**Non-isothermal multiphase flow and reactive transport benchmark for radioactive waste disposal**

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June 2023

# Executive Summary

This report presents the description of the non-isothermal multiphase flow and reactive transport benchmark for radioactive waste disposal to be carried out during WP DONUT.

As pointed out by   
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
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(2021), there is a need for benchmarking multiphase multicomponent reactive transport. Outside EURAD a benchmark entitled “Reactive Multiphase Flow in Porous Media at the Darcy Scale” has been initiated and recently discussed at the conference on Mathematical & Computational Issues in the Geosciences <https://meetings.siam.org/sess/dsp_talk.cfm?p=111450>.

This non-isothermal multiphase flow and reactive transport benchmark is an extension of the SIAM CO2 multiphase reactive transport benchmark to radioactive waste disposal. The proposed benchmark will provide a clear link between DONUT, GAS and ACED WP.

This report presents the description and several results of the non-isothermal multiphase flow and reactive transport benchmark for radioactive waste disposal to be carried out during WP DONUT. The benchmark case selected correspond to the FEBEX in situ test numerical model. The main features of the numerical model are the following: 1) 1D model; 2) Unsaturated bentonite; 3) Strong thermal gradients; 4) Gases: dry air and CO2; 5) Minerals: calcite and gypsum; 6) Geochemical processes: aqueous reactions, mineral dissolution/precipitation, cation exchange and gas dissolution/ex-solution. There were proposed 11 cases, 6 cases under isothermal conditions and 5 under non-isothermal conditions. The cases were designed increasing the complexity. By the moment, seven cases were performed by one or more participants the other cases will be performed in future works. In general, the results performed by the teams agree and follow the same trends, however there are some differences. Computed water content match for all the teams, but there are small discrepancies at the flow boundary (r = 1.14 m). Computed tracer concentrations are similar, but there are slightly differences at the diffusion front. Computed CO2(g) behaviour are similar for all teams but it shows differences especially at early times. Computed Ca2+ and sulphate concentrations show similar trend but there are variances at the unaltered bentonite. Computed calcite and gypsum follow the same trend, however there are differences due to the extremely small precipitation rate. Computed pH match for all the teams but there are small disagreements at early times.

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# Introduction

## Previous benchmarks

In addition to the specific work that will be conducted by each partner, a specific outcome of DONUT is the definition of the benchmarks that will be used both inside DONUT and outside to foster interactions. While international benchmarking initiatives are existing   
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
(Steefel et al., 2015; Birkholzer et al., 2019; Bildstein et al., 2021), the goal here is to define benchmarks of methods and tools to quantify efficiency and added-value in terms of :

* increase of knowledge (e.g. better physical representation, integration of coupled processes)
* accuracy, robustness, computational cost,
* robustness of scale-transition approaches
* ability to manage uncertainty and sensitivity analyses

Recently,   
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
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(2021) in a guest editorial to the subsurface environmental simulation benchmarks special issue mentioned emerging benchmarking opportunities. These authors stress the need for benchmarking in the context of multiphase multicomponent reactive transport. Outside EURAD a benchmark entitled “Reactive Multiphase Flow in Porous Media at the Darcy Scale” has been initiated and recently discussed at the SIAM 2021 conference on Mathematical & Computational Issues in the Geosciences <https://meetings.siam.org/sess/dsp_talk.cfm?p=111450>. The possibility to extend this SIAM benchmark to radwaste disposal has been previously discussed within the DONUT project due to the clear link between DONUT, GAS and ACED WP.

DONUT is also defining a benchmark relating to machine learning and geochemistry, which is considered as a recent disruptive technology in the field of reactive transport and will possibly unlock the next generation of simulation that require high demanding CPU time   
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
(Leal, 2017). The high computing cost associated with chemical equilibrium calculations is considering as the most demanding one in comparison to fluid flow or heat transfer and to circumvent this issue the use of surrogate model is promising   
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
  
(Laloy and Jacques, 2019; Prasianakis et al., 2020). The philosophy of the benchmark is described in DONUT D4.4.

In addition, within the WP HITEC two experiments have been selected as benchmarks for THM validation of constitutive and numerical models.

## Motivation of the multiphase flow and reactive transport benchmark for radioactive waste disposal

The proposal for the non-isothermal multiphase flow and reactive transport benchmark for radioactive waste is based on the previous experience of the group of the University of A Coruña (UDC) which has developed in the last 30 years coupled thermal (T), hydrodynamic (H) and geochemical (C) reactive transport models for laboratory and in situ heating and hydration tests for the engineered barrier systems of HLW repositories in granite and clay within the context of several EU research projects (FEBEX, NFPRO, FUNMIG, PAMINA, PEBS and CEBAMA). These models account simultaneously for the thermal gradients caused by the heat released from the waste, the multiphase flow of air, vapor and liquid water, the bentonite swelling, the canister corrosion, the concrete degradation and the geochemical reactions involving aqueous, exchanged, sorbed and mineral species.

The UDC group has developed a series of reactive transport codes with the generic name of CORE (COdes for modeling partly or fully saturated water flow, heat transport and multi-component REactive solute transport under both local chemical equilibrium and kinetic conditions). One of these codes is INVERSE-FADES-CORE V2 (Mon, 2017), which is a finite element code for modelling non-isothermal multiphase flow, heat transport and multicomponent reactive solute transport under both chemical equilibrium and kinetic conditions in deformable media.

1. **Benchmark cases for non-isothermal multiphase flow and reactive transport for radioactive waste disposal**
   1. **Main features of the benchmark cases**

The main features of the selected benchmark cases for non-isothermal multiphase flow and reactive transport for radioactive waste disposal include:

1. Multiphase flow and solute transport with liquid, gas and solid phases.
2. Non-isothermal conditions: heat source at around 100ºC.
3. Water evaporation near a heating source: phase change.
4. List of gases: air, water vapour, and reactive gases such as O2, CO2 and H2.
5. Chemical reactions: aqueous complexation, acid-base, redox, mineral dissolution/precipitation, cation exchange and gas dissolution/exsolution.
6. Materials: metallic canister, bentonite, concrete and the host rock (granite or clay).
7. Geometry: 1D parallel or 1D axi-symmetric.

*Figure 1* shows a schematic diagram of the thermal and hydrodynamic conditions in the initial heating and hydration stage of a radioactive waste repository.



*Figure 1* – *Schematic diagram of the thermal and hydrodynamic conditions in the initial heating and hydration stage of a radioactive waste repository.*

* 1. **Selected benchmark cases**

Two simulation benchmark cases have been selected for the non-isothermal multiphase flow and reactive transport benchmark for radioactive waste disposal. These cases are the following:

1. The FEBEX in situ test: 1D model. Unsaturated bentonite. Strong thermal gradients. Water evaporation in the heater and vapour condensation. Other gases: dry air, CO2 and H2. Materials: Bentonite and granite. Geochemical processes: aqueous reactions, mineral dissolution & precipitation, cation exchange and gas dissolution & ex-solution.
2. Long-term canister corrosion. 1D flow and multicomponent reactive solute transport model to simulate canister corrosion, the interactions of corrosion products with bentonite and the long-term hydrochemical evolution of porewater composition in the near field of a repository in fractured granite. Thermal gradient, water evaporation and vapour condensation could be less relevant. Other gases: H2.
   1. **Preliminary list of partners and computer codes**

Several teams have shown interest in participating in such benchmark. *Table 1* lists theteams and computer codes to be used for the non-isothermal multiphase flow and reactive transport for radioactive waste disposal. The participation of the teams at the benchmark could be as participant or observer.

*Table 1 – List of teams and computer codes to be used for the non-isothermal multiphase flow and reactive transport for radioactive waste disposal.*

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Participant | Modeling tool | DONUT partner | Type of participation | Contact  person |
| UDC | INVERSE-FADES-CORE | Yes | Producer | J. Samper  A. Mon |
| University of Pau | Reactive-DuMuX | Yes | Producer | Amaziane B.  Ahusborde E. |
| Jilin University | TOUGHREACT | No | Producer | Xu T. |
| TUL (Tech Univ Liberec) | FEFLOW & PHREEQC | Yes | Testing | Sembera J.  Hokr M. |
| BRGM & University of Orleans | OPENFOAM & PHREEQC | Yes | Testing | Francis Claret |
| LEI | COMSOL-PHREEQC | Yes | Testing | Narkuniene A. |
| SCK-CEN | OpenGeoSys (OGS) (to be confirmed) | Yes | Testing |  |
| PSI |  | No | Observer |  |

* 1. **Planning and schedule of the benchmark**

*Table 2* shows the planning and schedule of the non-isothermal multiphase flow and reactive transport for radioactive waste disposal from March 2022 to December 2023.

*Table 2 – Planning and schedule of the non-isothermal multiphase flow and reactive transport for radioactive waste disposal*

|  |  |
| --- | --- |
| **Date** | **Milestone** |
| March to June 2022 | Selection of the benchmark case and definition of the different benchmark levels of complexity. |
| June 2022 to February 2023 | Performing of the benchmark simulation by benchmark leaders. |
| February 2023 to June 2023 | Resolution of the benchmark by the different teams and exchange of information. |
| June 2023 | Workshop to discuss the results. |
| June to October 2023 | New calculations, if necessary, based on the workshop outcome. |
| October to December 2023 | Wrap up of common publications |

1. **Benchmark case 1: FEBEX in situ test**
   1. **Multiphase mathematical formulation**

This section presents the mathematical formulation of the coupled THC model. This formulation has been extracted from Zheng et al. (2011).

It is assuming no deformation. Water mass balance is given by Navarro and Alonso (2000):

|  |  |
| --- | --- |
|  | (1) |

where( ) is the divergence operator, and are the bulk densities of the liquid and gaseous phases (kg/m3), respectively, is the mass fraction of water in the liquid phase, is the mass fraction of the vapor in the gas phase, is the sink/source term of liquid water, is the vector of volumetric liquid flux (m/s) which is given by Eq. 15, is the vector of volumetric gas flux (m/s), which is given by Eq. 16, is the dispersive mass flux of vapor with respect to the mean gas velocity (kg/m2/s), which is given by Eq. 17, and is the mass of water per unit volume of porous medium (kg/m3), which is given by:

|  |  |
| --- | --- |
|  | (2) |

where is the porosity and is the liquid saturation degree. The dispersive mass flux of air and water with respect to the liquid phase are neglected.

The gas mass balance equation is given by:

|  |  |
| --- | --- |
|  | (3) |

where and is the mass of gas per unit volume of porous medium (kg/m3) and is the sink/source term of gas. The dispersive mass flux of air and the gas with respect to the gaseous phase are neglected.

The air mass balance equation is given by:

|  |  |
| --- | --- |
|  | (4) |

where is the mass fraction of air in the gaseous phase, is the Henry’s constant, and is the mass of air per unit volume of porous medium (kg/m3) which is given by:

|  |  |
| --- | --- |
|  | (5) |

Our formulation assumes that all phases are at local thermal equilibrium and therefore they are all at the same temperature. Hence, the energy balance is described in terms of an equation of internal energy, which is defined by the following balance of enthalpy:

|  |  |
| --- | --- |
|  | (6) |

where is the average specific enthalpy of the soil (J/m3), which in turn is given by:

|  |  |
| --- | --- |
|  | (7) |

where , , and are the specific enthalpies of free water, vapor, air and solid particles respectively, which are assumed to depend linearly on temperature and specific heat (Navarro and Alonso, 2000):

|  |  |
| --- | --- |
|  | (8) |
|  | (9) |
|  | (10) |
|  | (11) |

where , , and are the specific heat at the temperature of the liquid, vapor, air and solid, respectively; and is the specific enthalpy of water vapor at temperature .

is the vector of convective energy flux, which is given by:

|  |  |
| --- | --- |
|  | (12) |

where is the vector of volumetric vapor flux (m/s), which is given by the last terms of Eq. 1, that is, and is the bulk thermal conductivity tensor (W/mºC), which for unsaturated bentonite is computed as a volume-weighted average of the conductivities of the components according to:

|  |  |
| --- | --- |
|  | (13) |

where **w**, **v**, **a** and **s** are the thermal conductivities of water, vapor, air and solid, respectively. This equation is inspired in the formulation of De Vries’s (1963), which according to Tang et al. (2008) provides the best fit to measured thermal conductivity data for several bentonites such as FEBEX bentonite. The formulation in Eq. 13, however, may not be the appropriate for courser porous materials. According to Soler (2001), the Dufour effect is negligible compared to thermal conduction and, therefore, can be disregarded.

The volumetric liquid flux, , is given by:

|  |  |
| --- | --- |
|  | (14) |

where is the liquid pressure (Pa), is the intrinsic permeability tensor of the liquid (m2), is the relative permeability of the liquid, is the viscosity of the liquid (kg/m/s), is the elevation. The volumetric gas flux, , is given by:

|  |  |
| --- | --- |
|  | (15) |

where is the intrinsic permeability tensor of the gas (m2), is the relative permeability of gas, and is the viscosity of the gas phase (kg/m/s).

The dispersive mass flux of vapor, , is calculated by the Fick’s law:

|  |  |
| --- | --- |
|  | (16) |

where is the hydrodynamic dispersion tensor for vapor (m2/s) which includes the effects of mechanical dispersion (and molecular diffusion (). The effective molecular diffusion coefficient for the vapor was calculated from Pollock (1986):

|  |  |
| --- | --- |
|  | (17) |

where is the vapor tortuosity factor (dimensionless), in Celsius.

It should be noticed that in the model the gases dissolved in water (air and other gases) are transported by advection and dispersion in the fluid phase together with liquid water.

Solute transport processes include advection, molecular diffusion, and mechanical dispersion. Each of them produces a solute flux per unit surface and unit time. There are as many transport equations as primary chemical species or aqueous components in the system. The primary species are the building blocks of chemical systems of interest, upon which concentrations of secondary species are written through laws of mass action for reactions at thermodynamic equilibrium. Advection refers to solute migration associated to the volumetric liquid flux, . The advective solute flux, , is given by:

|  |  |
| --- | --- |
| . | (18) |

where is the total dissolved concentration of the of j-th species (mol/L).

Molecular diffusion in pure water **,** produces a mixing effect which obeys Fick’s law:

|  |  |
| --- | --- |
| . | (19) |

Where is the molecular diffusion coefficient in pure water of the j-th specie. In a porous medium the porewater molecular diffusion, , is related with the molecular diffusion in pure water, , through:

|  |  |
| --- | --- |
|  | (20) |

where is the medium tortuosity. For partially saturated porous media, tortuosity is related to water content through relationships such as (Millington and Quirk ,1961):

|  |  |
| --- | --- |
|  | (21) |

Therefore, the diffusive flux in a porous media is given by:

|  |  |
| --- | --- |
| . | (22) |

The hydrodispersive flux, **,** can be described as:

|  |  |
| --- | --- |
| . | (23) |

The hydrodynamic dispersion, , is a symmetric tensor which components in two dimensions and are the following:

|  |  |
| --- | --- |
|  | (24) |
|  | (25) |
|  | (26) |

where and are the longitudinal and transversal dispersivities, and are the velocity components in two dimensions, and is the velocity magnitude.

The dispersion coefficient (m2/s) includes the hydrodynamic or mechanical dispersion, and the porewater molecular diffusion, .Then, the dispersion coefficient , can be expressed as the following relation:

|  |  |
| --- | --- |
|  | (27) |

where **I** is the identity tensor.

The mass balance equation for the j-th primary species is given by:

|  |  |
| --- | --- |
|  | (28) |

where is the gas sink/source term, which includes the chemical reactions term (mol/m3/s), the water mass flux (kg/m3/s) source entering () or sink leaving () the system, according to:

|  |  |
| --- | --- |
|  | (29) |

where is the external concentration of the j-th solute species in the entering water flux.

Substitution of mass fluxes , andinto equation (28) and taking into account equation (28) leads to:

|  |  |
| --- | --- |
|  | (30) |

Expanding the mass term and the advective transport term and reordering the Eq. (30), the following equation can be rewritten as:

|  |  |
| --- | --- |
|  | (31) |

The following identity derived from the water mass balance in the liquid phase (Eq. 1) and multiplying by , was taken into account.

|  |  |
| --- | --- |
|  | (32) |

where and and are the condensation and evaporation rates (kg/m3/s), respectively. The net effect of the evaporation/condensation rate (kg/m3/s), , can be evaluated as:

|  |  |
| --- | --- |
|  | (33) |

Therefore, substituting the Eq. (29) and Eq. (32) into Eq. (31), one has the mass balance equation for the j-th primary species:

|  |  |
| --- | --- |
|  | (34) |

Defining the transport operator , as the following:

|  |  |
| --- | --- |
|  | (35) |

Finally, the mass balance equation for the j-th primary species is given by (Zheng and Samper, 2008):

|  |  |
| --- | --- |
|  | (36) |

where is the total dissolved concentration of the of j-th primary species (mol/L), is the mass of liquid water per unit volume of medium (kg/m3), which is equal to , where is the volumetric watercontent (m3/m3), and are the total precipitated minerals, the total exchanged and total dissolved gas concentrations (mol/L), respectively, of the j-th primary species, is the sink term (kg/m3/s), is the dissolved concentration of j-th species (mol/L) in the sink term , is the number of primary species.

The reactive transport of the f-th gas species was implemented as an additional mass balance equation of the f-th gas species in the gaseous phase. The gas mass balance accounts for: a) advection; b) molecular diffusion and c) mechanical dispersion.

The advection considers the movement of the gas species with the volumetric gas flux, (m3/s). The advective flux, of the f-th gas species is given by:

|  |  |
| --- | --- |
|  | (37) |

where is the gas density and is the concentration of the of f-th gas species (mol/kg) in the gaseous phase.

The diffusive flux of the f-th gas species,, is given by Fick’s Law according to:

|  |  |
| --- | --- |
|  | (38) |

where is the diffusion coefficient of the f-th gas species in an ideal gaseous phase which according to Lasaga (1998) is given by:

|  |  |
| --- | --- |
|  | (39) |

where is the gaseous phase pressure, is Avogadro’s number, and and are the molecular diameter and the molecular weight of the f-th gas species, respectively. In a partly saturated gaseous phase containing several gases, the molecular diffusion,, is affected by the gaseous phase tortuosity,, and the volumetric gas content, ( according to:

|  |  |
| --- | --- |
|  | (40) |

The tortuosity in the gaseous phase,, is computed from (Millington and Quirk ,1961):

|  |  |
| --- | --- |
|  | (41) |

Combining Eq. (38) and Eq. (40), the diffusive flux in the gaseous phase is given by:

|  |  |
| --- | --- |
|  | (42) |

The dispersive transport by the mechanical dispersion,, is assumed to follow Fick’s Law according to:

|  |  |
| --- | --- |
|  | (43) |

where is the mechanical dispersion tensor similar to that of the liquid phase presented in Eq. (24), Eq. (25) and Eq. (26). The molecular diffusion, , and the mechanical dispersion, , are commonly lumped into a single dispersion tensor, , according to:

|  |  |
| --- | --- |
|  | (44) |

where the , is the identity tensor.

The mass balance equation of the f-th gas species in the gaseous phase is given by:

|  |  |
| --- | --- |
|  | (45) |

where is the gas sink/source term, which includes: the gas chemical reactions term (mol/m3/s), the gas mass flux (kg/m3/s) source entering () or sink leaving () the system, according to:

|  |  |
| --- | --- |
|  | (46) |

where is the external concentration of the f-th gas species in the entering gas flux. Substituting the Eq. (37), Eq (42) and Eq. (43) into Eq. (45) and taken into account Eq. (50), one has:

|  |  |
| --- | --- |
|  | (47) |

Expanding the mass term and the advective transport term and substituting Eq (46), one has:

|  |  |
| --- | --- |
|  | (48) |

The gas mass balance in the gaseous phase Eq. (3) reordered and multiplied by the concentration is given by:

|  |  |
| --- | --- |
|  | (49) |

Combining Eq (48) and Eq (49), the transport equation is given by:

|  |  |
| --- | --- |
|  | (50) |

The gas transport equation can be rewritten in compact form as:

|  |  |
| --- | --- |
|  | (51) |

where is the mass of gas per unit volume of medium (kg/m3) which is equal to and is the following transport operator:

|  |  |
| --- | --- |
|  | (52) |

The chemical conceptual model for compacted bentonite accounts for the following reactions: aqueous complexation, acid/base, redox, cation exchange, mineral dissolution/precipitation (at equilibrium or in kinetic), gas dissolution/exsolution. The chemical system is defined in terms of the concentrations of the primary species. The concentrations of the secondary species are computed from the concentrations of the primary species through appropriate mass action laws (Samper et al., 2009). The concentrations of the precipitated, exchanged and adsorbed species are computed using similar equations. A detailed description of the calculations of the chemical reactions can be found in Samper et al. (2009) and Zheng et al. (2011). The Gaines-Thomas convention is used for cation exchange.

The total dissolved concentration, , can be written in an explicit form as a function of the Nc primary species by applying the Mass-Action Law:

|  |  |
| --- | --- |
|  | (53) |

where is the number of the secondary species; is the equilibrium constant of the k-th secondary specie reaction; is the thermodynamic activity coefficient and is the stoichiometric coefficient of the j-th primary specie on the k-th species.

The total concentration of the precipitated minerals of the j-th primary species, , can be written as:

|  |  |
| --- | --- |
|  | (54) |

where is the concentration (mol/L) of the m-th mineral phase and is the stoichiometric coefficient of the j-th primary specie on the m-th mineral. Under equilibrium conditions, dissolution-precipitation reactions can be described by the Law of Mass Action which states that:

|  |  |
| --- | --- |
|  | (55) |

where is the molar fraction of the m-th solid phase; is the thermodynamic activity coefficient ( and are taken equal to 1 for pure phases); and are the concentration and activity coefficient of the i-th specie; is the stoichiometric coefficient in the dissolution reaction of the m-th solid phase; and is the corresponding equilibrium constant.

The concentration of the i-th exchanged cation (mol/L) can be obtained from the i-th equivalent fraction , according to:

|  |  |
| --- | --- |
|  | (56) |

where CEC is the total cation exchange capacity (meq/100g); is the cation charge and; is the exchange coefficient or selectivity.

The total concentration of the dissolved gases concentrations of the j-th primary species, , can be written as:

|  |  |
| --- | --- |
|  | (57) |

where is the concentration of the f-th gas and is the stoichiometric coefficient of the j-th primary specie on the f-th gas. For reactions involving aqueous and gas phase, the Law of Mass-Action states that:

|  |  |
| --- | --- |
|  | (58) |

where is the partial pressure of the f-th species in the gas phase; is the activity coefficient and is the equilibrium constant of the reaction, and are the concentration and activity coefficient of the i-th dissolved primary specie, is the stoichiometric coefficient of the f-th gas on the i-th specie. The gaseous phase is assumed as an ideal mixture and the fugacity constant, is equal to 1.

The equilibrium constants for aqueous complexes and minerals depend on temperature under non-isothermal conditions. They are calculated with the following expression, which is valid for temperatures between 0 and 300 ºC:

|  |  |
| --- | --- |
|  | (59) |

where to are coefficients, which are derived by fitting Equation 43 to measured values at 0, 25, 60, 100 and 300ºC.The thermodynamic database of ThermoChimie v11.a (Giffaut et al, 2014) is used for aqueous complexes and minerals.

For the activity coefficients of the aqueous species the extended Debye-Hückel formula can be used:

|  |  |
| --- | --- |
|  | (60) |

where I is the ionic strength of the solution; and are the electric charge and the ionic radius in solution of the i-th species, respectively; A and B are constants which depends on the temperature and dielectric constant of water, and b is a constant determined from experimental data (A, B and b were taken from tabulated values from Helgeson and Kirkham (1974)). The value of the ionic strength is calculated as:

|  |  |
| --- | --- |
|  | (61) |

The activity of the water can be calculated according to the approximation of Garrels and Christ (1965):

|  |  |
| --- | --- |
|  | (62) |

* 1. **Description of the FEBEX in situ test reference case**

The FEBEX in situ test was performed in a gallery excavated in granite in the underground research laboratory of Grimsel operated by NAGRA in Switzerland. The test included the heating system, the clay barrier and the instrumentation, monitoring and control system (*Figure 2*). The drift was 70.4 m long and 2.27 m in diameter. The test zone was located in the last 17.4 m of the drift where heaters, bentonite and instrumentation were installed. The main elements of the heating system were two heaters, separated horizontally by 1 m, which simulated full-sized canisters. The heaters were placed inside a cylindrical steel liner having a diameter of 0.93 m, which had been installed concentrically with the drift. Each heater was made of carbon steel, measured 4.54 m in length and 0.90 m in diameter, had a wall thickness of 0.10 m and weighed 11 tons. The heaters were designed to maintain a maximum temperature of 100ºC at the liner/bentonite interface. The bentonite barrier was made of blocks of highly compacted bentonite. The test began in February 1997. The 1st operation period lasted from 1997 to 2002 when heater 1 was switched off and the surrounding area was dismantled. The 2nd operation period started after the emplacement of a shotcrete plug and ended in June 2015 when the entire bentonite barrier was fully dismantled.



*Figure 2 – General layout of the FEBEX in situ test indicating the instrumented and sampling sections used in this work. The x coordinates of the sections are referred to the concrete plug on the left.*

The bentonite barrier is hydrated from the external cylindrical surface and water flows towards the internal heater/bentonite interface. The bentonite barrier is initially unsaturated, and it progressively hydrates from the surrounding rock towards the canister. The water content of the bentonite increases near the hydration boundary. Bentonite hydration leads to bentonite swelling. Therefore, the porosity of the bentonite increases during bentonite hydration. Mechanical and swelling processes play an important role in the hydrodynamic and geochemical evolution of the EBS during the early heating and hydration stage of the EBS, when bentonite buffer is subjected simultaneous to heating and hydration.

The temperature is fixed at 100ºC on the heater/bentonite interface. Water evaporates near the heater. Vapor diffuses away from the heater and condenses in cooler places. Vapor condensation retards the hydration of the bentonite buffer and affects the concentration of the dissolved species (Villar et al., 2012; Zheng et al., 2011).

The conditions of the FEBEX in situ test call for a coupled non-isothermal multiphase flow conceptual model with: 1) Advection of water in the liquid phase; 2) Advection and diffusion of vapor and other gases in the gaseous phase; 3) Advection and diffusion of air in the liquid and gaseous phases; 4) Convection of heat in the liquid and gaseous phase and; 5) Heat conduction.

* 1. **Simplifications and benchmark test cases**

The conceptual model for the multiphase simulations needs to be simplified due to the complexity of the real system. It has been agreed to consider a simplified system in the reference case and to increase the complexity of the modelled processes.

The proposed test cases (TC) are the following (Table 3):

1. Hydration and conservative tracer.

* Bentonite hydration by prescribing the liquid pressure at r = 1.14 m equal to 100 kPa
* Constant temperature equal to 25ºC
* Granite Cl- concentration prescribed at r = 1.14 m

1. No hydration and air and CO2(g) diffusion.

* Constant liquid saturation equal to 60% and constant gas saturation equal to 40%
* Constant temperature equal to 25ºC
* CO2(g) partial pressure equal to 0.1 bar prescribed at r = 1.14 m

1. No hydration, CO2(g) diffusion and calcite at equilibrium

* Constant liquid saturation equal to 60% and constant gas saturation equal to 40%
* Constant temperature equal to 25ºC
* Granite porewater concentration prescribed at r = 1.14 m
* CO2(g) partial pressure equal to 0.1 bar prescribed at r = 1.14 m
* Calcite precipitation at equilibrium

1. Hydration, CO2(g) diffusion and calcite at equilibrium.

* Bentonite hydration by prescribing the liquid pressure at r = 1.14 m equal to 100 kPa
* Constant temperature equal to 25ºC
* Granite porewater concentration prescribed at r = 1.14 m
* CO2(g) partial pressure equal to 0.1 bar prescribed at r = 1.14 m
* Calcite precipitation at equilibrium

1. Hydration, CO2(g) diffusion and calcite and gypsum at equilibrium.

* Bentonite hydration by prescribing the liquid pressure at r = 1.14 m equal to 100 kPa
* Constant temperature equal to 25ºC
* Granite porewater concentration prescribed at r = 1.14 m
* CO2(g) partial pressure equal to 0.1 bar prescribed at r = 1.14 m
* Calcite and gypsum precipitation/dissolution at equilibrium

1. Hydration, CO2(g) diffusion and calcite and gypsum at equilibrium.

* Bentonite hydration by prescribing the liquid pressure at r = 1.14 m equal to 100 kPa
* Constant temperature equal to 25ºC
* Granite porewater concentration prescribed at r = 1.14 m
* CO2(g) partial pressure equal to 0.1 bar prescribed at r = 1.14 m
* Calcite and gypsum precipitation/dissolution at equilibrium
* Cation exchange reactions

1. Heating, hydration, evaporation and conservative tracer.

* Bentonite hydration by prescribing the liquid pressure at r = 1.14 m equal to 100 kPa
* Temperature prescribed at r = 0.45 equal to 100ºC and equal to 25ºC at r = 1.14 m
* Granite porewater concentration prescribed at r = 1.14 m
* Vapour generation

1. Heating, hydration, evaporation and CO2(g) diffusion.

* Bentonite hydration by prescribing the liquid pressure at r = 1.14 m equal to 100 kPa
* Temperature prescribed at r = 0.45 equal to 100ºC and equal to 25ºC at r = 1.14 m
* Granite porewater concentration prescribed at r = 1.14 m
* CO2(g) partial pressure equal to 0.1 bar fix at r = 1.14 m
* Vapour generation

1. Heating, hydration, evaporation, CO2(g) diffusion and minerals at equilibrium.

* Bentonite hydration by prescribing the liquid pressure at r = 1.14 m equal to 100 kPa
* Temperature prescribed at r = 0.45 equal to 100ºC and equal to 25ºC at r = 1.14 m
* Granite porewater concentration prescribed at r = 1.14 m
* CO2(g) partial pressure equal to 0.1 bar prescribed at r = 1.14 m
* Calcite, gypsum and anhydrite precipitation/dissolution at equilibrium
* Vapour generation

1. Heating, hydration, evaporation, CO2(g) diffusion, minerals at equilibrium and cation exchange.

* Bentonite hydration by prescribing the liquid pressure at r = 1.14 m equal to 100 kPa
* Temperature prescribed at r = 0.45 equal to 100ºC and equal to 25ºC at r = 1.14 m
* Granite porewater concentration prescribed at r = 1.14 m
* CO2(g) partial pressure equal to 0.1 bar prescribed at r = 1.14 m
* Calcite, gypsum and anhydrite precipitation/dissolution at equilibrium
* Vapour generation
* Cation exchange reactions

1. Heating, hydration, evaporation, CO2(g) diffusion, minerals at equilibrium, cation exchange, corrosion, corrosion products and H2(g) generation.

* Bentonite hydration by prescribing the liquid pressure at r = 1.14 m equal to 100 kPa
* Temperature prescribed at r = 0.45 equal to 100ºC and equal to 25ºC at r = 1.14 m
* Granite porewater concentration prescribed at r = 1.14 m
* CO2(g) partial pressure equal to 0.1 bar prescribed at r = 1.14 m
* Calcite, gypsum and anhydrite precipitation/dissolution at equilibrium
* Vapour generation
* Cation exchange reactions
* Corrosion, corrosion products and H2(g) generation

*Table 3 - Proposed benchmark test cases for the FEBEX in situ test.*

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| **Test case** | **Heating** | **Hydration** | **Aqueous species** | **Minerals** | **Gases** | **Cation exchange** | **Boundary r = 0.45 m** | **Boundary r = 1.14 m** |
| **TC1**  Tracer (Cl-) | No | Yes | Tracer | - | Air | - | T = 25ºC | T = 25ºC  Pliq = 100 kPa  Pgas = 100 kPa  Prescribed granite boundary water |
| **TC2**  Gas diffusion | No | No | H+  CO2(aq)  CO3-2 | - | Air, CO2(g) | - | T = 25ºC  Fix Sliq = 60% | T = 25ºC  Pgas = 100 kPa  Prescribed Sliq = 60%  Prescribed CO2(g) pp = 0.1 bar |
| **TC3**  Gas diffusion & mineral diss/prec | No | No | H+  CO2(aq)  CO3-2  Ca+2 | Calcite | Air, CO2(g) | - | T = 25ºC  Fix Sliq = 60% | T = 25ºC  Pgas = 100 kPa  Prescribed Sliq = 60%  Prescribed granite boundary water  Prescribed CO2(g) pp = 0.1 bar |
| **TC4**  Hydration, gas diffusion & mineral diss/prec | No | Yes | H+  CO2(aq)  CO3-2  Ca+2 | Calcite | Air, CO2(g) | - | T = 25ºC | T = 25ºC  Pliq = 100 kPa  Pgas = 100 kPa  Prescribed granite boundary water  Prescribed CO2(g) pp = 0.1 bar |
| **TC5**  Hydration, gas diffusion & several minerals diss/prec | No | Yes | H+  CO2(aq)  CO3-2  Ca+2  SO4-2 | Calcite, gypsum | Air, CO2(g) | - | T = 25ºC | T = 25ºC  Pliq = 100 kPa  Pgas = 100 kPa  Prescribed granite boundary water  Prescribed CO2(g) pp = 0.1 bar |
| **TC6**  Hydration, gas diffusion, minerals & cation exchange | No | Yes | H+  CO2(aq)  CO3-2  Ca+2  SO4-2  Na+  K+  Mg2+ | Calcite, gypsum | Air, CO2(g) | Na+, K+, Ca2+, Mg2+ | T = 25ºC | T = 25ºC  Pliq = 100 kPa  Pgas = 100 kPa  Prescribed granite boundary water  Prescribed CO2(g) pp = 0.1 bar |
| **TC7**  Nonisothermal water evaporation/condensation. Tracer (Cl-) | Yes | Yes | Tracer | - | Air, vapour, | - | T = 100ºC | T = 25ºC  Pliq = 100 kPa  Pgas = 100 kPa  Prescribed granite boundary water |
| **TC8**  Nonisothermal water evaporation/condensation + CO2(g) + CO2(aq) | Yes | Yes | H+  CO2(aq)  CO3-2 | - | Air, vapour, CO2(g) | - | T = 100ºC | T = 25ºC  Pliq = 100 kPa  Pgas = 100 kPa  Prescribed granite boundary water  Prescribed CO2(g) pp = 0.1 bar |
| **TC9**  Nonisothermal water evaporation/condensation + CO2(g) + CO2(aq) + minerals | Yes | Yes | H+  CO2(aq)  CO3-2  Ca+2  SO4-2 H4SiO4 | calcite, gypsum, anhydrite, quartz | Air, vapour, CO2(g) | - | T = 100ºC | T = 25ºC  Pliq = 100 kPa  Pgas = 100 kPa  Prescribed granite boundary water  Prescribed CO2(g) pp = 0.1 bar |
| **TC10**  Nonisothermal water evaporation/condensation + CO2(g) + CO2(aq) + minerals+ cation exchange | Yes | Yes | H+  CO2(aq)  CO3-2  Ca+2  SO4-2 H4SiO4  Na+  K+  Mg2+ | calcite, gypsum, anhydrite, quartz | Air, vapour, CO2(g) | Na+, K+, Ca2+, Mg2+ | T = 100ºC | T = 25ºC  Pliq = 100 kPa  Pgas = 100 kPa  Prescribed granite boundary water  Prescribed CO2(g) pp = 0.1 bar |
| **TC11**  Nonisothermal water evaporation/condensation + CO2(g) + CO2(aq) + minerals+ cation exchange + corrosion | Yes | Yes | H+  CO2(aq)  CO3-2  Ca+2  SO4-2 H4SiO4  Na+  K+  Mg2+  Fe+2  O2(aq) | calcite, gypsum, anhydrite, quartz, magnetite, siderite, goethite, Fe(s) (kinetic control), | Air, vapour, CO2(g), O2(g), H2(g) | Na+, K+, Ca2+, Mg2+ | T = 100ºC | T = 25ºC  Pliq = 100 kPa  Pgas = 100 kPa  Prescribed granite boundary water  Prescribed CO2(g) pp = 0.1 bar |

*\*chemical equilibrium is considered. Temperature dependency of thermodynamic parameters is included. \**\**under kinetic control*

* 1. **Model description**
     1. Physical properties

*Table 4* and *table 5* show the hydrodynamic and transport properties used in the numerical model of the Febex in situ test.

*Table 4 – Thermal and hydrodynamic parameters of the bentonite (Samper et al., 2018; Zheng and Samper, 2008; Zheng et al., 2011)*

|  |  |
| --- | --- |
| Porosity, | 0.4 |
| Intrinsic permeability for liquid flow, *kil* (m2) | *ko* = 3.75 10-21 m2 |
| Relative permeability to liquid, *krl* |  |
| Van Genuchten retention curve, (kPa) | kPa-1 |
| Elastic storage term | 0.0 |
| Liquid viscosity (kg/m s) (T in Celsius) |  |
| Vapor tortuosity factor | 0.10 |
| Solid density (kg/m3) (T in Celsius) |  |
| Liquid density (kg/m3) (T in Celsius) |  |
| Gas density (kg/m3) (T in Celsius) |  |
| Specific heat of the solid (J/kg ºC) | 835.5 |
| Thermal conductivity of the solid (W/m ºC) | 1.23 |
| Intrinsic permeability for gas flow (m2) | 5·10-10 |
| Relative permeability to gas, *k*rg (m2) |  |
| Gas viscosity (kg/m s) | 1.76·10-5 |
| Specific heat of the liquid (J/kg ºC) | 4202 |
| Specific heat of the air (J/kgº C) | 1000 |
| Specific heat of the vapor (J/kg ºC) | 1620 |
| Thermal conductivity of the liquid (W/m ºC) | 1.5 |
| Thermal conductivity of the air (W/m ºC) | 2.6·10-2 |
| Thermal conductivity of the vapor (W/m ºC) | 4.2·10-2 |
| Vaporization enthalpy (J/kg) | 2.45·106 |
| Thermal compressibility of the water (ºC-1) | 2.1·10-4 |
| Thermal compressibility of the solid (ºC-1) | 2·10-5 |

*Table 5 – Hydrodynamic and transport parameters of the numerical models (Samper et al., 2018; ENRESA, 2006; Zheng et al., 2010; Mon, 2017; Zheng and Samper, 2008; Zheng et al., 2011).*

|  |  |
| --- | --- |
| Molecular diffusion in water  in m2/s as a function of *T* and the molecular diffusion at the reference temperature *Tref* (ºC), *,* with = 25ºC |  |
| Longitudinal dispersivity (m) | 0.01 |
| Molecular diameter of the gases species (m) | 10-10 |
| Air Henry’s constant (T in Celsius) |  |

* + 1. Time and space discretization

A 1D row of rectangular elements was used (*Figure 3*). The model domain included the bentonite barrier, which extended from *r* = 0.45 m to *r* = 1.14 m. The spatial discretization is uniform where the grid size is equal to 1 cm. The simulation time horizon covered the entire duration of the in situ test from February 1997 to 2015 (18 years).



*Figure 3 – Finite element mesh.*

* + 1. Thermodynamic database

The benchmark cases consider the thermodynamic database ThermoChimie version 11a (Giffaut et al., 2014), available in different formats at <https://www.thermochimie-tdb.com/>.

* + 1. Geochemical properties

The primary species considered in the geochemical model of the benchmark case TC11 are the following: H2O, H+, O2(aq), Na+, Ka+, Ca+2, Mg+2, Cl-, SO4-2, CO32- and H4SiO4(aq). Table 6 shows the chemical reactions and the equilibrium constants at 25ºC for the secondary aqueous species, minerals and gases used in the numerical model of the Febex in situ test benchmark case. The Fe aqueous species and minerals for the benchmark test case TC11 (with Fe+2 as primary species), in which the canister corrosion is considered, are the same than in the long-term corrosion benchmark case (see *Table 3*). Table 7 shows the selectivity constants for the cation exchange reactions in the bentonite.

*Table 6 – Chemical reactions and equilibrium constants for aqueous complexes, minerals and gases at 25ºC taken from the thermodynamic database ThermoChimie v11.a (Giffaut et al., 2014) to use in the model of the Febex in situ test benchmark case.*

|  |  |
| --- | --- |
| **Aqueous complexes** | **Log K** |
| CaCO3(aq) Û Ca2+ + CO32- | -3.2200 |
| Ca(HCO3)+ Û Ca2+ + H+ + CO32- | -11.4300 |
| CaSO4(aq) Û Ca2+ + SO42– | -2.3100 |
| CaCl+ Û Ca2+ + Cl– | +0.2900 |
| CaCl2(aq) Û Ca2+ + 2Cl- | +0.6400 |
| Ca(H3SiO4)+ + H+ Û Ca2+ + H4SiO4(aq) | +8.8300 |
| CO2(aq) + H2O Û 2H+ + CO32- | -16.6800 |
| HCO3- Û H+ + CO32- | -10.3300 |
| H2(aq) + 0.5O2(aq) Û H2O | +46.0700 |
| H3(SiO4)- + H+ Û H4SiO4(aq) | +9.8400 |
| KCl(aq) Û K+ + Cl- | +0.5000 |
| KSO4- Û K+ + SO42– | -0.8800 |
| MgCO3(aq) Û Mg2+ + CO32- | -2.9800 |
| Mg(HCO3)+ Û Mg2+ + H+ + CO32- | -11.3700 |
| MgSO4(aq) Û Mg2+ + SO42– | -2.2300 |
| MgCl+ Û Mg2+ + Cl– | -0.3500 |
| Mg(H3SiO4)+ + H+ Û Mg2+ + H4SiO4(aq) | +8.5800 |
| NaHCO3(aq) Û Na+ + H+ + CO32- | -10.0800 |
| NaSO4- Û Na+ + SO42– | -0.9400 |
| NaCl(aq) Û Na+ + Cl- | +0.5000 |
| Na(CO3)- Û Na+ + CO32- | -1.2700 |
| OH- + H+ Û H2O | 14.000 |
| **Minerals** | **LogK** |
| Calcite Û Ca2+ + CO32- | -8.4800 |
| Anhydrite Û Ca2+ + SO42- | -4.4400 |
| Gypsum Û Ca2+ + SO42- + 2H2O | -4.6100 |
| Quartz + 2H2O Û H4SiO4(aq) | -3.7400 |
| **Gases** | **LogK** |
| CO2(g) + H2O Û 2H+ + CO32- | -18.1500 |
| H2(g) + 0.5O2(aq) Û H2O | +42.9900 |
| O2(g) Û O2(aq) | -2.9000 |

Table 7 - Selectivity constants for cation exchange reactions in the FEBEX bentonite (ENRESA, 2006).

|  |  |
| --- | --- |
| **Cation exchange** | **KNa-cation** |
| Na+ + X-K ⇔ K+ + X-Na | 0.138 |
| Na+ + 0.5 X2-Ca ⇔ 0.5 Ca2+ + X-Na | 0.294 |
| Na+ + 0.5 X2-Mg ⇔ 0.5 Mg2+ + X-Na | 0.288 |

* + 1. Initial conditions

Bentonite had an initial porosity of 0.40, a volumetric water content of 24%, which corresponds to a gravimetric water content of around 14.4%, a liquid saturation degree of 60% and a suction of 1.17·105 kPa. The gas pressure was set to 100 kPa. The initial temperature was uniform and equal to 25ºC. The initial compositions of the bentonite and the granite pore water, the initial mineral volume fractions and the initial concentrations of exchanged ions are listed in Table 8.

Table 8 – Equilibrated initial pore water composition and activities, initial mineral volume fractions and gas partial pressure in the bentonite and granite for TC1, TC2, TC3, TC4 and TC5.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
|  | **Bentonite** | | **Granite (r = 1.14 m)** | |
| **TC1** | **Concentration** | **Activity coefficent** | **Concentration** | **Activity coefficent** |
| Tracer (mol/L) | 1.6·10-1 mol/L |  | 1.3·10-5 mol/L |  |
| **TC2** | **Concentration** | **Activity coefficent** | **Concentration** | **Activity coefficent** |
| pH | 9.749 | 0.9921 | 7.70 | 0.9767 |
| CO2 (aq) | 3.388·10-8 mol/L | 1.0000 | 3.388·10-3 mol/L | 1.0000 |
| CO32- | 2.295·10-5 mol/L | 0.9689 | 2.088·10-4 mol/L | 0.9103 |
| CO2 (g) | 10-6 bar |  | 0.1 bar |  |
| **TC3 & TC4** | **Concentration** | **Activity coefficent** | **Concentration** | **Activity coefficent** |
| pH | 8.752 | 0.8122 | 7.495 | 0.9819 |
| CO2 (aq) | 3.374·10-8 mol/L | 1.0042 | 3.388·10-3 mol/L | 1.0000 |
| Ca2+ | 2.195·10-2 mol/L | 0.4405 | 4.799·10-5 mol/L | 0.9295 |
| CO32- | 7.701·10-7 mol/L | 0.4447 | 7.707·10-5 mol/L | 0.9296 |
| CO2 (gas) | 10-6 bar |  | 0.1 bar |  |
| Calcite | 0.01 vf |  | - |  |
| **TC5** | **Concentration** | **Activity coefficent** | **Concentration** | **Activity coefficent** |
| pH | 8.982 | 0.8007 | 7.491 | 0.9769 |
| CO2 (aq) | 3.372·10-8 mol/L | 1.0049 | 3.388·10-3 mol/L | 1.0000 |
| Ca2+ | 7.838·10-3 mol/L | 0.4166 | 4.879·10-5 mol/L | 0.9108 |
| SO42- | 1.790·10-2 mol/L | 0.4211 | 7.900·10-5 mol/L | 0.9109 |
| CO32- | 2.408·10-6 mol/L | 0.4211 | 7.818·10-5 mol/L | 0.9109 |
| CO2 (gas) | 10-6 bar |  | 0.1 bar |  |
| Calcite | 0.01 vf |  | - |  |
| Gypsum | 0.0015 vf |  | - |  |
| **TC6** | **Concentration** | **Activity coefficent** | **Concentration** | **Activity coefficent** |
| pH | 8.948 | 0.6691 | 7.489 | 0.9720 |
| CO2 (aq) | 3.309·10-8 mol/L | 1.0238 | 3.390·10-3 mol/L | 1.0001 |
| Ca2+ | 1.238·10-2 mol/L | 0.2055 | 4.879·10-5 mol/L | 0.8928 |
| Mg2+ | 3.335·10-2 mol/L | 0.2055 | 1.300·10-6 mol/L | 0.8928 |
| Na+ | 1.476·10-1 mol/L | 0.6691 | 3.800·10-4 mol/L | 0.9720 |
| K+ | 1.945·10-3 mol/L | 0.6691 | 7.800·10-6 mol/L | 0.9720 |
| SO42- | 4.169·10-2 mol/L | 0.2129 | 7.900·10-5 mol/L | 0.8930 |
| CO32- | 6.109·10-6 mol/L | 0.2129 | 7.978·10-5 mol/L | 0.8930 |
| CO2 (gas) | 10-6 bar |  | 0.1 bar |  |
| Calcite | 0.01 vf |  | - |  |
| Gypsum | 0.0015 vf |  | - |  |
| Exchanged Ca2+ | 19.04 |  | - |  |
| Exchanged Mg2+ | 55.20 |  | - |  |
| Exchanged Na+ | 26.04 |  | - |  |
| Exchanged K+ | 2.47 |  | - |  |

* + 1. Boundary conditions

The temperature and the liquid and gas pressure at the outer boundary (*r* = 1.14 m) were equal to 25ºC and 100 kPa, respectively (Figure 4). A constant temperature of 100ºC was prescribed at the internal boundary which coincides with the liner/bentonite interface (*r* = 0.45 m) from TC7 to TC11 cases. There was no gas and liquid flow at *r* = 0.45 m.



Figure 4.- Boundary conditions.

* + 1. Canister corrosion

Anaerobic canister corrosion is considered in the benchmark test case TC5. The canister is treated as a porous material made of 100% metallic iron, Fe(s). Under anaerobic conditions, H2O is the oxidizing agent of Fe(s) (Lu et al., 2011; Mon, 2017; Samper et al., 2016). The anaerobic Fe(s) corrosion reaction is given by:

|  |  |
| --- | --- |
|  | (63) |

By rewriting this reaction in terms of the primary species used in the numerical model, one obtains:

|  |  |
| --- | --- |
|  | (64) |

The carbon-steel corrosion is kinetically controlled and assumed to corrode at a constant rate of 2 μm/year (it should be noticed that η = 0 for constant canister corrosion), which amounts to 0.281 mol/m2/year.

* 1. **Calculated model results**

An excel file of each benchmark test case will be distributed to compare the computed results including the spatial distribution at selected times of:

* The computed liquid and gas saturation
* The computed total dissolved chemical species concentration and pH
* The computed concentration of precipitated and dissolved minerals
* The computed gases concentration
* The computed cation exchange concentration

The cases proposed include 11 cases: 6 cases under isothermal conditions and 5 cases are under non isothermal conditions. Due to the complexity of the test cases only the isothermal cases (TC1 to TC6) and one of the non-isothermal case (TC7) were solved by one or more teams. Here we present the results of the isothermal conditions, and the rest of the cases will be presented in futures works.

### Case TC1. Hydration and conservative tracer.

Figure 5 and Figure 6 show some preliminary benchmarking results for water content and Cl- concentration for Case TC1. There are results from 4 teams. Computed water content match for all the teams, but there are small discrepancies at the right boundary (r = 1.14 m). Computed Cl- are similar except the small differences at the diffusion front.





Figure 5.- Comparison of the spatial distribution of the computed water content at 1, 5 and 18 years for the Case TC1.



Figure 6.- Comparison of the spatial distribution of the computed Cl- concentration at 1, 5 and 18 years for the Case TC1.

Several sensitivity runs were performed to analysis if the differences in the results performed by each group could be due to the dispersion, diffusion and flow. The dispersion has been multiplied and divided by ten. The flow was set to null in the sensitivity run, in addition the diffusion coefficient was multiplied by ten. Figure 7 shows the computed results for the sensitivity runs to the dispersion, to the flow and diffusion. The computed concentrations for the sensitivity run to the increasing of the dispersion are faster than those for the base, on the other hand the concentrations are slower in the case of decreasing the dispersion. The tracer diffusion is slow if water flow is not considered, the tracer diffusion increases if the diffusion coefficient is increasing.

Figure 8 shows the comparison of the tracer concentrations for the sensitivity run to the dispersion multiplied by 0.1 performed by UDC and Lei. The results show the same trend but the are small differences at the diffusion profile. Figure 9 and Figure 10 shows the sensitivity runs without flow and increasing of the diffusion coefficient performed by UDC and Lei. The tracer concentrations match for both teams if the water flow is not considered.



Figure 7.- Spatial distribution of the computed Cl- concentration at 1, 5 and 18 years for the base run and sensitivity runs to the dispersion, flow, and diffusion for the Case TC1.



Figure 8.- Spatial distribution of the computed Cl- concentration at 1, 5 and 18 years for the sensitivity run to the dispersion multiplied by 0.1 for the Case TC1.



Figure 9.- Spatial distribution of the computed Cl- concentration at 1, 5 and 18 years for the sensitivity run to the flow for the Case TC1.



Figure 10.- Spatial distribution of the computed Cl- concentration at 1, 5 and 18 years for the sensitivity run to the flow and the diffusion multiplied by 10 for the Case TC1.

### Case TC2. Gas diffusion

Figure 11 shows some preliminary benchmarking results for CO2(g) concentration for Case TC2. There are results from 4 teams. There is a good agreement of the computed CO2(g) concentration from all teams.



Figure 11.- Comparison of the spatial distribution of the computed CO2(g) partial pressure at 0.001, 0.005 and 0.5 years for the Case TC2.

### Case TC3. Gas diffusion & mineral diss/prec

Figure 12 and Figure 13 show some preliminary benchmarking results for calcite and pH for Case TC3. There are results from 3 teams. Computed calcite follow the same trend, however there are differences due to the extremely small precipitation rate. Computed pH match for all the teams.



Figure 12.- Comparison of the spatial distribution of the computed calcite at 0.001, 0.005 and 0.5 years for the Case TC3.



Figure 13.- Comparison of the spatial distribution of the computed pH at 0.001, 0.005 and 0.5 years for the Case TC3.

### Case TC4. Hydration, CO2(g) diffusion and calcite at equilibrium.

Figure 14, Figure 15, Figure 16 and Figure 17 show some preliminary benchmarking results for CO2(g), Ca2+, calcite and pH for Case TC4. There are results from 3 teams. Computed CO2(g) are similar but shows differences at early times. Computed Ca2+ concentrations are similar for all teams. Computed calcite follow the same trend, however there are differences due to the small calcite concentrations. Computed pH match for all the teams.



Figure 14.- Comparison of the spatial distribution of the computed CO2(g) partial pressure at 0.005 and 0.5 years for the Case TC4.



Figure 15.- Comparison of the spatial distribution of the computed dissolved Ca+2 at 0.005, 1 and 18 years for the Case TC4.



Figure 16.- Comparison of the spatial distribution of the computed calcite at 0.005, 1 and 18 years for the Case TC4.



Figure 17.- Comparison of the spatial distribution of the computed pH at 0.5, 1 and 18 years for the Case TC4.

### Case TC5. Hydration, CO2(g) diffusion and calcite and gypsum at equilibrium.

Figure 18, Figure 19 and Figure 20 show some preliminary benchmarking results for Ca2+, sulphate and pH for Case TC5. Computed calcium and sulphate show similar trend but there are differences at the unaltered bentonite. Computed pH match for all the teams.

Figure 21 and Figure 22 show preliminary benchmarking results for calcite and gypsum for Case TC5. Computed calcite and gypsum show similar trends but there are differences at the flow boundary.



Figure 18.- Comparison of the spatial distribution of the computed dissolved Ca+2 at 0.005, 1 and 18 years for the Case TC5.



Figure 19.- Comparison of the spatial distribution of the computed dissolved SO4-2 at 0.005, 1 and 18 years for the Case TC5.



Figure 20.- Comparison of the spatial distribution of the computed pH at 0.5, 1 and 18 years for the Case TC5.



Figure 21.- Comparison of the spatial distribution of the computed calcite at 18 years for the Case TC5.



Figure 22.- Comparison of the spatial distribution of the computed gypsum at 18 years for the Case TC5.

### Case TC7. Hydration, heating and tracer.

Figure 23 and Figure 24 show some preliminary benchmarking results for water content and Cl- concentration for Case TC7. Computed water content and computed Cl- have similar trends are similar, however there are differences at the heating side due to the evaporation rate.



Figure 23.- Comparison of the spatial distribution of the computed water content at 1, 5 and 18 years for the Case TC7.

 

Figure 24.- Comparison of the spatial distribution of the computed Cl- concentration at 1, 5 and 18 years for the Case TC7.

# Benchmark case 2: Long-term corrosion

## Description of the long-term corrosion benchmark case

Samper et al. (2016) presented a non-isothermal multicomponent reactive transport model to study the long-term interactions of corrosion products and compacted bentonite in a high-level radioactive waste (HLW) repository in granite based on the Spanish reference concept (ENRESA, 2000). It consists on the disposal of spent fuel elements in cylindrical carbon steel canisters surrounded by blocks of compacted bentonite placed in horizontal disposal drifts, which are located at a depth of 500 m in a granite formation.

## Simplifications and benchmark test cases

The conceptual model for the non-isothermal multicomponent reactive transport model to study the long-term interactions of corrosion products and compacted bentonite in a HLW repository in granite needs to be simplified due to the complexity of the real system. It has been agreed to consider a simplified system in the reference case and to increase the complexity of the modelled processes.

One simplification is that the granite host rock is considered as a boundary condition and not as a material of the model. Bentonite swelling process is not considered. Surface complexation by sorption is not taken into account in the model.

The proposed benchmark test cases (TC) are the following (Table 9):

1. Conservative transport.
2. Conservative transport. Aqueous complexation, canister corrosion and H2(g) generation.
3. Conservative transport. Aqueous complexation, canister corrosion, H2(g) generation, bentonite minerals and corrosion products.
4. Conservative transport. Aqueous complexation, canister corrosion, H2(g) generation, bentonite minerals and corrosion products and cation exchange.
5. Adding the porosity feedback effect (PFE).

Table 9 - Proposed benchmark test cases of the non-isothermal multiphase and reactive transport for radioactive waste disposal (benchmark case 2 of hydrogen generation).

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **Test case** | **Aqueous complexation** | **Minerals** | **Gas** | **Cation exchange** |
| TC1 | Conservative tracer | - | - | - |
| TC2 | Yes | Fe(s) | H2(g) | - |
| TC3 | Yes | Fe(s), bentonite minerals and corrosion products | H2(g) | - |
| TC4 | Yes | Fe(s), bentonite minerals and corrosion products | H2(g) | Na+, K+, Ca2+, Mg2+ |
| TC5 | Yes | Fe(s), bentonite minerals and corrosion products | H2(g) | Na+, K+, Ca2+, Mg2+ |

## Conceptual model

### Hydrodynamic processes

Although the bentonite blocks are initially unsaturated, the reactive transport model of the HLW disposal cell in granite assumes that the bentonite is initially water-saturated because the bentonite barrier will become fully saturated in less than 50 years (Zheng and Samper, 2008).

The model accounts for molecular diffusion. The hydraulic conductivity of the bentonite is extremely low (6·10-14 m/s). Therefore, advection is negligible and solute diffusion is the main solute transport mechanism. All the water is assumed to be accessible to solutes.

Solute transport through the granite is simulated with a prescribed water flux parallel to the axis of the gallery at the bentonite/granite interface.

### Thermal processes

All the runs in the reactive transport model of the HLW disposal cell in granite are non-isothermal. The selected time evolution of the temperature at the canister-bentonite and the bentonite-granite interfaces in a HLW disposal cell in granite after 100 years of storage was used in the model (Figure 25). These data was computed by E. Neeft with the thermal parameters of the Febex bentonite and the Spanish Reference Granite (Neeft, 2020, personal communication).



Figure 25.- Time evolution of the temperature in the canister/bentonite and bentonite/granite interfaces used in the model of the HLW disposal cell in granite.

### Chemical processes

The conceptual geochemical model of the HLW disposal cell in granite includes the following processes: 1) Carbon-steel canister corrosion, 2) Aqueous complexation; 3) Acid/base; 4) Redox; 5) Mineral dissolution/precipitation; and 6) Cation exchange of Ca2+, Mg2+, Fe2+, Na+ and K+.

The geochemical system is defined in terms of 13 primary species (H2O, H+, O2(aq), Ca2+, Mg2+, Na+, K+, Fe2+, Al3+, Cl-, SO42-, HCO3-, H4SiO4,), 39 secondary aqueous species, 9 minerals and 5 cation exchange species. The secondary aqueous species were identified from speciation runs performed with EQ3/6 (Wolery, 1992). The Gaines-Thomas convention was used for cation exchange reactions (Appelo and Postma, 1993) only in the bentonite. Chemical reactions and the equilibrium constants at 25ºC for aqueous species and mineral dissolution/precipitation used in the model are listed in Table 10.

All the reactions are assumed at chemical equilibrium, except for the dissolution/precipitation of some minerals which are kinetically controlled such as the carbon-steel corrosion. The following kinetic rate law is used:

|  |  |
| --- | --- |
|  | (65) |

where rm is the dissolution/precipitation rate (mol/m2/s), is the kinetic rate constant (mol/m2/s) at 25ºC, Ea is the activation energy, R is the gas constant (J/K·mol), T is the temperature (K), is the saturation index which is equal to the ratio of the ion activity product to the equilibrium constant (dimensionless), ϴ and η are empirical parameters, is the absolute value operator, and is a catalytic term which accounts for the activities ai of the aqueous species and pmi is the exponent for the i-th aqueous species in the m-th mineral phase dissolution reaction. Variable sm is taken equal to -1 for precipitation and 1 for dissolution to ensure that the dissolution/precipitation rate is always positive for dissolution and negative for precipitation for any values of the parameters ϴ and η.

The dissolution/precipitation rate in mol/m2/s, rm, is multiplied by the mineral specific surface area, σ, to get the dissolution/precipitation rate in mol/m3/s, Rm. The specific surface area σ is defined as the surface area of the mineral per unit fluid volume. The reactive transport model of the HLW disposal cell in granite assumes that σ is constant in time.

Table 10 - Chemical reactions and equilibrium constants for aqueous complexes and minerals at 25ºC taken from the thermodynamic database ThermoChimie v11.a (Giffaut et al., 2014).

|  |  |
| --- | --- |
| Aqueous complexes | Log K |
| CaCO3(aq) + H+ Û Ca2+ + HCO3– | 7.1100 |
| CaHCO3+ Û Ca2+ + HCO3– | -1.100 |
| CaSO4(aq) Û Ca2+ + SO42– | -2.310 |
| CaOH+ + H+ Û Ca2+ + H2O | 12.78 |
| CO2(aq) + H2O Û H+ + HCO3– | -6.350 |
| CO32- + H+ Û HCO3– | 10.33 |
| KOH(aq) + H+ Û K+ + H2O | 14.460 |
| KSO4- Û K+ + SO42– | -0.8796 |
| MgCO3(aq) Û Mg2+ + CO32- | -2.980 |
| MgHCO3+ Û Mg2+ + HCO3– | -1.040 |
| MgSO4(aq) Û Mg2+ + SO42– | -2.230 |
| MgOH+  + H+ Û Mg2+ + H2O | 11.680 |
| NaHCO3(aq) Û Na+ + HCO3– | 0.250 |
| NaSO4- Û Na+ + SO42– | -0.940 |
| NaCO3- Û Na+ + CO32- | -1.270 |
| NaOH(aq)+ H+ Û Na+ + H2O | 14.750 |
| OH- + H+ Û H2O | 14.000 |
| HSO4- Û H+ + SO42- | 1.9791 |
| HS- + 2O2(aq) Û H+ + SO42– | 138.27 |
| Fe3+ + 0.5H2O Û H+ + 0.25O2 + Fe2+ | -8.485 |
| FeHCO3+Û Fe2++ HCO3– | -1.440 |
| FeCO3 (aq)Û Fe2++ CO32- | 4.640 |
| FeCl+ Û Fe2++ Cl- | -0.140 |
| FeCl2+ + 0.5H2O Û Fe2+ + Cl- + H+ + 0.25O2(aq) | -9.885 |
| FeOH++ H+ Û Fe2++ H2O | 9.500 |
| FeOH2+ Û Fe2++ 0.5H2O + 0.25O2(aq) | -6.295 |
| Fe(OH)2(aq) + 2H+ Û Fe2++ 2H2O | 20.60 |
| Fe(OH)3(aq) + 2H+ Û Fe2+ + 2.5H2O + 0.25O2(aq) | 4.075 |
| Fe(OH)4- + 3H+ Û Fe2+ + 3.5H2O + 0.25O2(aq) | 13.115 |
| Fe(OH)2+ + H+ Û Fe2+ + 1.5H2O + 0.25O2(aq) | -2.815 |
| Fe(SO4)2-  + 0.5H2O Û Fe2+ + 2SO42- + H+ + 0.25O2(aq) | -13.885 |
| FeSO4(aq)Û Fe2+ + SO42- | -2.200 |
| FeHSO42+  + 0.5H2O Û Fe2+ + 2H+ + SO42- + 0.25O2(aq) | -12.955 |
| Fe2(OH)24+ + 2H+Û 2Fe2+ + H2O + 0.5O2(aq) | -14.020 |
| H2(aq) + 0.5O2 Û H2O | 46.07 |
| Al(OH)2+ + 2H+ Û Al3+ + 2H2O | 10.580 |
| Al(OH)3(aq)+ 3H+ Û Al3+ + 3H2O | 16.420 |
| Al(OH)4- + 4H+ Û Al3+ + 4H2O | 22.870 |
| Al(OH)2+ + H+ Û Al3+ + H2O | 4.9500 |
| **Minerals** | **LogK** |
| Calcite + H+ Û Ca2+ + HCO3– | 1.850 |
| Magnetite + 6H+ Û 3Fe2+ + 0.5O2 (aq) + 3H2O | -6.560 |
| Siderite + H+ Û Fe2+ + HCO3– | -0.470 |
| Goethite + 2H+ Û Fe2+ + 1.5H2O + 0.25O2 (aq) | -8.090 |
| Fe(s) + 2H+ Û Fe2+ + 2H2O + 2OH- + H2(aq) | 58.85 |

#### Carbon steel corrosion

The available oxygen in the HLW disposal cell in granite will be consumed soon after its closure, and anaerobic conditions will prevail in the long term. The canister is treated as a porous material made of 100% metallic iron, Fe(s). Under anaerobic conditions, H2O is the oxidizing agent of Fe(s) (Lu et al., 2011; Mon, 2017; Samper et al., 2016). The anaerobic Fe(s) corrosion reaction is given by:

|  |  |
| --- | --- |
|  | (66) |

By rewriting this reaction in terms of the primary species used in the numerical model, one obtains:

|  |  |
| --- | --- |
|  | (67) |

The carbon-steel corrosion is kinetically controlled and assumed to corrode at a constant rate of 2 μm/year which amounts to 0.281 mol/m2/year.

## Numerical model

### Grid and simulated time

A 1-D numerical model of the canister and the bentonite was used to simulate the long term interactions of the corrosion products and the bentonite (Figure 26). Water flow and solute transport through the granite was simulated with a constant water flux of 4.6 L/y parallel to the axis of the gallery at the bentonite-granite interface. The finite element mesh has 93 nodes and 92 elements. Numerical simulations were performed for a time horizon of 10.000-50.000 years. The spatial mesh discretization is non uniform.



Figure 26.- Sketch of the engineered barrier system and 1D finite element grid of the 1D model.

### Flow and transport parameters

The FEBEX bentonite is considered initially saturated with a thickness of 75 cm. The hydraulic conductivity of the bentonite is extremely low, with a value of 6·10-14 m/s (Samper et al., 2016). Therefore, solute advection is negligible and diffusion is the main solute transport mechanism. All the water is assumed to be accessible to solutes.

The bentonite porosity, ф, is equal to 0.407. The effective diffusion coefficient, De, of the bentonite is equal to 4.07·10-11 m2/s (Samper et al., 2016). The solid density of the bentonite is 2700 kg/m3. The specific heat capacity and the saturated thermal conductivity of the bentonite are equal to 846.4 J/kgºC and 1.15 W/mºC, respectively (Samper et al., 2016).

The canister is assumed to have the same transport parameters, De and ф, as the bentonite.

The specific heat capacities of the bentonite and the canister are equal to 846 and 480 J/kgºC, respectively. The saturated thermal conductivities of bentonite and steel canister are equal to 1.15, and 50 W/mºC, respectively (ENRESA, 2000).

The thermal and hydrodynamic parameters of the bentonite considered in the reactive transport model of a HLW disposal cell in granite are listed in Table 11 (Samper et al., 2018; Samper et al., 2016).

Table 11 - Thermal and hydrodynamic parameters of the bentonite (Samper et al., 2018; Samper et al., 2016; Zheng and Samper, 2008; Zheng et al., 2011).

|  |  |
| --- | --- |
| Parameter | Bentonite |
| Hydraulic conductivity (m/s) | 6 ∙10-14 |
| Liquid viscosity (kg/m s) |  |
| Solid density (kg/m3) | 2700 |
| Specific heat of the solid (J/kg ºC) | 846.4 |
| Thermal conductivity of the solid (W/m ºC) | 1.23 |

### Chemical parameters

The chemical composition of the initial bentonite porewater (Samper et al., 2016) is listed in Table 12. The initial accessory mineral volume fraction of the calcite considered in the bentonite is 1%. Magnetite, siderite and goethite are not initially present in the system but are allowed to precipitate. The cation exchange capacity (CEC) of the bentonite is 102 meq/100 g (Fernández et al., 2004). Cation selectivity coefficients for exchanged Ca2+, Mg2+, K+ and Fe+ were derived from Samper et al. (Samper et al., 2008) and Tournassat (2003). Table 13 shows the selectivity constants for cation exchange reactions in the FEBEX bentonite.

The initial chemical composition of the canister porewater is assumed to be the same as that of the bentonite porewater. The canister is treated as a porous material made of 100% metallic iron, Fe(s). The chemical composition of the granite boundary water (Samper et al., 2016) is listed in Table 14.

Table 12 - Chemical composition of the initial FEBEX bentonite porewater (Samper et al., 2016).

| **Species**  (mol/L) | **FEBEX bentonite**  **porewater** |
| --- | --- |
| pH | 6.46 |
| Eh (V) | -0.078 |
| Ca2+ | 3.32·10-2 |
| Mg2+ | 3.67·10-2 |
| Na+ | 1.88·10-1 |
| K+ | 1.55·10-3 |
| Fe2+ | 1.43·10-4 |
| Al3+ | 1.0·10-8 |
| Cl- | 2.75·10-1 |
| HCO3- | 7.59·10-3 |
| SO42- | 2.05·10-2 |
| SiO2 (aq) | 9.67·10-5 |

Table 13 - Selectivity constants for cation exchange reactions in the FEBEX bentonite (ENRESA, 2006).

|  |  |  |
| --- | --- | --- |
| **Cation exchange** | | **KNa-cation** |
|  | Na+ + X-K Û K+ + X-Na | 0.138 |
|  | Na+ + 0.5 X2-Ca Û 0.5 Ca2+ + X-Na | 0.2924 |
|  | Na+ + 0.5 X2-Mg Û 0.5 Mg2+ + X-Na | 0.2881 |
|  | Na+ + 0.5 X2-Fe Û 0.5 Fe2+ + X-Na | 0.5 |

Table 14 - Chemical composition of the granite boundary water (Samper et al., 2016).

| **Species**  **(mol/L)** | **Granite boundary water** |
| --- | --- |
| pH | 7.825 |
| Eh (V) | -0.188 |
| Ca2+ | 1.522·10-4 |
| Mg2+ | 1.604·10-4 |
| Na+ | 4.350·10-3 |
| K+ | 5.371·10-5 |
| Fe2+ | 1.791·10-8 |
| Al3+ | 1.85·10-8 |
| Cl- | 3.949·10-4 |
| HCO3- | 5.049·10-3 |
| SO42- | 1.561·10-5 |
| SiO2 (aq) | 3.761·10-4 |

## Calculated model results

An excel file of each benchmark test case will be distributed to compare the computed results including the time evolution at selected locations and the spatial distribution at selected times of:

* The computed liquid and gas saturation
* The computed total dissolved chemical species concentration and pH
* The computed concentration of precipitated and dissolved minerals
* The computed concentration of exchanged cations
* The computed gases concentration

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