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*Supplement of*

# A parallelization scheme to simulate reactive transport in the subsurface environment with OGS#IPhreeqc 5.5.7-3.1.2

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# Part 1: PHREEQC script for the Engesgaard benchmark

The PHREEQC script for the Engegaard benchmark (Sect. 2.4, verification example 1) will be given below, in order to allow the reader to reproduce the results shown in Fig. 2. The USER_GRAPH data block in PHREEQC is also used here, so that the readers can directly visualize the results in the PHREEQC GUI for Windows. The script used for performance test is a little different from the one shown below. It does not include this USER_GRAPH data block and only prints out the results at the end of the simulation (to be in consistence with the OGS#IPhreeqc and OGS#ChemApp simulations).

The standard PHREEQC database (phreeqc.dat) is applied, which can be downloaded on the homepage of PHREEQC (http://wwwbrr.cr.usgs.gov/projects/GWC_coupled/phreeqc/).

```
SOLUTION 0 Mgcl2
    temp      25
    pH        7
    pe        4
    units     mol/kgw
    Cl        0.002
    Mg        0.001
    Ca        1e-10
    C(4)      1e-10

SOLUTION 1-100 Calcite
    temp      25
    pH        9.91 charge
    pe        4
    units     mol/kgw
    Ca        1.23e-4
    C(4)      1.23e-4
    Cl        1e-12
    Mg        1e-12


EQUILIBRIUM_PHASES 1-100
    Calcite   0 1.220005e-004

# 5.7412e-2 [mol/m3] * 0.002125 (0.002125 is the unit factor used to transfer
# unit from mol/m3 to mol/kgw for mineral, it can be calculated as follows:
# (1-porosity)*MolH2OPERKG /(water_concentration*porosity*WaterSaturation)
# Here, this 4 variables are 0.32[-], 55.508[mol/kgw],55508[molw/m3] and
# 1[-], respectively.

KINETICS 1-100
Dolomite
  -m 0

RATES
Dolomite
```

```
  -start
rem kmech = k25*exp(-Eact/R*(1/T-1/298.15))*Product([Ci]^nyi);
10  R = 8.314472
11  deltaT = 1/TK - 1/298.15
12  e = 2.7183
13  Ea = 36100
14  logK25 = -3.19
15  ny = 0.5
rem 16  mech_a = (10^logK25) * (e^(-Ea/R*deltaT)) * ACT("H+")^ny
16  mech_a = (10^logK25) * ACT("H+")^ny
23  Ea = 52200
24  logK25 = -7.53
rem 26  mech_b = (10^logK25) * (e^(-Ea/R*deltaT))
26  mech_b = (10^logK25)
30  rate = mech_a + mech_b
40  teta = 1
41  eta = 1
42  Area = .001
70  rate = Area * rate * (1 - SR("Dolomite")^teta)^eta
80  moles = rate * time
100 save moles
      -end

PRINT
 -reset true
 -selected_output true

SELECTED_OUTPUT
-file phout_sel-PQC.dat
-high_precision
-reset false

USER_PUNCH
-headings C(4) Ca Mg cl CO3-2 pH pe Calcite Dolomite
-start
20 PUNCH TOT("C(4)"), TOT("Ca"), TOT("Mg"), TOT("Cl"), mol("CO3-2")
30 PUNCH -LA("H+"), -LA("e-")
60 PUNCH EQUI("Calcite")
70 PUNCH KIN("Dolomite")
-end

TRANSPORT
        -cells           100
        -lengths         100*0.005
        -shifts          39
        -time_step       533.333
        -flow_direction  forward
        -boundary_conditions   flux  flux
        -diffusion_coefficient 0.0e-9
        -dispersivities  100*0.0067
        -correct_disp    true
END

TRANSPORT
       -shifts         1

USER_GRAPH 1
```

```
  -chart_title "Mg Cl Ca CO3-2 concentration"
  -headings Mg Cl Ca CO3-2
  -axis_titles "Distance" "mol/m3"
  -axis_scale x_axis 0 0.5
  -axis_scale y_axis 0 2
  -connect_simulations false
  -plot_concentration_vs  d
  -start
 10  x = DIST
 20 PLOT_XY x, TOT("Mg")*1000, symbol = Plus, symbol_size = 2
 30 PLOT_XY x, TOT("Cl")*1000, symbol = Plus, symbol_size = 2
 40 PLOT_XY x, TOT("Ca")*1000, symbol = Plus, symbol_size = 2
 50 PLOT_XY x, mol("CO3-2")*1000, symbol = Plus, symbol_size = 2
  -end
USER_GRAPH 2
  -chart_title "Mineral amount"
  -headings  Calcite Dolomite
  -axis_titles "Distance" "Calcite mol/m3" "Dolomite mol/m3"
  -axis_scale x_axis 0 0.5
  -axis_scale y_axis 0 6e-2
  -axis_scale sy_axis 0 1.5e-3
  -connect_simulations false
  -plot_concentration_vs  d
  -start
 10  x = DIST
 30 PLOT_XY x, EQUI("Calcite")/0.002125, symbol = Plus, symbol_size = 3
 60 PLOT_XY x, KIN("Dolomite")/0.002125, symbol = Plus, symbol_size = 3,y-
axis 2
  -end
END
```

# Part 2: Uranium leaching problem description

The test problem presented here is based on the 2-D example of Šimůnek *et al.* (2012) and Yeh and Tripathi (1991). The geometry, geochemical system and the groundwater flow regime of the problem are mainly adapted from Šimůnek *et al.* (2012). The major changes are for example some different definitions of boundary and initial conditions for water flow and geochemical system as well as spatial- and temporal discretization. These differences will be introduced in details below, and the simulation results will be presented.

1. Model description

In this scenario, uranium leaches from a mill tailing into the soil, reaches the groundwater body in the hillslope, and finally approaches a stream (BC 4 in Fig. 1). Additionally, acid solution and sulfate are also released from the tailing, which leads to the dissoultion of calcite and precipitation of dolomite. The initial groundwater table is shown in Fig. 1.

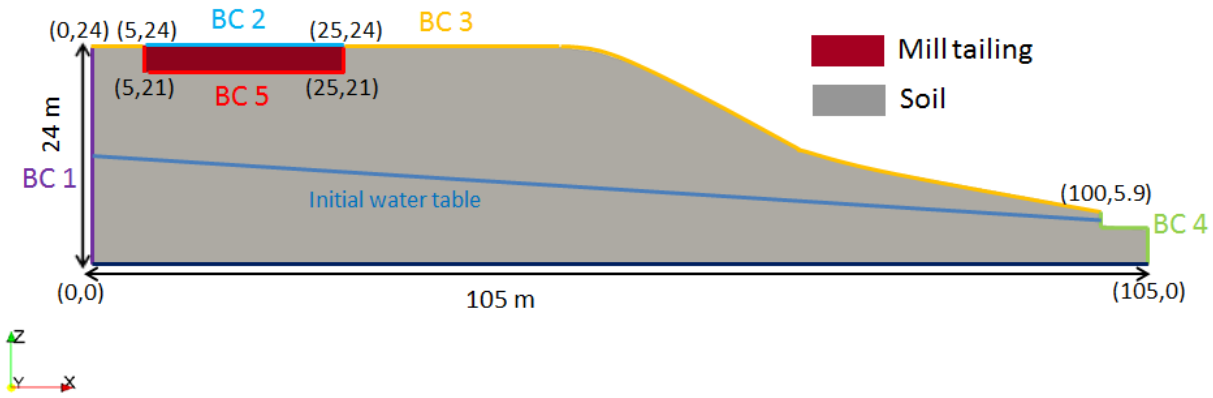


Fig.1 Geometry of the test example.

1.1. Water flow

Richards equation is applied to simulate the water flow in this unsaturated-saturated system. Same soil hydraulic parameters are applied for the tailing and the soil, which are listed in Tab. 1.

Tab.1 Soil properties of the model domain

| parameter | Residual saturation | Porosity | van Genuchten $\alpha$ | van Genuchten $n$ | Saturated hydraulic conductivity |
|---|---|---|---|---|---|
| Symbol and unit | $\theta_r(-)$ | $\phi\,(-)$ | $\alpha\ (m^{-1})$ | $n\,(-)$ | $K_s\ (cm \cdot d^{-1})$ |
| value | 0.078 | 0.43 | 0.036 | 1.56 | 378.43 |

The initial condition of pressure head is illustrated in Fig. 2, which can be obtained by defining the pressure head with the following equation:

$$h|(t=0) = 12 - 0.0714x - z \quad (1)$$

where *h* is the pressure head, *t* is the time, *x* and *z* are the coordinates in horizontal and vertical directions, respectively.

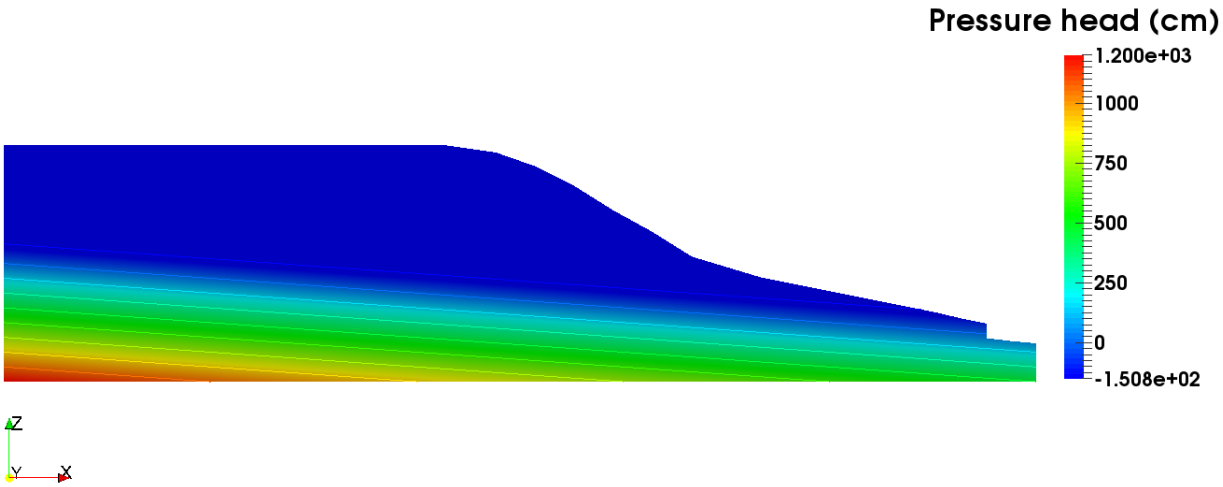


Fig 2. Initial pressure head.

Tab. 2 lists the boundary conditions for water flow on different boundaries illustrated in Fig. 1. Among these, a "constrained" head boundary condition is adopted for BC 1, which can be more realistic. This boundary condition switches between two different boundary condition types depending on the value of pressure head. If the pressure head is larger than 0 cm, then the Direchlet boundary condition will be applied; otherwise Neumann boundary condition (zero flux) will be used. This is different from Šimůnek *et al.* (2012), in which a constant pressure head of 12 m was applied. Additionally, we do not set a pumping well in the model domain as Šimůnek *et al.* (2012) did in their work.

Tab. 2 Boundary conditions for Richards flow.

| Name of Boundary | BC 1 | BC 2 | BC 3 | BC 4 | BC 5 |
|---|---|---|---|---|---|
| Type | Constrained head | Neumann | Neumann | Dirichlet | ---------- |
| Value | 12 m | 1.61E-7 m/s | 1.61E-8 m/s | 4.5 m | ---------- |

1.2. Mass transport and geochemical system.

In the present example, the same geochemical reaction networks (including aqueous complexation reactions and mineral precipitation/dissolution) and database from Šimůnek *et al.* (2012) are used. The amounts of aqueous species and minerals in the mill tailing are fixed as constant values during the entire simulation. For these purpose, we deactivate the calculation of solute transport and reactions in the mill tailing. At the interface between tailing and soil (i.e. BC 5) we set constant values for all species. Tab. 3 summarizes the values of all major components on BC 3, BC 5 and their initial distributions in mill tailing as well as soil. In the current study, longitudinal and transverse dispersivity are set as 1.0m and 0.2 m, respectively.

Tab. 3 Boundary conditions for solute transport and chemical reactions.

| | Values on Boundaries (mol/kgw) | | Initial values (mol/kgw) | |
|---|---|---|---|---|
| | BC 3 | BC 5 | Mill tailing | Soil |
| C(4) | 1.5E-3 | 1.0E-2 | 1.0E-2 | 1.5E-3 |
| Ca | 1.0E-3 | 1.2E-2 | 1.2E-2 | 1.55E-2 |
| U | 1.0E-8 | 5.0E-4 | 5.0E-4 | 1.0E-7 |
| P | 1.0E-6 | 1.0E-6 | 1.0E-6 | 1.0E-6 |
| S | 1.0E-4 | 5.81E-2 | 5.81E-2 | 1.48E-2 |
| Fe | 1.0E-7 | 3.5E-2 | 3.5E-2 | 1.0E-7 |
| O(0) | 4.5E-4 | 4.2E-4 | 4.2E-4 | 4.5E-4 |
| pH | 9.4 | 2.0 | 2.0 | 7.1 |
| pe | 4.0 | 18.5 | 18.5 | 13.5 |
| Calcite | 0 | 0 | 0 | 4.7E-4 |
| Gypsum | 0 | 0 | 1.4E-1 | 0 |

1.3. Spatial and temporal discretization.

Fig. 3 shows the finite element mesh employed for serial and parallel tests. The mesh consists of 14648 triangle elements and 7522 nodes. The total simulation time is 1000 days, which is discretized into 6369 time steps varying from 1E-7 to 24000 s.

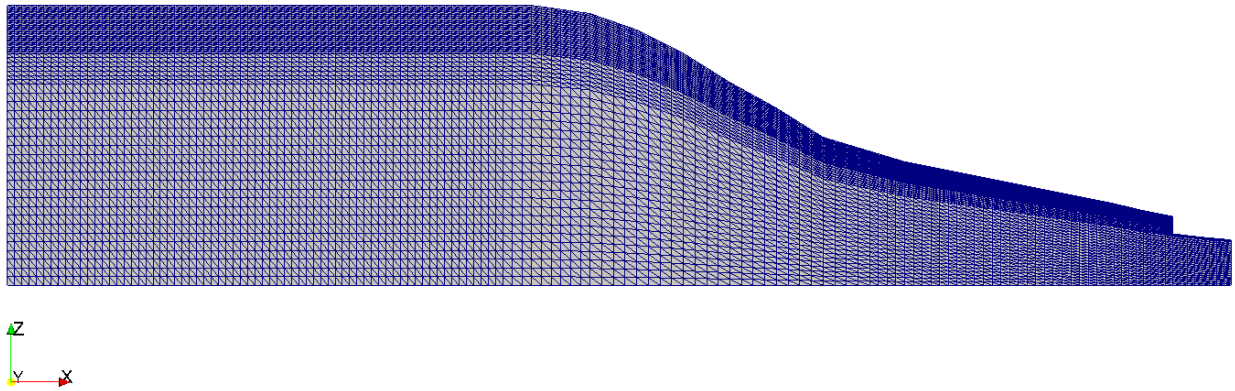


Fig. 3 Finite element mesh of the test problem.

## 2. Results

The distribution of water saturation and pressure head on the model domain after 1000 days is illustrated in Fig. 4. At this time point, an equilibrium state for water flow is reached. In the present example we did not set a pumping well at the location (40, 10), which can explain the different distribution of pressure head compared to Šimůnek *et al.* (2012) in the vicinity of the well.

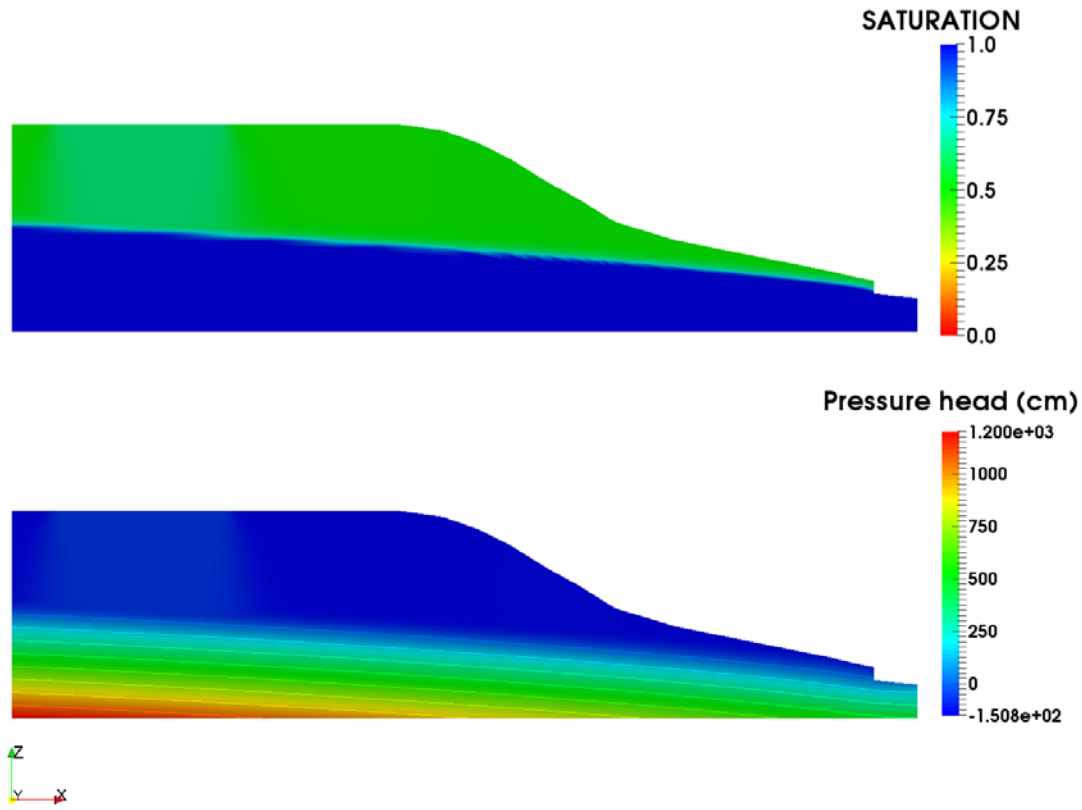


Fig. 4 Distribution of saturation and pressure head after 1000 days.

Fig. 5 illustrates the evolution of uranium concentration at time 200, 500 and 1000 days. The general trend is similar to the results obtained by Šimůnek *et al.* (2012). Due to a different flow field, the moving of uranium in our work is slower compared to theirs. Fig. 6 shows the concentration profiles of pH, calcite and gypsum at the end of simulation. The general features of all the three profiles match well to those presented by Šimůnek *et al.* (2012). In their work, the spread of acid solution and dissolution of calcite appear in a wider area of the vadose zone. The precipitation of gypsum happens mainly in the vicinity along the groundwater table, which is also the case in the present work. Precipitation of gypsum, however, does not appear in the lower left boundary in the present work, which can be due to the use of the constrained boundary.

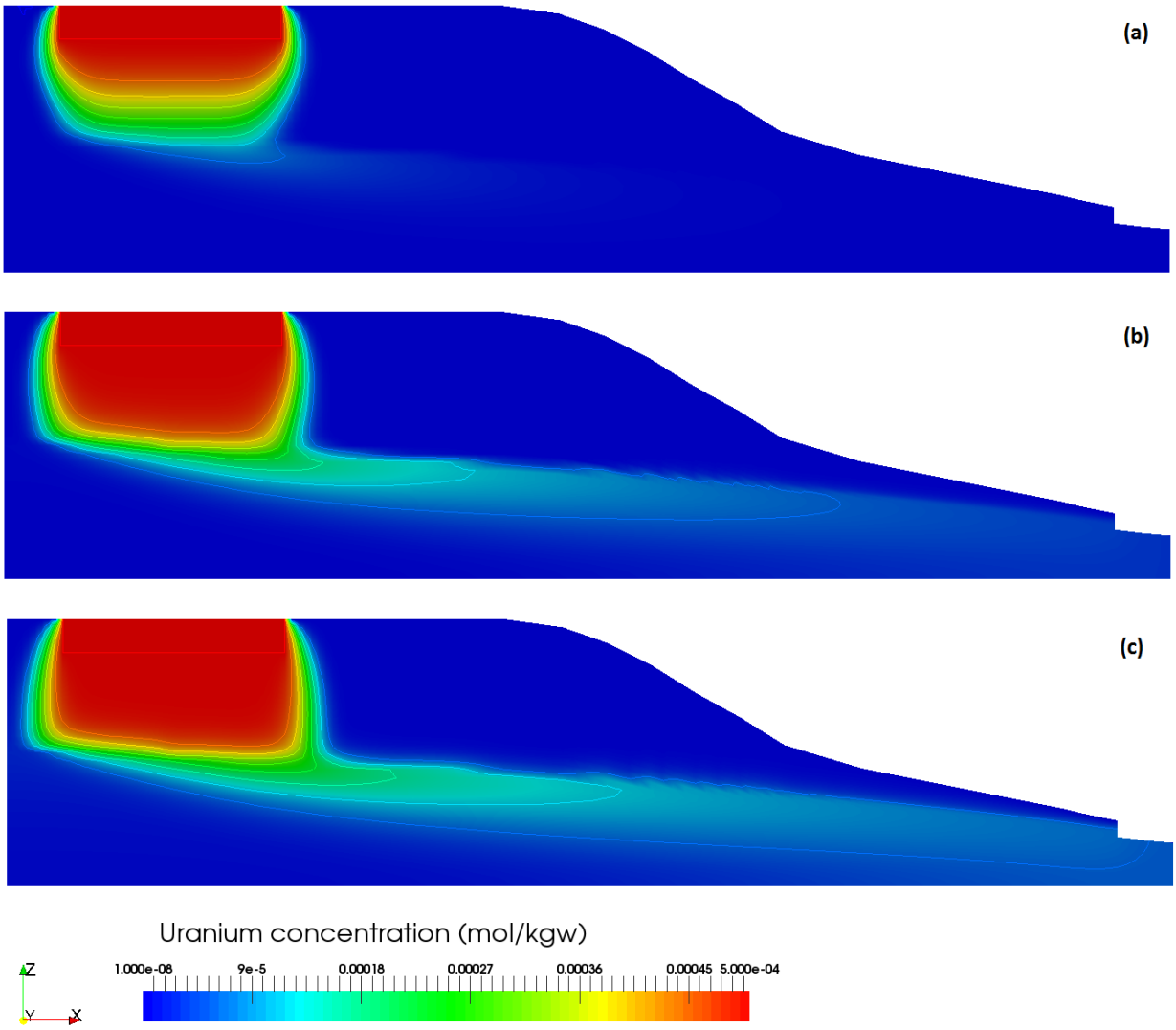


Fig. 5 Evolution of uranium concentration distribution at time 250 (a), 500 (b) and 1000 (c) day.

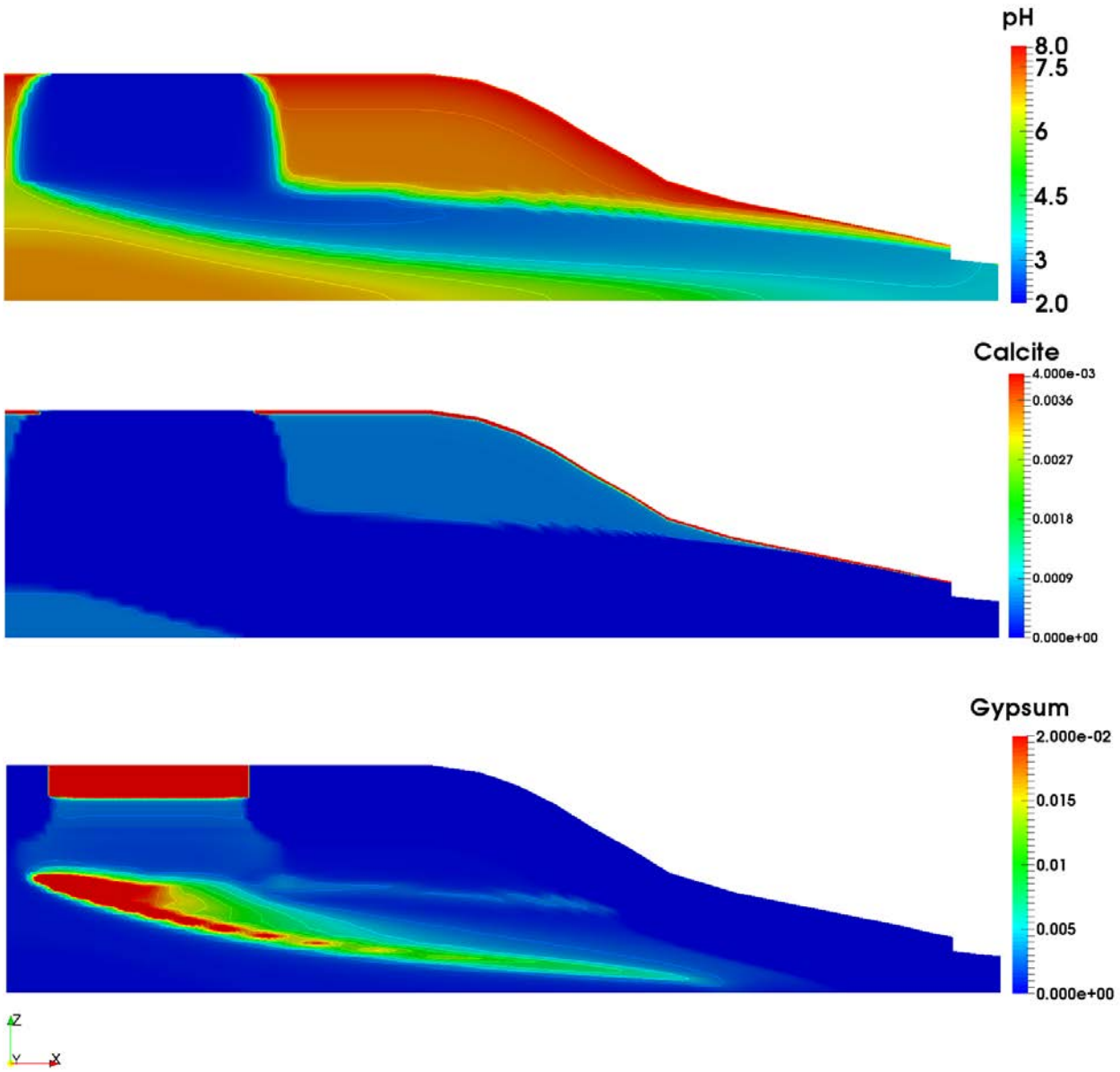


Fig. 6 Profiles of pH, calcite (mol/kgw) and gypsum (mol/kgw) at 1000 day.