Introduction to Reactive Transport with CrunchTope

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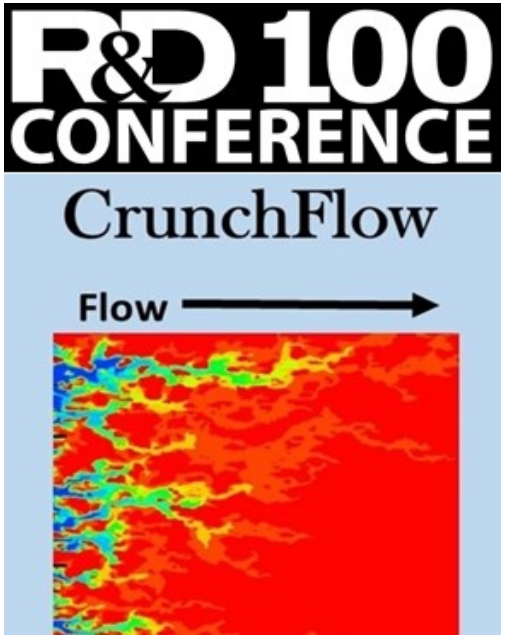
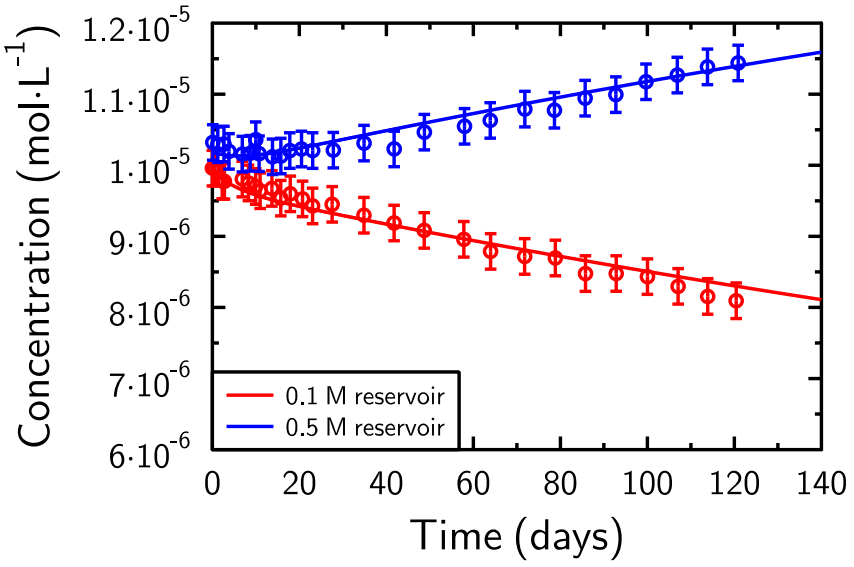




https://bitbucket.org/crunchflow/crunchtope/downloads/CrunchTope-Install.exe

Reactive Transport Equations

Fully Kinetic Approach

$$\frac{\partial(\phi S_L C_i)}{\partial t} = \nabla\cdot(\phi S_L D_i^* \nabla C_i) - \nabla\cdot(\mathbf{q} C_i) - \sum_{r=1}^{Nr} \nu_{ir} R_r - \sum_{m=1}^{N_m} \nu_{im} R_m - \sum_{l=1}^{N_g} \nu_{il} R_l$$

Accumulation Term | Dispersion-Diffusion | Advection | Aqueous Reactions | Mineral Reactions | Gas Reactions

Partial Equilibrium Approach

$$\frac{\partial(\phi S_L \Psi_i)}{\partial t} = \nabla\cdot(\phi S_L D_i^* \nabla \Psi_i) - \nabla\cdot(\phi S_L v \Psi_i) - \sum_{r=1}^{Nr} \nu_{ir} R_r - \sum_{m=1}^{N_m} \nu_{im} R_m - \sum_{l=1}^{N_g} \nu_{il} R_l$$

Total Concentration | **Secondary Species** | **Rewritten with Primary Species**

$$\psi_i = C_i + \sum_{l=1}^{N_s} \nu_{i,l} C_l = C_i + \sum_{l=1}^{N_s} \nu_{i,l} \left[\prod C_p^{\nu_{p,l}} K_{eq}^{-1} \right]$$

Reactive Transport Equations: Numerical

Accumulation Term | Dispersion-Diffusion | Advection | Aqueous Reactions

$$\phi S_L \frac{\left[\psi_{i,jx}^{n+1} - \psi_{i,jx}^{n}\right]}{\Delta t} - \phi S_L D \frac{\left[\psi_{i,jx-1}^{n+1} - 2\psi_{i,jx}^{n+1} + \psi_{i,jx+1}^{n+1}\right]}{\Delta x^2} + \phi S_L v \frac{\left[\psi_{i,jx-1}^{n+1} - \psi_{i,jx}^{n+1}\right]}{\Delta x} + \sum_{r=1}^{N_r}\left[R_{i,r}^{n+1}\right] = 0$$

Rewrite Ψ in terms of primary species concentrations

$$\frac{\phi S_L}{\Delta t}\left[\left(C_i + \sum_{l=1}^{N_s} \nu_{i,l}\left[\prod C_p^{\nu_{p,l}} K_{eq}^{-1}\right]\right)_{i,jx}^{n+1} - \psi_{i,jx}^{n}\right] + \sum_{r=1}^{N_r}\left[R_{i,r}^{n+1}\right]_{jx}$$

Accumulation + Reaction Terms

$$+ \frac{\phi S_L v}{\Delta x}\left[\left(C_i + \sum_{l=1}^{N_s} \nu_{i,l}\left[\prod C_p^{\nu_{p,l}} K_{eq}^{-1}\right]\right)_{i,jx}^{n+1} - \left(C_i + \sum_{l=1}^{N_s} \nu_{i,l}\left[\prod C_p^{\nu_{p,l}} K_{eq}^{-1}\right]\right)_{i,jx-1}^{n+1}\right]$$

Transport Terms

$$- \frac{\phi S_L D}{\Delta x^2}\left[\left(C_i + \sum_{l=1}^{N_s} \nu_{i,l}\left[\prod C_p^{\nu_{p,l}} K_{eq}^{-1}\right]\right)_{i,jx-1}^{n+1} - 2\left(C_i + \sum_{l=1}^{N_s} \nu_{i,l}\left[\prod C_p^{\nu_{p,l}} K_{eq}^{-1}\right]\right)_{i,jx}^{n+1} + \left(C_i + \sum_{l=1}^{N_s} \nu_{i,l}\left[\prod C_p^{\nu_{p,l}} K_{eq}^{-1}\right]\right)_{i,jx+1}^{n+1}\right] = 0$$

SHORT COURSE EXERCISES

Short Course Exercises

Introduction to speciation
- Example using the carbonate system featuring various constraints
- Stable isotopes of carbon (^{12}C and ^{13}C) implemented to demonstrate equilibrium fractionation

Advective transport
- Introduce a non-reactive tracer into an advective flow field
- Investigate numerical dispersion

Diffusive transport
- Introduce a non-reactive tracer into a purely diffusive transport problem
- No-flux versus Dirichlet boundary conditions

Multicomponent diffusion
- Concept of charged species diffusing at different rates and electrochemical migration
- Stable isotopes of Cl are implemented to consider the influence of diffusive fractionation

Transverse dispersion
- Example based on a recent 2D dispersion experiment, including multi-ion diffusion in an advective flow field

Ion exchange
- Introduce ion exchange of cesium in a 1D sediment column with competing Na^+

Surface complexation
- Surface complexation of zinc on iron-hydroxide (PHREEQc example 8)

CO_2 attack on reservoir rocks
- Diffusion of gas and flow of water, with variable liquid saturations and multi-mineral nucleation, precipitation, and dissolution

Calcite precipitation with isotopes
- Simulation of stable isotope kinetic fractionation of calcium during carbonate precipitation

Two-dimensional flow fields
- Xie et al (2015) benchmark on porosity and permeability change due to mineral reaction

Diffusion in clay
- Tournassat & Steefel, 2016

Inverse modeling with PEST-CrunchFlow
- Steefel et al, 2003

CrunchTope Files

1) Executable: `CrunchTope.exe`

2) Input file: *name*.in

1) Database(s): *name*.dbs

```
TITLE
Cs exchange on Hanford sediments:  Experiment 3
END


RUNTIME
time_units            hours
timestep_max          0.1
timestep_init         0.00001
time_tolerance        0.01
solver                gmres
preconditioner        ilu
precondition_level    1
lag_activity          on
debye-huckel          on
database_sweep        off
speciate_only         false
hindmarsh             true
gimrt                 true
courant_number        1.0
density_module        sodium_nitrate
graphics              kaleidagraph
screen_output         50
database              HanfordTanksColumnFit3Site-GT.dbs
save_restart          Column3NaNO3Flush1.rst
later_inputfiles      ShortCourse12b.in ShortCourse12c.in
END

OUTPUT
time_units             hours
spatial_profile        19.25
```

```
'temperature points' 8   0.  25.  60. 100. 150. 200. 250. 300.
'Debye-Huckel adh'   0.4939  0.5114 0.5465 0.5995 0.6855 0.7994 0.9593 1.2180
'Debye-Huckel bdh'   0.3253  0.3288 0.3346 0.3421 0.3525 0.3639 0.3766 0.3925
'Debye-Huckel bdt'   0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000
'H2O' 3.0  0.0    18.0153
'Ag+' 2.5  1.0   107.8682
'Al+++' 9.0  3.0    26.9815
'Am+++' 5.0  3.0   243.0000
'Ar(aq)' 3.0  0.0    39.9480
'Au+' 4.0  1.0   196.9665
'B(OH)3(aq)' 3.0  0.0    61.8330
'Ba++' 5.0  2.0   137.3270
'Be++' 8.0  2.0     9.0122
'Br-' 3.0 -1.0    79.9040
'Ca++' 6.0  2.0    40.0780
'Cd++' 5.0  2.0   112.4110
'Ce+++' 9.0  3.0   140.1150
'Cl-' 3.0 -1.0    35.4527
```

CrunchTope Files

```
OUTPUT
time_units          hours
spatial_profile      16.0  32.0
time_series          Rolle.out    11  20  1
time_series_print    K+  Mg++  Cl-
time_series_interval 1
END/
```

spatial_profile generated automatically at times specified (16, 32 hours)

time_series saved every *time_series_interval* in file `Rolle.out`

time_series_print writes species specified in file `Rolle.out`

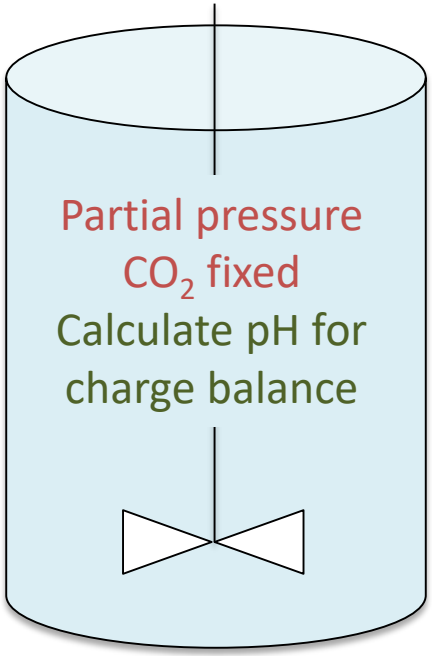
Spatial profile files include:

1. totcon#.tec — total concentrations in solution
2. pH#.tec — solution pH
3. conc#.tec — log concentrations of individual species
4. rate#.tec — mineral reaction rates (mol/L(bulk)/s)
5. aq_rate#.tec — aqueous reaction rates (mol/L/s)
6. volume#.tec — mineral volume fraction (dimensionless)
7. porosity#.tec — (dimensionless)
8. velocity#.tec — Darcy flux ($m^3/m^2/yr$)
9. toperatio_aq#.out — per mil
10. toperatio_min#.out — per mil

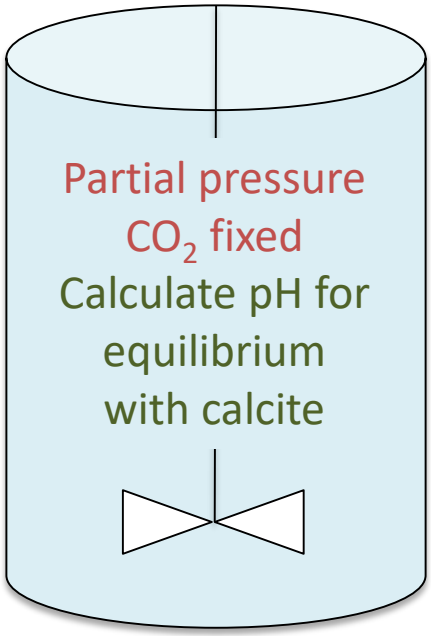
SPECIATION

Exercise 1: Carbonate Speciation

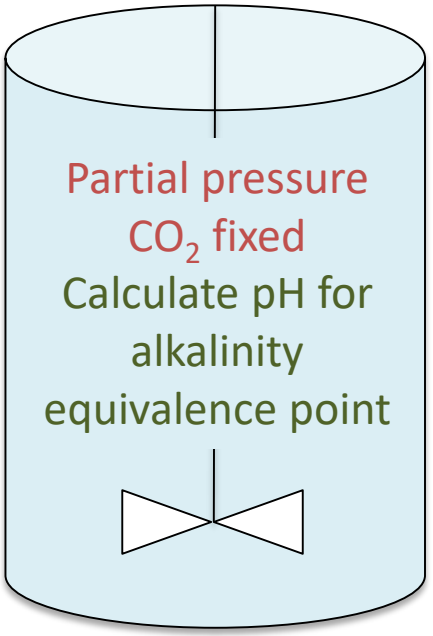
Condition: speciate 1



Condition: speciate 2



Condition: speciate 3



Input Blocks

```
RUNTIME
speciate_only       true
database_sweep  false
database              datacom_13C.dbs
graphics              tecplot
density_module  temperature
END
```

```
PRIMARY_SPECIES
H+
CO2(aq)
13CO2(aq)
Ca++
Na+
Cl-
END
```

```
GASES
CO2(g)
13CO2(g)
END
```

Log rate (mol/m^2/s)

```
MINERALS
Calcite     -label default  -rate  -11.00
END
```

```
SECONDARY_SPECIES
HCO3-
H13CO3-
CaCl+
CaCl2(aq)
CaOH+
HCl(aq)
NaCl(aq)
NaOH(aq)
OH-
CO3—
13CO3--
CaCO3(aq)
Ca13CO3(aq)
CaHCO3+
CaH13CO3+
NaCO3-
Na13CO3-
NaHCO3(aq)
NaH13CO3(aq)
END
```

Stoichiometric Reaction Matrix

HOMOGENEOUS REACTIONS

Species	log K	Stoichiometric Coefficients					
		H+	CO2(aq	13CO2(	Ca++	Na+	Cl-
HCO3-	6.3414E+00	-1.00	1.00	0.00	0.00	0.00	0.00
H13CO3-	6.3390E+00	-1.00	0.00	1.00	0.00	0.00	0.00
CaCl+	7.0039E-01	0.00	0.00	0.00	1.00	0.00	1.00
CaCl2(aq)	6.5346E-01	0.00	0.00	0.00	1.00	0.00	2.00
CaOH+	1.2850E+01	-1.00	0.00	0.00	1.00	0.00	0.00
HCl(aq)	-6.9993E-01	1.00	0.00	0.00	0.00	0.00	1.00
NaCl(aq)	7.8213E-01	0.00	0.00	0.00	0.00	1.00	1.00
NaOH(aq)	1.4799E+01	-1.00	0.00	0.00	0.00	1.00	0.00
OH-	1.3991E+01	-1.00	0.00	0.00	0.00	0.00	0.00
CO3--	1.6666E+01	-2.00	1.00	0.00	0.00	0.00	0.00
13CO3--	1.6664E+01	-2.00	0.00	1.00	0.00	0.00	0.00
CaCO3(aq)	1.3350E+01	-2.00	1.00	0.00	1.00	0.00	0.00
Ca13CO3(aq)	1.3348E+01	-2.00	0.00	1.00	1.00	0.00	0.00
CaHCO3+	5.2986E+00	-1.00	1.00	0.00	1.00	0.00	0.00
CaH13CO3+	5.2961E+00	-1.00	0.00	1.00	1.00	0.00	0.00
NaCO3-	1.6157E+01	-2.00	1.00	0.00	0.00	1.00	0.00
Na13CO3-	1.6155E+01	-2.00	0.00	1.00	0.00	1.00	0.00
NaHCO3(aq)	6.1857E+00	-1.00	1.00	0.00	0.00	1.00	0.00
NaH13CO3(aq)	6.1832E+00	-1.00	0.00	1.00	0.00	1.00	0.00

Stoichiometric Reaction Matrix

MINERAL REACTIONS

Mineral	log K	Stoichiometric Coefficients					
		H+	CO2(aq	13CO2(	Ca++	Na+	Cl-
Calcite	8.1957E+00	-2.00	1.00	0.00	1.00	0.00	0.00

GAS REACTIONS

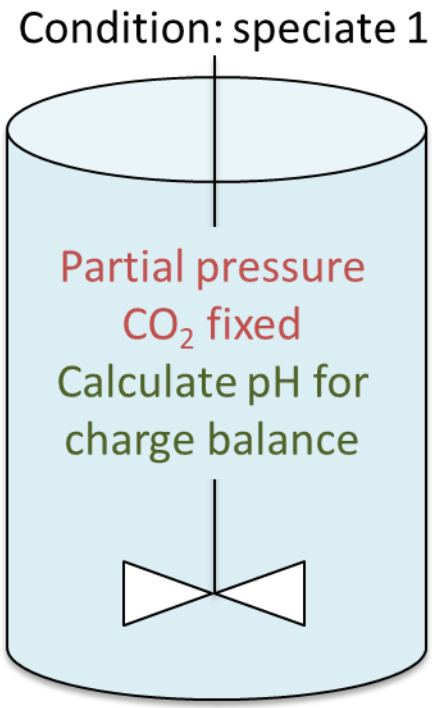
Gases	log K	Stoichiometric Coefficients					
		H+	CO2(aq	13CO2(	Ca++	Na+	Cl-
CO2(g)	-1.4677E+00	0.00	1.00	0.00	0.00	0.00	0.00
13CO2(g)	-1.4680E+00	0.00	0.00	1.00	0.00	0.00	0.00

Condition Blocks

Label for condition used in INITIAL_CONDITIONS and BOUNDARY_CONDITIONS and PUMP

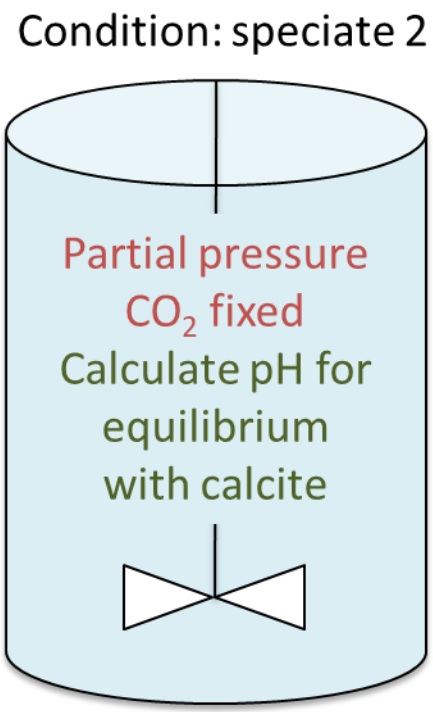
```
Condition       speciate1
!! Fix pCO2 and calculate pH based on charge balance
units           mol/kg
temperature     25.0
pH              charge
!!gas partial pressure in bars
CO2(aq)         CO2(g)      3.12E-04
13CO2(aq)       13CO2(g)    3.15E-06
Na+             0.01
Cl-             0.01
Ca++            0.00
END
```

Gas partial pressure in bars



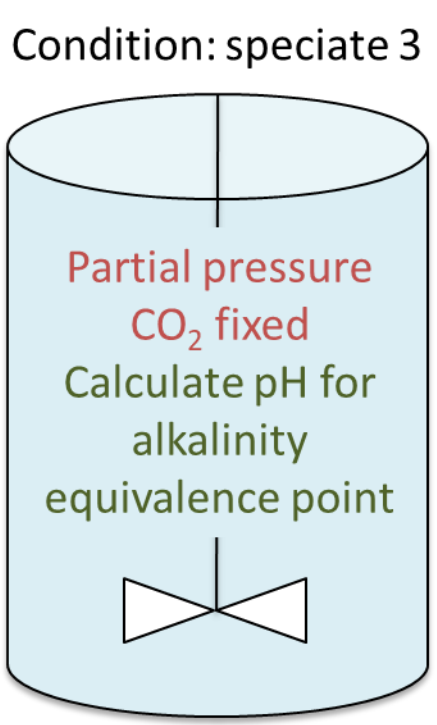
Condition Blocks

```
Condition       speciate2
!!  Fix pCO2 and calculate pH based on calcite equilibrium
units               mol/kg
temperature    25.0
pH                  Calcite
!! Gas partial pressure in bars
CO2(aq)           CO2(g)      3.12E-04
13CO2(aq)       13CO2(g)   3.15E-06
Na+               0.01
Cl-                charge
Ca++             0.01
END
```



Condition Blocks

```
Condition       speciate3
!! Fix pCO2 and calculate pH based on alkalinity at the CO2
!!    equivalence point (alkalinity = 0.00)
units           mol/kg
temperature     25.0
H+              0.00
!! gas partial pressure in bars
CO2(aq)         CO2(g)      3.12E-04
13CO2(aq)       13CO2(g)    3.15E-06
Na+             0.01
Cl-             0.01
Ca++            0.00
END
```



Total Hydrogen = -Alkalinity

Discretization and Initial and Boundary Conditions

```
DISCRETIZATION
xzones   1    1.0
END

INITIAL_CONDITIONS
speciate1   1-1
END
```

NOTE: No boundary conditions needed for initial value problem

Minimum 3 grid cells required for a boundary value problem (with transport

Exercise 1: Carbonate Speciation

View results in `ShortCourse1.out`

```
*********************************************
 ---> GEOCHEMICAL CONDITION: speciate1

 Temperature (C)          =     25.000
 Porosity                 =      1.000
 Liquid Saturation        =      1.000
 Liquid Density (kg/m^3)  =    997.075
 Solid Density (kg/m^3)   =      0.000
 Solid:Solution Ratio     =      0.000
 Ionic Strength           =      0.010
 Solution pH              =      5.658
 Total Charge             = -1.735E-18
```

```
*********************************************
 ---> GEOCHEMICAL CONDITION: speciate3

 Temperature (C)          =     25.000
 Porosity                 =      1.000
 Liquid Saturation        =      1.000
 Liquid Density (kg/m^3)  =    997.075
 Solid Density (kg/m^3)   =      0.000
 Solid:Solution Ratio     =      0.000
 Ionic Strength           =      0.010
 Solution pH              =      5.658
 Total Charge             = -1.735E-18
```

```
*********************************************
 ---> GEOCHEMICAL CONDITION: speciate2

 Temperature (C)          =     25.000
 Porosity                 =      1.000
 Liquid Saturation        =      1.000
 Liquid Density (kg/m^3)  =    997.075
 Solid Density (kg/m^3)   =      0.000
 Solid:Solution Ratio     =      0.000
 Ionic Strength           =      0.030
 Solution pH              =      7.717
 Total Charge             =  1.966E-02
```

Exercise 1: Carbonate Speciation with Isotopes

View results in `ShortCourse1.out`

```
*********************************************
 ---> GEOCHEMICAL CONDITION: speciate1
 Total Aqueous Concentrations of Primary Species
 -----------------------------------

 Species                    Molality     Constraint    Constraint Phase
 H+                      -6.4078E-19     Charge
 CO2(aq)                  1.3074E-05     Gas           CO2(g)
 13CO2(aq)                1.3206E-07     Gas           13CO2(g)
 Ca++                     1.0326E-30     Total
 Na+                      1.0000E-02     Total
 Cl-                      1.0000E-02     Total

Concentrations of Individual Species, Exchangers, and Surface Complex
-----------------------------------------------------------------------

                          Log            Log
Species                Molality       Activity       Molality       Activity
 H+                      -5.619         -5.658      2.403E-06      2.197E-06
 CO2(aq)                 -4.975         -4.974      1.060E-05      1.063E-05
 13CO2(aq)               -6.971         -6.970      1.070E-07      1.072E-07
 Ca++                   -29.987        -30.157      1.031E-30      6.968E-31
 Na+                     -2.001         -2.045      9.987E-03      9.009E-03
 Cl-                     -2.001         -2.047      9.987E-03      8.981E-03
 HCO3-                   -5.612         -5.657      2.443E-06      2.204E-06
 H13CO3-                 -7.606         -7.650      2.479E-08      2.236E-08
```

$\delta^{13}C = 0‰$

$\delta^{13}C = 4.6‰$

Speciation in ShortCourse1.out

From Speciate1

Concentrations of Individual Species, Exchangers, and Surface Complexes

Species	Log Molality	Log Activity	Molality	Activity	Activity Coefficient	Type
H+	-5.619	-5.658	2.403E-06	2.197E-06	9.141E-01	Aqueous
CO2(aq)	-4.975	-4.974	1.060E-05	1.063E-05	1.002E+00	Aqueous
13CO2(aq)	-6.971	-6.970	1.070E-07	1.072E-07	1.002E+00	Aqueous
Ca++	-29.987	-30.157	1.031E-30	6.969E-31	6.758E-01	Aqueous
Na+	-2.001	-2.045	9.987E-03	9.009E-03	9.022E-01	Aqueous
Cl-	-2.001	-2.047	9.987E-03	8.981E-03	8.994E-01	Aqueous
HCO3-	-5.612	-5.657	2.443E-06	2.204E-06	9.022E-01	Aqueous
H13CO3-	-7.606	-7.650	2.479E-08	2.236E-08	9.022E-01	Aqueous
CaCl+	-32.859	-32.904	1.383E-33	1.248E-33	9.022E-01	Aqueous
CaCl2(aq)	-34.905	-34.904	1.246E-35	1.249E-35	1.002E+00	Aqueous
CaOH+	-37.304	-37.349	4.967E-38	4.481E-38	9.022E-01	Aqueous
HCl(aq)	-7.006	-7.005	9.864E-08	9.887E-08	1.002E+00	Aqueous
NaCl(aq)	-4.875	-4.874	1.333E-05	1.336E-05	1.002E+00	Aqueous
NaOH(aq)	-11.187	-11.186	6.506E-12	6.521E-12	1.002E+00	Aqueous
OH-	-8.287	-8.333	5.158E-09	4.646E-09	9.008E-01	Aqueous
CO3--	-10.146	-10.323	7.146E-11	4.749E-11	6.645E-01	Aqueous
13CO3--	-12.140	-12.317	7.250E-13	4.817E-13	6.645E-01	Aqueous
CaCO3(aq)	-37.165	-37.164	6.836E-38	6.852E-38	1.002E+00	Aqueous
Ca13CO3(aq)	-39.159	-39.158	6.937E-40	6.953E-40	1.002E+00	Aqueous
CaHCO3+	-34.726	-34.771	1.879E-35	1.695E-35	9.022E-01	Aqueous

****** Partial pressure of gases (bars) *****

CO2(g)	3.12000000E-04
13CO2(g)	3.15000000E-06

****** Saturation state of minerals (log[Q/K] *****

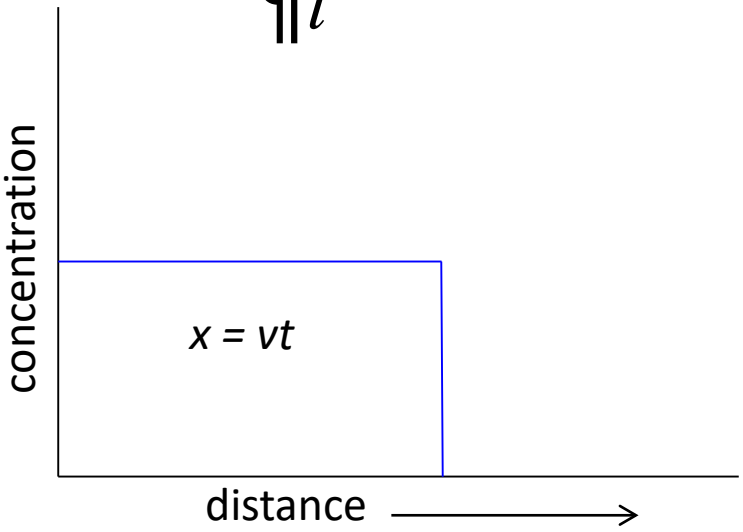
Calcite	-32.0097

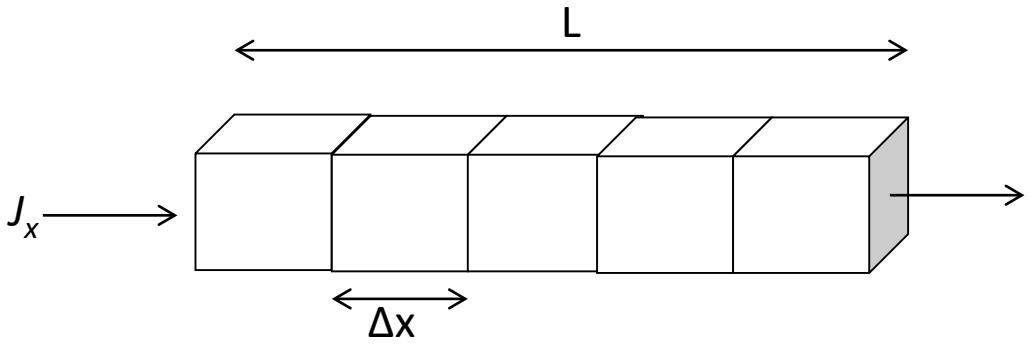
ADVECTION

Exercise 2: Advective Transport

$$\frac{\partial C}{\partial t} = -\nabla \cdot [vC] = -v\frac{\partial C}{\partial x}$$

For constant velocity and 1D





Initial condition: junk2
Left boundary: junk1 flux
Right boundary: junk2 flux

$$CFL = \frac{v\Delta t}{\Delta x}$$

Courant-Friedrichs-Lewy Condition

Numerical Dispersion

$$\frac{\left(C_i^{n+1} - C_i^n\right)}{\Delta t} = -v\frac{\left(C_i^n - C_i^n\right)}{\Delta x}$$

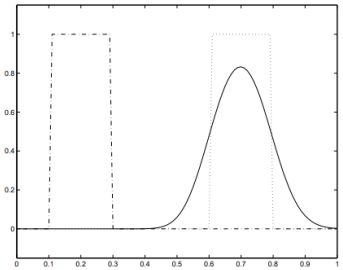
Upwind Scheme

$$C_i^{n+1} = C_i^n - \Delta t\left(\frac{\partial C}{\partial t}\right)_i + \frac{(\Delta t)^2}{2}\left(\frac{\partial^2 C}{\partial t^2}\right)_i + \ldots$$

$$C_i^{n+1} = C_i^n - \Delta x\left(\frac{\partial C}{\partial x}\right)_i + \frac{(\Delta x)^2}{2}\left(\frac{\partial^2 C}{\partial x^2}\right)_i + \ldots$$

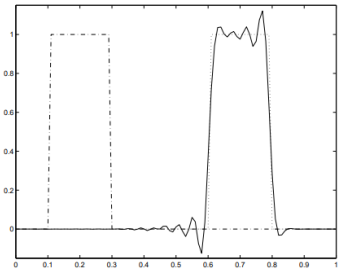
Taylor Series Expansions

Even terms result in smearing and amplitude errors Odd terms result in oscillatory phase errors



smearing (amplitude errors)

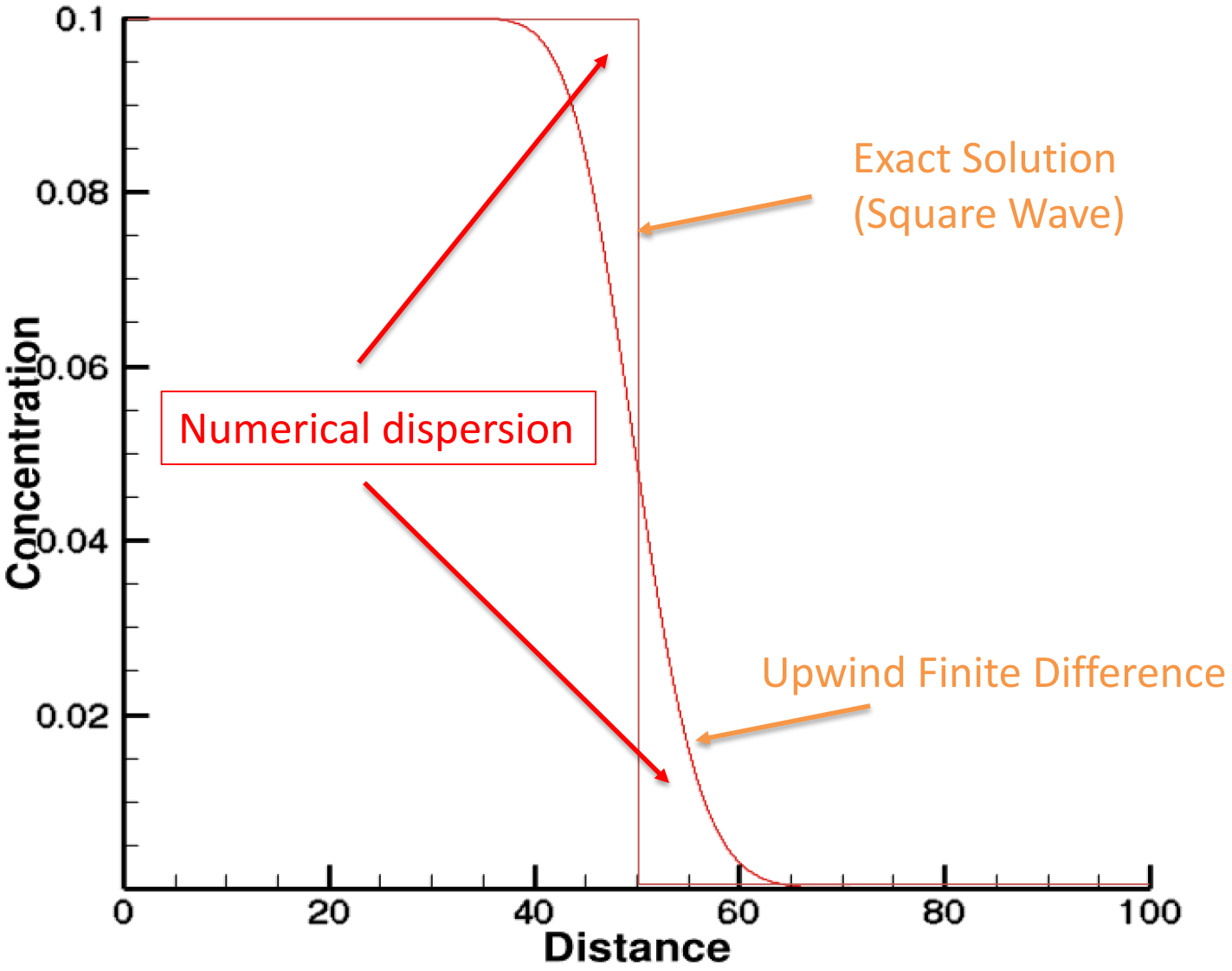
$$\frac{\partial u}{\partial t} + v\frac{\partial u}{\partial x} = 0$$



wiggles (phase errors)

http://www.mathematik.uni-dortmund.de/~kuzmin/cfdintro/lecture10.pdf

Numerical Dispersion



Exercise 2 Procedure

1. **Run CrunchTope in "GIMRT" mode, which uses 1st order upwind that introduces numerical dispersion**

```
RUNTIME
time_units      years
timestep_max    0.010
timestep_init   0.010
time_tolerance  0.1
hindmarsh       true
master          Tracer
database_sweep  no
speciate_only   false
gimrt           true
database        datacom.dbs
END
```

```
FLOW
time_units      years
distance_units  meters
constant_flow   1.0
END
```

```
TRANSPORT
distance_units meters
time_units    years
fix_diffusion  0.0
dispersivity   0.0
END
```

```
BOUNDARY_CONDITIONS
x_begin  junk1   flux
x_end    junk2   flux
END

INITIAL_CONDITIONS
junk2  1-100
END

DISCRETIZATION
distance_units  meters
xzones 100 1.00
END

Condition junk1
units          mol/kg
temperature    25.0
Tracer         0.1
END

Condition junk2
units          mol/kg
temperature    25.0
Tracer         0.000001
END
```

Boundary Condition

Initial Condition

Exercise 2 Procedure

1. **Run CrunchTope in "GIMRT" mode, which uses 1st order upwind that introduces numerical dispersion**
2. **Save "totcon1.out" as "totcon1_gimrt.out" to avoid being written over**
3. **Change to "gimrt false" so as to use TVD 3rd order accurate scheme with van Leer limiters**
4. **Rerun and compare "totcon1_gimrt.out" with "totcon1.out"**
5. **Now gradually increase dispersion in the input file (while still using OS3D mode ("gimrt false") until you get a match between TVD (OS3D) profile and Upwind (GIMRT) profile**

```
RUNTIME
time_units      years
timestep_max    0.010
timestep_init   0.010
time_tolerance  0.1
hindmarsh       true
master          Tracer
database_sweep  no
speciate_only   false
gimrt           false
database        datacom.dbs
END
```

Turns off upwinding, turns on higher order TVD scheme

```
TRANSPORT
distance_units meters
time_units     years
fix_diffusion  0.0
dispersivity   0.01
END
```

$\propto v$

Units of meters

Gradually increase until you have a match

What dispersivity do you need to match?

FICKIAN DIFFUSION

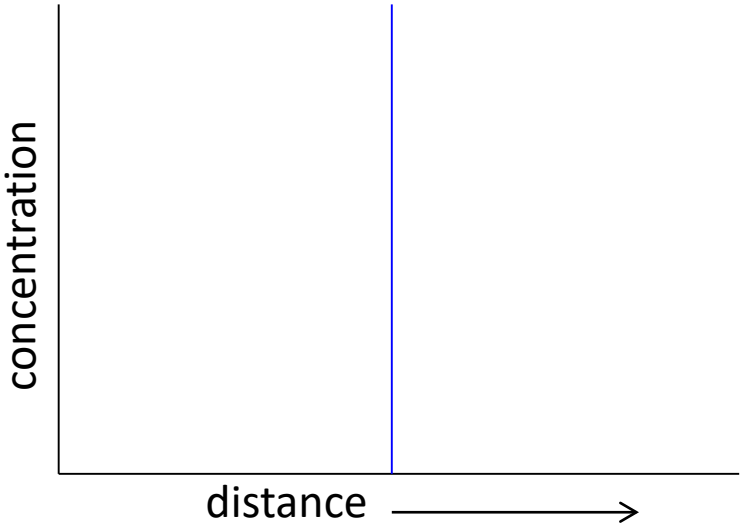
Exercise 3: Fickian Diffusion

(a) early

(b) intermediate

(c) late

Initial Condition



$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2}$$

Exercise 3: Fickian Diffusion

```
TRANSPORT
distance_units meters
time_units  second
fix_diffusion  1.E-09
dispersivity   0.0
END

DISCRETIZATION
xzones 501  0.0002
END

INITIAL_CONDITIONS
initial   1-501
boundary  251-251
END
```

Writes over earlier specified initial condition

```
BOUNDARY_CONDITIONS
x_begin   initial      flux
x_end     initial      flux
END
```

"flux" uses flow rate through boundary, if flow rate = 0, then it becomes a No Flux BC

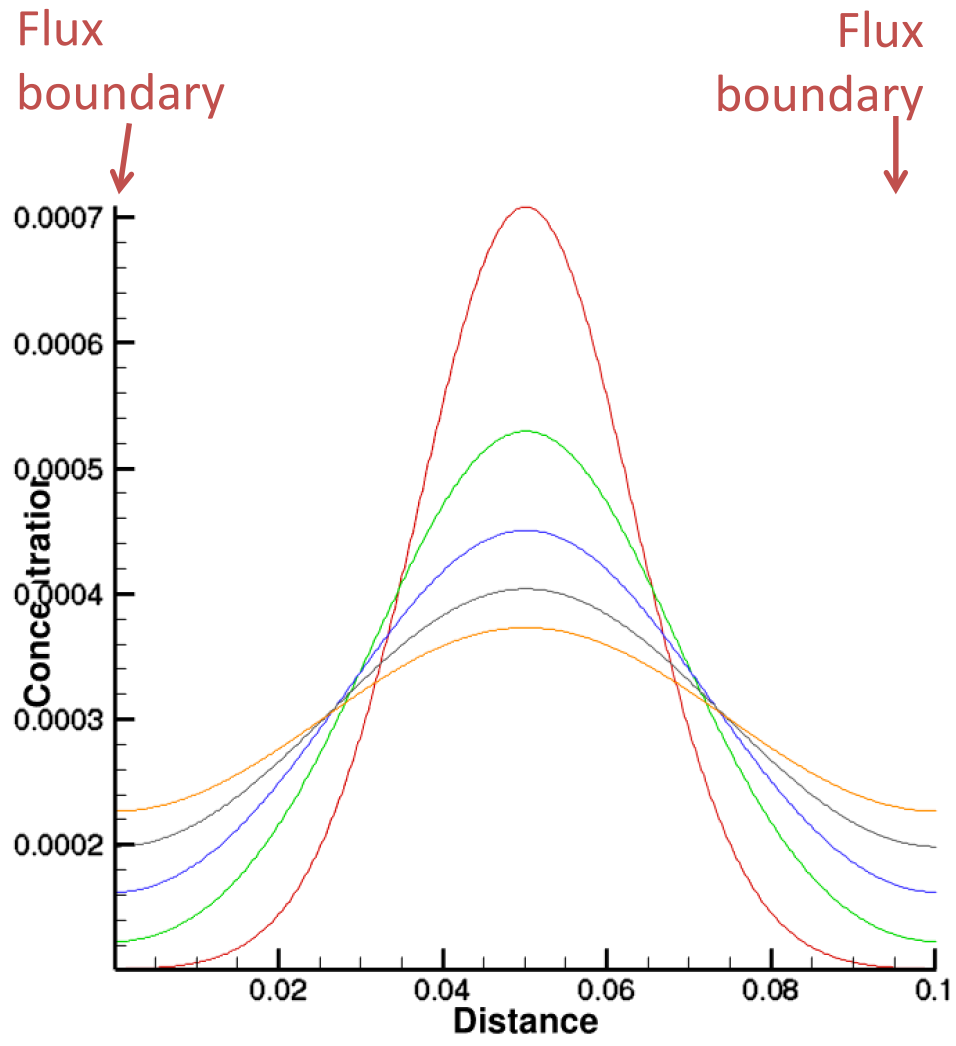
```
FLOW
time_units      years
distance_units   meters
constant_flow    0.0
END
```

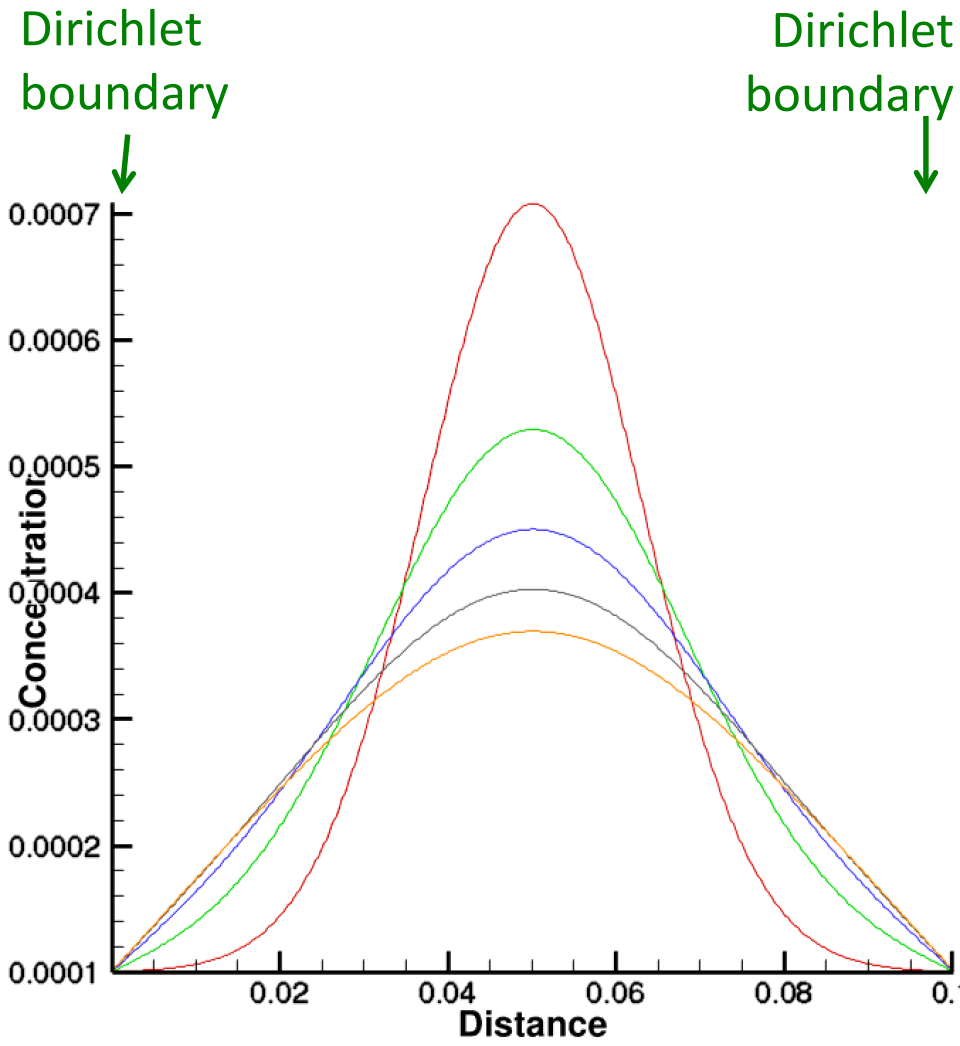
```
Condition boundary
units          mol/kg
temperature     25.0
Tracer          0.1
END
Condition initial
units          mol/kg
temperature     25.0
Tracer          0.0001
END
```

After running "flux" BC, switch to "Dirichlet" (fixed concentration) and compare results

```
BOUNDARY_CONDITIONS
x_begin   initial      Dirichlet
x_end     initial      Dirichlet
END
```

Exercise 3: Fickian Diffusion





NOTE: Error function analytical (ERF) solution only applies to infinite (or semi-infinite) boundary conditions, so would fail to describe system once mass reaches the boundary

NERNST-PLANCK
MULTICOMPONENT DIFFUSION

Exercise 4: Multicomponent Diffusion

Flux from chemical potential

$$J_i = L_{ij} \nabla \mu_i$$

Nernst-Planck Equation

Fickian **Electrical Potential** **Activity Coefficient**

$$J_i = -D_i \nabla C_i - \frac{z_i \mathrm{F} D_i C_i}{\mathrm{R}T} \nabla \psi - D_i C_i \nabla \ln \gamma_i$$

Diffusion Potential

$$\nabla \psi = -\frac{\mathrm{R}T}{\mathrm{F}} \frac{\sum_j z_j D_j \left[\nabla C_j + C_j \nabla \ln \gamma_j \right]}{\sum_j z_j^{\,2} D_j C_j}$$

Term vanishes if diffusion coefficients are all the same

CrunchTope Equation

$$J_i = -D_i \left[\nabla C_i \right] + z_i D_i C_i \frac{\sum_j z_j D_j \left[\nabla C_j \right]}{\sum_j z_j^{\,2} D_j C_j}$$

Fick's Law **Diffusion Potential**

Exercise 4: Multicomponent Diffusion
(with Nernst-Planck Equation)

```
BOUNDARY_CONDITIONS
X_begin   inlet       Dirichlet
X_end     initial     flux
END

TRANSPORT
distance_units centimeters
time_units  seconds
fix_diffusion  1.000e-05
formation_factor  1.0
cementation_exponent  1.0
D_25  H+     9.312e-05
D_25  Na+    1.334e-05
D_25  Cl-    2.032E-05
D_25  OH-    5.26e-05
D_25  NO3-   1.00e-05
END
```

Refers to Condition "inlet" and "initial"

Species-specific diffusion coefficients

```
Condition initial
temperature     25.0
pH              4.0
Cl-             1.e-04
Na+             1.e-04
NO3-            1.e-04
CO2(aq)         CO2(g)   1.0E-16
END

Condition inlet
temperature     25.0
pH              6.0
Cl-             1.e-04
Na+             1.e-04
NO3-            1.e-06
CO2(aq)         CO2(g)   1.0E-16
END
```

NOTE: Hydrogen ion will try to diffuse faster than Cl^- and Na^+

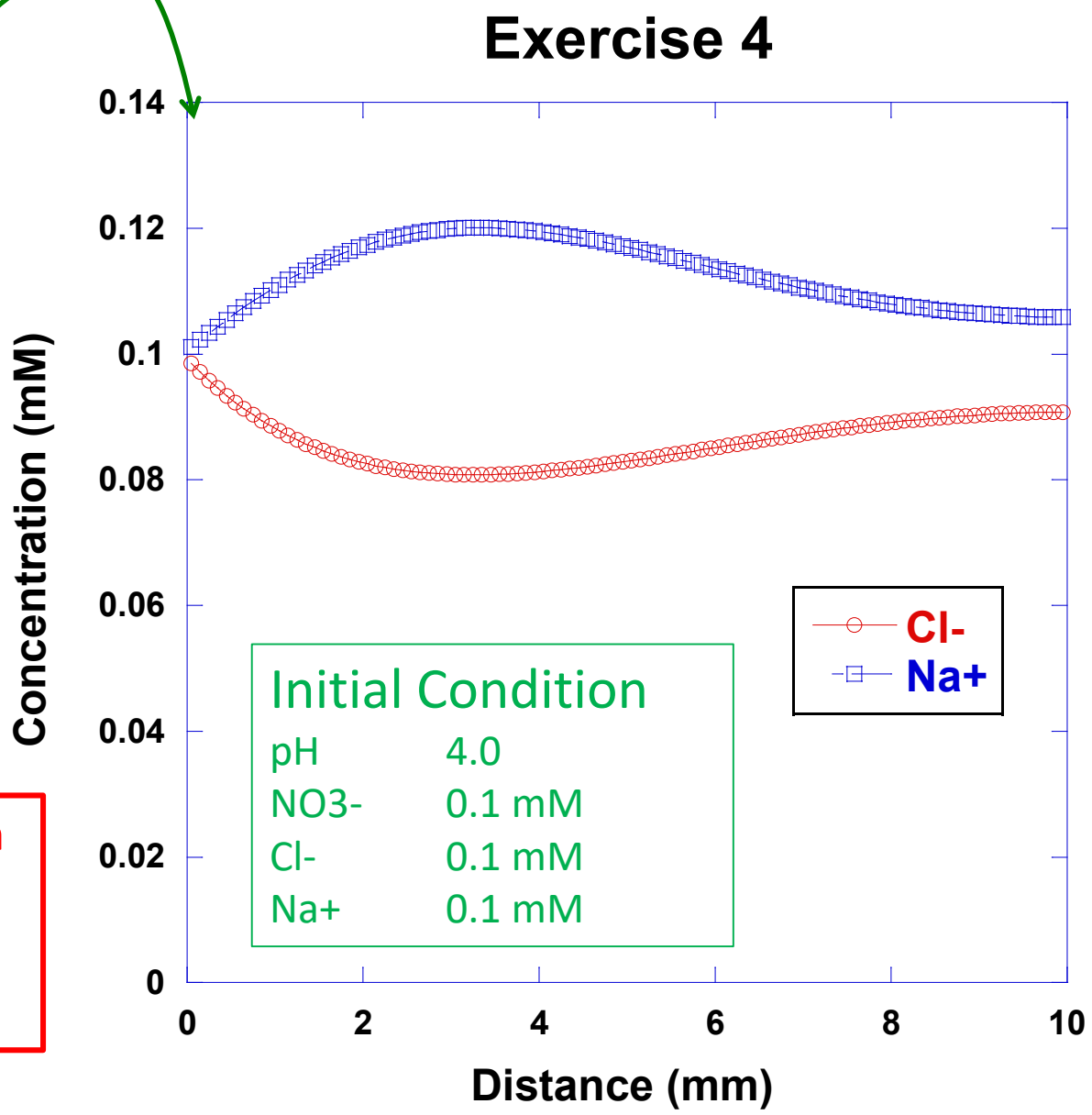
Change diffusion coefficients all to same number and compare results

```
TRANSPORT
D_25  H+     1.000e-05
D_25  Na+    1.000e-05
D_25  Cl-    1.000e-05
D_25  OH-    1.000e-05
D_25  NO3-   1.000e-05
END
```

Exercise 4: Nernst-Planck Equation

Left Boundary

pH	6.0
NO3-	0.001 mM
Cl-	0.1 mM
Na+	0.1 mM



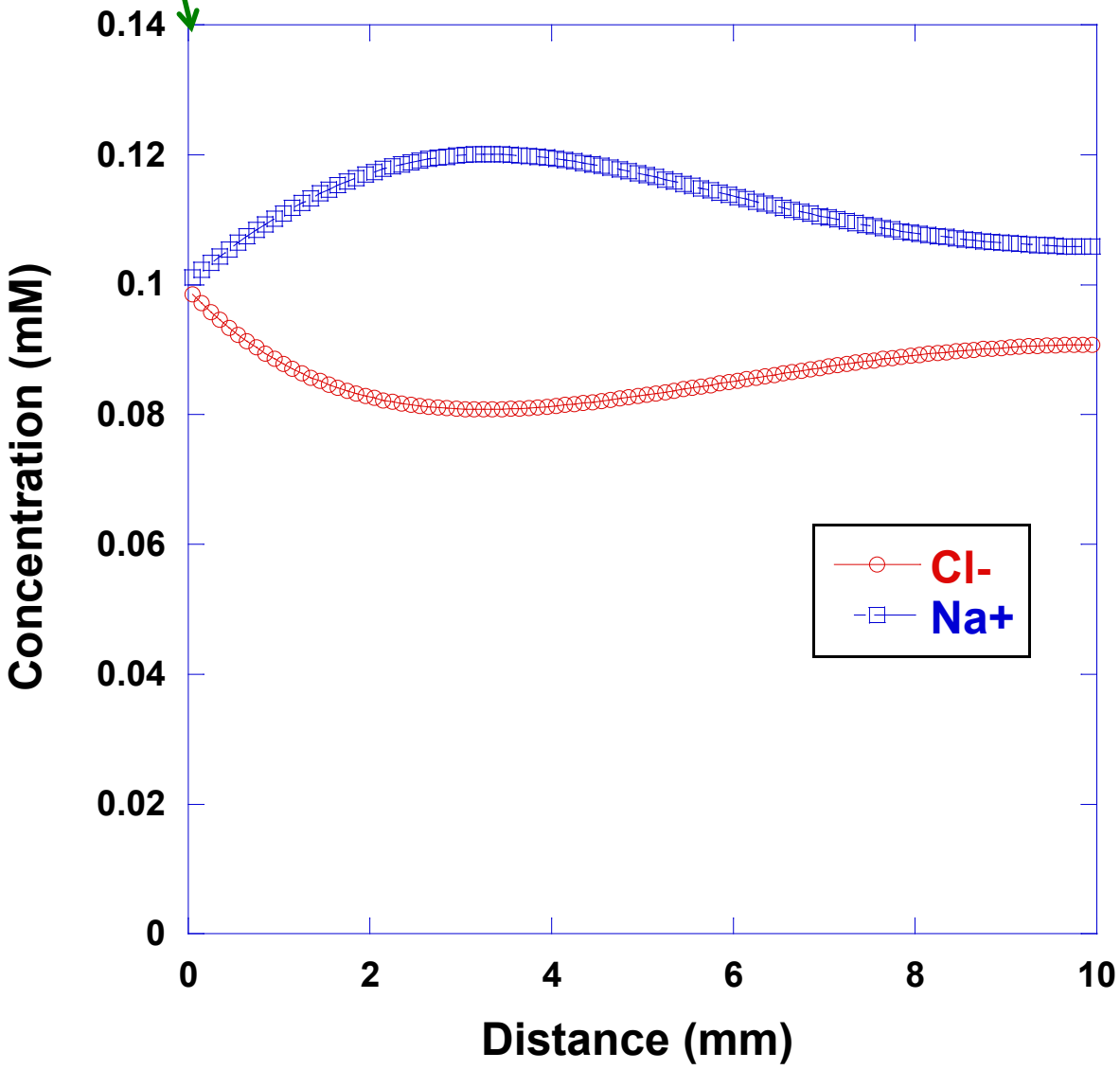
NOTE: No initial gradient in Na^+ or Cl^-, so Fick's Law would say there is no diffusion

Left Boundary

pH	6.0
NO3-	0.001 mM
Cl-	0.1 mM
Na+	0.1 mM

Initial Condition

pH	4.0
NO3-	0.1 mM
Cl-	0.1 mM
Na+	0.1 mM



Exercise 4: Nernst-Planck with $\delta^{37}Cl$

Isotopic fractionation expressed in per mil

```
ISOTOPES
primary  37Cl-  Cl-  0.333
END
```

Rare Isotope **Common Isotope**

$$\delta = \left[\frac{\left[{}^{37}Cl / {}^{36}Cl \right]_{sample}}{\left[{}^{37}Cl / {}^{36}Cl \right]_{std}} - 1 \right] \cdot 1000$$

Isotope ratio of standard

```
TRANSPORT
distance_units centimeters
time_units  seconds
fix_diffusion     1.000e-05
formation_factor  1.0
cementation_exponent  1.0
D_25  H+          9.312e-05
D_25  Na+         1.334e-05
D_25  Cl-         2.032E-05
D_25  37Cl-       2.028E-05
D_25  OH-         5.26e-05
D_25  NO3-        1.00e-05
END
```

Note difference in diffusion coefficients (source of fractionation)

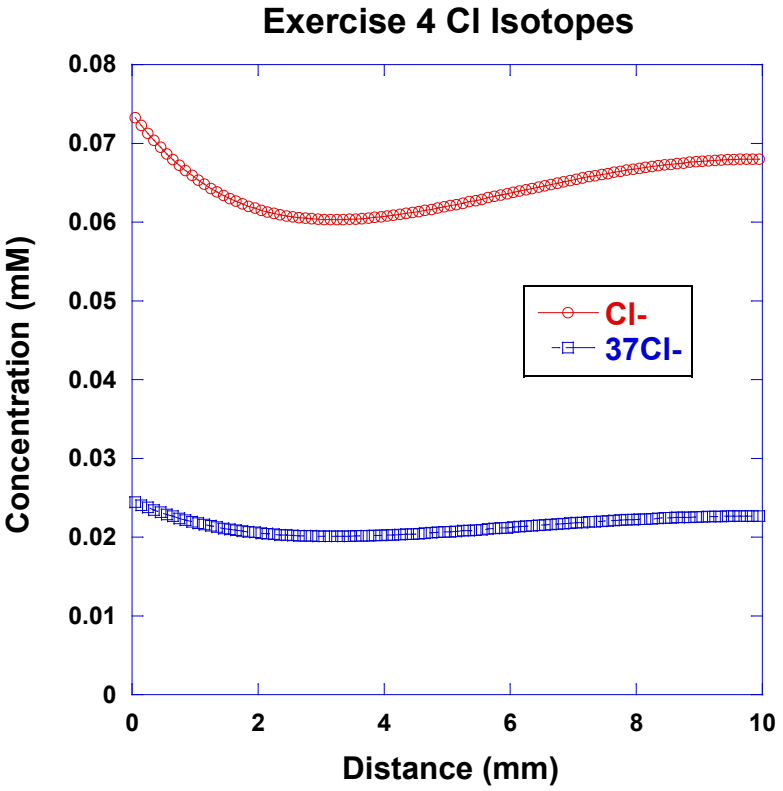
Find isotopic ratios in `toperatio_aq1.out`

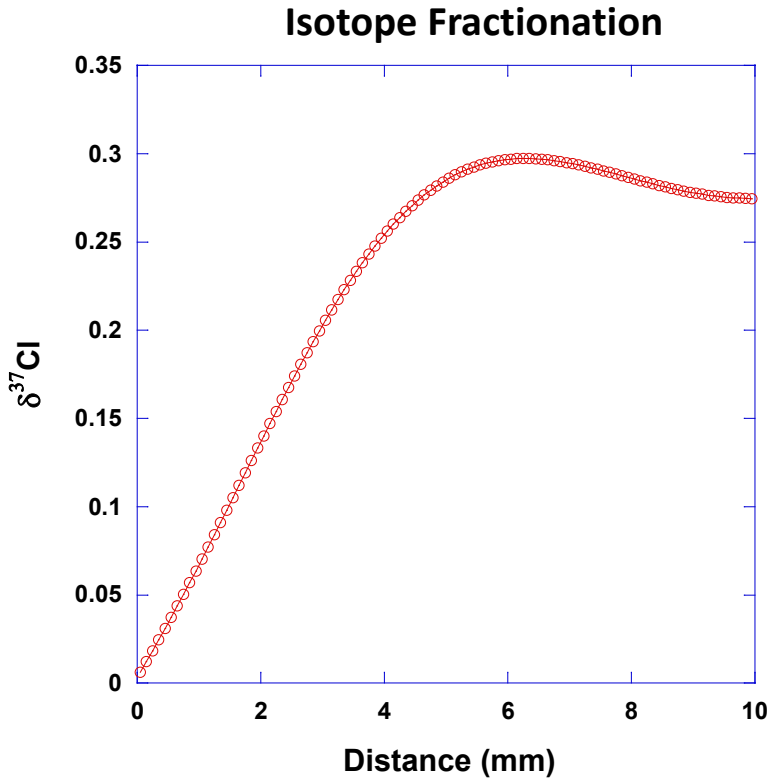
Exercise 4: Nernst-Planck with $\delta^{37}Cl$

Left Boundary	
pH	6.0
Cl-	0.075
37Cl-	0.025
Na+	0.1
NO3-	0.001

D_25	Cl-	2.032E-5
D_25	37Cl-	2.028E-5

$$\delta = \left[\frac{\left[{}^{37}Cl / {}^{36}Cl \right]_{sample}}{\left[{}^{37}Cl / {}^{36}Cl \right]_{std}} - 1 \right] \cdot 1000$$





Plot isotopic ratios in `toperatio_aq1.out`

SORPTION

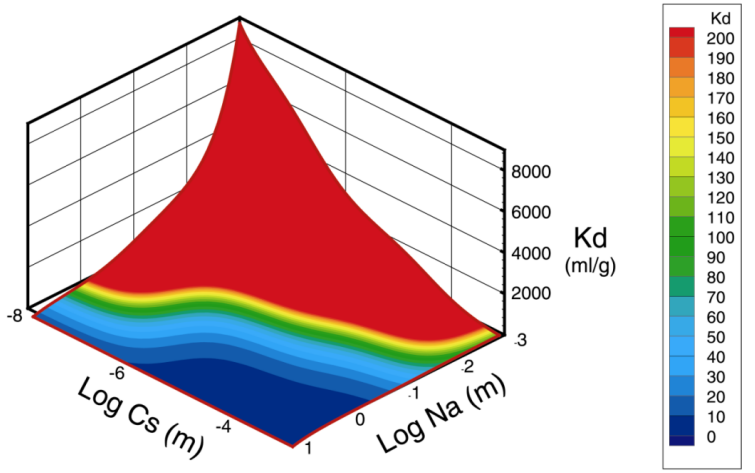
Contaminant Retardation

$$R = 1 + \frac{\rho_B K_d}{\phi}$$

ρ_B : bulk density (g/ml)

K_d : distribution coefficient (ml/g)

ϕ : porosity



$$R\frac{\partial C}{\partial t} = \frac{\partial}{\partial x_i}\left[D_{ij}\frac{\partial C}{\partial x_j}\right] - \frac{\partial}{\partial x_i}\left[v_i C\right]$$

Contaminant Velocity v_c

$$v_c = \frac{v_x}{R}$$

Exercise 6a: Cesium Ion Exchange

Exchange reaction involving Cs^+ and a competing Na^+

$$Cs^+ + X^- \leftrightarrow CsX$$

$$NaX \leftrightarrow Na^+ + X^-$$

$$Cs^+ + NaX \leftrightarrow CsX + Na^+$$

Gaines-Thomas convention for activity of an exchange species

$$\beta(i)_M = \frac{z_M q(i)_M}{\sum_M z_M q(i)_M}$$

Cation charge

Moles/g

Cation Exchange Capacity:

Single exchange site

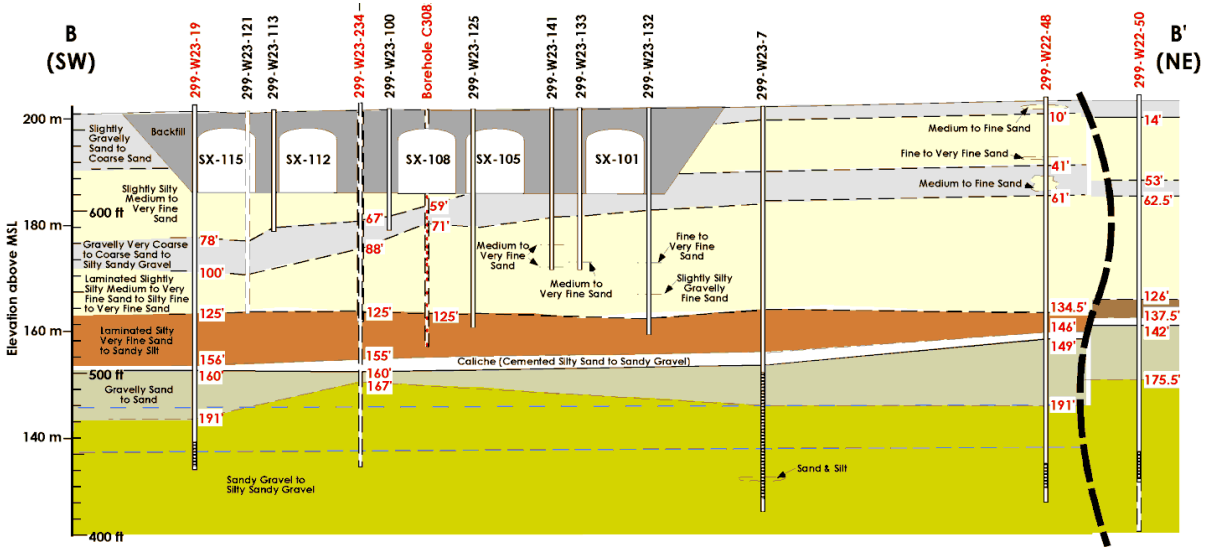
$$CEC = \sum_M z_M q_M$$

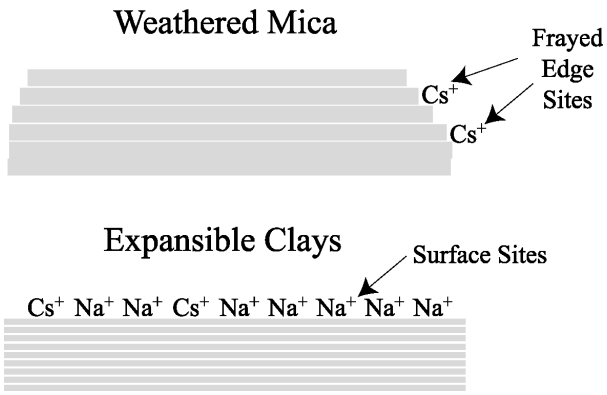
Multiple exchange sites

$$CEC = \sum_i \sum_M z_M q(i)_M$$

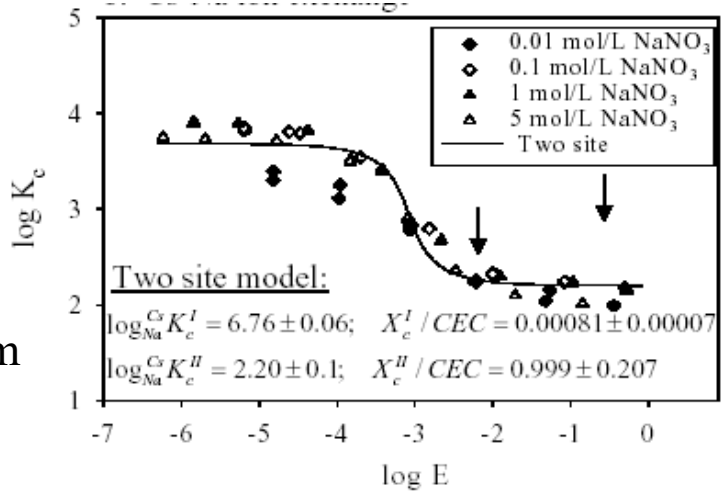
Real World Example for ^{137}Cs Cation Exchange

Leaking high ionic strength waste tanks led to contamination of the deep Hanford Vadose Zone





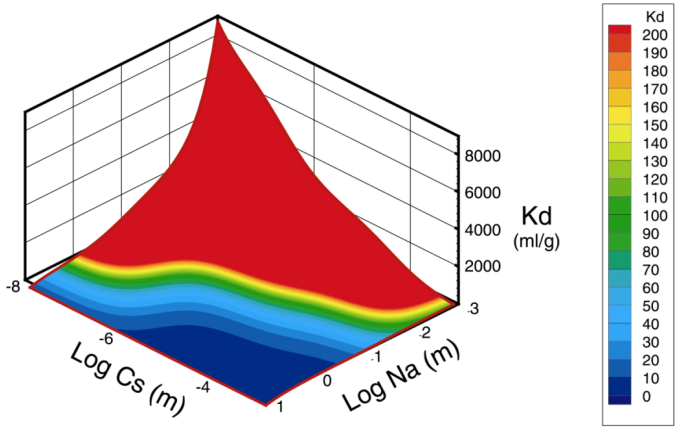
Failure of K_d models spawned a major Science and Technology Program at Hanford funded by the U.S. DOE



Binary exchange data from Zachara et al. (2002)

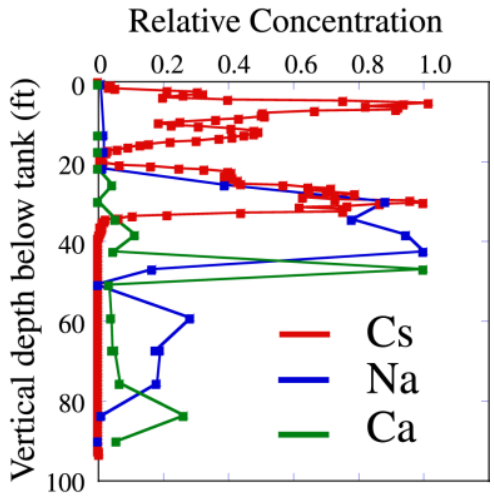
Cs Mobility in High Ionic Strength Solutions

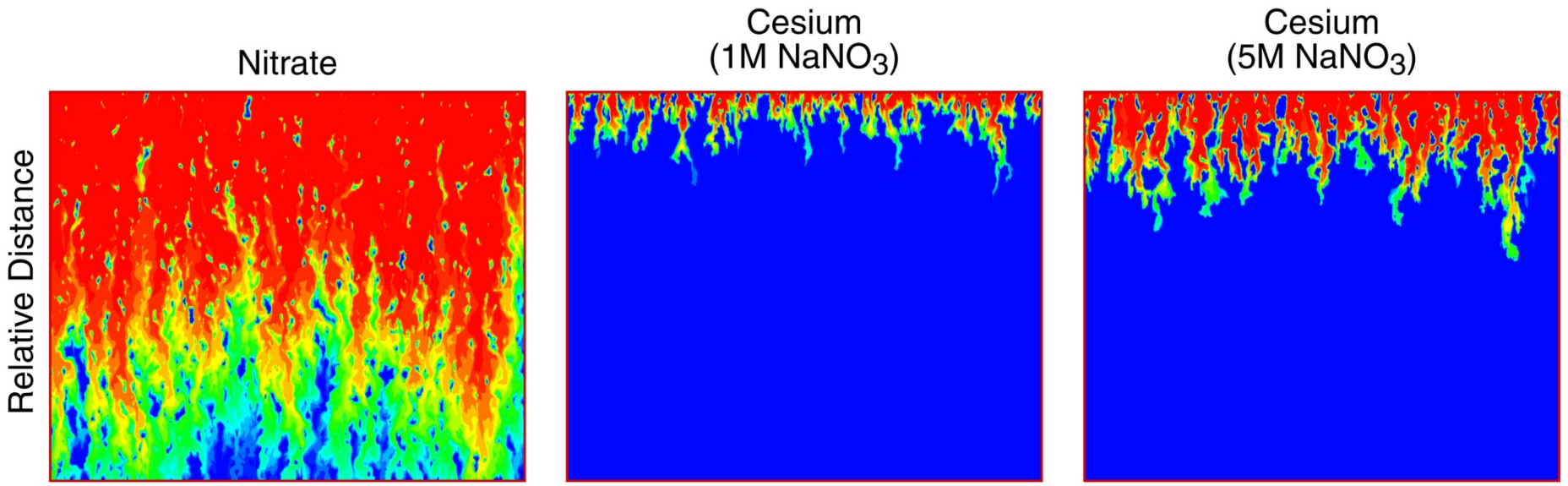
Greatest mobility of ^{137}Cs was below the Hanford SX-108 tank



Cesium K_d in Hanford Sediments

Steefel et al., 2003; 2005





Exercise 6a: Cesium Ion Exchange

Simulated sequence:

Input file	HanfordTank-A	HanfordTank-B	HanfordTank-C
$NaNO_3$ injectate concentration	5 M	5 M	5 M
CsI injectate concentration	0	0.1 mM	0
Duration	19.25 hrs	125 hrs	76.5 hrs
Purpose	Precondition sediment	Active exchange of Cs for Na	Flushing sediment

Exercise 6a: Cesium Ion Exchange

```
RUNTIME
density_module      sodium_nitrate
database            HanfordTanksColumnFit3Site-GT.dbs
save_restart        Column3NaNO3Flush1.rst
later_inputfiles    HanfordTank-B.in HanfordTank-C.in
END
```

```
OUTPUT
time_units          hours
spatial_profile     19.25
time_series         Expt3ColumnFit.out  100
time_series_print   Cs+  I-
time_series_output  0.00
END
```

```
BOUNDARY_CONDITIONS
x_begin   nano3flush        flux
x_end     initial_condition   flux
END
```

```
POROSITY
fix_porosity    0.405
porosity_update  false
END

ION_EXCHANGE
exchange   Xhan1-
exchange   Xhan2-
exchange   Xhan3-
convention Gaines-Thomas
END

DISCRETIZATION
distance_units  centimeters
xzones   100 0.15228
END
```

3 types of exchange sites

Database entries for log K (selectivity coefficients)
Assumes half-exchange reactions

Frayed edge site on illite

Planar sites on illite

```
Begin exchange
'NaXhan1' 2  1.0 'Na+' 1.0 'Xhan1-'        7.25224
'NaXhan2' 2  1.0 'Na+' 1.0 'Xhan2-'        4.93359
'NaXhan3' 2  1.0 'Na+' 1.0 'Xhan3-'        1.98868
'CsXhan1' 2  1.0 'Cs+' 1.0 'Xhan1-'        0.00
'CsXhan2' 2  1.0 'Cs+' 1.0 'Xhan2-'        0.00
'CsXhan3' 2  1.0 'Cs+' 1.0 'Xhan3-'        0.00
```

Exercise 6a: Cesium Ion Exchange

Initial Condition

```
Condition initial_condition
units          molar
temperature     25.0
pH             8.0
HCO3-          CO2(g)  3.15e-04
K+             0.0015
NO3-           0.001
Cs+            0.000
I-             0.000
Na+            0.001
Ca++           Calcite
Mg++           0.00005
Tracer         0.0
Cl-            charge
Xhan1-  -cec   2.277023E-08
Xhan2-  -cec   2.621486E-07
Xhan3-  -cec   1.20E-04

Calcite      0.01   specific_surface_area   0.1
SolidDensity  -ss_ratio  4698
END
```

Frayed edge site on illite (eq/g)

Planar sites on illite (eq/g)

```
BOUNDARY_CONDITIONS
x_begin   nano3flush          flux
x_end     initial_condition   flux
END
```

Sodium Nitrate Flush

```
Condition nano3flush
units          molar
temperature     25.0
pH             8.0
HCO3-          CO2(g)  3.15e-04
K+             1.e-5
Cs+            0.0
I-             0.0
Na+            1.00
NO3-           1.00
Ca++           0.0
Mg++           0.0
Tracer         0.001
Cl-            0.0
Xhan1-  -cec   2.277023E-08
Xhan2-  -cec   2.621486E-07
Xhan3-  -cec   1.20E-04
Calcite      0.01   specific_surface_area   0.1
SolidDensity  -ss_ratio  4698
END
```

```
FLOW
time_units     years
distance_units meters
constant_flow  638.2
END
```

Exercise 6a: Cesium Ion Exchange

Cesium Spike: `HanfordTank-B.in`

```
Condition cesiumflush
units          molar
temperature    25.0
pH             8.0
HCO3-          CO2(g)  3.15e-04
K+             1.e-5
Cs+            1.05e-4
I-             1.05e-4
Na+            1.00
NO3-           1.00
Ca++           0.000
Mg++           0.0
Tracer         0.001
Cl-            0.0
Xhan1-  -cec   2.277023E-08
Xhan2-  -cec   2.621486E-07
Xhan3-  -cec   1.20E-04
Calcite        0.01   specific_surface_area   0.1
SolidDensity  -ss_ratio  4698
END
```

This run "inherits" NaNO3 exchanged sediment from HanfordTank-A run

```
BOUNDARY_CONDITIONS
x_begin   cesiumflush          flux
x_end     initial_condition    flux
END
```

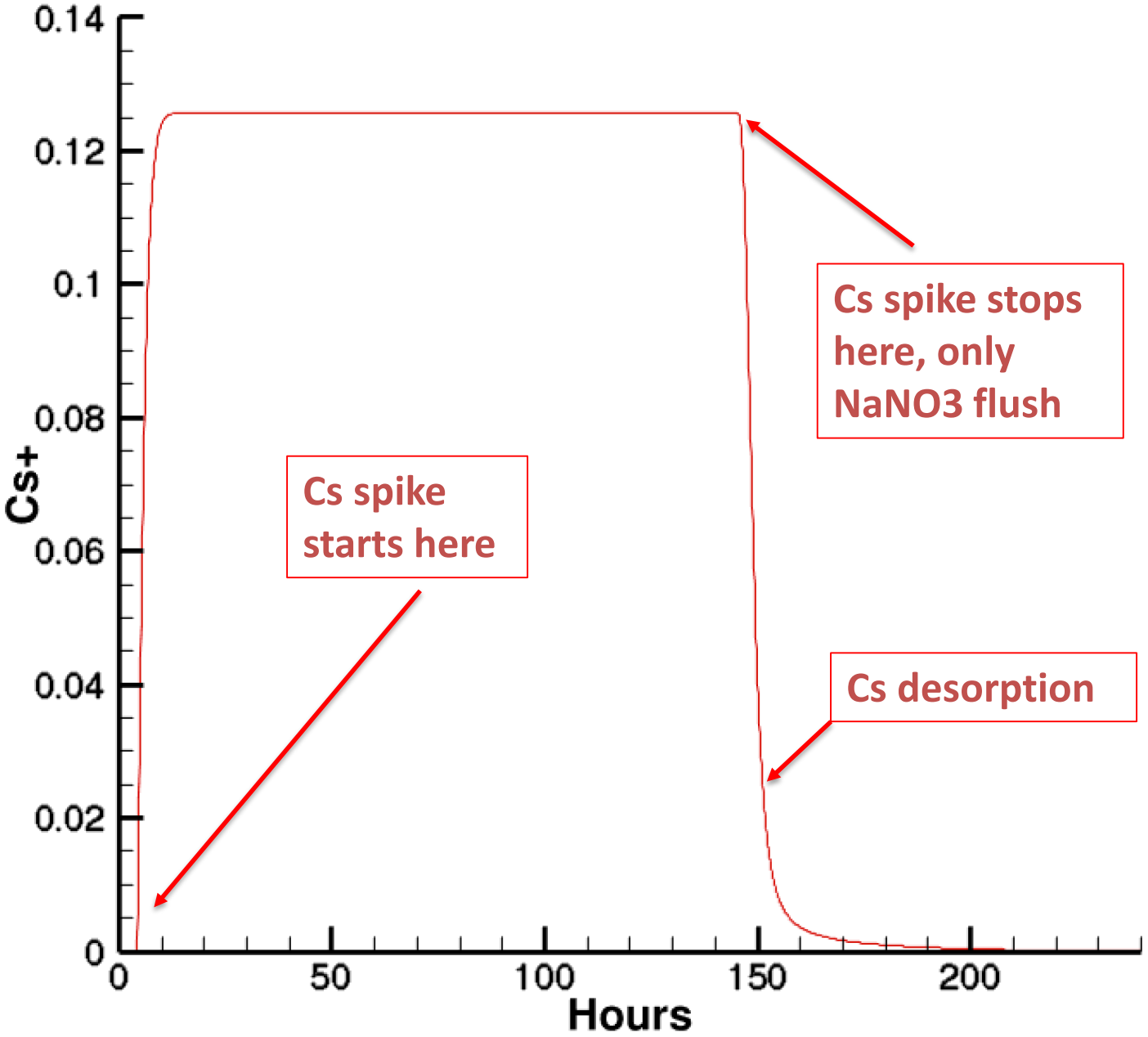
Sodium Nitrate Flush: `HanfordTank-C.in`

```
Condition nano3flush
units          molar
temperature    25.0
pH             8.0
HCO3-          CO2(g)  3.15e-04
K+             1.e-5
Cs+            0.0
I-             0.0
Na+            1.00
NO3-           1.00
Ca++           0.0
Mg++           0.0
Tracer         0.001
Cl-            0.0
Xhan1-  -cec   2.277023E-08
Xhan2-  -cec   2.621486E-07
Xhan3-  -cec   1.20E-04
Calcite        0.01   specific_surface_area   0.1
SolidDensity  -ss_ratio  4698
END
```

This run "inherits" Cs contaminated sediment from HanfordTank-B run

```
BOUNDARY_CONDITIONS
x_begin   nano3flush           flux
x_end     initial_condition    flux
END
```

Exercise 6a: Cesium Ion Exchange



Column effluent breakthrough curve

Cs spike starts here

Cs spike stops here, only NaNO3 flush

Cs desorption

Exercise 6b: Surface Complexation

Surface Hydroxyl

Protonation-deprotonation reactions controlling surface charge

$$SOH_2^+ \rightleftharpoons SOH^0 + H^+ \qquad SOH^0 \rightleftharpoons SO^- + H^+$$

$$K_{a1} = \frac{[SOH^0][H^+]}{[SOH_2^+]} \qquad K_{a2} = \frac{[SO^-][H^+]}{[SOH^0]}$$

First Acidity Constant — Second Acidity Constant

Electrostatic Effects

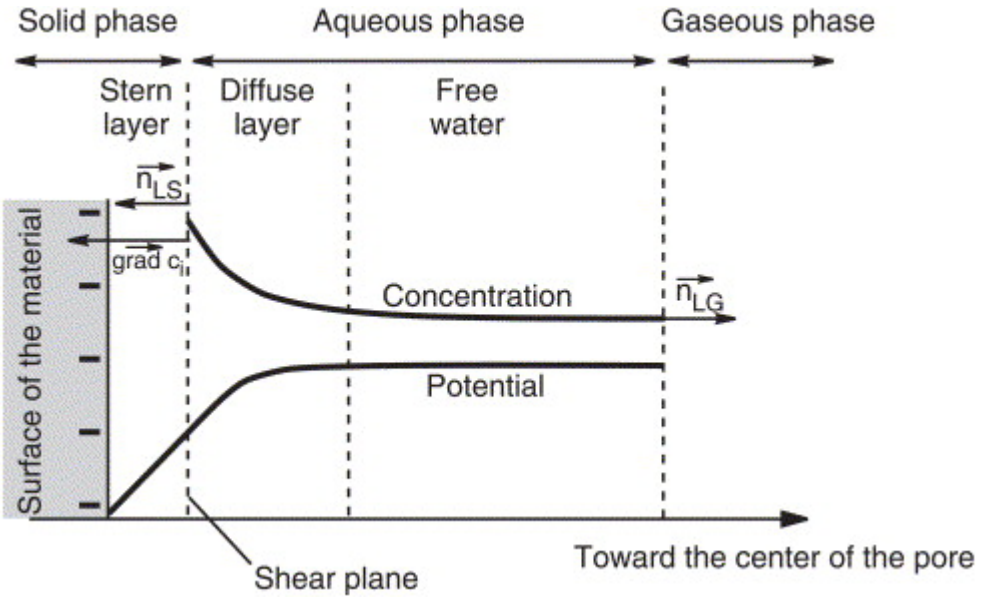
$$W = (+)_{\text{surface sites}} - (-)_{\text{surface sites}}$$

$$Q = W / \text{mass sorbent}$$

$$\sigma(C/m^2) = \frac{QF}{A}$$ ← Surface charge density

$$\Delta G_{ads} = \Delta G_{chem} + \Delta G_{coul}$$

$$K_a = K_{\text{intrinsic}} \exp\left[\frac{\Delta z F \Psi}{RT}\right]$$



Exercise 6b: Surface Complexation

Surface Complexation of Zn^{+2} on $Fe(OH)_3$

$$>FeOH2+\_str \rightleftharpoons >FeOH\_strong + H^+$$
$$>FeO-\_str + H^+ \rightleftharpoons >FeOH\_strong$$
$$>FeOHZn+\_str \rightleftharpoons >FeOH\_strong + H^+$$
$$>FeOH2+\_w \rightleftharpoons >FeOH\_weak + H^+$$
$$>FeO-\_w + H^+ \rightleftharpoons >FeOH\_weak$$
$$>FeOHZn+\_w \rightleftharpoons >FeOH\_weak + H^+$$

$$C_{sites} = \frac{\rho_{sites} A_{specific} MW_m \phi_m}{1000 V_m}.$$

```
!!!Site name     <site density mol/m**2>
>FeOH_weak       3.703704E-06
>FeOH_strong     9.259259E-08
Fe(OH)3          2.943109E-05  specific_surface_area  600.0
!!! Note: Gives 0.09 g/kgw water Fe(OH)3, 54 m**2 surface
```

Exercise will "sweep" the pH from 5.0 to 8.0 to show the Zn "pH edge"

Exercise 6b: Surface Complexation

```
OUTPUT
time_units            days
spatial_profile       365
time_series_at_node   PHREEQCexample8.out  1  1  1
```

```
SURFACE_COMPLEXATION
>FeOH_strong   on Fe(OH)3
>FeOH_weak     on Fe(OH)3
END
```

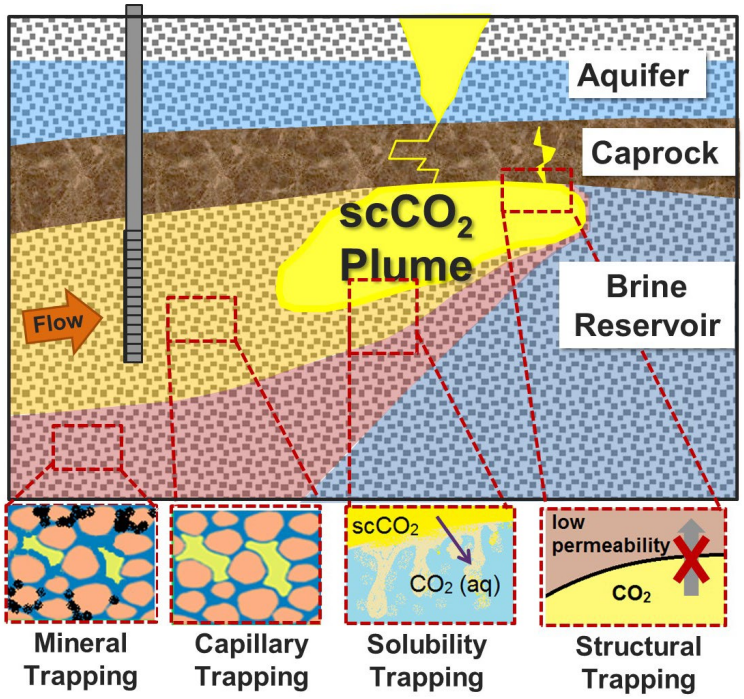
```
Condition Solution1
temperature       25.0
pH                5.00
Zn++              1.E-07        equilibrate_surface
Na+               charge
NO3-              1.0000E-01
Fe+++             0.00
O2(aq)            2.4647E-04
!Site name     <site density mol/m**2>
>FeOH_weak      3.703704E-06
>FeOH_strong    9.259259E-08
Fe(OH)3         2.943109E-05  specific_surface_area  600.0
SolidDensity    2600.0

 !! Note: Gives 0.09 g/kgw water Fe(OH)3, 54 m**2 surface
!!  Based on a density of 1017 kg/m**3, 1.017 g/cm**3
!!    Volume Fraction Fe(OH)3 [m**3/m**3]*0.001*Molecular Weight Fe(OH)3/(Porosity*Molar Volume Fe(OH)3
[m**3/mole]) = g/L, but we want g/kg water, so g/L * (1/ro) = g/kgw

END
```

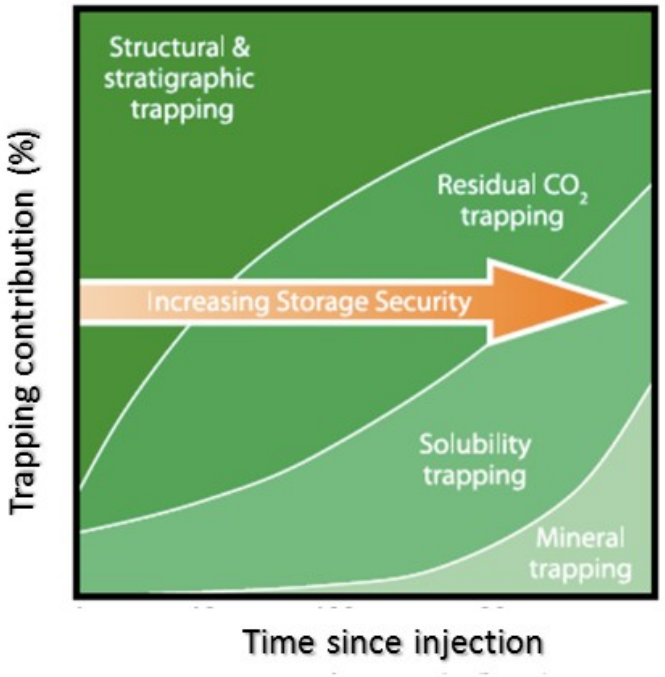
Partitions total concentration between surface and aqueous

Site densities for weak and strong sites

CO_2 ATTACK ON CEMENT

Exercise 7: CO_2 Attack on Cement





Diffusion-Reaction System

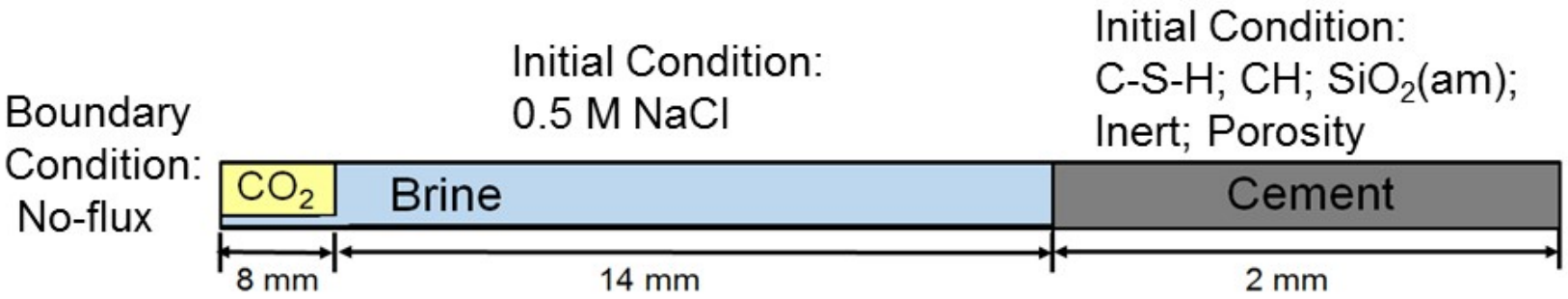
Dirichlet Boundary: Supercritical CO_2 at 100 bars

Mineralogy:

1. Portlandite
2. Calcium-silica hydrate (CSH)
3. Calcite precipitates

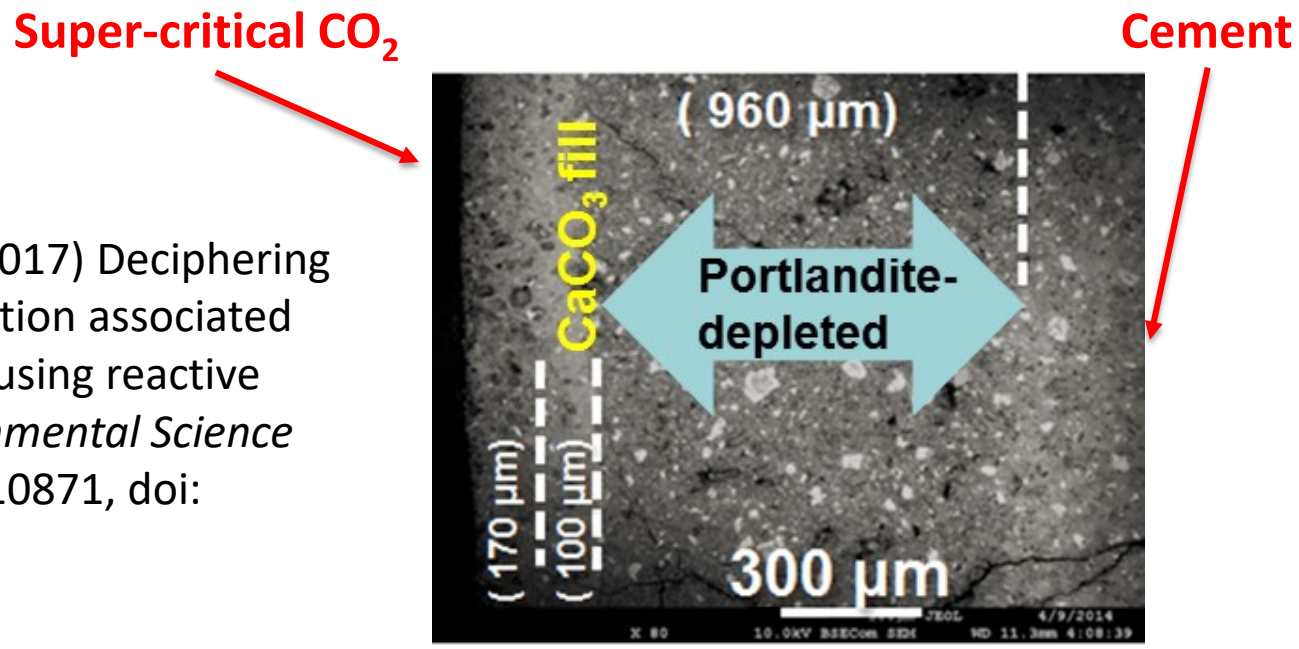
Li, Steefel, & Jun, 2017

Exercise 7: CO_2 Attack on Cement

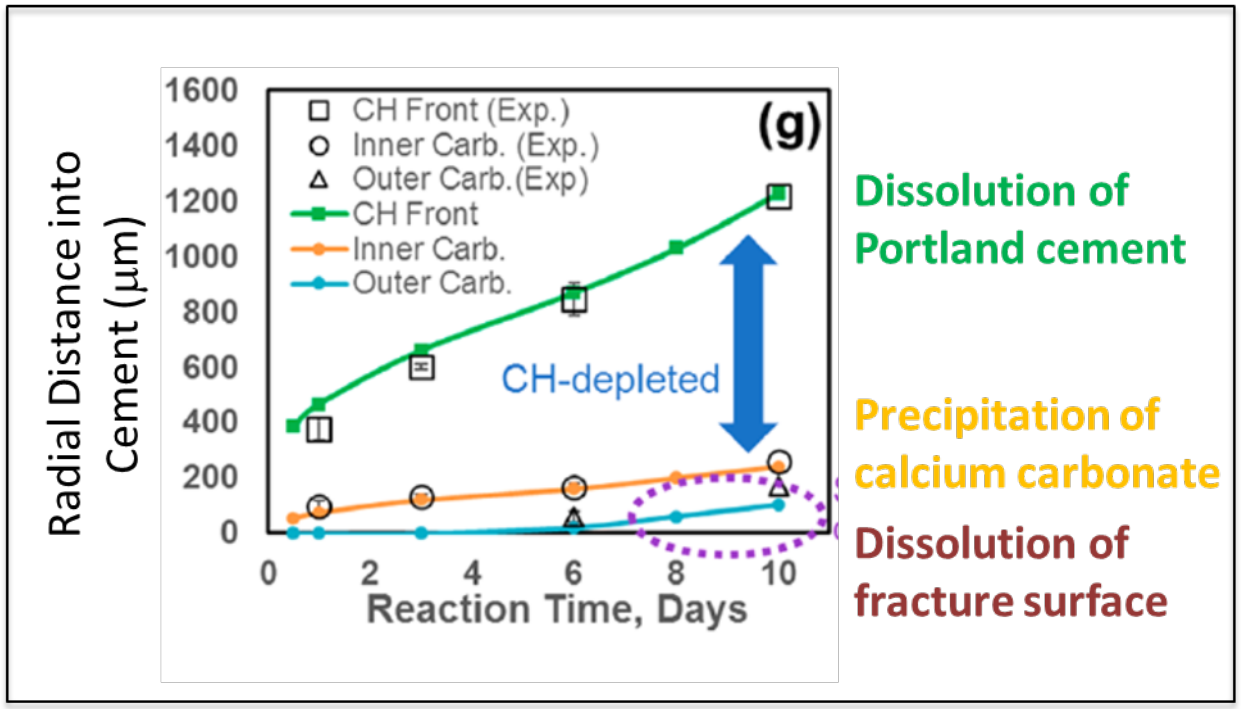


Based on:

Li, Q., C.I. Steefel, Y-S Jun (2017) Deciphering calcium carbonate precipitation associated with CO_2 attack on cement using reactive transport modeling. *Environmental Science and Technology* **51**: 10861-10871, doi: 10.1021/acs.est.7b00594.



Exercise 7: CO_2 Attack on Cement



Li, Q., C.I. Steefel, Y-S Jun (2017) Deciphering calcium carbonate precipitation associated with CO_2 attack on cement using reactive transport modeling. *Environmental Science and Technology* **51**: 10861-10871, doi: 10.1021/acs.est.7b00594.

Exercise 7: CO_2 Attack on Cement

```
RUNTIME
!!!fix_saturation  0.999
read_saturationfile QL_Saturation.dat
Duan          true
Qingyun       true
```

```
POROSITY
porosity_update     true
minimum_porosity    0.015
porosity_exponent   3.00
porosity_threshold  0.017
END
```

```
Calcite          -label nucleatecalcite
Calcite          -label h+  -rate     -3.0
Calcite_mix      -label h+  -rate     -3.0
SiO2(ammix)      -label default -rate  -6.5
SiO2(am)         -label default -rate  -6.5
SiO2(am)         -label nucleateSiO2(am)
Portlandite      -label default  -rate  -5.0
CSH(1.6)         -label default  -rate  -7.8
CSH(0.8)         -label default  -rate  -7.8
Bogusite         -rate  -35.00
Bogusite_i       -rate  -35.00
```

Two calcites with slightly different solubility

```
NUCLEATION
&Nucleation
 NameMineral     = Calcite
 label           = nucleatecalcite
 A_zero25C       = 0.00000001
 B_nucleation    = 0.000905
 Sigma_mJm2      = 47
 SSA_m2g         = 1
 Surface         = Bogusite_i
  /
END
NUCLEATION
&Nucleation
 NameMineral     = SiO2(am)
 label           = nucleateSiO2(am)
 A_zero25C       = 0.00000001
 B_nucleation    = 0.000905
 Sigma_mJm2      = 20000
 SSA_m2g         = 1
 Surface         = Bogusite_i
  /
END
```

Pre-exponential J_0

Constant terms

Interfacial free energy

Specific surface area of nucleated phase

Template for nucleation

$$R_{precipitation} = J_0 \exp\left[-\frac{\sigma^3 \upsilon^2}{3k_B^3 T^3 \left(\ln \Omega\right)^2}\right] A_{quartz}$$

Exercise 7: CO_2 Attack on Cement

```
Condition Brine-Seed
!!Solution w/o minerals
temperature     95.0
units           mol/kg
pH              charge
CO2(aq)         CO2(g)    100.0
Ca++            0.0
SiO2(aq)        0.000001
SO4--           0.0
Na+             0.5
Cl-             0.50064
Calcite                 0.0     ssa 1
Calcite_mix             0.0     ssa 1
SiO2(am)                0.0     ssa  1
SiO2(ammix)             0.0     ssa 1
CSH(1.6)                0.0
CSH(0.8)                0.0
Portlandite             0.0
Bogusite                0.0         0.0
Bogusite_i              0.01  ssa 1
set_porosity    16
!!set_saturation   0.95
```

```
DISCRETIZATION
distance_units  microns
xzones          4  2000   320 100  200  10
END
```

```
Condition Cement
temperature         95.0
pH                  Portlandite
CO2(aq)             1.E-10
Ca++                0.001
Na+                 charge
Cl-                 0.500
SiO2(aq)            0.0000001
Calcite_mix         0.00001    ssa 1
CSH(1.6)            0.31       ssa 1
CSH(0.8)            0.05       ssa 1
SiO2(ammix)         0.01       ssa 1
Portlandite         0.16       ssa 1
Bogusite            0.27       0.0
set_porosity        0.20
!!set_saturation      1
END
```

```
INITIAL_CONDITIONS
Brine       1-324
CO2         1-4
Brine-Seed    210-310
Cement      325-524
END
```

Li et al, 2017

Exercise 7: CO_2 Attack on Cement

Reactive Surface Area Options

```
Condition Cement
temperature          95.0
pH                   Portlandite
CO2(aq)              1.E-10
Ca++                 0.001
Na+                  charge
Cl-                  0.500
SiO2(aq)             0.0000001
Calcite              0.00001      ssa 1
CSH(1.6)             0.35         ssa 1
SiO2(am)             0.10         ssa 1
Portlandite          0.20         ssa 0.01
Bogusite             0.20          1.0
Teflon               0.0           1.0
set_porosity         0.15
END
```

Specific Surface Area (m^2/g)

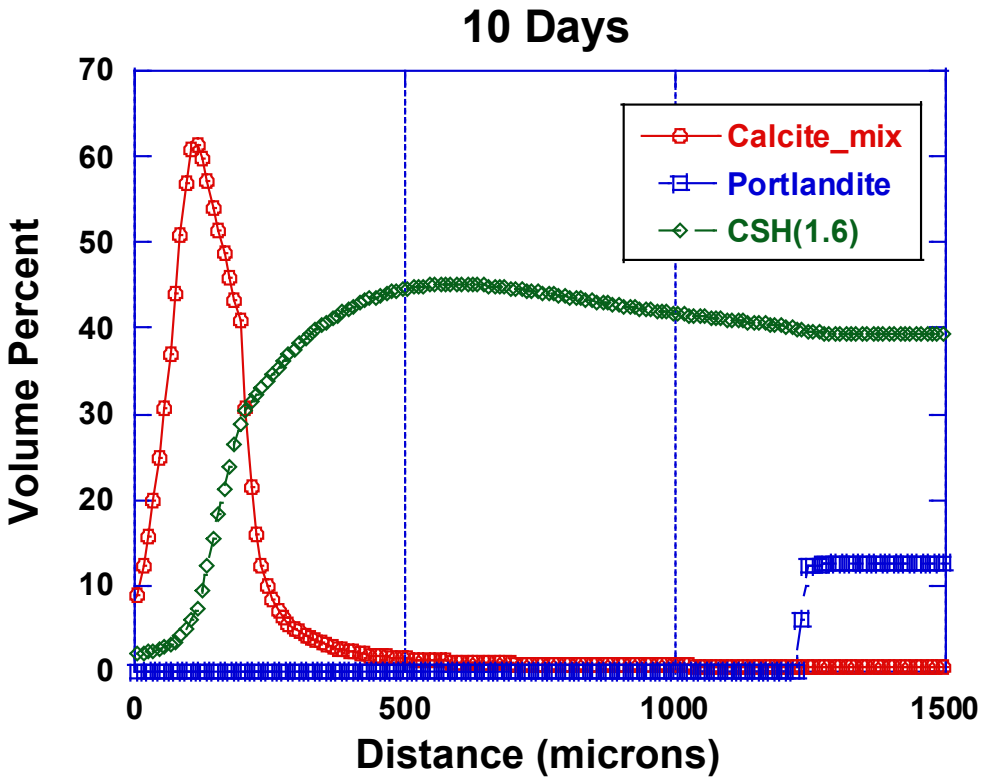
Bulk Surface Area (m^2/m^3)

```
1.0000000e-01
1.0000000e-01
1.0000000e-01
1.0000000e-01
1.0000000e+00
1.0000000e+00
```

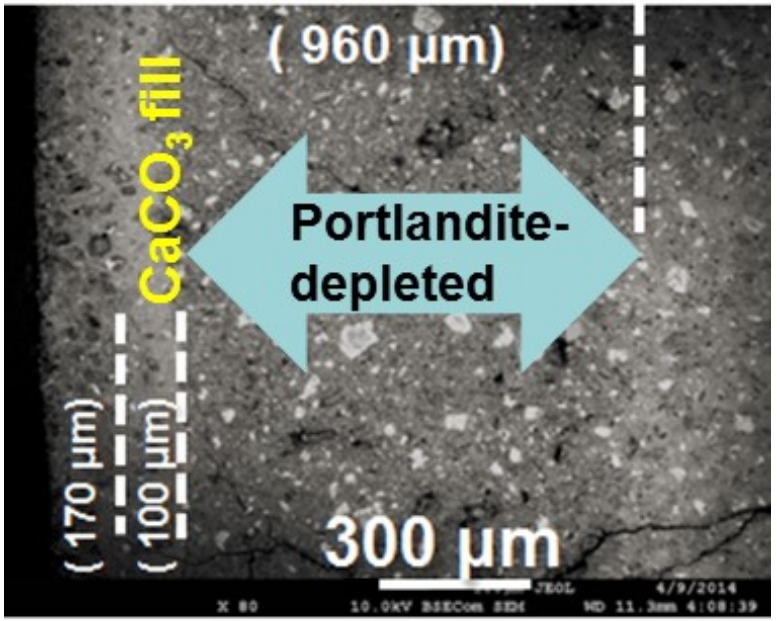
1st four grid cells are unsaturated (10%)

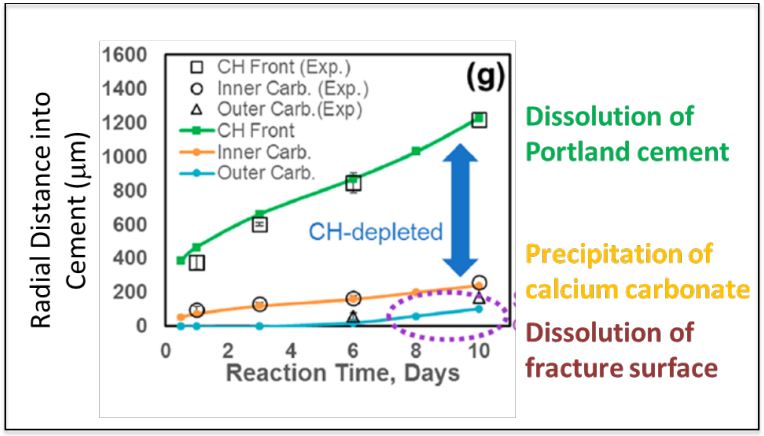
```
RUNTIME
time_units      days
!!fix_saturation  0.999
read_saturationfile   QL-saturation.dat
```

Exercise 7: CO_2 Attack on Cement



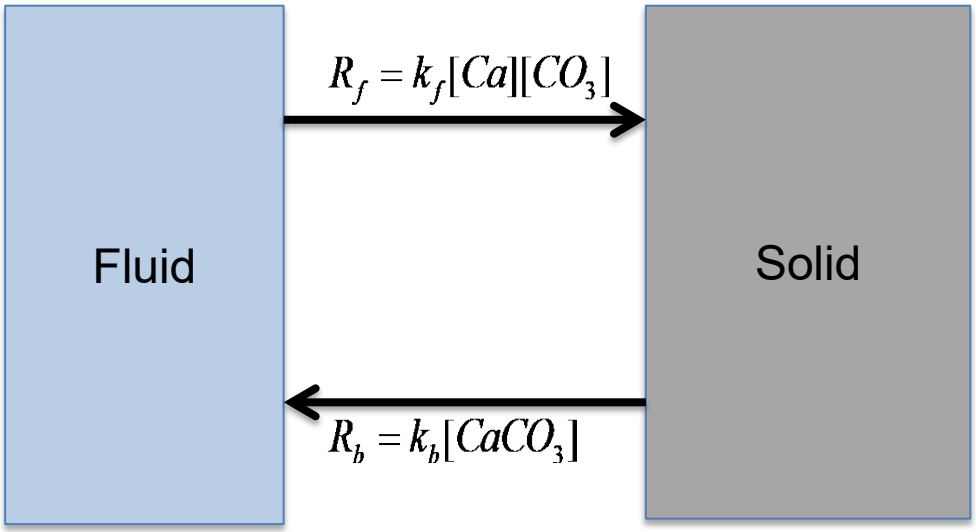
Li et al, ES&T, 2017

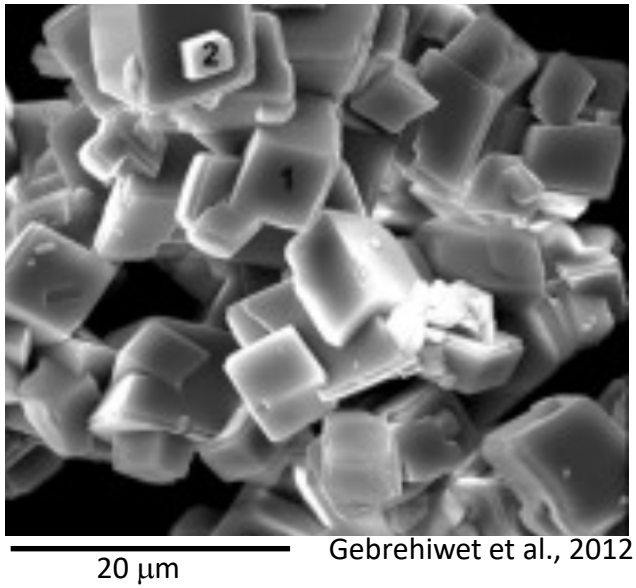




ISOTOPIC FRACTIONATION

Exercise 8: Calcite precipitation with $\delta^{44}Ca$





Gebrehiwet et al., 2012

$$R_{net} = R_f - R_b = k_f[Ca][CO_3] - k_f[CaCO_{3(s)}]$$

$$R_{net} = [CaCO_{3(s)}]k\left[\frac{[Ca^{2+}][CO_3^{2-}]}{[CaCO_{3(s)}]}\frac{1}{K_{eq}} - 1\right]$$

At equilibrium, $R_{net} = 0$

$$R_f = R_b$$

$$k_f[Ca^{2+}][CO_3^{2-}] = k_b[CaCO_{3(s)}]$$

$$\frac{k_b}{k_f} = \frac{[Ca^{2+}][CO_3^{2-}]}{[CaCO_{3(s)}]} = K_{eq}$$

Exercise 8: Calcite precipitation with $\delta^{44}Ca$

Isotope activities based on mole fractions

$$^{44}X = \frac{[^{44}CaCO_3]}{[CaCO_3]}$$

$$R_{net} = [CaCO_{3(s)}]k\left[\frac{[Ca^{2+}][CO_3^{2-}]}{[CaCO_{3(s)}]}\frac{1}{K_{eq}} - 1\right]$$

$$[^{40}CaCO_3] + [^{44}CaCO_3] = [CaCO_3]$$

$$^{40}R_N = {}^{40}k_b\ {}^{40}X\left(\frac{[^{40}Ca][CO_3]}{K_{sp}\ {}^{40}X} - 1\right)$$

$$^{44}R_N = {}^{44}k_b\ {}^{44}X\left(\frac{[^{44}Ca][CO_3]}{K_{sp}\ {}^{44}X} - 1\right)$$

Steefel et al. 2014

Exercise 8: Calcite precipitation with $\delta^{44}Ca$

```
INITIAL_CONDITIONS
amendment 1-1
END

DISCRETIZATION
distance_units     centimeters
xzones          1    1.0
END
```

```
condition   amendment
units          mmol/kg
temperature     25.0
H+            0.11544
Ca++           5.28
Ca44++         0.111997921
HCO3-          10.0
!! Mineral name <volume fraction m3/m3>
CalciteRifle              0.7833831  bsa 1.33E-02
Calcite44Rifle            0.0166170  bsa 1.33E-02
END
```

```
MINERALS
CalciteRifle    -label  default -rate    -4.10000000
!!!  2 per mil kinetic fractionation
Calcite44Rifle   -label  default -rate  -4.10217692
END

                                        Isotope
ISOTOPES                                Standard
primary    Ca44++        Ca++          0.021667
mineral    Calcite44Rifle  CalciteRifle  bulk
isotope_time_series      BatchExperiment.out     1  1
1
END
```

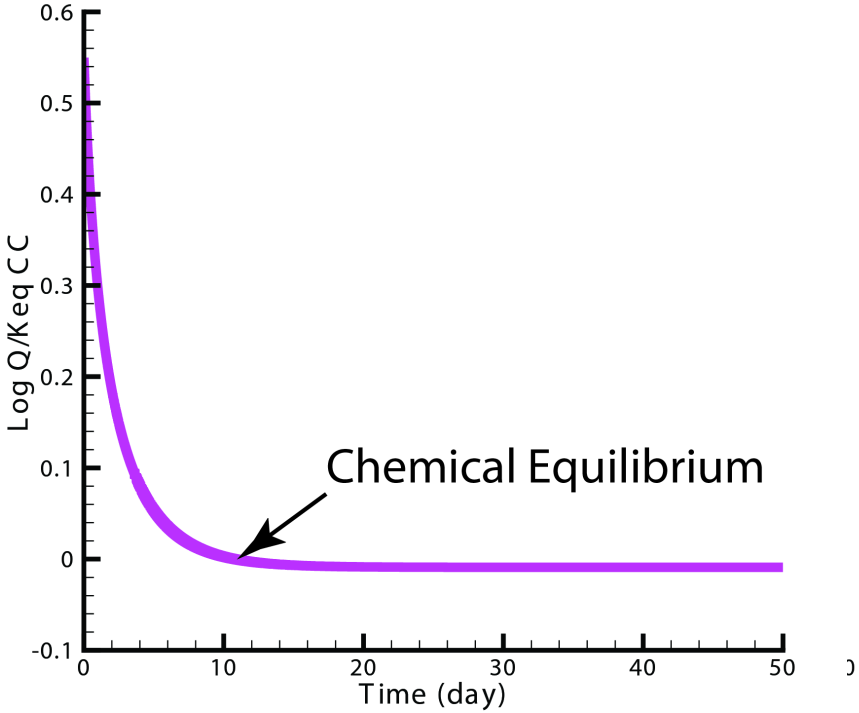
Kinetic fractionation

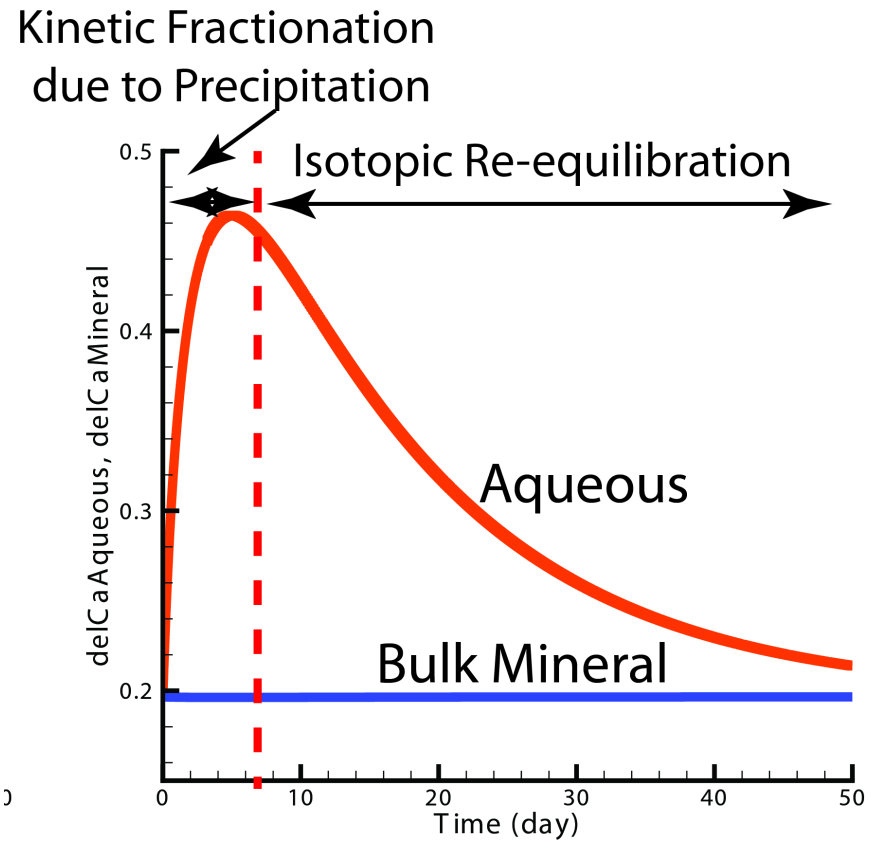
Isotopic back-reaction with

- **Bulk**
- **Surface**
- **None**

Output isotope time series to file at grid cell

Exercise 8: Calcite precipitation with $\delta^{44}Ca$

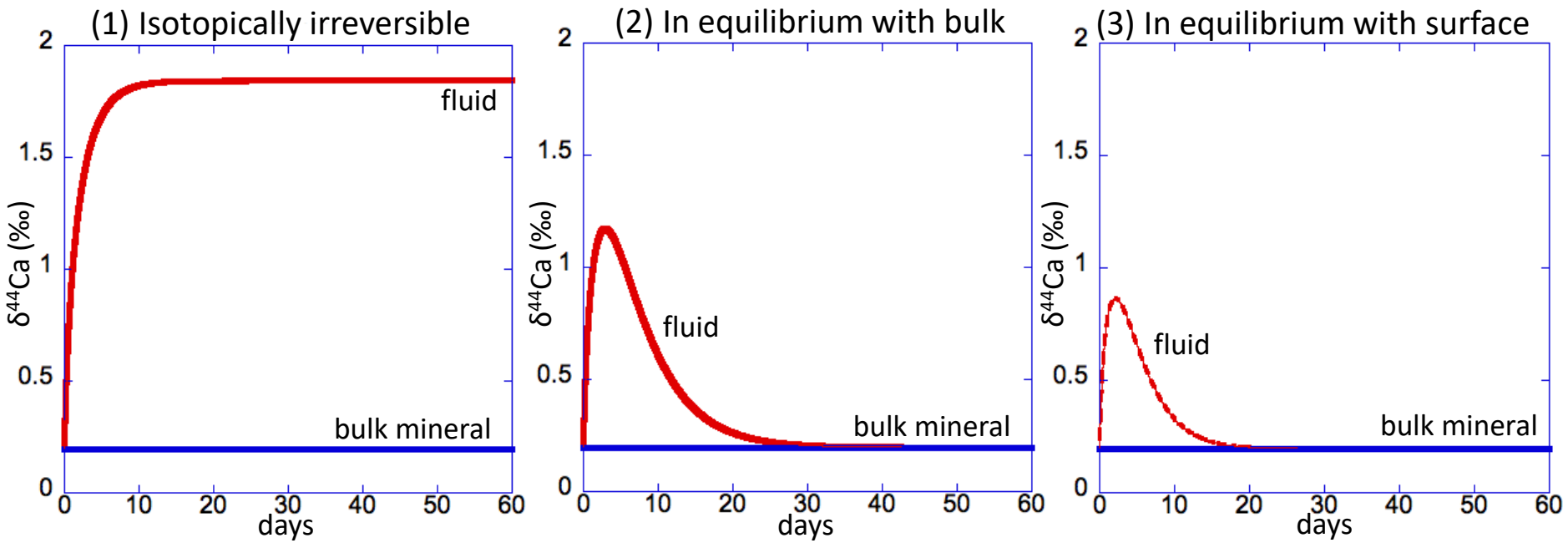




Steefel et al. 2014

Exercise 8: Calcite precipitation with $\delta^{44}Ca$

"None" "Bulk" "Surface"



Steefel et al. 2014

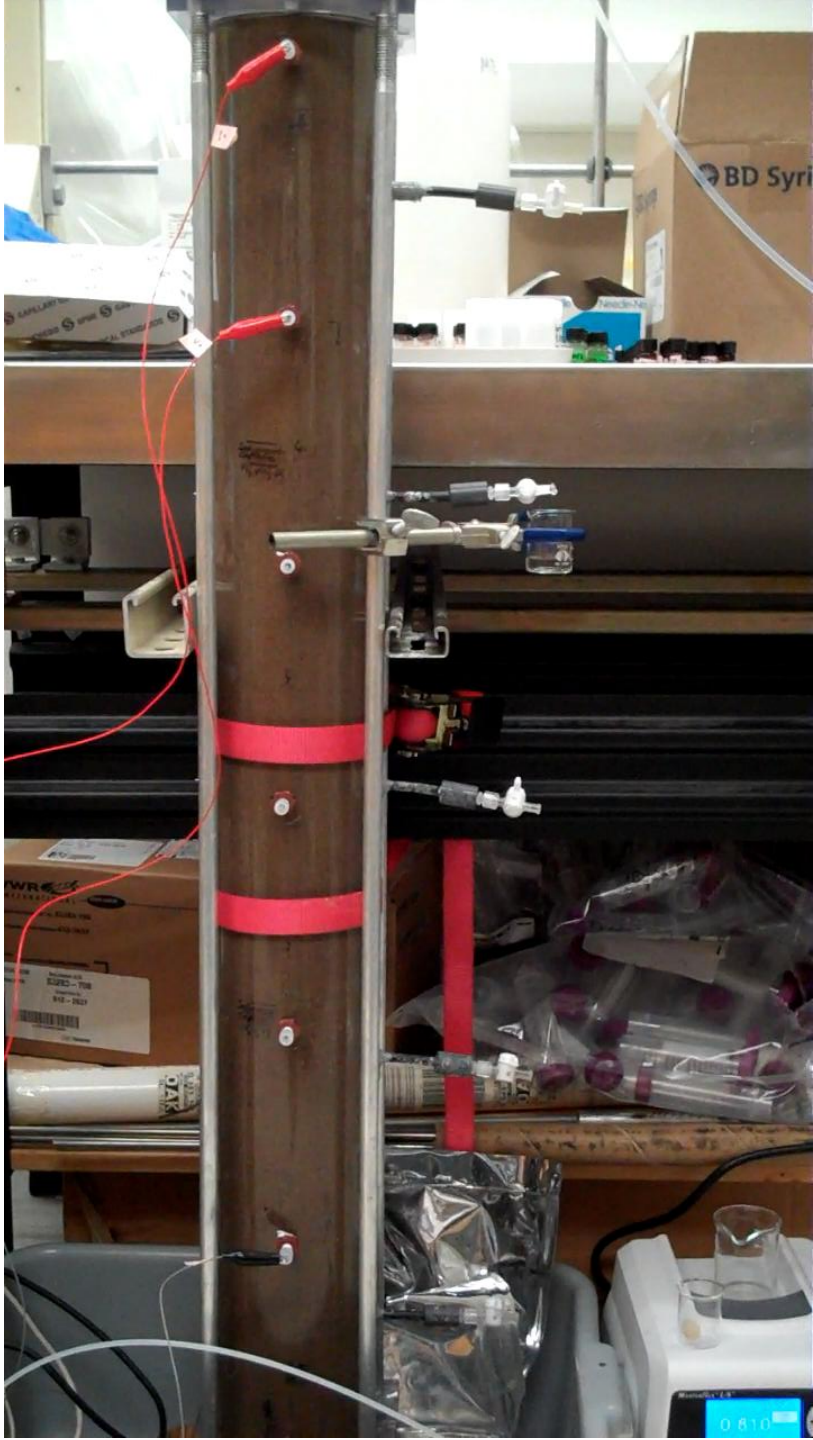
Exercise 9: Microbial Redox

Dual Monod

$$R_m = k_{\max}\left[\frac{[C_E]}{[C_E]+K_{S_E}}\frac{[C_D]}{[C_D]+K_{S_D}}\right]$$

E = electron acceptor

D = electron donor



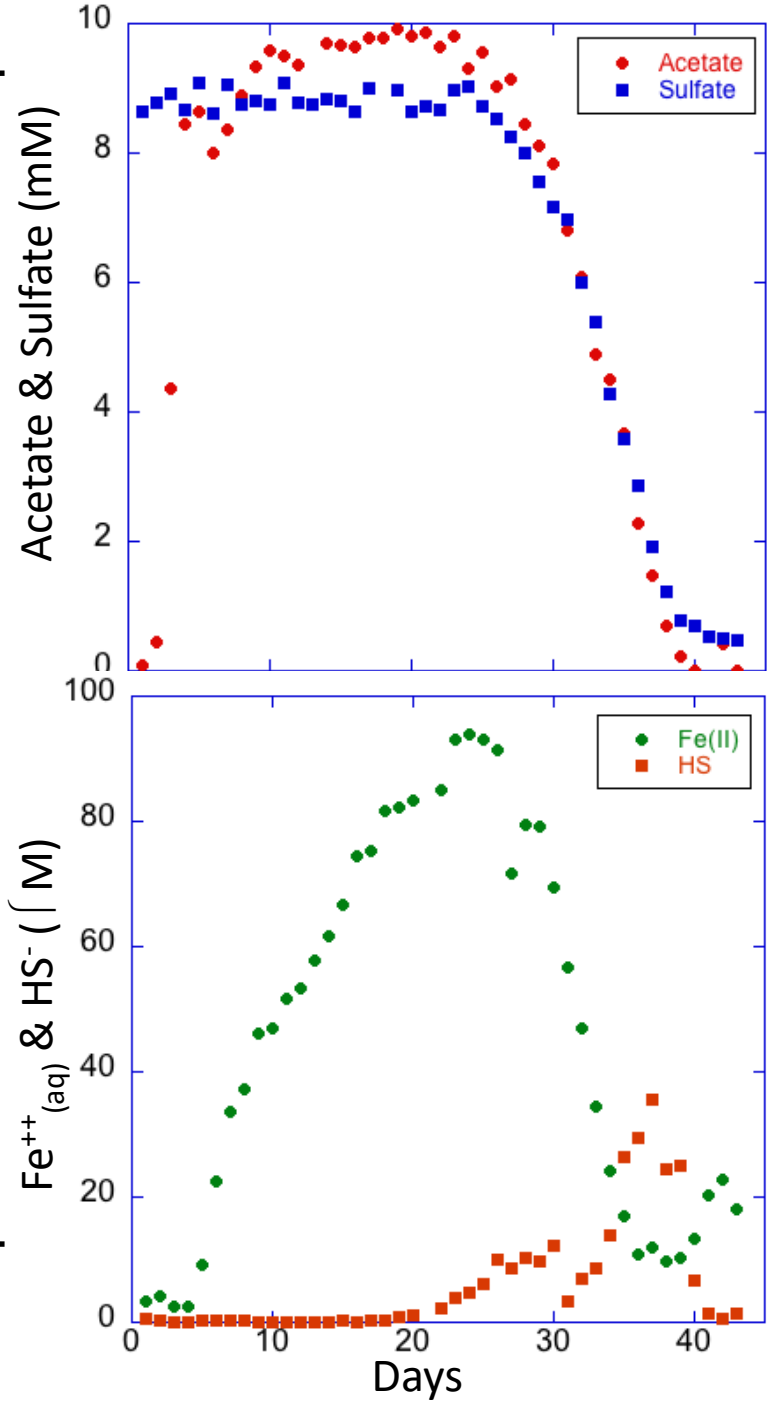
Druhan et al., 2014

Exercise 9: Microbial Redox

Rifle Sediment

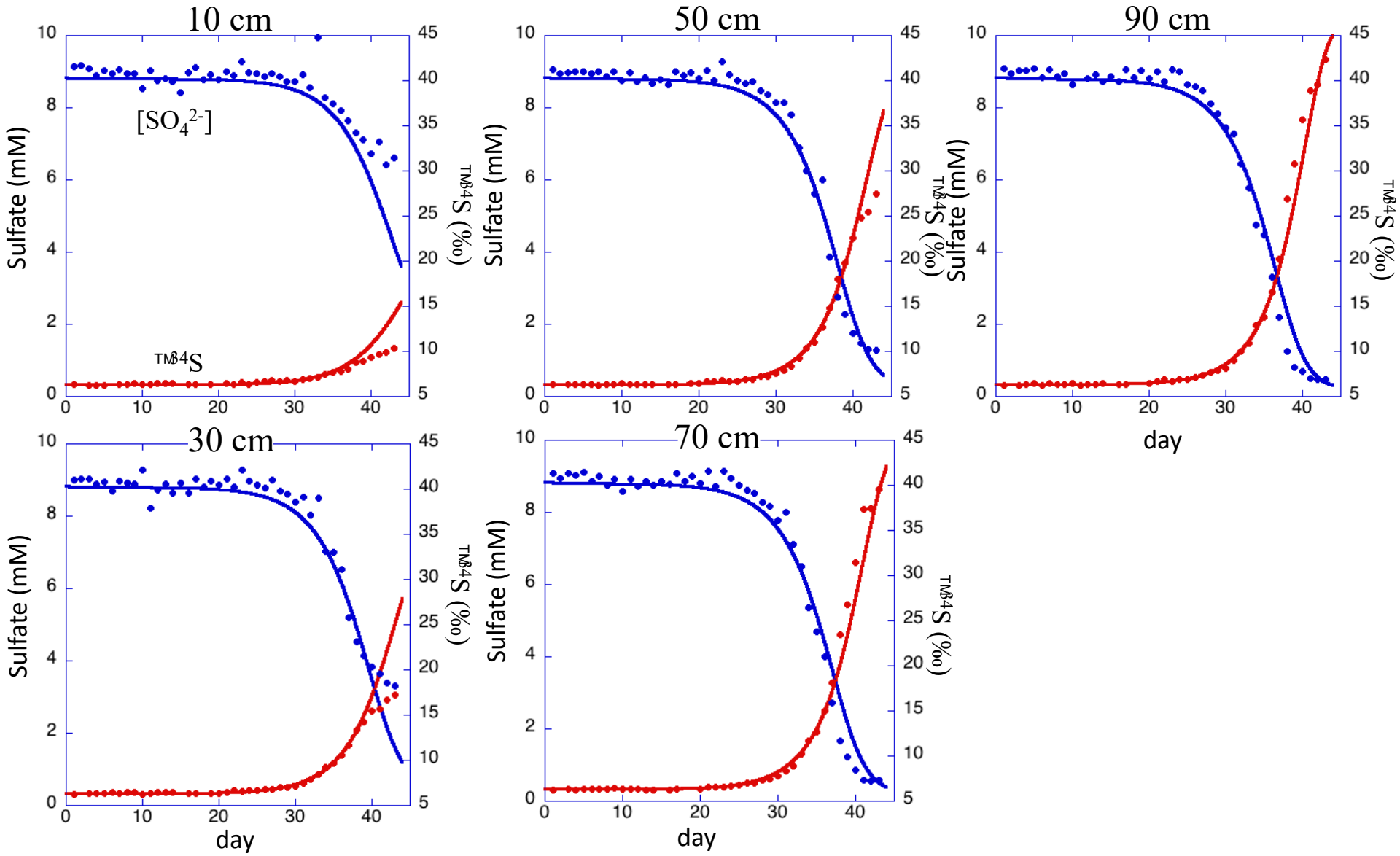
$CH_3COO^-_{(aq)}$
+ Rifle groundwater:

Uranium	0.7 – 1.5 μM
pH	7.0 – 7.2
Alkalinity	7 – 10 meq/L
Eh	-150 to 240 mV
DO	3 – 20 μM
Fe(II)	15 – 50 μM
Nitrate	2 – 3 μM
Sulfate	8 – 11 mM
Sulfide	0.03 – 0.5 μM



Druhan et al., 2014

Exercise 9: Microbial Redox



Druhan et al., 2014

POROSITY-PERMEABILITY CHANGE

Exercise 10: Porosity-Permeability

Mineral	Reaction	$\log K_{25}$
Calcite	$Ca^{2+} + CO_3^{2-} \leftrightarrow CaCO_3$	8.4750
Gypsum	$Ca^{2+} + SO_4^{2-} + 2H_2O \leftrightarrow CaSO_4{:}2H_2O$	4.5800
Ferrihydrite	$Fe^{3+} + 3H_2O \leftrightarrow Fe(OH)_3 + 3H^+$	-4.8910
Jarosite	$K^+ + 3Fe^{3+} + 2SO_4^{2-} + 6H_2O \leftrightarrow KFe_3(SO_4)_2(OH)_6 + 6H^+$	9.2100
Gibbsite	$Al^{3+} + 3H_2O \leftrightarrow Al(OH)_3 + 3H^+$	-8.1100
Siderite	$Fe^{2+} + CO_3^{2-} \leftrightarrow FeCO_3$	10.4500

Primary components	Unit	Initial condition	Boundary condition
pH	–	9.38	3.0
Ca^{2+}	mol l^{-1} H_2O	1.57×10^{-4}	1.00×10^{-4}
CO_3^{2-}	mol l^{-1} H_2O	2.57×10^{-4}	1.0×10^{-2}
SO_4^{2-}	mol l^{-1} H_2O	1.00×10^{-10}	6.46×10^{-4}

Xie, M., Mayer, K.U., Claret, F., Alt-Epping, P., Diederik, J., Steefel, C.I., Chiaberge, C., Simunek, J. (2015) Implementation and evaluation of permeability-porosity and tortuosity-porosity relationships linked to mineral dissolution-precipitation. *Computational Geosciences* **19**: 655-671. DOI 10.1007/s10596-014-9458-3

https://wci.llnl.gov/simulation/computer-codes/visit/executables

Exercise 10: Porosity-Permeability

```
Condition mingliang_boundary
temperature      25.0
pH               3.0
Ca++             0.0001
CO3--            0.01
SO4--            0.1
Fe++             0.000223
!!Fe++           8.0e-3
Fe+++            0.0143
Al+++            0.0143
K+               7.67e-5
O2(aq)           O2(g)   0.1005
Na+              9.092e-2
Tracer           0.01
Calcite          0.30      1.00
Gypsum           0.00      1.00
Ferrihydrite     0.00      1.00
Jarosite         0.00      1.00
Gibbsite         0.05      1.00
Siderite         0.05      1.00
TracerMineral    0.35      1.00
END
```

```
Condition initial
temperature      25.0
pH               7.0
Ca++             charge
!!Ca++           1.69512E-04
CO3--            CO2(g)   0.01
SO4--            1.69512E-04
Fe++             1.0e-5
Fe+++            1.0e-10
Al+++            1.0e-5
K+               1.0e-5
O2(aq)           O2(g)    1.E-15
Na+              1.0e-15
Tracer           0.00001
Calcite          0.22      1.00
Gypsum           0.00      1.00
Ferrihydrite     0.00      1.00
Jarosite         0.00      1.00
Gibbsite         0.05      1.00
Siderite         0.05      1.00
TracerMineral    0.33      1.00
END
```

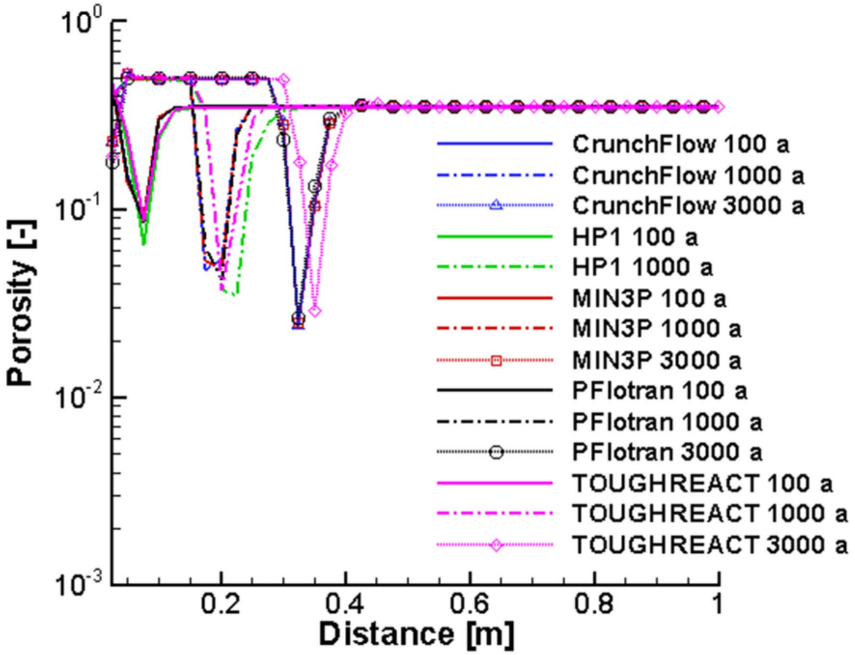
Exercise 10: 2D Porosity-Permeability

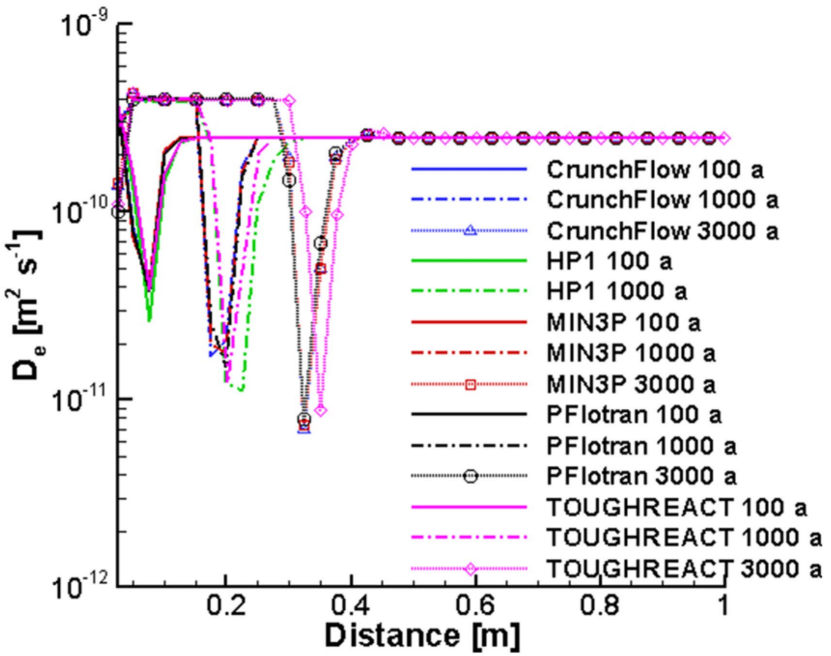
```
FLOW
distance_units      meters
time_units          second
calculate_flow      true
read_PermeabilityFile  perm5_2D.hyc  SingleFile3D
!!IF homogeneous flow:
!!permeability_x     1.18602E-11   default
!!permeability_x     2.61491E-10  zone  0-0    1-40     1-1
!!permeability_x     2.61491E-10  zone  31-31  1-40     1-1
permeability_y      0.00  zone  1-31    42-42     1-1
permeability_y      0.00  zone  1-31    0-0       1-1
pressure           30    default
pressure           104.4365949  zone 0-0   1-41    1-1 fix
pressure           0.0        zone 32-32 1-41    1-1 fix
gravity           90.0  90.0  90.0
END
```

```
DISCRETIZATION
distance_units  meters
xzones  1  0.050  29  0.10  1  0.050
yzones  1  0.025  39  0.05  1  0.025
END
```

```
MINERALS
!! Standard linear TST calcite
Calcite              -label default       -rate  -4.301029996
Gypsum               -label default       -rate  -4.301029996
Ferrihydrite         -label default       -rate  -5.301029996
Jarosite             -label default       -rate  -5.301029996
Gibbsite             -label default       -rate  -6.301029996
Siderite             -label default       -rate  -5.301029996
TracerMineral        -label default       -rate  -35.00
END
```

Exercise 10: 1D Porosity-Permeability

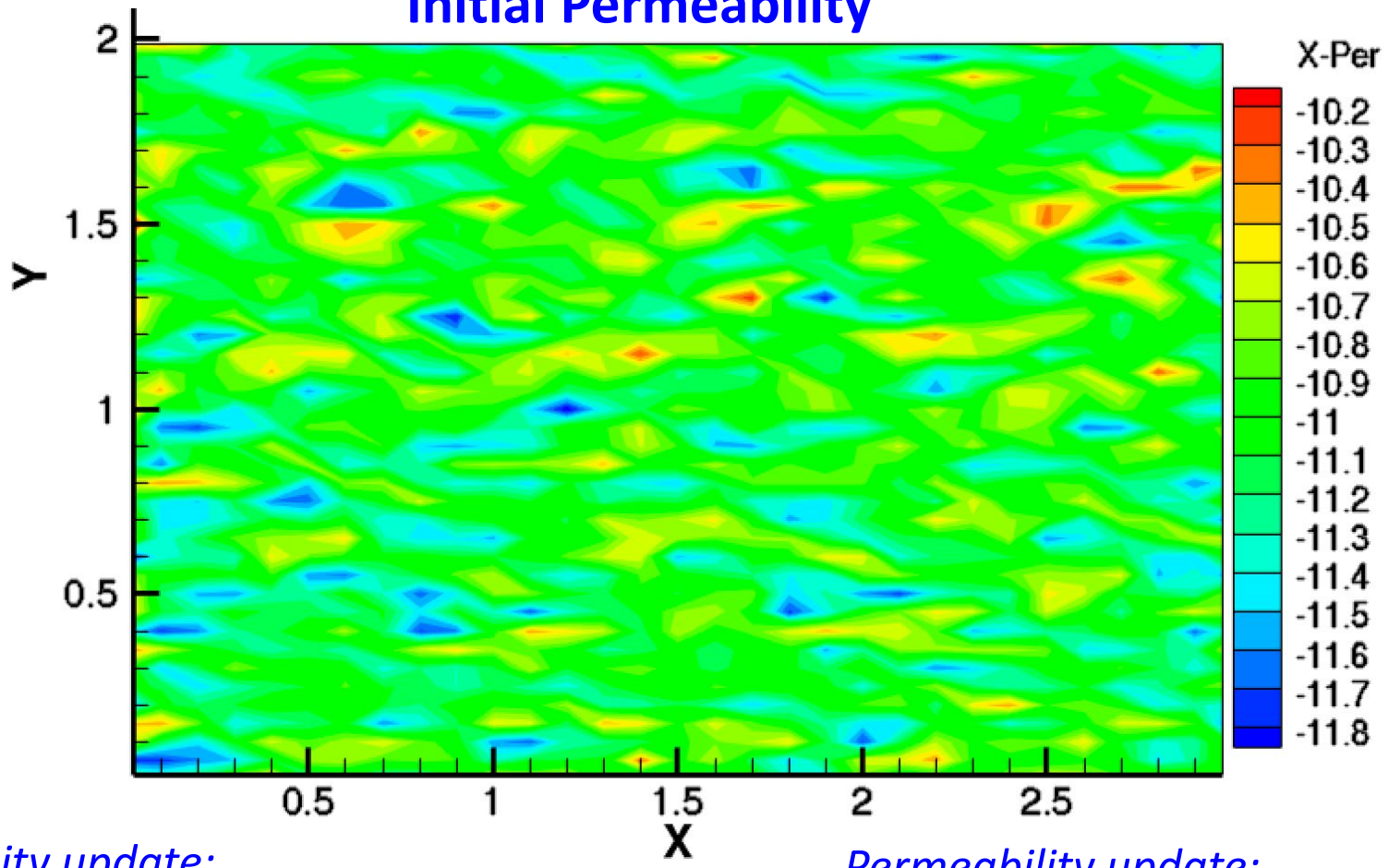




Xie et al, 2015

Exercise 10: 2D Porosity-Permeability

Initial Permeability



Porosity update:

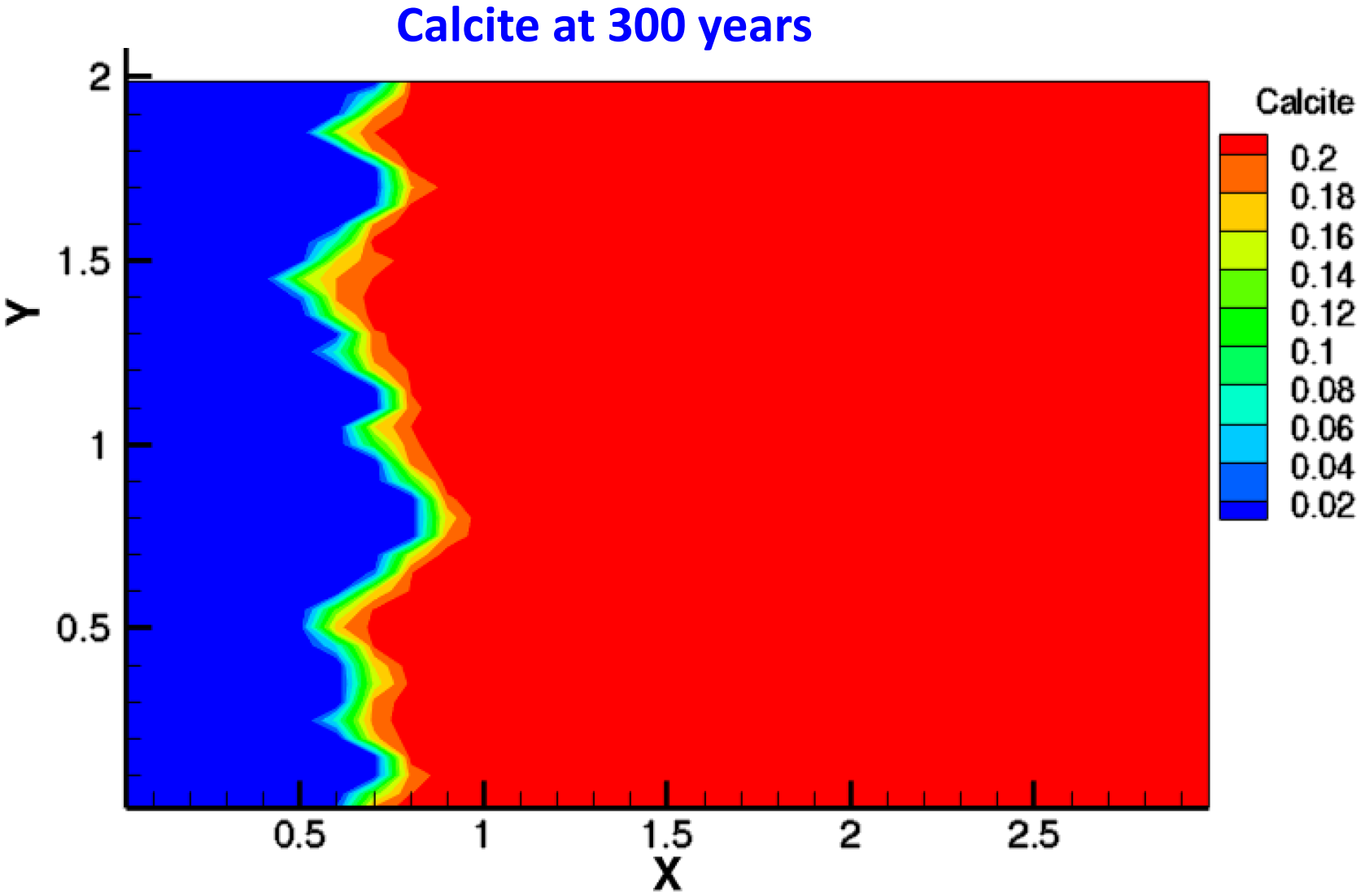
$$\phi = \sum_{m=1}^{N_m} 1 - \phi_m$$

Permeability update:

$$k_m = -k_{m,0}\left(\frac{\phi_t}{\phi_0}\right)^{2/3}$$

Xie et al., 2015

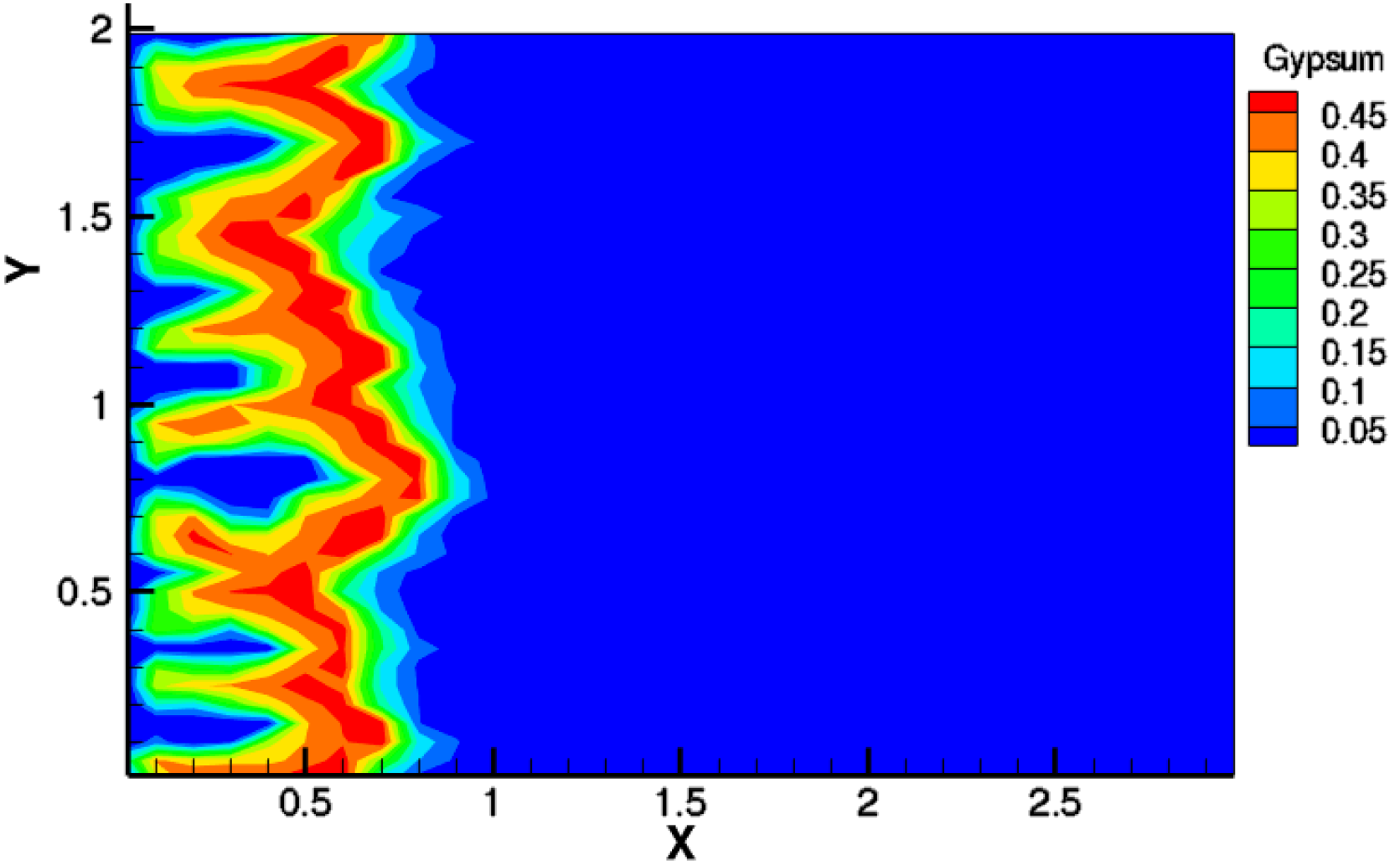
Exercise 10: 2D Porosity-Permeability



Xie et al., 2014

Exercise 10: 2D Porosity-Permeability

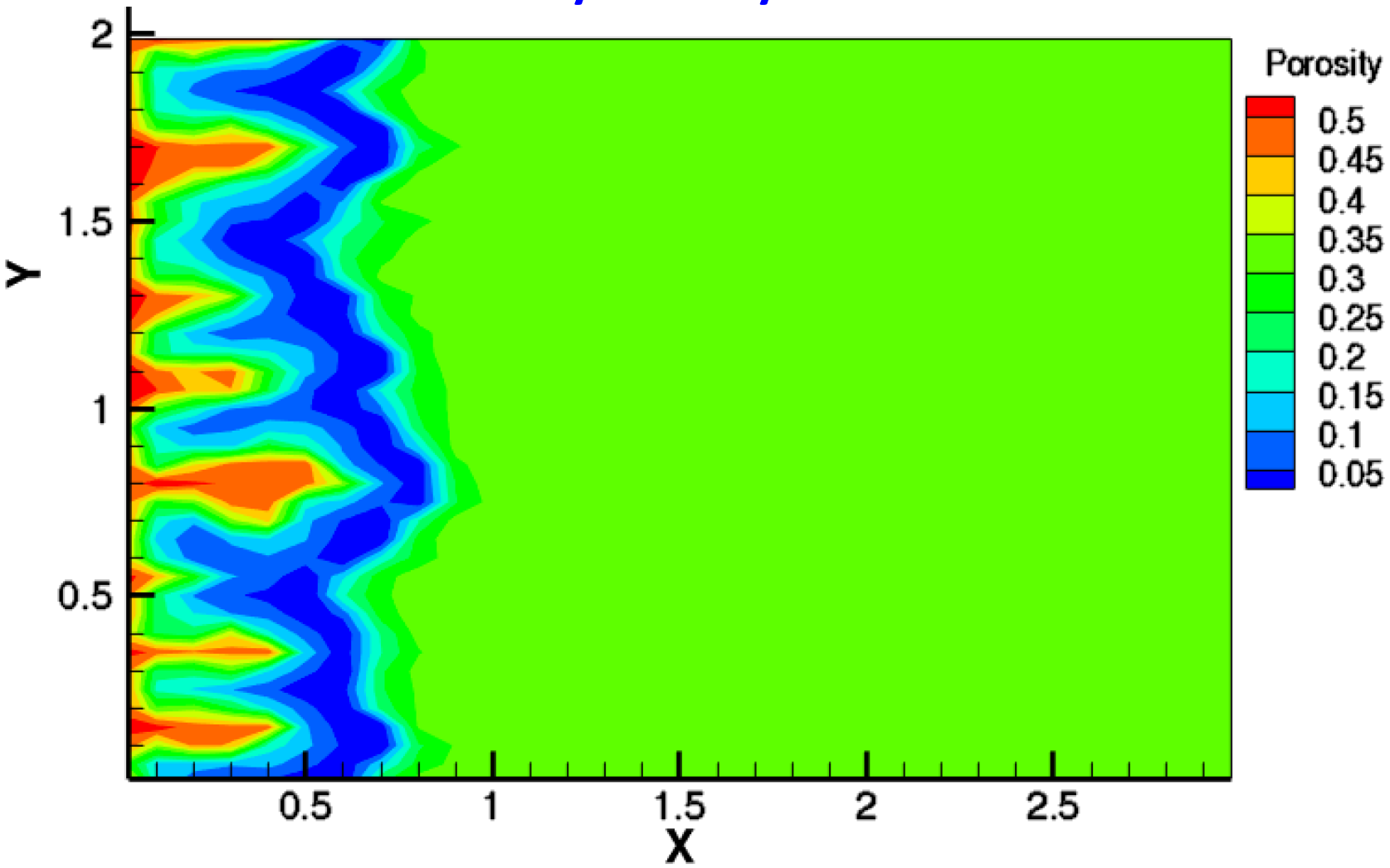
Gypsum at 300 years



Xie et al., 2015

Exercise 10: 2D Porosity-Permeability

Porosity at 300 years

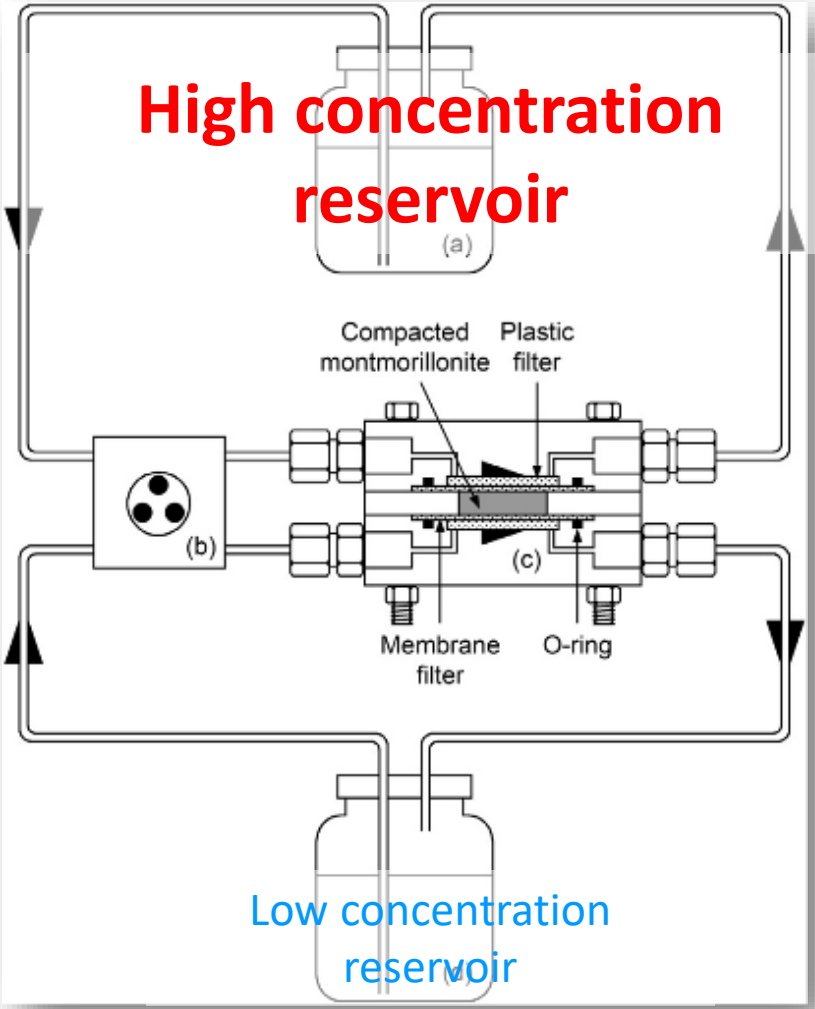


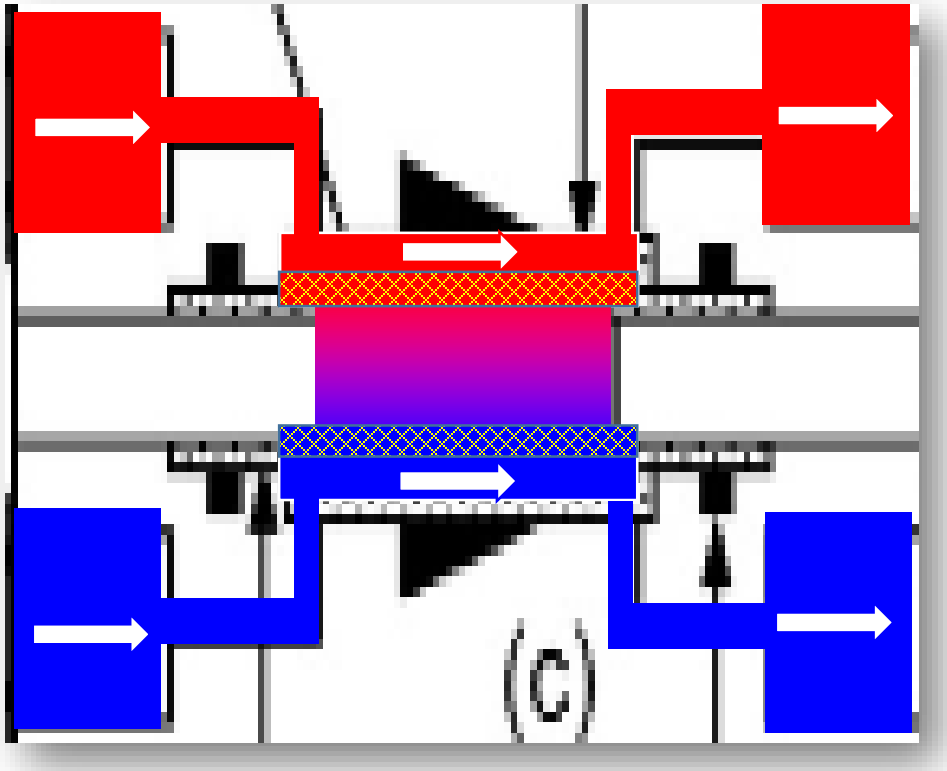
Xie et al., 2015

DIFFUSION IN CLAY

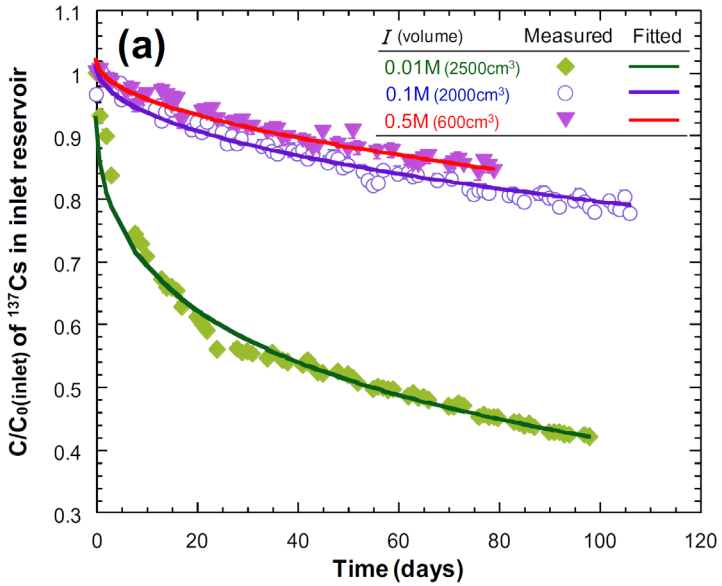
Exercise 11: Diffusion in Clay

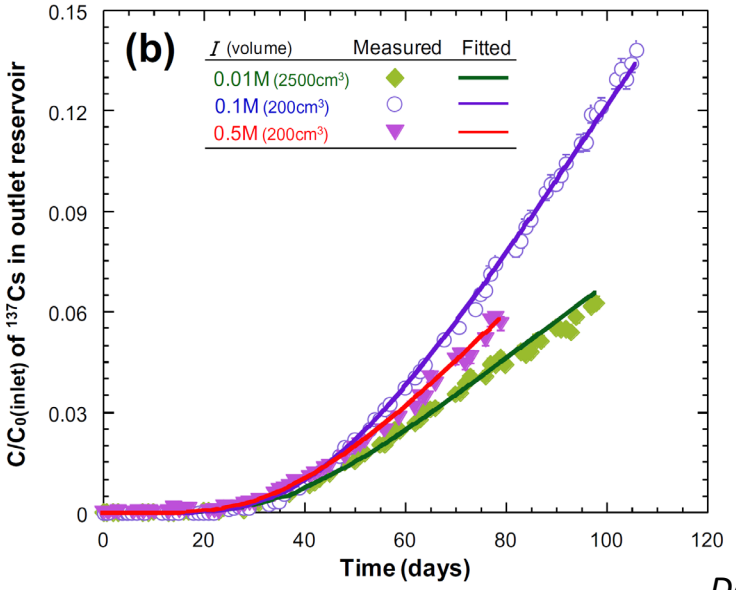
Experimental setup





Example of results

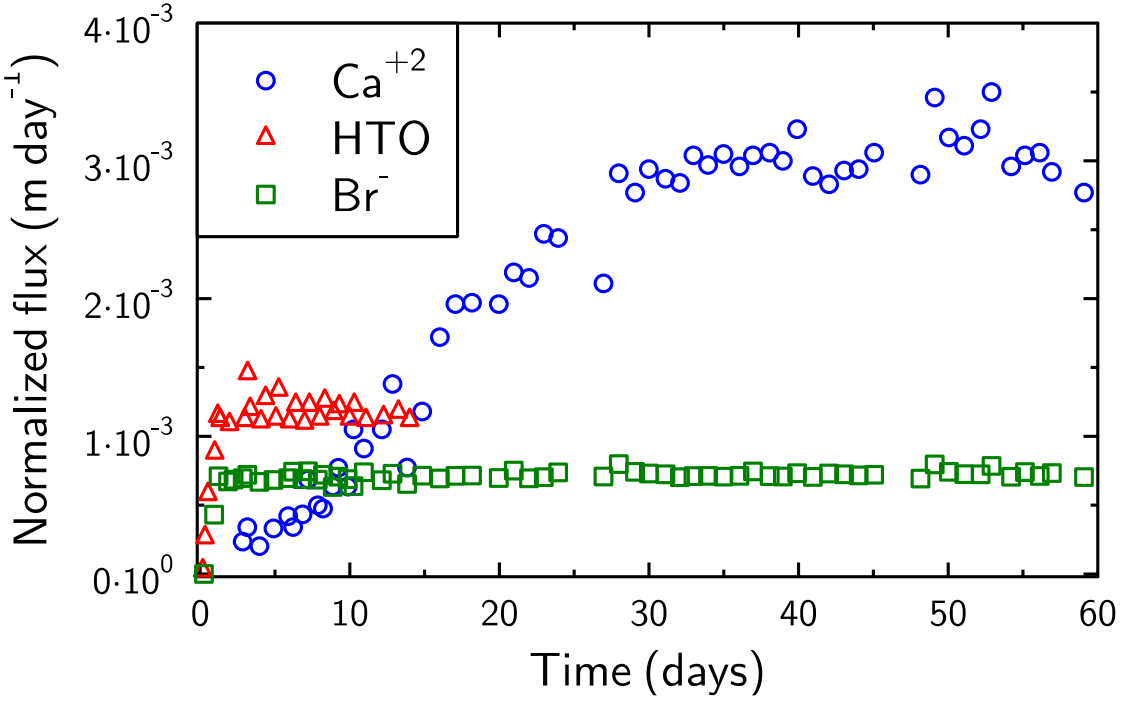




Data from Tachi & Yotsuji, 2014

$$Flux_{outlet} = \left.\frac{\partial C}{\partial t}\right|_{outlet} \times \frac{V_{outlet}}{S_{outlet}}$$ mol m^{-2} s^{-1}

$$Flux_{norm,outlet} = \frac{Flux_{outlet}}{C_{inlet}}$$ m s^{-1}



Data from Tinnacher et al. GCA, 2016

Geometry of the system, general properties

```
DISCRETIZATION
distance_units  meters
xzones      1 0.0001 50 0.0001 1 0.0001
yzones      1 100
zzones      1 1
END

INITIAL_CONDITIONS
HReservoir   1-1 1-1 1-1
Clay        2-51 1-1 1-1
LReservoir   52-52  1-1 1-1
END
```

Only one grid cell for the reservoir; large volume = 10 L

```
BOUNDARY_CONDITIONS
X_begin   HReservoir   Flux
X_end     Lreservoir   Flux
END

FLOW
space_units            meters              !!Default : meters ; km, cm, mm, um
time_units             seconds             !!Default : years ; days, hours, minutes, seconds
constant_flow          0.0  0.0            !!Default : 0.0
END
```

closed closed boundary conditions, only diffusion

Geometry of the system, general properties

```
POROSITY
fix_porosity          0.5
fix_microporosity     0.5
UpdateDDL             false
MultiplyPorosityTortuosity  true
END
```

New keywords that are specific to CrunchClay (ignored in CrunchTope)

```
TRANSPORT
distance_units         meters
time_units             second
fix_diffusion  1e-9

D_25  H+      9.31e-9
D_25  Bogus    1e-20
D_25  OH-     5.27e-9
D_25  Na+     1.3e-9
…

D_MP  H+      9.31e-9
D_MP  Bogus    1e-20
D_MP  OH-     5.27e-9
D_MP  Na+     1.3e-9
…
```

```
tortuosity 1 default
tortuosity 1   zone 1-1 1-1 1-1
tortuosity 0.037 zone 2-51 1-1 1-1
tortuosity 1   zone 52-52 1-1 1-1

tortuosityMP 1 default
tortuosityMP 1   zone 1-1 1-1 1-1
tortuosityMP 0.037 zone 2-51 1-1 1-1
tortuosityMP 1   zone 52-52 1-1 1-1
END
```

Chemistry, surfaces, DL properties

```
Condition HReservoir
temperature     25.0
units           mmol/kg
H2O             55.5
pH              7
Na+             100
Cl-             charge
Br-             1e0
Ca++            1e0
Hto             1e0
Bogus           Bogusite
Bogusite        3.1416e-8  specific_surface_area  750
>montmor-       1e-99 !!site per m2
set_porosity    0.999999999
set_microporosity  1e-10
END
```

Background electrolyte concentration is high compared to the concentration of the tracers.

Fake mineral with very low solubility that bears the surface

The surface charge is set to zero

Redefinition of the the bulk vs DL porosity for each of the domains
The reservoirs have a porosity value of 1

Chemistry, surfaces, DL properties

```
Condition Clay
temperature      25.0
units            mmol/kg
H2O              55.5
pH               7
Na+              100
Cl-              charge
Br-              1e-27
Ca++             1e-27
Hto              1e-27
Bogus            Bogusite
Bogusite         3.1416e-8   specific_surface_area  750
>montmor-        1.2e-99
set_porosity     5.655e-8
set_microporosity 5.0895e-7
END
```

Constant background electrolyte concentration

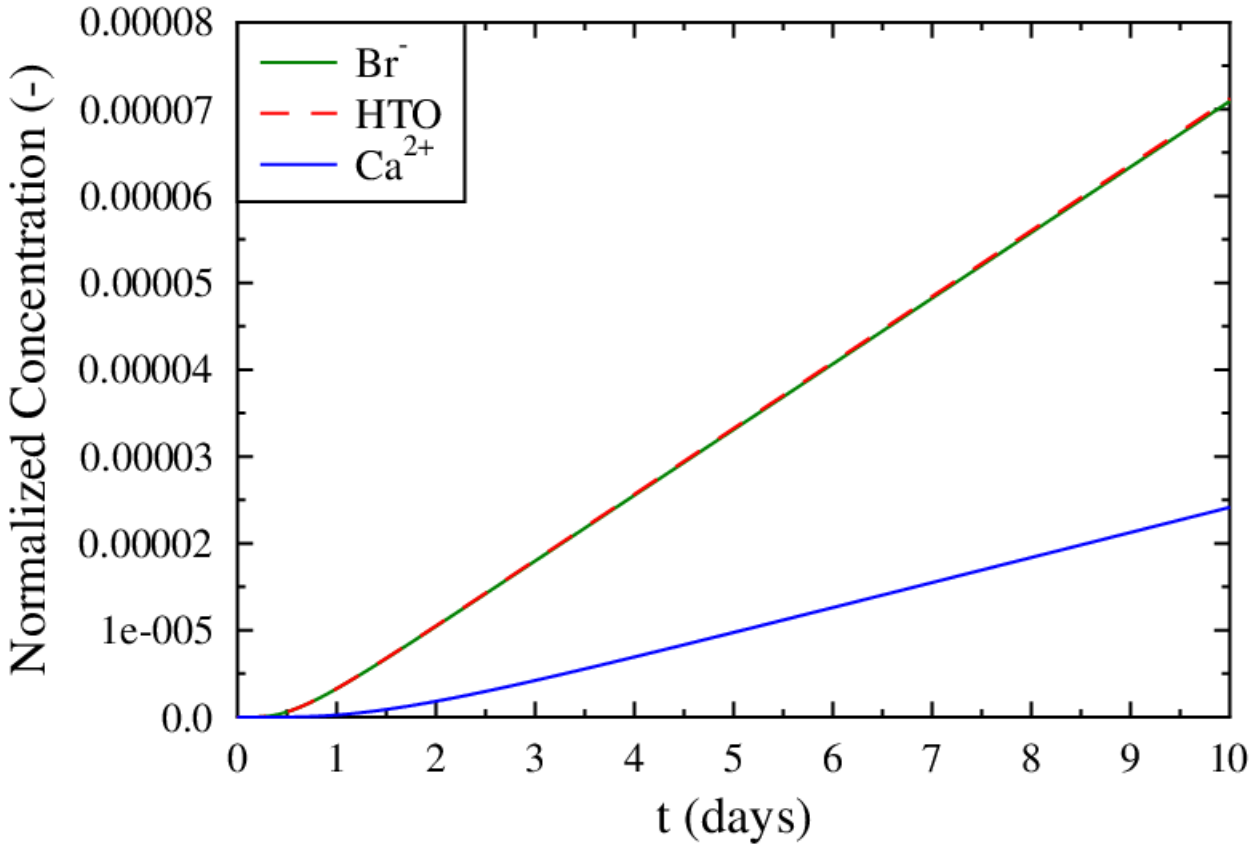
Fake mineral with very low solubility that bears the surface

The surface charge is set to zero

Redefinition of the the bulk vs DL porosity for each of the domains
See explanation in input files for calculation of these values
Here bulk porosity is 10 % of the total porosity

Results

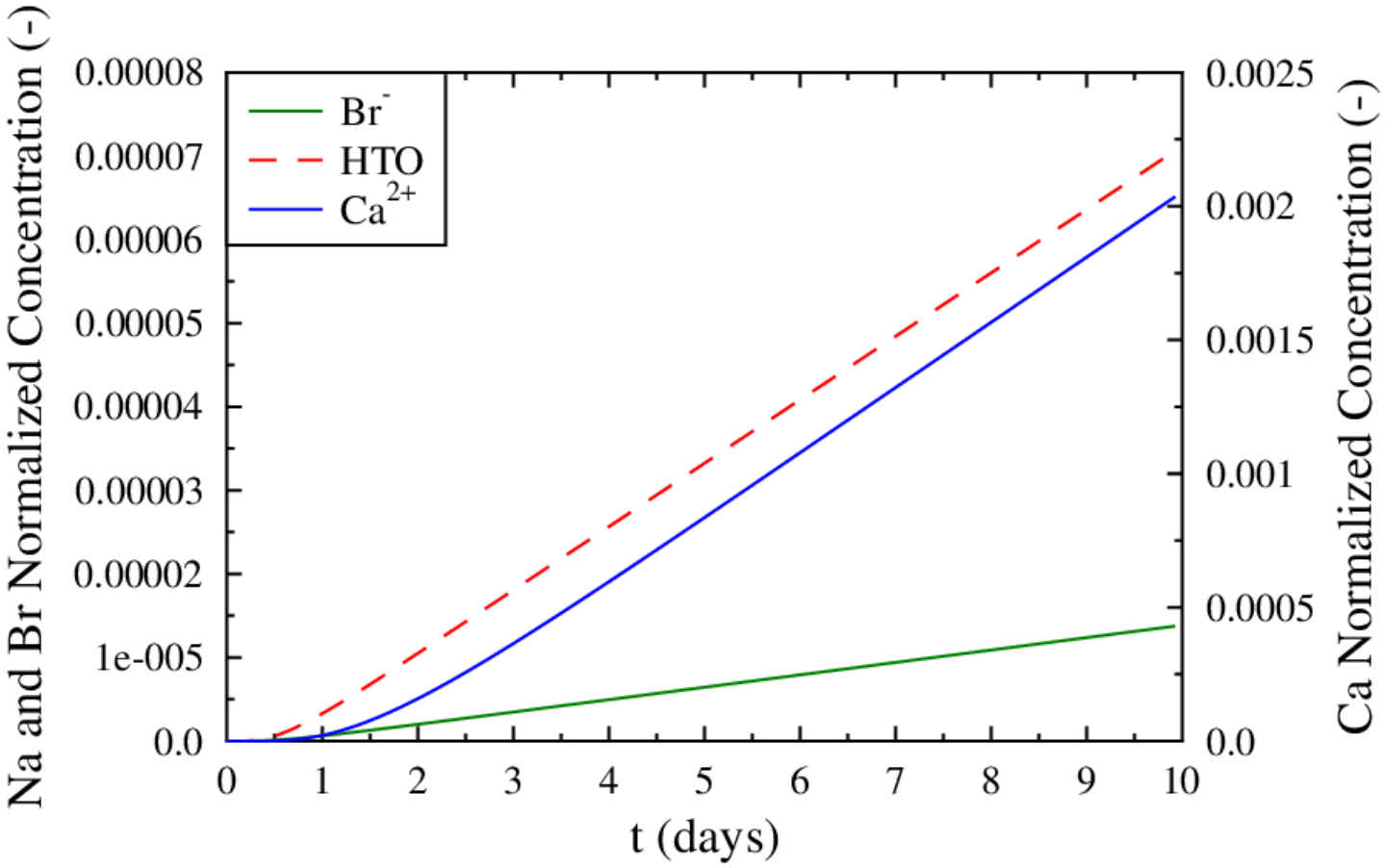
Concentration in the outlet reservoir



Why do the Br and HTO concentrations increase faster than the Ca concentration?

Results

Increase the surface charge in the clay plug to 0.9 mol charge/kg clay



What is the species that diffuse the fastest now ?

Results

Add surface complexation reactions:

>montmor- + Na+ = >montmorNa
2 >montmor- + Ca+2 = > >montmor2Ca

In database:

```
Begin surface complexation
'>montmorNa' 2 1.0 'Na+' 1.0 '>montmor-'  -0.5  -0.5  -0.5  -0.5  -0.5  -0.5  -0.5  -0.5
'>montmor2Ca' 2 1.0 'Ca++' 2.0 '>montmor-'  -1  -1  -1  -1  -1  -1  -1  -1
End of surface complexation
```

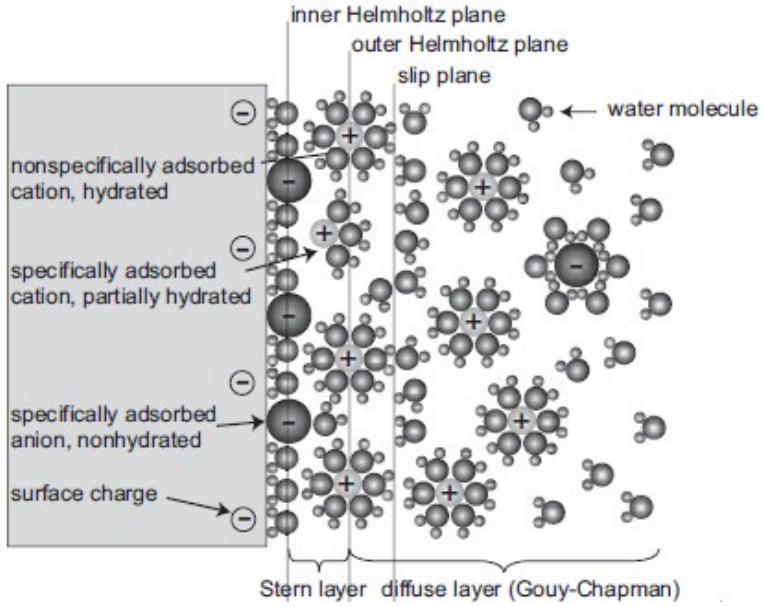
```
Begin surface complexation parameters
>montmor-       -1.0
>montmorNa       0.0
>montmor2Ca      0.0
End surface complexation parameters
```

Results

Add surface complexation reactions:

>montmor- + Na+ = >montmorNa
2 >montmor- + Ca+2 = > >montmor2Ca

The surface charge is partly compensated in the Stern layer (with no diffusion of sorbed species). The remaining charge is compensated in the diffuse layer



No surface complex

Total Charge in DDL (mol/m^3) = 5.6548800E-04
Total Fixed Charge (mol/m^3) = -5.6548800E-04

Microporosity = 1.470300000000000E-007
DonnanPotential = -9.386105664921650E-002

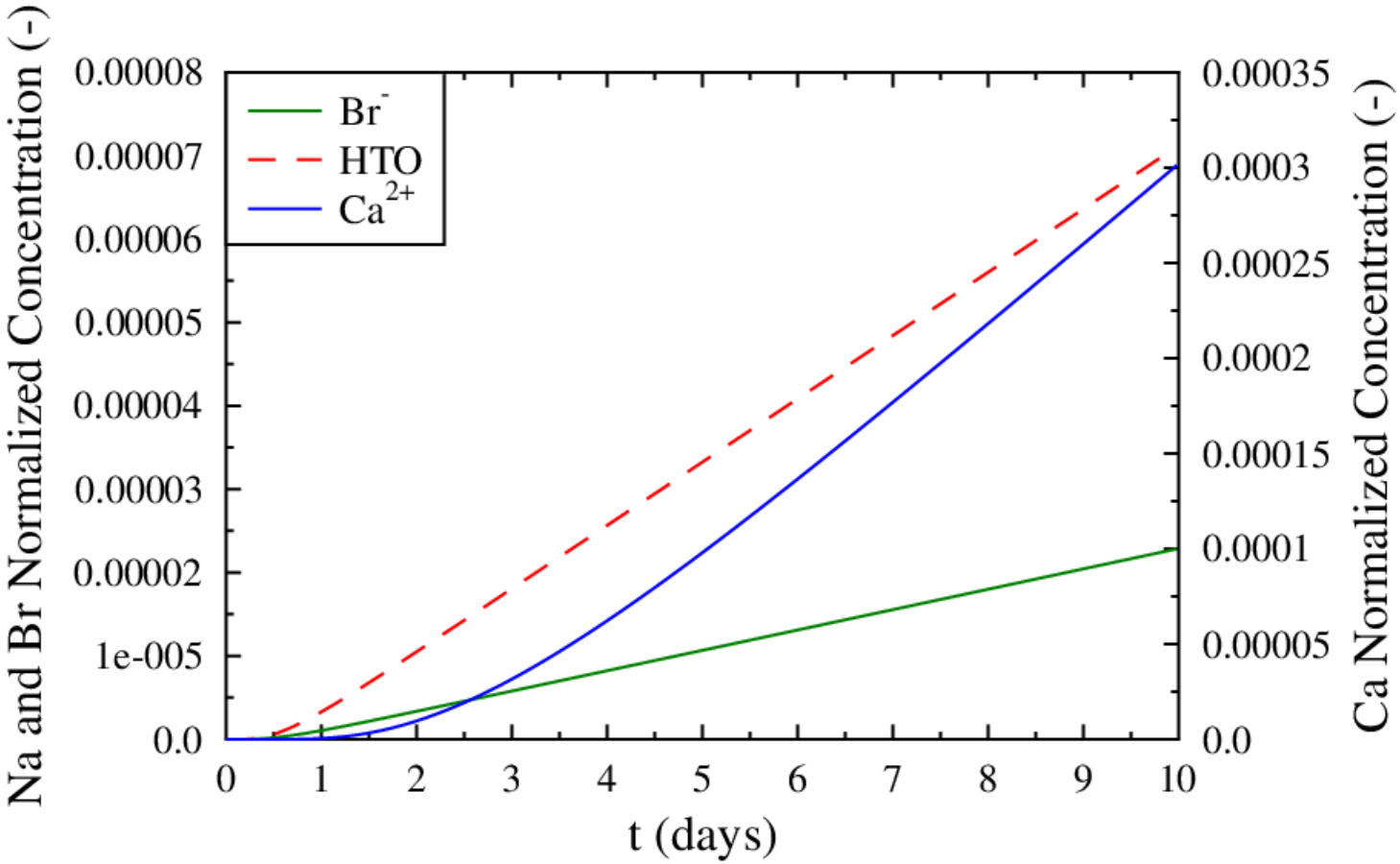
With surface complexes

Total Charge in DDL (mol/m^3) = 2.8973120E-04
Total Fixed Charge (mol/m^3) = -2.8973120E-04

Microporosity = 1.470300000000000E-007
DonnanPotential = -7.672779885055225E-002

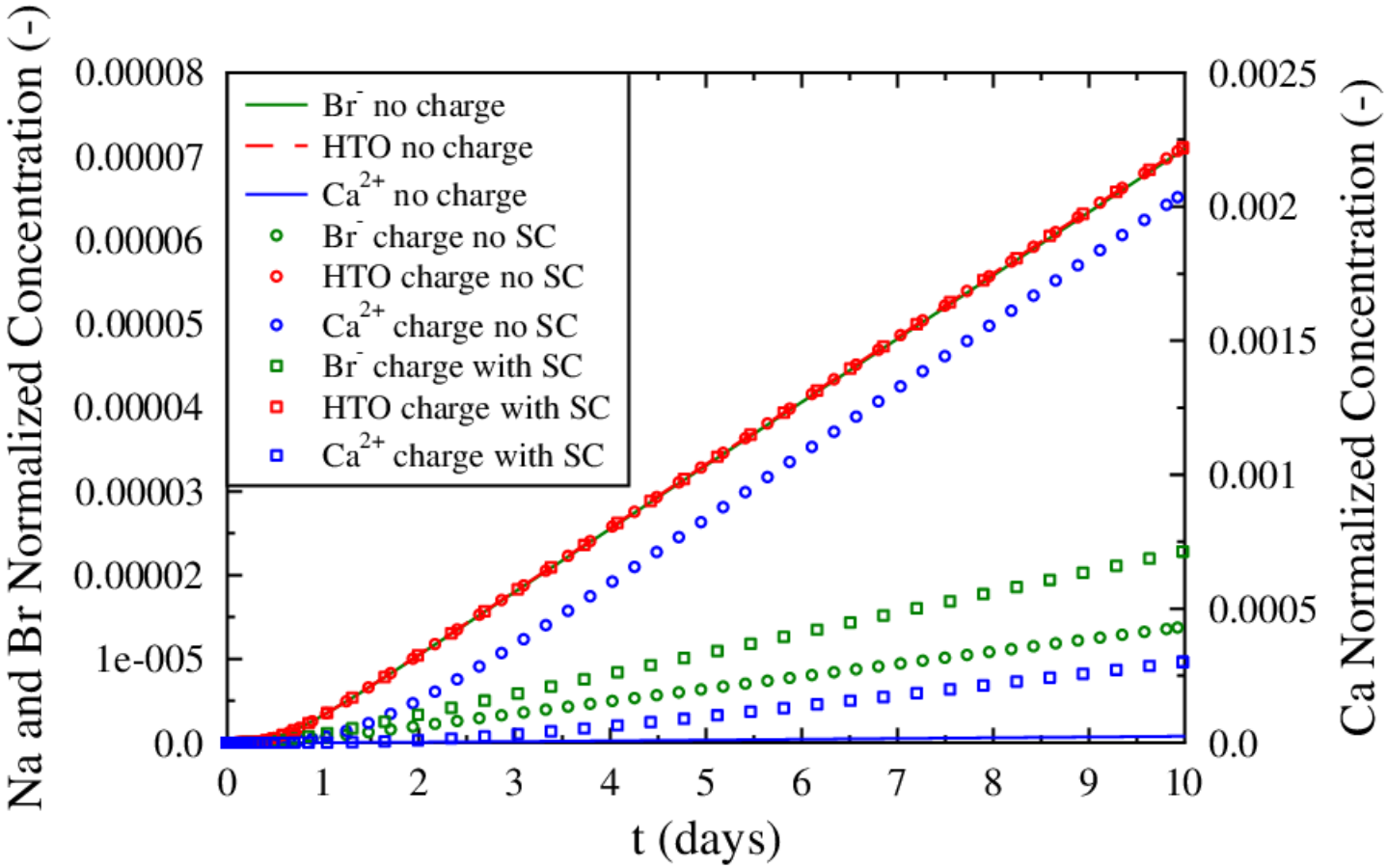
Results

Add surface complexation reactions:



What is the effect of Na and Ca surface complexation on Br and Ca diffusion?

Summary

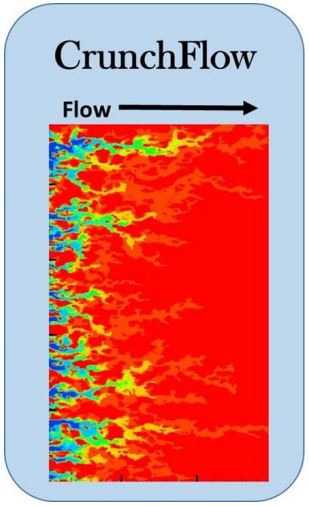

Na and Br Normalized Concentration (-)
Ca Normalized Concentration (-)
t (days)
Br- no charge
HTO no charge
Ca2+ no charge
Br- charge no SC
HTO charge no SC
Ca2+ charge no SC
Br- charge with SC
HTO charge with SC
Ca2+ charge with SC
0.00008
0.00007
0.00006
0.00005
0.00004
0.00003
0.00002
1e-005
0.0
0.0025
0.002
0.0015
0.001
0.0005
0.0
0
1
2
3
4
5
6
7
8
9
10

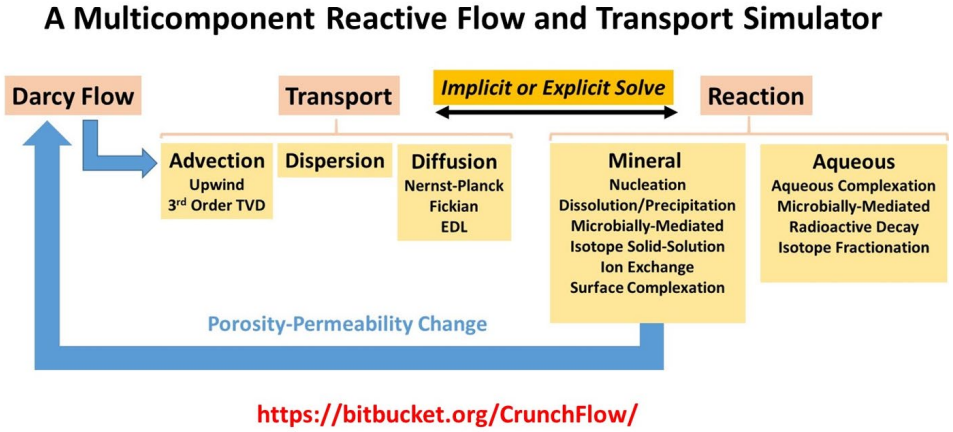
INVERSE MODELING WITH PEST-CRUNCH

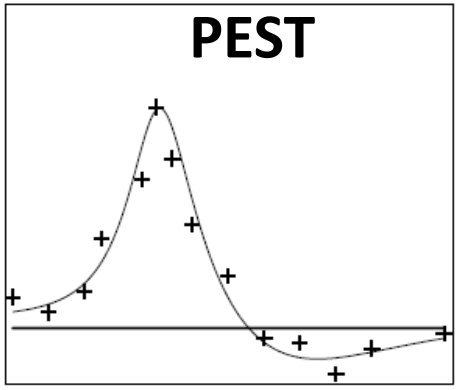
Exercise 12: Inverse Modeling with PEST-CrunchFlow

Use PEST together with CrunchFlow for inverse modeling and sensitivity analysis

http://www.pesthomepage.org/Home.php







Exercise 12: Inverse Modeling with PEST-CrunchFlow

BatchNoGmin.pst File

```
pcf
* control data
restart estimation
4 165 1 0 1
1 1 double point 1 0 0
5.0 2.0 0.1 0.005 10
3.0 3.0  0.001
0.01
50 .005 4 4 .010 5
1 1 1
* group definitions and derivative data
all  relative  0.01 0.0 switch 1.0 best_fit
* parameter data
k2a   none  relative  0.20000  -2.0  4.0  all 1.0 0. 1
k2b   none  relative  0.20000  -2.0  4.0  all 1.0 0. 1
k2c   none  relative  0.20000  -2.0  4.0  all 1.0 0. 1
k2d   none  relative  0.20000  -2.0  4.0  all 1.0 0. 1
```

Number of parameters to be fitted

Number of observations

Parameters

```
* observation groups
group_1
* observation data
SrCa-A11  0.00  1 group_1
SrCa-A12  0.00  1 group_1
SrCa-A13  0.00  1 group_1
SrCa-A14  42.37  1 group_1
SrCa-A15  0.05  1 group_1
SrCa-A21  1.19  1 group_1
SrCa-A22  0.56  1 group_1
SrCa-A23  0.37  1 group_1
SrCa-A24  40.50  1 group_1
SrCa-A25  0.00  1 group_1
```

```
* model command line
CrunchTope
* model input/output
datacom-SrExchange.tpl   datacom-SrExchange.dbs
PestExchange.ins   PestExchange.out
```

Template file for PEST so it knows where to update parameters in CrunchTope input file

PEST instruction file

Generated by CrunchTope

At command line: `i64pest BatchNoGmin.pst`

Exercise 12: Inverse Modeling with PEST-CrunchFlow

PestExchange.out File

```
 Primary Species   uEquiv/kgw    uEquiv/g solid
Ca++            3.6555E+01    1.8278E-01
K+              1.2860E+02    6.4298E-01
Mg++            9.7581E+00    4.8791E-02
Sr++            8.2991E+03    4.1495E+01
Na+             6.0143E+00    3.0071E-02
 Primary Species   uEquiv/kgw    uEquiv/g solid
Ca++            2.2798E+02    1.1399E+00
K+              2.0261E+02    1.0131E+00
Mg++            9.6190E+00    4.8095E-02
Sr++            8.0784E+03    4.0392E+01
Na+             1.3673E+00    6.8364E-03
```

Generated by CrunchTope per instructions in `BatchNoGmin.in` file

PestExchange.ins File

```
pif @
l2 [srca-a11]34:44
l1 [srca-a12]34:44
l1 [srca-a13]34:44
l1 [srca-a14]34:44
l1 [srca-a15]34:44
l2  [srca-a21]34:44
l1 [srca-a22]34:44
l1 [srca-a23]34:44
l1 [srca-a24]34:44
l1 [srca-a25]34:44
```

Tells PEST where to find the simulation data in `PestExchange.out` file to compare to observations

Datacom-SrExchange.tpl File

```
'Sr-XB8814-2' 2  1.0 'Sr++' 2.0 'XB8814-2'      0.00      0.000
'Ca-XB8814-2' 2  1.0 'Ca++' 2.0 'XB8814-2'      #k2a    # 0.000
'Na-XB8814-2' 2  1.0 'Na+' 1.0 'XB8814-2'       #k2b    # 0.000
'Mg-XB8814-2' 2  1.0 'Mg++' 2.0 'XB8814-2'      #k2c    # 0.000
'K-XB8814-2' 2  1.0 'K+' 1.0 'XB8814-2'         #k2d    # 0.000
End of exchange
```

Datacom-SrExchange.dbs File

```
'Sr-XB8814-2' 2  1.0 'Sr++' 2.0 'XB8814-2'      0.00          0.000
'Ca-XB8814-2' 2  1.0 'Ca++' 2.0 'XB8814-2'      .0918334263   0.000
'Na-XB8814-2' 2  1.0 'Na+' 1.0 'XB8814-2'       -.909927443   0.000
'Mg-XB8814-2' 2  1.0 'Mg++' 2.0 'XB8814-2'      .1465642933   0.000
'K-XB8814-2' 2  1.0 'K+' 1.0 'XB8814-2'         -1.88939379   0.000
End of exchange
```

Exercise 12: Inverse Modeling with PEST-CrunchFlow

BatchNoGmin.rec File

OPTIMISATION RESULTS

Parameters ----->

Parameter	Estimated value	95% percent confidence limits lower limit	upper limit
k2a	9.183343E-02	8.310404E-02	0.100563
k2b	-0.909927	-1.47566	-0.344194
k2c	0.146564	0.127452	0.165677
k2d	-1.88939	-1.96078	-1.81801

Note: confidence limits provide only an indication of parameter uncertainty.

They rely on a linearity assumption which may not extend as far in

parameter space as the confidence limits themselves - see PEST manual.

See file batchnogmin.sen for parameter sensitivities.

Observation	Measured value	Calculated value	Residual	Weight
srca-a11	0.00000	0.182780	-0.182780	1.000
srca-a12	0.00000	0.642980	-0.642980	1.000
srca-a13	0.00000	4.879100E-02	-4.879100E-02	1.000
srca-a14	42.3700	41.4950	0.875000	1.000
srca-a15	5.000000E-02	3.007100E-02	1.992900E-02	1.000
srca-a21	1.19000	1.13990	5.010000E-02	1.000
srca-a22	0.560000	1.01310	-0.453100	1.000
srca-a23	0.370000	4.809500E-02	0.321905	1.000
srca-a24	40.5000	40.3920	0.108000	1.000
srca-a25	0.00000	6.836400E-03	-6.836400E-03	1.000

Find summary of optimization results in *.rec file generated by PEST

Numerical Approach

Derivative of Total Concentration

$$\psi_i = C_i + \sum_{l=1}^{N_s} \nu_{i,l} C_l = C_i + \sum_{l=1}^{N_s} \nu_{i,l} \left[\prod C_p^{\nu_{p,l}} K_{eq}^{-1} \right]$$

The derivative of the total concentration with respect to the primary species concentrations

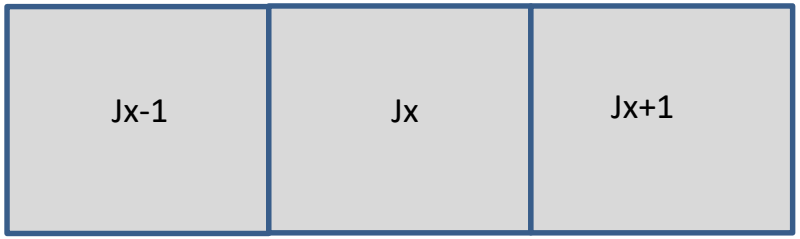
$$\frac{\partial}{\partial C_k} \left\{ \left[\psi_{i,jx}^{n+1} \right] \right\} = \frac{\partial}{\partial C_k} \left\{ C_i + \sum_{l=1}^{N_s} \nu_{i,l} C_l \right\} = \delta_{i,k} + \sum_{l=1}^{N_s} \left(\frac{\nu_{k,l}}{C_k} \right) \nu_{i,l} \left[\prod C_p^{\nu_{p,l}} K_{eq}^{-1} \right]$$

Or using the logarithms of the concentrations as the primary unknowns (which scales the Jacobian matrix, making it numerically more tractable)

$$d \ln X = \frac{dX}{X}$$

$$\frac{\partial}{\partial \ln C_k} \left\{ \left[\psi_{i,jx}^{n+1} \right] \right\} = \delta_{i,k} C_i + \sum_{l=1}^{N_s} \nu_{k,l} \nu_{i,l} \left[\prod C_p^{\nu_{p,l}} K_{eq}^{-1} \right] = \delta_{i,k} C_i + \sum_{l=1}^{N_s} \nu_{k,l} \nu_{i,l} C_l$$

Jacobian Matrix for Global Implicit Method



Jx

$$\frac{\phi}{\Delta t}\left[\delta_{i,k}C_i+\sum_{l=1}^{N_s}\nu_{k,l}\nu_{i,l}\left[\prod C_p^{\nu_{p,l}}K_{eq}^{-1}\right]\right]_{i,jx}^{n+1}+\frac{\phi v}{\Delta x}\left[\delta_{i,k}C_i+\sum_{l=1}^{N_s}\nu_{k,l}\nu_{i,l}\left[\prod C_p^{\nu_{p,l}}K_{eq}^{-1}\right]\right]_{i,jx}^{n+1}+$$
$$2\frac{\phi D}{\Delta x^2}\left[\delta_{i,k}C_i+\sum_{l=1}^{N_s}\nu_{k,l}\nu_{i,l}\left[\prod C_p^{\nu_{p,l}}K_{eq}^{-1}\right]\right]_{i,jx}^{n+1}$$

Jx-1

$$-\frac{\phi v}{\Delta x}\left[\delta_{i,k}C_i+\sum_{l=1}^{N_s}\nu_{k,l}\nu_{i,l}\left[\prod C_p^{\nu_{p,l}}K_{eq}^{-1}\right]\right]_{i,jx-1}^{n+1}-\frac{\phi D}{\Delta x^2}\left[\delta_{i,k}C_i+\sum_{l=1}^{N_s}\nu_{k,l}\nu_{i,l}\left[\prod C_p^{\nu_{p,l}}K_{eq}^{-1}\right]\right]_{i,jx-1}^{n+1}$$

Jx+1

$$-\frac{\phi v}{\Delta x}\left[\delta_{i,k}C_i+\sum_{l=1}^{N_s}\nu_{k,l}\nu_{i,l}\left[\prod C_p^{\nu_{p,l}}K_{eq}^{-1}\right]\right]_{i,jx+1}^{n+1}-\frac{\phi D}{\Delta x^2}\left[\delta_{i,k}C_i+\sum_{l=1}^{N_s}\nu_{k,l}\nu_{i,l}\left[\prod C_p^{\nu_{p,l}}K_{eq}^{-1}\right]\right]_{i,jx+1}^{n+1}$$

Newton's Method for Global Implicit Method

$$\frac{\phi}{\Delta t}\left[\delta_{i,k}C_i+\sum_{l=1}^{N_s}\nu_{k,l}\nu_{i,l}\left[\prod C_p^{\nu_{p,l}}K_{eq}^{-1}\right]\right]_{i,jx}^{n+1}$$

$$.+\frac{\phi v}{\Delta x}\left[\delta_{i,k}C_i+\sum_{l=1}^{N_s}\nu_{k,l}\nu_{i,l}\left[\prod C_p^{\nu_{p,l}}K_{eq}^{-1}\right]\right]_{i,jx}^{n+1}+2\frac{\phi D}{\Delta x^2}\left[\delta_{i,k}C_i+\sum_{l=1}^{N_s}\nu_{k,l}\nu_{i,l}\left[\prod C_p^{\nu_{p,l}}K_{eq}^{-1}\right]\right]_{i,jx}^{n+1}$$

$$.-\frac{\phi v}{\Delta x}\left[\delta_{i,k}C_i+\sum_{l=1}^{N_s}\nu_{k,l}\nu_{i,l}\left[\prod C_p^{\nu_{p,l}}K_{eq}^{-1}\right]\right]_{i,jx-1}^{n+1}-\frac{\phi D}{\Delta x^2}\left[\delta_{i,k}C_i+\sum_{l=1}^{N_s}\nu_{k,l}\nu_{i,l}\left[\prod C_p^{\nu_{p,l}}K_{eq}^{-1}\right]\right]_{i,jx-1}^{n+1}$$

$$.-\frac{\phi v}{\Delta x}\left[\delta_{i,k}C_i+\sum_{l=1}^{N_s}\nu_{k,l}\nu_{i,l}\left[\prod C_p^{\nu_{p,l}}K_{eq}^{-1}\right]\right]_{i,jx+1}^{n+1}-\frac{\phi D}{\Delta x^2}\left[\delta_{i,k}C_i+\sum_{l=1}^{N_s}\nu_{k,l}\nu_{i,l}\left[\prod C_p^{\nu_{p,l}}K_{eq}^{-1}\right]\right]_{i,jx+1}^{n+1}=$$

Nc x Nc Jacobian Submatrix

$$-\left\{\begin{array}{l}\phi\dfrac{\left[C_i+\sum_{l=1}^{N_s}\nu_{i,l}\left[\prod C_p^{\nu_{p,l}}K_{eq}^{-1}\right]_{i,jx}^{n+1}-\psi_{i,jx}^{n}\right]}{\Delta t}.\\ -\phi D\dfrac{\left[\left(C_i+\sum_{l=1}^{N_s}\nu_{i,l}\left[\prod C_p^{\nu_{p,l}}K_{eq}^{-1}\right]\right)_{i,jx-1}^{n+1}-2\left(C_i+\sum_{l=1}^{N_s}\nu_{i,l}\left[\prod C_p^{\nu_{p,l}}K_{eq}^{-1}\right]\right)_{i,jx}^{n+1}+\left(C_i+\sum_{l=1}^{N_s}\nu_{i,l}\left[\prod C_p^{\nu_{p,l}}K_{eq}^{-1}\right]\right)_{i,jx+1}^{n+1}\right]}{\Delta x^2}\\ .+\phi v\dfrac{\left[\left(C_i+\sum_{l=1}^{N_s}\nu_{i,l}\left[\prod C_p^{\nu_{p,l}}K_{eq}^{-1}\right]\right)_{i,jx}^{n+1}-\left(C_i+\sum_{l=1}^{N_s}\nu_{i,l}\left[\prod C_p^{\nu_{p,l}}K_{eq}^{-1}\right]\right)_{i,jx-1}^{n+1}\right]}{\Delta x}\end{array}\right\}$$

Nc Residual Vectors

Newton's Method for Global Implicit

For JX = 2

Nc x Nc

$$\mathbf{A_{22}} = \frac{\phi}{\Delta t}\left[\delta_{i,k}C_i + \sum_{l=1}^{N_s}\nu_{k,l}\nu_{i,l}\left[\prod C_p^{\nu_{p,l}}K_{eq}^{-1}\right]\right]_{i,2}^{n+1} + \frac{\phi v}{\Delta x}\left[\delta_{i,k}C_i + \sum_{l=1}^{N_s}\nu_{k,l}\nu_{i,l}\left[\prod C_p^{\nu_{p,l}}K_{eq}^{-1}\right]\right]_{i,2}^{n+1}$$
$$+2\frac{\phi D}{\Delta x^2}\left[\delta_{i,k}C_i + \sum_{l=1}^{N_s}\nu_{k,l}\nu_{i,l}\left[\prod C_p^{\nu_{p,l}}K_{eq}^{-1}\right]\right]_{i,2}^{n+1}$$

Nc x Nc

$$\mathbf{A_{21}} = -\frac{\phi v}{\Delta x}\left[\delta_{i,k}C_i + \sum_{l=1}^{N_s}\nu_{k,l}\nu_{i,l}\left[\prod C_p^{\nu_{p,l}}K_{eq}^{-1}\right]\right]_{i,1}^{n+1} - \frac{\phi D}{\Delta x^2}\left[\delta_{i,k}C_i + \sum_{l=1}^{N_s}\nu_{k,l}\nu_{i,l}\left[\prod C_p^{\nu_{p,l}}K_{eq}^{-1}\right]\right]_{i,1}^{n+1}$$

Nc x Nc

$$\mathbf{A_{21}} = -\frac{\phi v}{\Delta x}\left[\delta_{i,k}C_i + \sum_{l=1}^{N_s}\nu_{k,l}\nu_{i,l}\left[\prod C_p^{\nu_{p,l}}K_{eq}^{-1}\right]\right]_{i,3}^{n+1} - \frac{\phi D}{\Delta x^2}\left[\delta_{i,k}C_i + \sum_{l=1}^{N_s}\nu_{k,l}\nu_{i,l}\left[\prod C_p^{\nu_{p,l}}K_{eq}^{-1}\right]\right]_{i,3}^{n+1}$$

$$\begin{bmatrix} A_{1,1} & A_{1,2} & 0 & \cdots & & & \\ A_{2,1} & A_{2,2} & A_{2,3} & \cdots & & & \\ & & & \cdots & & & \\ & & & \cdots & A_{N-1,N-2} & A_{N-1,N-1} & A_{N-1,N} \\ & & & \cdots & 0 & A_{N,N-1} & A_{N,N} \end{bmatrix} \begin{bmatrix} \delta C_1 \\ \delta C_2 \\ \cdots \\ \delta C_{N-1} \\ \delta C_N \end{bmatrix} = -\begin{bmatrix} f_1 \\ f_2 \\ \cdots \\ f_{N-1} \\ f_N \end{bmatrix}$$