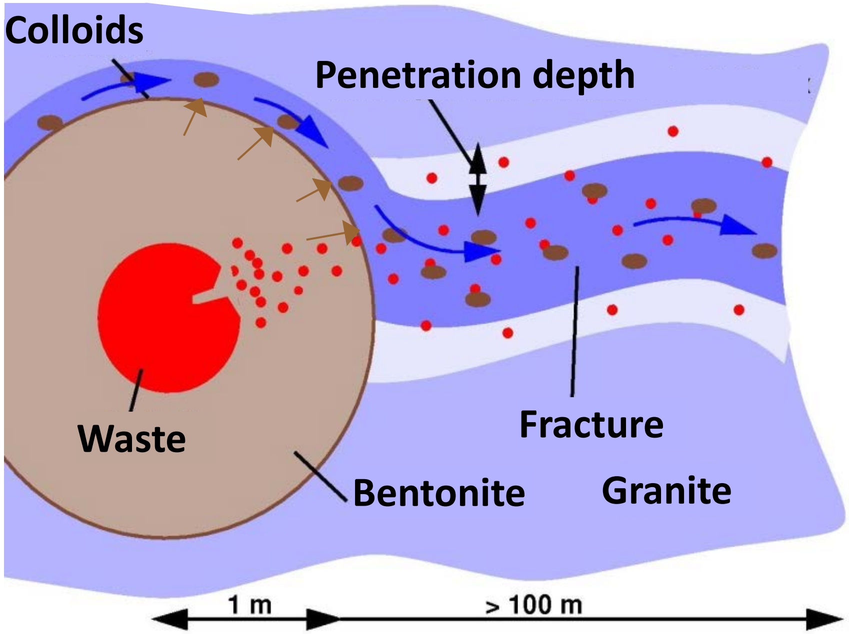
Nagra

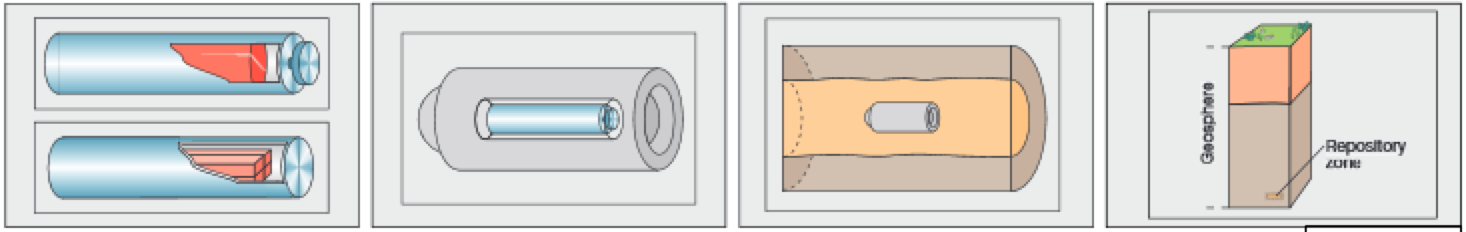
Consequence: transport of RNs may be significantly accelerated by colloids

Role of colloids for crystalline formations

Colloid generation in repositories in crystalline formations

- Inflow of low mineralized glacial melt water
- Bentonite erosion at the interface to the groundwater
- Colloid and RN release out of the bentonite
- Colloid facilitated RN transport through the fractures



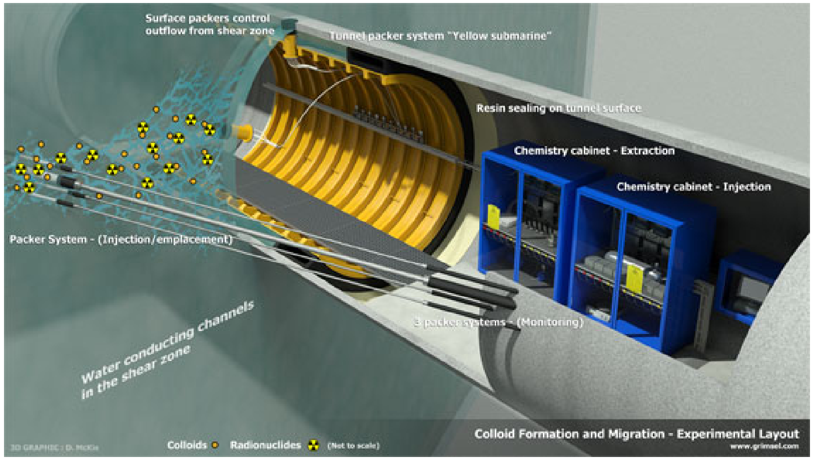


Nagra

Colloids are also present in all natural waters

CFM (Colloid Formation and Migration) experiments

- International project at Grimsel Test Site (GTS) with several international partners
- Field experiments under near-natural flow conditions indicate:
  - Sorption processes for RNs on colloids are kinetically controlled
  - Colloid filtration proceeds according to linear kinetic approach,
  - Colloid remobilization seems to be important



Nagra

Goal of this work[1],[2]:

- Modelling of colloid-facilitated RN transport capable of describing these experiments
- Numerical solution is realized in the transport code COFRAME
- Investigation of the impact of colloids and the effect of kinetics

---

[1] (in publishing) Reiche, T., Noseck, U., Schäfer, T.: Migration of contaminants in fractured-porous media in the presence of colloids: effects of kinetic interactions, Contaminant Hydrology, 2014

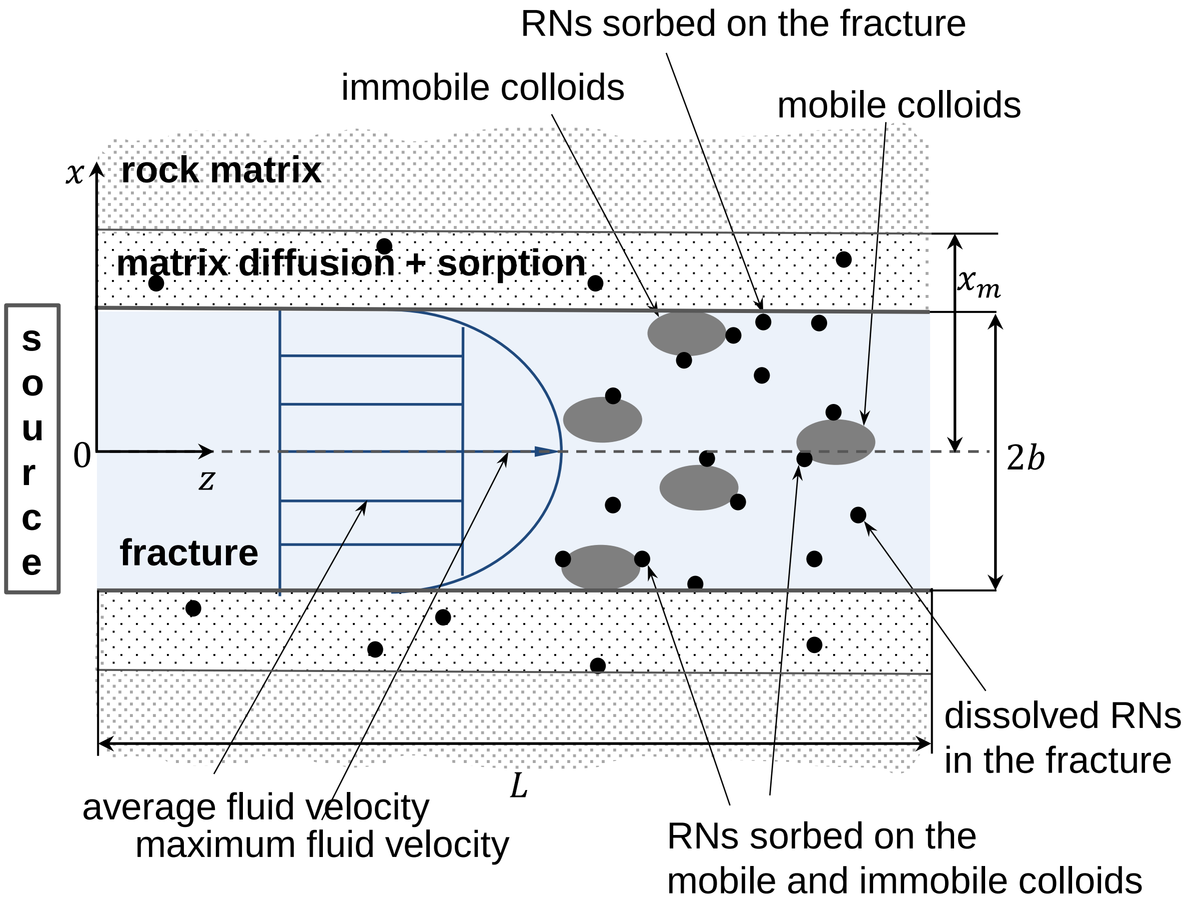
[2] Reiche, T., Noseck, U., Wolf, J. W.: Modellierung des Schadstofftransports in geklüftet-porösen Medien unter der Berücksichtigung von Kolloiden mit den Transportprogrammen FRAME und COFRAME, GRS-Bericht 333, Gesellschaft für Anlagen- und Reaktorsicherheit (GRS), Braunschweig, 2014

Model

Assumptions:

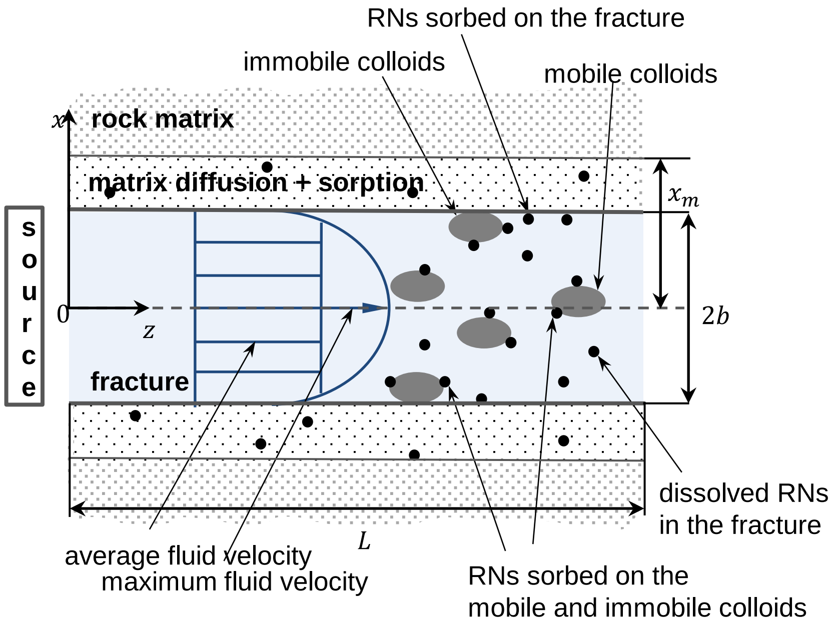
- Ground water flows only along fractures
- RNs can diffuse into stagnant matrix pore water but
- Colloids cannot diffuse into the rock matrix due to their larger size
- All colloids have the same size and properties

Fractured-porous medium as single planar fracture integrated in the porous rock matrix (double-porosity model)



modified after *Baek, I., Pitt, W.W.: Colloid-facilitated radionuclide transport in fractured porous rock, Waste Management, vol. 16, no. 4, 313-325, 1996*

Model



Assumptions:

1. No concentration gradient transverse the fracture

   ⇨ 1D modelling of the RN and colloid transport in the fracture

2. Ground water flow is laminar

   ⇨ Darcy’s low can be applied

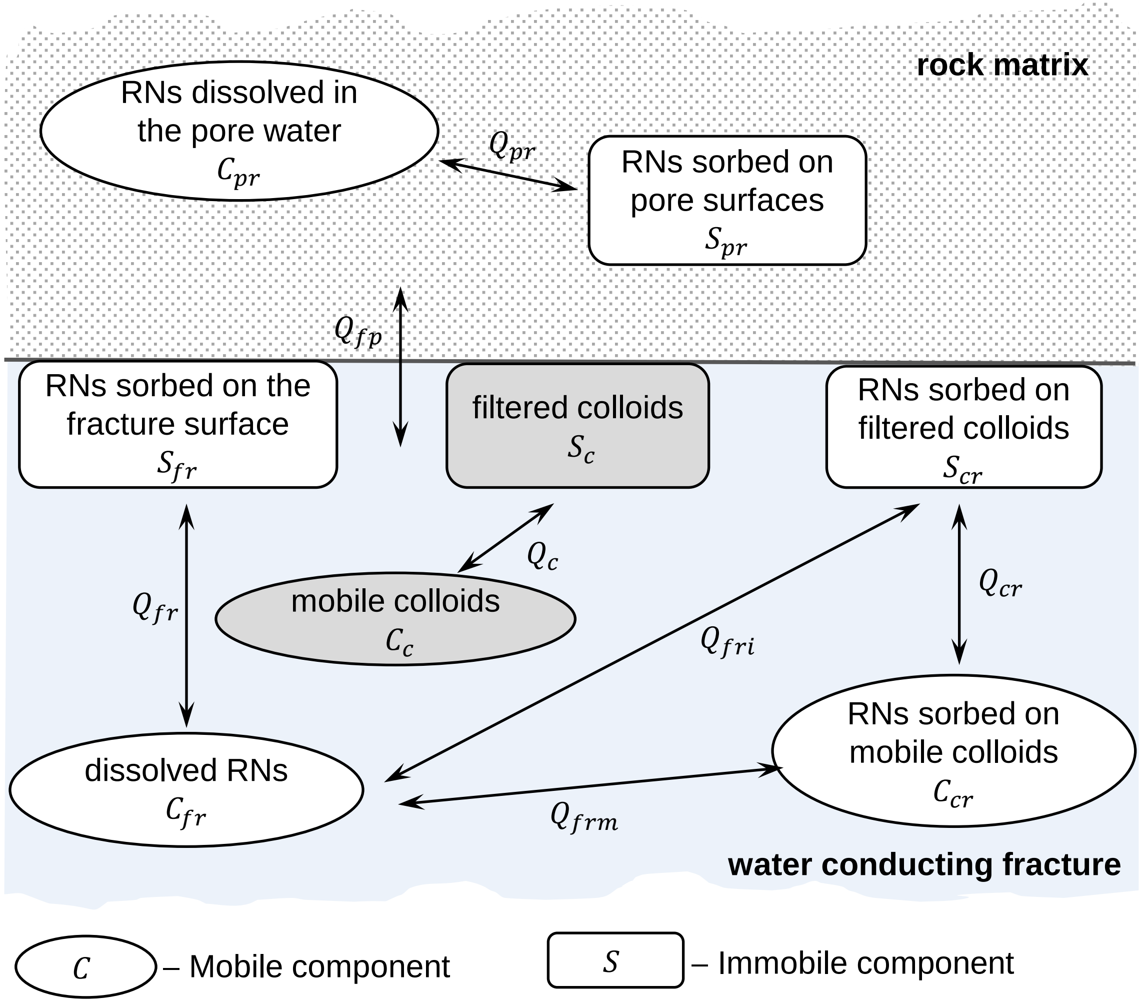
3. RN transport along the fracture is significant faster than the transport in the rock matrix

   ⇨ Matrix diffusion as 1D problem directed normal to the ground water flow

Model: components and processes

Components and its interactions:

- Colloids – mobile und filtered
  - filtration and remobilization, linear kinetic reaction
- RNs – dissolved in fracture and pore water, bound to pore surfaces, to fracture surface and to colloids
  - linear equilibrium sorption in the rock matrix
  - linear kinetically sorption on the fracture surface and on colloids
  - filtration and remobilization of colloid bound RNs
  - Flux through the fracture-matrix interface
  - Radioactive decay



rock matrix

RNs dissolved in the pore water C_{pr}

Q_{pr}

RNs sorbed on pore surfaces S_{pr}

Q_{fp}

RNs sorbed on the fracture surface S_{fr}

filtered colloids S_c

RNs sorbed on filtered colloids S_{cr}

Q_c

Q_{fr}

mobile colloids C_c

Q_{cr}

Q_{fri}

RNs sorbed on mobile colloids C_{cr}

dissolved RNs C_{fr}

Q_{frm}

water conducting fracture

C – Mobile component

S – Immobile component

advection, mechanical dispersion and molecular diffusion of RNs and colloids in the fracture

General transport equation

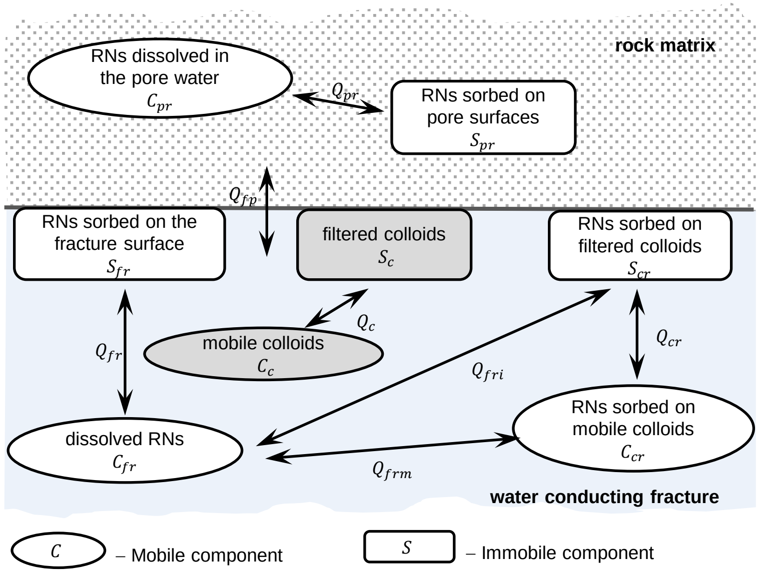
Mobile and immobile RNs and colloids are represented by 8 different components P

$$n\frac{\partial P}{\partial t} + n u_P \frac{\partial P}{\partial y} - n D_P \frac{\partial^2 P}{\partial y^2} = Q_P$$

	C_c	C_{cr}	C_{fr}	C_{pr}	S_c	S_{cr}	S_{fr}	S_{pr}
D_P	D_c	D_c	D_f	D_p	0	0	0	0
u_P	u_c	u_c	u	0	0	0	0	0

t	time [y],
y	relevant space coordinate [m] (x or z according to appropriate component),
n	porosity [-],
u_P	average velocity of the component P [m/y],
D_P	dispersion coefficient of the component P [m^2/y],
Q_P	source-sink-term of the component P (exchange terms, radioactive decay), volume- [$mol \cdot m^{-3} \cdot y^{-1}$] and surface-related [$mol \cdot m^{-2} \cdot y^{-1}$],
P	concentration of the component P, volume- [mol/m^3] and surface-related [mol/m^2].

Q_P – source-sink and exchange terms of the component P



Q_P is a sum of all source-sink and exchange terms relevant for P:

- RN-Sorption in the rock matrix – linear equilibrium reaction:

$$S_{pr} = K_{pr} C_{pr}$$

- RN-Sorption on colloids and on the fracture surface – linear kinetic reaction:

$$Q_P = k_P [K_P C_P - S_P]$$

- Filtration / remobilization of colloids and colloid bound RNs – linear kinetic reaction:

$$Q_P = \lambda_f u_c C_P b - R_{mb} S_P$$

- Diffusive RN flux normal to the fracture-matrix interface by Fick's law:

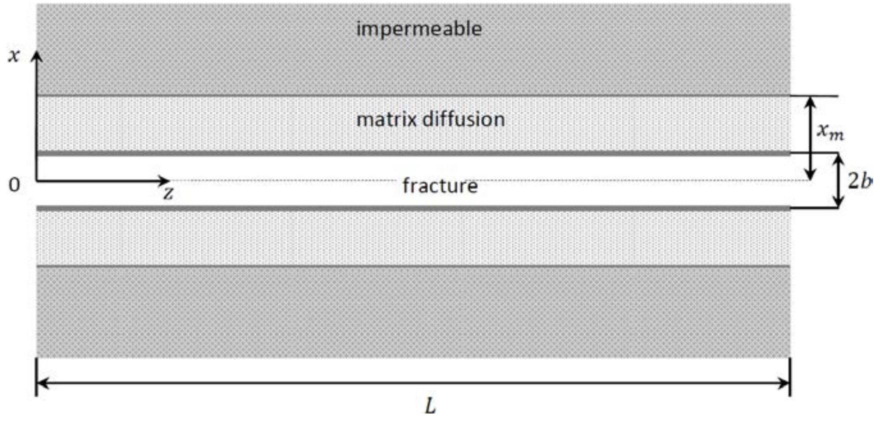
$$Q_{fp} = -nD \frac{\partial C_{pr}}{\partial x}\bigg|_{x=b}$$

- Radioactive decay:

$$Q_P = -\lambda C_P$$

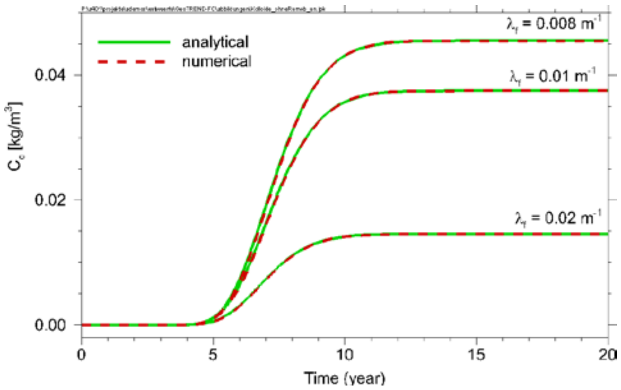
Equation system

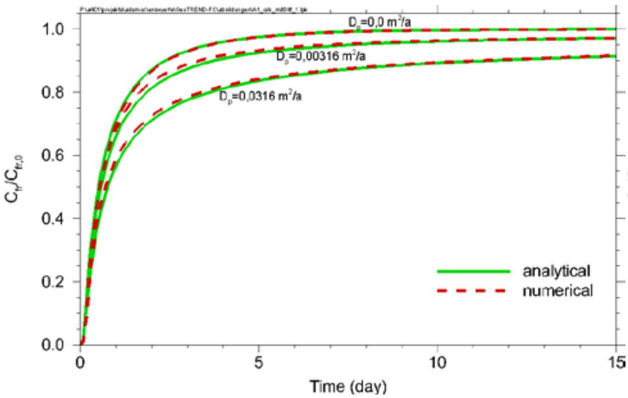
- 7 coupled equations:
  - 2 for colloids C_c and S_c independent from RN concentrations → solve at first
  - 5 for RNs C_{pr} , C_{fr}, C_{cr}, S_{cr}, S_{fr}
- Initial conditions ($t = 0$): zero concentrations or constant background concentrations
- Boundary conditions for mobile components:
  - inflow ($z = 0$) – *Dirichlet*: $C_P(0,t) = C_P(t)$
  - outflow ($z = L$) – *transmission*: $\left.\frac{\partial C_P}{\partial z}\right|_{z=L} = const$
  - x-axis
    - $x = b$: $C_{pr}(b,z,t) = C_{fr}(z,t)$
    - $x = x_m$ *impermeable*: $\left.\frac{\partial C_{pr}}{\partial x}\right|_{x=x_m} = 0$

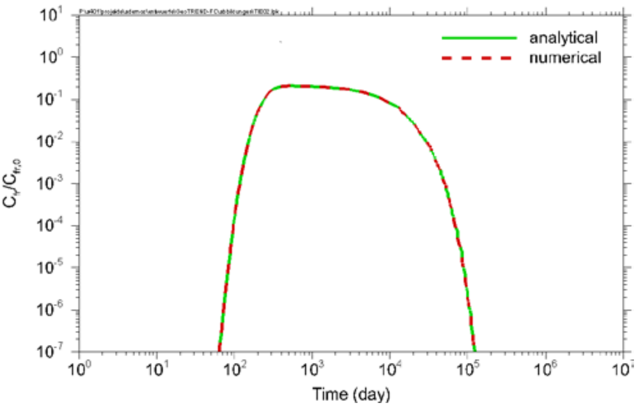


Numerical model

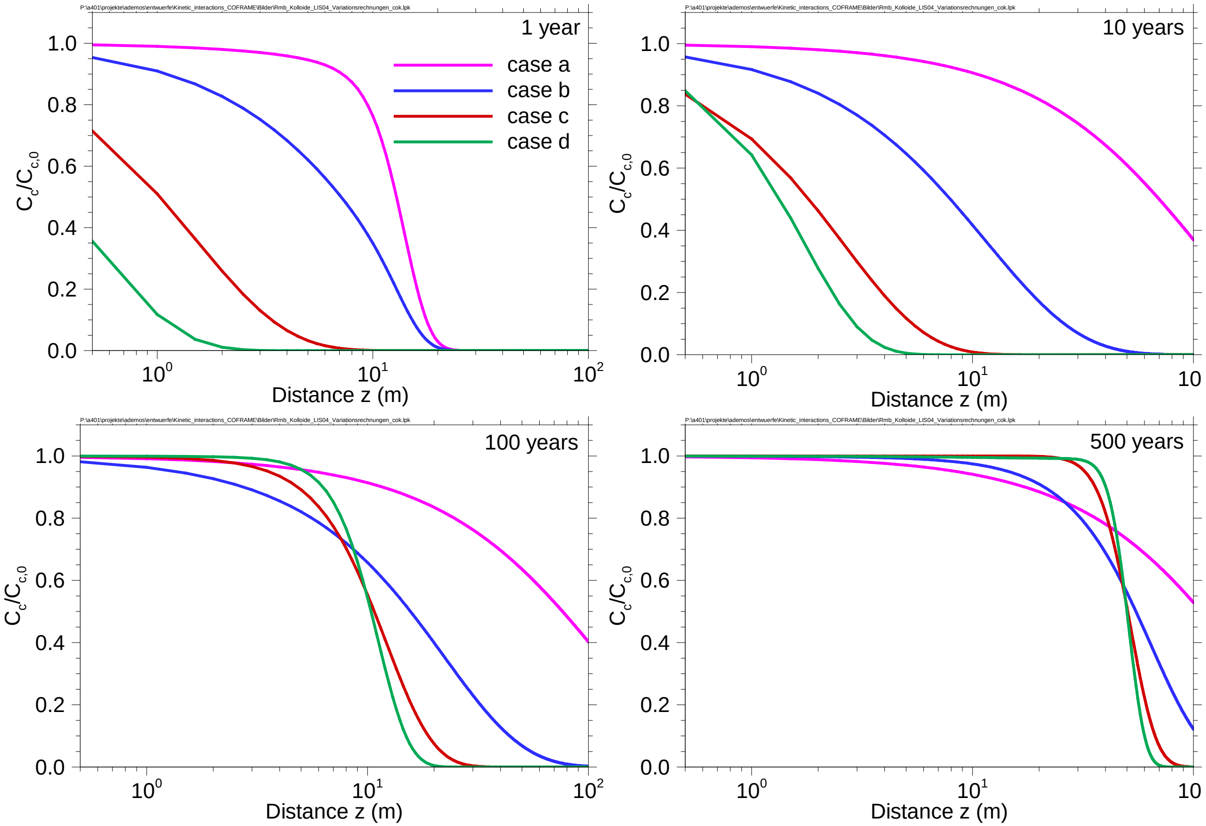
- **Finite Differences**
  - Time integration: *Crank-Nicolson*
  - Discretisation in spatial coordinate: *upwind* for first and *central difference* for second derivative
- Realized in the transport code COFRAME
- Verified using 3 analytical solutions:
  - Colloid transport
  - RN transport without colloids
  - RN transport in the presence of colloids (const concentration)







Effect of kinetics by filtration / remobilization of colloids

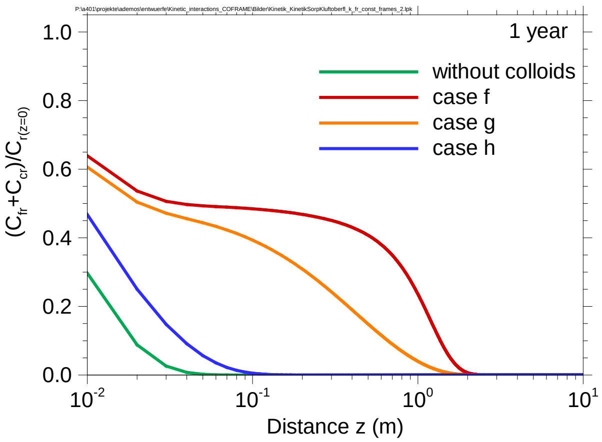


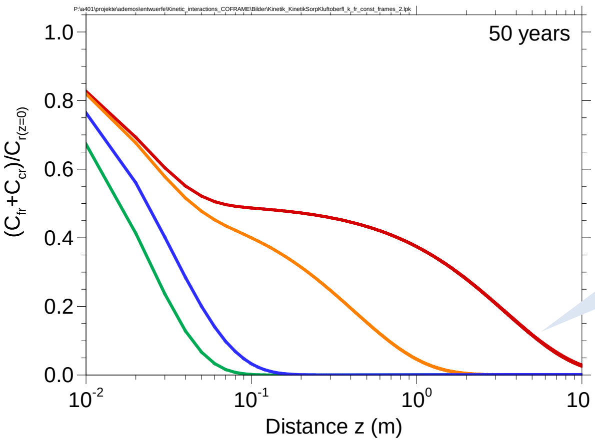
Case	λ_f, [m^{-1}]	R_{mb}, [y^{-1}]
a	0.01	0.001
b	0.1	0.01
c	1	0.1
d	10	1

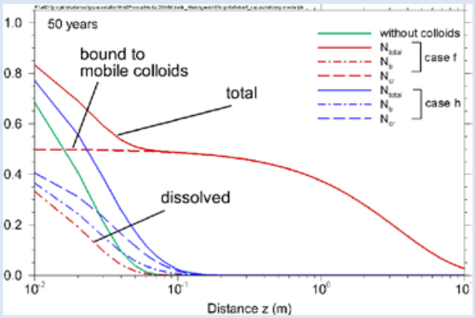
System parameters	Value
Fracture aperture	0.0001 m
Velocity	13.05 m/y
Diffusion coefficient	0 m^2/y
Longitudinal dispersion length	0.5 m

The higher the reaction rate the faster mobile colloids change into the immobile phase (until equilibrium is reached) → stronger retardation of the front.

Effect of kinetics by interacting processes for RN







Case	λ_f, [m^{-1}]	R_{mb}, [y^{-1}]	Reaction rates on colloids, [y^{-1}]
f	0.2	0.0001	0.1
g	2	0.001	1
h	200	0.1	100

- Velocity of RN front is mostly controlled by mobile colloids → **colloids can significantly accelerate the RN transport and increase RN concentration**
- Reaction rates for RN also affect the retarding processes, but the impact and extension of retarding processes depend as well on system parameters
- For system parameters used: higher reaction rates lead to faster immobilization of RNs due to their sorption on filtered colloids (stronger front retardation)

System parameters	Value
Colloid concentration	0.1 kg/m^3
Fracture aperture	0.001 m
Velocity	1 m/y
Molecular diffusion coefficient of colloids and RNs	0 m^2/y
Longitudinal dispersion length	0.1 m
Rock matrix porosity	0.01
Molecular diffusion coefficient in the rock matrix	0.0001 m^2/y

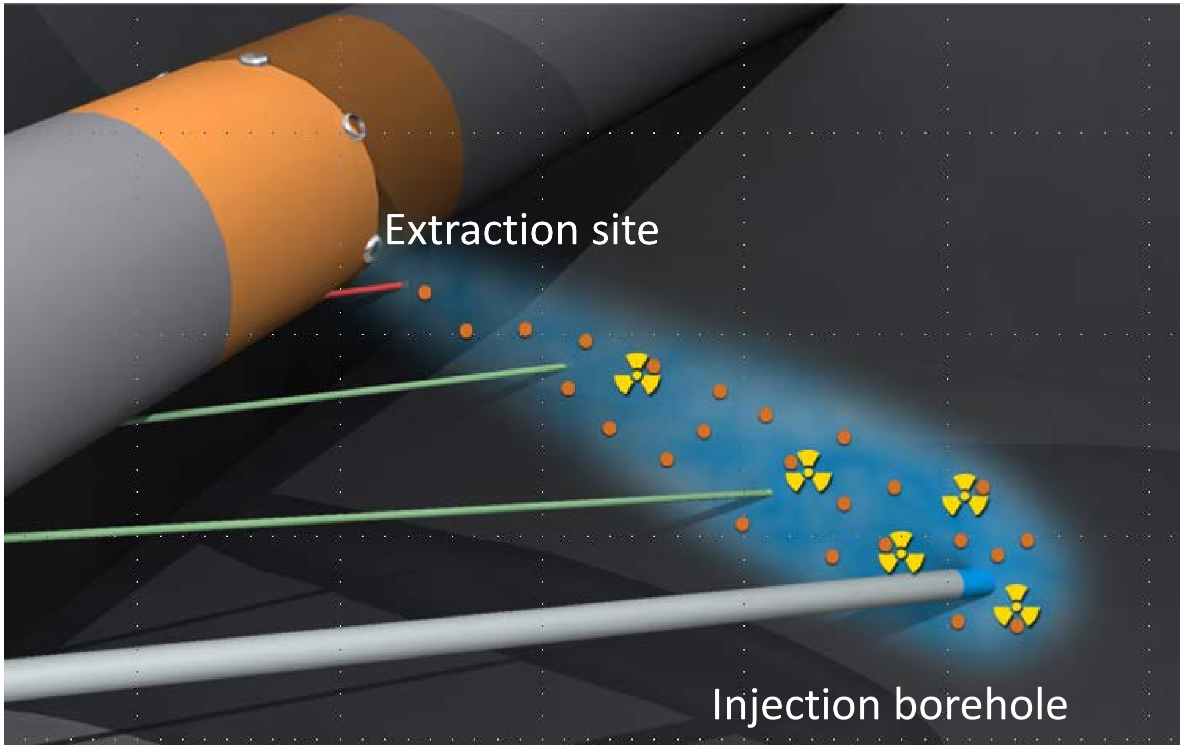
Sorprion parameters	Value
Distribution coefficients on colloids	10 m^3/kg
Distribution coefficients on fracture surface	10 m
Reaction rate on the fracture surface	0.1 y^{-1}

Application to a dipole test at the Grimsel Test Site

Field experiments with ideal tracer Ur, colloids, homologues (chemically similar elements): Eu, Tb (III), Hf, Th (IV)

Typical procedure

- Injection of a cocktail with bentonite colloids and homologues / RNs
- Homologues (III, IV) quantitatively bound to colloids
- Constant in- / outflow-rate
- Online- / offline-measurement of breakthrough curves (BTCs) at extraction site



Nagra

Model and system parameters

Interactions:

- filtration and remobilization of colloids, linear kinetic reaction
- linear equilibrium sorption of contaminants on the fracture surface
- linear kinetic sorption reaction for contaminants on colloids
- contaminants diffusion into the rock matrix
- Radioactive decay

System parameter	Value
Fracture length	6.2 m
Groundwater volume flow rate	25.44 m^3/y
Fracture aperture	0.0025 m
Porosity of the fracture fill	1 [-]
Colloid and contaminant dispersion length	0.6 m
Colloid and contaminant velocity	2175.08 m/y
Colloid molecular diffusion coefficient	0.003 m^2/y
Contaminant molecular diffusion coefficient in the fracture	0.03 m^2/y
Multiplication factor that defines which fraction of contaminants on inflow boundary is presented as dissolved in the groundwater	0.01 [-]
Maximum penetration depth in the rock matrix	0.02 m
Porosity of the rock matrix	0.05 [-]
Contaminant molecular diffusion coefficient in the rock matrix	0.008 m^2/y

Sorption coefficients of contaminants on colloids and on fracture derived from batch experiments[3]

Sorption rates for colloids derived by fitting the experimental breakthrough curves

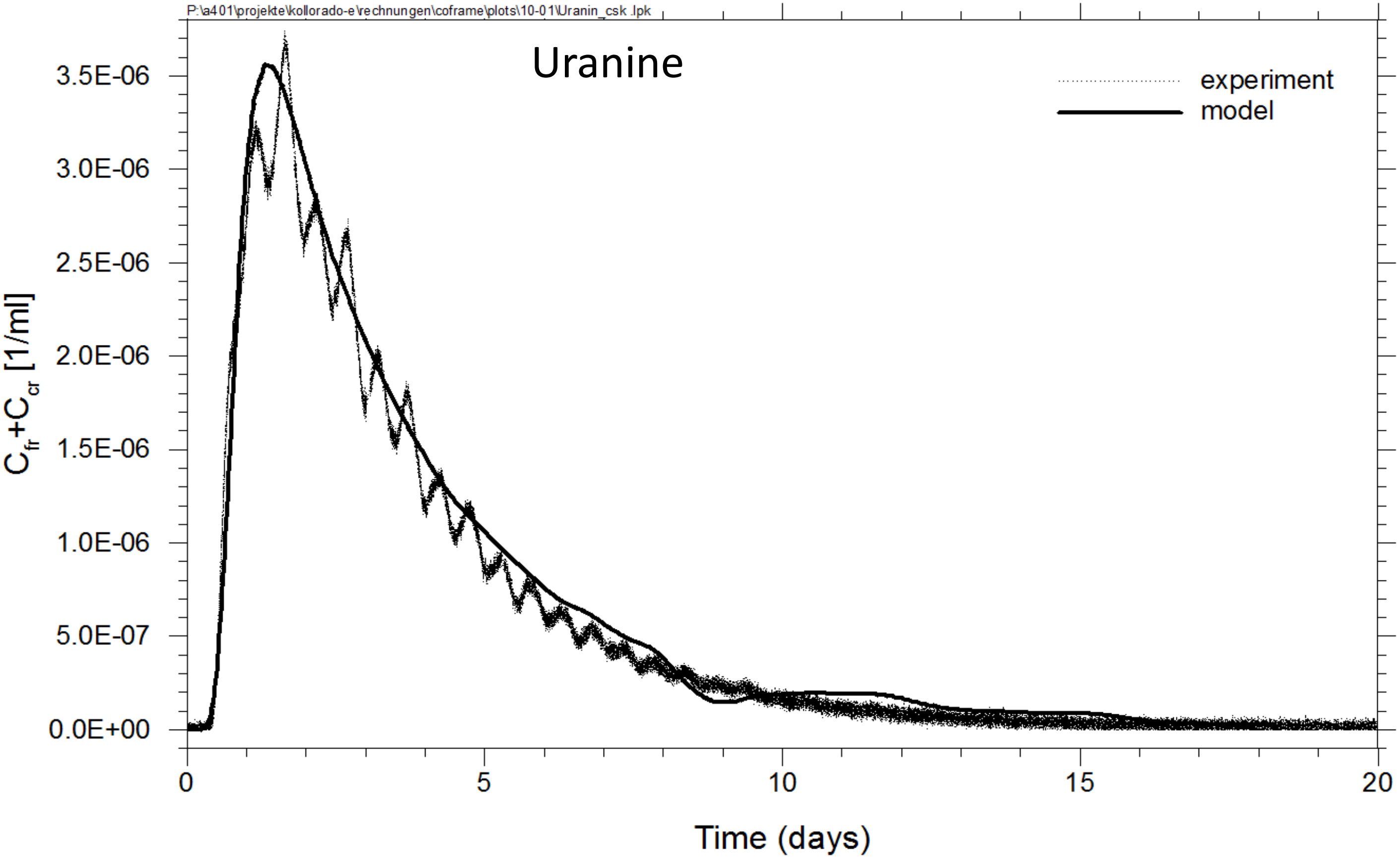
Sorption parameters	Ur	Tb	Hf	Eu	Th
K_{pr} [m^3/kg]	0	0.56	0.56	0.56	0.56
K_{fr} [m]	0	1.56	1.56	1.56	1.56
K_{frm}, K_{fri} [m^3/mol]	0	1500	1600	1500	1600
k_{fr} [y^{-1}]	-	$1 \cdot 10^6$	$1 \cdot 10^6$	$1 \cdot 10^6$	$1 \cdot 10^6$
k_{frm}, k_{fri} [y^{-1}]	0	450	250	600	200

---

[3] Schäfer, Th.; Noseck, U.; Huber, F.: Colloid/nanoparticle formation and mobility in the context of deep geological nuclear waste disposal (Project KOLLORADO-2; Final Report). KIT Scientific Report 7645. Karlsruhe 2012

Simulation of ideal tracer Uranine BTC

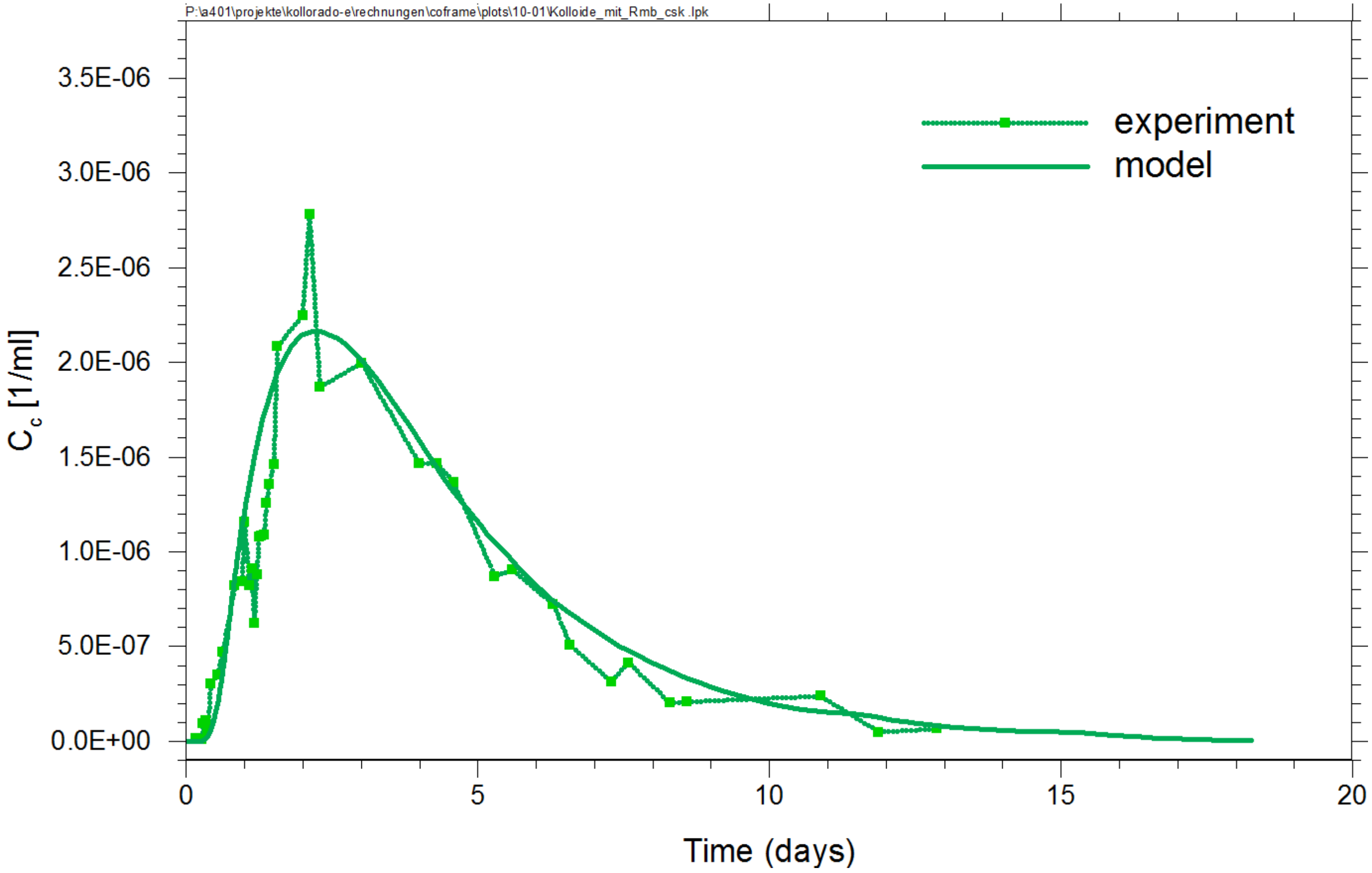
contaminant dispersion length and geometrical parameters were adapted



Simulation of colloid BTC

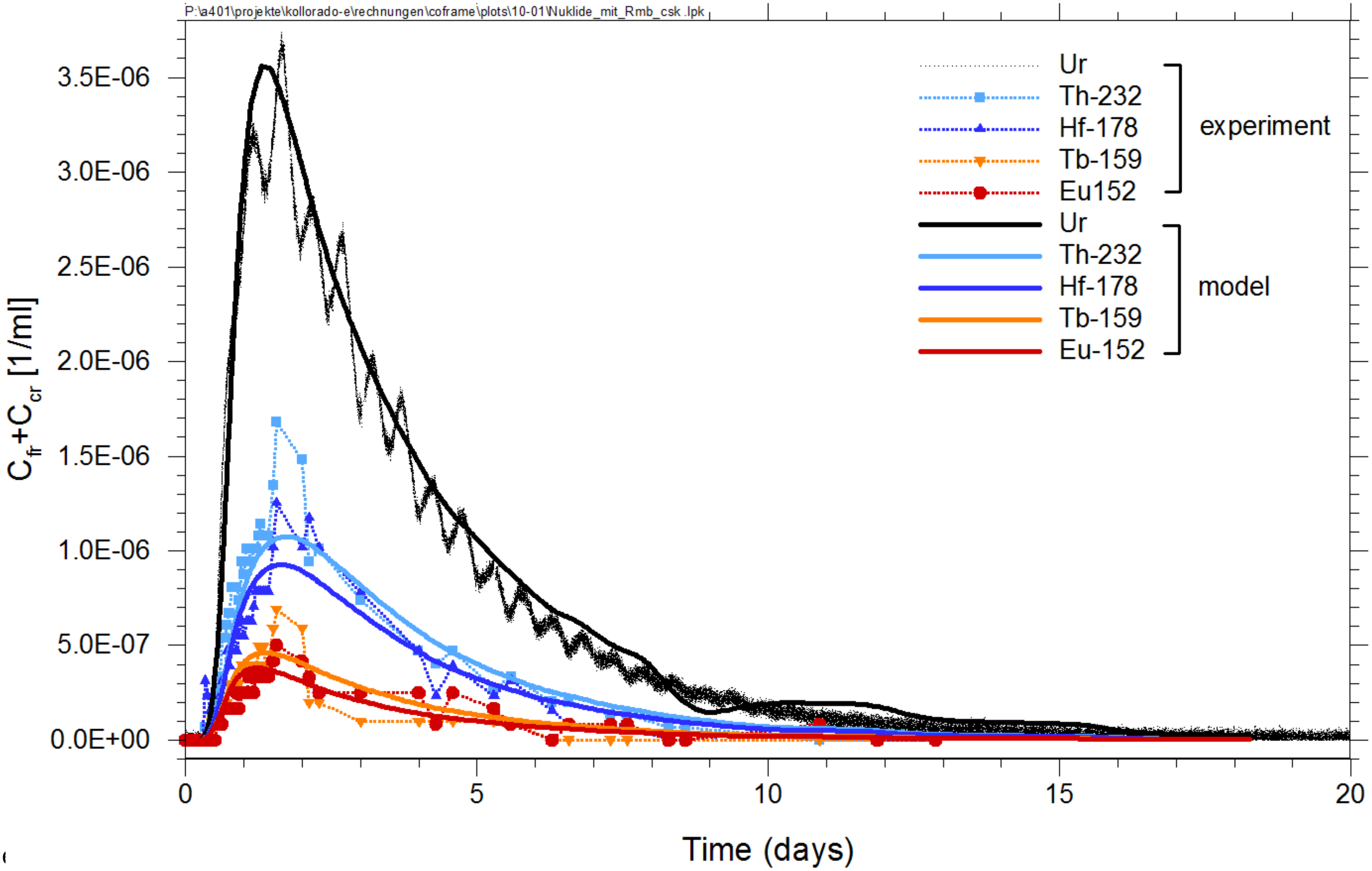
Modelling approach: reversible, kinetically controlled filtration and remobilization:

- filtration coefficient 0.33 m^{-1}
- remobilization coefficient 960 y^{-1}



Simulation Homologues / RNs BTC

- Resulting simulation curves coincide well with the experimental curves
- Confirmation that the experimental results can be best explained using a kinetic approach for sorption and filtration/remobilization processes



Summary and conclusions

- 1D-model of the migration of contaminants in a fractured-porous medium in the presence of colloids has been developed. Distinguishing features:
  - Sorption processes of contaminants on colloids and fracture surface are linear *kinetically controlled*
  - *Reversible* kinetically controlled interaction of colloids with fracture surface
- Realisation in transport code COFRAME (Finite Differences)
- Investigation of colloid impact and of effect of kinetics:
  - Colloids can significantly accelerate the contaminant transport and increase the contaminant concentration
- Application to a field dipole test at GTS:
  - modelled BTCs coincide well with experimental curves
  - Experimental data can be best explained using a kinetic approach of sorption and filtration/remobilization processes

Acknowledgement

This work was financed by the German Federal Ministry of Economic Affairs and Energy (BMWi)

Bundesministerium
für Wirtschaft
und Technologie

We also would like to thank the partners from the CFM project at Grimsel Test Site - KIT-INE (Germany), JAEA (Japan), SKB (Sweden), CRIEPI (Japan), KAERI (Republic of Korea), POSIVA (Finland), NAGRA (Switzerland), USDOE (USA).

Thank you for your attention!