9th Annual GTT-Technologies Workshop
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Speciation and Migration of Radionuclides in the Near-Field of an Underground Waste Repository in Salt Rock

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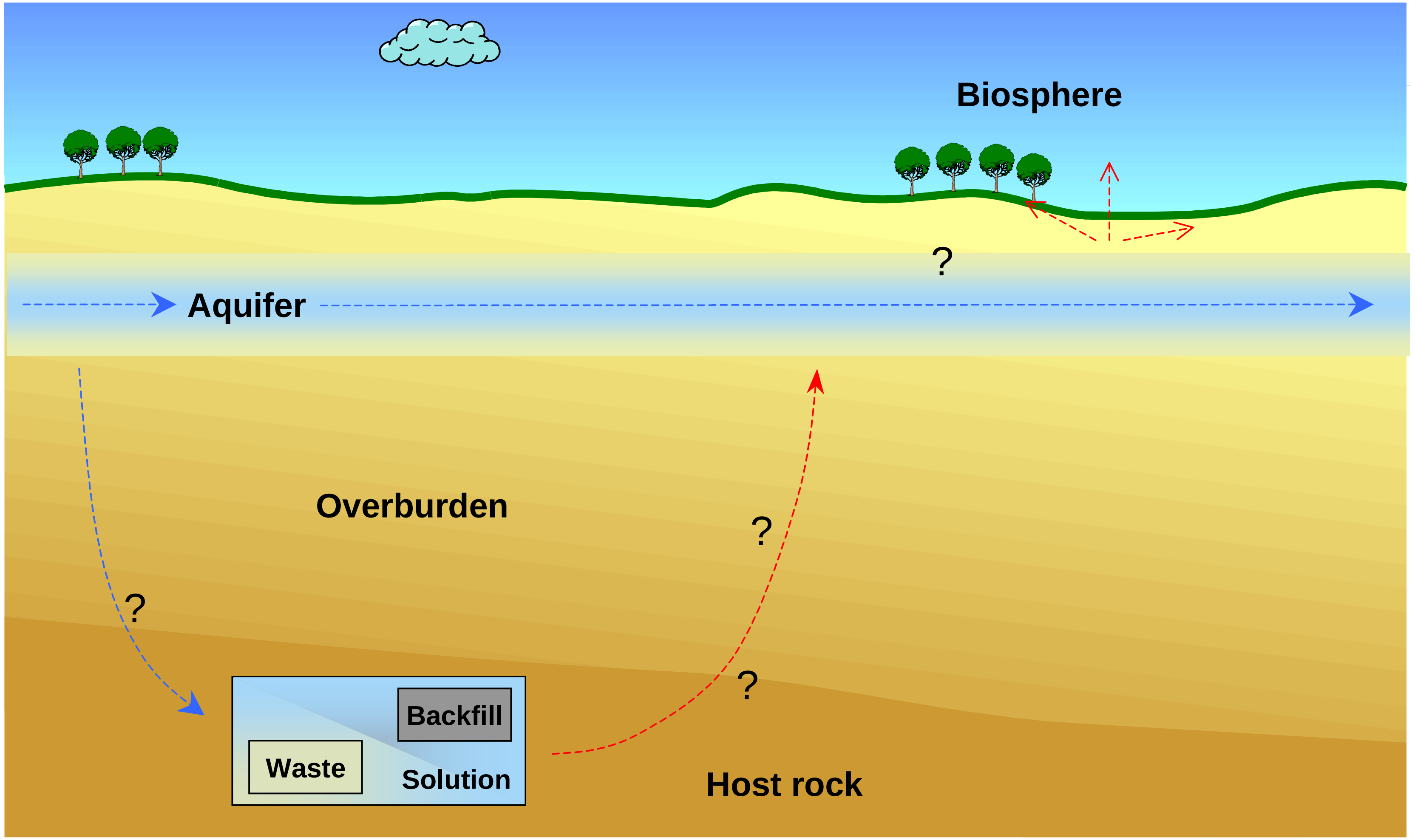
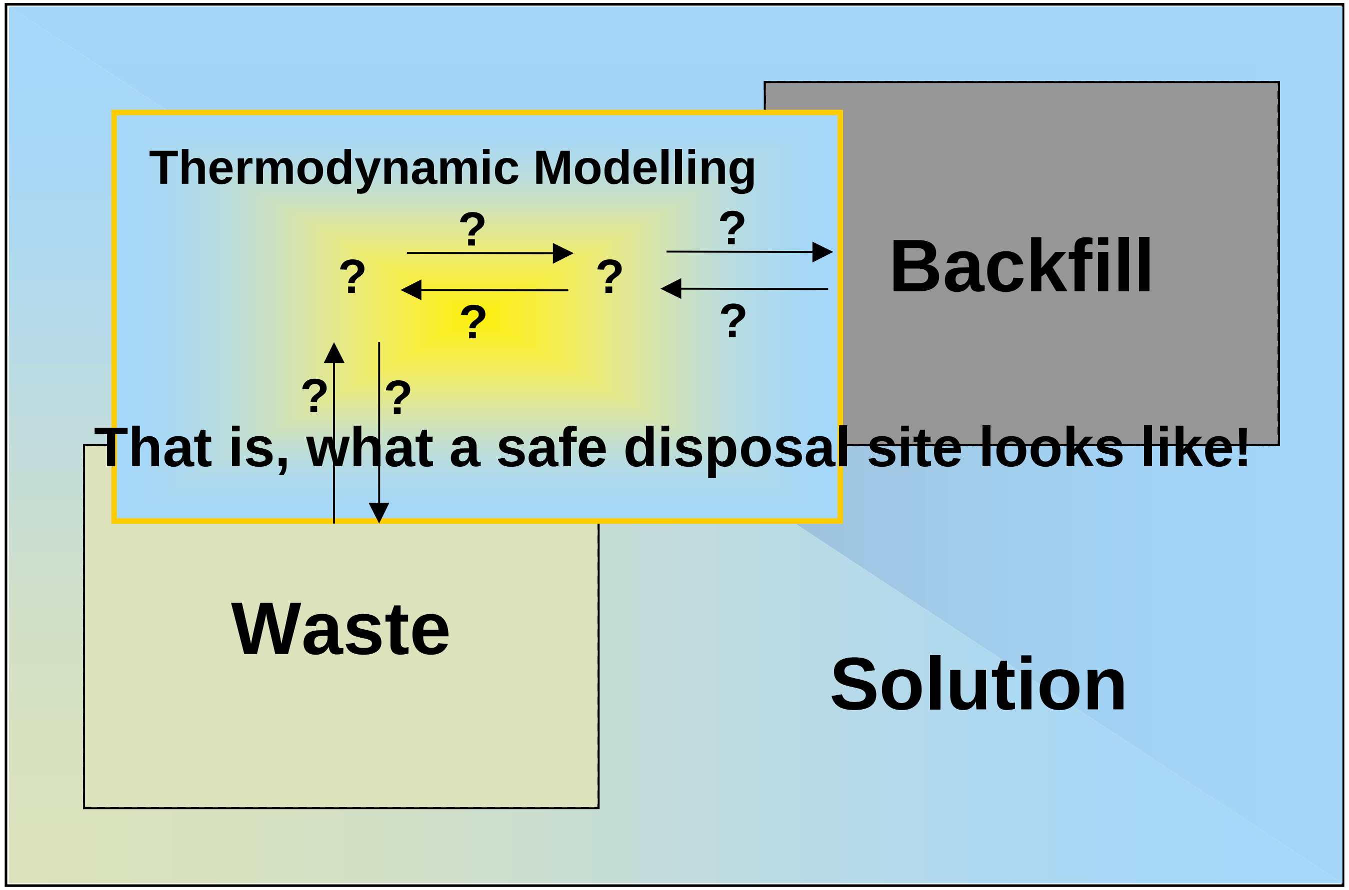
What you are going to learn …

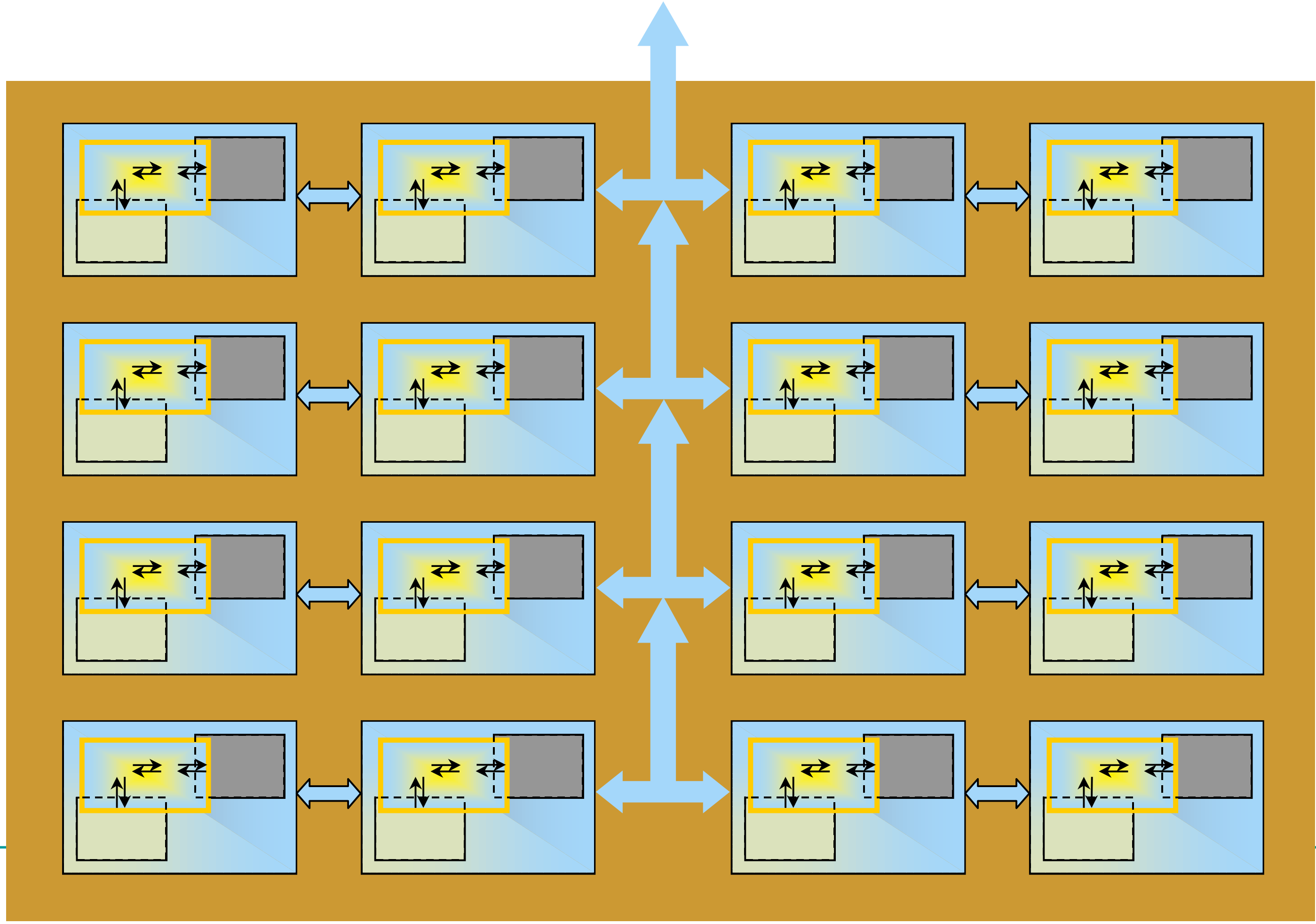
- What is „safety analysis“ about?
- How is thermodynamic modelling hooked in?
- Which data are needed?
- Applications
  - Some calculations of radionuclide solubility
  - Mobilization of radionuclides from vitrified waste
  - Diffusional transport in a clayey barrier
  - Reactive transport in geothermal fractured rock
  - Coupled CHM-behaviour of salt-based borehole-sealings
- What‘s about future developments?


Biosphere
?
Aquifer
Overburden
?
?
?
Backfill
Waste
Solution
Host rock

Disposal chamber for waste

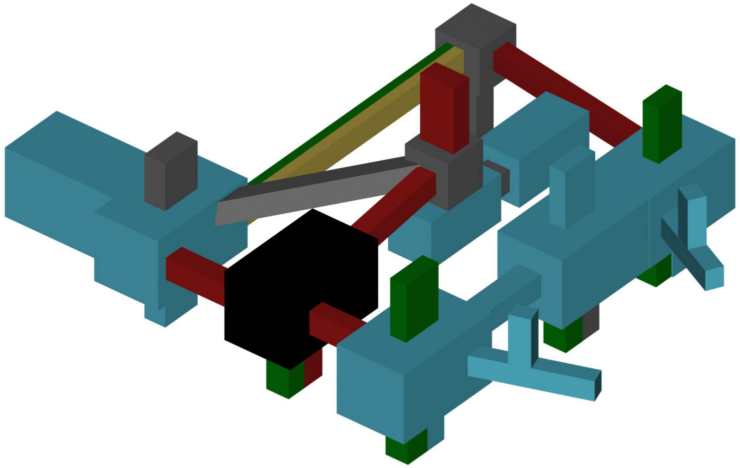


Many caverns form one system…

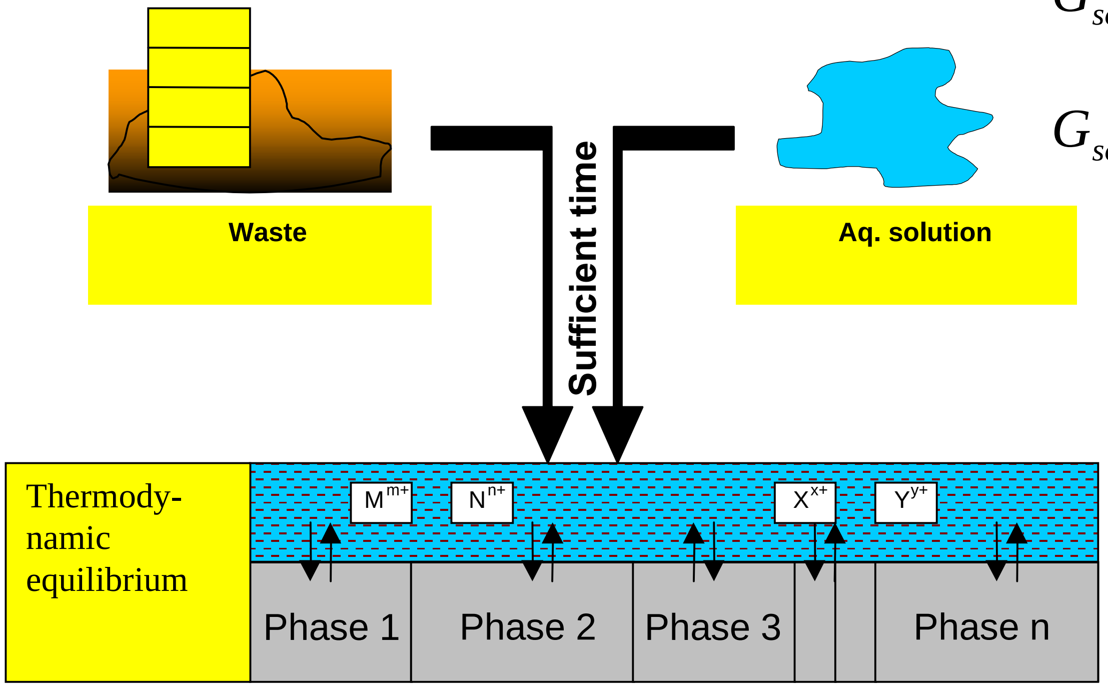


Of course, a real underground structure of a disposal site is much more complex…
This is just ONE base of an underground disposal site

- **Red** = Barriers
  Green = solid salt
  Blue = crushed salt
  Black = Disposal cavern
  Grey = Excavation-disturbed zone
- Up to 15 bases possible



Interaction Waste - Solution



Phasecomposition:

$$G_{solids} = \sum_{Phases\ i} n_i \cdot G^{\otimes}_{f,i}$$

$$G_{solution} = \sum_{i} n_i \left(G^{\otimes}_{f,i} + RT\left(\ln m_i + \ln \gamma_i\right)\right)$$

Equilibrium

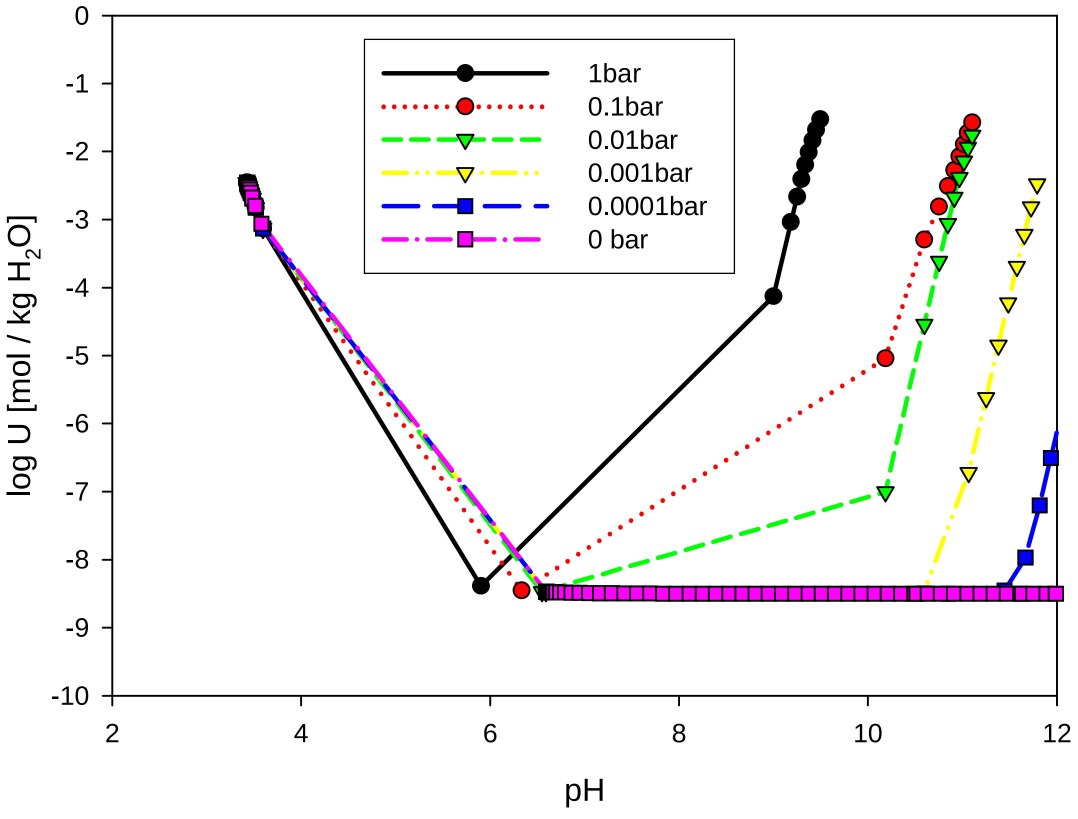
$$K = \prod_j a_j^{\nu_j} = \prod_j m_j^{\nu_j} \cdot \gamma_j^{\nu_j}$$

Application: Radionuclide solubility

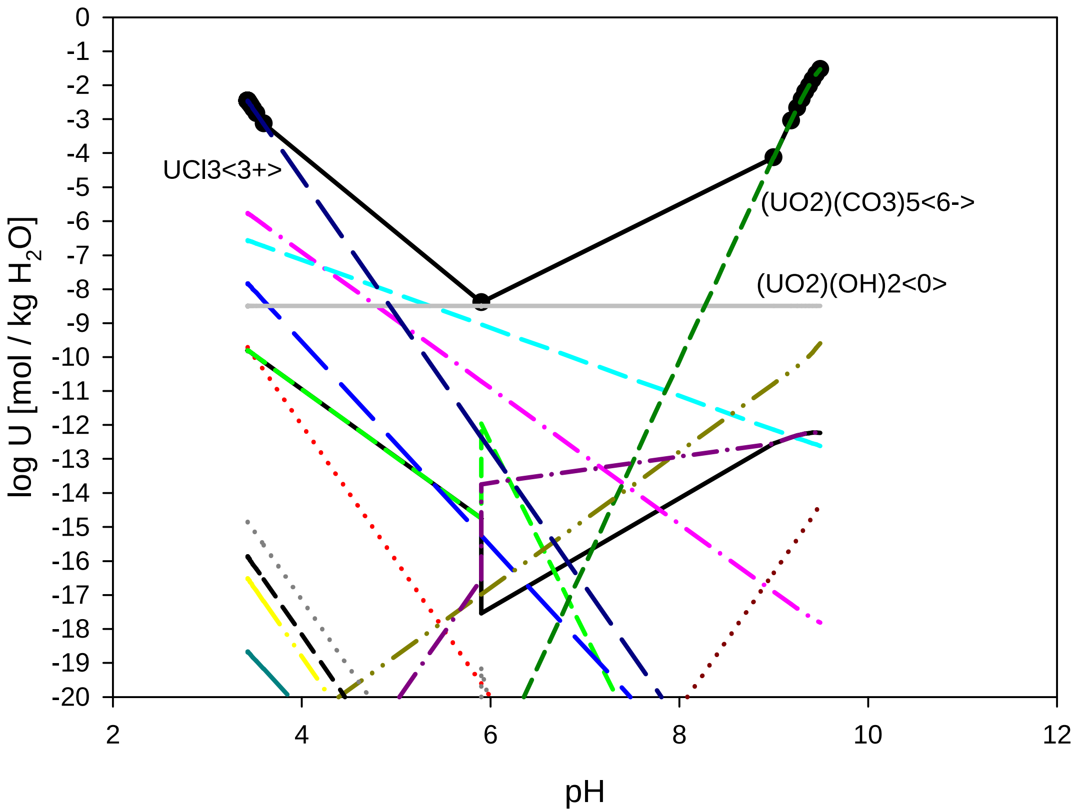
Example: UO_2

- Saturated NaCl-solution
- CO_2-fugacity = 1 … 0 bar
- Titration with NaOH

Solubility of U(IV) – diffferent pCO2



Solubility of U(IV) – (some) species (pCO2 = 1 bar)

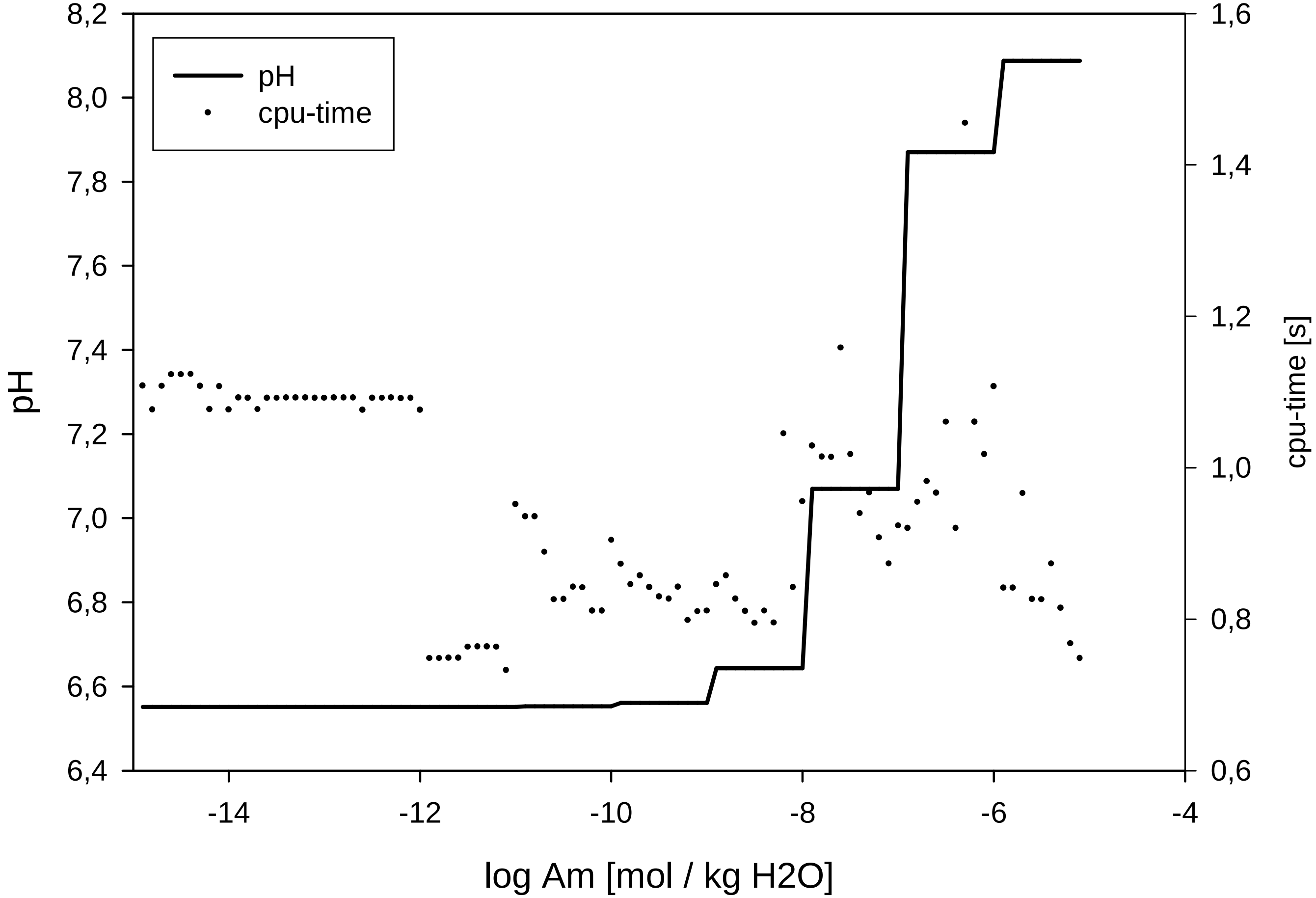


Application: Influence of radioactive decay

Example: Reaction Am(IV) + Np(IV) → Am(III) + Np(V)

- 1 kg H_2O
- 7 mol NaCl
- 1.2 mol N_2
- AmO_2: 1E-05 → 1E-15
- NpO_2: 1E-15 → 1E-05

Reaction Am(IV) + Np(IV) → Am(III) + Np(V)



Application: Mobilisation of radionuclides from waste

Example: vitrified waste (R7T7)

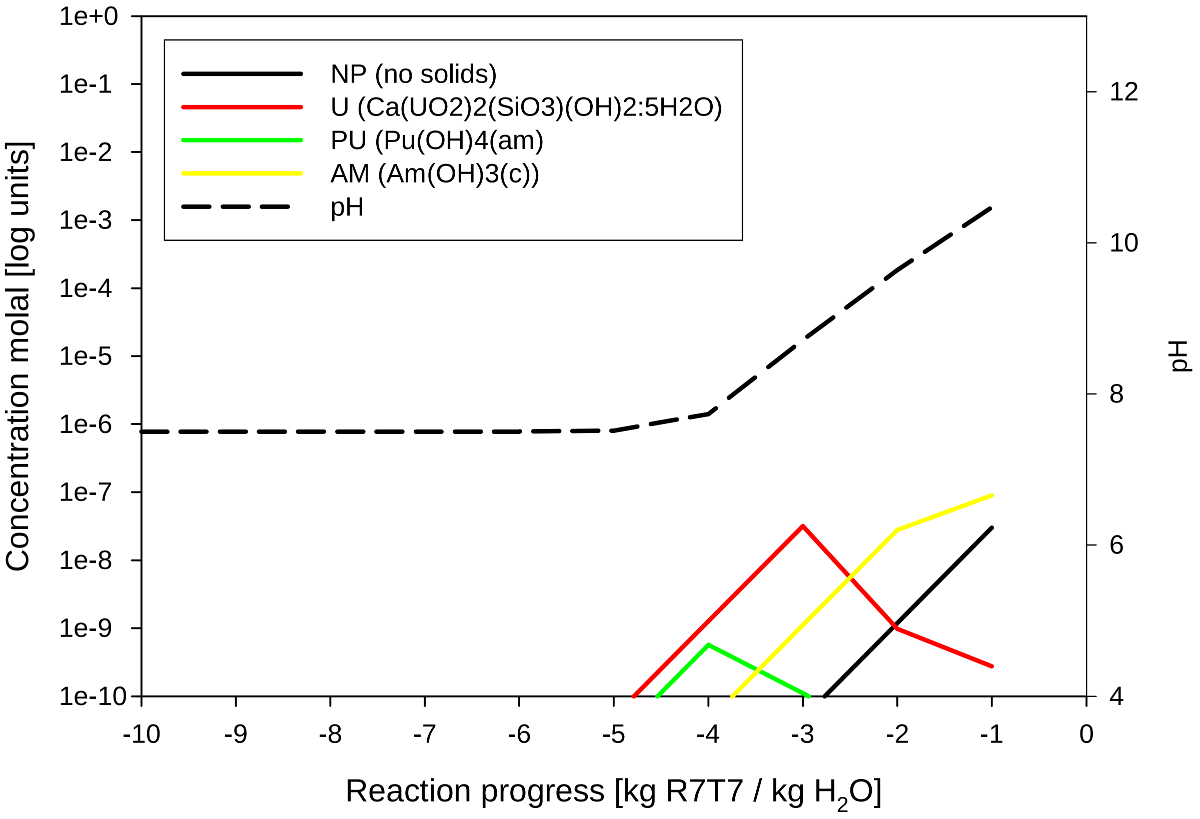
Inventory in terms of elements

	Element	Assumed Oxidationnumber	R7T7-glass [mol/kg]	spent fuel [mol/kg]
Matrix	Li	+1	1.34	$1.4 \cdot 10^{-4}$
	B	+3	4.11	$1.5 \cdot 10^{-5}$
	Na	+1	3.13	
	Ca	+2	0.73	$2 \cdot 10^{-4}$
	Si	+4	7.69	
	Al	+3	0.96	
	Fe	+3	0.34	
	Ni	+2	0.05	
	O		28.35	8.38
(modified by GRS)			27.10546	
Fission products	Sr	+2	0.032	0.006
	Se	+4		$9 \cdot 10^{-4}$
	I	±0		0.002
	Cs	+1		0.018
	Mo	+6	0.118	0.025
	Nd	+3	0.10	0.025
Actinides	U	+4	0.02	3.91
	Np	+4	$3 \cdot 10^{-5}$	0.04
	Pu	+4	0.009	0.045
	Am	+4	$7 \cdot 10^{-4}$	0.007

Boundary conditions

- 1 kg H_2O
- Saturated with halite (NaCl) and anhydrite ($CaSO_4$)
- „titrated“ with R7T7

R7T7: release of actinides



Application: diffusion in a clayey barrier

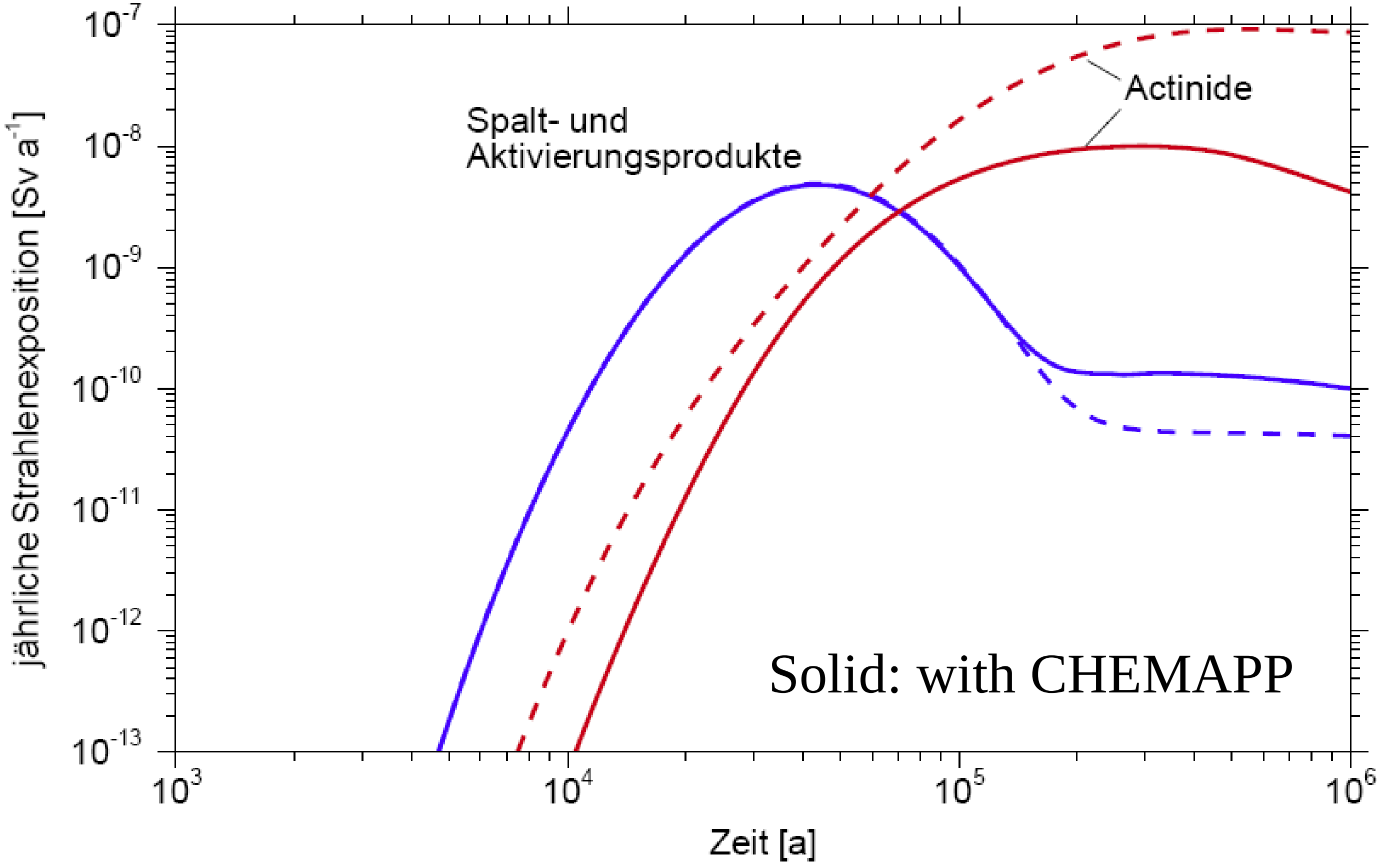
Moog, H. C.; Keesmann, S. (2007): Modellierung des reaktiven Stoff-transports im Nahfeld eines Endlagers, GRS-225, Abschlussbericht zu einem aus Mitteln des Bundesministeriums für Wirtschaft und Techno-logie (BMWi) geförderten Vorhaben, Fördernummer 02 E 9723, ISBN 978-3-931995-99-7, 179 Seiten.

Application: diffusion in a clayey barrier

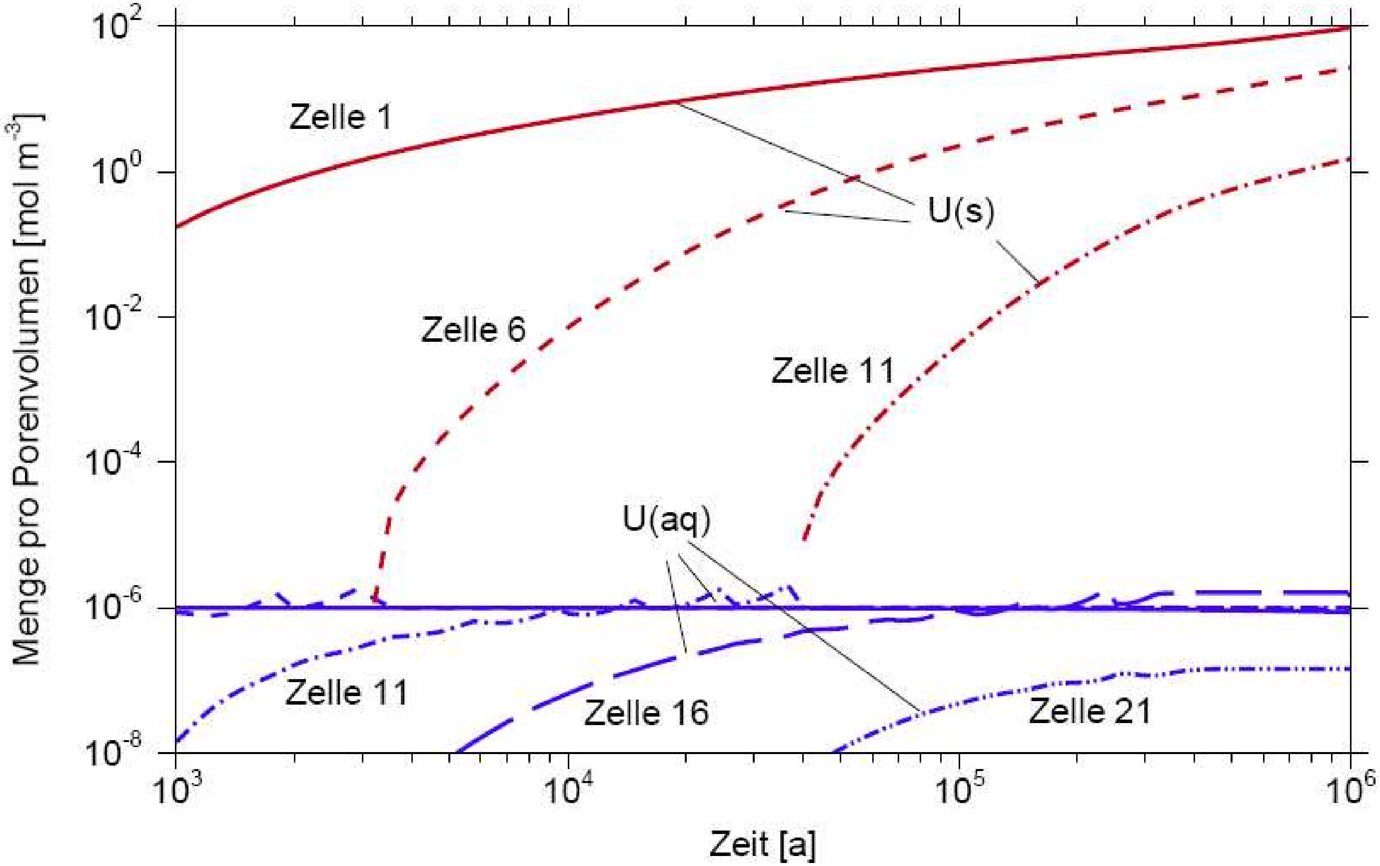
Example:

Behälter: BSK3-Kokille			**Transportstrecke**		
Länge	[m]	4,90	Dicke der Tonschicht	[m]	40,5
Radius	[m]	0,43	Dichte des Tonsteins	[kg m^{-3}]	2500
Zwischenlagerzeit	[a]	50	Porosität	[ ]	0,12
Standzeit	[a]	500	Diffusionskoeffizient	[$m^2 s^{-1}$]	$8{,}3 \cdot 10^{-11}$
Eisenmenge des Behältermaterials	[mol]	$4{,}387 \cdot 10^4$	**Randbedingung des Fernfeldes**		
Mobilisierungsrate des Behältermaterials	[a^{-1}]	10^{-6}	Volumenstrom im Aquifer	[m^3 a^{-1}]	10^6

Annual exposure of radiation



Development of U-inventory along the transportation path



Application: HTMC-coupled transport in fractured systems

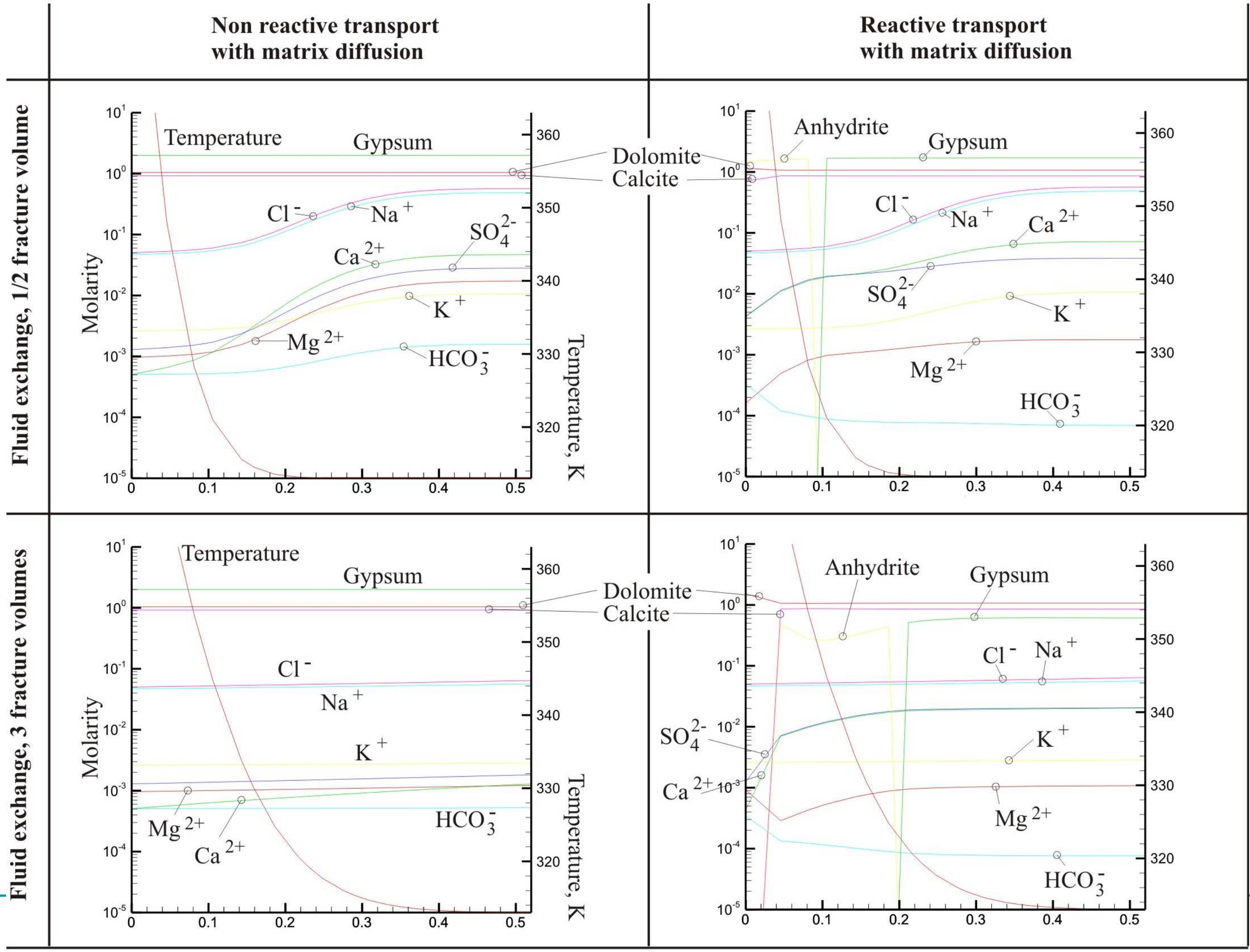
Example: mixing of seawater with geothermal water

C.I.McDermott, Georg Kosakowski, Ralph Mettier, H. Moog, O. Kolditz (2007): Geomechanical facies concept and the application of hybrid numerical and analytical techniques for the description of htmc coupled transport in fractured systems, PROCEEDINGS, Thirty-Second Workshop on Geothermal Reservoir Engineering Stanford University, Stanford, California, January 22-24, 2007, SGP-TR-183

Boundary conditions

Variable		*In situ* Sea Water	Geothermal Water
Temperature °C		40	120
pH		6.7	7.9
Aqueous Component	**Aq. Diff. Coeff. m²/s**	**Moles**	**Moles**
H2O		55.56	55.56
Na<+>	1.33E-09	4.85E-01	4.67E-02
K<+>	1.96E-09	1.06E-02	2.62E-03
Cl<->	2.03E-09	5.66E-01	5.01E-02
Mg<2+>	7.06E-10	1.72E-02	9.62E-04
Ca<2+>	7.92E-10	4.69E-02	5.05E-04
(SO4)<2->	1.07E-09	2.81E-02	1.29E-03
(HCO3)<->	1.00E-09	1.58E-03	5.05E-04
Solid Phase			
Ca(SO4)_Anhydrite		0	1.999
Ca(CO3)_Calcite		0.9247	1.002
CaMg(CO3)2_Dolomite		1.038	0.9991
Ca(SO4):2H2O_Gypsum		2.001	0

Result



Non reactive transport with matrix diffusion
Reactive transport with matrix diffusion
Fluid exchange, 1/2 fracture volume
Fluid exchange, 3 fracture volumes
Molarity
Temperature, K
Temperature
Gypsum
Anhydrite
Dolomite
Calcite
Cl -
Na +
Ca 2+
SO4 2-
K +
Mg 2+
HCO3 -

Application: Coupled CHM-behaviour in salt-based borehole-sealings

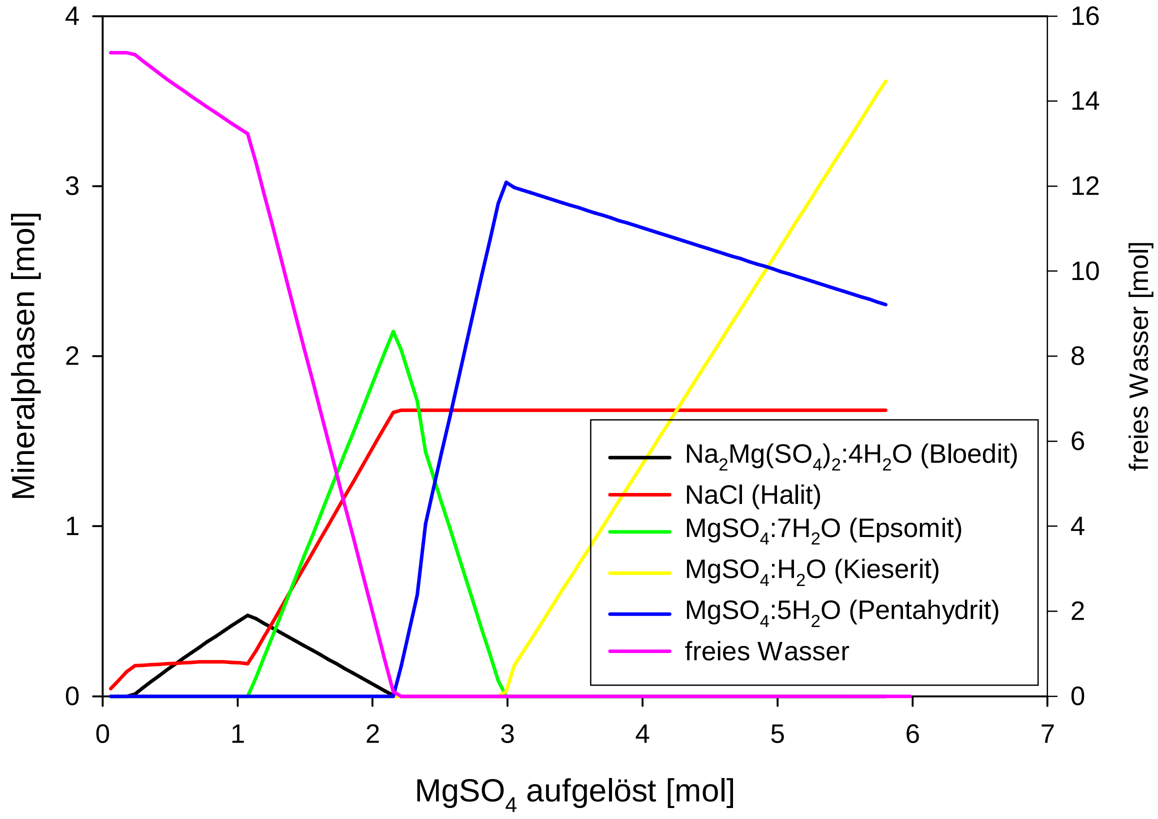
Example: Reaction of anhydrous MgSO4 with sat. NaCl-solution

F. Werunsky, Z. Hou, H. C. Moog (2007): Coupled modelling of the C:HM behaviour of self healing salt based backfill.

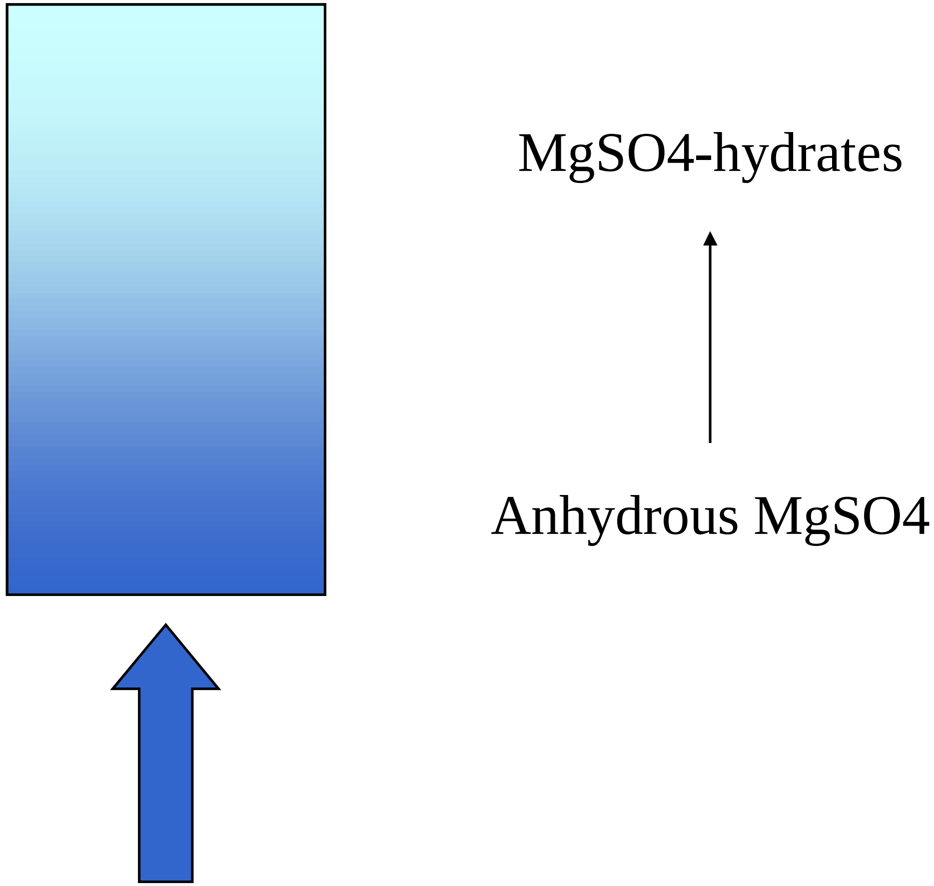
M. Xie, H. C. Moog, W. Wang, H.-J. Herbert, H. Shao, O. Kolditz (2007): Reactive transport modelling in salt material based on Gibbs energy minimization.

Both in: The Mechanical Behaviour of Salt - Under-standing of THMC Processes in Salt, Proceedings of the 6th Confer-ence on the Mechanical Behavior of Salt 'SALTMECH6', Hannover, Germany, 22-25 May 2007, ISBN 13: 978-0-415-44398-2, Taylor & Francis, London, UK.

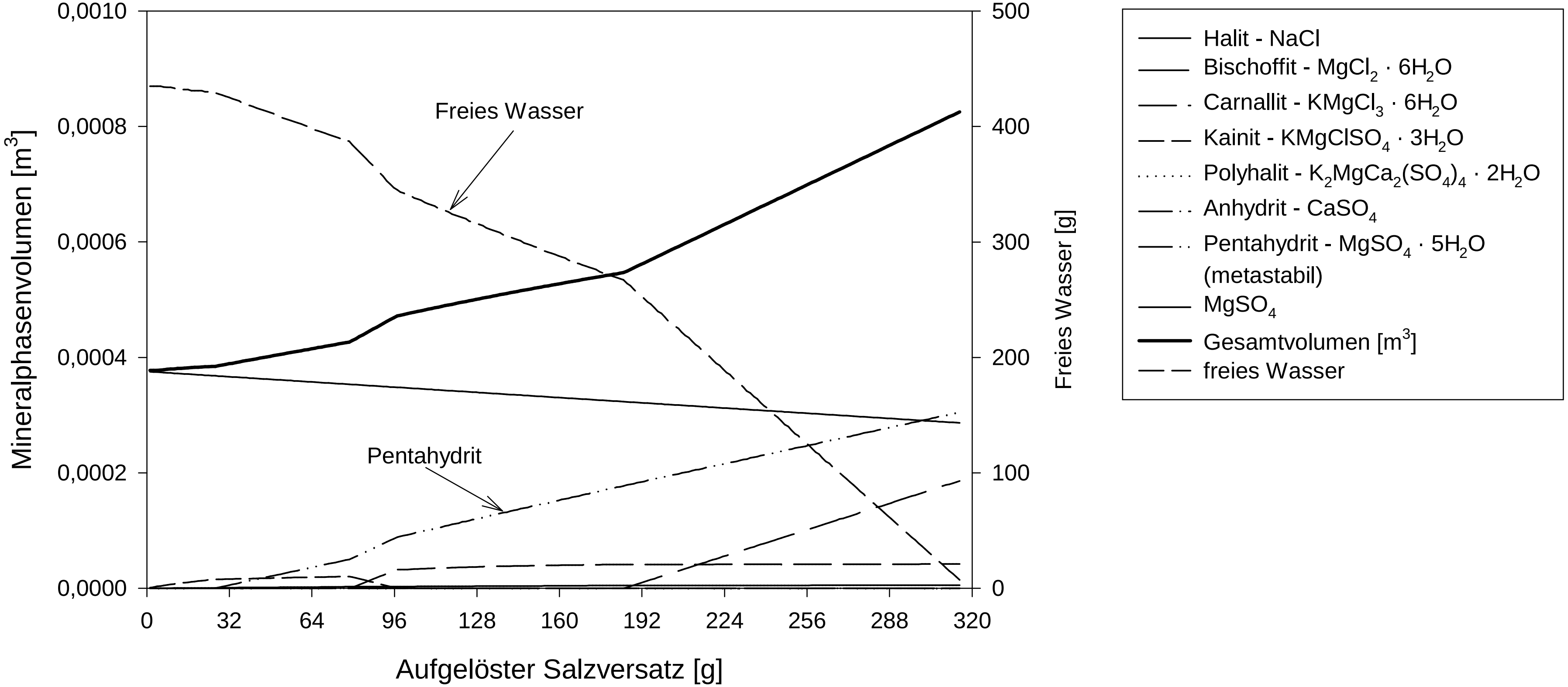
Formation of solids



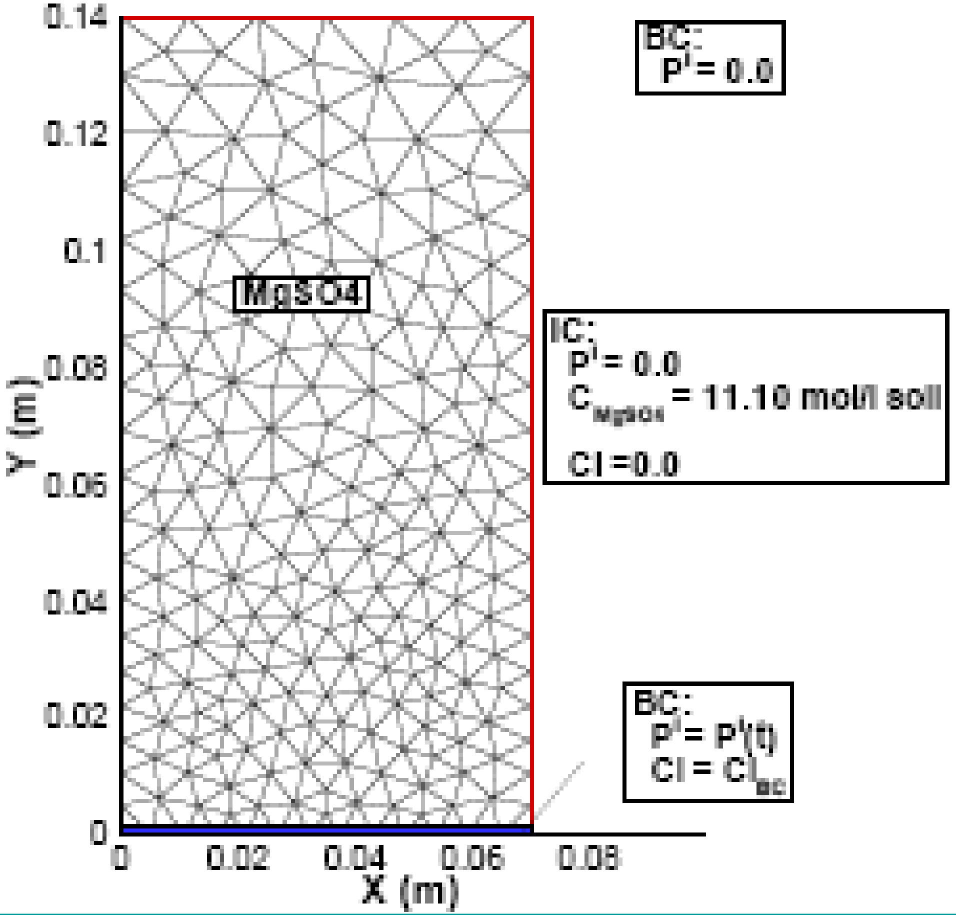
Principle



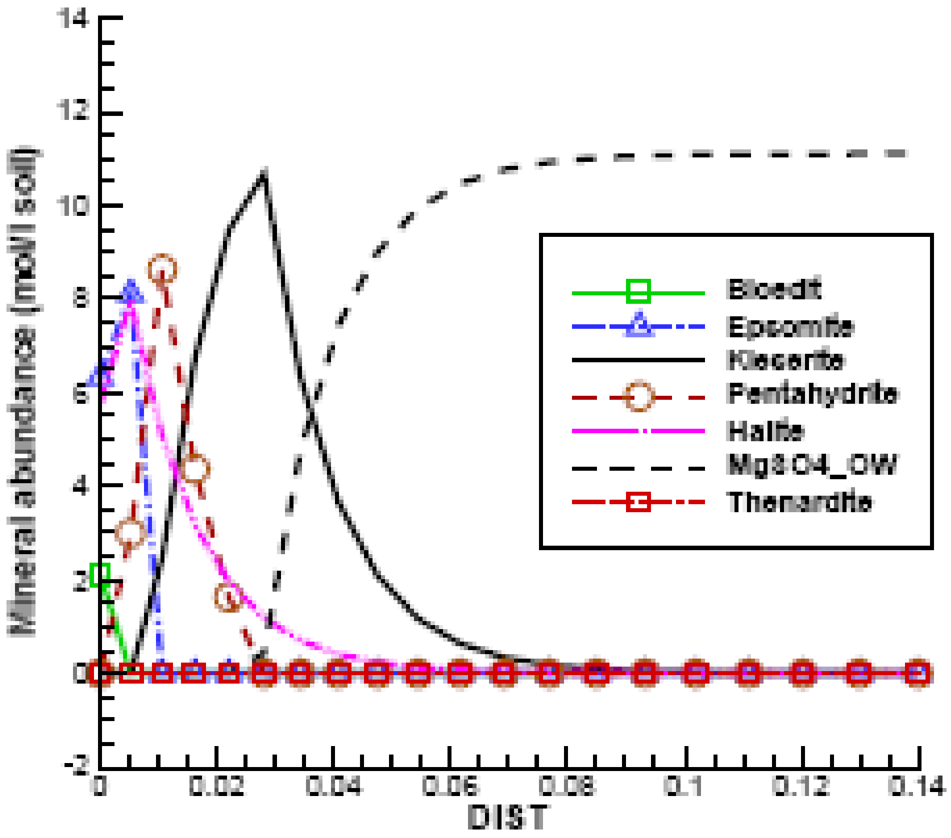
Total volume



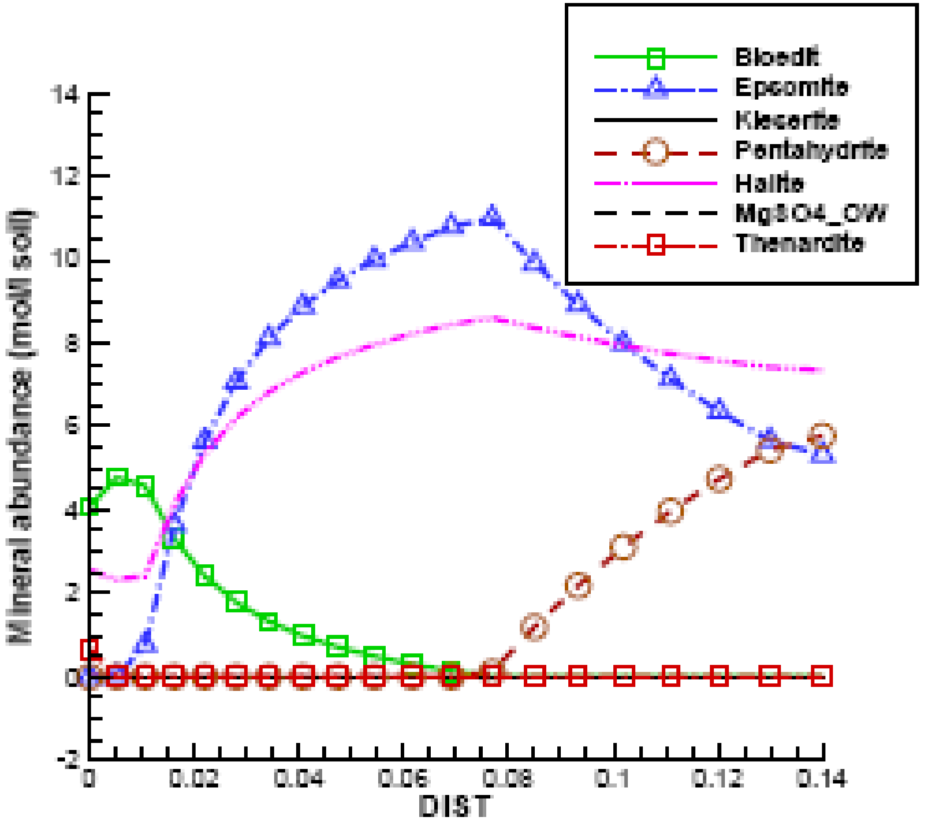
Model concept



Result: 1.1 * 10^3 sec



Result: 1.1 * 10^4 sec



Perspectives

- Implementation of coupling between volumetric changes due to chemical reaction and HM-behaviour (applications in clay and in geothermal systems)
- Steps to minimize computation time
- Performance assessment: Application to real systems with up to 150 caverns

Modells for the calculation of activity coefficients

- Debye-Hückel (1923): purely electrostatic interactions
- Extensions to the DH-equation…
- Approaches considering specific ionic iteractions …

$$\ln \gamma_i = DH \quad + \quad \sum_j \lambda_{i,j}(I) m_j \quad + \quad \sum_j \sum_k \mu_{i,j,k} m_j m_k$$

SIT -
Single Ion
Interaction Theory

Pitzer-Modell