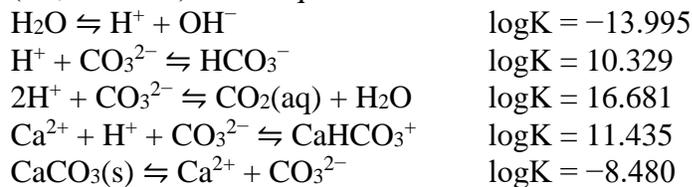


Description of the example CalE

This example models the dissolution of calcite by infiltrating water that is subsaturated with respect to calcite. Although the domain is in fact one-dimensional, a two-dimensional domain is used with a length of 100 m and a width of 1 m divided into 20 quadrilateral elements in the horizontal (x) direction. It has a uniform Darcy flux of 2 m/year (= $6.342 \cdot 10^{-5} \text{ kg m}^{-2} \text{ s}^{-1}$). The porosity is 0.1 and the dispersivity is 10 m. The simulated time is 5 years (= $1.58 \cdot 10^8 \text{ s}$), which equals the residence time in the domain. To model this, the Darcy flux is imposed on the left boundary and an (arbitrary) pressure of 0.0 MPa is imposed on the right boundary. The intrinsic permeability is set to 10^{-15} m^2 , but this parameter has no effect on the flow of water, only on the pressure gradient.

The chemical system together with chemical output options and numerical parameters is given in the file "Example_CalE_ChemSys.xml" (Figure 1). It has an aqueous phase with 7 chemical species and one mineral phase (calcite composed of one species CaCO_3). As the expression of Debye Hückel extended with \dot{b} term is used to calculate activities of aqueous species, parameters for this are required (IonSize and b_TD). It has 3 chemical components (Ca, C and H) and 5 equilibrium reactions:



Initially the water is saturated with calcite, has a pH of 8 and a total inorganic carbon concentration of 10^{-3} mol/kg . The inflowing water has a total inorganic carbon concentration of $3 \cdot 10^{-5} \text{ mol/kg}$, a total calcium concentration of $4 \cdot 10^{-5} \text{ mol/kg}$ and a pH of 5.5. These chemical compositions are called local chemistries and are given in the file "Example_CalE_LocalChem.xml" (Figure 2). Concentrations of all species have to be specified. In GiD the "solute" parameter of the "initial unknowns" and "flow B.C." refer to the number of local chemistry (in this file 1 for initial water and 2 for boundary water).

Both files use an xml format, which structures the input data. Its format is rather self-explanatory. A more exhaustive input description can be found in the documentation of CheProf (<https://github.com/upc-ghs/CheProf-for-Users>, chapter 3.1 and 3.2).

Figure 3 shows the pH after 5 years, calculated by the model. The pH increases at the inlet due to calcite precipitation.

```

<?xml version="1.0"?>
<ChemSys Name="Chemical system">

  <PhaseS>
    <Phase Name="Aqueous">
      <PhaseModel Type="Aqueous_DH"/>
      <Species Name="Ca+2" IonSize="5.0" b_TJ="0.165"/>
      <Species Name="HCO3-" IonSize="5.4" b_TJ="0.000"/>
      <Species Name="H+" IonSize="9.0" b_TJ="0.000"/>
      <Species Name="CaHCO3+" IonSize="6.0" b_TJ="0.000"/>
      <Species Name="CO3-2" IonSize="5.4" b_TJ="0.000"/>
      <Species Name="CO2" IonSize="3.0" b_TJ="0.100"/>
      <Species Name="OH-" IonSize="3.5" b_TJ="0.000"/>
    </Phase>
    <Phase Name="Calcite" Mob="Imm">
      <PhaseModel Type="Mineral" MolVol="0.36900E-04"/>
      <Species Name="CaCO3(s)"/>
    </Phase>
  </PhaseS>

  <ReactionS>
    <Reaction Name="OH- formation" Form=" = H+ + OH-" LogK="-13.995"/>
    <Reaction Name="HCO3- formation" Form="H+ + CO3-2 = HCO3-" LogK="10.329"/>
    <Reaction Name="CO2 formation" Form="2H+ + CO3-2 = CO2" LogK="16.681"/>
    <Reaction Name="CaHCO3+ formation" Form="Ca+2 + H+ + CO3-2 = CaHCO3+" LogK="11.435"/>
    <Reaction Name="Calcite dissolution" Form="CaCO3(s) = Ca+2 + CO3-2" LogK="-8.480"/>
  </ReactionS>

  <ComponentS Method="Manual">
    <Component Name="Ca" Form="Ca+2 + CaHCO3+ + CaCO3(s)"/>
    <Component Name="C" Form="HCO3- + CaHCO3+ + CO3-2 + CO2 + CaCO3(s)"/>
    <Component Name="H" Form="H+ - CO3-2 + CO2 - OH- - CaCO3(s)"/>
  </ComponentS>

  <Numerics Tol="0.10E-05" MaxIter="20" MaxFac="0.10E+04" UseLn="Yes"/>

  <Output>
    <Acti Species="H+; CaCO3(s)"/>
    <Comp Components="Ca; C"/>
    <VolF Phases="Calcite"/>
  </Output>

</ChemSys>

```

Figure 1. Chemical system of the example CalE.

```

<?xml version="1.0"?>
<LocalChemS>

  <!-- LocalChem 1 -->
  <LocalChem Name="InitialWater">
    <Phase Name="Aqueous" VolF="0.1">
      <Species Name="Ca+2" Conc="0.96030E-03"/>
      <Species Name="HCO3-" Conc="0.95920E-03"/>
      <Species Name="H+" Conc="0.10520E-07"/>
      <Species Name="CaHCO3+" Conc="0.94960E-05"/>
      <Species Name="CO3-2" Conc="0.52750E-05"/>
      <Species Name="CO2" Conc="0.20440E-04"/>
      <Species Name="OH-" Conc="0.10690E-05"/>
    </Phase>
    <Phase Name="Calcite" VolF="0.50000E-04">
      <Species Name="CaCO3 (s)" Conc="0.10000E+01"/>
    </Phase>
  </LocalChem>

  <!-- LocalChem 2 -->
  <LocalChem Name="BoundaryWater">
    <Phase Name="Aqueous" VolF="1.0">
      <Species Name="Ca+2" Conc="0.40000E-04"/>
      <Species Name="HCO3-" Conc="0.37330E-05"/>
      <Species Name="H+" Conc="0.31950E-05"/>
      <Species Name="CaHCO3+" Conc="0.18260E-08"/>
      <Species Name="CO3-2" Conc="0.57150E-10"/>
      <Species Name="CO2" Conc="0.26260E-04"/>
      <Species Name="OH-" Conc="0.32350E-08"/>
    </Phase>
    <Phase Name="Calcite" VolF="0.00000E+00">
      <Species Name="CaCO3 (s)" Conc="0.63096E-06"/>
    </Phase>
  </LocalChem>

</LocalChemS>

```

Figure 2. Chemical composition of the local chemistries of the example CalE.

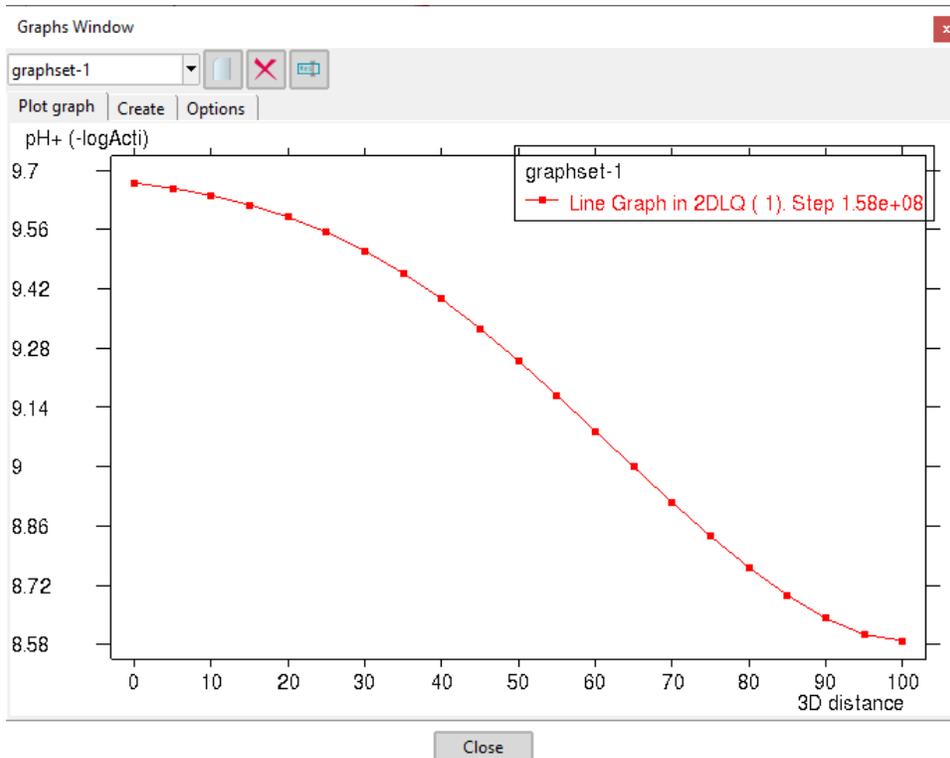


Figure 3. pH after 5 years of the example CalE, calculated by CODE_BRIGHT and produced by GiD.

Description of the example CalEPor

This example is the same as the previous example except that more calcite is dissolved, which effects porosity, permeability and pressure gradient. To do so, a longer time is simulated (500 years instead of 5 years) with a larger initial calcite mass fraction ($5 \cdot 10^{-2}$ instead of $5 \cdot 10^{-5}$) and calcite molar volume ($5 \cdot 10^{-2} \text{ m}^3 \text{ mol}^{-1}$ instead of $0.369 \cdot 10^{-4} \text{ m}^3 \text{ mol}^{-1}$).

Figure 4 to Figure 6 show some results. Rather sharp fronts can be seen of porosity change due to calcite dissolution at 40 and 80 m, after 244 and 500 years, respectively (Figure 4). Due to the lack of calcite pH can drop upstream (i.e., to the left) of these fronts (Figure 5). In the de-facto one-dimensional domain, the flow rate is uniform. As the permeability increases when porosity increases, pressure gradients must be lower upstream of the fronts (Figure 6) to maintain this uniform flow rate.

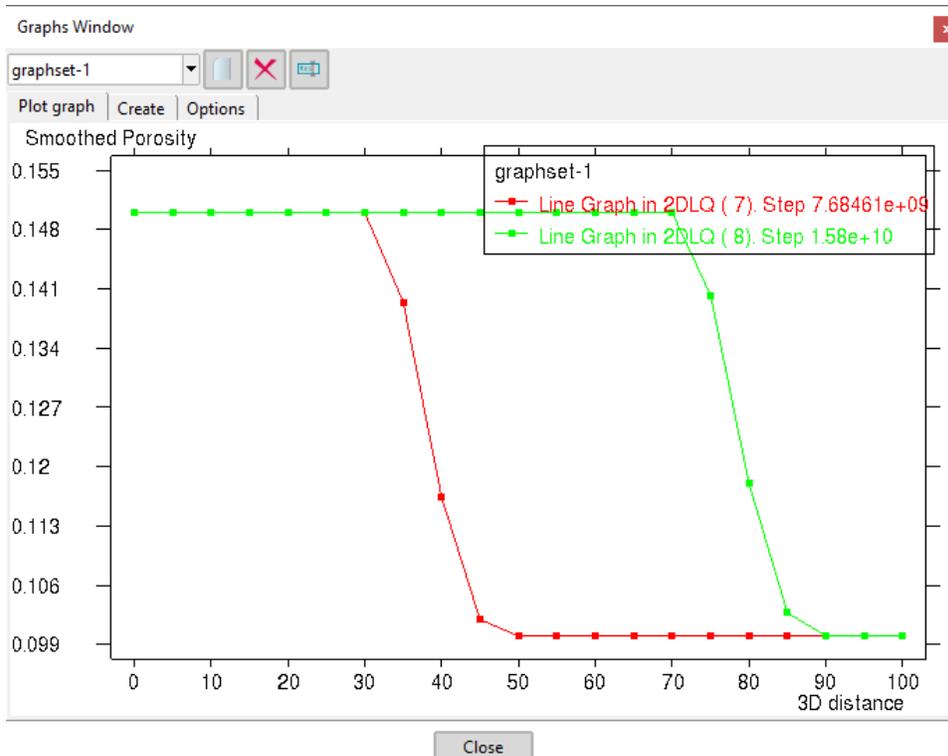


Figure 4. Porosity after 244 and 500 years ($7.68 \cdot 10^9$ and $1.58 \cdot 10^{10}$ s) of the example CalEPor, calculated by CODE_BRIGHT and produced by GiD.

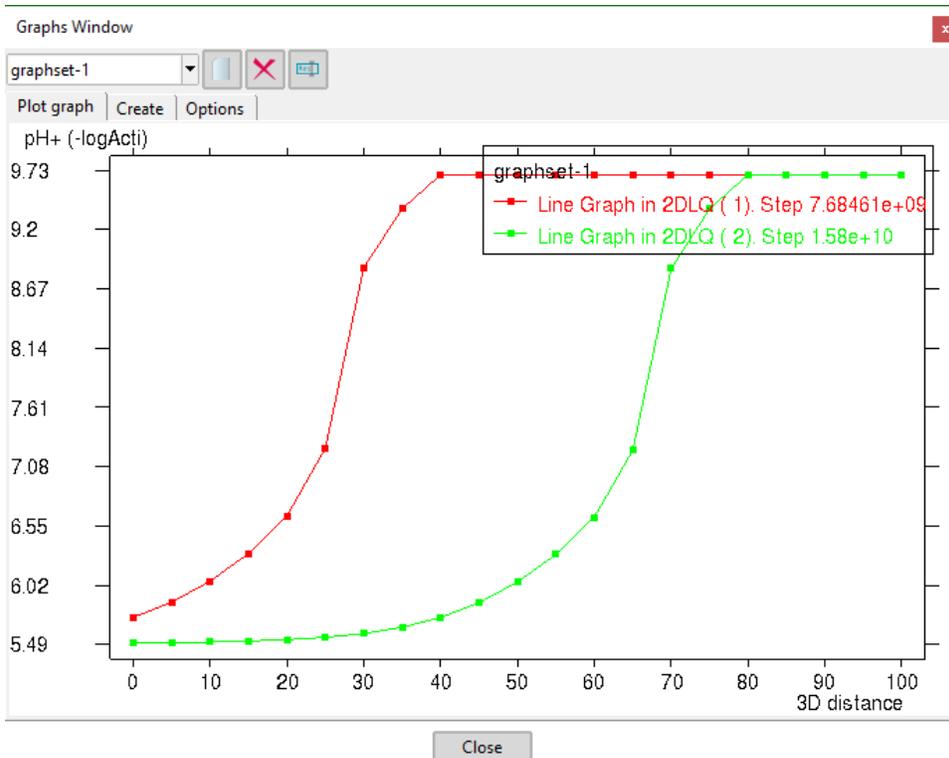


Figure 5. pH after 244 and 500 years ($7.68 \cdot 10^9$ and $1.58 \cdot 10^{10}$ s) of the example CalEPor, calculated by CODE_BRIGHT and produced by GiD.

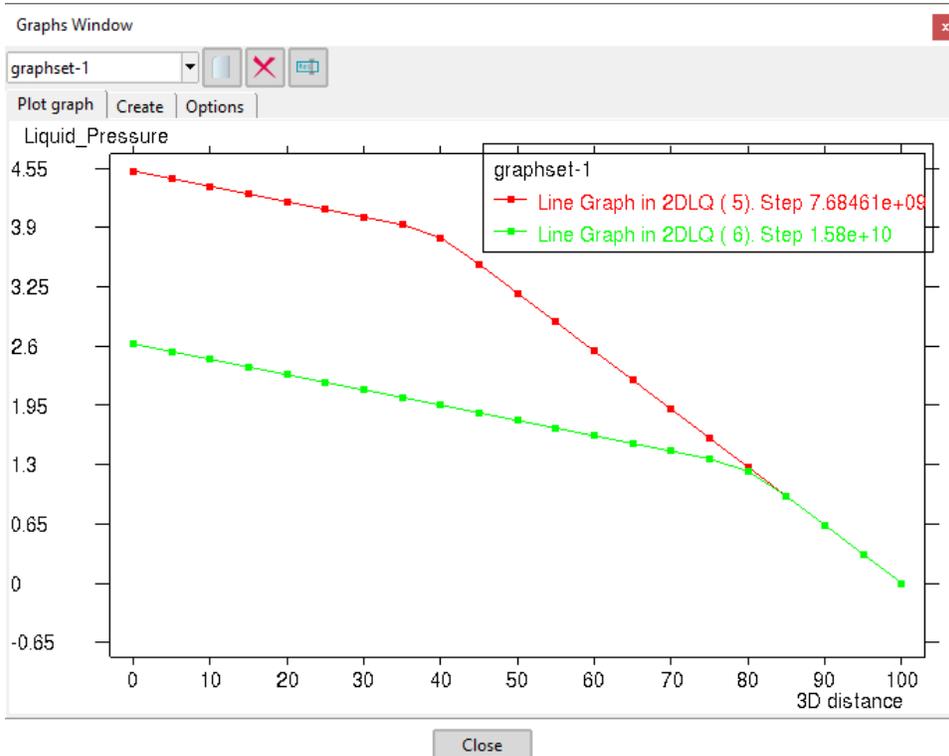


Figure 6. Liquid pressure (in MPa) after 244 and 500 years ($7.68 \cdot 10^9$ and $1.58 \cdot 10^{10}$ s) of the example CalEPor, calculated by CODE_BRIGHT and produced by GiD.