Geochemical and Reactive Transport modelling

Exercises

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Geochemical and Reactive Transport modelling

1. Speciation calculations
Speciation is the calculation of the concentrations of all the species in a chemical system

Speciation requires solution of a system of equations:

- **Mass action laws**
  - \( \text{H}_2\text{O} = \text{H}^+ + \text{OH}^- \)
  - \( \text{HCO}_3^- = \text{H}^+ + \text{CO}_3^{2-} \)
  - \( \text{CaCO}_3(s) = \text{Ca}^{2+} + \text{CO}_3^{2-} \)

- **Data equations** – based on our knowledge of the system
  - \( \text{pH} = -\log[\text{H}^+] \)
  - Charge balance: \( [\text{H}^+] + 2 [\text{Ca}^{2+}] - [\text{HCO}_3^-] - 2 [\text{CO}_3^{2-}] - [\text{OH}^-] \)
  - Total concentrations of dissolved species: \( C_{\text{tot}}, \text{Ca}_{\text{tot}} \)
  - Alkalinity: \( [\text{OH}^-] + [\text{HCO}_3^-] + 2 [\text{CO}_3^{2-}] \)
  - Electrical conductivity
  - Equilibrium with mineral
  - Equilibrium with gas
  - …
Gypsum solubility calculation

Calculate how much gypsum (CaSO₄·2H₂O) dissolves in clean water until equilibrium is reached

\[ \text{CaSO}_4\cdot2\text{H}_2\text{O} \rightarrow \text{Ca}^{2+} + \text{SO}_4^{2-} + 2\text{H}_2\text{O} \quad \text{log}K = -4.6 \]

- Mass action law: \( \log[\text{Ca}^{2+}] + \log[\text{SO}_4^{2-}] = -4.6 \)
- Mass balance:
  \[
  [\text{Ca}^{2+}] = x \quad x = \text{moles of dissolved gypsum / volume}
  [\text{SO}_4^{2-}] = x
  \]

- Solution
  \[
  [\text{Ca}^{2+}] = [\text{SO}_4^{2-}] = x = 10^{-2.3}
  \rightarrow \text{Moles of dissolved gypsum} = 10^{-2.3} = 5.0 \cdot 10^{-3} \text{ mol/l}
  \]
Speciation calculation for gypsum

✓ Mass Action Law:

\[ \text{CaSO}_4 \cdot 2\text{H}_2\text{O} = \text{Ca}^{2+} + \text{SO}_4^{2-} + 2\text{H}_2\text{O} \quad \log K = -4.6 \]

✓ Datum:

\[ \text{Ca}_{\text{tot}} = \text{Ca}^{2+} = 10^{-2} \text{ mol/l} \]

✓ Solution is trivial if \( a = c \rightarrow \text{SO}_4^{2-} = 10^{-4.6} \times 10^{-2} = 10^{-2.6} = 0.00251 \text{ mol/l} \)

✓ What if \( \gamma \neq 1 \)?
Speciation calculation for gypsum

✓ Mass Action Law:

$$\text{CaSO}_4 \cdot 2\text{H}_2\text{O} = \text{Ca}^{2+} + \text{SO}_4^{2-} + 2\text{H}_2\text{O} \quad \log K = -4.6$$

✓ Datum:

$$\text{Ca}_{\text{tot}} = \text{Ca}^{2+} = 10^{-2} \text{ mol/l}$$

✓ If $\gamma \neq 1$: iterative process

<table>
<thead>
<tr>
<th>iteration</th>
<th>m(Ca+)</th>
<th>m(SO4-)</th>
<th>l</th>
<th>$\gamma$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.01</td>
<td>0.002511886</td>
<td>0.025024</td>
<td>0.546336</td>
</tr>
<tr>
<td>1</td>
<td>0.01</td>
<td>0.008415521</td>
<td>0.036831</td>
<td>0.495419</td>
</tr>
<tr>
<td>2</td>
<td>0.01</td>
<td>0.0102342</td>
<td>0.040468</td>
<td>0.48311</td>
</tr>
<tr>
<td>3</td>
<td>0.01</td>
<td>0.010762362</td>
<td>0.041525</td>
<td>0.479757</td>
</tr>
<tr>
<td>4</td>
<td>0.01</td>
<td>0.010913333</td>
<td>0.041827</td>
<td>0.478815</td>
</tr>
<tr>
<td>5</td>
<td>0.01</td>
<td>0.010956295</td>
<td>0.041913</td>
<td>0.478549</td>
</tr>
<tr>
<td>6</td>
<td>0.01</td>
<td>0.010968506</td>
<td>0.041937</td>
<td>0.478473</td>
</tr>
<tr>
<td>7</td>
<td>0.01</td>
<td>0.010971975</td>
<td>0.041944</td>
<td>0.478452</td>
</tr>
<tr>
<td>8</td>
<td>0.01</td>
<td>0.01097296</td>
<td>0.041946</td>
<td>0.478446</td>
</tr>
<tr>
<td>9</td>
<td>0.01</td>
<td>0.01097324</td>
<td>0.041946</td>
<td>0.478444</td>
</tr>
</tbody>
</table>

Relative error (m SO4-2) 2.55E-05
Speciation requires solution of a system of equations:

- Mass action laws
  - \( \text{H}_2\text{O} = \text{H}^+ + \text{OH}^- \)
  - \( \text{HCO}_3^- = \text{H}^+ + \text{CO}_3^{2-} \)
  - \( \text{CaCO}_3(s) = \text{Ca}^{+2} + \text{CO}_3^{2-} \)

- Data equations – based on our knowledge of the system
  - \( \text{pH} = -\log[\text{H}^+] \)
  - Charge balance: \( [\text{H}^+] + 2 [\text{Ca}^{+2}] - [\text{HCO}_3^-] - 2 [\text{CO}_3^{2-}] - [\text{OH}^-] \)
  - Total concentrations of dissolved species: \( C_{\text{tot}}, \text{Ca}_{\text{tot}} \)
  - Alkalinity: \( [\text{OH}^-] + [\text{HCO}_3^-] + 2 [\text{CO}_3^{2-}] \)
  - Electrical conductivity
  - Equilibrium with mineral
  - Equilibrium with gas
  - …

Problem: it is a **non-linear system**

Iterative method is needed

A few codes exist to solve speciation
Programs to solve speciation

✓ Some of the most common codes:
  • Minteq (Pacific Northwest Laboratory)
  • EQ3NR (Lawrence Livermore National Laboratory)
  • Phreeqc (USGS)
  • …

✓ They use thermodynamic databases (logK and species properties)

✓ They calculate activity coefficients, $\gamma$, by means of the different models (Debye-Hückel, Trusdell Jones, Davis…)

✓ They have numerical methods to solve speciation (Picard, Newton-Raphson…)

✓ As output: they calculate concentrations of all species, saturation indices for minerals, pressure for gases, …
Phreeqc input file is organized in KEYWORDS and associated data blocks

- SOLUTION
- EQUILIBRIUM_PHASES
- REACTION
- KINETICS
- EXCHANGE
- SURFACE
- GAS_PHASE
- SOLID_SOLUTION
- SELECTED_OUTPUT
- END

To solve a speciation, the keyword SOLUTION is needed, followed by the water composition
PhreeqcII

---

**SOLUTION 1**

- **units**: ppm
- **pH**: 3.1
- **pE**: 16.0
- **Ca**: 489.3
- **Mg**: 69.8
- **Na**: 58.0
- **Fe**: 195.0
- **Al**: 92.2
- **Cl**: 35.0
- **C**: 100.0
- **S(6)**: 2820.0 or SO4

**REACTION 1**

# Calcite dissolution: 1.5 kg of Calcite are added in 100 steps

Calcite

0.015 moles in 100 steps

**EQUILIBRIUM_PHASES**

- **O2(g)**: -0.68
- **CO2(g)**: -3.5
- **gypsum**: 0.0 0.0
- **calcite**: 0.0 0.0
- **al(OH)3(a)**: 0.0 0.0 0.0
- **Fe(OH)3(a)**: 0.0 0.0

**SELECTED_OUTPUT**

- -file laboratorio.sel
- -ph
- -molalities Fe(OH)3 Al(OH)3 CaSO4
- -ai gypsum calcite

END
PhreeqcI
0.015 moles of calcite are added to the solution in 100 steps

\[ CaCO_3 \rightleftharpoons CO_3^{2-} + Ca^{2+} \quad \log K = -8.48 \]
PhreeqcI

2e-3 mol of calcite added
✓ EQUILIBRIUM_PHASES: to equilibrate the solution with a mineral or with a gas

Column 1: $\text{SI}=\log\Omega$ (for gases $= \log[\text{P}_i]$)
Column 2: initial quantity (default $= 10\text{mol}$)
SELECTED_OUTPUT: to print on file a series of output, chosen by the user

Open PhreeqcI on your computer and let's see how it works
Geochemical and Reactive Transport modelling

2. Reactive transport calculations
Phreeqc allows to solve 1D transport of solutes, water, colloids and heat

All the chemical processes modeled by Phreeqc, including kinetically controlled reactions, can be included in an advective-dispersive transport simulation

\[
\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} + v \frac{\partial c}{\partial x} + R
\]
One time step ("shift") contains 4 sub-steps in Phreeqc:

1. The mobile cell content is moved to the next cell
One time step ("shift") contains 4 sub-steps in Phreeqc:

2. Reactions between the solution and immobile phases (e.g., minerals, exchangers…) are calculated
Reactive transport modelling with Phreeqc

✓ One time step ("shift") contains 4 sub-steps in Phreeqc:

3. Dispersion is calculated by mixing the contents of adjacent cells
Reactive transport modelling with Phreeqc

✓ One time step (“shift”) contains 4 sub-steps in Phreeqc:

4. Again, reactions between the solution and immobile phases (e.g., minerals, exchangers…) are calculated

✓ The keyword to solve reactive transport is “TRANSPORT”
Reactive transport modelling with Phreeqc

Example of “TRANSPORT” block for Phreeqc input file:

```
Line 0:  TRANSPORT
Line 1:    -cells            5
Line 2:    -shifts           25
Line 3:    -time_step        1 yr 2.0
Line 4:    -flow_direction   forward
Line 5:    -boundary_conditions flux constant
Line 6:    -lengths          4*1.0 2.0
Line 7:    -dispersivities   4*0.1 0.2
Line 8:    -correct_disp     true
Line 9:    -diffusion_coefficient 1.0e-9
Line 10:   -stagnant         1  6.8e-6  0.3  0.1
Line 11:   -thermal_diffusion 3.0  0.5e-6
Line 12:   -initial_time     1000
Line 13:   -print_cells      1-3  5
Line 14:   -print_frequency  5
Line 15:   -punch_cells      2-5
Line 16:   -punch_frequency  5
```
Reactive transport modelling with Phreeqc

Example of “TRANSPORT” block for Phreeqc input file:

- **Line 0:** `TRANSPORT`
- **Line 1:** `-cells` 5
- **Line 2:** `-shifts` 25
- **Line 3:** `-time_step` 1 yr 2.0
- **Line 4:** `-flow_direction` forward
- **Line 5:** `-boundary_conditions` flux constant
- **Line 6:** `-lengths` 4*1.0 2.0
- **Line 7:** `-dispersivities` 4*0.1 0.2
- **Line 8:** `-correct Disp` true
- **Line 9:** `-diffusion_coefficient` 1.0e-9
- **Line 10:** `-stagnant` 1 6.8e-6 0.3 0.1
- **Line 11:** `-thermal_diffusion` 3.0 0.5e-6
- **Line 12:** `-initial_time` 1000
- **Line 13:** `-print_cells` 1-3 5
- **Line 14:** `-print_frequency` 5
- **Line 15:** `-punch_cells` 2-5
- **Line 16:** `-punch_frequency` 5

Number of cells in the column
Example of “TRANSPORT” block for Phreeqc input file:

Line 0:  TRANSPORT
Line 1:       -cells      5
Line 2:       -shifts    25  Number of time steps in simulation
Line 3:       -time_step 1 yr 2.0
Line 4:       -flow_direction forward
Line 5:       -boundary_conditions flux constant
Line 6:       -lengths    4*1.0 2.0
Line 7:       -dispersivities 4*0.1 0.2
Line 8:       -correct Disp true
Line 9:       -diffusion_coefficient 1.0e-9
Line 10:      -stagnant    1 6.8e-6 0.3 0.1
Line 11:      -thermal_diffusion 3.0 0.5e-6
Line 12:      -initial_time 1000
Line 13:      -print_cells 1-3 5
Line 14:      -print_frequency 5
Line 15:      -punch_cells 2-5
Line 16:      -punch_frequency 5
Reactive transport modelling with Phreeqc

Example of “TRANSPORT” block for Phreeqc input file:

Line 0: TRANSPORT
Line 1: -cells 5
Line 2: -shifts 25
Line 3: -time_step 1 yr 2.0
Line 4: -flow_direction forward
Line 5: -boundary_conditions flux constant
Line 6: -lengths 4*1.0 2.0
Line 7: -dispersivities 4*0.1 0.2
Line 8: -correct_disp true
Line 9: -diffusion_coefficient 1.0e-9
Line 10: -stagnant 1 6.8e-6 0.3 0.1
Line 11: -thermal_diffusion 3.0 0.5e-6
Line 12: -initial_time 1000
Line 13: -print_cells 1-3 5
Line 14: -print_frequency 5
Line 15: -punch_cells 2-5
Line 16: -punch_frequency 5

shifts / cells = number of pore volumes injected
Reactive transport modelling with Phreeqc

Example of “TRANSPORT” block for Phreeqc input file:

```plaintext
Line 0: TRANSPORT
Line 1: -cells 5
Line 2: -shifts 25
Line 3: -time_step 1 yr*2.0* [* = OPTIONAL ARGUMENT ]
Line 4: -flow_direction forward
Line 5: -boundary_conditions flux constant
Line 6: -lengths 4*1.0 2.0
Line 7: -dispersivities 4*0.1 0.2
Line 8: -correct_disp true
Line 9: -diffusion_coefficient 1.0e-9
Line 10: -stagnant 1 6.8e-6 0.3 0.1
Line 11: -thermal_diffusion 3.0 0.5e-6
Line 12: -initial_time 1000
Line 13: -print_cells 1-3 5
Line 14: -print_frequency 5
Line 15: -punch_cells 2-5
Line 16: -punch_frequency 5
```

time_step = L / velocity
Reactive transport modelling with Phreeqc

Example of “TRANSPORT” block for Phreeqc input file:

Line 0: TRANSPORT
Line 1: -cells 5
Line 2: -shifts 25
Line 3: -time_step 1 yr 2.0
Line 4: -flow_direction forward
Line 5: -boundary_conditions flux constant
Line 6: -lengths 4*1.0 2.0
Line 7: -dispersivities 4*0.1 0.2
Line 8: -correct_disp true
Line 9: -diffusion_coefficient 1.0e-9
Line 10: -stagnant 1 6.8e-6 0.3 0.1
Line 11: -thermal_diffusion 3.0 0.5e-6
Line 12: -initial_time 1000
Line 13: -print_cells 1-3 5
Line 14: -print_frequency 5
Line 15: -punch_cells 2-5
Line 16: -punch_frequency 5

Direction of flow into higher numbered cells
[alternative: backward]
Example of “TRANSPORT” block for Phreeqc input file:

```
Line 0: TRANSPORT
Line 1:   -cells          5
Line 2:   -shifts        25
Line 3:   -time_step     1 yr 2.0
Line 4:   -flow_direction forward
Line 5:   -boundary_conditions flux constant
Line 6:   -lengths       4*1.0 2.0
Line 7:   -dispersivities 4*0.1 0.2
Line 8:   -correct_disp true
Line 9:   -diffusion_coefficient 1.0e-9
Line 10: -stagnant      1 6.8e-6 0.3 0.1
Line 11: -thermal_diffusion 3.0 0.5e-6
Line 12: -initial_time 1000
Line 13: -print_cells 1-3 5
Line 14: -print_frequency 5
Line 15: -punch_cells 2-5
Line 16: -punch_frequency 5
```

B.C. for first and last cell:
1) **constant**: $c = c_0$ (Dirichlet)
2) **closed**: no flux at boundary, $v = 0$ (Neumann)
1) **flux (default)**: a given mass enters per unit time
Reactive transport modelling with Phreeqc

Example of “TRANSPORT” block for Phreeqc input file:

```plaintext
Line 0: TRANSPORT
Line 1:   -cells              5
Line 2:   -shifts             25
Line 3:   -time_step          1 yr 2.0
Line 4:   -flow_direction     forward
Line 5:   -boundary_conditions flux constant
Line 6:   -lengths

   4*1.0  2.0

Line 7:   -dispersivities     4*0.1  0.2
Line 8:   -correctDisp        true
Line 9:   -diffusionCoefficient 1.0e-9
Line 10:  -stagnant

   1   6.8e-6  0.3  0.1
Line 11:  -thermalDiffusion    3.0  0.5e-6
Line 12:  -initialTime         1000
Line 13:  -printCells          1-3  5
Line 14:  -printFrequency      5
Line 15:  -punchCells          2-5
Line 16:  -punchFrequency      5
```

List of lengths for each cell [m] (alternative to specify total length: `-length 100`)
Reactive transport modelling with Phreeqc

Example of “TRANSPORT” block for Phreeqc input file:

```
Line 0: TRANSPORT
Line 1:   -cells                     5
Line 2:   -shifts                   25
Line 3:   -time_step                1 yr 2.0
Line 4:   -flow_direction           forward
Line 5:   -boundary_conditions      flux constant
Line 6:   -lengths                  4*1.0 2.0
Line 7:   -dispersivities           4*0.1 0.2
Line 8:   -correct Disp             true
Line 9:   -diffusion_coefficient    1.0e-9
Line 10:  -stagnant                 1 6.8e-6 0.3 0.1
Line 11:  -thermal_diffusion        3.0 0.5e-6
Line 12:  -initial_time             1000
Line 13:  -print_cells              1-3 5
Line 14:  -print_frequency          5
Line 15:  -punch_cells              2-5
Line 16:  -punch_frequency          5
```

List of dispersivities for each cell [m]
### Reactive transport modelling with Phreeqc

Example of “TRANSPORT” block for Phreeqc input file:

<table>
<thead>
<tr>
<th>Line</th>
<th>Description</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>TRANSPORT</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>-cells</td>
<td>5</td>
</tr>
<tr>
<td>2</td>
<td>-shifts</td>
<td>25</td>
</tr>
<tr>
<td>3</td>
<td>-time_step</td>
<td>1 yr 2.0</td>
</tr>
<tr>
<td>4</td>
<td>-flow_direction</td>
<td>forward</td>
</tr>
<tr>
<td>5</td>
<td>-boundary_conditions</td>
<td>flux constant</td>
</tr>
<tr>
<td>6</td>
<td>-lengths</td>
<td>4*1.0 2.0</td>
</tr>
<tr>
<td>7</td>
<td>-dispersivities</td>
<td>4*0.1 0.2</td>
</tr>
<tr>
<td>8</td>
<td>correct_disp</td>
<td>true</td>
</tr>
<tr>
<td>9</td>
<td>diffusion_coefficient</td>
<td>1.0e-9</td>
</tr>
<tr>
<td>10</td>
<td>stagnant</td>
<td>1 6.8e-6 0.3 0.1</td>
</tr>
<tr>
<td>11</td>
<td>thermal_diffusion</td>
<td>3.0 0.5e-6</td>
</tr>
<tr>
<td>12</td>
<td>initial_time</td>
<td>1000</td>
</tr>
<tr>
<td>13</td>
<td>print_cells</td>
<td>1-3 5</td>
</tr>
<tr>
<td>14</td>
<td>print_frequency</td>
<td>5</td>
</tr>
<tr>
<td>15</td>
<td>punch_cells</td>
<td>2-5</td>
</tr>
<tr>
<td>16</td>
<td>punch_frequency</td>
<td>5</td>
</tr>
</tbody>
</table>

Dispersivity is multiplied by \((1+1/cells)\) for column ends with flux B.C. to improve modelling of effluent composition in case of few cells. Default: false
Reactive transport modelling with Phreeqc

Example of “TRANSPORT” block for Phreeqc input file:

```
Line 0:  TRANSPORT
Line 1:    -cells                5
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Line 4:    -flow_direction       forward
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Line 7:    -dispersivities       4*0.1 0.2
Line 8:    -correct_disp         true
Line 9:    -diffusion_coefficient 1.0e-9
Line 10:   -stagnant             1 6.8e-6 0.3 0.1
Line 11:   -thermal_diffusion    3.0 0.5e-6
Line 12:   -initial_time         1000
Line 13:   -print_cells          1-3 5
Line 14:   -print_frequency      5
Line 15:   -punch_cells          2-5
Line 16:   -punch_frequency      5
```

Effective diffusion coefficient [m²/s]  
Default: 0.3e-9 m²/s
Reactive transport modelling with Phreeqc

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<table>
<thead>
<tr>
<th>Line</th>
<th>Description</th>
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</tr>
</thead>
<tbody>
<tr>
<td>Line 0</td>
<td>TRANSPORT</td>
<td></td>
</tr>
<tr>
<td>Line 1</td>
<td>-cells</td>
<td>5</td>
</tr>
<tr>
<td>Line 2</td>
<td>-shifts</td>
<td>25</td>
</tr>
<tr>
<td>Line 3</td>
<td>-time_step</td>
<td>1 yr 2.0</td>
</tr>
<tr>
<td>Line 4</td>
<td>-flow_direction</td>
<td>forward</td>
</tr>
<tr>
<td>Line 5</td>
<td>-boundary_conditions</td>
<td>flux constant</td>
</tr>
<tr>
<td>Line 6</td>
<td>-lengths</td>
<td>4*1.0 2.0</td>
</tr>
<tr>
<td>Line 7</td>
<td>-dispersivities</td>
<td>4*0.1 0.2</td>
</tr>
<tr>
<td>Line 8</td>
<td>-correctDisp</td>
<td>true</td>
</tr>
<tr>
<td>Line 9</td>
<td>-diffusion_coefficient</td>
<td>1.0e-9</td>
</tr>
<tr>
<td>Line 10</td>
<td><strong>-stagnant</strong></td>
<td>1 6.8e-6 0.3 0.1</td>
</tr>
<tr>
<td>Line 11</td>
<td>-thermal_diffusion</td>
<td>3.0 0.5e-6</td>
</tr>
<tr>
<td>Line 12</td>
<td>-initial_time</td>
<td>1000</td>
</tr>
<tr>
<td>Line 13</td>
<td>-print_cells</td>
<td>1-3 5</td>
</tr>
<tr>
<td>Line 14</td>
<td>-print_frequency</td>
<td>5</td>
</tr>
<tr>
<td>Line 15</td>
<td>-punch_cells</td>
<td>2-5</td>
</tr>
<tr>
<td>Line 16</td>
<td>-punch_frequency</td>
<td>5</td>
</tr>
</tbody>
</table>

List of maximum immobile cells that can be associated to every mobile cell.
Reactive transport modelling with Phreeqc

Example of “TRANSPORT” block for Phreeqc input file:

```
Line 0: TRANSPORT
Line 1:    -cells  5
Line 2:    -shifts  25
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Line 4:    -flow_direction  forward
Line 5:    -boundary_conditions  flux constant
Line 6:    -lengths  4*1.0 2.0
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Line 10:   -stagnant  1 6.8e-6 0.3 0.1
Line 11:   -thermal_diffusion  3.0 0.5e-6
Line 12:   -initial_time  1000
Line 13:   -print_cells  1-3 5
Line 14:   -print_frequency  5
Line 15:   -punch_cells  2-5
Line 16:   -punch_frequency  5
```

Factors to calculate diffusive part of heat transport (T retardation factor, thermal diffusion coefficients)
Reactive transport modelling with Phreeqc

Example of “TRANSPORT” block for Phreeqc input file:

| Line 0: | TRANSPORT |
| Line 1: | -cells 5 |
| Line 2: | -shifts 25 |
| Line 3: | -time_step 1 yr 2.0 |
| Line 4: | -flow_direction forward |
| Line 5: | -boundary_conditions flux constant |
| Line 6: | -lengths 4*1.0 2.0 |
| Line 7: | -dispersivities 4*0.1 0.2 |
| Line 8: | -correct_disp true |
| Line 9: | -diffusion_coefficient 1.0e-9 |
| Line 10: | -stagnant 1 6.8e-6 0.3 0.1 |
| Line 11: | -thermal_diffusion 3.0 0.5e-6 |
| Line 12: | -initial_time 1000 |
| Line 13: | -print_cells 1-3 5 |
| Line 14: | -print_frequency 5 |
| Line 15: | -punch_cells 2-5 |
| Line 16: | -punch_frequency 5 |

Time to begin transport calculation (if omitted initial time is zero)
Example of “TRANSPORT” block for Phreeqc input file:

Line 0:  TRANSPORT
Line 1:    -cells          5
Line 2:    -shifts        25
Line 3:    -time_step     1 yr 2.0
Line 4:    -flow_direction forward
Line 5:    -boundary_conditions flux constant
Line 6:    -lengths     4*1.0  2.0
Line 7:    -dispersivities 4*0.1  0.2
Line 8:    -correct_disp   true
Line 9:    -diffusion_coefficient 1.0e-9
Line 10:   -stagnant   1  6.8e-6  0.3  0.1
Line 11:   -thermal_diffusion 3.0  0.5e-6
Line 12:   -initial_time    1000
Line 13:   -print_cells     1-3  5 List of cells for which results are written in the output file
Line 14:   -print_frequency  5
Line 15:   -punch_cells    2-5
Line 16:   -punch_frequency  5
Reactive transport modelling with Phreeqc

Example of “TRANSPORT” block for Phreeqc input file:

Line 0: TRANSPORT
Line 1:   -cells              5
Line 2:   -shifts            25
Line 3:   -time_step         1 yr 2.0
Line 4:   -flow_direction    forward
Line 5:   -boundary_conditions flux constant
Line 6:   -lengths           4*1.0 2.0
Line 7:   -dispersivities    4*0.1 0.2
Line 8:   -correctDisp       true
Line 9:   -diffusion_coefficient 1.0e-9
Line 10:  -stagnant          1  6.8e-6  0.3  0.1
Line 11:  -thermal_diffusion 3.0  0.5e-6
Line 12:  -initial_time      1000
Line 13:  -print_cells       1-3  5
Line 14:  **-print_frequency**  5  → List of shifts for which results are printed in the output file
Line 15:  -punch_cells       2-5
Line 16:  -punch_frequency   5
Example of “TRANSPORT” block for Phreeqc input file:

```
Line 0: TRANSPORT
Line 1:    -cells             5
Line 2:    -shifts           25
Line 3:    -time_step        1 yr 2.0
Line 4:    -flow_direction   forward
Line 5:    -boundary_conditions flux constant
Line 6:    -lengths           4*1.0 2.0
Line 7:    -dispersivities   4*0.1 0.2
Line 8:    -correct_disp     true
Line 9:    -diffusion_coefficient 1.0e-9
Line 10:   -stagnant          1  6.8e-6  0.3  0.1
Line 11:   -thermal_diffusion 3.0  0.5e-6
Line 12:   -initial_time     1000
Line 13:   -print_cells      1-3 5
Line 14:   -print_frequency  5
Line 15:   -punch_cells      2-5           
Line 16:   -punch_frequency  5
```

List of cells for which results are printed in the selected_output file.
Reactive transport modelling with Phreeqc

Example of “TRANSPORT” block for Phreeqc input file:

```
Line 0:  TRANSPORT
Line 1:    -cells          5
Line 2:    -shifts         25
Line 3:    -time_step      1 yr 2.0
Line 4:    -flow_direction forward
Line 5:    -boundary_conditions flux constant
Line 6:    -lengths        4*1.0 2.0
Line 7:    -dispersivities 4*0.1 0.2
Line 8:    -correct Disp   true
Line 9:    -diffusion_coefficient 1.0e-9
Line 10:   -stagnant       1 6.8e-6 0.3 0.1
Line 11:   -thermal_diffusion 3.0 0.5e-6
Line 12:   -initial_time   1000
Line 13:   -print_cells    1-3 5
Line 14:   -print_frequency 5
Line 15:   -punch_cells    2-5
Line 16:   -punch_frequency 5
```

List of shifts for which results are printed in the selected_output file.
Reactive transport modelling with Phreeqc

✓ The sequence of keywords for RT modelling is:

SOLUTION 1-5  # initial solution in the column
     ...(chemical composition)
END

SOLUTION 0  # solution injected in the column
     ...(chemical composition)

TRANSPORT  # transport parameters definition
     ...(transport parameters)

USER_GRAPH  # print (also SELECTED_OUTPUT is possible)
     ...

END
Reactive transport modelling with Phreeqc

✓ Today these commands are relevant:

SOLUTION 1-5  # initial solution in the column
...
(optional)EXCHANGE
...
(optional)EQUILIBRIUM_PHASES
...
END

SOLUTION 0    # solution injected in the column
...(chemical composition)

TRANSPORT    # transport parameters definition
...(transport parameters)

USER_GRAPH   # print (also SELECTED_OUTPUT is possible)
...
END
Reactive transport modelling with Phreeqc

✓ USER_GRAPH allows to plot results directly in Phreeqc:

```plaintext
USER_GRAPH # print (also SELECTED_OUTPUT is possible, see Slide 14)
-headings Ca Mg...
-chart_title "title"
-axis_titles "Pore Volumes" "c [mol/L]"
-plot_concentration_vs time
-start
10 graph_x (step_no + 0.5) / cell_no # to print pore_volume on x-axis
20 graph_y tot("Ca"), tot("Mg"), -la("H+"), SI("Goethite"), ... # You have to choose the appropriate variables
-end
```
Exercise 1: Acid mine drainage

✓ Objective: to simulate a treatment of an acidic water by means of adding calcite to the system

✓ Using the SOLUTION 1 of the previous exercises:

✓ Change the initial pH to 5.23
✓ Delete equilibrium conditions with calcite and CO2(g)
✓ Define a REACTION with calcite: add 1.0 moles in 20 steps
✓ Write the results in an Excel file (SELECTED_OUTPUT)
✓ Plot main results (pH, Saturation Index of calcite, Ca,tot, CO2) and comment: were you expecting this results? If so, why?
Exercise 2: Organic matter degradation

Consider the bed of a lake (1L), in equilibrium at first with atmospheric oxygen \((\log P[O_2(g)] = -0.7 \text{ bar})\) and organic matter, \(10^{-4} \text{ mol of } Fe(OH)_3(a)\) and \(10^{-4} \text{ mol of pyrolusite (MnO}_2(s))\), and, as regards the water, with pH = 7, TIC = \(10^{-3} \text{ mol/l}\) and a concentration of \(10^{-4} \text{ mol of NO}_3\) and \(10^{-4} \text{ mol of SO}_4\).

Evaluate the evolution of the system (pH, pe, concentrations) in parallel with the organic matter degradation.

Use the following syntax for the input file:

```plaintext
SOLUTION 1

pH 7
pe 13.6 equilibrium with P(O_2)
units mol/lbara
C(+4)
N(5)
S(6)
Fe equilibrium with Fe(OH)_3 (a)
Mn equilibrium with MnO_2(s)

EQUILIBRIUM_PHASES 1 # Equilibrium of the matter on the lake bed with Fe(OH)_3(a) and with pyrolusite

# Fe(OH)_3(a)
Pyrolusite

REACTION 1

CH2O 1.0
0.001 mol in 50 steps

SELECTED_OUTPUT ...
```
Exercise 3: 1D RT model with Phreeqc

✓ Consider a 1D domain, 8 mm long, filled with coarse sand (CEC = 1.1 meq/L) and pore water. The initial solution is 1mM NaNO₃.

✓ The pore water flow velocity is $3.17 \times 10^{-6}$ m/s and initial dispersivity and diffusion are null.

✓ The domain is flushed with 0.6 mM CaCl₂ solution.

✓ What chemical process do you think will be relevant in this model? How do you expect the fronts to be?
Exercise 3: 1D RT model with Phreeqc

1. Run this example with Phreeqc and plot the results using USER_GRAPH keyword. Comment the results: which species are exchanged?

2. Change diffusion_coefficient value to $1 \times 10^{-9}$ m$^2$/s: how do the results change?

3. Change the dispersivity value to 2 mm: how do the results change?

4. Add also 0.2 mM KNO$_3$ to the composition of the initial solution and comment the results: which species are exchanged?