Example 21.--Modeling diffusion of HTO, $^{36}Cl^-$, $^{22}Na^+$ and Cs^+ in a radial diffusion cell

This example illustrates how PHREEQC-3 can simulate a diffusion experiment, as is now often performed for assessing the properties of a repository for nuclear waste in a clay formation. A sample is cut from a core of clay, enveloped in filters, and placed in a diffusion cell (see Van Loon et al., 2004, for details). Solutions with tracers are circulated at the surfaces of the filters, the tracers diffuse into and out of the clay, and the solutions are sampled and analyzed regularly in time. The concentration changes are interpreted with Fick's diffusion equations to obtain transport parameters that permit to estimate the distances that elements could travel in thousands of years when escaped from the waste. Transport in clays is mainly diffusive because of the low hydraulic conductivity, and solutes are further retarded by sorption (cations) and by exclusion of part of the porespace (anions).

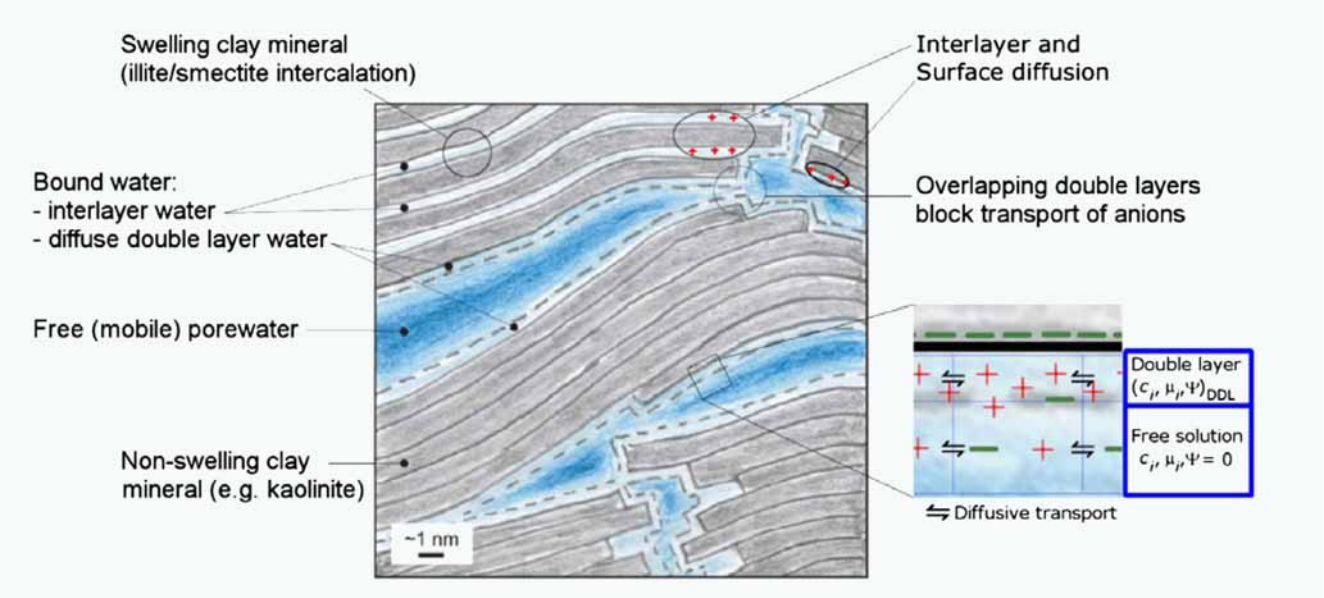

Figure 19. -- A diagram of the porespace in Opalinus Clay, showing three water-types with associated diffusion domains. Right hand side presents a pore as simplified in PHREEQC (Modified from NAGRA, 2002; Appelo et al., 2010).

For calculating diffusion, we need to account for the different diffusion coefficients of the tracers, the hindrance by the filters, and the properties of the clay. Figure 19 presents in a nutshell how the latter can be envisaged (Appelo et al., 2010). The pores in the clay are lined by clay minerals with a negative surface charge. The charge is partly neutralized by cations that are bound to the surface, partly by the electrostatic double layer that extends some distance in the pore, and contains an excess of cations (counter-ions, in

general) and a deficit of anions (co-ions, in general). In swelling clay minerals like montmorillonite, another part is neutralized by cations in the interlayer space. The concentration gradient that drives diffusion in free (uncharged) pore water is magnified in the double layer for counter-ions, diminished for co-ions, and remains the same for neutral species. The charge in the double layer lowers the dielectric permittivity of the water, which enhances the ion-association of cations and anions into neutral species. Also the viscosity of water may be higher than in free pore water. The double layers can overlap in pore constrictions, obstructing then the passage of anions which are forced to take longer routes than cations and neutral species that can go through.

PHREEQC can calculate an averaged double layer composition with identifier **-Donnan** in keyword **SURFACE**, which, in essence, neutralizes the surface charge. Solute species can be assigned an enrichment factor in the Donnan porespace to emulate the additional concentration change as a result of different ion association. For diffusion, the viscosity can be set differently with respect to free pore water. All these properties may be adjusted for the tracers HTO, Na^+, Cs^+ and Cl^- in this example.

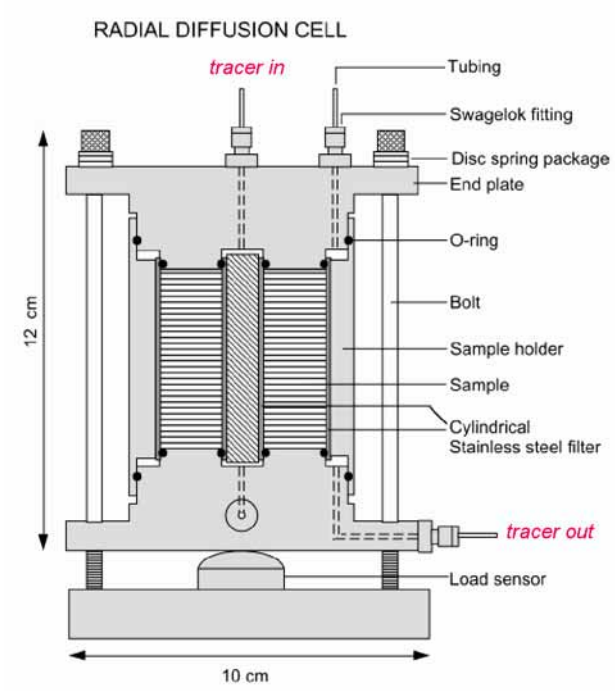

Figure 20. -- Radial diffusion cell used for analyzing diffusion parallel to the bedding plane of clay (Van Loon et al., 2004).

The experiments to be modeled were done in a radial diffusion cell, shown in Figure 20. The radial cell enables to measure diffusion parallel to the bedding plane of the clay (Van Loon et al., 2004). A solution with tracers is circulated at the surface of the inner filter, and another solution with the same major ions, but without tracers, contacts the surface of the outer filter. The latter solution is replaced regularly to keep the tracer concentration zero, and analyzed for the tracer that has diffused through the filters and the clay.

For a linear column, PHREEQC calculates diffusion automatically using the parameters entered with identifier **-multi_D** in keyword **TRANSPORT**. However, diffusion in the experiment is radial, and the filters have other properties than the clay. Also, the boundary solutions for the default (linear) column have a constant composition, whereas we want to know the concentration changes in these solutions during

the diffusion experiment. All these experimental details can be matched by calculating diffusion in a stagnant column, and defining the mixing factors among the individual cells with keyword **MIX**.

The mixing factors can be derived from Fick's diffusion equations, $F = -D_e \nabla C$ and $\frac{\partial C}{\partial t} = -\nabla \cdot F$, which transform to finite differences for an arbitrarily shaped cell *j*:

$$c_j^{t2} = c_j^{t1} + D_w \Delta t \sum_{i \neq j}^{n} \frac{\varepsilon_{ij}}{G_{ij} h_{ij}} \frac{A_{ij}}{V_j} (c_i^{t1} - c_j^{t1}) f_{bc}, \tag{22}$$

where c_j^{t1} is the concentration in cell *j* at the current time (mol/m^3), c_j^{t2} is the concentration in cell *j* after the time step, D_w is the tracer diffusion coefficient (m^2/s), Δt is the time step (seconds), *i* is an adjacent cell, ε_{ij} is the porosity over the interface of cells *i* and *j* (-), G_{ij} is the geometrical factor which corrects for tortuosity of the porous medium (-), h_{ij} is the distance between midpoints of the cells (m), A_{ij} is the shared surface area of cell *i* and *j* (m^2), V_j is the volume of cell *j* (m^3), and f_{bc} is a factor for boundary cells (-). The summation is for all cells (up to *n)* adjacent to *j*. When A_{ij} and h_{ij} are equal for all cells, a central difference algorithm is obtained that has second-order accuracy [$O(h)^2$], also for a radial geometry (Appelo et al., 2008). It is therefore advantageous to make the grid regular. However, the same accuracy is achievable for a heterogeneous domain, even with widely variable gridsize, if the harmonic mean of the parameters in $\frac{\varepsilon_{ij}}{G_{ij} h_{ij}}$ is used. These parameters together, translate the tracer diffusion coefficient D_w into the effective diffusion coefficient D_e.

The harmonic mean can be derived in general (omitting the activity coefficient for simplifying the formulas) as follows. The fluxes inside cells *i* and *j*, and over the interface of the two cells, must be the same and are given by:

$$J_{ij} = -\frac{\varepsilon_{ij}}{G_{ij}} D_w \frac{c_j - c_i}{h_{ij}}, \tag{23}$$

$$J_i = -\frac{\varepsilon_i}{G_i} D_w \frac{c_{ij} - c_i}{h_i/2}, \text{ and} \tag{24}$$

$$J_j = -\frac{\varepsilon_j}{G_j} D_w \frac{c_j - c_{ij}}{h_j/2}, \tag{25}$$

where h is the cell-length (m), and c_{ij} is the concentration at the interface. Substituting $\varepsilon_i / G_i = g_i$, in equation 24 and similar in equation 25, and combining the two equations while eliminating the concentration c_{ij} gives:

$$J_{ij} = J_i = J_j = -\frac{2}{h_j/g_j + h_i/g_i} D_w (c_j - c_i) . \quad (26)$$

**Refer in transport to this example, delete the derivation there **

By multiplying the flux with the surface area, the timestep and the boundary factor, and dividing by the volume of the cell for which the concentration change is calculated (here: cell j), the mixing factor is obtained:

$$mixf_{ij} = \frac{2}{h_j/g_j + h_i/g_i} D_w \frac{A_{ij}\Delta t}{V_j} f_{bc} \quad (47)$$

where f_{bc} is 2 for cells in contact with a constant concentration cell, and 1 otherwise. When calculating *mixf*, V_j is set to 10^{-3}m^3, and for D_w the default diffusion coefficient is used, entered with identifier **-multi_D**. In multicomponent diffusion-mode, PHREEQC adapts the volume V_j (entered as 10^{-3}m^3 in equation 47), to the actual volume of water in cell j, and multiplies the mixing factor for each solute species a by the ratio of the tracer diffusion coefficient for a and the default diffusion coefficient (= $D_{w,a}/ D_w$).

To avoid numerical oscillations, it is necessary that *mixf* < 0.5, which can be realized generally by limiting the timestep to a maximum. This maximum is usually determined by the cell with the smallest volume (in the model) and the proton, which normally has the highest tracer diffusion coefficient. However, if the proton concentration is sufficiently buffered by alkalinity or other species, and the solutions are uniform except for the tracers, the tracer with the highest D_w may be selected for calculating the maximal permissible timestep. If, nevertheless, PHREEQC warns that negative concentrations are calculated (and the program stops since the system may reach an infeasible state), the timestep can be substepped. For example, **-time_step** 5e2 3 will subdivide the time step of 500 seconds in three equal ones of 166.7 seconds.

The input file in table 57 defines the physical and chemical properties of the clay pore space, and writes the mixing factors for diffusional transport in the filters and the clay. The filters used by Van Loon have geometrical factor of 4 for all the tracers, whether charged or not (Glaus et al., 200**). In the clay, the geometrical factor for HTO is 6.2. For cations, the geometrical factor appears to be 2 - 4 times smaller than for tritium. However, in the example, we will use, in the clay, the same geometrical factor for HTO and the cations, but obtain the smaller apparent geometrical factors by subdividing the porespace in free pore water

and double layer water. The concentrations of cations are higher in double layer water than in free pore water, and hence, also the concentration gradient of cations are higher, enhancing their diffusion as noted before. In models that do not account for this physical aspect of the clay porespace, the faster diffusion is mimicked by diminishing the geometrical factor. For anions, the geometrical factor is about 1.5 times higher than for tritium. This is related to narrowing of the pores, where overlapping double layers obstruct the passage of anions while tritium and the cations can go through unhindered. The model accounts for the observed, smaller accessible porosity for anions than for tritium and cations by anion exclusion in the double layer.

Table 57.--Input file for example 21, calculating diffusion of HTO and other tracers in a radial cell.

```
TITLE Radial diffusion cell, Van Loon et al., 2004, EST 38, 5721.
SOLUTION_MASTER_SPECIES
# element   species   alk gfw_formula element_gfw
  Hto       Hto       0.0   20        20
  Na_tr     Na_tr+    0.0   22        22
  Cl_tr     Cl_tr-    0.0   36        36
  Cs        Cs+       0.0  132.905   132.905
SOLUTION_SPECIES
  Hto = Hto;        log_k 0; -gamma 1e6 0;     -dw 2.236e-9
  Na_tr+ = Na_tr+;  log_k 0; -gamma 4.0 0.075; -dw 1.33e-9; -erm_ddl 1.23
  Cl_tr- = Cl_tr-;  log_k 0; -gamma 3.5 0.015; -dw 2.03e-9
  Cs+ = Cs+;        log_k 0; -gamma 3.5 0.015; -dw 2.07e-9; -erm_ddl 1.23
SURFACE_MASTER_SPECIES
  Su_fes Su_fes-   # Frayed Edge Sites
  Su_ii Su_ii-     # Type II sites of intermediate strength
  Su_ Su_-         # Double layer, planar sites are modeled with EXCHANGE
SURFACE_SPECIES
  Su_fes- = Su_fes-; log_k 0
  Na+ + Su_fes- = NaSu_fes; log_k 10
  Na_tr+ + Su_fes- = Na_trSu_fes; log_k 10
  K+ + Su_fes- = KSu_fes; log_k 12.4
  Cs+ + Su_fes- = CsSu_fes; log_k 17.14

  Su_ii- = Su_ii-; log_k 0
  Na+ + Su_ii- = NaSu_ii; log_k 10
  Na_tr+ + Su_ii- = Na_trSu_ii; log_k 10
  K+ + Su_ii- = KSu_ii; log_k 12.1
  Cs+ + Su_ii- = CsSu_ii; log_k 14.6

  Su_- = Su_-; log_k 0

EXCHANGE_SPECIES
  Na_tr+ + X- = Na_trX; log_k 0.0;  -gamma 4.0 0.075
  Cs+ + X- = CsX;       log_k 2.04; -gamma 3.5 0.015

SOLUTION 0-2 column with only cell 1, two boundary solutions 0 and 2.
  Na 1; Cl 1
END
```

```
KNOBS; -iter 2000; -pe_step 5; -step 10; -diag true; -conv 1e-7

SOLUTION 3 tracer solution
  pH 7.6; pe 14 O2(g) -1.0; temp 23
  Na 240; K 1.61; Mg 16.9; Ca 25.8; Sr 0.505
  Cl 300; S(6) 14.1; Fe(2) 0.0; Alkalinity 0.476
# uncomment tracer concentration 1 by 1
  Hto 1.14e-3;   -water 0.2 # 1.14e-6 mM in the xpt
#  Cl_tr 2.505e-2; -water 0.502
#  Na_tr 1.87e-4; -water 1.02 # 1.87e-7 mM in the expt
#  Cs 1; -water 1.02
SELECTED_OUTPUT
  -file radial; -reset false
USER_PUNCH
       # Define symbols and pi...
  1    nl$ = CHR$(10) # newline, in unix use CHR$(13)
  2    q$  = CHR$(34)            # quote '"'
  3    x$  = CHR$(35)            # cross '#'
  4    sc$ = CHR$(59)            # semicolon ';'
  5    pi  = 2 * ARCTAN(1e10)    # 3.14159...

       # Define experimental parameters...
  10   height = 0.052           # length of the clay cylinder / m
  20   r_int = 6.58e-3          # inner radius of clay cylinder / m
  30   r_ext = 25.4e-3          # outer radius
  40   thickn_filter1 = 1.8e-3  # tracer-in filter thickness / m
  50   thickn_filter2 = 1.6e-3  # tracer-out filter thickness / m
  60   por_filter1 = 0.418      # porosity
  70   por_filter2 = 0.367
  80   G_filter1 = 4.18         # geometrical factor. (for filters, por / G = 10)
  90   G_filter2 = 3.67
  100  V_end = 0.2              # volume of the tracer-out solution / L
  110  thickn_clay = r_ext - r_int # clay thickness / m
  120  por_clay = 0.159
  130  rho_b_eps = 2.7 * (1 - por_clay) / por_clay  # clay bulk density / porosity / (kg/L)
  140  CEC = 0.12 * rho_b_eps   # CEC / (eq/L porewater)
  150  A_por = 37.0e3 * rho_b_eps # pore surface area / (m2/L porewater)

       # Define model parameters...
  160  Dw = 2.5e-9              # default tracer diffusion coefficient / (m2/s)
  170  nfilt1 = 1               # number of cells in filter 1
  180  nfilt2 = 1               # number of cells in filter 2
  190  nclay = 11               # number of clay cells
  200  f_free = 0.117           # fraction of free pore water (0.01 - 1)
  210  f_DL_charge = 0.45       # fraction of CEC charge in electrical double layer
  220  tort_n = -0.99           # exponent in Archie's law, -1.045 without filters
  230  G_clay = por_clay^tort_n # geometrical factor
  240  interlayer_D$ = 'false'  # 'true' or 'false' for interlayer diffusion
  250  G_IL = 750               # geometrical factor for clay interlayers
  260  punch_time = 60 * 60 * 6 # punch time / seconds

       # See which tracer is present...
  280  if tot("Hto") > 1e-10 THEN tracer$ = 'Hto' ELSE GOTO 330
  290    exp_time = 60 * 60 * 24 * 20  # time of the experiment / seconds
```

```
  300    scale1$ = '1e-15'             # scales the flux in the chart
  310    scale2$ = '1e-11'             # scales the mass
  320    GOTO 480
  330  if tot("Cl_tr") > 1e-10 THEN tracer$ = 'Cl_tr' ELSE GOTO 390
  340    exp_time = 60 * 60 * 24 * 40
  350    scale1$ = '1e-11'             # scales the flux in the chart
  360    scale2$ = '1e-7'              # scales the mass
       # Anions have higher tortuosity in clay...
  370    IF INSTR(tracer$, "Cl") THEN G_clay = G_clay * 1.57
  380    GOTO 480
  390  if tot("Na_tr") > 1e-10 THEN tracer$ = 'Na_tr' ELSE GOTO 440
  400    exp_time = 60 * 60 * 24 * 45
  410    scale1$ = '1e-15'             # scales the flux in the chart
  420    scale2$ = '1e-11'             # scales the mass
  430    GOTO 480
  440  if tot("Cs") > 1e-10 THEN tracer$ = 'Cs'
  450    exp_time = 60 * 60 * 24 * 1000
  460    scale1$ = '1e-9'             # scales the flux in the chart
  470    scale2$ = '1e-4'             # scales the mass

       # Define solution composition...
  480  sol$ = nl$ + ' pH 7.6' + sc$ +' pe 14 O2(g) -1.0' + sc$ +' temp 23'
  490  sol$ = sol$ + nl$ + ' Na 240' + sc$ +' K 1.61' + sc$ +' Mg 16.9' + sc$ +' Ca 25.8'
+ sc$ +' Sr 0.505'
  500  sol$ = sol$ + nl$ + ' Cl 300' + sc$ +' S(6) 14.1' + sc$ +' Fe(2) 0.0' + sc$ +'
Alkalinity 0.476'

       # Define phases in which the tracers precipitate...
  510  tracer_phases$ = nl$ + 'PHASES '
  520  tracer_phases$ = tracer_phases$ + nl$ + ' A_Hto' + nl$ + ' Hto = Hto' + sc$ +'
log_k -15'
  530  tracer_phases$ = tracer_phases$ + nl$ + ' A_Na_tr' + nl$ + ' Na_trCl = Na_tr+ +
Cl-' + sc$ + ' log_k -14'
  540  tracer_phases$ = tracer_phases$ + nl$ + ' A_Cl_tr' + nl$ + ' NaCl_tr = Na+ +
Cl_tr-' + sc$ +' log_k -14'
  550  tracer_phases$ = tracer_phases$ + nl$ + ' A_Cs' + nl$ + ' CsCl = Cs+ + Cl-' + sc$
+ ' log_k -13'
  560  tracer_equi$ = nl$ + 'A_' + tracer$ + ' 0 0'

       # Write solutions for the cells...
  600  punch nl$ + 'PRINT ' + sc$ + ' -reset false' + sc$ + ' -echo_input true' + sc$ +
' -user_print true'
  610  IF nfilt1 = 0 THEN GOTO 800
  620  punch nl$ + x$ + ' filter cells at tracer-in side...'
  630  r1 = r_int - thickn_filter1
  640  xf1 = thickn_filter1 / nfilt1
  650  FOR i = 1 TO nfilt1
  660    num$ = TRIM(STR$(i + 3)) + sc$
  670    V_water = 1e3 * height * por_filter1 * pi * (SQR(r1 + xf1) - SQR(r1))
  680    punch nl$ + 'SOLUTION ' + num$ + ' -water ' + STR$(V_water)
  690    punch sol$ + nl$
  700    r1 = r1 + xf1
  710  NEXT i
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```
  800  punch nl$ + nl$ + x$ + ' cells in Opalinus Clay...'
  810  r1 = r_int
  820  x = thickn_clay / nclay
  830  FOR i = 1 TO nclay
  840    num$ = TRIM(STR$(i + 3 + nfilt1)) + sc$
  850    V_water = 1e3 * height * por_clay * pi * (SQR(r1 + x) - SQR(r1))
  860    punch nl$ + 'SOLUTION ' + num$ + ' -water ' + STR$(V_water * f_free)
  870    punch sol$
  880    IF f_free = 1 and tracer$ = 'Hto'  THEN GOTO 960
  890    punch nl$ + 'SURFACE ' + num$ + ' -equil ' + num$
  900    punch nl$ + ' Su_ ' + TRIM(STR$(f_DL_charge * CEC * V_water)) + STR$(A_por) +
' ' + STR$(V_water)
  910    punch nl$ + ' Su_ii ' + TRIM(STR$(7.88e-4 * rho_b_eps * V_water))
  920    punch nl$ + ' Su_fes ' + TRIM(STR$(7.4e-5 * rho_b_eps * V_water))
  930    IF f_free < 1 THEN punch nl$ + ' -Donnan ' + TRIM(STR$((1 - f_free) * 1e-3 /
A_por))
  940    punch nl$ + 'EXCHANGE ' + num$ + ' -equil ' + num$
  950    punch nl$ + ' X ' + TRIM(STR$((1 - f_DL_charge) * CEC * V_water)) + nl$
  960    r1 = r1 + x
  970  NEXT i

 1000 IF nfilt2 = 0 THEN GOTO 1200
 1010 punch nl$ + nl$ + x$ + ' tracer-out filter cells...'
 1020 r1 = r_ext
 1030 xf2 = thickn_filter2 / nfilt2
 1040 FOR i = 1 TO nfilt2
 1050   num$ = TRIM(STR$(i + 3 + nfilt1 + nclay)) + sc$
 1060   V_water = 1e3 * height * por_filter2 * pi * (SQR(r1 + xf2) - SQR(r1))
 1070   punch nl$ + 'SOLUTION ' + num$ + ' -water ' + STR$(V_water)
 1080   punch sol$ + nl$
 1090   r1 = r1 + xf2
 1100 NEXT i

 1200 punch nl$ + x$ + ' outside solution...'
 1210 num$ = TRIM(STR$(4 + nfilt1 + nclay + nfilt2)) + sc$
 1220 punch nl$ + 'SOLUTION ' + num$ + ' -water ' + STR$(V_end)
 1230 punch sol$
 1240 punch nl$ + 'END'

      # Write phases in which the tracers precipitate...
 1300 punch nl$ + tracer_phases$
 1310 punch nl$ + 'EQUILIBRIUM_PHASES ' + num$ + tracer_equi$
 1320 punch nl$ + 'END'

      # Define mixing factors for the diffusive flux between cells 1 and 2:
      #    J_12 = -2 * Dw / (x_1 / g_1 + x_2 / g_2) * (c_2 - c_1)
     # Multiply with dt * A / (V = 1e-3 m3).  (Actual volumes are given with SOLUTION;
-water)
      # Use harmonic mean: g_1 = por_1 / G_1, g_2 = por_2 / G_2, x_1 = Delta(x_1), etc.
 1400 IF nfilt1 > 0 THEN gf1 = por_filter1 / G_filter1
 1410 IF nfilt2 > 0 THEN gf2 = por_filter2 / G_filter2
 1420 g = por_clay / G_clay
      # Find max time step = 0.5 * V_water * dx * G_factor / (Dw * por * A * fbc)
      #            V_water = por * pi * height * ((r + dr)^2 - r^2)
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```
       #                  A = por * pi * height * r * 2
       # At the inlet of the tracers, fbc = 2...
  1500 IF nfilt1 = 0 THEN GOTO 1530
  1510   r1 = r_int - thickn_filter1
  1520   ff = (SQR(r1 + xf1) - SQR(r1)) * xf1 * G_filter1 / (r1 * 2) / 2
  1530 ff1 = (SQR(r_int + x) - SQR(r_int)) * x * G_clay / (r_int * 2) / 2
       # Perhaps the clay has very small cells...
  1540 IF nfilt1 = 0 THEN ff = ff1 ELSE IF ff1 * 2 < ff THEN ff = ff1 * 2
       # Or at the filter-clay transition, fbc = 1...
  1550 IF nfilt1 > 0 THEN ff1 = (SQR(r_int + x) - SQR(r_int)) * (xf1 / gf1 + x / g) /
(2 * r_int * 2)
  1560 IF nfilt1 > 0 AND ff1 < ff THEN ff = ff1
  1570 dt_max = 0.5 * ff / Dw
       # Check with punch times, set shifts...
  1580 IF punch_time < dt_max THEN dt = punch_time ELSE dt = dt_max
  1590 punch_fr = 1
  1600 IF dt < punch_time THEN punch_fr = ceil(punch_time / dt)
  1610 dt = punch_time / punch_fr
  1620 shifts = ceil(exp_time / dt)

       # Write mixing factors...
  1700 punch nl$ + nl$ + x$ + ' mixing factors...'
  1710 r1 = r_int
  1720 IF nfilt1 > 0 THEN r1 = r_int - thickn_filter1
  1730 A = height * 2 * pi
  1740 FOR i = 0 TO nfilt1 + nclay + nfilt2
  1750   IF i = 0 OR i = nfilt1 + nclay + nfilt2 THEN fbc = 2 ELSE fbc = 1
  1760   IF i > nfilt1 OR nfilt1 = 0 THEN GOTO 1810
  1770     IF i < nfilt1 THEN mixf = Dw * fbc / (xf1 / gf1) * dt * A * r1 / 1e-3
  1780     IF i = nfilt1 THEN mixf = 2 * Dw / (xf1 / gf1 + x / g) * dt * A * r1 / 1e-3
  1790     IF i < nfilt1 THEN r1 = r1 + xf1 ELSE r1 = r1 + x
  1800     GOTO 1880
  1810   IF i > nfilt1 + nclay THEN GOTO 1860
  1820     mixf = Dw * fbc / (x / g) * dt * A * r1 / 1e-3
  1830     IF i = nfilt1 + nclay AND nfilt2 > 0 THEN mixf = 2 * Dw / (xf2 / gf2 + x /
g) * dt * A * r1 / 1e-3
  1840     IF i < nfilt1 + nclay THEN r1 = r1 + x ELSE r1 = r1 + xf2
  1850     GOTO 1880
  1860   mixf = Dw * fbc / (xf2 / gf2) * dt * A * r1 / 1e-3
  1870   r1 = r1 + xf2

  1880   punch nl$ + 'MIX ' + TRIM(STR$(i + 3)) + sc$ + STR$(i + 4) + STR$(mixf)
  1890 NEXT i
  1900 punch nl$ + 'END'

       # Write TRANSPORT...
  2000 punch nl$ + 'TRANSPORT'
  2010 stag = 2 + nfilt1 + nclay + nfilt2
  2020 punch nl$ + ' -warnings true'
  2030 punch nl$ + ' -shifts ' + TRIM(STR$(shifts))
  2040 punch nl$ + ' -flow diff' + sc$ + ' -cells 1' + sc$ + ' -bcon 1 2' + sc$ + ' -stag
' + TRIM(STR$(stag))
  2050 punch nl$ + ' -time ' + STR$(dt)
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```
  2060 punch nl$ + ' -multi_D true ' + STR$(Dw) + STR$(por_clay) + ' 0.0 ' +
TRIM(STR$(-tort_n))
  2070 punch nl$ + ' -interlayer_D ' + interlayer_D$ + ' 0.04 0.0 ' + TRIM(STR$(G_IL))
  2080 punch nl$ + ' -punch_fr ' + TRIM(STR$(punch_fr)) + sc$ + ' -punch_c ' + TRIM(STR$(2
+ stag))

       # Write USER_GRAPH...
  2200 punch nl$ + 'USER_GRAPH'
  2210 punch nl$ + ' -plot_csv_file ' + tracer$ + '_rad.csv'
  2220 punch nl$ + ' -axis_scale x_axis 0 ' + TRIM(STR$(exp_time / (3600 * 24)))
  2230 punch nl$ + ' -axis_titles ' + q$ + 'Time / days' + q$ + ' ' + q$ + 'Flux / ('
+ scale1$ + ' mol/m2/s)' + q$ + ' ' + q$ + 'Accumulated mass / (' + scale2$ + ' mol)' + q$
  2240 punch nl$ + ' -plot_concentration_vs time'
  2250 punch nl$ + ' 10 days = total_time / (3600 * 24)'
  2260 punch nl$ + ' 20 if INSTR(' + q$ + tracer$ + q$ + ', ' + q$ + 'C' + q$ + ') THEN
mm = 1 ELSE mm = 1e-3'
  2270 punch nl$ + ' 30 s1 = ' + STR$(1 / val(scale1$)) + ' * mm'
  2280 punch nl$ + ' 40 s2 = ' + STR$(1 / val(scale2$)) + ' * mm'
  2290 punch nl$ + ' 50 a = equi(' + q$ + 'A_' + tracer$ + q$ + ') * s2'
  2300 punch nl$ + ' 60 IF get(1) = 0 AND total_time > 0 THEN put(total_time, 1)'
  2310 punch nl$ + ' 70 dt = get(1)'
  2320 A = 2 * pi * r_ext * height
  2330 punch nl$ + ' 80 plot_xy days - dt / (2 * 3600 * 24), (a - get(2)) * s1 / s2 /
dt /' + STR$(A) +', color = Green, symbol = None'
  2340 punch nl$ + ' 90 put(a, 2)'
  2350 punch nl$ + ' 100 plot_xy days, equi(' + q$ + 'A_' + tracer$ + q$ + ') * s2,
y_axis = 2, color = Red, symbol = None'
  2360 punch nl$ + 'END '

END
USER_PUNCH
 10
INCLUDE$ radial
END
```

The file starts with the tracer species, where, for the monovalent tracers $^{22}Na^+$ (="Na_tr$^+$") and Cs^+, an enrichment factor for the double layer is entered with **-erm_ddl**. The enrichment is related to increased complexation of the polyvalent cations in the low dielectric permittivity of the double layer. Sorption of Cs^+ is much stronger than of Na^+, which is modeled by 2 surface complexes and one exchange reaction with very high constants. The constants are based on the measured adorption isotherm for Opalinus Clay, but may be generally applicable since they are associated primarily with strong sorption sites on illite. Next, the file writes **SOLUTION** 0-2 for a regular column, followed by **SOLUTION** 3, which forms the start of the stagnant column and circulates at the inner filter of the diffusion cell. This solution contains the tracers that should be uncommented one by one to run the file each time with only a single tracer. When **SOLUTION** 3 is calculated, **USER_PUNCH** is processed to write a **SELECTED_OUTPUT** file 'radial', which contains

the **SOLUTION**s for the cells in the filters and the clay, the mixing factors, and the **TRANSPORT** and **USER_GRAPH** datablocks. The Basic lines in **USER_PUNCH** do the following tasks.

Lines 1 - 5 define a few variables that facilitate printing of special symbols like the semicolon, and π, for calculating the radial configuration of the experimental cell.

Lines 10 - 150 define the dimensions of the experimental cell and properties of the filters and the clay that have been measured and thus, should be considered as constant.

Lines 160 - 270 give model parameters that may be varied to simulate the experiments, and can be changed to check the diffusion model. Typically, for checking the numerics, the number of cells for the filters (variables `nfilt1` and `nfilt2`) and for the clay (`nclay`), and the timestep (`punch_time`) can be altered without affecting the calculated results. It is also interesting to set `nfilt1` and/or `nfilt2` to zero and inspect the effects that the filters have on the flux. (The program will probably crash when `nclay` is set to zero.) Values of the other model parameters were derived from the geometrical factors, obtained in the traditional way by fitting the measured tracer diffusion curves (Appelo et al., 2010). And also here, the Basic program and PHREEQC's functioning can be verified. For example, `f_free` the fraction of free pore water, partitioning the porespace in free and double layer water. The value may be changed to anything between 0.01 and 1 for tritium which, as an uncharged species, diffuses equally quickly in free and double layer water (if the latter is given the viscosity of free pore water) . However, the variable has major effect on the through-diffusion of $^{36}Cl^-$. The parameter `f_DL_charge` partitions the Cation Exchange Capacity (`CEC`) over the double layer and exchange sites. Increasing its value will not affect the diffusion of tritium, but decrease the flux of Cl^- and increase it of Na^+.

Lines 280 - 500 check which tracer is present (the file should be run for a single tracer to show the model lines together with the experimental data), and define the solid phases in which the tracers precipitate in the outer solution. The moles of this phase will record the amounts that have diffused. The phases have such a low solubility that the tracer concentration is maintained at zero concentration, essentially.

Lines 600 - 1100 write the solutions for the filter cells and the clay, with radially increasing amounts of water. For the clay, keyword **SURFACE** is used to define the moles of the surface sites of Su_, Su_ii and Su_fes, for the double layer, and the sites on illite that sorb the alkaline cations with intermediate and very high strength, respectively. The fixed sites of the Cation Exchange Capacity (`CEC`) are defined with **EXCHANGE**.

Lines 1200 - 1320 write the external **SOLUTION** and the **EQUILIBRIUM_PHASES** in which the tracers are captured.

Lines 1400 - 1900 calculate and write the mixing factors as explained above in equation 22-47. First, the maximal time step is derived, either from the innermost filter cell, or from the transition of the inner filter and the clay, or from the innermost clay cell. The timestep is decreased when it is larger than desired by `punch_time`. With this timestep, the mixing factors are calculated for each cell and written to the file, taking care of the heterogeneities at physical boundaries and the radial outline of the field.

Lines 2000 - 2360 write datablocks for **TRANSPORT** and **USER_GRAPH**. The experimental data (courtesy of L.R. van Loon) will be plotted ('**-plot_csv_file** *file_name*') together with the calculated accumulated mass in the outer solution and the flux, obtained by dividing the the mass that has accumulated by the time interval and the outer surface area of the clay.

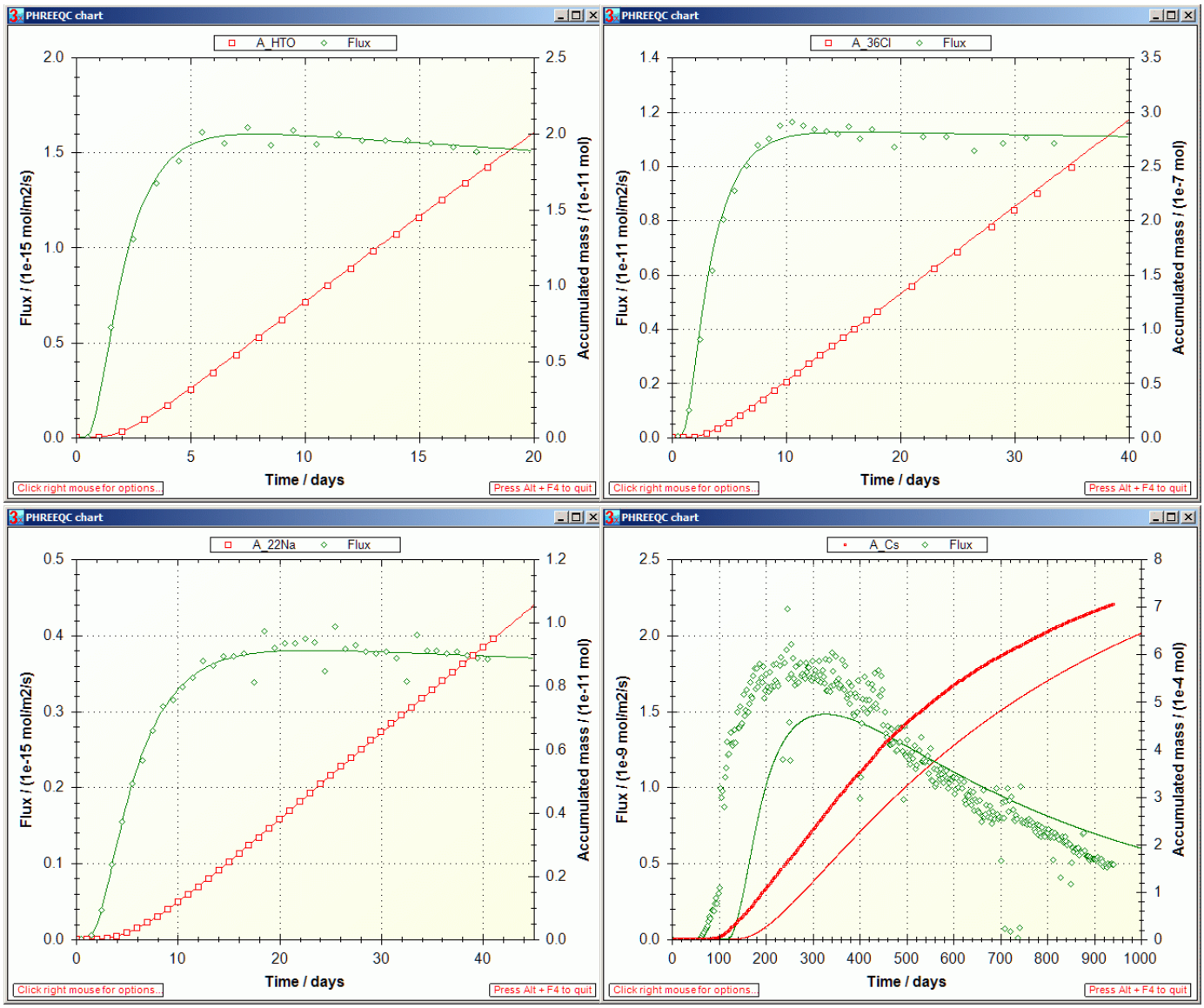

Figure 21. --Mass outflow (red) and corresponding flux (green) by diffusion through the radial cell for, clock-wise from the upper-left, HTO, $^{36}Cl^-$, Cs^+ and $^{22}Na^+$. Lines are modeled, symbols indicate measured data.

Following the **END** after **USER_PUNCH**, the file 'radial' is loaded in the input file with **INCLUDE$** and then processed. Before the file is included, **USER_PUNCH** is reset by just giving a single Basic line number without instruction, thus avoiding that the file is written over and over again, each time that a solution is calculated.

The file should be run separately for the tracers HTO, ^{36}Cl, ^{22}Na and Cs by uncommenting the tracers in **SOLUTION** 3 one by one. The results are shown in figure 21. Briefly, the arrival of the tracer,

accumulating in the outer solution, is delayed by the storage in porewater and the sorption on minerals in the clay. The delay increases from $^{36}Cl^-$, HTO, $^{22}Na^+$ to Cs^+. The total storage can be obtained from the graphs by extrapolating the straight-line segment of the accumulated mass to time zero, and reading the value from the secondary Y-axis (a negative number, since mass is lost). The flux, the derivative of the mass with time, shows that the accumulation of HTO, and of Cs^+ in particular, decreases already during the experiment because the concentration is diminishing in the tracer solution. The volume of the solution with HTO, the first experiment performed, was 0.2 L and relatively small. Sorption of Cs^+ is so strong (more than 99.5% of Cs^+ resides in the solid phase) that 1 L simply contains insufficient mass to fill all the sorption sites on the clay.

The model can calculate the experimental results very well, except for Cs^+. The calculated arrival time of Cs^+ is almost 100 days later than observed and then the mass accumulates too slowly. This behavior of Cs^+ has been found in many similar experiments. It has been modeled by increasing the diffusion coefficient and decreasing the sorption capacity for Cs^+ relative to batch experiments, and it can be tried out easily in this example.

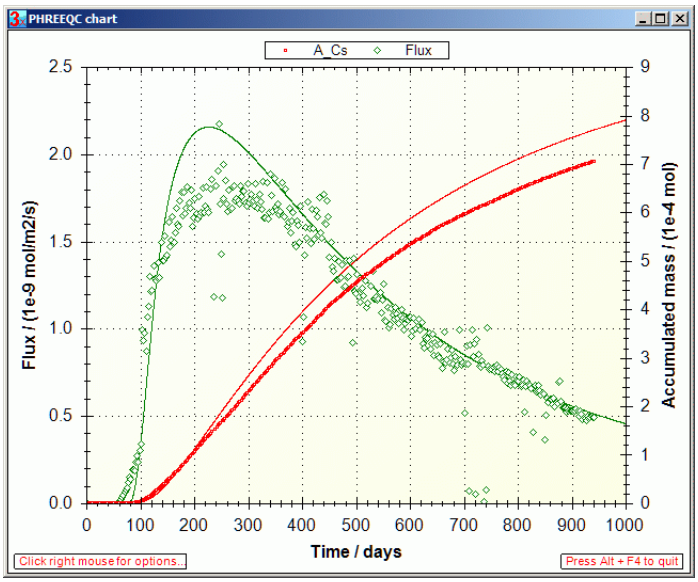

Figure 22. --Mass outflow (red) and corresponding flux (green) of Cs^+ in the diffusion cell when interlayer diffusion is included.

The diffusion of Cs^+ can be increased by setting interlayer diffusion 'true' in Line 240:

```
  240  interlayer_D$ = 'true'  # 'true'
or 'false' for interlayer diffusion
```

(It is of interest to see the different effects of interlayer diffusion on $^{22}Na^+$ and on Cs^+.)

The results, shown in figure 22, illustrate that the arrival time of Cs^+ can be matched by increasing diffusion, but that the mass accumulates too quickly. Another option for reducing the delay of the tracer arrival is by decreasing the sorption of Cs^+, either by lowering the moles of surface and exchange sites or the complexation constants, or by lowering both. By adjusting both the sorption and the diffusion coefficient, it may be possible to simulate the experimental data for Cs^+. However, it will remain difficult to explain why the sorption capacity is different between batch- and diffusion experiments for Cs^+ and not for the other cations.

Alternatively, and in line with the heterogeneous distribution of Cs^+ in the clay after the experiment, the relatively fast arrival time can be modeled with a dual-porosity structure in which the porespace is subdivided in continuous and stagnant pores that can exchange by diffusion. The continuous pores guide Cs^+ more rapidly through the clay than is calculated for a homogeneous medium, depending on the proportion, the flow velocity, and the diffusional exchange with the stagnant pores. With equation 47, and some effort, the dual-porosity structure can be introduced in the Basic program. Otherwise, the c-file can be used which is given as supplementary information in Appelo et al. (2010). Similar to the Basic program, it writes a complete PHREEQC input file for diffusion of Cs^+, but in a dual porosity clay, while in addition, it permits distributing the surface and exchange sites differently over the stagnant and continuous pores.