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

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Abstract:
Indurated clays are candidate host rock formations for high level radioactive wastes (HLW) repositories. Clay pore water can corrode the containers and interact with the high level waste, whereby toxic components are released into the pore water. During this process large amount of water will be consumed, leading to a solution with higher ionic strength beyond the range where extended Debye-Hückel or Davies approach may be applied.

This study focuses on the modeling of the release and transport of heavy metals and toxic anions from three BSK3 canisters with spent fuel rods emplaced in a 50 m deep borehole backfilled with bentonite. The geochemical modeling was undertaken using CHEMAPP. Solute activities were calculated using the Pitzer formalism. It is assumed that 6.6 m^3 Opalinus clay pore water reacts with the containers with spent fuel and as a result 1.5 m^3 contaminated solution fills the remaining pore space in the borehole after completion of the corrosion. This solution is allowed to diffuse over a distance of 30 m through the Opalinus clay formation. The comparison of the 1D-analytic solution with 2D isotropic and anisotropic mass transport results demonstrated the capacity of the numerical tools and the influence of the transport parameters on the contaminant migration path.

1 INTRODUCTION

Clay formations are candidate rocks for HLW repositories in Germany and in several other European countries. A release and migration of radionuclide, heavy metals and other toxic substances in the aqueous phase is conceivable. Water from the saturated clay pore space can enter the disposal drifts and boreholes and interact with the containers and the wastes. The different types of canisters contain huge amounts of iron and heavy metals. So far safety assessment analyses have been focussed primarily on the reactions with the waste and the release of radionuclides. This study is focused on the release of heavy metals and anionic toxic substances from the repository. The reaction of clay pore water with the containers has been modeled. In the reaction high amounts of water are consumed and the ionic strength of the resulting solutions will be soon beyond the range where Extended Debye-Hückel or Davies approach may apply. Better results can be obtained with the Pitzer formalism which is able to describe solubilities up to high ionic strength. In a recent GRS project Pitzer parameters were developed for the heavy metals Hg, As, Cu, Co, Cr, and Ni (Hagemann et al. 2008). These data are consistent with the HMW Pitzer database for the system of oceanic salts (Harvie et al. 1984). Other Pitzer data, for instance for Al and Si, were added from the literature (Reardon et al. 1990). The completeness and quality of these data will be discussed and results of the modeling of the corrosion of three BSK3 containers (German containers for spent fuel rods) in a 50 m deep Borehole in Opalinus clay will be presented. The underlying scenario takes into account a water inflow from the surrounding clay formation into the backfilled borehole, the corrosion of the containers, the consumption of water by the reaction, the replenishing of the water supply from the surrounding rock and the partial release of the hydrogen generated by the corrosion. This is the scenario of the normal evolution of a repository in clay. The evolution of pH and Eh as well as of the solution composition and the formation of mineral phases will be shown. The composition of the resulting final solution is used for 1D and 2D transport modeling from the near field through a 30 m thick clay layer. Only diffusive flow is considered. Diffusion coefficients and sorption coefficients were taken from the literature. The time dependant spreading of the contaminants through the clay formation will be shown up to one million years. The concentrations of heavy metals and anionic toxic substances at the boundary of the clay formation will be compared with the drinking water ordinance in Germany.

2 GEOCHEMICAL MODELING

For thermodynamic equilibrium modeling we applied the commercial programmer's library CHEMAPP (Eriksson et al. 1997). It consists of a set of subroutines which provides all the necessary tools for the calculation of complex multicomponent, multiphase chemical equilibria and the determination of the associated energy balances. CHEMAPP locates thermodynamic equilibrium on the basis of minimization of the global Gibbs Free Energy with the mass balances as linear subsidiary constraints. As such, it is to be distinguished from programs like PHREEQC (Parkhurst and Appelo 1999) or Geochemist's Workbench (Bethke 1994), where equilibria are identified on the basis of equations for law of mass action. For the minimization purpose Lagrange's method of undetermined multipliers is applied. Since the multipliers turn out to be the chemical potentials of the system components at equilibrium, they can thus be used to simply calculate the relative activities of all phase constituents and pure stoichiometric phases contained in the system.
The chemical composition of one BSK3-container was listed in Tab. 1.
The chemical simulation was conducted under the following assumptions:

- 25°C and 1 bar initial pressure.
- Opalinus clay (OPC) pore water (Tab. 2) enters into a borehole with 50 m in depth and 0.46 m in diameter.
- Within the borehole there were three BSK3-container surrounded with compacted bentonite, which has a porosity of 50%.
- Each BSK-container is cylindrical with 4.98 m in height and 0.43 m in diameter. The total free pore space in the borehole amounts 3.068 m^3.
- With the intrusion of OPC pore water into the borehole, the corrosion process of the canisters was initiated and water was consumed. Large quantities of gas (mainly H2) were released.
- The maximal gas pressure was set to be the static liquid pressure surrounding the borehole.

The simulated results were listed in Tab. 3.

Tab. 1 Chemical composition of one BSK3-container with spent fuel

Element	**Inventory** [mol]
C	340.44
Si	356.32
Mn	790.94
P	14.04
S	7.26
Ni	694.25
Al	42.93
As	5.39
Cr	1395.86
Cu	27.83
Mo	13.16
N	28.86
Nb	1.09
Sn	62.56
Ti	63.18
V	9.92
B	332.84
Zr	5091.48
UO2	6840.63
Al2O3	20.89
Fe	48220.16

Tab. 2 Pore water chemical composition of Opalinus clay (Pearson et al. 2002)

Chemical component	Concentration (g/kg H2O)
NaCl	6.13
KCl	0.06
MgCl2	0.47
CaCl2	0.77
SrCl2	0.05
Na2SO4	1.63
NaHCO3	0.05
pH	7.9

Tab. 3 Total inventory and mobile contaminants in 1.5 m^3 solution after the corrosion of three BSK3 containers by 6.6 m^3 Opalinus clay pore water

Element	Total inventory in the borehole		Mobile inventory in 1.5 m3 solution after corrosion	
	mol	g	mol	g
Fe	144660.49	8078565.06	5.53E+01	3.09E+03
Al	254.12	6856.63	7.10E-06	1.90E-04
U	20521.89	4884804.02	4.76E-06	1.13E-03
P	42.11	1304.39	4.21E+01	1.30E+03
As	16.18	1212.48	1.62E+01	1.21E+03
Ni	2082.75	122243.76	1.16E-04	6.81E-03
Zr	15274.45	1393396.29	9.64E-07	9.00E-05
Mn	2372.83	130358.40	2.37E-08	1.30E-06
Mo	39.49	3789.00	1.30E-01	1.25E+01
Cu	83.48	5304.60	8.91E-10	5.66E-08
Cr	4187.59	217738.26	1.08E-08	5.63E-07
Sn	187.68	22280.04	2.88E-11	3.42E-09
Ti	189.53	9072.03	3.38E-07	2.00E-05
V	29.75	176.79	1.59E-03	1.00E-02

3 TRANSPORT SIMULATION

3.1 Theoretical Background

The simulator GeoSys/RockFlow is adopted for the mass transport modelling (Kolditz and Shao 2009). This software is developed for fully or partially saturated porous media, in which the aqueous and/or gaseous phases are considered mobile, while the solid phases are assumed to be immobile. The current work is assumed to be saturated isotropic/anisotropic porous media.
The mass transport in a homogeneous, saturated porous media is determined by convection, diffusion, decay, biodegradation, sorption and chemical reaction. Conservative mass transport normally refers to mass transport without decay, biodegradation and chemical reaction. For a steady state 1D flow through a homogenous porous media the following equation is applied for the conservative mass transport (Kolditz et al. 2008):

$$\frac{\partial C}{\partial t} + \frac{\rho_b}{R} \cdot \frac{\partial S}{\partial t} + \frac{q}{R} \cdot \frac{\partial C}{\partial z} = D_{zz} \cdot \frac{\partial^2 C}{\partial z^2} \qquad \textbf{(1)}$$

In which
C - dissolved concentration (kg $\cdot$m^{-3})
t - time (s)
S - sorbed concentration (kg $\cdot$kg^{-1})
ρ_b - bulk density (kg $\cdot$m^{-3})
q - flow rate (m $\cdot$s^{-1})
z - distance (m)
D_{zz} - dispersion coefficient in z direction (m^2 $\cdot$s^{-1})
R - retardation factor (-)

The retardation coefficient R for the Henry isotherm is related to the Henry sorption coefficient K_D as described in the following equation:

$$R = 1 + \frac{\rho_b}{\phi} \cdot K_D = 1 + \frac{1-\phi}{\phi} \cdot \rho_s \cdot K_D \qquad (2)$$

with
ρ_s - density (kg ·m^{-3})
ϕ - porosity (-)
The sorbed concentration S represents the exchange process between the solid and the liquid phase and is described by:
$S = K_D \cdot C$
For clay material with extremely low permeability, diffusive mass transport is dominant. The following analytical solution can be obtained for homogeneous media:

$$C(z,t) = C_0 \cdot erf\left(\frac{z}{2\sqrt{D_a \cdot t}} \right) \qquad (3)$$

in which D_a is the apparent diffusion coefficient as:
$$D_a = \frac{\phi D_{zz}}{R} = \frac{D_e}{R}$$
with
D_e - effective diffusion coefficient (m^2 ·s^{-1}).

3.2 Assumptions

Most of the assumptions are the same as described in NAGRA (2002). The main points concerning toxic contaminant migration in the HLW system are:

- The host rock consists of the Opalinus Clay (OPC).
- Transport relevant properties of OPC are constant in space and time.
- Tunnel, ramp and shaft are considered to be sealed to a quality that is comparable to the original host rock properties, the propagation via these paths does not contribute significantly to the overall diffusion though the host rock, and especially no by-pass effects are assumed.
- Chemotoxic constituents are present either in solution or as sorbed phases.
- Dissolved chemotoxic contaminants are transported by diffusion.
- Transport is retarded by linear, reversible, equilibrium sorption, described by an element-dependent sorption coefficient (K_D).
- After the canister breaching, dissolved chemical components from the canister are fully exposed to bentonite.
- Bentonite and OPC are fully saturated.
- The effective porosity of anions and non-anions are different (Tab. 4) (NAGRA 2002; Bourg et al. 2003).

3.3 Material properties

The material properties of Opalinus Clay and bentonite for the mass transport modelling are listed in Tab. 4 and Tab. 5.

Tab. 4 Material properties of Opalinus Clay and bentonite (NAGRA 2002)

Parameter		Opalinus Clay	Bentonite
Density	kg/m^3	2394	1600
Effective Porosity for cation	-	0.12	0.50
Effective Porosity for anion	-	0.06	0.05

Tab. 5 Sorption (K_D) and effective diffusion coefficient (De) of Opalinus Clay (OPC) and Bentonite (NAGRA 2002)

	Opalinus Clay			Bentonite	
Element	K_D (m^3/kg)	D_e (m^2/s) horizontal	D_e (m^2/s) vertical	K_D (m^3/kg)	D_e (m^2/s)
Al	0	5.0×10^{-11}	1.0×10^{-11}	0	2.0×10^{-10}
As	0	5.0×10^{-12}	1.0×10^{-12}	0	3.0×10^{-12}
B	0	5.0×10^{-12}	1.0×10^{-12}	0	3.0×10^{-12}
C	0.001	5.0×10^{-12}	1.0×10^{-12}	6×10^{-5}	3.0×10^{-12}
Ca	0.001	5.0×10^{-11}	1.0×10^{-11}	0.003	2.0×10^{-10}
Cl	0	5.0×10^{-12}	1.0×10^{-12}	0	3.0×10^{-12}
Cr	0	5.0×10^{-11}	1.0×10^{-11}	0	2.0×10^{-10}
Cu	0	5.0×10^{-11}	1.0×10^{-11}	0	2.0×10^{-10}
Fe	0	5.0×10^{-11}	1.0×10^{-11}	0	2.0×10^{-10}
H	0	5.0×10^{-11}	1.0×10^{-11}	0	2.0×10^{-10}
K	0	5.0×10^{-11}	1.0×10^{-11}	0	2.0×10^{-10}
Mg	0	5.0×10^{-11}	1.0×10^{-11}	0	2.0×10^{-10}
Mn	0	5.0×10^{-11}	1.0×10^{-11}	0	2.0×10^{-10}
Mo	0.01	5.0×10^{-12}	1.0×10^{-12}	0	3.0×10^{-12}
N	0	5.0×10^{-12}	1.0×10^{-12}	0	3.0×10^{-12}
Na	0	5.0×10^{-11}	1.0×10^{-11}	0	2.0×10^{-10}
Ni	0.9	5.0×10^{-11}	1.0×10^{-11}	0.2	2.0×10^{-10}
O	0	5.0×10^{-12}	1.0×10^{-12}	0	3.0×10^{-12}
P	0	5.0×10^{-12}	1.0×10^{-12}	0	3.0×10^{-12}
S	0	5.0×10^{-12}	1.0×10^{-12}	0	3.0×10^{-12}
Si	0	5.0×10^{-12}	1.0×10^{-12}	0	3.0×10^{-12}
Sn	100	5.0×10^{-11}	1.0×10^{-11}	800	2.0×10^{-10}
Ti	0	5.0×10^{-11}	1.0×10^{-11}	0	2.0×10^{-10}
U	20*	5.0×10^{-11}	1.0×10^{-11}	40	2.0×10^{-10}
V	0	5.0×10^{-11}	1.0×10^{-11}	0	2.0×10^{-10}

* Rübel et al. 2007

3.4 Model setup

Based on the symmetrical geometry and material properties, a 2D symmetrical model is applied for the numerical mass transport in the OPC-Clay (Fig. 1). The vertical borehole is in the center with a radius of 0.23 m and 50 m in height. Three canisters are evenly distributed in the borehole. The rest of the borehole is filled with bentonite. An observation point was set 30 m above the center of the borehole for comparison of simulated results by various scenarios. With the intrusion of pore water from the surrounding OPC clay, chemical reactions is supposed to occur and is assumed that the end solution with toxic contaminants can easily reach the borehole/clay boundary due to the small gap between them. The concentration of all contaminants within the borehole is assumed to be constant for the whole simulation time. The flow field is set to be diffusion only.

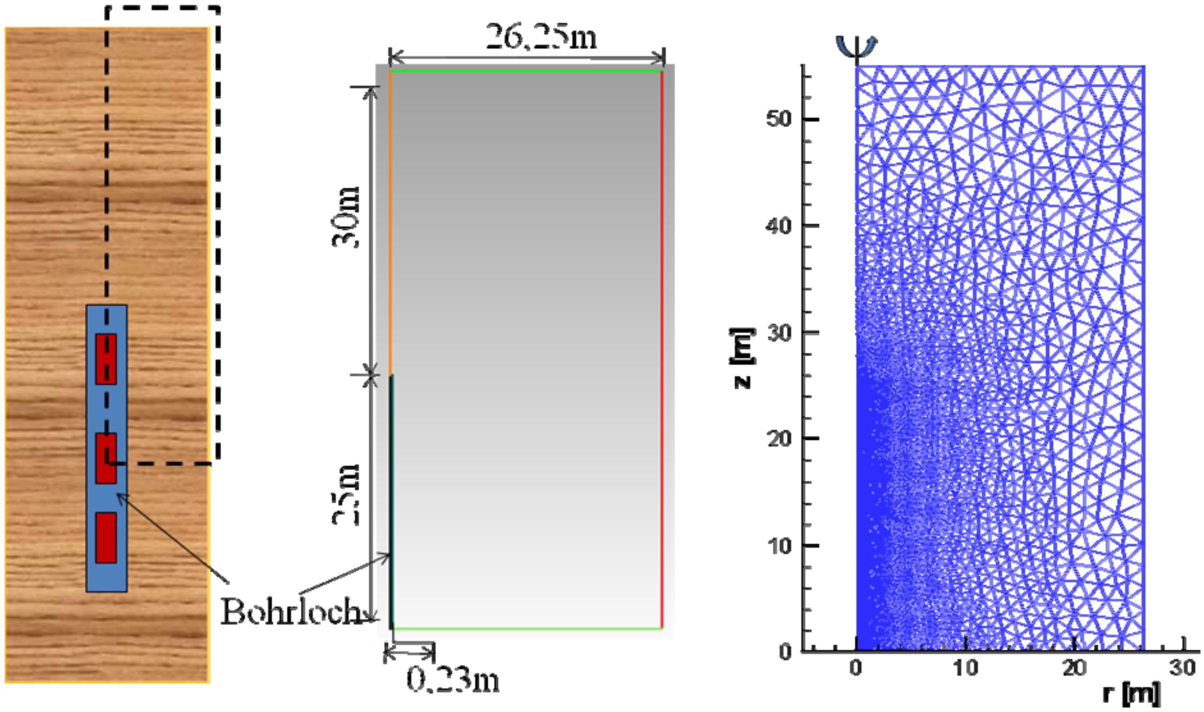

Fig. 1: 2D symmetrical model set-up and discretization

The pore space in the borehole was filled with contaminated solution that was separatedly calculated using CHEMAPP (Tab. 3). In the Opalinus Clay, it was initially saturated with OPC pore water, for which chemical composition from experiments was found in the literature (Tab. 2).

4 RESULTS AND DISCUSSION

The conservative mass transport modeling was undertaken by 1D analytic calculation (in vertical direction at the central of the borehole), 2D symmetric isotropic and anisotropic numerical modeling.

The 1D analytic calculations were conducted with a model starting at the center on top of the borehole and ending 30 m vertically through the OPC. This represents the shortest path for the contaminants from borehole to reach the biosphere. The effective diffusion coefficients were set for all cations with 1×10^{-11} m^2/s and for anions with 1×10^{-11} m^2/s. The sorption coefficient (k_D) of the elements differs from each other. The k_D values were found in the literature. If no suitable values found, the sorption effect of that element was than not considered (k_D =0). After 1 million years the moving front of several elements without sorption effect like V could reach the observation point (30 m above the borehole). The higher the k_D –value, the slower the contaminants were transported (Fig. 2). The k_D of Sn, for instance, was 100 m^3/kg, which is much higher than the other elements. The migration front of Sn remained within 0.5 m even after one million years.

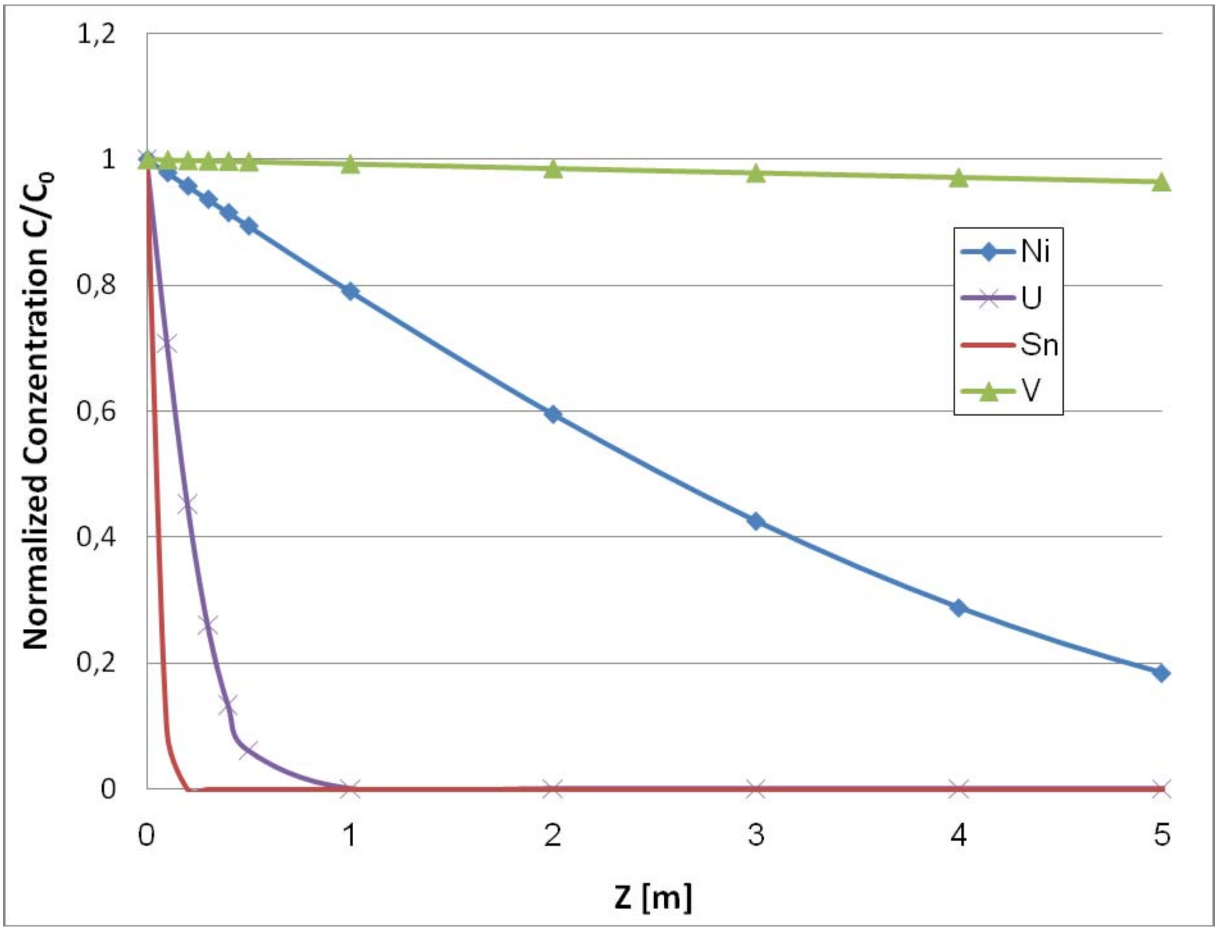

Fig. 2: Concentration profiles of Ni, U, Sn and V after one million years (1D-analytic)

The 2D symmetric isotropic as well as anisotropic simulations were also undertaken. The vertical diffusion coefficients were applied for the isotropic case. For comparison, the concentration evolutions of Vanadium (V) at the observation point were plotted in Fig. 3. The result of 2D isotropic case was close to the 1D analytic solution. However, the 2D anisotropic case showed quite different results from the 2D isotropic case. This reveals the fact that the five times higher horizontal effective diffusion coefficient enables the contaminants to diffuse preferably horizontal. Consequently, the vertical transport will be delayed (Fig. 4). For anions the same trend was observed as shown in Fig. 5 as an example of Arsenic (As) migration in an anisotropic OPC.

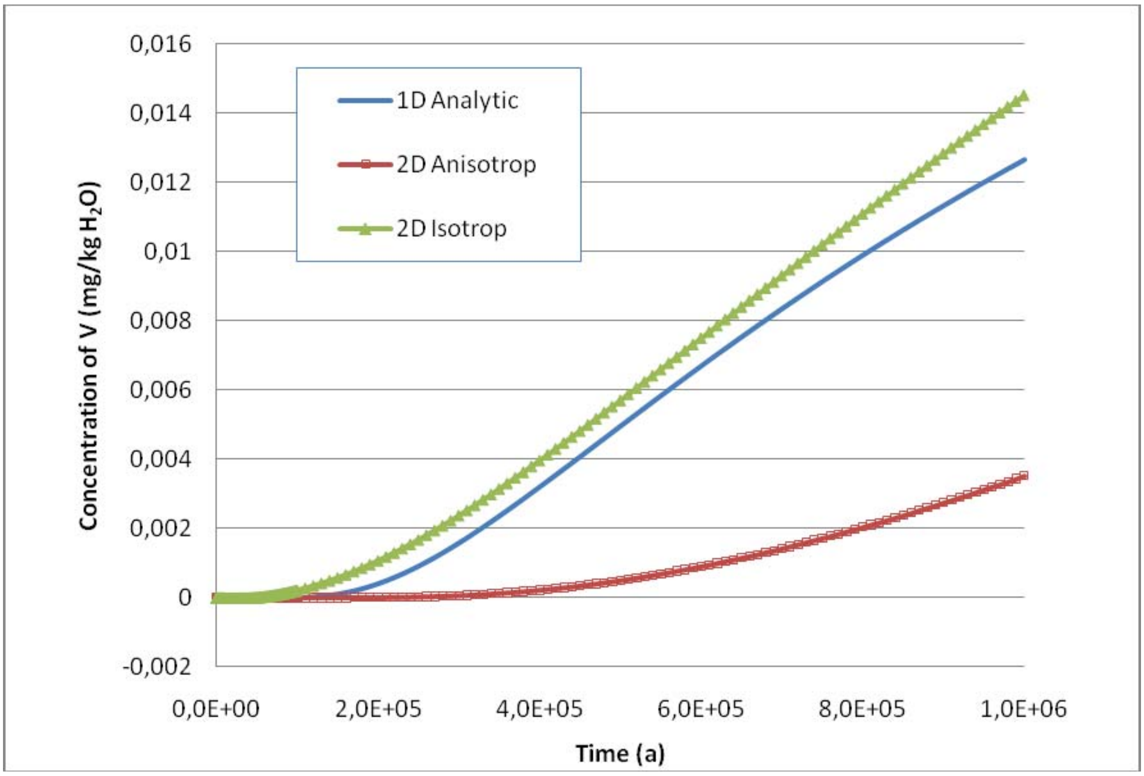

Fig. 3: Evolution of V concentrations with time in the 1D and 2D transport modeling

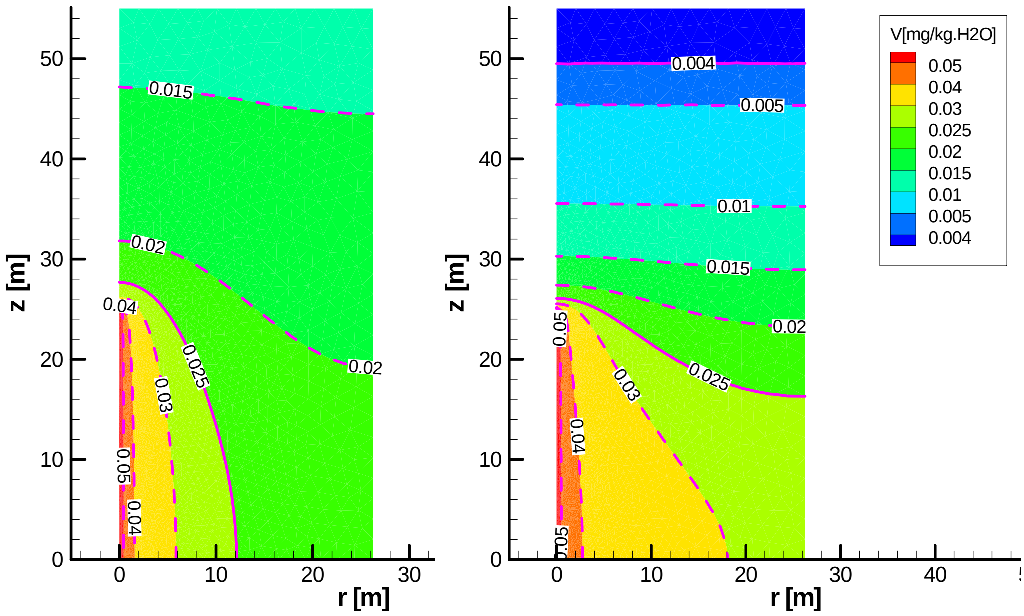

Fig. 4: V concentration profiles after 1 million years, comparison of 2D isotropic (left) and anisotropic (right) modeling

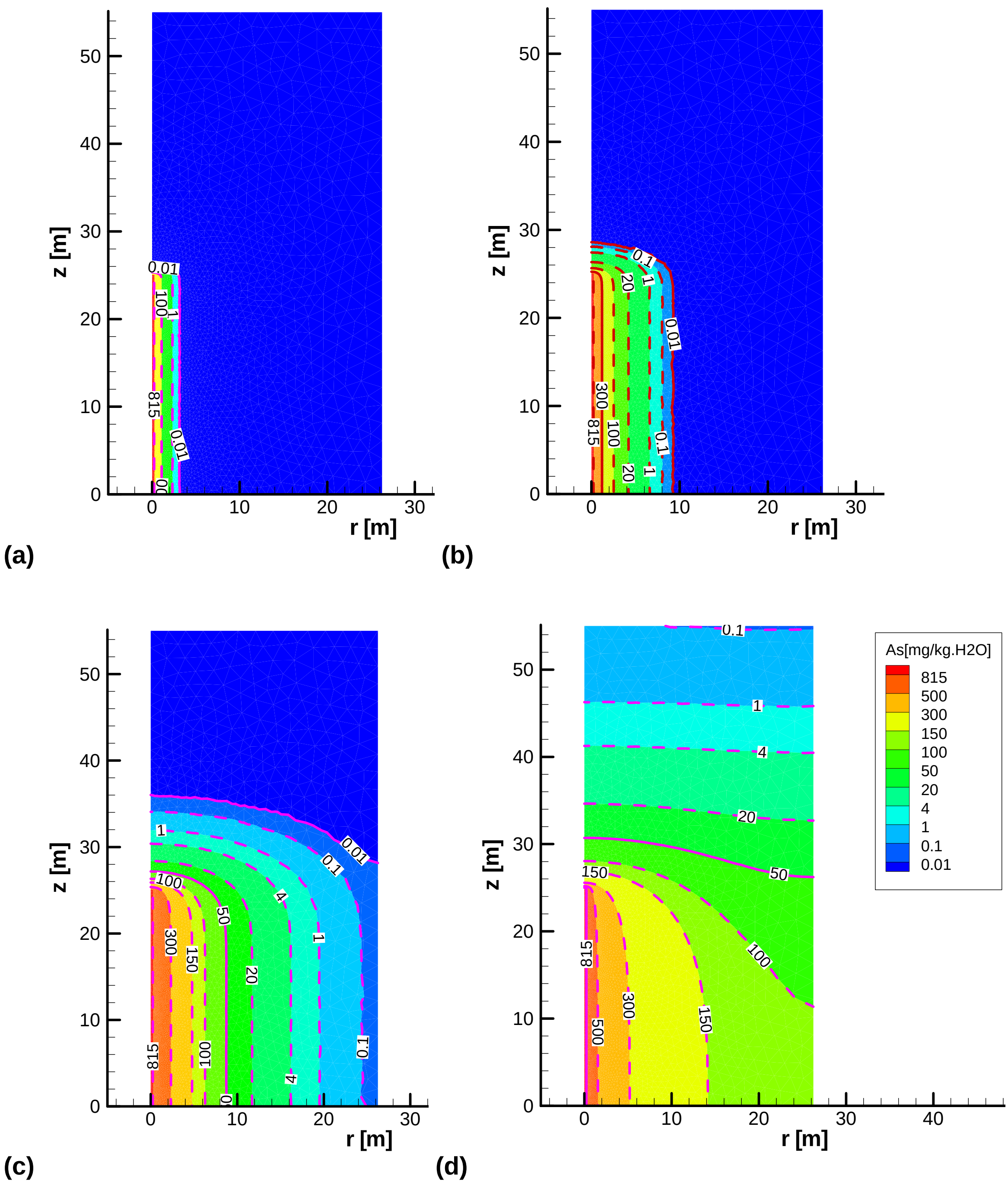

Fig. 5 As concentration profile after (a) 1000, (b) 10 000, (c) 100 000 and (d) 1000 000 years

5 CONCLUSION

Inflow of pore water into the emplacement borehole may lead to an intermittent corrosion process at the surface of the containment. Corrosion is triggered by the approaching pore solution and is halted by the total consumption of free water.

Solutes in the vicinity of the containment get progressively enriched by the depletion of free water. Depending on reaction kinetics the rate of consumption of free pore water is likely to exceed that resulting from the transport within the host rock. As a consequence, highly concentrated salt solutions are likely to form in the direct vicinity of the containment, even though the native pore solution present in the host rock may be of groundwater type. Thus, as a remarkable result of this study, it turns out, that for the modeling of chemical reactions

taking place in the vicinity of a containment embedded in a clay stone formation, it might be necessary to employ other models for the calculation of solute activities than Davies, like for example the Pitzer formalism.
Assuming unlimited access of pore solution to the containment, this will eventually be entirely corroded, leaving corrosion products filling the free space in the pore hole. Depending of the remaining free volume, a variety of solutions may form: Small solution volumes lead to even higher concentrations.
We therefore conclude that the employment of Pitzer formalism in geochemical modeling gives more realistic results for the corrosion processes in repositories in clay formations, even if the original composition of the pore waters is not saline.
The 1D analytical calculation and 2D symmetric isotropic/anisotropic simulations demonstrated the capability of the numerical tools for mass transport modeling. The higher horizontal effective mass transport process delayed the vertical migration of contaminants.

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REFERENCES

C. M. Bethke (1994): The Geochemist's Workbench™, Version 2.0, A Users Guide to Rxn, Act2, Tact, React, and Gtplot, Hydrogeology Program, University of Illinois.

G. Eriksson, K. Hack, S. Petersen (1997): ChemApp - A programmable thermodynamic calculation interface, Werkstoffwoche '96, Symposium 8 Simulation, Modellierung, Informationssysteme, 47 (ISBN 3-88355-236-4, published by DGM Informationsgesellschaft mbH, Hamburger Allee 26, D-60486 Frankfurt, Germany), Language: English.

Hagemann, S., Scharge, T.; Willms, Th. (2008): Entwicklung einer thermodynamischen Datenbasis für Arsen, Chrom, Kobalt, Kupfer, Mangan, Nickel und Quecksilber, Gesellschaft für Anlagen- und Reaktorsicherheit (GRS) mbH, GRS-Abschlußbericht, Braunschweig, 2008, in press.

Harvie, C.E.; Møller, N.; Weare, J.H. (1984): The Prediction of Mineral Solubilities in Natural Waters: The Na-K-Mg-Ca-Cl-SO4- OH-HCO3-CO3-CO2-H2O System to High Ionic Strengths at 25°C.- Geochim. Cosmochim. Acta 48 (1984), S. 723-751.

Kolditz, O. and Shao, H.: Developer benchmark book on THMC components of numerical codes GeoSys/RockFlow version 4.7. – UFZ Leipzig 2008

NAGRA (2002): Models, Codes and Data for Safety Assessment, NAGRA technical report 02-06.

Parkhurst, D.L. and Appelo, C.A.J. (1999): User's guide to PHREEQC (Version 2) - A computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations: U.S. Geological Survey Water-Resources Investigations Report 99-4259, 310 p.

Pearson, F.J.; Arcos, D.; Bath, A.; Boisson, J.Y.; Fernández, A.Ma.; Gäbler, H-E. Gaucher, E.; Gautschi, A.; Griffault, L.; Hernán, P.; Waber, H.N.: Geochemistry of Water in the Opalinus Clay Formation at the Mont Terri Rock Laboratory. SNHGS, Geological Report No. 30, Bern, 2002.

Rübel, A.; Becker, D.A.; Fein, E.:. Radionuclide transport modelling, Performance assessment of repositories in clays, Gesellschaft für Anlagen- und Reaktorsicherheit (GRS) mbH, GRS-228, Braunschweig, 2007.