Problem No. 1: Reactive Transport in Groundwater Systems

1.1 Aqueous Transport with NaCl solution

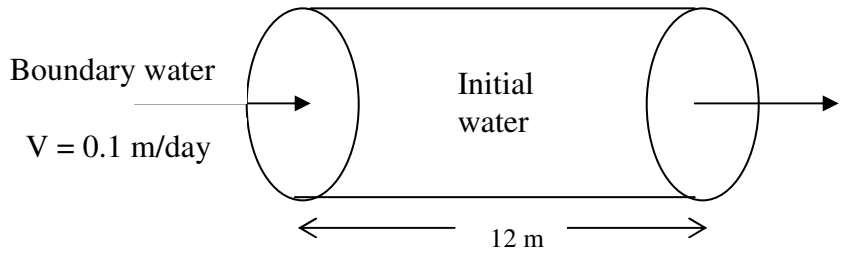

Figure 1-1 Simplified conceptual model for 1-D transport of NaCl solution.

A 1-D homogeneous fully water-saturated porous medium is considered (Figure 1-1), using the following parameters: a porosity of 0.1, a pore velocity v of 0.1 m/day, a solid density of 2600 kg/m^3. The flow system is a cylindrical, horizontal porous medium with cross-sectional area of 1 m^2 and 12 m length, divided into 60 grid blocks of 0.2 m thickness. Parameters for water flow are specified in file *flow.inp*. Water chemical compositions are assigned through data in files *solute.inp* and *chemical.inp*. In *chemical.inp*, the record starting with "(1 1)" following the record 'INITIAL AND BOUNDARY WATER TYPES' specifies that one initial water composition will be read, as well as one boundary water composition. The data entered in *solute.inp* under "default values of chemical zone codes for grid blocks" assign the first (and only) initial water type to all grid blocks in the problem, as well as assigning the first (only) boundary water composition to all injection grid blocks. Injection occurs only in block "F 1" (GENER block in file flow.inp), and with the boundary water chemical composition.

The EOS1 flow module (water and heat transfer) is used. **The complete input and output files are given in subdirectory: ~/problem-1/run_RT**).

A total of four species are simulated, H_2O, H^+, Na^+, and Cl^-. The species names must appear in the primary species block of the thermodynamic database. Initial concentrations for all four species are set equal to a very small value of 10^{-10} mol/kg (practically zero, because TOUGHREACT uses log10 calculations for concentrations in order to avoid convergence problems). The inlet concentrations are set equal to 10^{-1} mol/kg for all four species. The results are presented in Figure 1-2.

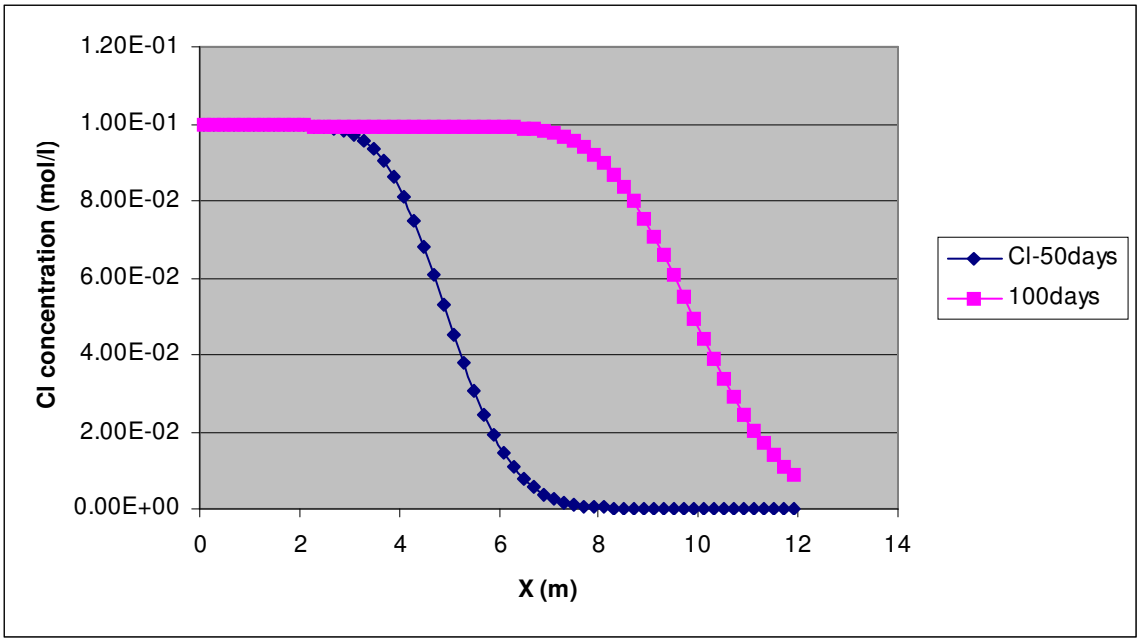

Figure 1-2. Distribution of Cl concentration (mol/l) at different times.

Steps to Run this Problem

Install TexPad

Step 1: Create a subdirectory *~practice/RT_water/NaCl*

Step 2: Copy all files from *~/problem-1/run_RT*: *flow.inp*, *solute.inp*, *chemical.inp*, *databas1.dat*, and *treact121_eos1*

Step 3: Browse through the input files

Step 4: Run the problem

Step 5: Look at the results. The spreadsheet *Cl_x.xls* can be used to plot concentrations by cut-an-pasting data from the *kdd_conc.dat* file at specific time periods

1.2 Aqueous transport with calcite, gypsum and dolomite

Batch system

Start with dilute water, then add calcite, CO_2 gas, gypsum and dolomite to obtain an initial solution for reactive geochemical transport. The batch system can be considered as a porous medium box. The 0.1 porosity is filled with dilute water initially.

Step 1: Create a subdirectory *~practice/RT_water/calcite/batch*

Step 2: Copy all input files from the previous problem (transport of NaCl solution): *flow.inp*, *solute.inp*, *chemical.inp*, *databas1.dat*, and *treact121_eos1*

- Modify file *flow.inp*: leave only one grid block under "ELEME", delete all connections under "CONNE", remove the lines under "GENER" (don't remove key words !!!)
- Modify file *solute.inp*: change grid block for the printout

Step 3: Add calcite and related species to file *chemical.inp*

- Add primary species: 'hco3-' and 'ca+2'
- Add secondary species: 'co2(aq)', 'co3-2', 'naco3-', and 'nahco3(aq)', 'caco3(aq)', and 'cahco3+'
- Add mineral: calcite as equilibrium (copy from the bottom of the file)

- Set nbwtype=0, delete boundary water zone
- Add initial water: 'hco3-' and 'ca+2' (copy from 'cl-' one, modify the name)
- Add initial mineral zone: ‘calcite’ (copy from the bottom of the file)
- Change file *solute.inp*: make sure grid block name for printing consistent with one in flow.inp, and allow printing calcite amounts
- Run
- See results in file *kdd_time.dat*
- Open *flow.inp*, change the simulation time from 8.64E6 to 8.64E3 s, change the time step from 8.64E3 to 8.64E0 s (*because carbonate reaction is fast*)

Step 4: Add co2(g) to file *chemical.inp*

- Add CO_2 to gas list: ‘co2(g)’
- Add initial gas zone: 'co2(g)' 0.01 ! bar
- Run
- Look at the results in file *kdd_time.dat*. Look at pH
- Change Pco2 form 0.01 to 0.1 bar
- Run
- Look at pH

Step 5: Add gypsum and related species to file *chemical.inp*

- Add primary species: 'so4-2'
- Add secondary species: 'naso4-', 'caso4(aq)'
- Add mineral: gypsum as equilibrium (copy from 'calcite', then modify)
- Add initial water: 'so4-2'
- Add initial mineral zone: ‘gypsum’ (copy from calcite, then modify)
- Adjust the sum of mineral volume fractions <=1.0
- Edit file *solute.inp* to specify more printout for both aqueous species and minerals
- Run
- Look at the results in file *kdd_time.dat*

Step 6: Add dolomite ($CaMg(CO_3)_2$)

- Add primary species: 'mg+2' (copy from 'ca+2' line, then modify the name)
- Add secondeary species: 'mgco3(aq)', 'mghco3+', 'mgso4(aq)'

- Add mineral: 'dolomite' as equilibrium
- Add initial water: 'mg+2'
- Add initial mineral zone: ‘dolomite’ (copy from calcite, then modify)
- Adjust the sum of mineral volume fractions <=1.0
- Change solute.inp for more printout for both aqueous species and minerals
- Run
- Look at the results in file *kdd_time.dat*

Step 7: Change all minerals from equilibrium to kinetic mode

- Change from equilibrium to kinetic mode for all minerals in the system definition (copy from the bottom of the file, and then replace)
- Change in “initial mineral zone’ (copy from the bottom and replace)
- Run
- Look at the results in files *kdd_time.dat* and *iter.dat*

Problem variations: change Pco2, or mineral reactive surface areas, then plot.

Reactive transport

This problem is based on the previous 1-D flow field for NaCl transport and the batch geochemical system. We now set up a 1-D reactive transport model.

Step 1: Create a subdirectory ~ */calcite/flow-through*

Step 2: Copy *flow.inp* and *treact121_eos1.exe* from the previous problem (transport of NaCl solution)

Step 3: Copy *chemical.inp*, *solute.inp*, and *Databas1.dat* from the batch problem

Step 4: From the *batch* folder,

- Open *chdump.out* and copy the bottom part (chemical composition)
- Paste in *chemical.inp,* and leave the previous initial water for recharge water

Step 5: Change nbwtype from 0 to 1

Step 6: Run and check the results

Step 7: Plot the results

Problem variations: Increase the Ca concentration by one order of magnitude, or change the concentration of other species for recharge waters, or use seawater from folder ~/problem-1/input_RT/chemical_seawater.inp

Different mineral zones

This problem is based on the previous 1-D reactive transport with an initial homogeneous mineral distribution. We now let the first half the column filled with calcite and gypsum, and the second with dolomite and gypsum.

Step 1: Create a subdirectory *~/calcite/mineral-zones*

Step 2: Copy files *flow.inp*, *solute.inp*, *chemical.inp*, *Databas1.dat* and *treact121_eos1.exe* from *~/calcite/flow-through*

Step 3: Make two mineral zones in file *chemical.inp*

- Change nmtype from 1 to 2
- Copy the mineral zone 1 down below the original data
- Change imtype from 1 to 2
- Modify zone 1 with calcite Vf=0.5, dolomite Vf=0.0, gypsum Vf=0.5
- Modify zone 2 with calcite Vf=0.0, dolomite Vf=0.5, gypsum Vf=0.5

Step 4: Make two mineral zones connected to grid blocks in file *solute.inp*. Use default values (one) for grid blocks 1-30

- Connect the mineral zone 2 to grid blocks 31-60 (copy from the bottom)

Step 5: Run and plot the results

Problem variation: Make three mineral zones (zone 3 with with calcite Vf=0.5, dolomite Vf=0.5, gypsum Vf=0.0)

SPACE FOR NOTES

INPUT FILES – CHEMICAL.INP

```
# Transport of NaCl solution'
'--------------------------------------------------------------------------'
'DEFINITION OF THE GEOCHEMICAL SYSTEM'
'PRIMARY AQUEOUS SPECIES'
'h2o'
'h+'
'na+'
'cl-'
'*'
'AQUEOUS COMPLEXES'
'oh-'           'nacl(aq)'
'*'
'MINERALS'
'*'         0  0   0            0
'GASES'
'*'
'SURFACE COMPLEXES'
'*'
'species with Kd and decay    decay constant(1/s)'
'*'                    0.0   0.0   0.0
'EXCHANGEABLE CATIONS'
'                 master     convention     ex. coef.'
'*'                 0            0            0.0
'--------------------------------------------------------------------------'
'INITIAL AND BOUDARY WATER TYPES'
1   1        !niwtype, nbwtype = number of initial and boundary waters
1    25.0                          !iwtype initial, temp (C)
'       icon        guess         ctot          '
'h2o'      1        1.000d+0      1.000d+0       ,  ,   0.
'h+'       3        1.0000d-7     1.000d-7       ,  ,   0.
'na+'      1        1.000d-10     1.000d-10      ,  ,   0.
'cl-'      1        1.000d-10     1.000d-10      ,  ,   0.
'*'        0         0.0          0.0            ,  ,   0.
1    25.0                           !itype boundary, temp (C)
'       icon        guess         ctot          '
'h2o'      1        1.000d+0      1.000d+0       ,  ,   0.      ! 1 kg H2O
'h+'       3        1.0000d-7     1.000d-7       ,  ,   0.
'na+'      1        1.000d-01     1.000d-01      ,  ,   0.      ! mol/kg H2O
'cl-'      1        1.000d-01     1.000d-01      ,  ,   0.
'*'        0         0.0          0.0            ,  ,   0.
'--------------------------------------------------------------------------'
'INITIAL MINERAL ZONES'
1                                  !nmtype= number of mineral zones
1                                  !imtype
'mineral         vol.frac.'
'*'                0.0      0
'--------------------------------------------------------------------------'
'INITIAL gas ZONES'
1                                       !ngtype= number of gas zones
1                                       !igtype
'gas      partial pressure'
'*'                0.0
'--------------------------------------------------------------------------'
'Permeability-Porosity Zones'
 1
 1
'perm law   a-par   b-par tcwM1'
    3    0.0000E+00    0.0000E+00
'--------------------------------------------------------------------------'
'INITIAL SURFACE ADSORPTION ZONES'
0                     !ndtype= number of sorption zones
```

```
'zone       ad.surf.(m2/kg)  total ad.sites (mol/l)'
'-------------------------------------------------------------------------------'
'INITIAL LINEAR EQUILIBRIUM Kd ZONE'
1                                  !kdtpye=number of Kd zones
1                                  !idtype
'species   solid-density(Sden,kg/dm**3)  Kd(l/kg=mass/kg solid / mass/l'
'*'                0.0                 0.0
'---------------------------------------if Sden=0 Kd store retardation factor'
'INITIAL ZONES OF CATION EXCHANGE'
0                       !nxtype= number of exchange zones
'zone            ex. capacity'
'-------------------------------------------------------------------------------'
'end'
```

INPUT FILES – SOLUTE.INP

```
'Transport of NaCl solution'
options for reactive chemical transport
    2    1    5 0.00    0    0    2    0    0 ! ISPIA,INIBOUND,ISOLVC,rcour,NGAS1,ichdump,kcpl,Ico2h2o,numdr
constraints for reactive chemical transport (4e10.4)
   1.00e-4   0.000     4.0     1.0       !sl1min, d1min, stimax, cnfact
Read input and output file names:
databas1.dat                    ! thermodynamic database
iter.dat                        ! iteration information
kdd_conc.dat                    ! aqueous concentrations in tecplot form
kdd_min.dat                     ! mineral data  in tecplot form
kdd_gas.dat                     ! gas data  in tecplot form
kdd_tim.dat                     ! concentrations at specific elements over time
Weighting parameters
       1.0       1.0    0.d-10   0.0d-05           ! itime wupc,dffun,dffung
data to convergence criteria:
    1 0.100E-03  300 0.100E-04   30 0.100E-05  0.00E-05  0.00E-05    !  ........ TOLDC,TOLDR
writing control variables:
   40    1    2    0    1    1    1   ! NWTI,NWNOD,NWCOM,NWMIN,IWCOMT,conflag(=1:mol/l),minflag(=1:Vf)
pointer of nodes for writing in time:
A11 8
pointer of components for writing:
    3    4
pointer of minerals for writing:

default values of chemical zone codes for grid blocks:
    1    1    1    1    0    0    1    1
chemical zone codes for nodes:

nodes connected to gas supply (i.e.) atmosphere

end
```

INPUT FILES – FLOW.INP

```
# Transport of NaCl solution
# EOS9 flow input
ROCKS----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
ROCK1    1     2600.       0.1  6.51E-12  6.51E-12  6.51E-12  0.00E+00     952.9
                                  0.00

MULTI----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
    1    1    2    6
! Isothermal case
START----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
REACT----1MOPR(20)-2----*----3----*----4----*----5----*----6----*----7----*----8
0002
PARAM----1----*-123456789012345678901234----*----5----*----6----*----7----*----8
   21000     50000000000000020571005000
 0.00000E0  8.6400E6    1.e+01  8.64E+03F   1      -9.806650
    1.E-06
           1.001E+05                25.0

RPCAP----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
    1           .333       -.1        1.        0.
    1      9.79020E3      .333        1.
TIMES----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
    2
   4.32e+6  8.6400E6
ELEME----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
A11 1             10.2000E+000.4000E+00          0.1000E+000.5000E+00-.5000E+00
A11 2             10.2000E+000.4000E+00          0.3000E+000.5000E+00-.5000E+00
A11 3             10.2000E+000.4000E+00          0.5000E+000.5000E+00-.5000E+00
 :
 :
 :
A1159             10.2000E+000.4000E+00          0.1170E+020.5000E+00-.5000E+00
A1160             10.2000E+000.4000E+00          0.1190E+020.5000E+00-.5000E+00

CONNE----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
A11 1A11 2                  10.1000E+000.1000E+000.1000E+01
A11 2A11 3                  10.1000E+000.1000E+000.1000E+01
A11 3A11 4                  10.1000E+000.1000E+000.1000E+01
 :
 :
 :
A1157A1158                  10.1000E+000.1000E+000.1000E+01
A1158A1159                  10.1000E+000.1000E+000.1000E+01
A1159A1160                  10.1000E+000.1000E+000.1000E+01

GENER----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
A11 1    0                  1     WATE  1.1576E-4          0.
v=0.1m/d
A1160    0                  1     WATE -1.1576E-4          0.
v=0.1m/d

INCON----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8

ENDCY
```

Input block for MESHMAKER

```
MESHM----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
XYZ
      90.0
NX      60        0.2
NY       1        1.0
NZ       1        1.0

ENDFI
```

Problem No. 2: Plug-Flow Reactor Experiment

2.1 Steps to Run this Problem

Step 1: Create a subdirectory *~practice/plugflow_quartz*

Step 2: Copy all files from *~/problem-2/quartz/input_quartz/*

Step 3: Read the problem description below. Browse through the input files and spreadsheet *quartz.xls*. The paper related to the experiment is also provided (Johnson et al., 1998).

Step 4: Run the problem, including exercises noted in Section 2.4. The calculated silica concentrations from file *time.dat* can be cut-and-pasted in worksheet *3.results* of spreadsheet *quartz.xls* to display and compare results with an analytical solution

Step 5: Compare computed silica concentrations at the plug outlet with the measured data (~105 ppm as Si), and with results in folder *~/problem-2/quartz/output_quartz/*

Step 6: Increase the quartz dissolution rate, by increasing either the surface area or the rate constant, and verify that the quartz solubility cannot be exceeded (use worksheet *6.Quartz solubility* in spreadsheet *quartz.xls* to compute the quartz solubility)

Step 7: As time allows, run the tuff plug-flow reactor experiment in a similar fashion (Section 2.4)

2.2 Description of Experiment

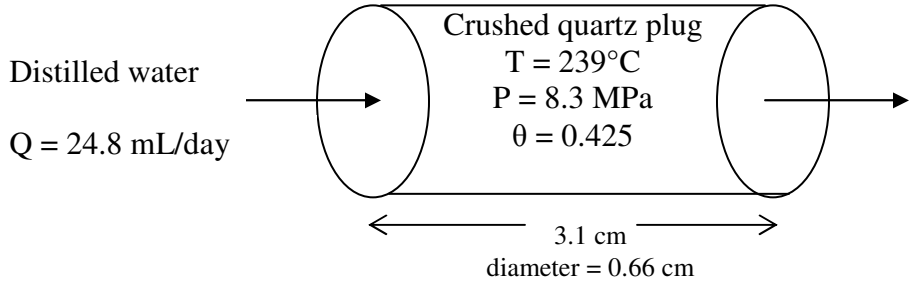

Figure 2-1. Quartz plug-flow reactor experiment.

This problem is based on the quartz dissolution experiment carried out by Johnson et al. (1998) using a plug-flow reactor, under experimental conditions shown in Figure 2-1 (details can be found in the attached paper). The problem is setup in a similar fashion as Problem No. 1. It is modeled as a 1-D, homogeneous, fully water-saturated porous medium, using the module EOS3. The general setup and calculation of input parameters for this problem are described below. The attached spreadsheet *quartz.xl*s summarizes setup parameters and their calculation, and provides a means to plot model results (silica concentrations at the plug outlet) and compare these results with an analytical solution.

2.3 General Setup

Refer to worksheet *1.Set-up* of spreadsheet *quartz.xls*. The problem is setup with 31 grid blocks of 1 mm length each (Δx = 1 mm), and 1 outlet boundary grid block (*rt 32*) with a given infinite volume to maintain constant pressure and temperature conditions. Flow is prescribed into the first gridblock (*rk 1*), and the computed silica concentration in the last gridblock (*rk 31*) is monitored.

MESHMAKER can be used to setup the numerical grid (see folder *~/problem-2/ quartz/input_quartz/test_meshm*). The grid spacing is constant at Δx = 0.001 m. Because the plug is circular in cross-section, the values Δy and Δz input into MESHMAKER must be specified such that the product of these values yield the plug cross-sectional area (Area [m^2] = π $(0.0066/2)^2$ with $\Delta y = \Delta z = \text{area}^{0.5}$). This ensures that the correct volume will be computed for each gridblock.

2.4 Calculation of Input Parameters

Refer to worksheet *2.flow rate* of spreadsheet *quartz.xls*. The calculation of various input parameters are implemented in this spreadsheet and discussed below.

Flow Rate

Mass injection rates for specific gridblocks are input in the GENER block of file *flow.inp*, or in a separate *GENER* file (see the TOUGH2 user manual). It is therefore necessary to convert the

known flow rate (Q, in this case in mL/day) to a mass injection rate (R_{mass} in kg/s) using the water density (ρ_w):

$$R_{mass}\ [\text{kg/s}] = Q\ [\text{mL/day}]\ 10^{-6}\ [\text{m}^3/\text{mL}]\ \rho_w\ [\text{kg/m}^3]\ /$$
$$\{60\ [\text{s/min}]\ 60\ [\text{min/hr}]\ 24\ [\text{hr/day}]\ \}$$

The fluid seepage velocity (v) in the plug relates to the mass injection rate through the plug cross-sectional area (A), porosity (θ) and the water density (ρ_w) as follows:

$$v\ [\text{m/sec}] = R_{mass}\ [\text{kg/sec}]\ /\ \{\ A\ [\text{m}^2]\ \theta\ \rho_w\ [\text{kg/m}^3]\ \}$$

Exercise: verify that the velocity output in file *flow.out* (given the correct input mass rate in the GENER block) matches the value calculated with the above expressions.

Input Water Composition

The water injected in the plug inlet is pure (distilled) water. The concentration of components H_2O and H^+ always need to be specified with TOUGHREACT. The value input in the concentration field for H_2O (in file *chemical.inp*) is always the liquid water mass in kilograms (generally 1 kg). The amounts ("concentrations") of other aqueous components are entered in moles. These amounts are divided (internally, after input) by the input water mass in kilograms to yield molal concentrations.

In the thermodynamic database of TOUGHREACT, H_2O and H^+ are defined as primary species, whereas OH^- is defined as a secondary species, thus associated with a negative stoichiometric coefficient for H^+ (e.g., $OH^- = H_2O - H^+$). Therefore, using this convention, the total (numerical) concentration hydrogen ion is zero for pure neutral water, because neutral conditions dictate equal OH^- and H^+ activities (about equal concentrations). Therefore, $Total_{H+} = [H^+] + [OH^-] = [H^+] - [H^+] = 0$. For this reason, in file *chemical.inp*, the composition of distilled water is input with a total hydrogen ion concentration of zero, from which a neutral pH is then calculated (neutral pH is ~5.6 at 239°C). Alternatively, pH can be specified by entering the H^+ activity (10^{-pH}) and setting the ICON flag = 3 in file *chemical.inp*, in which case

TOUGHREACT will compute the total H^+ (numerical) concentration. Note that the total H^+ (numerical) concentration is negative for alkaline solutions.

In this problem, we are only interested in the concentration of silica in the outlet. In this case, the input silica concentration is set to a small number (10^{-10} molal) to approximate a zero concentration. Note that for components other than H^+ and the redox species used to balance redox reactions, total (numerical) concentrations should not be specified as values equal to, or less than, zero.

Exercise: run the problem using input total $H^+ = 0$ (with ICON=1), then check the computed pH in file *chdump.out*. Restart the problem, this time entering the pH (with ICON=3), and check that the speciation results in file *chdump.dat* are identical.

Time Discretization

In general, time should be discretized such that the specified maximum time step remains less than one half the fluid travel time through one gridblock. This can be done by entering, in the *flow.inp* file, a maximum time step that meets this criterion, or by entering a non-zero *rcour* value in the *solute.inp* file. The *rcour* variable corresponds to the Courant Number, which is used by TOUGHREACT to automatically limit the time step size according to the fluid velocity as follows:

The maximum time step (Δt_{max}) is calculated as

$$\Delta t_{max} = \Delta t_{max0} \, |rcour|$$

with

$$\Delta t_{max0} = \Delta x / v_{max}$$

where Δx is the grid block length and v_{max} is the maximum liquid or gas velocity. When *rcour* is non-zero, v_{max} is taken as the maximum of the gas and liquid velocities at all grid blocks.

Exercise: using the above expressions, calculate a maximum time-step size corresponding to a Courant Number of 0.1. Verify that the maximum time step calculated in this way is not exceeded when running TOUGHREACT with *rcour* = 0.1 in file *solute.inp*. Also, evaluate the sensitivity of model results to the time step size.

Input Surface Areas

Refer to worksheet *5.suface area* of spreadsheet *quartz.xls* for calculations of the geometric surface area. Approximate surface areas can be calculated assuming spherical grains, although the method can be improved by assuming various types of grain packing. Here, areas are calculated simply assuming full spheres of radius *r*, as follows:

Area (sphere) = 4 *pi* r^2
Volume (sphere) = 4/3 *pi* r^3
Surface area [$Length^2/Length^3$] = *3*/*r*
Surface area [$Length^2$ / Mass] = 3/(*r density*)

Exercise: run the problem assuming different values of surface areas, until the computed concentration of silica in the plug outlet matches the measured value in the experiment (~105 ppm).

2.5 Tuff Plug-Flow Reactor Experiment

An experiment similar to the quartz plug-flow experiment was carried out by Johnson et al. (1998) using crushed volcanic tuff instead of quartz. The problem is modeled in the same manner and with the same setup as the quartz dissolution problem (Sections 2.2 to 2.4). The spreadsheet *tuff.xls* shows the model input parameters, which are essentially unchanged from the quartz dissolution problem. Most of the input changes are reflected in the file *chemical.inp*, which now includes all the volcanic tuff components (Al, Na, K, Mg, Ca, etc.) and the tuff composition. To run this problem:

Step 1: Create a subdirectory ~practice/1D-plugflow_tuff
Step 2: Copy all files from ~/problem-2/tuff/input_tuff/
Step 3: Browse through *tuff.xls* and through the input files

Step 4: Run the problem. The calculated concentrations of dissolved species from file *time.dat* can be cut-and-pasted in worksheet *3.results* of spreadsheet *tuff.xls* to display and compare results with measured data. Measured concentrations at the plug outlet in this experiment are the following:

Component	1 day (ppm)	35 days (ppm)
Si	392	353
Na	15	15
Al	7	7.5
K	3.8	2.4
Ca	0.07	0.08

Step 5: Vary input parameters such as surface area and/or rate constants to improve the match of model results to measured data

2.6 References

Johnson, J.W., Knauss, K.G., Glassley, W.E., DeLoach, L.D., and Tompson, A.F.B., 1998. Reactive Transport Modeling of Plug-Flow Reactor Experiments: Quartz and Tuff Dissolution at 240°C. Journal of Hydrology, 209, 81-111.

SPACE FOR NOTES

INPUT FILES – CHEMICAL.INP (QUARTZ PROBLEM)

```
'PFR-3 EXPT: Quartz Dissolution at 239 C'
'------------------------------------------------------------------------'
'DEFINITION OF THE GEOCHEMICAL SYSTEM'
'PRIMARY AQUEOUS SPECIES'
'h2o'
'h+'
'sio2(aq)'
'*'
'MINERALS'
'quartz'  1  1 0  0
0.2724e-07 0 1.0 1.0 0.0  0.0 0.0 0.0
'*'       0  0 0  0
'GASES'
'*'
'SURFACE COMPLEXES'
'*'
'species with Kd and decay    decay constant(1/s)'
'*'                    0.0d0
'EXCHANGEABLE CATIONS'
'                 master     convention     ex. coef.'
'*'                 0            0            0.0
'------------------------------------------------------------------------'
'INITIAL AND BOUDARY WATER TYPES'
1   1       !niwtype, nbwtype = number of initial and boundary waters
1    239.0                          !iwtype initial, temp (C)
'        icon        guess         ctot    '
'h2o'      1        1.000d+0       1.000d+0   ' ' 0.
'h+'       1       2.5881d-6      0.0         ' ' 0.
'sio2(aq)' 1       1.000d-10      1.000d-10   ' ' 0.
'*'        0         0.0           0.0        ' ' 0.
1    239.0                                    !itype boundary, temp (C)
'       icon        guess         ctot    '
'h2o'      1        1.000d+0       1.000d+0   ' ' 0.
'h+'       1       2.5881d-6       0.0        ' ' 0.
'sio2(aq)' 1       1.000d-10       1.000d-10  ' ' 0.
'*'      0         0.0           0.0          ' ' 0.
'------------------------------------------------------------------------'
'INITIAL MINERAL ZONES'
1                                  !nmtype= number of mineral zones
1                                  !imtype
'mineral         vol.frac.'
'quartz'           1.0000   1
0.0      300.0     0
'*'                0.0      0
'------------------------------------------------------------------------'
'INITIAL gas ZONES'
0
'gas         partial pressure'
'------------------------------------------------------------------------'
'Permeability-Porosity Zones'
 1
 1
'perm law   a-par   b-par tcwM1'
    3    0.0000E+00    0.0000E+00
'------------------------------------------------------------------------'
'INITIAL SURFACE ADSORPTION ZONES'
0                     !ndtype= number of sorption zones
'zone       ad.surf.(m2/kg)  total ad.sites (mol/l)'
'--------------------------------------if Sden=0 Kd store retardation factor'
'INITIAL LINEAR EQUILIBRIUM Kd ZONE'
1                                  !kdtpye=number of Kd zones
```

```
1                                    !idtype
'species   solid-density(Sden,kg/dm**3)  Kd(l/kg=mass/kg solid / mass/l'
'*'                 0.0                  0.0
'-------------------------------------if Sden=0 Kd store retardation factor'
'INITIAL ZONES OF CATION EXCHANGE'
0                       !nxtype= number of exchange zones
'zone            ex. capacity'
'-------------------------------------------------------------------------'
'end
```

INPUT FILES – CHEMICAL.INP (VOLCANIC TUFF PROBLEM)

```
'PFR-5 EXPT: Tuff Dissolution at 240 C'
'--------------------------------------------------------------------------------
'
'DEFINITION OF THE GEOCHEMICAL SYSTEM'
'PRIMARY AQUEOUS SPECIES'
'h2o'
'h+'
'ca++'
'na+'
'sio2(aq)'
'k+'
'alo2-'
'*'
'MINERALS'
'kaolinite'    1 3 0 0
0.4043e-8 0 1.0 1.0 0.0 0.0 0.0 0.0
0.4043e-8 0 1.0 1.0 0.0 0.0 0.0 0.0  1.e-6   0
0.0   0.    000.00
'paragonite'   1 3 0 0
0.1994e-9 0 1.0 1.0 0.0 0.0 0.0 0.0
0.1994e-9 0 1.0 1.0 0.0 0.0 0.0 0.0  1.e-6   0
0.0   0.    000.00
'muscovite'    1 3 0 0
0.1994e-9 0 1.0 1.0 0.0 0.0 0.0 0.0
0.1994e-9 0 1.0 1.0 0.0 0.0 0.0 0.0  1.e-6   0
0.0   0.    000.00
'gibbsite'     1 3 0 0
0.1213e-7 0 1.0 1.0 0.0 0.0 0.0 0.0
0.1213e-7 0 1.0 1.0 0.0 0.0 0.0 0.0  1.e-6   0
0.0   0.    000.00
'pyrophyllite' 1 3 0 0
0.4043e-8 0 1.0 1.0 0.0 0.0 0.0 0.0
0.4043e-8 0 1.0 1.0 0.0 0.0 0.0 0.0  1.e-6   0
0.0   0.    000.00
'boehmite'     1 3 0 0
0.1213e-7 0 1.0 1.0 0.0 0.0 0.0 0.0
0.1213e-7 0 1.0 1.0 0.0 0.0 0.0 0.0  1.e-6   0
0.0   0.    000.00
'diaspore'     1 3 0 0
0.1213e-7 0 1.0 1.0 0.0 0.0 0.0 0.0
0.1213e-7 0 1.0 1.0 0.0 0.0 0.0 0.0  1.e-6   0
0.0   0.    000.00
'k-feldspar'   1 3 0 0
0.3631e-8 0 1.0 1.0 0.0 0.0 0.0 0.0
0.3631e-8 0 1.0 1.0 0.0 0.0 0.0 0.0  1.e-6   0
0.0   0.    000.00
'albite_low'   1 3 0 0
0.7943e-7 0 1.0 1.0 0.0 0.0 0.0 0.0
0.7943e-7 0 1.0 1.0 0.0 0.0 0.0 0.0  1.e-6   0
0.0   0.    000.00
'anorthite'    1 3 0 0
0.1587e-6 0 1.0 1.0 0.0 0.0 0.0 0.0
0.1587e-6 0 1.0 1.0 0.0 0.0 0.0 0.0  1.e-6   0
0.0   0.    000.00
'quartz'       1 1 0 0
0.2836e-07 0 1.0 1.0 00.0 0.0 0.0 0.0
'cristobalite(alpha)'  1 1 0 0
0.3942e-7 0 1.0 1.0 0.0 0.0 0.0 0.0
'sio2(am)_G'    1 3 0 0
7.9433e-13 0 1.0 1.0 62.8 0.0 0.0 0.0
1.0 0 1.0 1.0 0.0 -7.07 0.0 -2598.0  1.e-6   0
```

```
0.0   0.    000.00
'*'       0  0 0  0
'GASES'
'*'
'SURFACE COMPLEXES'
'*'
'species with Kd and decay    decay constant(1/s)'
'*'                  0.0d0
'EXCHANGEABLE CATIONS'
'                 master     convention     ex. coef.'
'*'                 0           0            0.0
'-------------------------------------------------------------------------'
'INITIAL AND BOUDARY WATER TYPES'
1   1      !niwtype, nbwtype  = number of initial and boundary waters
1    240.0     0                    !iwtype initial, temp (C)
'        icon        guess         ctot          '
'h2o'       1        1.000d+0      1.000d+0   ' ' 0.
'h+'        1        2.5881d-6     0.0        ' ' 0.
'ca++'      1        1.000d-10     1.000d-10  ' ' 0.
'na+'       1        1.000d-10     1.000d-10  ' ' 0.
'sio2(aq)' 1         1.000d-10     1.000d-10  ' ' 0.
'k+'        1        1.000d-10      1.000d-10 ' ' 0.
'alo2-'      1        1.000d-10     1.000d-10 ' ' 0.
'*'         0        0.0           0.0        ' ' 0.
1    240.0     0
'       icon        guess         ctot
'h2o'       1        1.000d+0      1.000d+0   ' ' 0.
'h+'        1        2.5881d-6     0.0        ' ' 0.
'ca++'      1        1.000d-10     1.000d-10  ' ' 0.
'na+'       1        1.000d-10     1.000d-10  ' ' 0.
'sio2(aq)' 1         1.000d-10     1.000d-10  ' ' 0.
'k+'        1        1.000d-10     1.000d-10  ' ' 0.
'alo2-'      1       1.000d-10     1.000d-10  ' ' 0.
'*'       0         0.0           0.0        ' ' 0.
'-------------------------------------------------------------------------'
'INITIAL MINERAL ZONES'
1                              !nmtype= number of mineral zones
1                              !imtype
'mineral          vol.frac.'
'kaolinite'         0.0000   1
1.0e-3       300.     0
'paragonite'        0.0000   1
1.0e-3       300.     0
'muscovite'         0.0000   1
1.0e-3       300.     0
'gibbsite'          0.0000   1
1.0e-3       300.     0
'pyrophyllite'      0.0000   1
1.0e-3       300.     0
'boehmite'          0.0000   1
1.0e-3       300.     0
'diaspore'          0.0000   1
1.0e-3       300.     0
'k-feldspar'        0.2294   1
1.0e-3       300.     0
'albite_low'        0.1694   1
1.0e-3       300.     0
'anorthite'         0.0057   1
1.0e-3       300.     0
'quartz'            0.1507   1
1.0e-3       300.     0
'cristobalite(alpha)'   0.4449   1
1.0e-3       300.     0
'sio2(am)_G'        0.0000   1
```

```
1.0e-3       300.    0
'*'                0.0      0
'--------------------------------------------------------------------------------'
'INITIAL gas ZONES'
0
'gas         partial pressure'
'--------------------------------------------------------------------------------'
'Permeability-Porosity Zones'
 1
 1
'perm law   a-par   b-par tcwM1'
    3    0.0000E+00    0.0000E+00
'--------------------------------------------------------------------------------'
'INITIAL SURFACE ADSORPTION ZONES'
0                 !ndtype= number of sorption zones
'zone       ad.surf.(m2/kg)  total ad.sites (mol/l)'
'---------------------------------------if Sden=0 Kd store retardation factor'
'INITIAL LINEAR EQUILIBRIUM Kd ZONE'
1                             !kdtpye=number of Kd zones
1                             !idtype
'species   solid-density(Sden,kg/dm**3)  Kd(l/kg=mass/kg solid / mass/l'
'*'                0.0                 0.0
'---------------------------------------if Sden=0 Kd store retardation factor'
'INITIAL ZONES OF CATION EXCHANGE'
0                 !nxtype= number of exchange zones
'zone            ex. capacity'
'--------------------------------------------------------------------------------'
'end'
```

INPUT FILES – SOLUTE.INP (QUARTZ PROBLEM)

```
'PFR-3  Isothermal Quartz dissolution - solute transport input of TOUGHREACT '
options for reactive chemical transport
    2    1    5 0.50    0    0    0    0    0 ! ISPIA,INIBOUND,ISOLVC,rcour,NGAS1,ichdump,kcpl,Ico2h2o,numdr
constraints for chemical solver (3e10.4)
   1.00e-4   0.000     2.0              !sl1min, d1min, stimax
Read input and output file names:
ther_ympR4c.dat                ! thermodynamic database
iter.dat                       ! iteration information
tec_conc.dat                   ! aqueous concentrations in tecplot form
tec_min.dat                    ! mineral data  in tecplot form
tec_gas.dat                    ! gas data in tecplot form
time.dat                       ! concentrations at specific elements over time
Weighting parameters
       1.0       1.0    1.d-09       0.0    ! itime wupc,dffun,dffung
data for convergence criteria:
    1 0.100E-03  300 0.100E-04   30 0.100E-05  0.00E-05  0.00E-05
            !MAXITPR,TOLTR,MAXITPCH,TOLCH,MAXITPAD,TOLAD,TOLDC,TOLDR
writing control variables:
    2    1    1    1    1    0    1   ! NWTI,NWNOD,NWCOM,NWMIN,IWCOMT,conflag(=1:mol/l),minflag(=1:Vf)
pointer of nodes for writing in time:
rk 31
pointer of components for writing (15 per line, 15I5):
    3
pointer of minerals for writing (20 per line, 20I5):
    1
default values of chemical zone codes for grid blocks:
    1    1    1    1    0    0    1    1
chemical zone codes for nodes:

nodes connected to gas supply (i.e.) atmosphere

end
```

INPUT FILES – FLOW.INP (QUARTZ PROBLEM)

```
# PFR-3  Isothermal Quartz dissolution (239 C) (after ELS file for PFR-2)
ROCKS----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
rock1    1     2650.       .425  6.51E-12  6.51E-12  6.51E-12  0.00E+00       0.0
   0.0       0.0       0.0           0.20

START
PARAM----1----*-123456789012345678901234----*----5----*----6----*----7----*----8
   49999    99990000000000000020571003000   2.14e-5     2.334       0.0
 0.00000E0 3.600E+03    1.E+00  100.E+00dummy      -9.806650
    1.E-06
              8.3E+6          0.00000      2.39E2

REACT----1MOPR(20)-2----*----3----*----4----*----5----*----6----*----7----*----8
00000003


TIMES
    2
     600.0    3600.0

MULTI----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
    2    2    2    6


ELEME
rk  1          rock10.3421E-070.0000E+00               0.000     0.000     0.000
rk  2          rock10.3421E-070.0000E+00               0.001     0.000     0.000
rk  3          rock10.3421E-070.0000E+00               0.002     0.000     0.000
 :
 :
 :
rk 31          rock10.3421E-070.0000E+00               0.030     0.000     0.000
rt 32          rock10.3421E+530.0000E+00               0.031     0.000     0.000

CONNE
rk  2rk  1                  10.5000E-030.5000E-030.3421E-040.0000E+00
rk  3rk  2                  10.5000E-030.5000E-030.3421E-040.0000E+00
 :
 :
 :
rk 31rk 30                  10.5000E-030.5000E-030.3421E-040.0000E+00
rt 32rk 31                  10.5000E-030.5000E-030.3421E-040.0000E+00

GENER
rk  1    0                  1     WATE 2.34000E-70.7561E+05    0.

ENDCY
```

Input block for mesh generation

```
MESHMAKER1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
XYZ
  90.0
NX      31   0.001
NY       1 5.849E-03
NZ       1 5.849E-03

ENDFI
```