Modeling of release and transport of toxic substances in a high level waste repository in clay formations

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Objectives

Documentation of:

Available tools and data

Possibilities and limitations

for the modeling of release and transport of toxic elements in HLW repositories in clay formations

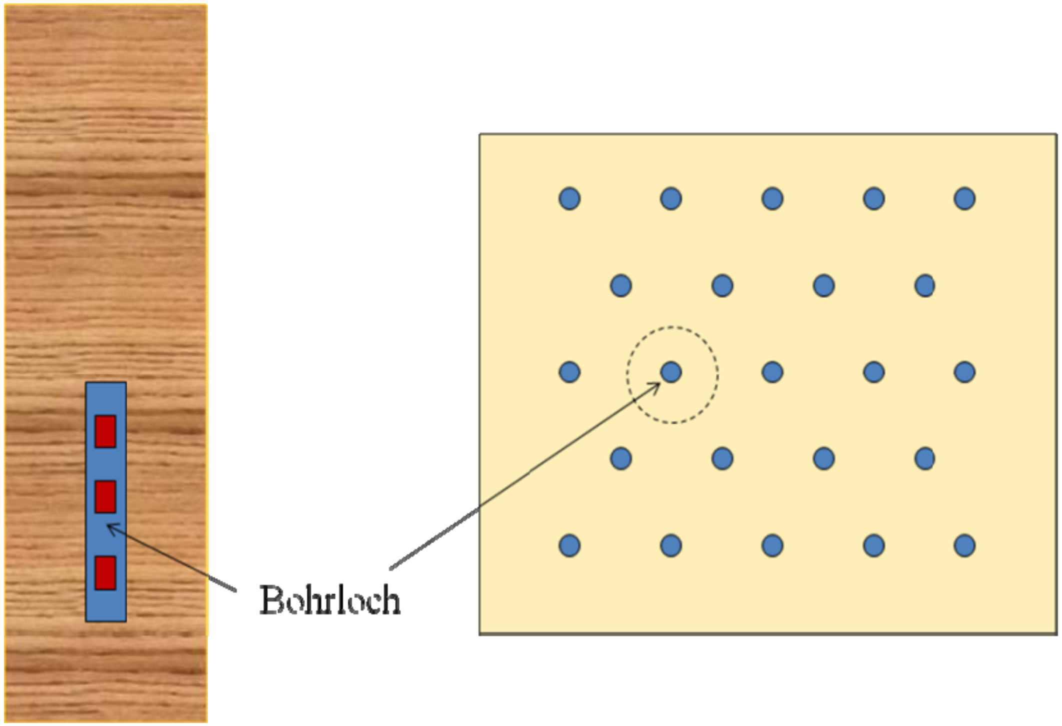
Approach

Geochemical equilibrium modeling
followed by
Transport modeling

The disposal concept regarded was the disposal of spent fuel in vertical boreholes in clay formations in Southern and Northern Germany

Disposal concept:

3 spent fuel canisters (BSK3) in 50m deep boreholes



Geochemical Modeling

What has been modeled?

The mobilization of toxic elements

heavy metals: U, Cr, Ni, Zr, Mn, Sr, Mo, Cu, Sn, Ti, V and toxic anions: P, As, B, N

due to the corrosion of 3 BSK3 canisters

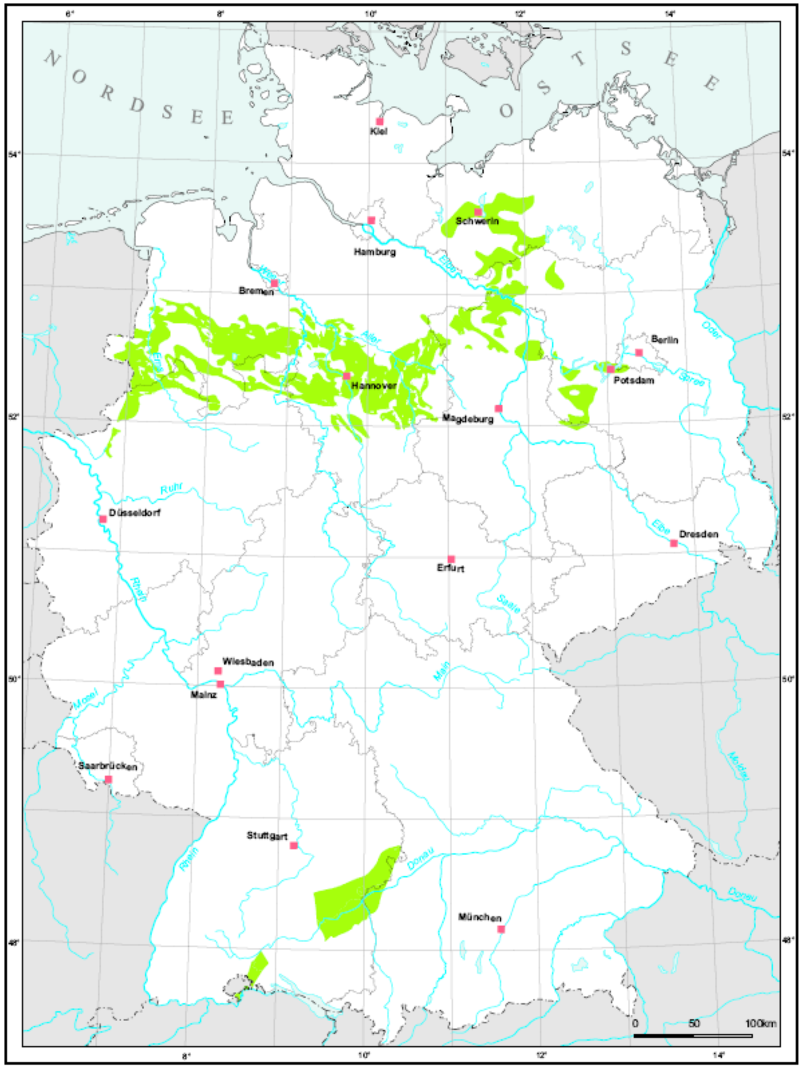
by clay pore waters of different salinities

Which examples were chosen for the modeling and why?

Corrosion by:

- **Opalinus clay water**
- **NaCl saturated solution**

Clay formations in Germany



untersuchungswürdige Tongesteinsformationen in Deutschland

Geochem. Modeling - Tools

Code – CHEMAPP

Pitzer model for the calculation of activities in high saline solutions

Thermodynmic Data – generated by GRS

- **Pb, Zn** (Herbert, Mönig 1997)
- **Pb** (Hagemann 1999, Diss.)
- **Pb, Zn, Cd** (Hagemann 2007)
- **Fe, S** (Moog et al. 2004)
- **Si, Al** (Reardon et al. 1999, Th. Meyer 2009)
- **As, C, Co, Cu, Mn, Ni, Hg** (Hagemann et al. 2008)

Geochem. Modeling - boundary conditions:

25°C, 1bar

Pore waters: OPW, NaCl solution

Vertical borehole: 50 m deep, Ø 0,46 m

3 BSK3 canisters with 3 spent fuel rods, 15 tons of metals

Bentonit buffer, 50 % porosity

Initial volume of corroding pore water 3,06 m^3

H_2 generated by the corrosion can leave the system

Geochem. Modeling - boundary conditions:

Chemical elements regarded:

- **aqueous system:** H, O
- **sea water system:** Na, K, Ca, Mg, Cl, SO_4, CO_3
- **silicate matrix:** Si, Al
- **heavy metals:** Fe, U, Ni, Ti, V, Cr, Cu, Mo, Mn, Sn, Sr, Zr
- **anions:** B, As, P, N

Not regarded: Ne, Y (no thermodyn. data)

Geochemical Modeling - Results

Step 1 1:

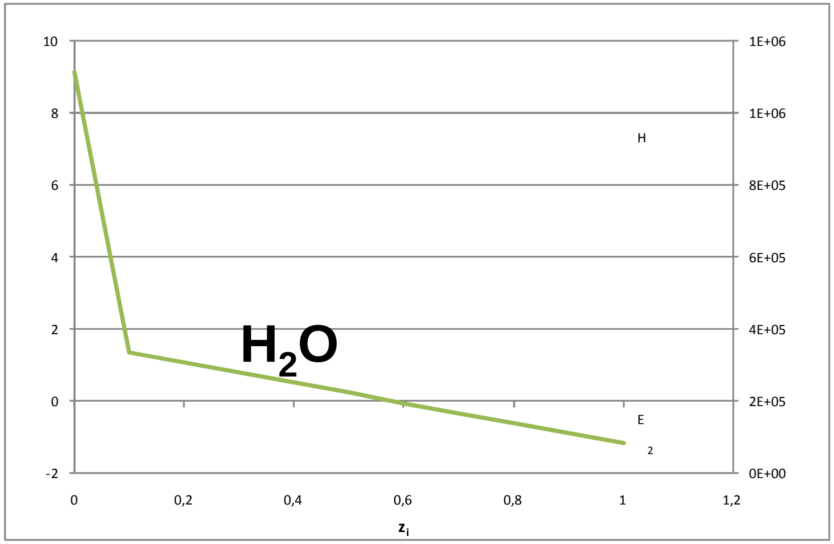
assumptions:

borehole filled with 3,06 m^3 pore water

no replenishment of consumed water

Result:

pore water completely consumed



Geochemical modellig - Results

Step 2:

Assumptions:

consumed pore solution can be replenished

enough solution is available for the total corrosion of 3 BSK3

Results:

for the corrosion of the15 tons of metals in 3 BSK3 containers

5,0 m^3 OPW,

5,6 m^3 NaCl are consumed

no toxic elements are released.

the entire inventory is mobilized but immediately reintegrated in the corrosion products

Results of the geochmical modeling

Step 3: more pore water available – formation of EQS

If more pore water is available than needed for the total corrosion, a solution in equilibrium with the corrosion products (EQS), will be formed

Examples

5,1 m³ OPW	5,16 m³ OPW	6,6 m³ OPW
no EQS	0,06 m³ EQS	1,5 m³ EQS
	density: 1,716 g/cm³	1,049
	ionic strength. 38,8 mol/kg	0,7

Results of the geochmical modeling

After the formation of 1.5 m3 ES
Most bof the toxic elements are imibilised in the corrosion products

Element	OPW	NaCl	IP21
% Imobilisiert			
Fe	99,96	99.89	100,00
Al	100,00	100,00	100,00
U	100,00	100,00	100,00
P	0	0	0
As	0	0	0
Ni	100,00	100,00	100,00
Zr	100,00	100,00	100,00
Mn	100,00	100,00	100,00
Mo	99,67	99,67	0
Cu	100,00	100,00	100,00
Cr	100,00	100,00	100,00
Sn	100,00	100,00	100,00
Ti	100,00	100,00	100,00
V	99.99	99.99	98,65

Geochemical modeling – Results

Chemical composition of 1,5m³ ES
Comparison with legally allowed concentrations in groundwater

Element	OPW	NaCl	Legal limit
Composition 1,5 m³ EQS	mg/l	mg/l	mg/l
As	804	810	0,010
B	4381	2330	0,740
N	804	810	44,300
Ni	4,5E-3	2,1E-3	0,014
Zr	5,8E-5	3,0E-5	*
Mn	8,6E-7	5,1E-6	0,05
Mo	8	2531	0,035
Cu	3,8E-8	4,0E-7	0,014
Cr	3,7E-7	0,160	0,007
Sn	2,2E-9	4,6E-8	*
Ti	1,0E-5	6,6E-6	*
V	0,053	1012	0,004

* No legal limit

Discussion results of Geochemical Modeling

Metal corrosion involves high H_2O consumption

Is required amount of water available ?

In clay formations probably yes

How fast can pore water be supplied?

ca. 230 ml/a i.e. ca. 20.000 a for 5 m^3 OPW

How fast is corrosion?

at a rate of 1 µm/a ca.152 g/a

Which process is faster, consumption or supply of pore water?

230 ml/a supply, 50 ml/a consumption

Volumes of ES low, density and ionic strength high

Conclusions

The release, mobilization and transport of toxic elements has been modeled and the results have been compared with legal limits

The available tools for Geochemical and Transport Modeling have been successfully tested

Results of the Geochemical Modeling:

- Concentrations of contaminants are much higher in highly concentrated solutions
- Such high salinity EQS are likely to be formed not only in the clay formations Northern Germany with NaCl saturated pore waters but also in Switzerland and Souterh Germany in the Opalinus clay with low salinity pore waters
- For the Geochemical Modeling of the geochemical processes in clay formations of all types the Pitzer Formalism and Pitzer data seem to be the better option

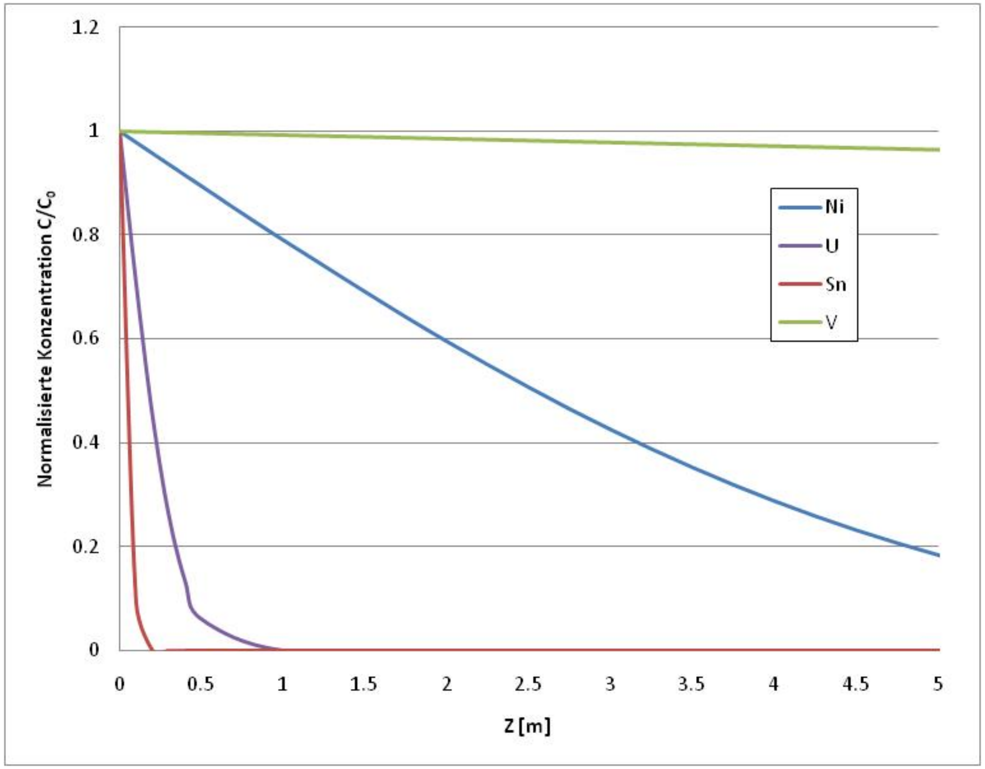
Results of the Transport Modeling:

- The transport of contaminants horizontally and perpendicular to the bedding slows down considerably the contaminant concentrations reaching the clay formation boundary
- Retention in in the clay formation is an important safety factor
- According to the 2D Transport Modeling only contaminants for which no retention was considered reached the clay formation boundary after 1 million years

Transport Modeling - results

1D-Transport in Bentonite

Strongly dependant on sorption

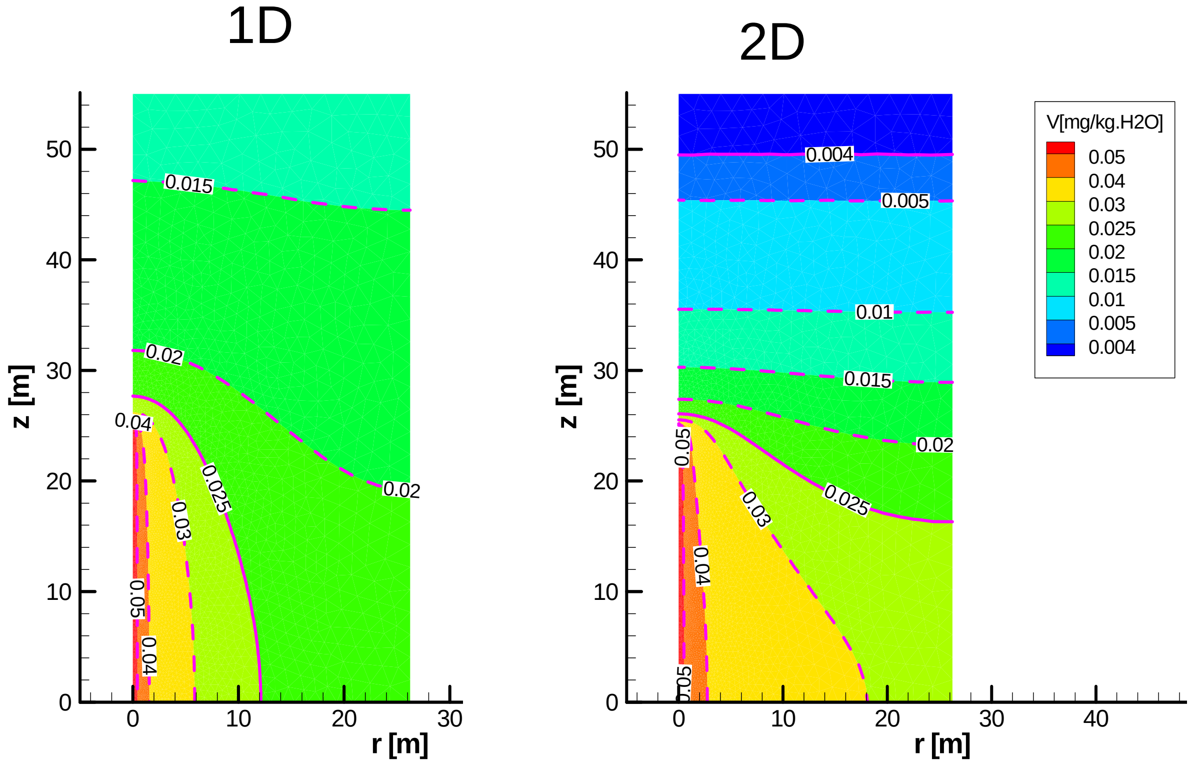


Concentration profiles of Ni, U, Sn und V after 1 Mio. years

(a)

Transport Modeling - results

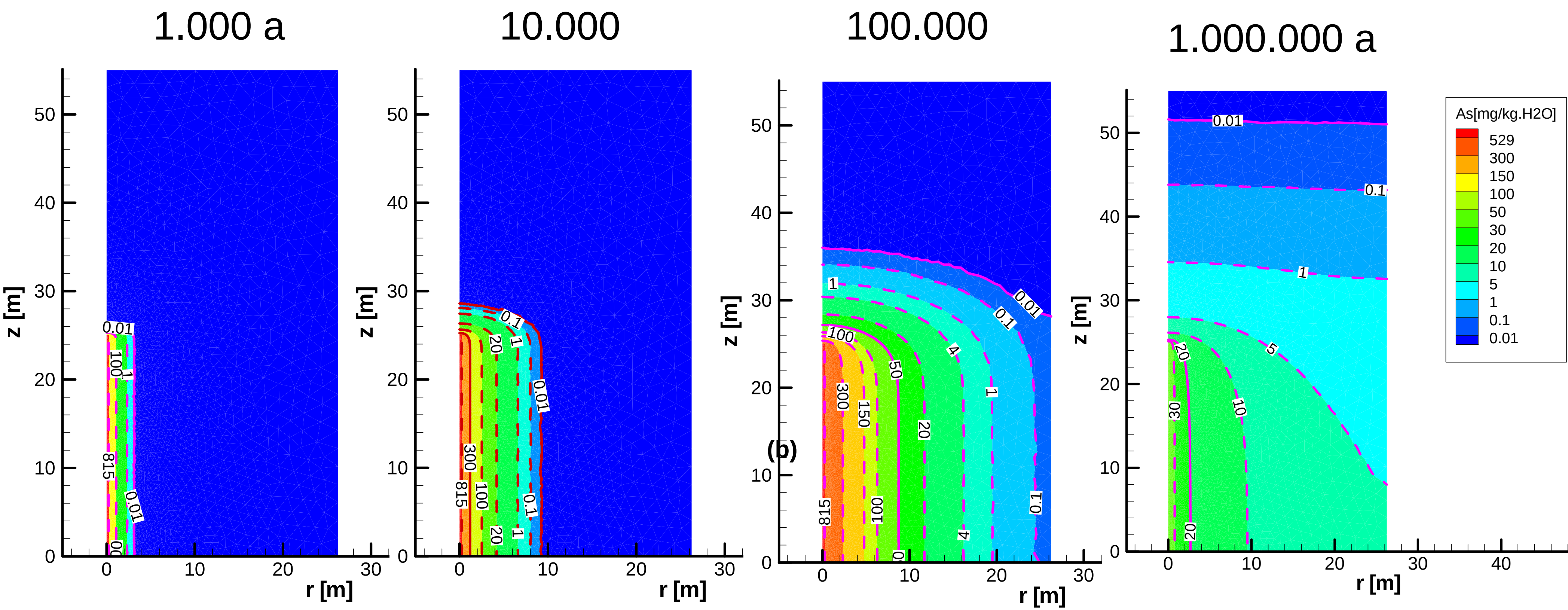
Opalinus clay



V concentration profiles in OPWW after 1 Mio.

Transport Modeling - results

2D Opalinus clay



As ile in OPW, Beurteilungswert: 0,01 mg/kg H_2O