



Final report on benchmark calculations in granite Deliverable (D-N°:4.1.2)

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Summary

Performance assessment (PA) models for radionuclide migration through the near field of a high-level radioactive waste (HLW) repository usually rely on simplifying assumptions such as the use of the "K_d approach" for nuclide sorption and "the limited solubility" for nuclide precipitation. Testing the validity of these assumptions has been limited by: 1) The lack of nuclide surface complexation and cation exchange data; and 2) Unavailability of computer codes which could handle simultaneously the migration, sorption and precipitation of radionuclides together with the geochemical evolution of the near field. Laboratory experiments performed in recent years have provided substantial data and understanding on the mechanisms of nuclide sorption. On the other hand, sophisticated research-oriented process-based computer codes and models have been developed which allow for the simultaneous modelling of migration, sorption, nuclide precipitation and multicomponent geochemical evolution of the near field. This report presents the work done by by UDC and ENRESA to test the validity of the "K_d approach" and "limited solubility" assumptions for nuclide sorption and precipitation for the 0.75 m thick compacted bentonite barrier included in the Spanish reference concept in granite (ENRESA, 2001a). Such testing has been performed by comparing the results of a PA model, created by ENRESA with Goldsim, with those obtained by UDC with CORE, a reactive transport model (Samper et al., 2003). The elements considered in the calculations are Ni, Cs, and U.

CORE^{2D}V4 (Samper et al., 2003) has been updated to simulate the reactive transport of Cs, Ni and U in compacted bentonite. A 1-D axisymmetric numerical model has been used which contains a finite element grid of 167 elements and 168 nodes to represent the length of the disposal drift corresponding to a single canister. An extra element of 0.01mm has been added at the bentonite outer surface to simulate the 'mixing tank' boundary condition. Solutes diffuse out of the bentonite into this outermost element and the equivalent groundwater flow is injected and extracted from this element. An 'equivalent flux" of 0.06 L/year per canister has been in the calculations.

Most of the available U thermodynamic sorption data correspond to U (VI). Data for U(IV) are limited. The model of U sorption has revealed that there are significant uncertainties in: 1) The redox state and the form in which U is present in the spent fuel. Although $UO_2(am)$ is the most likely mineral phase, other mixed forms such as U_4O_9 , U_3O_7 and U_3O_8 cannot be discarded; 2) The mineral phases controlling U solubility at the conditions of the repository. Such mineral phases have been analyzed in Eh-pH-U solubility plots, but there are uncertainties in the controlling phases; 3) The thermodynamic data for some U mineral





phases such as coffinite; 4) The thermodynamic sorption data for U(VI) and U(IV) which are not comprehensive. Data for the sorption of uranyl carbonates are lacking. There is a need for a complete sorption data for multisite sorption materials. Due to these uncertainties, it was not possible to create a satisfactory reactive transport model for Uranium and no comparisons with the simplified PA models could be done.

The reactive transport models created with CORE have been used to study the evolution of the geochemistry of the bentonite barrier, simultaneously to the transport of radionuclides. The calculations performed for the base run plus many different sensitivity cases have provided a good understanding of the evolution of the system and the importance of the different parameters. The most useful result obtained with the reactive transport models is the dependence of the distribution coefficients (K_d) of the transported species on environmental parameters, such as pH, Eh and ionic strength. For Nickel, it was found that the K_d was strongly affected by the dissolved concentration of Ni²⁺ (for concentrations higher than 10⁻⁶ mol/I) and pH. For Cesium, K_d was found unsensitive to the dissolved concentration of Cs+ but very sensitive to the ionic strength of bentonite porewater.

For Ni and Cs it has been found that the results obtained with the reactive transport models can not be reproduced with the simplified PA model using a constant value of K_d . But using a K_d that depends on environmental parameters (such as pH, ionic strength or the dissolved concentration of the transported species) that are known to control sorption, the simplified model is capable of reproducing with great precission the results obtained with the reactive transport models.

Finally, the reactive transport model has been used to study the effects of considering the simultaneous transport of two radioactive species (Ni and Cs) or one radioactive species (Ni or Cs) and corrosion products from the carbon steel canister. The reduction in K_d due to the competition for sorption sites is of little importance. The competition between Cs⁺ and Ni²⁺ is not significant because Cs⁺ sorbs by cation exchange while Ni²⁺ is mainly sorbed by surface complexation. Corrosion products have a significant effect on Ni²⁺ sorption compared with the base run, due to the changes in pH and Eh induced by the corrosion products.





1. Introduction

1.1. Objectives

As stated in Annex I of PAMINA's contract, within Task 4.1.B "the validity of the simplifying assumptions " K_d approach" and "limited solubility" used in PA type models will be tested by means of benchmarks with detailed chemical process-models and codes for radionuclide migration in the near field. Calculations will be done for reference disposal concepts of spent fuel and vitrified waste in granite and clay rock".

ENRESA and UDC are teamed within Task 4.1.B to analyse the transport in the near field of a spent fuel repository in granite, based on the repository concept described in ENRESA2000 (ENRESA, 2001). ENRESA has performed the PA calculations using GoldSim code (GoldSim, 2007) and UDC has performed the detailed chemical calculations using CORE^{2D}4V (Samper et al, 2003). ENRESA and UDC have compared the results obtained following both approaches. Conclusions on the validity of the "Kd approach" and "limited solubility" have been drawn by comparing such models.

1.2. Structure of the report

The Spanish reference concept in granite is briefly described in Chapter 2. ENRESA model and data are presented in Chapter 3. UDC model and data are presented in Chapter 4. The source term used in Ni, Cs and U calculations is presented in Chapter 5. Chapter 6 presents the geochemical evolution in the reference run without radionuclides. Nickel simulations are described in Chapter7. The results for the testing of Cs are presented in Chapter 8. Simulations of U migration are presented in Chapter 9. Since other radionuclides and corrosion products may compete for sorption sites, the possible competition effects are analyzed in Chapter 10. A detailed comparison of the TSM models of UDC with the classical K_d models performed by ENRESA is presented in Chapter 11. The main conclusions are presented in Chapter 12.





2. Description of the reference concept

Calculations are performed for the Spanish reference concept case in granite, as described in ENRESA (2001a). This concept is based on the disposal of spent fuel in carbon steel canisters in long horizontal drifts excavated in the granite by means of tunnel boring machines. Canisters are surrounded by high-density compacted bentonite.

The canister measures 4.54 m in length and 0.90 m in diameter, and contains 4 PWR or 12 BWR fuel elements (although calculations are done only for canisters with 4 PWR fuel elements) in a subcritical configuration. The thickness of the wall of the canister is 0.10 m at the cylindrical wall and 0.12 m at the ends, and it is capable of withstanding the pressures to which it is subjected under disposal conditions and of providing a minimum period of containment of one thousand years. A total of 3,600 canisters are required for the final waste inventory of spent fuel estimated for the Spanish nuclear power programme.



Figure 2.1. Longitudinal section of a disposal drift.

Canisters are disposed in cylindrical disposal cells, built with blocks of pre-compacted bentonite having a dry density of 1,700 kg/m³ (in order to achieve a final dry density of 1,600 kg/m³). The blocks are initially unsaturated (water content of 14%). The disposal drifts, of 500 m in length and 2.4 m in diameter (see Figure 2.1), are located at a depth of 500 m in the host formation. In order not to exceed a temperature of 100 °C in the bentonite, separations of 1.4m between canisters and 35m between disposal drifts have been established. The detailed dimensions of an individual "cell" (length of disposal drift that corresponds to one canister) are shown in Figure 2.2.







Figure 2.2. Dimensions of an individual disposal cell





3. ENRESA model and data (GoldSim)

3.1. Conceptual model

After several thousands of years the disposal canister is expected to fail and groundwater will contact the waste. Radionuclides will start to be released and will pass to the water in the canister cavity, where they dissolve or precipitate, depending on their solubility limits.

The radionuclides in dissolution in the canister cavity diffuse into the bentonite buffer and after some time cross the bentonite and pass to the groundwater flowing in the proximity of the disposal drift.

The processes considered for the transport in the near field are the following:

- Diffusive transport in the bentonite.
- Advective transport at the bentonite-granite interface.
- Sorption on bentonite.
- Precipitation/redissolution.
- Isotopic dilution.
- Anion exclusion.
- Radioactive decay/ingrowth.

The following hypotheses are used in the model:

- Bentonite buffer is fully saturated when transport starts.
- Advective transport in the bentonite is negligible.
- After failure the canister presents no resistance to transport.
- The canister internal water volume is always prefectly mixed.
- Sorption of radionuclides on bentonite is linear and reversible and can be represented using a distribution coefficient (K_d).
- Sorption on canister corrosion products and materials in the canister cavity (cladding, glasss beads,...) is neglected.
- The flow of solute leaving the bentonite by diffusion passes to the groundwater that flows around the disposal drift.

3.2. Mathematical model

The radionuclides and stable isotopes released from the waste pass to the water inside the canister (0.5 m^3 /canister), where they dissolve or precipitate depending on their solubility limits. Radionuclides released from the waste enter the canister internal water volume and





leave this water by transport into the bentonite. The balance allows knowing the mass of each radionuclide in the canister cavity (M_{RN}) at each instant, taking into account radioactive decay/ingrowth. The total mass in the canister cavity of each chemical species is known too. The dissolved concentration of radionuclide RN in the canister internal water (c_{RN}) is:

$$c_{RN} = \min\left(\frac{M_{RN}}{V_{water canister}}, \frac{M_{RN}}{M_{CE}} So \operatorname{lub} ility_{CE}\right)$$

where M_{CE} is the mass in the canister internal volume of the chemical element to which radionuclide RN belongs and Solubility_{CE} is the solubility limit of the chemical element.

The radionuclides dissolved in water transport radially through the bentonite buffer only by diffusion, since the low permeability of the saturated bentonite makes advection negligible. The 1D axysimmetric diffusion equation for the transport in bentonite is:

$$\theta R \frac{\partial c}{\partial t} = De \left[\frac{\partial^2 c}{\partial r^2} + \frac{1}{r} \frac{\partial c}{\partial r} \right] - \lambda \theta R c$$
$$R = 1 + \frac{1 - \theta}{\theta} \rho K_d \qquad De = Dp \theta$$

where:

- c = solute concentration in bentonite porewater
- De = effective diffusion coefficient in bentonite
- Dp = diffusion coefficient in bentonite porewater
- θ = bentonite accessible porosity (radionuclide dependent, due to anion exclusion)
- λ = radioactive decay constant
- R = retardation factor due to sorption on bentonite
- ρ = density of the solid of the bentonite
- K_d = distribution coefficient bentonite-water

The following boundary conditions for transport in the bentonite are imposed:





- at <u>bentonite inner surface</u>, the calculated dissolved concentration in the canister internal water volume,
- at <u>bentonite outer surface</u>, a "mixing tank" condition is imposed, and the water flow leaving the bentonite by diffusion is equal to the flow extracted from the near field by an equivalent flow rate (Q_F) with the solute concentration existing in the bentonite porewater at the bentonite-drift interface.

$$Q_F c(r=1.2m) = De \frac{\partial c}{\partial t}\Big|_{r=1.2m}$$

3.2.1. Geometric model

Both ENRESA and UDC use 1D-axysimmetric models that represent the length of disposal drift that corresponds to a single canister (disposal cell). A "mixing tank" boundary condition is imposed at the outer surface of the bentonite, with an "equivalent flow" of groundwater leaving the outermost part of bentonite. In ENRESA2000 /1/ a value of 0.06 litre/yr-canister was derived.

The model used in the near field transport calculations is shown in Figure 3.1.



Figure 3.1. Model for transport in the near field.

In GoldSim model the bentonite is discretized into several "mixing cells" of annular shape, which is equivalent to solve the transport problem using finite differences. The effect of the number of cells used on results was thoroughly explored in /4/, and it was found that





discretizing the bentonite into 99 cells of annular shape (0.75cm thickness) gave very precise results, and for PAMINA Task 4.1.B the model of 99 cells for the bentonite is used.

3.2.2. The mixing cells algorithm

GoldSim solves the transport in the near field problem using a "mixing cell algorithm" for transport in porous media, that is based in the discretisation of the medium into a number of mixing cells, with the following characteristics:

- The mixing in the cell is complete and instantaneous.
- A cell can contain different media (water, bentonite, granite,...).
- Radionuclides in a cell are distributed between the different media in the cell following their distribution coefficients (K_d).
- Diffusive and advective solute transports between cells are modelled.

In the cells, the following processes are considered:

- Radioactive decay/ingrowth for decay chains. There is no limit in the number of members.
- Precipitation (solubility limits)/redissolución.
- Diferent isotopes of the same chemical element. As a consequence, elemental solubility is shared between the diferent isotopes of the element.
- Anion exclusión (accesible porosity can be element specific).

The equation describing the evolution of the mass of radionuclide i in a cell is:

$$\frac{dm_{in}}{dt} = S_{in} - \lambda_i m_{in} + \lambda_j k_{ji} m_{jn} \frac{A_i}{A_j} + \sum_{c=1}^{NCn} f_{cin}$$

where:

m_{in} = mass of radionuclide i in cell n

- S_{in} = mass release rate of radionuclide i to cell n from the waste
- λ_i = radioactive decay constant of radionuclide i
- λ_i = radioactive decay constant of radionuclide j
- m_{jn} = mass of radionuclide j (parent of radionuclide i) in cell n





 k_{ji} = fraction of radionuclide j disintegrations that produce radionuclide i

A_i = mass number of radionuclide i

A_j = mass number of radionuclide j

NC_n = number of mass transfer connections of cell n

 f_{cin} = mass transfer rate of radionuclide i to cell n through connection c

First term in the equation is the mass input rate of radionuclide i to cell n from the waste. In ENRESA 2000 all the radionuclides released from the waste pass to a first cell that represents the free water around the waste inside the buffer.

Second and third terms represent radioactive decay/ingrowth. Fourth term represents the mass transfer rates of radionuclide i between cell n and the other cells of the system.

For each radionuclide a differential equation is obtained for each cell. For a decay chain, a system of differential equations of obtained, that are coupled through the decay/ingrowth terms and the terms of mass transfer between cells (f_{cin}).

The concentration of radionuclide i in the water of cell n is calculated taking into account sorption on solid materials in the cell and the radionuclide solubility limit:

$$C_{in} = MIN \left[\frac{m_{in}}{V_n + MS_n K_{din}}, Cmax_{in} \right]$$

where:

 V_n = water volume in cell n

 MS_n = mass of solid material in cell n

 $K_{d in}$ = solid-water distribution coefficient for radionuclide i in cell n

Cmaxin = solubility limit of radionuclide i in the water of cell n

When several isotopes of the same chemical element are considered, the element solubility limit (Solubility_k) is shared between all the isotopes and

$$C \max_{in} = So \operatorname{lub} ility_k \frac{m_{in}}{\sum_k m_{kn}}$$





where the denominator is the sum of the masses in cell n of all the isotopes of element k (radionuclide i is an isotope of element k).

The input/output of radionuclide i in cell n from/to the other cells is made through the different connections c. The input/output rate for radionuclide i in cell n through connection c (f_{cin}), has different expression for advective and diffusive transport.

For a *diffusive connection* between cells n and m, the mass transfer rate for radionuclide i to cell n through connection c ($f_{cin}(dif)$) is:

$$f_{cin}(dif) = D_{ci} (-C_{in} + C_{im})$$

where:

 D_{ci} = diffusive transport factor for radionuclide i in connection c.

 C_{in} = concentration of radionuclide i in cell n water.

C_{im} = concentration of radionuclide i in cell m water.

Factor D_{ci} is defined from the transport parameters in both cells:

$$D_{ci} = \frac{S_{c}}{\frac{L_{n}}{De_{in}} + \frac{L_{m}}{De_{im}}}$$

where:

 S_c = contact surface for diffusive connection c between cells n and m.

 L_{cn} = diffusion length for connection c in cell n.

 L_{cm} = diffusion length for connection c in cell m.

 De_{in} = effective diffusion coefficient for radionuclide i in cell n.

De_{im} = effective diffusion coefficient for radionuclide i in cell m.

The effective diffusion coefficient for radionuclide i in cell n is defined as:

$$De_{in} = Dw_i \left(\frac{\delta}{\tau^2}\right)_{in} \theta_{in} = Dp_{in} \theta_{in}$$





where:

 Dw_i = diffusion coefficient in free water for radionuclide i.

 Dp_{in} = pore diffusion coefficient for radionuclide i in cell n.

 $(\delta/\tau^2)_{in}$ = pore geometry factor for the porous medium in cell n for radionuclide i.

 θ_{in} = accesible porosity for radionuclide i in cell n.

For an *advective connection* between cells n and m, the mass transfer rate of radionuclide i to cell n through connection c ($f_{cin}(adv)$) is as follows:

 $f_{cin}(adv) = -q_c C_{in}$ (if water flows from n to m)

 $f_{cin}(adv) = q_c C_{im}$ (if water flows from m to n)

where:

 q_c = water flow through connection c.

 C_{in} = concentration of radionuclide i in the water of cell n.

 C_{im} = concentration of radionuclide i in the water of cell m.

(NOTE: advective connections are not used in the model of GoldSim used in PAMINA Task 4.1.B, only diffusive transport is considered).

The system of differential equations is solved in an iterative way, starting at t=0 using a timestep Δt . If radionuclide masses and concentrations in water for all radionuclides are known at instant t in all cells, the masses at instant t+ Δt will be:

$$m_{in}\left(t + \Delta t\right) = m_{in}(t) + \left(S_{in}(t) - \lambda_i m_{in}(t) + \lambda_j k_{ji} m_{jn}(t) \frac{A_i}{A_j} + \sum_{c=1}^{NCn} f_{cin}(t)\right)^* \Delta t$$

After calculating the masses at instant $t+\Delta t$, the new concentrations in water are calculated and a new iteration is done. For a decay chain of m members in a system of n mixing cells, a system of n x m equations is generated and solved in the same way.





3.3. Data

The values assigned to the transport parameters in bentonite for different species are present in Table 3.1.

	Cations	Anions
Porosity	0.407	0.08
Pore water diffusion coefficient (Dp) (m ² /s)	10 ⁻¹⁰	10 ⁻¹⁰

Table 3.1.	Transport	parameters	in	bentonite	of	GoldSim	model	
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Density of the solid material of bentonite is 2700 kg/m³ and total porosity is 40.7%. An "equivalent flow" of 0.06 liter/yr-canister is used for the "mixing tank" boundary condition at the bentonite outer surface.

The maximum concentration of dissolved Ni is 10^{-3} mol/L in the porewater.





4. UDC model and data

4.1. Conceptual model

The UDC model considers the following two materials: canister and bentonite. Detailed numerical predictions show that bentonite barrier will become fully water-saturated after 20 to 30 years for the Spanish reference concept (ENRESA, 2005; 2006). Therefore, the model assumes that bentonite is initially water-saturated.

The geochemical model accounts for the following geochemical reactions: aqueous complexation, acid-base, redox, canister corrosion, dissolution/precipitation of calcite, goethite, gypsum, magnetite, quartz and siderite, cation exchange of Ca^{2+} , Mg^{2+} , Na^+ , K^+ , Fe^{2+} , Ni^{2+} , Cs^+ and UO_2^{2+} , and protonation/deprotonation by surface complexation.

The chemical system is defined in terms of the following primary species: H_2O , $O_2(aq)$, H^+ , Na⁺, K⁺, Ca²⁺, Mg²⁺, Fe²⁺, HCO₃⁻, Cl⁻, SO₄²⁻, Ni²⁺, Cs⁺, UO₂²⁺ and SiO₂(aq).

Relevant aqueous complexes were identified from speciation runs performed with EQ3/6 (Wolery, 1992). All these reactions are assumed at local chemical equilibrium. The Gaines-Thomas convention is used for cation exchange (Gaines and Thomas, 1953). The surface complexation is simulated as proposed by Bradbury and Baeyens (2005) without electrostatic contributions, considering one strong and two weak surface sites. Surface complexation reactions are not considered inside the canister.

Chemical reactions and their equilibrium constants at 25 °C for aqueous complexes and minerals (Wolery, 1992) are listed in Table 4.1 and Table 4.2, chemical reactions and their equilibrium constants for aqueous uranium complexes are listed in Table 4.3.

Minerals	Log K (25 °C)
$CaCO_3(s) + H^+ \Leftrightarrow Ca^{2+} + HCO_3^-$	1.8487
$CaSO_4 \cdot 2H_2O(s) \Leftrightarrow Ca^{2+} + SO_4^{2-} + 2H_2O$	-4.4823
$SiO_2(s) \Leftrightarrow SiO_2(aq)$	-3.9993
$Fe_{3}O_{4}(s) + 6H^{+} \Leftrightarrow 3Fe^{2+} + 0.5O_{2}(aq) + 3H_{2}O$	-6.5076
$FeOOH(s) + 2H^{+} \Leftrightarrow Fe^{2+} + 0.25O_2(aq) + 1.5H_2O$	-7.9555
$FeCO_3(s) + H^+ \Leftrightarrow Fe^{2+} + HCO_3^-$	-0.1920
$NiCO_3(s) + H^+ \Leftrightarrow Ni^{2+} + HCO_3^-$	3.5118
$Ni(OH)_2(s) + 2H^+ \Leftrightarrow Ni^{2+} + 2H_2O$	12.748
UO_2 :2H ₂ O(am) + 4H ⁺ \Leftrightarrow U ⁴⁺ + 4H ₂ O	1.5000
$USiO_4(s) + 4H^+ \Leftrightarrow U^{4+} + SiO_2(aq) + 2H_2O$	-8.0477
$UO_{2\cdot 25}(s) + 4H^+ \Leftrightarrow U^{4+} + 0.125O_2(aq) + 2H_2O$	-11.793

Table 4.1. Equilibrium constants for minerals





Aqueous complexes	Log K (25 °C)
CaCl ⁺ ⇔ Ca ²⁺ + Cl [−]	0.6956
CaCl₂(aq) ⇔ Ca ²⁺ + 2Cl [−]	0.6436
$CaCO_3(aq) + H^+ \Leftrightarrow Ca^{2+} + HCO_3^-$	7.0017
CaHCO ₃ ⁺ ⇔ Ca ²⁺ + HCO ₃ ⁻	-1.0467
$CaH_3SiO_4^+ + H^+ \Leftrightarrow Ca^{2+} + 2H_2O + SiO_2(aq)$	8.7916
$CaSO_4(aq) \Leftrightarrow Ca^{2+} + SO_4^{2-}$	-2.1111
$CaOH^+ + H^+ \Leftrightarrow Ca^{2+} + H_2O$	12.850
$CO_2(aq) + H_2O \Leftrightarrow H^+ + HCO_3^-$	-6.3447
$\text{CO}_3^{2-} + \text{H}^+ \Leftrightarrow \text{HCO}_3^-$	10.329
$CsCl (aq) \Leftrightarrow Cs^+ + Cl^-$	0.0900
$Fe^{3+} + 0.5H_2O \Leftrightarrow Fe^{2+} + H^+ + 0.25O_2(aq)$	-8.4900
FeCl ⁺ ⇔ Fe ²⁺ + Cl ⁻	0.1605
$FeCO_3(aq) + H^+ \Leftrightarrow Fe^{2+} + HCO_3^-$	5.5988
FeHCO ₃ ⁺ ⇔ Fe ²⁺ + HCO ₃ ⁻	-2.0500
$FeSO_4(aq) \Leftrightarrow Fe^{2+} + SO_4^{2-}$	-2.2000
$HCI(aq) \Leftrightarrow H^+ + CI^-$	0.6700
$HSO_4^- \Leftrightarrow H^+ + SO_4^{2-}$	-1.9791
$HSiO_3^- + H^+ \Leftrightarrow H_2O + SiO_2(aq)$	9.9525
$H_6(H_2SiO_4)_4^{-} + 2H^{+} \Leftrightarrow 8H_2O + 4SiO_2(aq)$	13.446
$KCl(aq) \Leftrightarrow K^+ + Cl^-$	1.4946
$KSO_4^- \Leftrightarrow K^+ + SO_4^{2-}$	-0.8796
$MgCl^+ \Leftrightarrow Mg^{2+} + Cl^-$	0.1349
$MgCO_3(aq) + H^+ \Leftrightarrow Mg^{2+} + HCO_3^{-2}$	7.3499
$MgHCO_3^+ \Leftrightarrow CaMg^{2+} + HCO_3^-$	-1.0357
$MgH_2SiO_4(aq) + 2H^+ \Leftrightarrow Mg^{2+} + SiO_2(aq) + 2H_2O$	17.482
$MgH_{3}SiO_{4}^{+} + H^{+} \Leftrightarrow Mg^{2+} + SiO_{2}(aq) + 2H_{2}O$	8.5416
$MgSO_4(aq) \Leftrightarrow Mg^{2^+} + SO_4^{2^-}$	-2. 4117
NaCl (aq) ⇔ Na ⁺ + Cl ⁻	0.7770
$NaCO_3^- + H^+ \Leftrightarrow Na^+ + HCO_3^-$	9.8144
$NaHCO_3(aq) \Leftrightarrow Na^+ + HCO_3^-$	-0.1541
$NaHSiO_3(aq) + H^+ \Leftrightarrow Na^+ + SiO_2(aq) + H_2O$	8.3040
$NaOH(aq) + H^+ \Leftrightarrow Na^+ + H_2O$	14.180
$NaSO_4^- \Leftrightarrow Na^+ + SO_4^{2-}$	-0.8200
NiCl ⁺ ⇔ Ni ²⁺ + Cl [−]	0.9962
$Ni(OH)^{-} + H^{+} \Leftrightarrow Ni^{2+} + H_2O$	11.535
$Ni(OH)_2(aq) + 2H^+ \Leftrightarrow Ni^{2+} + 2H_2O$	19.990
$Ni(OH)_3^+ + 3H^+ \Leftrightarrow Ni^{2+} + 3H_2O$	30.985
$Ni_2(OH)^{3+} + H^+ \Leftrightarrow 2Ni^{2+} + H_2O$	10.700
$Ni_4(OH)_4^{4+} + 4H^+ \Leftrightarrow 4Ni^{2+} + 4H_2O$	27.680
$NiSO_4(aq) \Leftrightarrow Ni^{2+} + SO_4^{2-}$	-2.1257
$OH^- + H^+ \Leftrightarrow H_2O$	13.995

Table 4.2. Equilibrium	constants for	r aqueous	complexes.
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Aqueous complexes	Log K (25 °C)
$U^{3+} + 0.75O_2(aq) + 0.5 H_2O \Leftrightarrow UO_2^{2+} + H^+$	65.045
U^{4+} + 0.5 $O_2(aq)$ + $H_2O \Leftrightarrow UO_2^{2+}$ + 2 H^+	33.945
$UOH^{3+} + 0.5O_2(aq) \Leftrightarrow UO_2^{2+} + H^+$	34.485
$U(OH)_{2}^{2+} + 0.5O_{2}(aq) \Leftrightarrow UO_{2}^{2+} + H_{2}O$	35.045
$U(OH)_{3}^{+} + 0.5O_{2}(aq) + H^{+} \Leftrightarrow UO_{2}^{2+} + 2H_{2}O$	38.645
$U(OH)_4(aq) + 0.5O_2(aq) + 2H^+ \Leftrightarrow UO_2^{2+} + 3H_2O$	43.945
$U_{6}(OH)_{15}^{9+} + 3O_{2}(aq) + 3H^{+} \Leftrightarrow 6UO_{2}^{2+} + 9H_{2}O$	220.57
$U(CO_3)_4^{4-} + 0.5O_2(aq) + 2H^+ + H_2O \iff UO_2^{2+} + 4HCO_3^{-}$	40.140
$U(CO_3)_5^{6-}$ + 0.5O ₂ (aq) + 3H ⁺ + H ₂ O \Leftrightarrow UO ₂ ²⁺ + 5HCO ₃ ⁻	51.589
$USO_4^{2++0.5O_2(aq)+H_2O} \Leftrightarrow UO_2^{2++SO_4^{2-}+2H^+}$	27.365
$U(SO_4)_2(aq) + 0.5O_2(aq) + H_2O \iff UO_2^{2+} + 2SO_4^{2-} + 2H^+$	23.435
UCI^{3+} + 0.5 $O_2(aq)$ + $H_2O \iff UO_2^{2+}$ + CI^- + $2H^+$	32.225
$UO_2^+ + 0.25O_2(aq) + H^+ \Leftrightarrow UO_2^{2+} + 0.5H_2O$	20.016
$UO_2 CI_2(aq) \Leftrightarrow UO_2^{2+} + 2CI^{-}$	1.1000
$UO_2 CIO_3^+ \Leftrightarrow UO_2^{2^+} + 1.5 O_2(aq) + CI^-$	16.770
$UO_2 CO_3(aq) + H^+ \Leftrightarrow UO_2^{2+} + HCO_3^-$	0.3888
$UO_2(CO_3)_2^{2-} + 2H^+ \Leftrightarrow UO_2^{2+} + 2HCO_3^{-}$	4.0476
$UO_2(CO_3)_3^{4-} + 3H^+ \Leftrightarrow UO_2^{2+} + 3HCO_3^{-}$	9.1464
$UO_2(CO_3)_3^{5-} + 0.25O_2(aq) + 4H^+ \Leftrightarrow UO_2^{2+} + 3HCO_3^{-} + 0.5H_2O$	44.053
$(UO_2)_3(CO_3)_6^{-6-} + 6H^+ \Leftrightarrow 3UO_2^{-2+} + 6HCO_3^{-6-}$	7.9728
$(UO_2)_2CO_3(OH)_3 + 4H^+ \Leftrightarrow 2UO_2^{2+} + HCO_3 + 3H_2O$	11.189
$(UO_2)_3CO_3(OH)_3^+ + 4H^+ \Leftrightarrow 3UO_2^{2+} + HCO_3^- + 3H_2O$	9.6688
$(UO_2)_{11}(CO_3)_6(OH)_{12}^{2-} + 18H^+ \Leftrightarrow 11UO_2^{2+} + 6HCO_3^{-} + 12H_2O$	25.543
$UO_2OH^+ + H^+ \Leftrightarrow UO_2^{2^+} + H_2O$	5.2500
$UO_2(OH)_2(aq) + 2H^+ \Leftrightarrow UO_2^{2+} + 2H_2O$	12.150
$UO_2(OH)_3^- + 3H^+ \Leftrightarrow UO_2^{2+} + 3H_2O$	20.250
$UO_2(OH)_4^{2-} + 4H^+ \Leftrightarrow UO_2^{2+} + 4H_2O$	32.400
$(UO_2)_2OH^{3+} + H^+ \Leftrightarrow 2UO_2^{2+} + H_2O$	2.7000
$(UO_2)_2(OH)_2^{+2} + 2H^+ \Leftrightarrow 2UO_2^{-2+} + 2H_2O$	5.6200
$(UO_2)_3(OH)_4^{+2} + 4H^+ \Leftrightarrow 3UO_2^{+2} + 4H_2O$	11.900
$(UO_2)_3(OH)_5^+ + 5H^+ \Leftrightarrow 3UO_2^{2+} + 5H_2O$	15.550
$(UO_2)_3(OH)_7^- + 7H^+ \Leftrightarrow 3UO_2^{-2+} + 7H_2O$	32.200
$(UO_2)_4(OH)_7^+ + 7H^+ \Leftrightarrow 4UO_2^{2+} + 7H_2O$	21.900
$UO_2SO_3(aq) + 0.5O_2(aq) \Leftrightarrow UO_2^{2+} + SO_4^{2-}$	40.024
$UO_2SO_4(aq) \Leftrightarrow UO_2^{2^+} + SO_4^{2^-}$	-3.1500
$UO_2(SO_4)_2^{2-} \Leftrightarrow UO_2^{2+} + 2SO_4^{2-}$	-4.1400
$UO_2(SO_4)_3^{4-} \Leftrightarrow \overline{UO_2^{2+} + 3SO_4^{2-}}$	-3.0200
$UO_2S_2O_3(aq) + 2O_2(aq) + H_2O \Leftrightarrow UO_2^{2+} + 2SO_4^{2-} + 2H^+$	130.74

Table 4.3. Ec	quilibrium co	onstants for	aqueous ι	uranium	complexes.

Selectivity coefficients for exchangeable cations and protolysis constants for surface complexation (Bradbury and Baeyens, 2005; BENIPA, 2003; Fernández et al., 2004; Samper et al., 2007) are listed in Table 4.4.





Table 4.4. Selectivity coefficients for cation exchange reactions and protolysis constants for surface complexation reactions. = SOH denotes strong sites, = W^1OH weak sites type 1 and = W^2OH weak sites type 2.

Cation exchange	K _{Na-cation}
$Na^{+} + K-X \Leftrightarrow K^{+} + Na-X$	0.138
Na⁺ + 0.5Ca-X₂ ⇔ 0.5Ca²⁺ + Na-X	0.292
$Na^{+} + 0.5Mg - X_2 \Leftrightarrow 0.5Mg^{2+} + Na - X$	0.288
$Na^{+} + 0.5Fe-X_2 \Leftrightarrow 0.5Fe^{2+} + Na-X$	0.500
$Na^{+} + Cs - X \Leftrightarrow Cs^{+} + Na - X$	0.025
$Na^{+} + 0.5Ni-X_2 \Leftrightarrow 0.5Ni^{2+} + Na-X$	0.519
Na ⁺ + 0.5UO ₂ -X ₂ ⇔ 0.5 UO ₂ ²⁺ + Na-X	0.841
Surface complexation	Log K _{int}
\equiv SOH ₂ ⁺ $\Leftrightarrow \equiv$ SOH + H ⁺	-4.5
\equiv SO ⁻ + H ⁺ $\Leftrightarrow \equiv$ SOH	7.9
\equiv SONi ⁺ + H ⁺ $\Leftrightarrow \equiv$ SOH + Ni ²⁺	0.6
$\equiv \text{SONiOH} + 2 \text{ H}^{+} \Leftrightarrow \equiv \text{SOH} + \text{Ni}^{2+} + \text{H}_2\text{O}$	10.0
$\equiv \text{SONi}(\text{OH})_2^- + 3 \text{ H}^+ \Leftrightarrow \equiv \text{SOH} + \text{Ni}^{2+} + 2\text{H}_2\text{O}$	20.0
\equiv SOUO ₂ ⁺ + H ⁺ $\Leftrightarrow \equiv$ SOH + UO ₂ ²⁺	-3.1
$\equiv \text{SOUO}_2\text{OH} + 2 \text{ H}^+ \Leftrightarrow \equiv \text{SOH} + \text{UO}_2^{2^+} + \text{H}_2\text{O}$	3.4
$\equiv \text{SOUO}_2(\text{OH})_2^- + 3 \text{ H}^+ \Leftrightarrow \equiv \text{SOH} + \text{UO}_2^{2+} + 2 \text{ H}_2\text{O}$	11.0
$\equiv \text{SOUO}_2(\text{OH})_3^{2^-} + 4 \text{ H}^+ \Leftrightarrow \equiv \text{SOH} + \text{UO}_2^{2^+} + 3 \text{ H}_2\text{O}$	20.5
\equiv SOU ⁴⁺ + H ⁺ $\Leftrightarrow \equiv$ SOH + U ⁴⁺	-7.7
$\equiv \text{SOH}_2\text{UO}_2(\text{CO}_3)_2^- \Leftrightarrow \equiv \text{SOH} + \text{H}^+ + \text{UO}_2(\text{CO}_3)_2^{-2}$	-11.79
$\equiv \text{SOH}_2\text{UO}_2(\text{CO}_3)_3^{3-} \Leftrightarrow \equiv \text{SOH} + \text{H}^+ + \text{UO}_2(\text{CO}_3)_3^{4-}$	-13.82
$\equiv W^{1}OH2^{+} \Leftrightarrow \equiv W^{1}OH + H^{+}$	-4.5
$\equiv W^1O^- + H^+ \Leftrightarrow \equiv W^1OH$	7.9
\equiv W ¹ ONi ⁺ + H ⁺ \Leftrightarrow \equiv W ¹ OH + Ni ²⁺	3.3
$\equiv W^{1}OUO_{2}^{+} + H^{+} \Leftrightarrow \equiv W^{1}OH + UO_{2}^{2+}$	-0.7
$\equiv W^{1}OUO_{2}OH + 2H^{+} \Leftrightarrow \equiv W^{1}OH + UO_{2}^{2+} + H_{2}O$	5.7
$\equiv W^2 O H 2^+ \Leftrightarrow \equiv W^2 O H + H^+$	-6.0
$\equiv W^2 O^- + H^+ \Leftrightarrow \equiv W^2 O H$	10.5

4.2. Mathematical formulation

In UDC model, aqueous (dissolved) species are subject to transport in the liquid phase as well as chemical interactions with other aqueous species (homogeneous reactions), and solid species (heterogeneous reactions). Solid species, including precipitated, exchanged and adsorbed surface species, only participate in local chemical reactions.

For aqueous systems in chemical equilibrium, "multi-species reactive transport" can be reduced to "multi-component reactive transport" (Yeh and Tripathi, 1991; Walter et al., 1994; Steefel and Lasaga, 1994; and Lichtner, 1996) if diffusion and dispersion coefficients can be assumed to be the same for all the aqueous species. Under these conditions, transport equations can be written in terms of total dissolved components. Based on mass conservation, transport equations for chemical components can be expressed as





$$\nabla \cdot \left(\theta \mathbf{D} \nabla C_{j}\right) - \mathbf{q} \cdot \nabla C_{j} + w \left(C_{j}^{*} - C\right) + \theta R_{j} = \theta \frac{\partial C_{j}}{\partial t} \qquad j = 1, 2, ..., N_{C}$$
(1)

where N_c is the number of chemical components, C_j is the total dissolved concentration of component j, C_j^* is the dissolved concentration of fluid sources of water flow w, D is the hydrodynamic dispersion tensor, and R_j is the reactive sink/source term which includes all the chemical interactions of the j-th component with solid (or gas) species. In general, the chemical sink/source term depends on the concentrations of all dissolved species in a nonlinear manner, which renders the transport equations (1) highly non-linear. These primary governing equations need to be complemented with constitutive chemical relationships.

For representing a geochemical system, it is convenient to select a subset of N_c aqueous species as basis species which are the so-called components, or primary species. The remaining species are called "secondary", and the number of secondary species must be equal to the number of reactions. All the secondary species can be represented as linear combinations of primary species such as

$$S_{i}^{s} = \sum_{j=1}^{N_{c}} v_{ij} S_{j}^{p}$$
 $i = 1, ..., N_{R}$ (2)

where S_j^p is the chemical formula of the j-th primary species, S_i^s is the chemical formula of the i-th secondary species, N_R is the number of reactions (or secondary species), and v_{ij} is the stoichiometric coefficient of the j-th primary species in the i-th reaction.

<u>Aqueous complexation</u>. By assuming local equilibrium for aqueous complexation reactions, the mass action law provides an expression which relates the concentration of the i-th aqueous complex to the concentrations of primary species:

$$\mathbf{x}_{i} = \mathbf{K}_{i}^{-1} \gamma_{i}^{-1} \prod_{j=1}^{N_{C}} c_{j}^{\nu_{ij}^{x}} \gamma_{j}^{\nu_{ij}^{x}} \qquad i = 1, ..., N_{x}$$
(3)

where N_x is the number of aqueous complexes, x_i are molal concentrations of aqueous complexes, c_j are molal concentrations of primary species, ν_{ij}^x is the stoichiometric coefficient of the j-th primary species in the i-th aqueous complex, γ_i and γ_j are thermodynamic





activity coefficients which can be calculated from available expressions such as that of Debye-Hückel, and K_i is the equilibrium constant.

<u>Acid-base and redox reactions</u>. Acid-base and redox reactions can be treated in a manner similar to aqueous complexation reactions (Yeh and Tripathi, 1989). Contrary to the proton, which exists as a dissolved species, the electron is a hypothetical species. Considering the electron as a dissolved species is convenient because it allows one to complete redox half-reactions such as $Fe^{2+} \Leftrightarrow Fe^{3+} + e^-$. A virtual concentration is attached to the electron which by convention has an activity coefficient equal to 1. Consideration of redox reactions only requires an additional equation for the electron balance ("operational electrons" according to Yeh and Tripathi, 1989).

<u>Mineral dissolution/precipitation</u>. The dissolution or precipitation of pure mineral phases under local equilibrium conditions is governed by the following expression

$$K_{m} = \prod_{j=1}^{N_{C}} c_{j}^{\nu_{mj}^{p}} \gamma_{j}^{\nu_{mj}^{p}} \qquad m = 1, ..., N_{P}$$
(4)

where m is the mineral index, N_p is the number of minerals, v_{mj}^p is the stoichiometric coefficient of the j-th basis species in the m-th mineral, and K_m is the solubility constant.

<u>Cation exchange</u>. According to the Gaines-Thomas convention, cation exchange reactions can be written as (Appelo and Postma, 1993):

$$\frac{1}{z_i}S_i + \frac{1}{z_j}\left(S_j - X_{z_j}\right) \Leftrightarrow \frac{1}{z_i}\left(S_i - X_{z_i}\right) + \frac{1}{z_j}S_j$$
(5)

where S_i and S_j denote dissolved cation species having electrical charges z_i and z_j , respectively, and $(S_i - X_{z_i})$ and $(S_j - X_{z_j})$ represent exchange sites occupied by exchanged cations. The equilibrium equation for cation exchange is obtained by applying the mass-action law to (5):

$$\mathbf{K}_{\mathbf{S}_{i}\mathbf{S}_{j}} = \frac{\beta_{i}^{\frac{j}{z_{i}}} \cdot \left(\gamma_{j}\mathbf{c}_{j}\right)^{\frac{j}{z_{j}}}}{\beta_{j}^{\frac{j}{z_{j}}} \cdot \left(\gamma_{i}\mathbf{c}_{i}\right)^{\frac{j}{z_{i}}}}$$
(6)





where $K_{S_iS_j}$ is the selectivity constant for cations S_i and S_j , and β_i and β_j are the activities of the exchanged cations which in the Gaines-Thomas convention are assumed to be equal to the equivalent fractions (Appelo and Postma, 1993). Here Na⁺ is taken as the reference cation. For a system with only three cations (Na⁺, K⁺, and Ca²⁺), the exchange reactions are written as:

$$Na^{+} + K-X = K^{+} + Na-X$$

 $Na^{+} + 0.5Ca-X_{2} = 0.5Ca^{2+} + Na-X$

and their selectivities are denoted by $K_{\text{Na/K}}$ and $K_{\text{Na/Ca}},$ respectively.

<u>Surface complexation</u>. The sorption of solutes at the solid surfaces is described as a chemical reaction between the aqueous species and the specific surface site (SC). These surface reactions include proton exchange, cation binding and anion binding via ligand exchange at surface hydroxyl sites (represented here as XOH to avoid confusion with other chemical species). For example, the sorption of a metal is described as:

$$XOH + M^{z^+} = XOM^{(z-1)^+} + H^+$$

At equilibrium, this reaction can be described by:

$$K_{\text{int}r} = \frac{\left[XOM^{(z-1)+}\right]\alpha_{H^+}}{\left[XOH\right]\alpha_{M^{z+}}}$$

where K_{intr} is the equilibrium constant related to the chemical reaction, usually referred to as the intrinsic constant (Dzombak and Morel, 1990), *a* denotes thermodynamic activity of aqueous species and the terms in brackets represent the concentrations of the surface complexes (mol/kg).

In aqueous complexation reactions the electric charge is assumed to be homogeneously distributed in the solution. However, surface reactions take place on an electrostatic charged surface which creates an electrostatic field. An additional energetic term accounting for the work needed for the aqueous species to travel across the surface electric field is required:

$$K_{ads} = K_{\text{int}\,r} e^{\frac{\Delta z F \psi_d}{RT}}$$





where R is the gas constant (8.314 J/mol/K), T is the absolute temperature (K), K_{ads} is the apparent equilibrium constant of the overall adsorption process, and Δz is the charge of the reaction. Although the contribution of the electrostatic term to the total sorption energy is not determined experimentally, it is useful to take into account the variations of surface charge effects on surface complexation reactions. In this equation the thermodynamic activities of the surface complexes are substituted by their concentrations. This is based on the assumption that all non ideal behavior of the surface species is attributed to the mean surface potential and is accounted for by the electrostatic term.

Our computer code CORE^{2D}V4 (Samper et al., 2003) accounts for adsorption via surface complexation using the double layer model. More details can be found in Xu (1996).

4.3. Model geometry

A 1D axisymmetric flow model is used corresponding to a single canister. The grid has 167 elements and 168 nodes. An extra element of 0.01mm thickness is added at the bentonite outer surface in order to simulate the 'mixing tank' boundary condition. Solutes diffuse into this outermost element and the equivalent groundwater flow is injected and extracted from this element. An 'equivalent flux' of 0.06 litre/year (for a canister length of 5.94m) is used for the 'mixing tank' boundary condition at the bentonite outer surface (see Figure 4.1). The first 16 elements represent the canister internal volume up to a radius of 0.45m and the remaining 151 elements represent the bentonite up to a radius of 1.2m.



Figure 4.1. Finite element mesh used in the 1-D axisymmetric model.

4.4. Model parameters

In UDC model the canister internal volume is treated as a dummy porous medium with a very large porewater diffusion coefficient (3 orders of magnitude greater than that in bentonite) is used to ensure always perfect mixing. A porosity of 0.132 is used for the canister to ensuring that the internal water volume is $0.5m^3$.





		· ·
Material	Initial porosity	Initial effective diffusion (m ² /s)
Bentonite	4.07·10 ⁻¹	4.070·10 ⁻¹¹
Canister	1.32·10 ⁻¹	6.713·10 ⁻⁰⁹

Table 4.5. Flow and transport parameters.

Given the low hydraulic conductivity of the bentonite, diffusion is the main solute transport mechanism in the engineered barrier. All dissolved chemical species are assumed to have the same effective diffusion coefficient which is equal to $4.07 \cdot 10^{-11} \text{m}^2/\text{s}$. The model assumes that porosity is constant and all water is accessible for chemical reactions, that is, the geochemical porosity coincides with total porosity. Flow and transport parameters are listed in Table 4.5 (BENIPA, 2003; Samper et al., 2007).

4.5. Initial and boundary conditions

The chemical composition of inflow water coincides with that of initial granite porewater. The initial porewater composition in the canister and the bentonite is the same. The chemical composition of the boundary inflow water and the initial bentonite are listed in Table 4.6 (BENIPA, 2003; Samper et al., 2007).

Primary species	Initial bentonite water (mol/L)	Boundary water (mol/L)
Ca ²⁺	3.101·10 ⁻²	1.522·10 ⁻⁴
Cl	2.756·10 ⁻¹	3.949·10 ⁻⁴
Fe ²⁺	6.583·10 ⁻⁵	1.791·10 ⁻⁸
рН	6.435	7.825
HCO ₃ ⁻	1.689·10 ⁻³	5.049·10 ⁻³
K ⁺	1.507·10 ⁻³	5.371·10 ⁻⁵
Mg ²⁺	3.473·10 ⁻²	1.604·10 ⁻⁴
Na⁺	1.841·10 ⁻¹	4.350·10 ⁻³
Eh (V)	-0.059	-0.188
SiO ₂ (aq)	3.761·10 ⁻⁴	3.761·10 ⁻⁴
SO4 ²⁻	2.049·10 ⁻²	1.561·10 ⁻⁵

Table 4.6. Chemical composition of the boundary and initial water concentration.

The initial composition of bentonite porewater is controlled by mineral dissolution/precipitation at chemical equilibrium (calcite and quartz), proton surface complexation and cation exchange.





S-OH	2·10 ⁻⁶		
W ¹ -OH	4·10 ⁻⁵		
W ² -OH	4·10 ⁻⁵		

Table 4.7. Surface complexes site densities of bentonite (in mol/g dry bentonite).

Initial volume fractions of calcite and quartz in bentonite are both equal to 0.01 (BENIPA, 2003; Samper et al., 2007). Gypsum, magnetite, siderite and goethite are minerals which are not initially present in the system, but are allowed to precipitate.

Cation exchange capacity (CEC) in bentonite is 87 meq/100g. Surface complexation site densities in bentonite are listed in Table 4.7.

4.6. Numerical methods

The numerical formulation adopted for solving the coupled equations of solute transport and chemical reactions is based on the sequential iteration approach (SIA) (Yeh and Tripathi, 1991; Walter et al., 1994) which consists on solving transport and chemical equations separately in a sequential manner. The transport equations are solved first and then those of chemical reactions. This sequential process is repeated until convergence is attained. The essence of the SIA is therefore the sequential solution of two independent sets of equations: the transport equations and the chemical equations. While the former are solved in a component manner, the later are solved node-wise. These two sets of equations are coupled by means of chemical sink/source terms. CORE^{2D}V4 uses a mixed explicit-implicit scheme based on the standard operator which enjoys adequate convergence properties (Samper et al., 1995; Xu, 1996). This scheme is given by

$$\nabla \cdot \left(\theta \mathbf{D} \nabla C_{j}^{s+1/2}\right) - \mathbf{q} \cdot \nabla C_{j}^{s+1/2} + w \left(C_{j}^{*} - C_{j}^{s+1/2}\right) + \theta R_{j}^{s} = \theta \frac{\partial C_{j}^{s+1/2}}{\partial t} \qquad j = 1, \dots, N_{C}$$
(7)

where superscript s denotes the transport+reaction iteration number. A transport+reaction iteration consists of two parts, a transport part denoted by s+1/2 (it should be noted that $\frac{1}{2}$ does not mean $\Delta t/2$ where Δt is the time step) and the reaction part denoted by s+1. If the reaction sink/source terms R_j^s in equation (7) are known, the resulting equations are linear and have the same structure as the standard transport equation of a conservative solute.





These equations are solved by the Galerkin finite element method (Xu, 1996). After space and time discretization, the equation for the j-th component becomes

$$\left[\epsilon \mathbf{E} + \frac{\mathbf{F}}{\Delta t}\right] \mathbf{C}_{j}^{k+1,s+1/2} = \mathbf{g}_{j}^{k+1} + \theta \mathbf{R}_{j}^{k+1,s} + \left[(\epsilon - 1)\mathbf{E} + \frac{\mathbf{F}}{\Delta t}\right] \mathbf{C}_{j}^{k}$$
(8)

where ε is a time weighting parameter (ε =0 for explicit and ε =1 for implicit), E is a square matrix containing dispersion and advection terms, F is also a square matrix of storage terms, \mathbf{g}_{j}^{k+1} is a column vector containing boundary terms as well as external fluid sink/source terms and superscript k denotes the time step and $\Delta t = t^{k+1} - t^{k}$. The actual expressions of E, F and \mathbf{g}_{j}^{k+1} are given by Xu (1996). The terms $R_{j}^{k+1,s}$ can be evaluated from the solution of the chemical reaction system at the previous iteration (see the following section). Transport and chemical equations are solved iteratively. In each iteration the reaction terms $R_{j}^{k+1,s}$ are updated until a specified convergence tolerance is satisfied. The sequential non-iterative approach (SNIA) is a particular case of the sequential iteration approach (SIA) in which the sequence of transport and reaction equations is solved only once.

Our numerical formulation applies to problems with any type of homogeneous reactions (aqueous complexation, acid-base and redox) as well as any combination of heterogeneous reactions (mineral dissolution/precipitation, gas dissolution/ex-solution, cation exchange and adsorption). The formulation is based on mass balances in terms of the basis species (Parkhurst et al., 1980; Yeh and Tripathi, 1991). The total analytical concentration of basis species, T_j, in the system are given by

$$T_{j} = c_{j} + \sum_{i=1}^{N_{X}} v_{ij}^{x} x_{i} + \sum_{i=1}^{N_{p}} v_{ij}^{p} p_{i} \qquad j = 1, ..., N_{C}$$
(9)

where p_i is the i-th mineral concentration and the first two terms of the right-hand side are total dissolved component concentrations, C_i

$$C_{j} = c_{j} + \sum_{i=1}^{N_{x}} v_{ij}^{x} x_{i}$$
 $j = 1,..., N_{C}$

which are subject to transport (see Eqs.7). Here c_j denote the dissolved concentrations of primary species.





The set of nonlinear chemical reactions is solved by the Newton-Raphson iterative method. The iterative procedure is repeated until a specified convergence tolerance is satisfied. Once the concentrations of the primary variables are obtained, all other secondary variables can be computed in a straightforward manner. The changes in mineral concentrations, Δp_i , are used to calculate the rate of mass transfer of component j from the mineral phase to the aqueous phase. The expression of the chemical sink/source term in Equation (8) is computed as:

$$R_{j} = -\frac{1}{\Delta t} \sum_{i=1}^{N_{p}} \nu_{ij}^{p} \Delta p_{i}$$
⁽¹⁰⁾

Notice that these sink/source terms may have also contributions from other heterogeneous reactions such as gas dissolution/ex-solution, cation exchange and surface adsorption.

4.7. Computer code

UDC has used its finite element code CORE^{2D} V4 (Samper et al., 2003) which is a code for transient saturated and unsaturated water flow, heat transport and multicomponent reactive solute transport under both local chemical equilibrium and kinetic conditions in heterogeneous and anisotropic media. Flow and transport equations are solved with Galerkin triangular finite elements and an Euler scheme for time discretization. CORE^{2D} V4 solves problems with a wide range of geochemical reactions including homogeneous and heterogeneous reactions such as acid-base, aqueous complexation, redox, mineral dissolution/precipitation, gas dissolution/ex-solution, cation exchange and surface complexation. The chemical formulation is based on ion association theory and uses an extended version of Debye-Hückel equation (B-dot) for activity coefficients of aqueous species. CORE^{2D} V4 can be found in Samper et al. (2003).





5. Nuclide source term

Calculations have been made for 3 nuclides which are present in significant amounts in the spent fuel: Uranium, Nickel and Caesium.

The masses of radioactive and stable isotopes of Nickel after 50 years of cooling are listed in Table 5.1 (ENRESA, 2001b). More than 99% of nickel is located in the structural components of the fuel assembly made of Inconel (INC-718) and stainless steel (SS-304). Nickel release will be controlled by the degradation of these alloys under repository conditions. Although these alloys are very resistant to corrosion usually a short duration is assigned to them in Safety Assessment exercises. For instance, in ENRESA2000 (ENRESA, 2001a) a duration of 1000 years was assumed, leading to complete Ni release 1000 years after canister failure.

	Activation products				Fission
	INC-718	SS-304	ZRY-4	UO ₂ impurities	products
^{58,60,61,62,64} Ni (stable)	2.68·10 ³	1.38·10 ³	2.65	11.1	
⁵⁹ Ni	17.3	2.53	1.53·10 ⁻²	6.68·10 ⁻²	
⁶³ Ni	2.50	0.333	2.29·10 ⁻³	9.60·10 ⁻³	
Ratio Ni (stable)/ ⁵⁹ Ni	155	545	173	166	
Ratio Ni (stable)/ ⁶³ Ni	1070	4140	1150	1150	
¹³³ Cs (stable)					605
¹³⁵ Cs					241
¹³⁷ Cs					206
Ratio Cs(stable)/ ¹³⁵ Cs					2.51
Ratio Cs(stable)/ ¹³⁷ Cs					2.93

 Table 5.1. Mass and location of radioactive and stable isotopes after 50 years of cooling (g/fuel element).

Cesium is a fission product that is created in the UO_2 pellets during irradiation in the reactor. A small fraction (6% in the calculations) migrates to the gap pellet-cladding and the pellet crack and is released quickly after canister and cladding failure (Instant Release Fraction or IRF). The remaining 94% of Cesium remains immobilised in the UO_2 matrix and is released very slowly when the Uranium matrix oxidizes due to alpha radiolysis.

The masses of Ni and Cs in a canister which contains 4 fuel elements after 50 years of cooling are presented in Table 5.2. The inventories in mol are calculated using a mass number of 60 for stable Ni and 133 for stable Cs.





	Half-life (years)	Mass (g/canister)	Mass (mol/canister)
Ni stable		1.63·10 ⁴	272
⁵⁹ Ni	7.50·10 ⁴	79.6	1.35
⁶³ Ni	96	11.4	0.181
Cs stable		2420	18.2
¹³⁵ Cs	2.30·10 ⁶	964	7.14
¹³⁷ Cs	30	824	6.01

Table 5 2 Masses	of Ni and Ce	ner canister	after 50 v	lears of cooling
Table 5.2. Masses	UI INI AHU US	per carrister	aller 50 y	years or cooling.

Due to the short life of ⁶³Ni and ¹³⁷Cs, when the canister fails after several thousands of years their inventories will be negligible and need not to be taken into account in the calculations. The inventories of stable Ni and Cs remain constant with time while the inventories of ⁶³Ni and ¹³⁵Cs will decrease exponentially with time.

Each disposal canister contains around to two tons of Uranium and by far the most abundant isotope is ²³⁸U. Due to its very long life (4.47 billion years) it can be treated as a stable isotope. Its inventory per canister is listed in Table 5.3.

Table 5.3. Masses of Uranium in canister.

	Half-life	Activity	Mass	Mass
	(years)	(Bq/canister)	(kg/canister)	(mol/canister)
²³⁸ U	4.47·10 ⁹	2.15·10 ¹⁰	1.73·10 ³	7266

 238 U is the main component of the UO₂ matrix and will be released slowly when the uranium matrix oxidises due to alpha radiation.

In ENRESA2000 (ENRESA, 2001a) the minimum duration of the canister used in the calculations was 1,300 years, which is a very conservative value. In ENRESA2003 (ENRESA, 2004) a more realistic model of canister failure due to generalised corrosion was developed, and the value obtained for the minimum duration of the canister was 20,000 years. This is the value that has been used in the calculations performed in PAMINA.

Figure 5.2 shows the cumulative masses of the different isotopes released from the waste after the canister failure (at t=20,000 years). These masses have been calculated using the waste alteration models of ENRESA2000 (ENRESA, 2001a), and have been used in the benchmark calculations.







Figure 5.2. Cumulative amounts of U, Ni and Cs released from the waste (in g per canister)





6. Results of the hydrogeochemical evolution fot the reference run without nuclides

Initial concentrations of most of species in bentonite porewater are larger than those in granite groundwater, except for bicarbonate. The solute mass flow from bentonite into granite or from granite to bentonite takes place until concentrations get steady values. In this section we present the results of the time evolution of chemical species in the bentonite.

Figure 6.1 and Figure 6.2 show the time evolution of the concentrations of the dissolved species at a radial distance of 1.2 m. Except for HCO_3^- , dissolved anions and cations decrease due to solute diffusion from the bentonite into the granite. HCO_3^- concentration in granite is greater than that of bentonite and therefore it increases with time.

Figure 6.3 shows the time evolution of pH. Initially, pH remains constant. Later, it increases because pH in granite is larger than that of bentonite. Calcite dissolution also contributes to increase pH.

Figure 6.4 shows the time evolution of the concentration of exchanged Ca^{2+} and Na^+ . They are constant for t < 10⁴ years. Later, dissolved Ca^{2+} displaces exchanged Na^+ from the exchanger.

lonic strength, *I*, is a measure of the total ion content of a solution. It is defined as:

$$I = \frac{1}{2} \cdot \sum_{i=1}^{N} c_{i} \cdot z_{i}^{2}$$
(11)

where z_i and c_i are the ion charge and the concentration of the i-th aqueous species, respectively. Computed ionic strength remains constant for t < 10³ years at a value of / = 0.36. Later, it decreases because most ions diffuse out from bentonite. At the end it reaches a value similar to that of the boundary granite water (see Figure 6.5).

The time evolution of cumulative calcite precipitation is shown in Figure 6.6 . Calcite precipitates near the bentonite-granite interface before $2 \cdot 10^5$ years, because the increase of HCO_3^- and pH are quicker than the decrease of dissolved Ca^{2+} by the exchange between bentonite and granite. After $2 \cdot 10^5$ years, the decrease of dissolved Ca^{2+} concentration controls the dissolution of calcite. Near the canister, calcite dissolves always. Figure 6.7 shows the radial distribution of calcite dissolution/precipitation. This plot illustrates that calcite





precipitats near the bentonite-granite interface until $2 \cdot 10^5$ years, later, however, calcite dissolves everywhere in the bentonite.









Figure 6.2. Time evolution of computed concentrations of dissolved anions at r = 1.2 m in logarithmic time scale (top) and natural time scale (bottom), respectively.










Figure 6.5. Time evolution of computed ionic strength at r = 1.2 m in logarithmic time scale (top) and in natural time scale (bottom). It is the same at all radial distances.



Figure 6.6. Time evolution of cumulative calcite dissolution/precipitation at r = 0.5 m and r = 1.2 m (negative values indicate dissolution and positive values indicate precipitation).







Activity coefficients, γ_i , are calculated according to the extended Debye-Hückel formula:

$$\log \gamma_i = -\frac{A \cdot z_i^2 \cdot (I)^{0.5}}{1 + B \cdot \alpha_i \cdot (I)^{0.5}} + b \cdot I$$
(12)

where α_i is the ionic radius in solution of the i-th species; *A* and *B* are constants which depend on the temperature and the dielectric constant of water, and *b* is a constant determined from fitting experimental data.

The activities of aqueous species increase due to the decreasing of the ionic strength when aqueous species out diffuse from bentonite. Activity increasements of bivalent cations are larger than those of monovalent ions (see Figure 6.8). The activity coefficient of Na⁺ increases from 0.708 to 0.896; but that of Ca²⁺ increases from 0.293 to 0.658.



The equation of cation exchange between Ca^{2+} and Na^+ is given by:

$$0.5Ca - X_2 + Na^+ = Na - X + 0.5Ca^{2+}$$
(13)





The equilibrium equation for the exchange rreaction is given by:

$$\frac{\left[Ca^{2+}\right]^{0.5}}{\left[Na^{+}\right]} = K_{Na/Ca} \cdot \frac{\beta_{Ca}^{0.5}}{\beta_{Na}}$$
(14)

where [] denotes activities of dissolved species, β_i is the equivalent fraction of exchanged species and $K_{Na/Ca}$ is the Na-Ca selectivity coefficient.

The activities of dissolved species are calculated from concentrations c_i and activity coefficients, γ_i , through:

$$[i] = \gamma_i \cdot c_i \tag{15}$$

Figure 6.9 shows the time evolution of several ratios of Ca^{2+} to Na^+ : (1) The ratio of dissolved concentrations (meq/L), $\frac{C_{Ca^{2+}}}{C_{Na^+}}$ which decreases indicating that dissolved Ca^{2+} decreases faster than dissolved Na^+ ; (2) The ratio of $(C_{Ca^{2+}})^{0.5}/(C_{Na^+})$, which increases indicating that Ca^{2+} is capable of displacing X-Na; (3) The ratio of activities, $[Ca^{2+}]^{0.5}/[Na^+]$, which increase indicating that dissolved Ca^{2+} displaces exchanged Na^+ when the chemical composition of bentonite porewater changes.









7. Nickel simulations

Nickel is a transition metal of the tenth group which is mainly found in the +2 oxidation state in aqueous and solid states. The solubility of Ni can be controlled either by NiCO₃(s) or Ni(OH)₂(s), depending on the pH of the system. One of the conceptual uncertainties that may affect Ni solubility is the reduction of sulphate to sulphide (Duro et al., 2006). Ni sorption onto bentonite occurs via cation exchange and surface complexation. Bradbury and Baeyens (1997a, 1997b, 1999 and 2005) presented a mechanistic description and a model of Ni sorption on montmorillonite. Doménech and Duro (2008) report the sorption properties of montmorillonite and the parameters affecting Ni sorption on montmorillonite. Grambow et al. (2006) used an experimental approach to assess model uncertainty of sorption of Ni on MX-80 bentonite. Bradbury and Baeyens (1997a, 1997b, and 1999) found that the sorption of Ni^{2+} is constant and only via cation exchange for pH < 5. Sorption of Ni^{2+} via surface complexation (SC) is strongly non-linear and exhibits a strong non linear pH dependency. Ni²⁺ uptake by SC sorption occurs on at least two types of pH-dependent sites. For the conditions relevant to nuclear waste disposal (pH > 7, Ni trace concentrations), the sorption of Ni²⁺ is governed by surface complexation on the edge surface sites (Montavon et al., 2006). Ni²⁺ sorption increases with pH regardless of temperature (Tertre et al., 2005; Boonfueng et al., 2006; Bhattacharyya and Gupta, 2007). At low pH, where surface complexation is mild, sorption varies strongly with ionic strength, whereas at high pH, where surface complexation is stronger, the effect of ionic strength becomes less relevant (Bradbury and Baevens, 1997b; Boonfueng et al., 2006). Ni²⁺ sorption at low radionuclide concentrations is large and linear and occurs on a relatively small number of sites with a high binding affinity. These are the so-called "strong sites". For intermediate Ni²⁺ concentrations the sorption is non-linear because sorption takes place on a second set of sites having a larger concentration but a weaker binding constant. These are the so-called "weak sites". Groundwater composition can affect the sorption of Ni²⁺ onto bentonite because it determines the aqueous form in which Ni is found in solution and the conditions under which Ni can form stable solid phases (Domenech and Duro, 2008). Ni²⁺ sorption decreases with increasing initial concentration of dissolved Ni²⁺, but the amount of Ni²⁺ sorbed per unit mass of bentonite increases. Bradbury and Baeyens (2006) studied the influence of dissolved carbonate concentration on Ni²⁺ sorption onto bentonite. They concluded that Ni carbonated complexes do not sorb due to their low complexation constants.

In the model presented in this report, we performed first runs in which the solubility of Ni was controlled either by $NiCO_3(s)$ or $Ni(OH)_2(s)$. Model results show that the concentration of





dissolved Ni²⁺ at the beginning is too large compared to experimental data. Therefore, in the following runs, a dummy Ni mineral was used in the canister to release Ni at a constant dissolved concentration of 10^{-3} mol/L. The section of sensitivity analyses includes the results obtained with a smaller solubility of 10^{-5} mol/L and those of the runs in which the Ni solubility is controlled by NiCO₃(s) and Ni(OH)₂(s).

7.1. Verification of Ni calculation

CORE^{2D}V4 was updated during PAMINA to deal with the requirements of the project (see Milestone 4.1.4). The updated version of CORE^{2D}V4 (Samper et al., 2003) was verified in the simulation of sorption with a concentration of 0.1M NaCl. Results of CORE were compared directly with those of the 2SPNE SC/CE titration model of Bradbury and Baeyens (1997a). The total strong site capacity is $2.10 \cdot 10^{-3}$ mol kg⁻¹ and the total weak site capacity is $6.65 \cdot 10^{-2}$ mol kg⁻¹. Two different Ni surface complexes, $\equiv S^{S}ONi^{+}$ and $\equiv S^{S}ONiOH$, were assumed to occur at strong sites. A Ni surface complex $\equiv S^{W}ONi^{+}$ is assumed to occur at weak sites. Protonation/deprotonation is assumed to occur at both types of sites. The aqueous species and their concentrations are the same as those used in the simulation of the titration model for pH 6.0. The Ni²⁺ concentration at the granite boundary is $9.13 \cdot 10^{-8}$ mol/L.

Once steady state is reached, a constant Ni distribution coefficient K_d of 399 L/Kg is attained. This K_d at pH 6 is plotted together with the Ni sorption isotherm. One can see in Figure 7.1 that the computed K_d at pH 6 matches perfectly the value of the isotherm.

After the verification, the base run of Ni was performed using the reactive transport conditions indicated in Chapter 3.

7.2. Base run

The amount of available Ni is 20Kg per canister. A constant solubility of 10^{-3} mol/L was adopted for the base run. The water flow at the 'mixing tank' boundary is 0.06 L/year per canister.

Ni dissolution in the canister releases dissolved Ni²⁺ which diffuses into the bentonite. This makes the concentrations of dissolved and sorbed Ni²⁺ in bentonite to increase. They increase fast near the canister (see Figure 7.2) and more slowly at r = 1.2m. The Ni solid source is exhausted when all the Ni in the canister has dissolved. This makes the concentration of dissolved Ni²⁺ in bentonite to decrease. The concentration of sorbed Ni²⁺





however, remains almost constant at the end of the simulation (see Figure 7.3). Concentrations of dissolved and sorbed Ni^{2+} are different at different places for t < 6350 years. After 6350 years, the concentrations of sorbed and dissolved Ni^{2+} are the same throughout the bentonite.



Figure 7.1. Comparison of Ni sorption isotherm on conditioned Na-montmorillonite (line) and the K_d computed with the reactive transport model at r = 0.5 and 0.8 m (symbols).

The distribution coefficient, K_d , of Ni is calculated from the output results of the TSM with the following equation:

$$K_d = \frac{Y + W}{C}$$

where Y is the concentration of total sorbed Ni^{2+} (mol/kg of soil) by surface complexation, W is the concentration of sorbed Ni^{2+} by cation exchange (mol/Kg of soil) and C is the total dissolved concentration of Ni^{2+} (in mol/L) which includes the concentration of free Ni^{2+} and those of all the Ni^{2+} aqueous complexes.

The concentrations of aqueous species other than Ni species at a given time are the same in all the bentonite. Because the water flow at the boundary is very small. The mass flow transported out by the water flow is much smaller than the diffusive mass flow.





Calcite is a mineral initially present in the bentonite. It is dissolved in bentonite when the concentrations of other aqueous species decrease, especially the concentration of Ca^{2+} (see Figure 7.4). Then, the concentration of HCO_3^{-} increases with time. Calcite dissolution is largest at the interface bentonite-canister.



Figure 7.2. Time evolution of the concentration of dissolved Ni²⁺ at different locations of the bentonite in log-log (top) and semi log plot (bottom).







Figure 7.3. Time evolution of the concentration of sorbed Ni²⁺ at different locations of the bentonite in log-log (top) and semi log plot (bottom).



Figure 7.4. Radial distribution of cumulative calcite precipitation-dissolution at different times (positive for precipitation and negative for dissolution).

The dissolution of calcite releases Ca^{2+} . The concentration of dissolved Ca^{2+} in the bentonite decreases due to the out diffusion of dissolved Ca^{2+} and cation exchange. Dissolved Ca^{2+} exchanges. The concentration of exchanged Ca^{2+} increases with time while that of exchanged Na⁺ decreases (see Figure 7.5).

The initial K_d at ambient conditions is around 350 L/Kg. K_d decreases for t<6350 years because the concentration of dissolved Ni²⁺ increases faster than that of sorbed Ni²⁺. Later, K_d increases because the concentration of dissolved Ni²⁺ decreases while that of sorbed Ni²⁺ remains constant. The increase of K_d after 10⁵ years is also related to an increase of pH (see Figure 7.6). The time evolution of K_d is different at different places for t < 6350 years. Later, K_d is the same everywhere.

Figure 7.7 shows the radial distribution of the concentration of dissolved Ni^{2+} at different times. The dissolved Ni^{2+} transports from the canister into the bentonite. The concentration of dissolved Ni^{2+} in the bentonite increases to a value similar to that in the canister. After 6350 years, when Ni in the canister has dissolved completely, the concentrations of dissolved Ni^{2+} in the bentonite start to decrease.



Figure 7.5. Time evolution of the concentration of exchanged Ca and Na (r=0.5 m).









Figure 7.7. Radial distribution of the concentration of dissolved Ni²⁺ at different times in semi log (top) and natural scale (bottom).

Figure 7.8 shows the relationship between K_d and the concentration of dissolved Ni²⁺ at different locations. The K_d of Ni²⁺ is nearly constant when the concentration of dissolved Ni²⁺ is smaller than 10⁻⁶ mol/L. This corresponds to part AB in Figure 7.8. During the time in which the concentration of dissolved and sorbed Ni²⁺ increase (t < 6350 years), the K_d of Ni²⁺





decreases because the concentration of dissolved Ni²⁺ increases faster than that of sorbed Ni²⁺ (part BC). Later, the K_d of Ni²⁺ increases because the concentration of dissolved Ni²⁺ decreases while that of sorbed Ni²⁺ remains constant (part CD of the curve) due to the increase in pH.

When the Ni²⁺ front transports into the bentonite, Ni²⁺ is sorbed by surface complexation and H⁺ are released from the surface complexes. Then, the pH decreases slightly for $10^3 < t < 10^4$ years (see Figure 7.9). This effect of Ni²⁺ sorption on pH lasts until t=10⁴ years. Later, the pH increases due to calcite dissolution and the out diffusion of protons from the bentonite. The Eh in the bentonite remains equal to its initial value of -0.059 until it decreases to the value of the boundary water of -0.188 (see Figure 7.10).



Figure 7.8. Relationship between the apparent K_d and the concentration of dissolved Ni²⁺ at different locations.



Figure 7.10. Time evolution of computed Eh. Its value is the same at all locations.

Figure 7.11 shows the plot of K_d versus pH at several locations within the bentonite. The interpretation of this figure can be made by analyzing simultaneously Figure 7.6 and Figure 7.9. For t<10⁴ years, K_d versus pH describes S-shape curves within the pH range of 6.3-6.5.





During this stage, K_d changes mostly due to changes in the concentration of dissolved Ni²⁺. For t>10⁴ years, both K_d and pH increase steadily. Their values plot on a parabola of a mild curvature. Therefore, at early times, K_d is controlled by the concentrations of dissolved Ni²⁺. Later, for t > 10⁴ year, K_d increases because pH increases.

The ionic strength of the bentonite water decreases because the concentrations of aqueous species in bentonite decrease (see Figure 7.12). In the first 10^4 years, ionic strength remains constant while K_d decreases. In this period, changes of K_d are not related to the ionic strength (see Figure 7.13). After 10^4 years, K_d increases and ionic strength decreases. Their values plot on a parabola.

Initially, when the concentration of dissolved Ni^{2+} is small, Ni^{2+} is mainly adsorbed at strong and weak sites (see Figure 7.14). The strong sites get saturated quickly and the concentration of sorbed Ni^{2+} at strong sites remains constant. The concentration of Ni^{2+} sorbed at weak sites increases with the concentration of dissolved Ni^{2+} in the bentonite. Sorption at weak sites is the main component of sorbed Ni^{2+} . After 6350 years, the concentration of dissolved Ni^{2+} decreases, that of sorbed Ni^{2+} at weak sites decreases while the concentration of exchanged Ni^{2+} increases.





1.2m.







strong and weak sites at r = 0.5 m.

7.3. Sensitivity to the effective diffusion of bentonite

A sensitivity run was performed with an effective diffusion an order of magnitude smaller than that of the base run ($D_e = 4 \ 10^{-11} \ m^2/s$).

The effect of surface complexation on pH in the sensitivity run is smaller than that of the base run (see Figure 7.15). There is almost no gradient of dissolved Ni²⁺ in the bentonite after 9000 years in the base run. The transport of Ni²⁺ is slower when the effective diffusion is an order of magnitude smaller. The concentrations of dissolved Ni²⁺ in the bentonite still show noticeable gradients after 10⁴ years (see Figure 7.16). Sorption is retarded also because dissolved Ni²⁺ transports slower (see Figure 7.17 and Figure 7.18). Since the dissolved Ni²⁺ transports slower, the Ni in the canister dissolves also slower. The concentration of dissolved Ni²⁺ also decreases slower when all the Ni in the canister has dissolved (Figure 7.17). As a result of these, the total sorbed Ni²⁺ in bentonite increases slower. It takes a longer time to reach constant concentration of sorbed Ni²⁺ (55750 years) than in the base run (6350 years). The concentration of total sorbed Ni²⁺ in the sensitivity run is larger than that in the base run at the end of the simulation (see Figure 7.18). All these features affect the evolution of K_d (see Figure 7.19). One can see that the trends of K_d are similar in both runs. There is a time lag factor of 10. The final K_d is slightly smaller in the sensitivity run.



Figure 7.16. Radial distribution of the concentration of dissolved Ni^{2+} at different times in the sensitivity run in which D_e is 10 times smaller than that in the base run.



Figure 7.17. Sensitivity of the concentration of dissolved Ni²⁺ to a change in the effective diffusion coefficient of bentonite in log-log (top) and semi-log plot (bottom).







Figure 7.18. – Sensitivity of computed concentration of sorbed Ni²⁺ to a change in the effective diffusion coefficient of bentonite in log-log (top) and semi-log plot (bottom).



Figure 7.19. Sensitivity of the apparent K_d of Ni²⁺ to a reduction of the effective diffusion of the bentonite.

7.4. Sensitivity to the concentration of surface complexation sites

 Ni^{2+} sorption occurs mostly via surface complexation on weak sites which have a concentration of 0.04 mol/Kg in the base run. In order to evaluate the sensitivity of K_d to the concentration of weak sites, two sensitivity runs were performed by adopting the following values of the densities of weak complexation sites: 0.02 and 0.06 mol/Kg.

The concentration of sorbed Ni^{2+} is smaller while that of dissolved Ni^{2+} is slightly larger when the amount of sorption sites is smaller. However, the differences are not very large at the beginning. Differences are larger when the concentrations of dissolved Ni^{2+} decrease. When there are more sorption sites, more Ni^{2+} is sorbed and more dissolved Ni^{2+} transports into bentonite (see Figure 7.20 and Figure 7.21). When the total weak sorption sites are smaller, the dissolved Ni^{2+} transports faster than the base run (Figure 7.21), and the gradient of the concentration of Ni^{2+} in bentonite dissipates earlier (see Figure 7.22 and Figure 7.23).

During the period in which the concentration of dissolved Ni^{2+} increases, the larger the concentration of sorption sites, the greater the concentration of sorbed Ni^{2+} (see Figure 7.24). The Ni in the canister is exhausted earlier when the concentration of sorption sites is larger. The concentration of dissolved Ni^{2+} decreases faster with more sorption sites, thus the





concentration of sorbed Ni²⁺ decreases faster (see Figure 7.24 and Figure 7.25). In the sensitivity run with a smaller concentration of sorption sites, the concentration of dissolved Ni²⁺ increases until 10⁵ years, accordingly the sorbed Ni²⁺ keeps increasing until 10⁵ years. Later, it remains constant. Thus, at the end of the simulation, the concentration of sorbed Ni²⁺ in the run with 0.02 mol/Kg of weak sorption sites is larger than those in the base run and the run with 0.06 mol/Kg of weak sorption sites. The K_d of Ni²⁺ in the run with more sorption sites is larger than that of the base run (see Figure 7.26). When the density of sites is smaller, less Ni²⁺ is sorbed by surface complexation and less relevant are protonation/deprotonation reactions. Therefore, less protons are released into the water and the effect of surface complexation on pH is smaller (see Figure 7.27).



Figure 7.20. Sensitivity of the concentration of dissolved Ni^{2+} at r = 0.5 m to changes in the density of weak sorption sites of bentonite.



Figure 7.21. Sensitivity of the concentration of dissolved Ni^{2+} at r = 1.2 m to changes in the density of weak sorption sites of bentonite.



Figure 7.22. Radial distribution of the concentration of dissolved Ni²⁺ at different times in the sensitivity run in with 0.02 mol/Kg of weak sorption sites.



Figure 7.23. Radial distribution of the concentration of dissolved Ni²⁺ at different times in the sensitivity run with 0.06 mol/Kg of weak sorption sites.



Figure 7.24. Sensitivity of computed concentration of sorbed Ni^{2+} at r = 0.5 m to changes in the density of weak sorption sites of bentonite.



Figure 7.25. Sensitivity of computed concentration of sorbed Ni^{2+} at r = 1.2 m to changes in the density of weak sorption sites of bentonite.



Figure 7.26. Sensitivity of the apparent K_d of Ni²⁺ at r = 1.2 m to changes in the density of weak sorption sites of bentonite.



sites of bentonite.

7.5. Fixed chemical conditions

The K_d of Ni²⁺ may depend on the concentration of dissolved Ni²⁺, pH and the concentration of other cations. To elucidate the effect of the environmental chemistry on K_d and distinguish it from the effect of the concentrations of dissolved Ni²⁺, a set of runs were performed in which the environmental chemical conditions were maintained constant. In a first step, the chemical composition of the granite water was taken equal to that of bentonite. This was not enough to ensure a constant pH in the bentonite. Therefore, in a second step, pH was fixed to its initial value in addition to taking the granite water composition equal to that of the bentonite.

7.5.1. Same water composition

The concentrations of Cl⁻ and SO₄²⁻ remain constant when the composition of the granite water is taken equal to that of bentonite. Cation exchange causes slight changes in the concentrations of dissolved K⁺, Fe²⁺, Na⁺ and Mg²⁺. The concentration of dissolved HCO₃⁻ changes slightly during the simulation due to the calcite dissolution (see Figure 7.28).





Concentrations of exchanged K^+ , Fe^{2^+} , Na^+ and Mg^{2^+} remain constant during the simulation. The concentration of exchanged Ni^{2^+} in the bentonite changes due to the release of Ni^{2^+} from the canister (see Figure 7.29).







Dissolved Ni²⁺ transports slightly faster than in the base run (see Figure 7.30). This makes Ni in the canister to dissolve faster. The 20Kg of solid Ni are completely dissolved after 5950 years. Then, the concentration of dissolved Ni²⁺ decreases earlier than that in the base run (see Figure 7.31). But, the decrease rate is slower compared to that in base run. At later times (t > 10^5 years), the concentration of dissolved Ni²⁺ in the run with constant chemistry remains nearly constant while that in the base run decreases fast.

Figure 7.32 shows the time evolution of the release rate of dissolved Ni²⁺ from bentonite. The release rates of both runs are similar for t < 3 10³ years. Later, the release of Ni²⁺ for the base run is larger than that of the fixed chemistry because the K_d for the constant chemistry is larger than that of the base run for 7 10³ < t < 3 10⁴ years (see Figure 7.34). For t > 4 10⁴ years, the trend changes and the release rate for the run of fixed chemistry is larger than that of the base run because the K_d of the base run increases up to 300 L/Kg while for the constant chemistry run it remains smaller than 30 L/Kg. The time evolution of the concentration of sorbed Ni²⁺ in the bentonite is similar to that of dissolved Ni²⁺ in bentonite for t < 10⁴ years (see Figure 7.33). Later, however, the concentration of sorbed Ni²⁺ in the base run at radial distances of 0.5 and 1.2 m. They are the similar when K_d decreases. But when the K_d increases, the K_d of Ni²⁺ in the base run increases faster and reaches a value an order of magnitude larger than that in the run with constant chemistry. These differences in K_d are caused by the difference in the pH (see Figure 7.35). Changes in the pH affect the K_d of Ni²⁺ mostly after 10⁴ years.

Even though there are no gradients in the chemistry caused by the boundary water, the dissolved Ni²⁺ migrates through the bentonite and affects pH (see Figure 7.35). Ni²⁺ is sorbed in bentonite mostly by surface complexation. The sorption of dissolved Ni²⁺ releases protons and affects pH. When the concentration of dissolved Ni²⁺ in the bentonite decreases, protons are sorbed on surface complexes and the pH increases slightly.



Figure 7.30. Radial distribution of the concentration of dissolved Ni²⁺ at different times in the run in which the chemical composition is constant.



Figure 7.31. Time evolution of the concentration of dissolved Ni²⁺ at different locations for the base run and the run with constant chemistry.



Figure 7.32. Release rate of dissolved Ni²⁺ from the bentonite for the base run and the run with fixed chemistry.



Figure 7.33. Time evolution of the concentration of sorbed Ni²⁺ at different locations for the base run and the run with constant chemistry.







Figure 7.36 shows the K_d versus the concentration of dissolved Ni²⁺ at r = 1.2 m. K_d is approximately constant when the concentration of dissolved Ni²⁺ is smaller than 10⁻⁶ mol/L. For larger concentrations, K_d decreases because the concentration of sorbed Ni²⁺ in bentonite increases slower than that of dissolved Ni²⁺. After reaching a maximum, the concentration of dissolved Ni²⁺ in the bentonite decreases. Sorbed Ni²⁺ also decreases, but at a much slower rate, so K_d increases.

Figure 7.37 shows the K_d versus pH at r = 1.2 m for the base run and the sensitivity run. For t < 5950 years, the pH and the concentration of dissolved Ni²⁺ and sorbed Ni²⁺ are the same. Therefore, K_d values versus pH describe S-shape curves around pH=6.4 which are similar in both runs. During this stage, K_d changes are not related to pH but to the concentration of dissolved Ni²⁺. For t > 5950 years, K_d versus pH describes different curves compared to the base run.

Similar to the base run, at the beginning, Ni^{2+} is sorbed mostly at the strong sites (see Figure 7.38). Later, when the concentration of dissolved Ni^{2+} increases, strong sites get saturated. Then, Ni^{2+} is sorbed mostly on weak sites. When the concentration of dissolved Ni^{2+} in the bentonite decreases, that of Ni^{2+} sorbed at strong sites remains constant. Ni^{2+} sorbed by cation exchange decreases in the sensitivity run while it increases in the base run because the concentrations of other cations decrease. On the contrary, the concentration of Ni^{2+} sorbed on weak sites remains constant, while it decreases in the base run.







Figure 7.36. –Apparent K_d versus the concentration of dissolved Ni^{2+} at r = 1.2 m for the base run and the run with constant chemistry.



Figure 7.37. Apparent K_d versus pH at at r = 1.2 m for the base run and the run with constant chemistry.







Figure 7.38. Time evolution of the concentrations of exchanged and sorbed Ni^{2+} on strong and weak sites at r = 1.2 m for the base run and the run with constant chemistry.

7.5.2. Constant chemistry and fixed pH

Based on the previous sensitivity run, the pH of the system was fixed by including a dummy mineral which releases or consumes protons to maintain a constant pH equal to 6.543 which is the initial pH of the bentonite pore water.

pH affects the protonation/deprotonation reactions and the sorption of Ni²⁺ on surface sorption sites. So, when the pH is fixed, Ni²⁺ sorption is more stable. The concentration of dissolved Ni²⁺ in the bentonite remains constant for t > 8 10³ years (see Figure 7.39). At the same time, the concentration of sorbed Ni²⁺ in bentonite increases first and then remains constant for t > 8 10³ years (see Figure 7.40). The K_d of Ni²⁺ in bentonite decreases at the beginning like in the base run. K_d of Ni²⁺ keeps constant for t > 8 10³ years (see Figure 7.41). K_d is constant for concentrations of dissolved Ni²⁺ smaller than 10⁻⁶ mol/L. Then, it decreases when the concentration of dissolved Ni²⁺ increases. At the end of the simulation, K_d remains constant (see Figure 7.42).







Figure 7.39. Time evolution of the concentration of dissolved Ni²⁺ at different locations for the base run and the run in which chemistry and pH are fixed.











Figure 7.41. Time evolution of K_d of Ni²⁺ for the base run and the run with fixed chemistry and pH.



Figure 7.42. K_d of Ni²⁺ versus the concentration of dissolved Ni²⁺ at r = 1.2 m for the base run and the run with fixed chemistry and pH.

7.6. Sensitivity to the boundary water flow

The "equivalent flux" of groundwater flowing the outermost surface of the bentonite barrier in the base run is 0.06 L/year per canister (ENRESA 2000). Two runs were performed with water flowes 10 and 20 times larger than that of the base run to evaluate the effect of the boundary water flow on the K_d of Ni²⁺.

The dissolved species diffuse out faster and their concentrations in bentonite decrease faster when the water flow is larger than that of the base run. Figure 7.43 shows the concentrations of dissolved species at r = 1.2 m for the base run and the run with a flow 20 times larger than that of the base run. Cl⁻ and SO₄²⁻ are conservative species. They reach steady values equal to those of the boundary water in granite after 10⁵ years. Their concentrations describe straight lines in the semilog plot.

Similar to the base run, the concentration of sorbed Ni^{2+} in the bentonite in the run with a larger water flow increases at the beginning due to the increase of exchanged Ni^{2+} and




sorbed Ni²⁺ on weak sites. Then, it decreases attaining a constant value (see Figure 7.44). Exchanged Ni²⁺ keeps increasing and becomes the largest component of sorbed Ni²⁺ at the end of the simulation (see Figure 7.44). Strong sites get saturated at the beginning of the simulation. Figure 7.45 shows the concentrations of exchanged cations in bentonite. One can see that an increase in water flow enhances cation exchange. The concentration of exchanged Na⁺ decreases more than that in the base run. This makes more important the exchange of Ca²⁺ and Ni²⁺. The concentrations of other cations such as Fe²⁺ and Mg²⁺ remain constant during the simulation.

When the water flow is larger, the out diffusion of dissolved species is faster than in the base run (see Figure 7.46). Therefore, Ni in the canister dissolves faster. The concentration of dissolved Ni²⁺ is smaller than 10^{-3} mol/L (see Figure 7.47 and Figure 7.48). The concentration of dissolved Ni²⁺ in bentonite is smallest in the run with the largest water flow (see Figure 7.48). The differences in the concentration of sorbed Ni²⁺ in the bentonite, on the other hand, are small (see Figure 7.49). So K_d of Ni²⁺ is largest when the flow rate is largest (see Figure 7.50).

Figure 7.51 shows the comparison of the pH time evolution in the bentonite. The larger the water flow, the faster protons diffuse away from bentonite and the faster pH increases. At the end of the simulation, pH reaches a same higher value in the runs with 0.6 L/yr and 1.2 L/yr.













re 7.44. Time evolution of computed concentrations of exchanged and sorbed Ni^{2+} at r = 0.5 m in the run with a water flow 20 times larger than the base run.



Figure 7.45. Time evolution of the concentrations of exchanged Ca^{2+} and Na^{+} at r = 0.5 m in the base run and the run with a larger water flow 20 times larger than the base run.



changes in the water flow q.



in the water flow.



Figure 7.49. Sensitivity of the computed concentration of sorbed Ni^{2+} at r =1.2 m to changes in the water flow q.



Figure 7.50. Sensitivity of the apparent K_d of Ni²⁺ at r = 1.2 m to changes in the water flow q.



Figure 7.51. Sensitivity of pH at r=1.2m to changes in the water flow q.

7.7. Sensitivity to the solubility of Ni in the canister

NAGRA adopted a solubility of Ni of 10^{-5} mol/L (NAGRA, 2003) which is much smaller than the value used here for the base run (10^{-3} mol/L). A sensitivity run was performed with a Ni solubility of 10^{-5} mol/L to evaluate the effect of the Ni solubility limit on the Ni release rate and K_d.

Solid Ni in the canister dissolves more slowly for the small Ni solubility (see Figure 7.52). In fact, the solid Ni in the canister does not dissolve completely at the end of the simulation for solubility of 10^{-5} mol/L (see Figure 7.53).

The maximum concentration of dissolved Ni²⁺ for a solubility of 10⁻⁵ mol/L is two orders of magnitude smaller than that of the base run (see Figure 7.54). The concentration of sorbed Ni²⁺ in the bentonite at r = 0.5 m increases more slowly and is always smaller than that of the base run (see Figure 7.55). Concentrations of sorbed Ni²⁺ are always smaller than those of the base run because dissolved concentrations are also smaller.







values for dissolution) to the Ni solubility.





1.2 m to the Ni solubility in the canister.

It is known that the K_d of Ni²⁺ decreases when the concentration of dissolved Ni²⁺ increases. Therefore, K_d values for a Ni solubility of 10⁻⁵ mol/L are generally larger than those of the





base run. In addition, the time variability of K_d for the low solubility run is much smaller than that of the base run. The K_d of Ni²⁺ in the sensitivity run at r = 1.2 m is nearly constant for t < 10⁵ years and later increases slightly (see Figure 7.56).

The time evolution of the concentration of sorbed Ni^{2+} in the bentonite in the sensitivity run shows that Ni^{2+} sorption takes place mostly at strong sites which are not saturated because the concentration of dissolved Ni^{2+} in the bentonite is small (see Figure 7.57). Ni^{2+} sorption at weak sites is an order of magnitude smaller. Exchanged Ni^{2+} is the smallest component.

The concentrations of dissolved Ni^{2+} in the base run are larger than in the sensitivity run. The strong sorption sites become saturated from the beginning in the base run. Ni^{2+} sorbed at weak sites increases and becomes the main component at the end of the simulation. Therefore, Ni^{2+} sorption mechanisms are different in the base run and in the sensitivity run because Ni^{2+} is mostly sorbed on strong sorption sites when the concentration of dissolved Ni^{2+} is small while Ni^{2+} sorbs mostly on weak sorption sites when the concentration of dissolved Ni^{2+} is large.





Figure 7.57. Time evolution of the concentration of sorbed Ni^{2+} at r = 0.5 m for the sensitivity run with a Ni solubility of 10^{-5} mol/L.

Since the concentration of sorbed Ni^{2+} in the sensitivity run is smaller than in the base run, Ni^{2+} sorption has no effect on surface protonation/deprotonation. Therefore, contrary to the base run, the pH in the sensitivity run is not affected by Ni^{2+} sorption (see Figure 7.58).



Figure 7.58. Sensitivity of pH at r = 1.2 m to the Ni solubility limit.

7.8. Variable Ni solubility limit

The solubility of Ni²⁺ can be controlled either by NiCO₃(s) or Ni(OH)₂(s), depending on the pH of the system. The maximum concentration of dissolved Ni²⁺ in the canister is not constant when the solubility of Ni²⁺ is controlled by a Ni mineral phase. In order to evaluate the uncertainties related to the Ni solubility, the following three runs were performed:

1) Solubility in the canister is controlled only by NiCO₃(s).

2) Solubility in the canister is controlled only by $Ni(OH)_2(s)$.

3) Solubility in the canister is controlled simultaneously by $Ni(OH)_2(s)$ and $NiCO_3(s)$ which are assumed to be present in the same amount.

Regardless of the mineral phase, the Ni²⁺ solubility at the geochemical conditions of the canister pore water is larger than 10^{-3} mol/L for t < 10^{3} years (see Figure 7.59). Later, the concentration of dissolved Ni²⁺ decreases faster than in the base run and becomes smaller. Ni(OH)₂(s) has a solubility smaller than that of NiCO₃(s). The run with Ni(OH)₂(s) leads to a concentration of dissolved Ni²⁺ in the canister which is smaller than that of the run with NiCO₃(s), but larger than that of the base run for t < 10^{3} years. The solubility of Ni(OH)₂(s) is





strongly controlled by pH. Therefore, the dissolution rate of $Ni(OH)_2(s)$ decreases when the pH is high. For this reason, the concentrations of dissolved Ni^{2+} in the $Ni(OH)_2(s)$ run are much smaller than those of the base run for t > 10^3 years (see Figure 7.60).

The overall patterns of the time evolution curves of the concentrations of dissolved Ni^{2+} at r = 1.2m are similar in all cases (see Figure 7.60). However, there are significant differences in the:

1) Arrival time of the Ni²⁺ front. Ni²⁺ arrives first in the case of NiCO₃(s). The largest retardation of the arrival of Ni occurs in the case of Ni(OH)₂(s).

2) Peak Ni²⁺ concentrations. The largest concentration of dissolved Ni²⁺ corresponds to the constant solubility case (base run) which has the smallest K_d values after 10⁴ years (see Figure 7.62). The smallest concentration of dissolved Ni²⁺ occurs for the case of Ni(OH)₂(s) which has the largest K_d.

There are differences in the concentrations of sorbed Ni^{2+} at r = 1.2 m for t < 10⁴ years. Later, however, they are similar in all cases (see Figure 7.61).

The K_d of Ni²⁺ at r = 1.2 m is largest in the run with Ni(OH)₂(s) (see Figure 7.62) because this run has the smallest concentrations of dissolved Ni²⁺. Since the dissolution of 1 mol Ni(OH)₂(s) consumes 2 moles of H⁺, the run with Ni(OH)₂(s) leads to a significant increase of pH (see Figure 7.63).







Figure 7.59. Time evolution of the concentration of dissolved Ni²⁺ in the canister for different hypotheses about the source of Ni in the canister.



Figure 7.60. Time evolution of the concentration of dissolved Ni^{2+} at r = 1.2 m for different hypotheses about the source of Ni in the canister.







Figure 7.61. Time evolution of computed concentration of sorbed Ni²⁺ at r = 1.2 m for different assumptions about the source of Ni in the canister in log-log (top) and semi-log plot (bottom).







Figure 7.62. Time evolution of the apparent K_d of Ni²⁺ at r = 1.2 m for different assumptions about the source of Ni in the canister.



Figure 7.63. Time evolution of pH at r = 1.2 m for different assumptions about the source of Ni in the canister.





7.9. Sorption with a constant K_d

The results of the previous models in which the transport of Ni^{2+} was simulated with a reactive transport and thermodynamic sorption model are compared here with those obtained with a single-species constant K_d model. Inasmuch as K_d is not constant, simulations are performed for a set of values of K_d ranging from 10 to 50 L/Kg.

The concentrations of dissolved Ni²⁺ at r = 1.2 m for a K_d of 20 L/Kg have trends similar to that of the base run at the increasing part. However, once all the Ni²⁺ in the canister is released, computed concentrations of dissolved Ni²⁺ in the base run decrease faster than in the runs with constant K_d (see Figure 7.64). Clearly, a model with a constant K_d fails to reproduce correctly the breakthrough curve of Ni²⁺ and therefore the release rate from the bentonite into the granite.

A more detailed comparison of the results of the reactive transport and thermodynamic sorption model with other models of constant and variable K_d are presented in Chapter 8.



Figure 7.64. Comparison of the release rates of Ni^{2+} at r = 1.2m computed with a reactive transport model and a constant K_d model.





7.10. Summary of all the sensitivity runs

The results of all the runs including the base run (BR) and the sensitivity runs (SR) are summarized in this section. Model parameters and boundary conditions of the runs are listed in Table 7.1. These runs differ on:

The chemical conditions and pH (variable or constant)

The effective diffusion of the bentonite

The density of weak sorption sites

The boundary water flow

The solubility limit of Ni

Runs	рН	D _e (m²/s)	Density of weak sorption sites 1 (mol/Kg)	Water flow (L/year)	Ni solubility (mol/L)
BR	Variable	4 10 ⁻¹¹	0.04	0.06	10 ⁻³
SR1	Constant	4 10 ⁻¹¹	0.04	0.06	10 ⁻³
SR2	Variable	4 10 ⁻¹²	0.04	0.06	10 ⁻³
SR3	Variable	4 10 ⁻¹¹	0.02	0.06	10 ⁻³
SR4	Variable	4 10 ⁻¹¹	0.06	0.06	10 ⁻³
SR5	Variable	4 10 ⁻¹¹	0.04	0.6	10 ⁻³
SR6	Variable	4 10 ⁻¹¹	0.04	1.2	10 ⁻³
SR7	Variable	4 10 ⁻¹¹	0.04	0.06	10 ⁻⁵

Table 7.1. Parameters of the base run and sensitivity runs for Ni.

Figure 7.66 shows the comparison of the concentration of dissolved Ni^{2+} for the base and sensitivity runs. The following remarks can be made from the analysis of the computed concentrations of dissolved Ni^{2+} :





1) The change in the density of weak sorption sites changes the scale of the curves but not their shape (see runs BR, SR3 and SR4)

2) The breakthrough curve of Ni is retarded by a factor of 10 when the effective diffusion of the bentonite is decreased (see runs BR and SR2)

3) The change in the boundary water flow affects mostly the receding part of the breakthrough curve while the rising part is similar to that of the base run (see runs BR, SR5 and SR6)

4) The effect of fixing the pH and the chemical conditions affects mostly the final part of the breakthrough curve. The concentration of dissolved Ni remains constant after 10⁴ years in SR1 while it decreases in the base run (see runs BR and SR1)

5) The reduction of the solubility limit of Ni by two orders of magnitude from 10^{-3} to 10^{-5} mol/L results in a reduction of dissolved concentrations of two orders of magnitude (see runs BR and SR7)

The release rate of Ni^{2+} from the bentonite into the granite is equal to the water flow times the concentration of dissolved Ni^{2+} at r = 1.2 m. The release rates for the base and sensitivity runs are shown in Figure 7.66. The sensitivity of the release rates to model parameters are similar to those of the concentration of dissolved Ni^{2+} except for the sensitivity runs to water flow (runs SR5 and SR6). The following remarks can be made from the analysis of the release rates:

1) The change in the density of weak sorption sites changes the scale of the release curves but not their shape (see runs BR, SR3 and SR4)

2) The release curve is retarded by a factor of 10 when the effective diffusion of bentonite is decreased (see runs BR and SR2)

3) The change in the boundary water flow affects strongly the release rate which reaches its maximum for the largest flow (run SR6).

4) Fixing the pH and the chemical conditions affects mostly the final part of the release curve (see runs BR and SR1).

5) The reduction of the solubility limit of Ni by two orders of magnitude results in a reduction of the release rates of two orders of magnitude (see runs BR and SR7)





The computed K_d of Ni²⁺ in the bentonite for all the runs are shown in Figure 7.67. The following remarks can be made from the analysis of the K_d curves in Figure 7.67:

1) The change in the density of weak sorption sites changes the K_d by a constant factor (see runs BR, SR3 and SR4)

2) The reduction in K_d is retarded by a factor of 10 when the effective diffusion coefficient of bentonite is decreased (see runs BR and SR2)

3) The change in the boundary water flow affects strongly the K_d which starts to increase sooner for the largest flow (see runs BR, SR5 and SR6)

4) Fixing the pH and the chemical conditions affects mostly the final part of the K_d curve (see runs BR and SR1).

5) The reduction of the solubility limit leads to a nearly constant K_d which is equal to its initial value of 350 L/kg (see runs BR and SR7)

The plot of K_d versus the concentration of dissolved Ni²⁺ (see Figure 7.68) shows that almost all runs plot on the same trajectories, indicating that the relationship between K_d and the concentration of dissolved Ni²⁺ (sorption isotherm) is not affected significantly by the changes in model parameters, chemical hypotheses and boundary conditions.

The plot of K_d versus pH (Figure 7.69) shows that the S-shaped curves in the range 6.3 < pH < 6.5 are the same for all runs. All runs except SR3 and SR4 plot on the same curve in the range 6.5 < pH < 8.5. The parabolas of runs SR3 and SR4 are similar to the parabola of the base run except for a constant displacement. This means that the parabolic relationship between log- K_d and pH is an intrinsic function of the system. Changing the density of weak sites affects only the scale of the function.

The overall pattern of the time evolution of pH is similar in all runs except for the runs in which the water flow is changed (Figure 7.70). The larger the water flow, the faster pH increases. At the end of the simulation, pH reaches a same higher value in runs SR5 and SR6.



Figure 7.65. Comparison of the concentrations of dissolved Ni^{2+} at r = 1.2 m for the base run and the sensitivity runs in log-log plot (top) and semilog plot (bottom).







Figure 7.66. Comparison of the release rate of Ni^{2+} at r = 1.2 m for the base run and the sensitivity runs.



Figure 7.67. Comparison of the apparent K_d of Ni²⁺ at r = 1.2 m for the base run and all the sensitivity runs.



Figure 7.69. Apparent K_d of Ni²⁺ versus pH at r = 1.2 m for the base run and all the sensitivity runs.

7.5 pH 8

6.5

7

10¹

10⁰

6

9

SR5 SR6

8.5



Figure 7.70. Comparison of pH at r = 1.2 m for the base run and the sensitivity runs.





8. Cesium simulation

8.1. Sorption of Cs on montmorillonite

 Cs^+ sorption onto bentonite occurs mainly via cation exchange. Cs^+ sorbs rapidly onto bentonite and achieves equilibrium almost instantaneously (Tsai et al. 2001; Murali and Mathur 2002; Shahwan and Erten 2002; Khan 2003; Atun and Kilislioglu 2003; Jan et al. 2006; Montavon et al. 2006). This is supported by the negative value of ΔG^0 for sorption of Cs^+ onto bentonite calculated by Shahwan and Erten (2002) (-18±1 KJ mol-1) indicating that Cs^+ sorption is spontaneous.

Table 8.1 summarises the log K for Cs^+ exchange reported in the literature according to the Gaines-Thomas approach. One can see that the log K of Cs^+ exchange is large, meaning that Cs^+ tends to displace Na⁺ from the interlayer positions because the hydrated radius of Cs^+ is smaller than that of Na⁺ (Table 8.2).

reaction	Log K	Reference
	1.6 ^a	Ochs et al. (2001)
	1.6 ^a	Ochs et al. (2003)
	1.7	Sabodina et al. (2006a)
	1.7	Sabodina et al. (2006b)
$NaX + Cs^{+} = CsX + Na^{+}$	1.58 ^b	Klika et al. (2007)
	3.16 ^c	Klika et al. (2007)
	1.65	Montavon et al. (2006)
	1.2	Hurel et al. (2002)
	2.0 ^d	De Windt et al. (2006)
NaY+ Cs ⁺ = CsY + Na ⁺	1.14	Grambow et al. (2006)
$NaX^* + Cs^+ = CsX^* + Na^+$	6.0 ^e	Montavon et al. (2006)
$KX + Cs^+ = CsX + K^+$	1.85 ^f	Atun and Kilislioglu (2003)
$HX + Cs^{+} = CsX + H^{+}$	1.08±0.13	Filipska and Stamberg (2006)

Table 8.1. Log K of exchange reactions (according to Gaines-Thomas convention) of Cs⁺ in montmorillonite (Doménech and Duro, 2008).

^aFrom Wanner et al. (1994); ^bFrom Gast (1969); ^cFrom Lewis and Thomas (1963); ^dFrom Gorgeon (1994); ^ea second exchange site; ^fEquilibrium constant.

<i>Table 8.2.</i> Ionic and hydrated radii of Na, Ca, Mg, Ni, CS and U (Domenech and Duro, 200	<i>le 8.2.</i> Ionic and hydrated radii of Na, Ca, Mg, Ni, Cs and U (Domér	iech and Duro, 200	8).
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	Ionic radii (Å)	Hydrated radii (Å)	Reference
Na(I)	1	3.6	Woods and Gunter (2001)
Ca(II)	1	4.1	Woods and Gunter (2001)
Mg(II)	0.7	4.3	Woods and Gunter (2001)
Cs(I)	1.7	3.3	Woods and Gunter (2001)
Ni(II)	0.7	4	Tansel et al. (2006)
U(VI)	0.74	6.5	Krestou et al (2003)





The effects of different parameters on Cs^+ sorption have been identified using bibliographic data, and are summarized in the following paragraphs.

<u>Effect of pH</u>: No important changes in Cs⁺ sorption are observed with pH because Cs⁺ speciation and cation exchange are not pH-dependent (Gutiérrez and Fuentes 1996; Hurel et al. 2002; Missana et al. 2004; Tertre et al. 2005; Filipska and Stamberg 2006; Doménech and Duro, 2008).

<u>Effect of ionic strength</u>: The dependence of Cs⁺ sorption on ionic strength is normally due to an increase of the competition from other cations that exchange preferentially. Therefore, Cs⁺ sorption decreases when the ionic strength of the solution increases due to the effect of other cations which compete for exchange positions (Atun and Bodur 2002; Hurel et al. 2002; Murali and Mathur 2002; Atun and Kilislioglu 2003; Missana et al. 2004; Tertre et al. 2005; Doménech and Duro, 2008).

<u>Effect of groundwater composition</u>: Groundwater composition can affect the sorption of a cation onto montmorillonite because it determines the aqueous form in which the element is found in solution. Dissolved Cs^+ is usually found as Cs^+ , except for high Cl^- concentrations, when the concentration of CsCl(aq) is similar to that of Cs^+ . The most important anion affecting Cs^+ sorption is Cl^- . High Cl^- concentrations may decrease Cs^+ sorption (Doménech and Duro, 2008). In our model, computed results show that concentration of CsCl(aq) is much smaller than that of Cs^+ , thus, Cl^- does not affect Cs^+ sorption.

<u>Effect of Cs⁺ concentration</u>: The experimental results obtained in different studies show that sorbed Cs⁺ decreases when dissolved Cs⁺ increases (Atun and Bodur 2002; Murali and Mathur 2002; Shahwan and Erten 2002; Khan 2003; Atun and Kilislioglu 2003). However, dissolved Cs⁺ concentration does not affect K_d when the total concentration of sorbed Cs⁺ is much smaller than CEC. In the model presented in this chapter, concentrations of sorbed Cs⁺ are smaller than 0.01 mol/L which are much smaller than CEC (3.42 mol/L). Therefore, K_d is not expected to depend on Cs⁺ concentration.

<u>Effect of bentonite dry density or S/L ratio</u>: Cs^+ sorption is related to the S/L ratio of the experiments and the bentonite dry density. Tsai et al. (2001) and Khan et al. (2003) observed that Cs^+ sorption increases with the bentonite dry density. This is explained by the fact that when the ratio S/L increases the available exchange sites also increase. In addition, an increase of the dry density decreases the interlayer space and favours the sorption of the cations having the lowest hydration radii. Khan et al. (2003) reported also no changes on Cs^+





sorption beyound a certain value of dry density, given the high excess of exchange sites. However, other studies revealed the opposite effect. Oscarson and Hume (1998) performed sorption experiments with unconfined and compacted bentonite at different S/L ratios. They observed that about 1/3 less Cs⁺ was sorbed on compacted versus unconfined bentonite and that the decrease of K_d with increasing S/L ratio was more pronounced in compacted bentonite. A decrease of K_d when S/L increases was also observed by Murali and Mathur (2002) and Klika et al. (2007). Oscarson and Hume (1998) suggested that the particleparticle effects were more relevant in compacted clay systems. It is likely that Cs⁺ cannot access the same number of sites on the compacted clay as it can on the unconfined clay because the number of unaccessible pores increases in compacted clay. Montavon et al. (2006) did not observe important differences between dispersed and compacted bentonite. The cation exchange capacity and the selectivity constants are, therefore, not affected significantly by bentonite dry density. Van Loon et al. (2009) measured Cs⁺ isotherms on crushed (<63 µm) and intact Opalinus Clay (OPA). They found an excellent agreement between both approachs indicating that all sorption sites for Cs⁺ in intact OPA are available. Therefore, the effect of the bentonite dry density or S/L ratio is unclear and it seems to depend on the specific conditions of each experiment (Doménech and Duro, 2008).

8.2. Results of the base run

When the canister fails the cesium in the Instant Release Fraction (IRF) inventory is assumed to be released immediately to the canister cavity. The mass of cesium in the IRF is 202.9g which amounts to a concentration of 3.058×10^{-3} mol/L in the canister cavity water. Additionally, there is a gradual release of Cs⁺ from the Uranium matrix, as shown in Figure 8.1 (ENRESA, 2000). The total mass of cesium released from the waste in 1 million years is 601.62g per canister. This release rate was set as a prescribed Cs⁺ flow in the left boundary of the model corresponding to the canister. The initial concentration of Cs⁺ in the bentonite was set equal to 10^{-20} mol/L.



Figure 8.2. Model for transport in the near field with indications of the flowes F_1 , F_2 and F_3 .

Figure 8.3 shows the computed time evolution of the concentration of dissolved Cs^+ at several locations within the bentonite. The concentrations of dissolved Cs^+ increase with time in the bentonite due to the in-diffusion of Cs^+ from the canister. At r = 0.5m (i.e. 5 cm from the canister-bentonite interface), the concentration of Cs^+ reaches its maximum value after 500 years and then decreases. After approximately $4 \cdot 10^4$ years, the concentrations of dissolved





 Cs^+ become uniform in the bentonite barrier. After this time, Cs^+ concentrations decrease due to: (1) the out-diffusion of dissolved Cs^+ from bentonite to the granite and (2) the increase of the exchanged Cs^+ .

The time evolution of the concentration of exchanged Cs⁺ shows patterns similar to those of dissolved Cs⁺ (see Figure 8.4). Exchanged concentrations become uniform throughout the bentonite buffer at t ~ $4 \cdot 10^4$ years. Later, concentrations of exchanged Cs⁺, w, keep increasing in spite of the decrease of concentrations of dissolved Cs⁺, c. The increase of w and the decrease of c for t> $4 \cdot 10^4$ years lead to an increase of the apparent K_d (see Figure 8.5). K_d has an almost constant value of 41 L/Kg for t < 10^4 years. Then, it increases to 584 L/Kg at t = 10^6 years.

Figure 8.5 shows the time evolution of the K_d of Cs^+ in the bentonite. K_d is constant and equal to 41 L/Kg for t < 10⁴ years. After 10⁴ years, K_d increases due to the effect of other cations such as Na⁺, Ca²⁺ and Mg²⁺. The concentrations of these cations decrease with time because they are transported out of the bentonite. Dissolved Cs⁺ exchanges with other exchanged cations. This makes the K_d of Cs⁺ to increase with time until a value of 584 L/Kg. The concentration of CsCl(aq) is very smaller than that of Cs⁺ that it does not affect Cs⁺ sorption.

Figure 8.6 shows the time evolution of computed pH. It increases after 10^5 years due to calcite dissolution and the out-diffusion of protons because the pH of boundary water (7.825) is larger than that of bentonite.

Figure 8.7 shows the plot of K_d versus the concentration of dissolved Cs^+ . There are two branches in the plot. In the first one, K_d is constant and does not change with the concentrations of dissolved Cs^+ . In the second branch, K_d increases from 41 L/Kg to 584 L/Kg when the concentration of dissolved Cs^+ decreases.

Figure 8.8 shows the time evolution of computed concentrations of exchanged Cs^+ , Ca^{2+} and Na^+ at r = 1.2 m. One can see that the concentration of exchanged Cs^+ increases after 10^3 years. Its concentration is 3 orders of magnitude smaller than those of the major cations, Ca^{2+} and Na^+ .

Figure 8.9 shows the plot of K_d versus ionic strength. K_d of Cs^+ decreases when ionic strength increases. The potential competition of other cations on Cs^+ exchange decreases and the activity of dissolved species increases when ionic strength decreases.





Figure 8.10 shows the time evolution of computed Eh in bentonite. There is a slight increase of Eh after 10^5 years which is due to a slight reduction of Fe³⁺ into Fe²⁺ caused by the exchange of Fe²⁺. The Eh of bentonite decreases at the end of the simulation because the Eh of boundary water is smaller than that of bentonite.

To illustrate mass balance, three Cs^+ release rates have been calculated, including: (1) Cs^+ release rate into the canister, F_1 ; (2) Cs^+ release rate from the canister into the bentonite, F_2 , and (3) Cs^+ release rate from the bentonite into the granite, F_3 (see Figure 8.2). The cumulative masses, M_i , corresponding to each release rate have been also calculated.

Figure 8.11 shows the time evolution of Cs^+ release rate from the near field. Peak release rate occurs at $5 \cdot 10^4$ years.

Figure 8.12 shows the concentrations of dissolved cations versus ionic strength. One can see that the slope of bivalent cations is larger than those monovalent cations. For a given ionic strength, Na^+ is the dominating cation, therefore, ionic strength is mostly determined by the concentration of Na^+ .

Figure 8.13 shows the cumulative amount of Cs^+ released into the canister and from bentonite into the granite. After 1 Ma the total amount of Cs^+ released from bentonite into the granite is 3.80g (0.0286mol), and about 99.3% of Cs^+ is still sorbed in the near field (see the computed mass balance of Cs^+ in Table 8.3). Due to the high solubility of cesium, the cumulative amount of Cs^+ released into the canister coincides approximately with the amount of Cs^+ that enters into the bentonite.

	Mass of Cs^+ (g)
Canister: dissolved Cs^+	0.016
Bentonite: dissolved Cs^+	0.278
Bentonite: exchanged Cs^{+}	598.855
Released from the near field	3.803
Total	602.952
Error	0.22%

<i>Table 8.3.</i> Computed mass balance of Cs ⁺ at the end of the	simulation	$(10^{\circ} \text{ years}).$
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Figure 8.3. Time evolution of the computed concentration of dissolved Cs⁺ in the bentonite at different radial distances.



Figure 8.4. Time evolution of the computed concentration of exchanged Cs⁺ at different radial distances.







and Ca^{2+} at r = 1.2m.

















Figure 8.12. Concentrations of dissolved cations versus ionic strength.



logarithmic time scale (top) and in natural time scale (bottom).





8.3. Sensitivity to CEC

The reference value of CEC is 87 meq/100g. A sensitivity run with a larger CEC of 102 meq/100g was made to evaluate the sensitivity of Cs^+ sorption to CEC.

Figure 8.14 shows the comparison of the time evolution of K_d for two different values of CEC. The larger the CEC the greater the K_d . The relative sensitivity, RS, has been calculated from:

$$RS = \left(\frac{K_d^{s} - K_d^{b}}{K_d^{b}}\right) \left/ \left(\frac{CEC^{s} - CEC^{b}}{CEC^{b}}\right)$$

where superscripts *s* and *b* indicate sensitivity run and base run, respectively. The relative sensitivity of K_d to changes in CEC is approximately equal to 1. This means that a p% change in CEC translates into an equal p% of change in K_d . Therefore, an uncertainty of 15% in the value of CEC will translate in an uncertainty of 15% in K_d of Cs⁺.



Figure 8.15 and Figure 8.16 show the sensitivity of the concentrations of dissolved and exchanged Cs^+ to changes in CEC. A larger CEC means more sorption sites and larger retardation. The concentration of dissolved Cs^+ is smaller at all radial distances when CEC increases. For CEC = 102meq/100g, the concentration of exchanged Cs^+ at radial distances r = 0.5 m is larger than that of base run, which indicates that more Cs^+ is sorbed near the




bentonite-canister interface. Thus, the concentrations of exchanged Cs^+ at r = 0.8 m and r = 1.2 m are smaller than those of base run. pH and calcite dissolution are not sensitive to CEC changes (not shown here).



CEC in logarithm scale (top) and in semi-logarithm scale (bottom).







Figure 8.16. Sensitivity of computed concentrations of exchanged Cs⁺ to changes in CEC in logarithm scale (top) and in semi-logarithm scale (bottom).





8.4. Sensitivity to effective diffusion coefficient

The effective diffusion coefficient of bentonite in the reference run D_e is $4 \cdot 10^{-11}$ m²/s. Model results are not sensitive to an increase of D_e . Therefore, a D_e of $4 \cdot 10^{-12}$ m²/s was used in the sensitivity run.

Figure 8.17 shows the comparison of computed dissolved Cs⁺ concentration for different values of D_e at r = 0.5m and 1.2m. It can be seen that the Cs⁺ diffusive transport is slowed down significantly when D_e is reduced. For D_e = $4 \cdot 10^{-12} \text{ m}^2/\text{s}$, the concentration of Cs⁺ near the canister (r = 0.5m) decreases slowly and remains always larger than the Cs⁺ concentration of Cs⁺ at r = 1.2m. Concentrations of dissolved Cs⁺ are not uniform in the bentonite even after 10^6 years in the sensitivity run.

Figure 8.18 shows the comparison of computed concentrations of exchanged Cs^+ for different values of D_e . The sensitivity of exchanged concentrations to a decrease D_e is similar to that of dissolved concentrations.

Figure 8.19 shows the comparison of the time evolution of the K_d for different values of D_e . K_d values for different diffusion coefficients coincide before 10^5 years. There are some small differences later. K_d increases at a slower rate for the small D_e case because a smaller D_e slows the out-diffusion of cations from bentonite into granite and the decrease of the ionic strength.

Figure 8.20 shows the comparison of the pH time evolution for different values of D_e at r = 1.2m. The increase in pH at late times is smaller when D_e is decreased possibly due to the fact that calcite precipitation at r = 1.2 m in the case of low D_e is larger than in the base run (see Figure 8.21) and protons are released when calcite precipitates.

Figure 8.21 shows the comparison of cumulative calcite dissolution/precipitation for different values of D_e at r = 1.2 m. The HCO₃⁻ concentration and the pH of boundary water are larger than those of bentonite. Both HCO₃⁻ and OH⁻ diffuse from the granite into the bentonite. For $D_e = 4 \cdot 10^{-12} \text{ m}^2/\text{s}$, diffusion is slowed down, making the HCO₃⁻ concentration and pH to increase in r=1.2 m, and increasing calcite precipitation at this location.

Figure 8.22 and Figure 8.23 illustrate the sensitivity of dissolved concentrations of Cl⁻, SO₄²⁻, Na⁺, and Ca²⁺ to changes in D_e at r = 1.2 m. The mass flow of dissolved species from bentonite to granite, *F*, is equal to: $F = q \cdot (c_{1,2} - c_b)$ where *q* is the boundary water flow





(0.06 liter/year) and $c_{1.2}$ and c_b are the dissolved concentrations in the bentonite at r = 1.2 m and in boundary water, respectively. For most solutes except for bicarbonate, species are released by the boundary flow because $c_{1.2} > c_b$. Cl⁻ out-diffuses from bentonite into granite. Concentrations of Cl⁻ are not sensitive to a decrease of D_e by a factor of 10 because the diffusive flow is faster than the advective solute boundary flow. A pure diffusion model (no chemical reactions) was performed for Cl⁻ (see Figure 8.24). Cl⁻ is only sensitive to D_e for very low D_e values = $3 \cdot 10^{-14}$ m²/s. Reactive species diffuse from bentonite into granite at a rate slower than that of Cl⁻. They are retarded by sorption and aqueous complexation reactions. One can see that the concentrations of SO₄²⁻ are sensitive to a decrease of D_e while those of Cl⁻ are not (Figure 8.22).



Figure 8.17. Sensitivity of the computed concentrations of dissolved Cs^{*} to changes in D_{e} .







Figure 8.19. Sensitivity of K_d to changes in D_e at r = 1.2m, it is the same for all radial distances.



Figure 8.21. Sensitivity of computed cumulative calcite dissolution/precipitation at r = 1.2 m to changes in D_e (negative for dissolution and positive for precipitation).







changes in D_e at r = 1.2m.











Figure 8.24. Sensitivity of computed concentrations of Cl⁻ to changes in D_e in the case of pure diffusion (no chemical reactions) at r = 1.2m in logarithm scale (top) and semi-logarithm (bottom).





8.5. Sensitivity to the boundary flow

Concentrations of most species in bentonite are larger than in granite except for bicarbonate. The exchange of species between granite and bentonite is carried out by the boundary flow. The flow takes out solute mass from bentonite when the concentration in bentonite is larger than in granite until species get the same concentrations in both materials. The boundary water flow q takes solutes away. The mass flow F is directly proportional to q. In this section, the sensitivity of model results to q is evaluated. Model runs were performed for water flowes 10 and 100 times larger than the reference value of 0.06 L/year.

Figure 8.25 shows the computed concentrations of Cl⁻ and SO₄²⁻ at r = 1.2m for boundary flowes of 0.06, 0.6 and 6.0 L/year. Concentrations of Cl⁻ and SO₄²⁻ decrease at earlier times when q increases. Concentration fronts are advanced 10 and 100 times compared to the base run. For flowes of 0.6 and 6.0 L/year, concentrations attain steady values after $1.5 \cdot 10^5$ and $1.5 \cdot 10^4$ years, respectively. The concentrations of Cl⁻ and SO₄²⁻ in a semilog-plot are lines of constant slope. This confirms that the concentrations of these species vary in an exponential form

$$C - C_b = (C_0 - C_b) \exp(-\alpha t)$$

where C_0 is the initial concentration, C_b is the boundary concentration and α is a recession coefficient $[T^{-1}]$ which for a flow q is equal to q/V_w where V_w is the total volume of water in the bentonite and the canister.

Reactive species such as Ca^{2^+} and Na^+ show similar sensitivities to the boundary flow. However, these cations are affected by cation exchange and calcite dissolution/precipitation and present more complex patterns (see Figure 8.26). The time evolution of the concentration of dissolved Ca^{2^+} (see Figure 8.26) shows two phases. In the first one, the concentration of dissolved Ca^{2^+} is larger than the boundary concentration of Ca^{2^+} . Dissolved Ca^{2^+} diffuses out from bentonite, and exchanged Ca^{2^+} increases. In the second one, when Ca^{2^+} concentration is smaller than the boundary concentration, dissolved Ca^{2^+} diffuses back into bentonite, while Ca^{2^+} keeps exchanging with Na^+ . For q = 6.0 L/year, the concentration of dissolved Ca^{2^+} starts recovering after 10^5 years due to the backwards diffusion of Ca^{2^+} when exchanged Ca^{2^+} starts to decrease.













Exchanged concentrations of Ca^{2+} , Mg^{2+} , Na^+ and Cs^+ are sensitive to the boundary flow (see Figure 8.27). The larger the flow, the greater the exchange between exchanged Na^+ and dissolved Ca^{2+} and Mg^{2+} . Dissolved Ca^{2+} and Mg^{2+} exchange with exchanged Na^+ , Na-X,

the concentration of which decreases with time.

The reaction of cation exchange between Ca^{2+} and Na^{+} is given by:

$$0.5Ca - X_2 + Na^+ = Na - X + 0.5Ca^{2+}$$

Its equilibrium expression is:

$$\frac{\left[Ca^{2+}\right]^{0.5}}{\left[Na^{+}\right]} = K_{Na/Ca} \cdot \frac{\beta_{Ca}^{0.5}}{\beta_{Na}}$$

where [] denotes activity of dissolved species, β_i are equivalent fractions of exchanged species and $K_{Na/Ca}$ is the Na-Ca selectivity coefficient. Figure 8.28 shows the sensitivity of the activity ratio [Ca²⁺]^{0.5}/[Na⁺] to changes in q. The activity ratio controls the exchange





between Ca^{2+} and Na^+ . When this ratio increases, dissolved Ca^{2+} exchanges with Na^+ and vice versa. One can see in Figure 8.28 that the ratio remains constant initially, and then it increases steadily.

The sensitivity of HCO_3^- concentrations to the boundary flow is shown in Figure 8.29. The HCO_3^- concentration increases at early times because the initial HCO_3^- concentration of bentonite is smaller than that of granite. Later, it reaches a maximum which is greater than the HCO_3^- concentration of granite water due to calcite dissolution.

The sensitivity of pH to water flow is shown in Figure 8.30. The increase of pH in bentonite is due to the combination of: (1) H^+ out diffusion because the pH of bentonite is smaller than that of granite and (2) calcite dissolution (see also Figure 8.31).

Calcite equilibrium sets up a relationship between pH, HCO_3^- and Ca^{2+} according to the following reaction:

$$CaCO_{3}(s) + H^{+} = Ca^{2+} + HCO_{3}^{-}$$

The amount of calcite dissolution/precipitation is related to the time evolution of H⁺, Ca²⁺ and HCO₃⁻ which are controlled by diffusion. In addition, dissolved Ca²⁺ is affected by cation exchange. For q = 0.06 L/year, calcite dissolves at the end of simulation. For q = 6.0 L/year, calcite precipitates first due to the increase of pH and HCO₃⁻ concentration caused by solute diffusion. Later, after 10⁴ years, calcite dissolves because dissolved Ca²⁺ has decreases due to Ca-Na exchange. At late times (t > 10⁵ years), calcite precipitates again.

Figure 8.32 and Figure 8.33 show that the concentrations of both dissolved and exchanged Cs^+ at r = 1.2 m are very sensitive to the boundary flow. In general, the larger the flow q, the greater the solute flow and, therefore, the lesser the concentration of dissolved Cs^+ . The same is true for the concentration of exchanged Cs^+ .

Figure 8.34 shows the sensitivity of K_d of Cs^+ to the boundary flow. K_d is very sensitive to the boundary flow because the water flow controls the release rate of aqueous species through the boundary and, therefore, it controls the rate of decrease of the ionic strength, which affects directly the K_d of Cs^+ .



Figure 8.27. Sensitivity of computed concentrations of exchanged cations at r = 1.2m to changes in the boundary flow.



Figure 8.28. Sensitivity of the activity ratio $[Ca^{2+}]^{0.5}/[Na^+]$ at r = 1.2m to changes in the boundary flow.







to changes in the boundary flow.









changes in the boundary flow.



Figure 8.33. Sensitivity of computed concentrations of exchanged Cs^+ at r = 1.2m to changes in the boundary flow.



Figure 8.34. Sensitivity of K_d of Cs⁺ at r = 1.2m to changes in the boundary flow.





8.6. Constant K_d

Several runs were performed with a non-reactive constant- K_d model for K_d values of 30, 50 and 70 L/Kg, respectively. These results are compared with those of the reference run which is denoted as the thermodynamic sorption model, TSM. Figure 8.35 shows the comparison of the concentration of dissolved Cs⁺ computed with a TSM and with the constant- K_d models. One can see that the constant K_d model fails to reproduce the concentrations computed with the TSM, especially at large times (t > 2·10⁵ years).









Figure 8.35. Comparison of concentrations of dissolved Cs⁺ computed with the TSM and with constant K_d models in logarithmic time scale (top), in natural time scale (intermediate) and natural concentration scale (bottom).





8.7. Results for constant chemistry

The base run assumes a boundary flow of 0.06 L/year. This water flow has a chemical composition typical of granite water. Most species in bentonite have concentrations larger than in granite (except for HCO_3^- , see Table 4.6). The differences of concentrations cause diffusive transport and chemical reactions such as aqueous complexation, cation exchange and mineral dissolution/precipitation.

In order to evaluate the relevance of chemical reactions on the sorption of Cs^+ , a run was performed in which the composition of the granite boundary water was set equal to that of the bentonite. In this way, the only chemical processes which take place in the bentonite barrier are those involving Cs^+ .

Figure 8.36 shows a comparison of the K_d obtained with the reference run and that with constant chemistry. The K_d of Cs^+ is constant in the absence of chemical reactions. This means that the increase of K_d in the reference run is caused by the reduction of the ionic strength when major ions diffused out the bentonite.



Figure 8.36. Comparison of the K_d obtained with the reference run and the run with constant chemistry.

Figure 8.37 shows the comparison of the concentrations of dissolved Cs^+ for both runs. After 10^5 years, the concentration of dissolved Cs^+ decreases in the reference run while it





increases in the constant chemistry run. This means that the decrease of the concentration of dissolved Cs^+ in the base run is related to the competition diminishment of other cations for the exchange positions. The concentration of exchanged Cs^+ is similar in both runs (not shown here).



reference run and the run with constant chemistry.

8.8. Summary of Cs⁺ sensitivity runs

The results of all the runs including the base run (BR) and the sensitivity runs (SR) are summarized in this section. Parameters and conditions of the base run and the sensitivity runs are listed in Table 8.4. These runs differ on:

- 1) The cation exchange capacity, CEC;
- 2) The effective diffusion coefficientof bentonite, De;
- 3) The boundary water flow;
- 4) The chemical conditions (variable or constant).
 - Table 8.4. Parameters of the base run and sensitivity runs.

Runs	CEC	De	Water flow	Chemical
	(meq/100g)	(m²/s)	(L/year)	condition





BR	87	4·10 ⁻¹¹	0.06	Variable
SR1	102	4·10 ⁻¹¹	0.06	Variable
SR2	87	4·10 ⁻¹²	0.06	Variable
SR3	87	4·10 ⁻¹¹	0.6	Variable
SR4	87	4·10 ⁻¹¹	6.0	Variable
SR5	87	4·10 ⁻¹¹	0.06	Constant

Figure 8.38 shows the comparison of the concentration of dissolved Cs^+ for the base and sensitivity runs. The following remarks can be made from the analysis of the computed concentrations of dissolved Cs^+ :

1) The change in the CEC changes slightly the scale of the curves but not their shape;

2) The concentration curve is retarded by a factor of 10 when the effective diffusion coefficient of bentonite is decreased by a factor of 0.1;

3) The change in the boundary water flow has a strong effect on the receding part of the concentration curve while the rising part is similar to that of the base run;

4) The effect of fixing the chemical conditions affects mostly the final part of the concentration curve.

The release rate of Cs^+ from bentonite into granite is equal to the product of the water flow times the concentration of dissolved Cs^+ at r = 1.2 m. The release rates for the base and sensitivity runs are shown in Figure 8.39. The sensitivity of release rates to model parameters are similar to those of the concentration of dissolved Cs^+ except for the sensitivity runs to water flow. The following remarks can be made from the analysis of the release rates:

1) The change in the CEC changes slightly the scale of the release curves but not their shape;

2) The release curve is retarded by a factor of 10 when the effective diffusion coefficient of bentonite is decreased by a factor of 0.1;

3) The change in the boundary water flow affects strongly the release rate which reaches its maximum for the largest flow;





4) The effect of the fixing chemical conditions affects mostly the final part of the release curve.



sensitivity runs in semi-log scale (top) and in log-log scale (bottom).



Figure 8.39. Release rate of Cs⁺ for the base and sensitivity runs.

Computed K_d of Cs^+ in bentonite for all the runs are shown in Figure 8.40. The following remarks can be made from the analysis of the K_d curves:

1) The change in the CEC changes the K_d by a constant factor;

2) The $K_{\rm d}$ is not affected by the reduction of the effective diffusion coefficient of bentonite;

3) The change in the boundary water flow affects strongly the K_d which starts to increase sooner for the largest flow (see runs BR, SR3 and SR4);

4) The K_d remains constant when the chemical conditions are constant.

The time evolutions of ionic strength for all the runs are shown in Figure 8.41. All curves coincide with that of the base run except for the runs with larger boundary water flow. Ionic strength decreases sooner when the flow increases.

Figure 8.42 shows the plot of K_d versus ionic strength for all runs. All curves plot on the same straight line except for the run with a larger CEC. The latter lies on a line parallel to the line of the base run. This implies that the K_d is directly proportional to CEC and an increase in CEC introduces a scale factor in K_d .





Therefore, CEC controls directly the K_d value while the boundary flow and D_e affect K_d value by controlling the time evolution of ionic strength.





coincides with BR).





9. Uranium simulations

Uranium in porous media can be present either as dissolved species in the pore water, adsorbed onto reactive mineral surfaces, or precipitated in mineral phases. Only U(IV) and U(VI) are important in natural waters where uranium concentrations range from a few parts per billion to several parts per million depending largely on pH, Eh and carbonate concentration (Ivanovich and Harmon, 1992; Read and Hooker, 1992). The chemistry of uranium in aqueous systems is mainly controlled by the pH, the redox potential, and the type of available complexing agents such as carbonates, phosphates, vanadates, fluorides, sulfates and silicates (Langmuir, 1997).

In a deep underground HLW repository, the subsurface water has reducing properties in natural conditions. The mineralogical indication of reducing conditions is the overall stability of minerals containing a ferrous component (pyrite, magnetite, chlorite, biotite, etc.) and U(IV) minerals. The products of secondary alteration of Fe- and Ti-bearing minerals serve as the main sorbents of uranium. In water solutions, U(IV) has a very low migration ability due to the formation of the poorly soluble hydroxide U(OH)₄. Under reducing conditions, the subsurface water is always saturated with uranium. Omel'yanenko et al. (2007) studied the behavior of uranium under conditions of interaction of rocks and ores with surbsurface water. They found that the stability conditions of uranium ore are quite suitable for safe isolation of spent fuel (SF) which consists of 95% uraninite (UO₂) and is a confinement matrix for all other radionuclides. The disposal of SF in massifs of crystalline rocks at depths below 500m, where reducing conditions are predominant, is a reliable guarantee of a high SF stability (Omel'yenenko et al., 2007). Due to the low solubility of U under near-neutral and reducing conditions, the equilibrium uranium concentration in subsurface water is not larger than 10⁻⁸ mol/L. In water from an orebody that contains 40% U at the Cigar Lake deposit in Canada, the U concentration does not differ from the background value of 10⁻⁸ mol/L (Cramer, 1986). Experiments on solubility of uraninite under near-neutral and reducing conditions yielded a similar U concentration in the equilibrium solution (Johnson and Shoesmith, 1988; Red'kin et al., 1989). Within the depth interval of the expected location of a HLW repository (0.5-1.5 km), subsurface water is characterized by near-neutral slightly-alkaline properties. Under such conditions, uraninite is virtually insoluble. This fact is important for the safe long-term storage and disposal of SF (Omel'yenenko et al., 2007).

Duro et al. (2006) found that under reducing conditions, solids of the type UO_{2+x} are able to control the aqueous concentration of uranium. Gómez et al. (2006) also reported that U(IV)





minerals such as uraninite, pitchblende and coffinite are the most abundant in uraniferous deposits, but the low solubility of U(IV) aqueous complexes leads to the low U concentrations found in reduced waters. They found that all the sampled groundwaters in a uranium mine were undersaturated with respect to uranium oxides $(UO_2(am))$ and oversaturated with respect to uraninite $(UO_2(crystalline))$ and coffinite $(USiO_4)$. This supports the hypothesis that coffinite neoformation may take place in the fracture fillings, the existence of which was reported by Buil (2004). It has also been observed in other uranium ores in Salamanca (Spain) (Pérez del Villar et al., 2002). The precipitation of coffinite as a secondary mineral has also been observed (Bros et al., 2003; Fayek et al., 1997; Pomies et al., 2004). In the sampling of Gómez et al. (2006) from an uranium mine, uranium concentrations were around 4-9 10^{-8} mol/L. They reported a geochemical model which predicts the uranium concentration in water samples based on the equilibrium between the water itself and partially oxidized uraninites together with the precipitation of coffinite.

Under oxidizing conditions, subsurface waters are commonly undersaturated with respect to uranium minerals as a precondition of its leaching from rocks and ores. U(VI) has a higher migration ability in comparison with U(IV). However, because of the insufficient duration of interaction with rocks, the U concentration in subsurface water under oxidizing conditions are usually much smaller than the equilibrium value and approaches 10^{-7} mol/L (Omel'yenenko et al., 2007). Due to the susceptibility of U(VI) to complexation, complex uranyl compounds with various anions are the main migration species. The most common aqueous complexes are $UO_2(CO_3)_3^{4-}$, $UO_2(CO_3)_2^{2-}$, $UO_2(CO_3)^0$ and less frequently $UO_2(SO_4)_2^{2-}$. For water equilibrated with calcite at a concentration of $CO_3^{2-}\approx 10^{-5}$ mol/L, the equilibrium U concentration in the water interacting with rocks is approximately equal to 10^{-5} mol/L (Liu and Neretnieks, 1999). But the U content in natural water is commonly smaller than this value.

Uranium absorbed by secondary minerals, particularly by iron hydroxides and leucoxene, is its single stable species under oxidizing conditions. The interaction of uranium mineral with oxygen-bearing water results in oxidation of uraninite (Shoesmith, 2000), accompanied by loosening of the mineral surface, formation of microfractures, and an increase in solubility with the enrichment of water in uranium up to 10⁻⁴ mol/L. Secondary U(VI) minerals, first of all, uranyl hydroxides (schoepite, becquerelite, etc.) and silicates (uranophane, soddyite, etc.), replace uraninite (Omel'yanenko et al., 2007). Schoepite or dehydrated schoepite forms first, followed by uranyl oxide hydrates with interlayer cations (e.g., becquerelite and compreignacite), then soddyite, and finally uranyl alkaline silica hydrates such as uranophane and boltwoodite (Wronkiewicz and Buck, 1999). Under oxidizing conditions, and





for the pH and carbonate concentrations found in natural waters, the predominant aqueous species of U(VI) are carbonate complexes. Uranophane has been found to form as a secondary phase in the vicinity of massive uranium ores. Soddyite can form at lower pH values depending on the environmental conditions (Duro et al., 2006).

U sorption occurs by cation exchange and surface comlexation. It depends on pH (Hyun et al., 2001; Kowal-Fouchard et al., 2004), ionic strength (Hyun et al., 2001; Kowal-Fouchard et al., 2004; Sabodina et al., 2006b) and initial U concentration (Stamberg et al., 1999; Missana et al., 2004). Cation exchange dominates the sorption for pH below 5 (Kowal-Fouchard et al., 2004; Sabodina et al., 2006b). Surface complexation dominates the sorption process at higher pH and presents high pH dependence (Catalano and Brown, 2005; Sabodina et al., 2006b). It is observed a maximum sorption of U around pH 7-8 when carbonate aqueous concentration is significant. At higher pH, the negative U-carbonate species does not sorb and forms uranyl-carbonate complexes. Then, an increase of carbonate concentration produces a decrease of sorbed U (Stamberg et al., 1999; Bradbury and Baeyens 2006; Sabodina et al., 2006b). Stamberg et al. (1999, 2003), Turner and Sassman (1996), Catalano and Brown (2005) considered the sorption of U carbonate species on montmorillonite and found a good match to the experimental data. According to SKB (2006), the K_d for U in bentonite ranges from 3.6 10^3 to 1.113 10^6 L/Kg for U(IV) and from 500 to 1.8 10^4 L/Kg for U(VI).

Given the large amount of uranium in the canister, some uranium minerals are put initially in the canister. The initial amount is assigned an arbitrary value to make sure that there is always enough uranium in the canister to be released depending on U solubility.

Prior to the simulation, solubilities of U minerals were analyzed with EQ3/6. First, the solubility runs were performed for different pH values for the initial chemical conditions of the bentonite pore water. Then, the solubility runs were performed for several Eh values for those chemical conditions. Figure 9.1 shows the solubility of U minerals versus pH (Eh = -0.059 V). The solubility of the U(IV) mineral is very small and that of U(VI) mineral is very large for pH < 7. The solubility of the U(IV) mineral increases with pH and that of U(VI) minerals remains almost constant. Figure 9.2 shows the solubility of U minerals versus Eh (pH = 6.435). Under reducing conditions, the U(IV) mineral increases with Eh when the redox conditions become oxiditing. For the condition of the bentonite buffer (6.4 < pH < 7.8 and -0.188 < Eh < -0.050), the uranium phases controlling U solubility are Uraninite and coffinite.







Figure 9.1. Solubility of U minerals versus pH for the initial chemical conditions of the bentonite porewater.



the bentonite porewater.





9.2. Runs with UO₂·2H₂O (am)

First, a model was run by assuming that U in the canister is mostly in the form of a U(IV) mineral phase. The phase selected is $UO_2:2H_2O$ (am). Its initial volume fraction is 0.999999.

9.2.1. Run with UO₂²⁺ sorption

Most U sorption models reported in the literature consider the sorption of $UO_2^{2^+}$ because the parameters of $UO_2^{2^+}$ sorption are commonly available. Here, we start by considering that $UO_2^{2^+}$ is the only U species.

Model results show that U minerals do not precipitate in the system. Figure 9.3 shows the time evolution of the dissolution of UO₂:2H₂O (am). Although this U oxide dissolves always, the total amount of dissolved mineral is very small. Therefore, the concentration of dissolved uranium is very small (see Figure 9.4 and Figure 9.5). This run considers the sorption of $UO_2^{2^+}$. But in reducing conditions, the most abundant U species is $U(OH)_4(aq)$. The concentration of free $UO_2^{2^+}$ is very small (see Figure 9.5). Therefore, the computed concentration of sorbed U is small. Figure 9.6 shows the pH evolution in the bentonite. pH is the same everywhere in the bentonite. The dissolution of $UO_2^{2^+}$ (am) is very small and has no effect on pH. pH is affected by the transport of aqueous species and calcite dissolution. Figure 9.7 shows that the total sorbed $UO_2^{2^+}$ is also very small. Most of it is sorbed at strong sorption sites. The K_d of U is nearly constant for t < 10⁵ years with a value of 0.1 L/Kg which is abnormally low for U(IV). Later, it decreases because the concentration of sorbed $UO_2^{2^+}$ decreases (see Figure 9.8) while the concentration of dissolved uranium remains constant, probably due to the long term increase in pH.



Figure 9.3. Time evolution of the cumulative UO₂:2H₂O(am) dissolution in the canister (negative values for dissolution).



Figure 9.4. Time evolution of the concentration of total dissolved U at different locations.







the bentonite.



locations.



Figure 9.8. Time evolution of the apparent K_d of U(IV) at different locations when $UO_2^{2^+}$ is the sorbing species.





9.2.2. Run with U⁴⁺ sorption

U sorption in the previous run was too small because $UO_2^{2^+}$ is not the dominant U aqueous species. Under reducing conditions, the dominant U aqueous species is $U(OH)_4(aq)$. Therefore, the sorption of U^{4^+} should be considered (Grambow et al., 2006).

When the sorption of U^{4+} is considered, there is more U sorbed by surface complexation. The K_d of U increases to values which range from 4 10³ to 6 10⁴ L/Kg (see Figure 9.9 and Figure 9.10). However, the concentration of dissolved U in the bentonite is very low and much smaller than that in the canister due to the strong sorption (see Figure 9.11 and Figure 9.12).



Figure 9.9. Time evolution of the apparent K_d of U(VI) at different locations when U⁴⁺ is the sorbing species.





Figure 9.11. Time evolution of the computed concentration of dissolved uranium at different locations when U^{4+} is the sorbing species.







Figure 9.12. Time evolution of the concentration of dissolved U at r = 1.2 m when the sorbing species are either U⁴⁺ or UO₂²⁺.

9.3. Runs with U₄O₉

The dominant chemical environment of a deep geologic repository is characterized by the absence of free atmospheric oxygen and other oxidizing species. Uranium dioxide in its U(IV) state has a very low solubility in water (Rai et al., 2003). However, radioactive α -decay in spent fuel causes the emission of α -particles. These, in turn, may generate oxidizing species close to the fuel surface duo to α -radiolysis of water (Carbol et al., 2009). Because the concentration of dissolved U is too small when U is assumed to be in the form of UO₂:2H₂O (am), another run was performed by assuming that uranium in the canister is in the form of a partly oxidized uranium mineral such as U₄O₉.

9.3.1. Only sorption of UO₂²⁺

First, a run was performed which considers that $UO_2^{2^+}$ is the sorbing species. At the same time that U_4O_9 dissolves in the canister, coffinite and goethite are allowed to precipitate (see Figure 9.13). Goethite precipitates only in the canister. Coffinite precipitates in the canister and in the bentonite, although the amount precipitated in bentonite is very small compared to that in the canister. The concentration of dissolved uranium in the canister increases continuously as the dissolution of U_4O_9 progresses (see Figure 9.14). At the end of the




simulation, the concentration of dissolved $UO_2^{2^+}$ in the canister and the bentonite are larger than those computed in the run with $UO_2(am)$. Consequently, there is more $UO_2^{2^+}$ sorbed (see Figure 9.15) and the K_d of U is larger, but not large enough for U (see Figure 9.16). The reason for the moderate K_d is that the dominant U aqueous species are $UO_2(CO_3)_3^{4^-}$ and $UO_2(CO_3)_2^{2^-}$ while the concentration of sorbing species $UO_2^{2^+}$ is much smaller than those of uranyl carbonates (see Figure 9.17). Most of the sorbed $UO_2^{2^+}$ is sorbed on strong sorption sites. The amount of exchanged $UO_2^{2^+}$ is very small (see Figure 9.18). The dissolution of U_4O_9 makes the Eh to increase in the bentonite until 10⁵ years. Later, Eh decreases because it is controlled by the outer boundary water flow (see Figure 9.19). The time evolution of pH in this run is similar to that of the previous run. The final pH is 7.48 while it was 7.73 in the run with $UO_2(am)$.



Figure 9.13. Time evolution of cumulative mineral dissolution-precipitation in the canister (positive for precipitation and negative for dissolution).



Figure 9.14. Time evolution of the concentration of total dissolved uranium at different locations.



Figure 9.15. Time evolution of the concentration of sorbed UO_2^{2+} at different locations.



Figure 9.16. Time evolution of the apparent K_d of mixed U(IV) and U(VI) at different locations when $UO_2^{2^+}$ is the sorbing species.



Figure 9.17. Time evolution of the concentrations of U aqueous species in bentonite.



Figure 9.18. Time evolution of the concentration of sorbed $UO_2^{2^+}$ at r = 1.2 m. The curve of total sorbed $UO_2^{2^+}$ coincides with that of $UO_2^{2^+}$ sorbed on strong sites.



Figure 9.19. Time evolution of Eh at different locations.





9.3.2. Run with the sorption of U⁴⁺ and uranyl carbonates

When U in the canister is assumed to be in the form of U_4O_9 , the dominant U aqueous species are $UO_2(CO_3)_3^{4-}$ and $UO_2(CO_3)_2^{2-}$. An additional run was performed in which the sorbing species are these uranyl carbonates together with U^{4+} . Sorption data for uranyl carbonate species were taken from Stamberg (1999, 2003).

The results show that there is more U sorbed. This prevents the concentration of dissolved U to increase (see Figure 9.20 and Figure 9.21). The K_d of U increases (see Figure 9.22). Most of the sorbed U is sorbed on strong sorption sites. Coffinite precipitates in the canister, but it does not precipitate in the bentonite due to the low concentration of dissolved U.



Figure 9.20. Time evolution of the concentration of total dissolved uranium at different locations when U_4O_9 is considered.







9.4. Summary of all the runs

The results of all the runs are summarized in this section. The conditions runs are listed in Table 9.1.

Figure 9.23 shows the time evolution of dissolved U in all runs. When there is no U mineral precipitate and no U^{4+} sorption (Run 1), the concentration of dissolved U is larger at the beginning. At the end of the simulation, the run considering partial oxidized U mineral (Run 3) provides largest concentration of dissolved U. When the sorption of U^{4+} and U carbonates is included, the concentration of dissolved U decreases (Runs 2 and 4).

Figure 9.24 shows the time evolution of sorbed U for all the runs. Under reducing conditions, the K_d is very small if the sorption of U^{4+} is not considered (Run 1). When the sorption of U carbonates is included, the K_d in creases to a large value in the run with U_4O_9 (Figure 9.25).

Figure 9.25 shows the time evolution of K_d for all the runs.

	Initial U mineral	U mineral allowed to precipitate	Sorbing species
Run 1	UO2:2H2O (am)	No	UO2 ²⁺
Run 2	UO ₂ :2H ₂ O (am)	No	$\mathrm{UO_2}^{2^+}$ and U^{4^+}
Run 2	U ₄ O ₉	Coffinite	UO2 ²⁺
Run 3	U ₄ O ₉	Coffinite	UO ₂ ²⁺ , U ⁴⁺ and U carbonates

Table 9.1. Chemical conditions of the runs for U.







Figure 9.23. Time evolution of the concentration of dissolved U for all the runs.



Figure 9.24. Time evolution of the concentration of sorbed U for all the runs.



Figure 9.25. Time evolution of the $K_{\rm d}$ of U for all the runs.





10. Competition effects

10.1. Competition between nuclides

Based on the models presented in Chapters 7 and 8, the migration and sorption of Ni and Cs are solved simultaneously. The chemistry is the same to that used in the separated base runs. The results of the Cs+Ni run are compared with those of the separate base runs.

10.1.1. Competition effect of Cs on Ni

Ni dissolution in the canister for the Cs+Ni run takes a slightly longer time than in the Ni base run. This means that the competition of Cs influences slightly the transport of Ni²⁺, and then influences the Ni dissolution in the canister. The concentration of Ni²⁺ in the bentonite increases to a larger value and then decreases faster than that in the Ni base run (see Figure 10.1). The sorbed Ni²⁺ in the bentonite is slightly smaller in some times and larger at others due to the competition of Cs (see Figure 10.2). For the most part, the K_d of Ni²⁺ in the bentonite for the Cs+Ni run is slightly larger than that in the Ni base run (see Figure 10.3). The competition of Cs reduces the concentration of Ni²⁺ sorbed on weak sites and that of exchanged Ni²⁺ (see Figure 10.4). This influences the transport of dissolved Ni²⁺ and then the dissolution of Ni in canister. The difference of Eh is very small in both runs. Since Cs sorbs by cation exchange and Ni²⁺ is mainly sorbed by surface complexation, the effect of Cs on Ni sorption is not significant.



Figure 10.1. Time evolution of the concentration of dissolved Ni^{2+} at r = 1.2 m for the base run and the Cs+Ni run.



Figure 10.2. Time evolution of the concentration of sorbed Ni^{2+} at r = 1.2 m for the base run and the Cs+Ni run.







in bentonite for the Ni base run and the Cs+Ni run.



Figure 10.4. Comparison of the time evolution of the concentration of sorbed Ni^{2+} evolution at r = 1.2 m in bentonite for the Ni base run and Cs+Ni run.





10.1.2. Competition effect of Ni on Cs

Nickel is a potential competing cation for Cs^+ exchange. The effect of competition of Ni^{2+} on Cs^+ has been evaluated by performing a run in which both Ni^{2+} and Cs^+ are modeled simultaneously.

Figure 10.5 shows the time evolution of the K_d of Cs^+ in the Cs^+ base run and in the run with Cs-Ni competition. The competition of Ni²⁺ is not relevant for t < 10⁴ years because other cations (Na⁺, Ca²⁺, Mg²⁺ and K⁺, etc.) have much larger concentrations in bentonite. The effect of the competition starts to be relevant after 10⁵ years when the concentrations of other cations have decreased. The K_d of Cs⁺ decreases due to the Ni competition effect.





10.2. Competition with corrosion products

All the model runs presented so far did not account for the effect of canister corrosion. In this section, numerical models of the competition of corrosion products on Cs and Ni sorption are presented.

Canister corrosion is modeled using the model developed within the IP NF-PRO (see Samper et al., 2008). The carbon-steal canister has an internal radius of 0.35 m and a





thickness of 0.1 m. The corrosion of carbon-steel layer by water is simulated with the following reaction:

$$Fe(s) + 2H^+ + 0.5O_2(aq) \Leftrightarrow Fe^{2+} + H_2O$$

Corrosion is assumed to proceed kinetically with a corrosion rate of 0.05 μ m/year. Magnetite and siderite are allowed to precipitate in the bentonite according to:

$$Fe_{3}O_{4}(s) + 6H^{+} \Leftrightarrow 3Fe^{2+} + 0.5O_{2}(aq) + 3H_{2}O \qquad LogK = -6.5076$$

$$FeCO_{3}(s) + H^{+} \Leftrightarrow Fe^{2+} + HCO_{3}^{-} \qquad LogK = -0.1920$$

These two reactions are assumed at local equilibrium.

Fe²⁺ also can be sorbed by cation exchange and surface complexation. The following Fe surface complexes are included: S^SOFe⁺, S^SOFeOH, S^WOFe⁺. The parameters of Fe surface complexation are taken equal to those of Ni (see Bradbury and Baeyens, 2005).

10.2.1. Competition effect of corrosion products on Ni

Corrosion products cause an increase in the concentration of dissolved Fe^{2+} in the bentonite. Magnetite and siderite precipitate in the bentonite (see Figure 10.6 and Figure 10.7). The iron released from corrosion products competes with Ni for sorption sites and causes an increase in Ni sorption (see Figure 10.8). During the period of dissolution of Ni in the canister, the concentration of dissolved Ni²⁺ increases in bentonite. At the receding stage, the concentration of dissolved Ni decreases faster than in the base run (see Figure 10.10). The overall effect of corrosion products on the K_d of Ni are (see Figure 10.11):

1) A reduction of K_d at early times (t < 10⁴ years) due to the competition effect.

2) An increase of K_d at late times (t > 10⁴ years) due to the large increase of pH caused by corrosion.

For t > 2 10^3 years, Ni²⁺ and Fe²⁺ sorb mostly on weak surface sites (see Figure 10.12 and Figure 10.13). Because of the Fe competition on Ni sorption, the Ni²⁺ sorbed on strong sites does not remain constant. Canister corrosion affects significantly the Eh and the pH in the bentonite. The Eh decreases and the pH increases (see Figure 10.14 and Figure 10.15). However, the pH does not increase to a very high value because it is buffered by protonation/deprotonation.











precipitation).









Figure 10.11. Time evolution of the apparent K_d of Ni²⁺ in bentonite at r=1.2 m for the Ni base run and the run with corrosion products.







Figure 10.12. Time evolution of the concentration of sorbed Ni^{2+} in bentonite at r = 1.2 m for the run with corrosion products.



Figure 10.13. Time evolution of the concentration of sorbed Fe in bentonite at r = 0.5 m for the run with corrosion products.







Figure 10.14. Time evolution of Eh in bentonite at r = 1.2 m for the Ni base run and the run with corrosion products.



the run with corrosion products.

The plot of K_d versus the concentration of dissolved Ni²⁺ reveals that (Figure 10.16):





The K_d decreases for concentrations of dissolved Ni²⁺ smaller than 10⁻⁵ mol/L. The function relating K_d to the concentration of dissolved Ni²⁺ (sorption isotherm) changes due to the competition of corrosion products.

Corrosion products do not affect the second stage of the curve which depends only on pH.



10.2.2. Competition of corrosion products on Cs⁺ sorption

Canister corrosion releases a large amount of dissolved Fe which may compete with Cs⁺ for exchange positions. The competition is more relevant after 10^5 years when other cations have diffused out through the boundary (see Figure 10.17). The K_d of Cs⁺ decreases compared to that of the base run after 10^5 years.

Figure 10.18 shows the time evolution of computed concentrations of dissolved and Cs^+ in the base run and in the run with corrosion products.



Canister corrosion consumes protons and increases pH (see Figure 10.19). Figure 10.20 shows the time evolution of the concentration of dissolved Fe in the base run and in the run



10⁻⁵

10⁻⁶

10⁻⁷

10¹



with corrosion products. Concentrations of dissolved Fe in the corrosion run are larger than those of the base run after 2×10³ years. The oscillation of Fe concentration is caused by the increase of sorbed Fe on weak sites from 10^4 to 10^5 years (see Figure 10.21).



10⁵ Time (year) Figure 10.20. Time evolution of the concentration of total dissolved Fe in the base run and the run with corrosion products

10⁴

10²

Base run Corrosion run

10³

10⁶



Figure 10.21. Time evolution of the concentration of sorbed Fe via cation exchange and via surface complexation on weak and strong sites in the run with corrosion products.

10.3. Summary of competition runs for Ni

Figure 10.22 shows the time evolution of the concentration of dissolved Ni^{2+} of the base run and the competition runs. The effect of Fe on the dissolved Ni^{2+} is more significant than that of Cs. Fe competion increases the concentration of dissolved Ni^{2+} at early time and decreases the concentration of dissolved Ni^{2+} later.

Figure 10.23 shows the time evolution of the K_d of the base run and the competition runs. Fe competition decreases the K_d before 5 10^3 years. Later, it increases the K_d because it increases the pH significantly. The effect of Cs competition is very small.

Figure 10.24 shows the plot of K_d versus the concentration of dissolved Ni²⁺ for the base run and the competition runs. The competition of Fe decreases the straight line of log- K_d versus log-C for t < 10⁴ years. The run of Ni+Cs shows a similar trend to base run.



Figure 10.22. Time evolution of the concentration of dissolved Ni^{2+} at r = 1.2 m for the base run and the competition runs.



Figure 10.23. Time evolution of the K_d of Ni²⁺ at r = 1.2 m for the base run and the competition runs.







Figure 10.24. K_d versus the concentration of Ni²⁺ at r = 1.2 m for the base run and the competition runs.

10.4. Summary of the competition runs for Cs

Figure 10.25 shows the time evolution of ionic strength of the base run and the competition runs. Both Ni and Fe retard slightly the decrease of ionic strength. In a semi-log plot, the results of all runs coincide and plot along straight lines for $t < 10^5$ years.

Figure 10.26 shows the time evolution of the K_d for the base run and the competition runs. Ni decreases the K_d of Cs^+ by a combination of two factors: 1) By affecting the decreasing rate of the ionic strength (Figure 10.25), and 2) By competing for exchange positions. The effect of Fe on K_d of Cs^+ is similar to that of Ni, although the patterns of Fe are more complex.

Figure 10.27 shows the plot of K_d versus ionic strength for all runs. The competition of Fe and Ni tend to decrease the slope of the straight line of log- K_d versus log-I.



Figure 10.25. The time evolution of the ionic strength in the base run and in the competition runs in logarithmic scale (top) and in semi-logarithmic scale (bottom).



Figure 10.27. $K_{\rm d}$ versus ionic strength for the base run and the competition runs.





11. Comparison of UDC results with ENRESA results

11.1. Calculations for Nickel

11.1.1. UDC and ENRESA results in the base case

The calculations performed by UDC using a thermodynamic sorption model showed that the $K_d(Ni)$ is a function of both the dissolved concentration of nickel and the pH. The dependence of $K_d(Ni)$ on [Ni] and pH has been included in GoldSim model through the values listed in Table 11.1, provided by UDC and obtained from a set of calculations in which constant pH values were imposed.

[Ni]	рН								
(mol/L)	6.2	6.4	6.543	6.6	6.8	7.0	7.2	7.4	7.6
10 ⁻⁸	171.0	271.0	375.0	426.0	659.0	1000	1500	2160	3010
5 10 ⁻⁸	170.0	270.0	373.0	423.0	651.0	986.0	1460	2080	2850
10 ⁻⁷	170.0	268.0	370.0	418.0	642.0	963.0	1410	1990	2680
5 10 ⁻⁷	165.0	256.0	346.0	389.0	574.0	820.0	1130	1460	1810
10 ⁻⁶	159.0	242.0	321.0	357.0	508.0	693.0	899.0	1110	1310
5 10 ⁻⁶	124.0	169.0	206.0	220.0	272.0	323.0	372.0	419.0	467.0
10 ⁻⁵	97.6	125.0	148.0	152.0	178.0	205.0	233.0	266.0	302.0
5 10 ⁻⁵	39.6	46.2	52.6	53.6	63.3	76.4	93.8	116.0	141.0
10 ⁻⁴	25.3	29.7	34.3	35.8	44.4	56.0	71.0	89.7	111.0
5 10 ⁻⁴	10.9	14.2	17.3	18.7	24.3	31.2	38.6	45.9	52.4
10 ⁻³	8.6	11.3	13.7	14.7	18.6	22.7	26.7	30.1	33.0

Table 11.1.Values of $K_d(Ni)$ as a function of [Ni] and pH obtained by UDC in the constant pHcalculations

In TSM calculations, for a given pair of values of [Ni] and pH, the K_d values obtained in the base case and the calculations with prescribed pH can be quite different. Below pH=6.4 differences are very small, but increase with pH and the differences are larger than 2 at pH close to 7.4. To take into account these differences a pH dependent correction factor has been calculated to transform the K_d values in Table 11.1 into the K_d values in the base run.

Table 11.2. Correction factors to transform the K_d values in Table 11.1 into the Kd values in

the	base	run.
-----	------	------

	рН						
	6.2	6.4	6.6	6.8	7.0	7.2	7.4
Correction factor for K _d	1	1	1.67	1.87	2.18	2.18	2.29

ENRESA has performed two different calculations using GoldSim:

- A calculation using the values of $K_d(Ni)$ in Table 11.1 (identified as ENRESA 2 in the figures), and





- A calculation using the values of K_d(Ni) in corrected with the factor in Table 11.2 (identified as ENRESA in the figures).
- In both cases, the dependence of pH with time is taken into account with the evolution calculated by UDC (see Figure 11.1).

The calculation identified as ENRESA should provide results very similar to those obtained by UDC in the base run.



Figure 11.1. Evolution of pH in bentonite porewater in the base run.

Calculations are performed assuming that 20 kg of stable nickel are released from the waste in 1000 years at a constant rate.

The Ni release rates from the near field calculated by ENRESA and UDC are plot together in Figure 11.2. The cumulative Ni releases from the bentonite obtained by ENRESA and UDC are shown in Figure 11.3.

There exists a good agreement between UDC and ENRESA results after 10,000 years (especially in the case identified as ENRESA). At earlier times there are significant differences, because in UDC calculations the initial transport of nickel is much faster than in ENRESA calculations. A similar result has been obtained in the calculations for Cs.



Figure 11.2. Ni release rate from the bentonite in the base case. Comparison of ENRESA and UDC results.



Figure 11.3. Cumulative Ni release from the bentonite in the base case. Comparison of ENRESA and UDC results.





11.1.2. GoldSim calculations with constant K_d

Calculations have been done using a constant K_d , as usually done in PA calculation. Different values of K_d between 10 and 1000 L/kg have been used to cover the range of values of K_d obtained by UDC in the base run (see Table 11.1). Results are shown in Figure 11.4 and Figure 11.5.

Figure 11.4 and Figure 11.5 clearly show that the results of the mechanistic model cannot be reproduced using a constant K_d value. In order to obtain a good agreement with the results of the mechanistic model (UDC) the PA model needs to include the dependence of $K_d(Ni)$ on Nickel concentration in the porewater and the time evolution of the porewater pH.



Figure 11.4. Total Ni release rate from the bentonite (mol/year) for different values of the K_d also shown is the curve computed with the base run of the UDC model.



Figure 11.5. Cumulative Ni release from bentonite (mol) for different values of the K_d and the base run of the TSM.

11.1.3. UDC and ENRESA calculations for a constant pH 6.543.

Figure 11.6 and Figure 11.7 show the release rate and the cumulated release from the bentonite calculated by ENRESA and UDC for the case of constant pH. In this case $K_d(Ni)$ are only a function of the Nickel concentration in bentonite porewater and the values of K_d in column "6.543" of Table 11.1 are used. The K_d values used in GoldSim calculations are identical to those obtained by UDC in their calculation.

Figure 11.6 and Figure 11.7 show a good agreement between ENRESA and UDC results after 10⁵ years but the behaviour is quite different at earlier times. Again, in UDC calculations the initial transport of Nickel is much faster than in ENRESA calculations.



Figure 11.6. Comparison of ENRESA and UDC for total Ni release rate from bentonite (mol/year) using a constant pH of 6.543 in the bentonite porewater.



Figure 11.7. Comparison of ENRESA and UDC for the cumulative Ni release from bentonite (mol) for a constant pH of 6.543 in the bentonite porewater.





11.2. Calculations for Cesium

11.2.1. UDC and ENRESA results for the base run

The calculations performed by UDC have shown that $K_d(Cs)$ is affected only by the ionic strength (I) of the bentonite porewater with no significant influence of the concentration of Cs dissolved. For a given time, the I of bentonite porewater is nearly the same along the bentonite barrier. The time evolution of I at different locations in the bentonite (0.5, 0.6, 0.8, 1.0 and 1.2m) are shown in Figure 11.1. It can be seen that they all overlap:



Figure 11.8. Evolution of the ionic strength of bentonite porewater at different locations in the bentonite for r = 0.5m to 1.2m.

UDC results show that $K_d(Cs)$ dependes only on the ionic strength. Figure 11.9 shows K_d as a function of the ionic strength at r=0.8m. Nearly identical curves are obtained the K_d as a function of ionic strength at other locations in the bentonite. Results can be fitted to a straight line in log-log (Figure 11.9).

From Figure 11.8 and Figure 11.9 the time evolution of $K_d(Cs)$ in the bentonite can be obtained (see Figure 11.10).



Figure 11.9. Dependence of $K_d(Cs)$ on the ionic strength of porewater.



Figure 11.10. Time evolution of $K_d(Cs)$ in the bentonite. All the points of the bentonite have the same value.





A run of the GoldSim model has been performed using the releases from the waste of ¹³⁵Cs and stable Cesium shown in Chapter 5. The model takes into account the evolution with time of the I of the bentonite porewater using the values in Figure 11.8. The dependence of $K_d(Cs)$ on I, as shown in Figure 11.9, has been included in the model too.

The results obtained with GoldSim model are shown in Figure 11.11 and Figure 11.12.

Four additional calculations were done using the time evolutions of the ionic strength at r = 0.5m, 0.6m, 1.0 and 1.2m in all the thickness of bentonite. The results are nearly identical to the base case in which the time evolution of the I at r=0.8m is used.



The results obtained by UDC and ENRESA are compared in Figure 11.13 to Figure 11.17.

Figure 11.11. Release rate of Cs from bentonite (mol/year) calculated by ENRESA with GoldSim.






Figure 11.12. Cumulative release of Cs⁺ from bentonite (mol) calculated by ENRESA with GoldSim.



Figure 11.13. Total Cs release rate for bentonite (mol/year). Comparison of ENRESA and UDC results with the release rate in linear scale.







Figure 11.14. Total Cs release rate from the bentonite (mol/year). Comparison of ENRESA and UDC results with the release rate in logarithm scale.



Figure 11.15. Cumulative flow of Cs from the bentonite (mol). Comparison of ENRESA and UDC results.



Figure 11.16. Concentrations of total dissolved Cs in bentonite porewater in the base case calculated by ENRESA with GoldSim.



Figure 11.17. Concentrations of total Cs in the bentonite porewater in the base case by UDC calculated with a TSM.

11.2.2. GoldSim calculations with a constant K_d(Cs)

Calculations have been done using a constant K_d , as usually done in PA calculations. Different values of K_d between 40.9 and 550 L/kg have been used to cover the range of values of K_d obtained by UDC in the base case (Figure 11.9). Results are shown in Figure 11.18 and Figure 11.19.

The release rates obtained with a variable K_d and those of a constant K_d equal to 40.9 L/kg are very similar up to 10,000 years values. This result was expected because in that time period the K_d value is equal or slightly higher than 40.9 L/kg (Figure 11.10). In the long term the release rate with a variable K_d is similar to the release rate with a constant of K_d =550 L/kg. In the variable K_d calculation the release rate at each time is roughly the same as the release rate in the calculations with constant K_d equal to the K_d value in Figure 11.10 at that time.

The results in Figure 11.18 and Figure 11.19 clearly show that the results of the mechanistic model cannot be reproduced using a constant K_d value. But when the dependence of $K_d(Cs)$ on ionic strength, and the time evolution of I are included in the PA model, there is a good agreement with the results of the mechanistic model (UDC).

Figure 11.18. Total Cs release rate from the bentonite (mol/year) with constant and variable $K_{\rm d}$

Figure 11.19. Cumulative Cs release from bentonite (mol/year) with constant and variable K_d values.

11.2.3. UDC and ENRESA calculations for a constant K_d of 40.9 L/kg

Figure 11.20 and Figure 11.21 show the release rate and the cumulative release from the near field calculated by ENRESA and UDC for the same case of constant chemistry leading to a constant $K_d(Cs)$ of 40.9 L/kg.

Figure 11.22 and Figure 11.23 show the evolution of the total Cs concentration in the porewater at different locations in the bentonite calculated by ENRESA and UDC for the case of constant chemistry.

The comparison of Figure 11.20 to Figure 11.23 shows a good agreement after 10,000 years but the behaviour is quite different at earlier times. The initial transport of Cs in UDC calculations is much faster than in ENRESA calculations.

Figure 11.20. Total Cs release rate from the bentonite (mol/year) using a constant chemistry leading to a constant $K_d(Cs) = 40.9 L/kg$. Comparison of ENRESA and UDC results.

Figure 11.21. Total Cs cumulative release from bentonite (mol) using a constant chemistry leading to a constant $K_d(Cs)$ =40.9 L/kg. Comparison of ENRESA and UDC results.

Figure 11.22. Total Cs concentration in bentonite porewater for a constant K_d of 40.9 L/kg calculated by ENRESA with GoldSim.

Figure 11.23. Total Cs concentration in bentonite porewater calculated by UDC using a constant chemistry corresponding to a constant $K_d(Cs) = 40.9$ L/kg.

11.3. Analysis of discrepancies

In sections 11.1 and 11.2 there is a good agreement in the long term results obtained by ENRESA and UDC, but there are important differences at early times. Some of the differences between UDC and ENRESA calculations may be caused by numerical truncation errors of the numerical scheme used by CORE to solve for the cupled transport+chemistr equations.

In order to explore such errors, several sensitivity runs were performed with different time increments and convergence transport+chemistry tolerances (see Table 11.3). Three sensitivity runs were performed based on the run with a constant chemistry by: 1) Reducing all the time increments by a factor of 2; 2) Reducing the convergence tolerance by a factor of 10; and 3) Reducing the time increments by a factor of 2 and the tolerance by a factor of 10. The results of three runs are then compared with those of a constant K_d model (K_d =40.9 L/Kg) without chemistry which is supposed contain less errors.

Figure 11.24 shows the comparison of the computed Cs concentrations at r = 1.2 m. It can be seen that

Decreasing the time increments improves the solution in the log-scale for t < 1000 years but not for larger times;

For large times, the errors decrease only when the tolerance is decreased.

Table 11.3. Numerical model	setting for	mumerical	sensitivity	runs.
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Runs	Numerical model setting
CKNC	Constant K_d no chemistry : K_d = 40.9 L/Kg
NSR1	Numerical sensitivity run 1: constant chemistry base run (tolerance = 10 ⁻⁴)
NSR2	Reduce the time increments by a factor of 2 based on NSR1
NSR3	Reduce the tolerance by a factor of 10 based on NSR1
NSR4	Reduce the time increments and the tolerance by a factor of 2 and 10,
	respectively, based on NSR1

12. Conclusions

The validity of the " K_d approach" commonly used to represent sorption in the radionuclide migration through the near field of a high-level radioactive waste (HLW) repository has been tested. Detailed reactive transport with thermodynamic sorption models (TSMs) have been compared with simplified models that use distribution coefficients (K_d) for the 0.75 m thick compacted bentonite barrier included in the Spanish disposal concept in granite (ENRESA, 2005). Such testing has been performed by comparing the results of a PA model, solved by ENRESA with Goldsim, with those obtained by UDC with CORE, a reactive transport model (Samper et al., 2003).

Testing has been performed for Ni and Cs. For U this comparison was not done because it was not possible to create a satisfactory mechanistic model including TSM (for sorption) and solid phases (for Uranium solubility).

12.1. Conclusions for Ni

Mechanistic calculations have been done for Ni using a thermodynamic sorption model (TSM) and a solubility limit of of 10^{-3} mol/l. Calculations showed that the apparent distribution coefficient, K_d, was strongly affected by the dissolved concentration of Ni²⁺ and the pH of bentonite porewater. The K_d of Ni²⁺ is nearly constant when the concentration of dissolved Ni²⁺ is below 10^{-6} mol/l. When the Ni²⁺ front transports into bentonite, Ni²⁺ is sorbed by surface complexation and H⁺ are released from the surface complexes, producing a small decrease in pH between 10^3 and 10^4 years. Later, pH increases due to calcite dissolution and the out diffusion of protons from the bentonite.

The Eh in bentonite remains equal to its initial value of -0.059 until it decreases to the value of the boundary water of -0.188. Initially when the concentration of dissolved Ni^{2+} is small, Ni^{2+} is mainly adsorbed at strong and weak sites. The strong sites are saturated quickly and the concentration of sorbed Ni^{2+} at strong sites remains constant. The concentration of sorbed Ni^{2+} at weak sites increases with the concentration of dissolved Ni^{2+} in bentonite. Sorption at weak sites is the main component of sorbed Ni^{2+} .

The results of the TSM have been compared with those of classical models based on the use of a K_d . A constant K_d model can not reproduce the release rates of Ni²⁺ from the bentonite into the granite obtained with the TSM model. The results obtained with a variable K_d which

depends on the concentration of dissolved Ni^{2+} and the pH are in very good agreement with those provided by the TSM model.

The effect of the simultaneous transport of Cs or corrosion products with Ni has been analyzed. The competition effect of Cs^+ on Ni^{2+} sorption is not significant because Cs^+ sorbs by cation exchange while Ni^{2+} is maily sorbed by surface complexation. The corrosion products change the pH and Eh in the bentonite significantly, so the presence of corrosion products affects significantly the sorption of Ni^{2+} in the bentonite due to the change of environmental conditions, while the competition between corrosion products and Ni^{2+} for sorption sites is of secondary importance.

12.2. Conclusions for Cs

Mechanistic calculations have been done for Cs using a thermodynamic sorption model (TSM) and no solubility limit. Calculations have shown that the K_d of Cs does not depend on the concentration of dissolved Cs⁺ because the concentration of exchanged Cs⁺ is much smaller than the concentrations of other exchanged cations in the bentonite. By the contrary, a significant dependence of the K_d with the ionic strength in bentonite porewater was identified. In this case with constant chemistry, the K_d of Cs remains constant during all the simulation.

In one million years, only 3.80g of Cs^+ (out of 600g released from the waste) have been released from bentonite into the granite. This means that 99.3% of Cs^+ is still sorbed in the bentonite barrier after 10^6 years.

The results of the TSM have been compared with those of classical models based on the use of a K_d . A constant K_d model fails to reproduce the release rates of Cs⁺ from the bentonite into the granite. The results obtained with a variable K_d which depends on the ionic strength are in very good agreement with those provided by the TSM model.

The competition of Ni and corrosion products on Cs sorption has been evaluated. Ni affects slightly the K_d of Cs⁺ by a combination of two factors: 1) By affecting the decreasing rate of ionic strength, and 2) By competing for exchange positions. The competition effect of corrosion products on the K_d of Cs⁺ is also small.

12.3. Conclusions for U

The detailed CORE model has revealed that there are significant uncertainties in: 1) The redox state and the form in which U is present in the spent fuel. Although $UO_2(am)$ is the most likely mineral phase, other mixed forms such as U_4O_9 , U_3O_7 and U_3O_8 cannot be discarded; 2) The mineral phases controlling U solubility at the conditions of the repository. Such mineral phases have been analyzed in Eh-pH-U solubility plots, but there are uncertainties in the controlling phases; 3) The thermodynamic data for some U mineral phases such as coffinite; 4) The thermodynamic sorption data for U(VI) and U(IV) which are not comprehensive. Data for the sorption of uranyl carbonates are lacking. There is a need for a complete sorption data for multisite sorption materials.

Due to the previous uncertainties it was not possible to create a satisfactory mechanistic model with TSM for Uranium. The comparison of TSM and K_d models for U should be made once the previous uncertainties in the TSM of uranium are solved.

12.4. General conclusions

For Ni and Cs it has been found that the results obtained with the mechanistic models that include a TSM can not be reproduced using a constant value of K_d . But using a K_d that depends on environmental parameters (such as pH, ionis strength or the dissolved concentration of the transported species) that control sorption, has proved to be capable of reproducing with great precission the results obtained with a TSM model.

The main lesson learned is that mechanisitic models with TSM should be used to study the evolution of the geochemistry of the system with simulataneous transport of radionuclides. This detailed model allows identifying the parameters that control the soption of the radionuclide and creating a function that describes the dependence of the distribution coefficient on relevant parameters: radionuclide dissolved concentration, pH, eH, I,....The inclusion of this variable Kd in the simplified Performance Assessment model probably will be enough to reproduce with precission the results obtained with the mechanistic model.

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