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# Coupling of Transport Processes and Geochemical Processes - a New Feature in the EMOS-Code

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**Abstract:** For the assessment of long-term safety of underground waste repositories the program-package EMOS is used in the GRS. Up to now calculations are performed with constant solubility limits which do not change in time. Recently EMOS was coupled with a commercially available code feasible of calculating thermodynamic equilibria (CHEMAPP). This allows to calculate solubilities which are dependent from actual geochemical conditions and their change in space and time. A database was set up which allows it to employ the Pitzer formalism to extend the validity of calculations to high-saline media. First runs of the coupled model indicate that solubilities explicitly calculated from thermodynamic equilibria may differ orders of magnitude in comparison to utilizing constant limits for solubility. Other results indicate that lacking knowledge about the kinetics of solid phase formation or the predominance of meta-stable phases may pose a problem to safety assessment.

## 1. INTRODUCTION

The final objective of performance assessment (PA) for underground waste repositories is the prediction of the maximum likely flow of hazardous substances such as heavy metals or radionuclides from the near-field into the biosphere. While for heavy metals specific boundary concentrations have to be observed due to their toxicity, the hazardous potential of radionuclides originate from their radioactive decay.

In particular, PA involves a conception of processes considered to be taking place successively and in part simultaneously. For those supposed to be relevant to the ultimate goal of PA models are needed, most desirable mechanistic but often rather phenomenologically. Processes considered may include the failure of the waste containment followed by leaching of the waste as source term for hazardous species, convergence of host rock giving rise to progressive closure of path ways and displacement of fluids, sorption on native or newly formed solid phases and precipitation/dissolution.

Processes relating to the mobility of hazardous substances like sorption, precipitation/dissolution or charge-transferring reactions highly depend on the actual geochemical setting of the system rendering it very difficult to find fixed parameters which suit to a given system at any time relevant for the modelling. Perhaps even more important is that flow characteristics within the considered system, e. g., a drift within an underground repository, may change as consequence of geochemical alterations of solid and liquid phases.

It is therefore desirable to have a model which links physical processes to geochemical reactions. The latter may be identified by thermodynamic modelling. This paper reports on first steps to accomplish this task.

## 2. THEORY

### 2.1 Thermodynamic modelling

In general the purpose of thermodynamic modelling is to find a state where the global change in Gibbs Free Energy relative to the chosen standard states of all its constituents is minimum. For the present case we assume that temperature and pressure are set to standard values. As boundary condition for

thermodynamic equilibrium the total elemental composition is given. The task of calculating thermodynamic equilibrium is accomplished when all elements are assorted into aqueous phase constituents and solid phases in such a way that the sum of the respective changes in Gibbs Free Energy attains a minimum.

As for the present case we do not deal with mixed solid phases (solid solutions), and leave temperature and pressure at their standard values, we may assume unit activity for each solid phase. The contribution to the global Gibbs Free Energy change due to the formation of solid phases is then

$$\Delta G_{\text{solid}} = \sum_i n_i \Delta G_{f,i}^0 \quad [1]$$

where  $\Delta G_{f,i}^0$  is the Standard Gibbs Free Energy of formation of any solid phase  $i$  and  $n_i$  is the number of moles of it in the system.

For the aqueous phase, however, we have to account for its non-ideality. The contribution to the global Gibbs Free Energy change due to the formation of aqueous phase constituents is then given by

$$\Delta G_{\text{aqueous}} = \sum_i n_i \Delta G_{f,i}^0 + RT \sum_i \ln m_i + RT \sum_i \ln g_i \quad [2]$$

where  $\Delta G_{f,i}^0$  is the Standard Gibbs Free Energy of formation of any aqueous phase constituent and  $n_i$  is the number of moles of it in the system,  $m_i$  is the molality of aqueous phase constituent  $i$ , and  $g_i$  is the respective activity coefficient. The last term on the right hand side of equation [2], taken negatively, gives the change in Gibbs Free Energy for an aqueous phase constituent by virtue of its charge relative to a hypothetical state where the same species wouldn't bear any charge at all. An activity coefficient of less than unity means that the aqueous phase constituent in its actual environment is energetically stabilized relative to a (hypothetical) uncharged state.

The global change in Gibbs Free Energy may be calculated by summing up equations [1] and [2]. Thermodynamic equilibrium is defined to be attained when

$$\Delta G_{\text{solid}} + \Delta G_{\text{aqueous}} = \min \quad [3]$$

## 2.2 Calculation of activity coefficients

The calculation of activity coefficients in aqueous solutions has been subject of extensive research. For a very dilute solution with a concentration below  $10^{-2}$  M the Debye-Hückel limiting law works:

$$\log_{10} g_i = -Az_i^2 \sqrt{I} \quad [4]$$

where  $A \approx 0.5$  at  $T = 298.15$  K,  $z_i$  is the charge of species  $i$ , and  $I$  is the ionic strength. At higher concentrations, however, extensions to the Debye-Hückel limiting law apply. For the treatment of high-saline solutions up to saturation the Pitzer theory proved to be a suitable tool. Pitzer and coworkers developed a model which extends the Debye-Hückel expression for the calculation of ion activity coefficients by terms for specific interactions between two or three ions (Pitzer, 1973; Pitzer and Kim, 1974; Pitzer, 1975; Pabalan and Pitzer, 1987). These contain specific parameters ("Pitzer parameters") which have to be determined for each individual ionic interaction. Harvey et al. (1984) developed a set of Pitzer parameters which enables one the modeling of solubilities at 298 K in the hexary system of oceanic salts (Na-K-Mg-Ca-Cl-SO<sub>4</sub>) with a high degree of precision. This result was confirmed by Herbert (1996), who demonstrated that long term in-situ experiments concerning the dissolution of salt formations in flooded potash mines could be closely reproduced by geochemical modeling using the data base created by Harvey, Møller, and Weare (1984).

## 2.3 Research into further Pitzer parameters

Concerns about the long-term safety of underground toxic waste repositories in salt formations have sparked the interest in the solubilities of toxic heavy metal salts in brine solutions. This initiated efforts to continue the work begun by Harvey and coworkers and to extend the available set of Pitzer parameters for lead (Hagemann, 1995 and 1999), and zinc and cadmium (Herbert and Mönig, 1996).

Pitzer parameters for Cu(II), Cr(VI) and Ni were evaluated by Voigt (1998). At present GRS is working on Pitzer parameters for Fe(III), Fe(II), S(-II), Se(IV), Se(VI), and I.

The need to model cementitious phases in brines has given rise to further efforts to obtain Pitzer parameters for Si and Al (Reardon, 1990). GRS is continuing this work to explicitly account for individual hydrolysis products of the elements.

The modelling of actinide solubility in brine solutions has been a field of extensive research for INE and PSI, leading to Pitzer parameters for U, Am, Np, Tc, and Cm in some oxidation states (Neck et al. 1998a and b, Neck et al. 1999, Berner 1990, Plyasunov 1998, Fanghänel et al. 1995, Neck and Kim 2001, Novak et al. 1997). However, the present data sets for actinides do not cover all possible interactions with ions of the oceanic system, and data for lower oxidation states of U, Np, and Tc are even more sparse.

### 3. METHODS

For the present purpose EMOS (Buhmann 1999) was linked with CHEMAPP, a commercially available, pre-compiled library of routines for the calculation of thermodynamic equilibria. A new database was established containing data from the above mentioned sources. Additionally, thermochemical data and solubility constants for cementitious phase were taken from Glasser et al. (2001) and Revertegat et al. (1997). Standard Gibbs Free Energies of Formation were taken from NEA publications (Silva et al. 1995, Lemire et al. 2001, Rard et al. 1998, Wanner and Forest 1992). Some Pitzer parameters for carbonates were modified in comparison to the original data by Harvey et al. (1984) according to Peiper and Pitzer (1982).

Tables 1 and 2 give an overview about solution phase constituents and solid phases presently accounted for in the database for the coupling. Sorption is not accounted for yet.

**Table 1:** List of solution phase constituents in the present database for the coupling between EMOS and CHEMAPP.

Nr.	Name	Nr.	Name	Nr.	Name
1	H <sub>2</sub> O	25	TcO <sub>4</sub> <->	49	(UO <sub>2</sub> ) <sub>2</sub> (OH) <sub>2</sub> <2+>
2	H<+>	26	TcO<2+>	50	(UO <sub>2</sub> ) <sub>3</sub> (OH) <sub>4</sub> <2+>
3	Na<+>	27	TcO(OH)<+>	51	(UO <sub>2</sub> ) <sub>3</sub> (OH) <sub>5</sub> <+>
4	OH<->	28	TcO(OH) <sub>2</sub> <aq>	52	Am<3+>
5	HCO <sub>3</sub> <->	29	TcO(OH) <sub>3</sub> <->	53	AmCl<2+>
6	CO <sub>3</sub> <2->	30	Tc(OH) <sub>2</sub> (CO <sub>3</sub> )<aq>	54	AmCl <sub>2</sub> <+>
7	CO <sub>2</sub> (aq)	31	Tc(OH) <sub>3</sub> (CO <sub>3</sub> )<->	55	AmOH<2+>
8	Cl<->	32	NpO <sub>2</sub> <+>	56	Am(OH) <sub>2</sub> <+>
9	K<+>	33	NpO <sub>2</sub> (OH)<aq>	57	Am(OH) <sub>3</sub> <aq>
10	Mg<2+>	34	NpO <sub>2</sub> (OH) <sub>2</sub> <->	58	AmCO <sub>3</sub> <+>
11	Ca<2+>	35	NpO <sub>2</sub> (CO <sub>3</sub> )<->	59	Am(CO <sub>3</sub> ) <sub>2</sub> <->
12	SO <sub>4</sub> <2->	36	NpO <sub>2</sub> (CO <sub>3</sub> ) <sub>2</sub> <3->	60	Am(CO <sub>3</sub> ) <sub>3</sub> <3->
13	HSO <sub>4</sub> <->	37	NpO <sub>2</sub> (CO <sub>3</sub> ) <sub>3</sub> <5->	61	Am(CO <sub>3</sub> ) <sub>4</sub> <5->
14	CaCO <sub>3</sub> <aq>	38	UO <sub>2</sub> <2+>	62	Pu<3+>
15	MgCO <sub>3</sub> <aq>	39	UO <sub>2</sub> OH<+>	63	PuCl<2+>
16	MgOH<+>	40	UO <sub>2</sub> (OH) <sub>2</sub> <aq>	64	PuCl <sub>2</sub> <+>
17	Fe<2+>	41	UO <sub>2</sub> (OH) <sub>3</sub> <->	65	PuOH<2+>
18	SiO <sub>2</sub> <aq>	42	UO <sub>2</sub> (OH) <sub>4</sub> <2->	66	Pu(OH) <sub>2</sub> <+>
19	Al<3+>	43	UO <sub>2</sub> Cl<+>	67	Pu(OH) <sub>3</sub> <aq>
20	H <sub>3</sub> SiO <sub>4</sub> <->	44	UO <sub>2</sub> Cl <sub>2</sub> <aq>	68	PuCO <sub>3</sub> <+>
21	H <sub>2</sub> SiO <sub>4</sub> <2->	45	UO <sub>2</sub> CO <sub>3</sub> <aq>	69	Pu(CO <sub>3</sub> ) <sub>2</sub> <->
22	Al(OH) <sub>4</sub> <->	46	UO <sub>2</sub> (CO <sub>3</sub> ) <sub>2</sub> <2->	70	Pu(CO <sub>3</sub> ) <sub>3</sub> <3->
23	Pb<2+>	47	UO <sub>2</sub> (CO <sub>3</sub> ) <sub>3</sub> <4->	71	Pu(CO <sub>3</sub> ) <sub>4</sub> <5->
24	Fe<3+>	48	(UO <sub>2</sub> ) <sub>2</sub> OH<3+>		

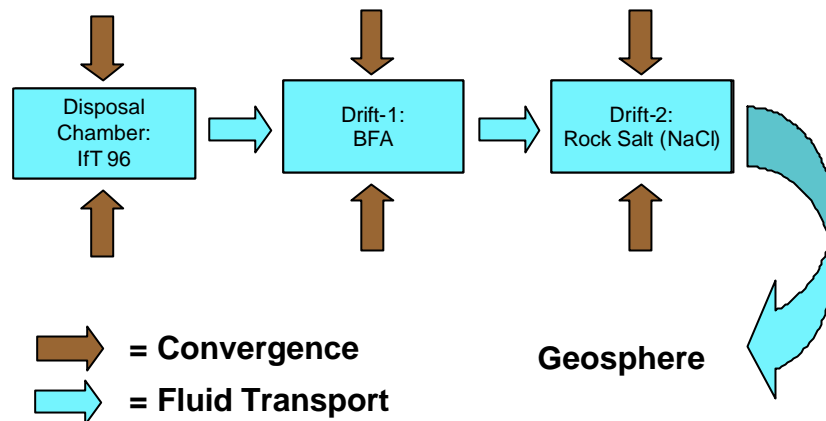
**Table 2:** List of solid phases in the present database for the coupling between EMOS and CHEMAPP.

Nr.	Name	Trivialname	Nr.	Name	Trivialname	Nr.	Name
3	NaHCO <sub>3</sub>	Nahcolite	51	Na <sub>2</sub> CO <sub>3</sub> *H <sub>2</sub> O	Thermonatrit	99	TcO <sub>2</sub> *1.6H <sub>2</sub> O
4	Na <sub>2</sub> CO <sub>3</sub> *10H <sub>2</sub> O	Natron	52	Na <sub>3</sub> H(CO <sub>3</sub> ) <sub>2</sub> *2H <sub>2</sub> O	Trona	100	KTcO <sub>4</sub>
5	NaCl	Halite	53	K <sub>2</sub> NaH(CO <sub>3</sub> ) <sub>2</sub> *2H <sub>2</sub> O	Trona-K	101	NpO <sub>2</sub> OH (am)
6	KCl	Sylvite	54	KAl <sub>3</sub> (OH) <sub>6</sub> (SO <sub>4</sub> ) <sub>2</sub>	Alunite	102	NpO <sub>2</sub> OH (aged)
7	CaCl <sub>2</sub> *6H <sub>2</sub> O	Antarcticite	55	AlOOH	Boehmite	103	NaNpO <sub>2</sub> CO <sub>3</sub>
8	CaCl <sub>2</sub> *4H <sub>2</sub> O		56	Mg <sub>3</sub> Si <sub>2</sub> O <sub>5</sub> (OH) <sub>4</sub>	Chrysotile (Serpentine)	104	NaNpO <sub>2</sub> CO <sub>3</sub> *3.5H <sub>2</sub> O
9	MgCl <sub>2</sub> *6H <sub>2</sub> O	Bischoffite	57	Mg <sub>2</sub> SiO <sub>4</sub>	Forsterite	105	Na <sub>3</sub> NpO <sub>2</sub> (CO <sub>3</sub> ) <sub>2</sub>
10	NaK <sub>3</sub> (SO <sub>4</sub> ) <sub>2</sub>	Aphtitalite	58	Al(OH) <sub>3</sub>	Gibbsite	106	KNpO <sub>2</sub> CO <sub>3</sub>
11	Na <sub>2</sub> Mg(SO <sub>4</sub> ) <sub>2</sub> *4H <sub>2</sub> O	Bloedite	59	Ca <sub>4</sub> (Al <sub>2</sub> O <sub>6</sub> )SO <sub>4</sub> *12H <sub>2</sub> O	Monosulfate	107	K <sub>3</sub> NpO <sub>2</sub> (CO <sub>3</sub> ) <sub>2</sub>
12	Mg(OH) <sub>2</sub>	Brucite	60	Ca <sub>6</sub> (Al <sub>2</sub> O <sub>6</sub> )Cl <sub>6</sub> *30H <sub>2</sub> O	Trichloride	108	UO <sub>3</sub> *2H <sub>2</sub> O
13	KMgCl <sub>3</sub> *6H <sub>2</sub> O	Carnallite	61	Ca <sub>3</sub> (Al <sub>2</sub> O <sub>6</sub> )*6H <sub>2</sub> O	Hydrogarnet	109	UO <sub>2</sub> CO <sub>3</sub>
14	MgSO <sub>4</sub> *7H <sub>2</sub> O	Epsomite	62	Ca <sub>4</sub> (Al <sub>2</sub> O <sub>7</sub> )*13H <sub>2</sub> O	Tetracalciumaluminat	110	Am <sub>2</sub> O <sub>3</sub>
15	MgSO <sub>4</sub> *6H <sub>2</sub> O	Hexahydrate	63	Ca <sub>3</sub> (Al <sub>2</sub> SiO <sub>8</sub> )*4H <sub>2</sub> O	Si-Hydrogarnet	111	Am(OH) <sub>3</sub>
16	KMgClSO <sub>4</sub> *3H <sub>2</sub> O	Kainite	64	Ca <sub>9</sub> (Si <sub>6</sub> O <sub>21</sub> )*11H <sub>2</sub> O	Jennite	112	Am(OH)CO <sub>3</sub> *0.5H <sub>2</sub> O<cr>
17	MgSO <sub>4</sub> *H <sub>2</sub> O	Kieserite	65	Ca <sub>6</sub> Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> (OH) <sub>12</sub> *26H <sub>2</sub> O	Ettringite	113	Am <sub>2</sub> (CO <sub>3</sub> ) <sub>3</sub> *4H <sub>2</sub> O(am)
18	K <sub>2</sub> Mg(SO <sub>4</sub> ) <sub>2</sub> *4H <sub>2</sub> O	Leonite	66	Ca <sub>5</sub> (Si <sub>6</sub> O <sub>17</sub> )*9H <sub>2</sub> O	Tobermorite	114	NaAm(CO <sub>3</sub> ) <sub>2</sub> *5H <sub>2</sub> O
19	K <sub>2</sub> Mg(SO <sub>4</sub> ) <sub>2</sub> *6H <sub>2</sub> O	Picromerite	67	Ca <sub>2</sub> (Al <sub>2</sub> SiO <sub>7</sub> )*8H <sub>2</sub> O	Gehlenithydrate	115	Pu <sub>2</sub> O <sub>3</sub>
20	K <sub>2</sub> MgCa <sub>2</sub> (SO <sub>4</sub> ) <sub>4</sub> *2H <sub>2</sub> O	Polyhalite	68	Ca <sub>2</sub> Al <sub>2</sub> O <sub>5</sub> *8H <sub>2</sub> O	Dicalciumaluminat	116	Pu(OH) <sub>3</sub>
21	CaSO <sub>4</sub>	Anhydrite	69	Ca <sub>3</sub> (Al <sub>2</sub> (Si <sub>0.5</sub> )O <sub>7</sub> )	Tricalciumhemisilikate	117	Pu(OH)CO <sub>3</sub> *0.5H <sub>2</sub> O<cr>
22	K <sub>2</sub> SO <sub>4</sub>	Arcanite	70	Ca(Al <sub>2</sub> Si <sub>4</sub> O <sub>12</sub> )*6H <sub>2</sub> O	Chabazite	118	Pu <sub>2</sub> (CO <sub>3</sub> ) <sub>3</sub> *4H <sub>2</sub> O(am)
23	Na <sub>2</sub> Ca(SO <sub>4</sub> ) <sub>2</sub>	Glauberite	71	Mg <sub>4</sub> (Si <sub>6</sub> O <sub>15</sub> )(OH) <sub>2</sub> *6H <sub>2</sub> O	Sepiolite	119	NaPu(CO <sub>3</sub> ) <sub>2</sub> *5H <sub>2</sub> O
24	CaSO <sub>4</sub> *2H <sub>2</sub> O	Gypsum	72	Mg <sub>3</sub> (Si <sub>4</sub> O <sub>11</sub> )*H <sub>2</sub> O	Talcite		
25	K <sub>3</sub> H(SO <sub>4</sub> ) <sub>2</sub>		73	Mg <sub>4</sub> (Al <sub>2</sub> O <sub>7</sub> )*10H <sub>2</sub> O	Hydrotalcite		
26	KHSO <sub>4</sub>	Mercallite	74	SiO <sub>2</sub> (am)	SiO <sub>2</sub> (am)		
27	Na <sub>2</sub> SO <sub>4</sub> *10H <sub>2</sub> O	Mirabilite	75	Ca <sub>4</sub> (Al <sub>2</sub> O <sub>6</sub> )Cl <sub>2</sub> *10H <sub>2</sub> O	Friedel's Salt		
28	Na <sub>3</sub> H(SO <sub>4</sub> ) <sub>2</sub>		76	(Ca <sub>0.8</sub> )(SiO <sub>2.8</sub> )*H <sub>2</sub> O	CSH(0.8)		
29	K <sub>2</sub> Ca(SO <sub>4</sub> ) <sub>2</sub> *H <sub>2</sub> O	Syngenite	77	(Ca <sub>1.1</sub> )(SiO <sub>3.1</sub> )*3H <sub>2</sub> O	CSH(1.1)		
30	Na <sub>2</sub> SO <sub>4</sub>	Thenardite	78	(Ca <sub>1.8</sub> )(SiO <sub>3.8</sub> )*5H <sub>2</sub> O	CSH(1.8)		
31	Ca <sub>2</sub> Cl <sub>2</sub> (OH) <sub>2</sub> *H <sub>2</sub> O		79	PbSO <sub>4</sub>	Anglesite		
32	Ca(OH) <sub>2</sub>	Portlandite	80	PbCl <sub>2</sub>	Cotunnite		
33	CaCO <sub>3</sub> (Aragonit)	Aragonite	81	2PbCl <sub>2</sub> *KCl			
34	Na <sub>6</sub> CO <sub>3</sub> (SO <sub>4</sub> ) <sub>2</sub>	Burkeite	82	3PbCl <sub>2</sub> *3KCl*H <sub>2</sub> O			
35	Ca <sub>4</sub> Cl <sub>2</sub> (OH) <sub>6</sub> *13H <sub>2</sub> O		83	PbCl <sub>2</sub> *3MgCl <sub>2</sub> *19H <sub>2</sub> O			
36	CaCO <sub>3</sub> (Calcit)	Calcite	84	PbCl <sub>2</sub> *PbSO <sub>4</sub> *2Na <sub>2</sub> SO <sub>4</sub> *5w			
37	CaMg(CO <sub>3</sub> ) <sub>2</sub>	Dolomite	85	PbSO <sub>4</sub> *K <sub>2</sub> SO <sub>4</sub>	Palmierite		
38	CaNa <sub>2</sub> (CO <sub>3</sub> ) <sub>2</sub> *5H <sub>2</sub> O	Gaylussite	86	PbCO <sub>3</sub>	Cerussite		
39	K <sub>2</sub> CO <sub>3</sub> *1.5H <sub>2</sub> O		87	2PbCO <sub>3</sub> *Pb(OH) <sub>2</sub>	Hydrocerussite (Schock)		
40	K <sub>8</sub> H <sub>4</sub> (CO <sub>3</sub> ) <sub>6</sub> *3H <sub>2</sub> O		88	Pb <sub>3</sub> (CO <sub>3</sub> ) <sub>2</sub> (OH) <sub>2</sub>	Hydrocerussite (RIC)		
41	KNaCO <sub>3</sub> *6H <sub>2</sub> O		89	Pb(OH)Cl	Laurionite		
42	KHCO <sub>3</sub>	Kalicinite	90	3Pb(OH) <sub>2</sub> *PbCl <sub>2</sub>			
43	MgCO <sub>3</sub>	Magnesite	91	Pb(OH) <sub>2</sub> *PbSO <sub>4</sub>			
44	K <sub>8</sub> H <sub>6</sub> (SO <sub>4</sub> ) <sub>7</sub>	Misenite	92	3Pb(OH) <sub>2</sub> *PbSO <sub>4</sub>			
45	Na <sub>2</sub> CO <sub>3</sub> *7H <sub>2</sub> O		93	PbCO <sub>3</sub> *PbCl <sub>2</sub>	Phosgenite		
46	Na <sub>4</sub> Ca(SO <sub>4</sub> ) <sub>3</sub> *2H <sub>2</sub> O		94	Pb <sub>2</sub> (O)SO <sub>4</sub>	Lanarkite		
47	MgCO <sub>3</sub> *3H <sub>2</sub> O	Nesquehonite	95	NaPb <sub>2</sub> (CO <sub>3</sub> ) <sub>2</sub> OH	Auerbachs Salz		
48	Mg <sub>2</sub> Cl(OH) <sub>3</sub> *4H <sub>2</sub> O	Oxychloride-Mg	96	FeCl <sub>2</sub> *4H <sub>2</sub> O			
49	Na <sub>2</sub> Ca(CO <sub>3</sub> ) <sub>2</sub> *2H <sub>2</sub> O	Pirssonite	97	FeSO <sub>4</sub> *7H <sub>2</sub> O	Melanterite		
50	Mg <sub>2</sub> CaCl <sub>6</sub> *12H <sub>2</sub> O	Tachyhydrite	98	TcO <sub>2</sub>			

## 4. RESULTS

### 4.1 Mobilization of Pb from chemical waste

For a first test of the coupling the following szenario was set as is depicted in Figure 1.



**Figure 1:** Szenario for the mobilization of Pb from an underground waste disposal site

IfT 96 is a toxic waste originating from glass producing industry. It contains sulfates of Na, K, Mg, Ca, and Pb. The disposal chamber is connected to two succeeding drifts. The first is filled with brown coal fly ash (BFA), the second is filled with rock salt. All three chambers are supposed to be flooded instantaneously with saturated NaCl-solution. Convergence of the host rock gives rise to the transport of fluid. Lead is considered to be released instantaneously from the waste.

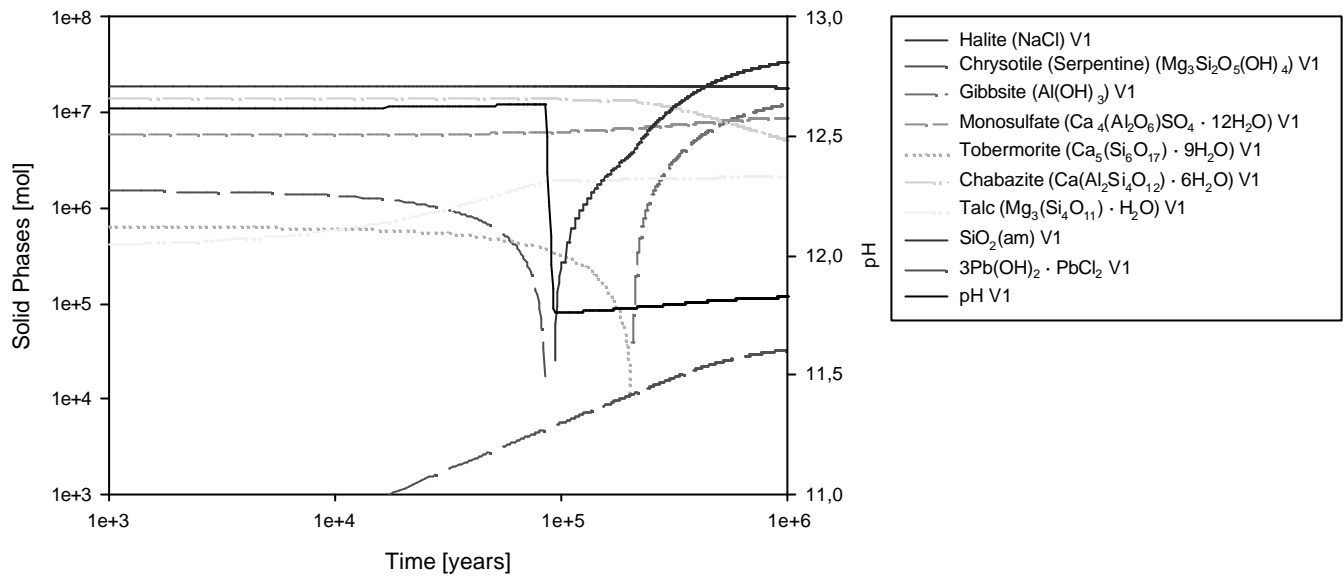
In each time step the total elemental composition is taken as boundary condition for the calculation of thermodynamic equilibrium within each chamber. Hence, from a modelling point of view each chamber is treated as an ideal mixing chamber where all constituents of solid and liquid phases can interact. As a result of Gibbs Energy minimization total moles of elements, partitioned into mobile and immobile fractions are returned to EMOS.

As an example figure 2 gives the computed composition of solid phases for drift-1. Due to the presence of BFA a much higher pH develops in this drift than in the disposal chamber for the waste. As a consequence Pb entering drift-1 from the disposal chamber becomes precipitated. This is a fine example for a case where two waste forms are combined in a way to favour the precipitation of heavy metals. The model predicts the formation of a basic Pb-chloride (laurionite).

The inflow of acid solution from the disposal chamber into the alkaline environment of drift-1 leads to the progressive dissolution of silicon-bearing minerals, which for a long time act as pH-buffer for the system. When these minerals are consumed, the model predicts a drop of pH and the subsequent formation of new solid phases.

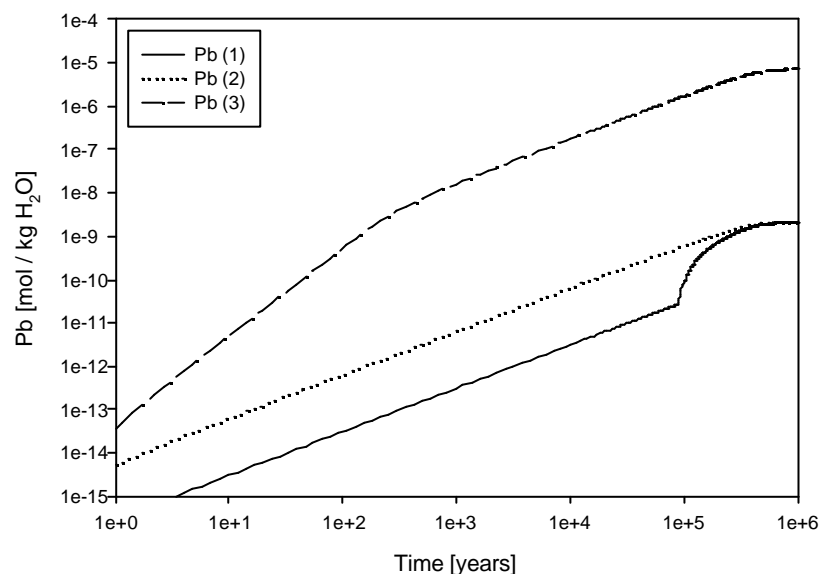
It is important to note that the pH evolving over long times is connected to the actual composition of solid phases. The choice of solid phases as taken from the literature leads to the result shown below. But not all solid phases found therein correspond to everyday laboratory experience and there are good reasons that some of them might not form at all.

While it is not the case of the present work to judge on the "right" assortment of Si/Al-phases for a thermodynamic database, we were curious as to which extent a variation in the entered solid phases for Si/Al might have an impact on the final release of Pb from the disposal site in the present scenario.



**Figure 2:** Evolution of solid phase composition in drift-1

For this purpose we did two additional runs of the model. In the second version we allowed only for those phases to form which according to own laboratory experience really appear. In a third run we were even more restrictive and allowed for the formation of very few phases only, most of them being amorphous and CSH-phases. As an example from the results figure 3 illustrates the lead concentration in drift-2, the "exit" of the system.



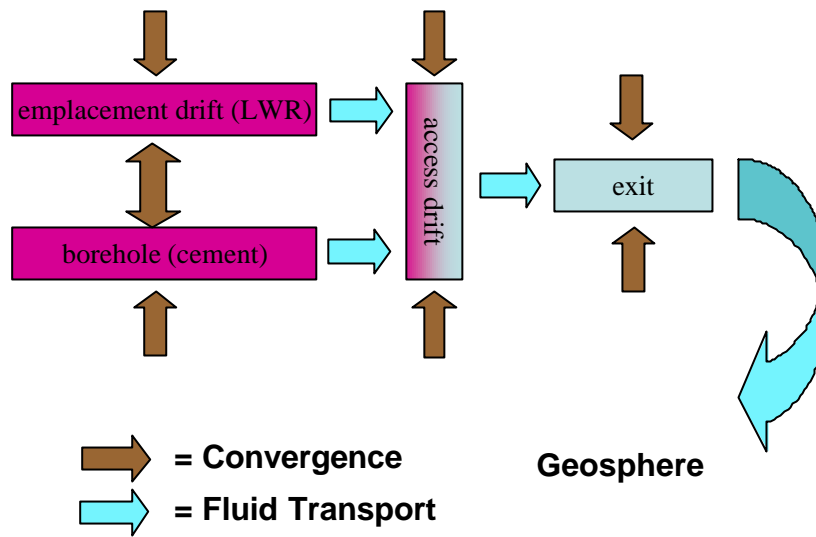
**Figure 3:** Evolution of lead concentration, calculated with different sets of entered solid phases for Si/Al

Critical for the evolution of pH is the ensemble of entered Si/Al-phases. With fewer Si/Al-phases allowed for the calculation of thermodynamic equilibrium pH tends to be lower giving rise to higher lead concentrations. Note that while the final lead concentration for scenario 1 and 2 is the same (see figure 3) the cumulative stream of lead to the environment is different !

As with a given oxidation state the pH for most heavy metals, and in fact for radionuclides also, plays a predominant role, we conclude from the "computer experiment" that for the modelling of heavy metal or radionuclide mobility in a cementitious environment the choice of solid phases for the database has to be founded on experimental evidence to invoke confidence into the results of thermodynamic modelling.

### 4.2 Mobilization of radionuclides from LWR- and cemented waste

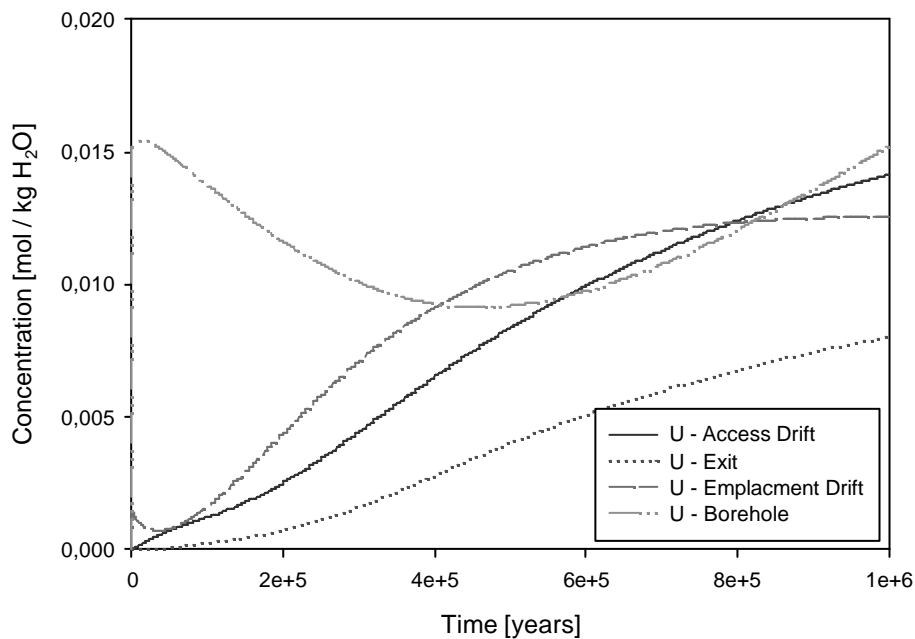
For a first test involving radionuclides the following scenario was set up as depicted in figure 4.



**Figure 4:** Szenario for the mobilization of radionuclide from an underground repository

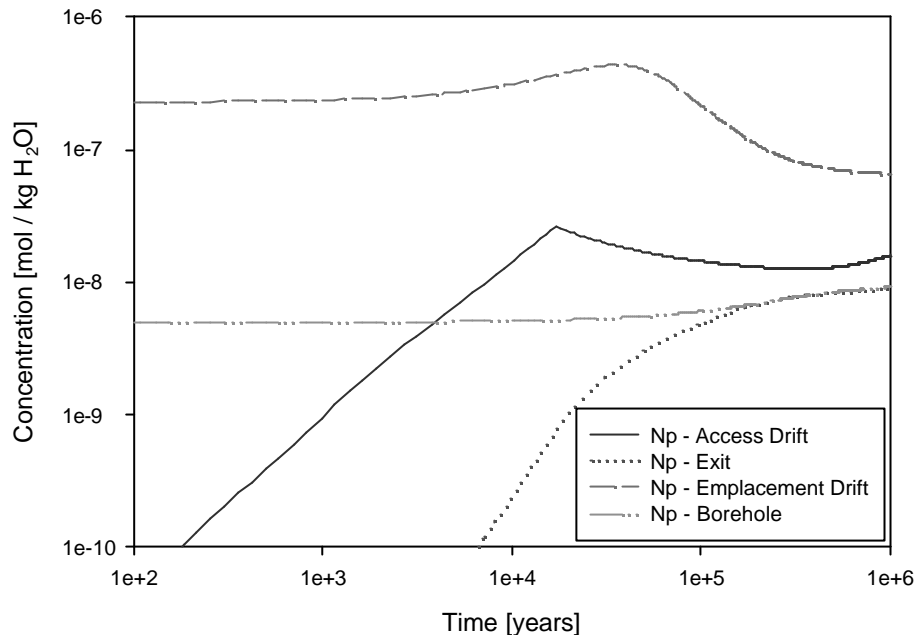
Emplacement drift and borehole contain different forms of radioactive waste while access drift and exit are filled with rocksalt. As in the previous case the entire system is supposed to be flooded with saturated NaCl-solution. In the contrary to the previous case the mobilization of radionuclides from the waste is considered to proceed during 100 (borehole) or 1000 (LWR) years.

While the borehole solution is likely to be alkaline due to the presence of cementitious phases, it will be lower in all other segments. By the convergence these solutions become mixed and the pH increases outside the borehole while within the borehole it will remain constant or decrease. Additionally, carbonate leaching out of the borehole will contribute to the mobility of radionuclides in the emplacement drift. The present database allows for the formation of chloro-, hydroxo-, and carbonato-complexes (see table 1).



**Figure 5:** Evolution of U-concentration in all segments of the model

In figures 5 and 6 is depicted how the total concentrations of U and Np evolve in any of the segments. The very high concentrations for U are the result of high pH-values of 12 or even more. Comparisons with transport modelling without thermodynamic modelling indicate considerable differences.



**Figure 6:** Evolution of Np-concentration in all segments of the model

## 5. CONCLUSIONS AND PERSPECTIVES

Transport code was coupled with thermodynamic equilibrium calculations. The results allow for a more substantiated PA for an underground repository for hazardous materials. The method is also suitable for the assessment of underground disposal sites for non-radioactive chemical-toxic waste. However, lacking knowledge about the kinetics of solid phase dissolution/precipitation or the predominance of meta-stable phases poses a potential problem to the reliability of the model predictions.

The presented coupling will be further developed to account for the gaseous phase and changes in volumetric properties inside the system.

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