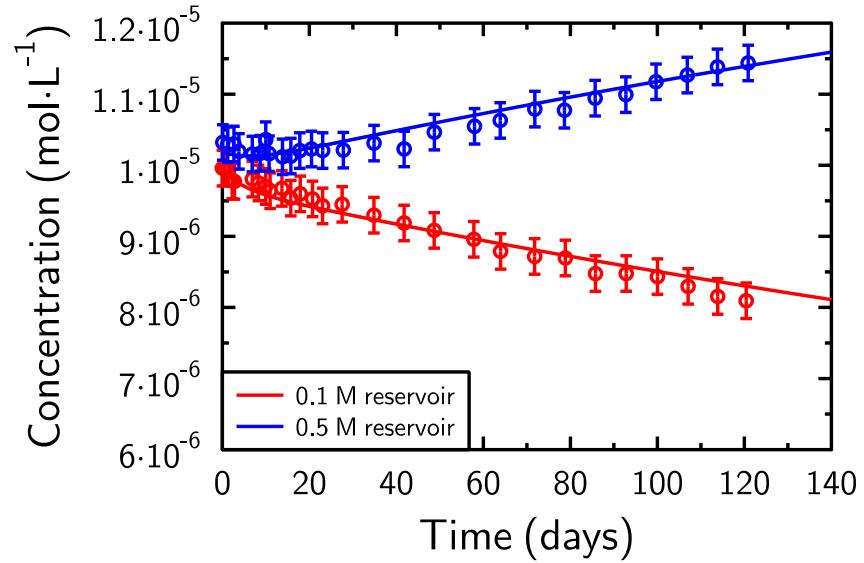
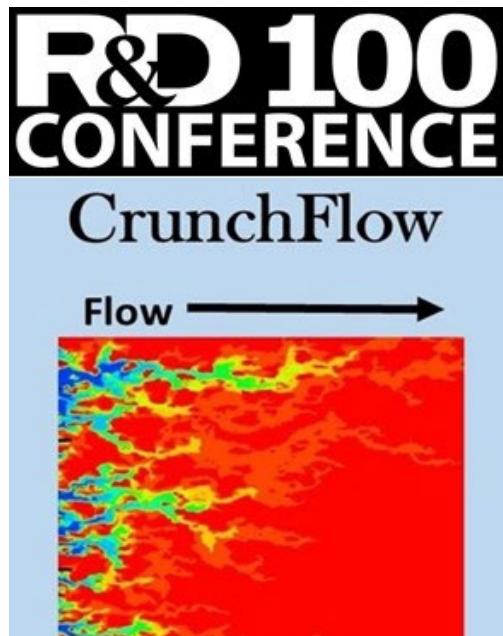


Introduction to Reactive Transport with CrunchTope

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Christophe Tournassat

Lawrence Berkeley National Laboratory



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Latest Open Source CrunchTope

<https://github.com/CISteefel/CrunchTope>

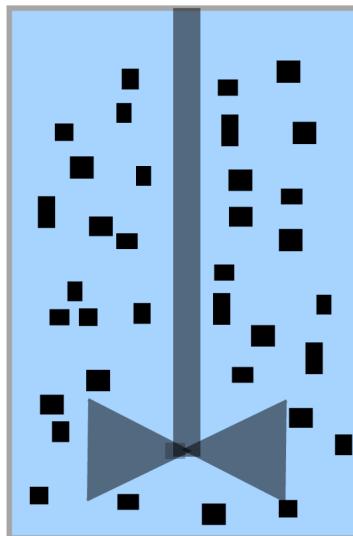
Latest CrunchTope Executables

CrunchTope Release v2.0.1 (April 13, 2022)

<https://github.com/CISteefel/CrunchTope/releases/tag/v2.0.1>

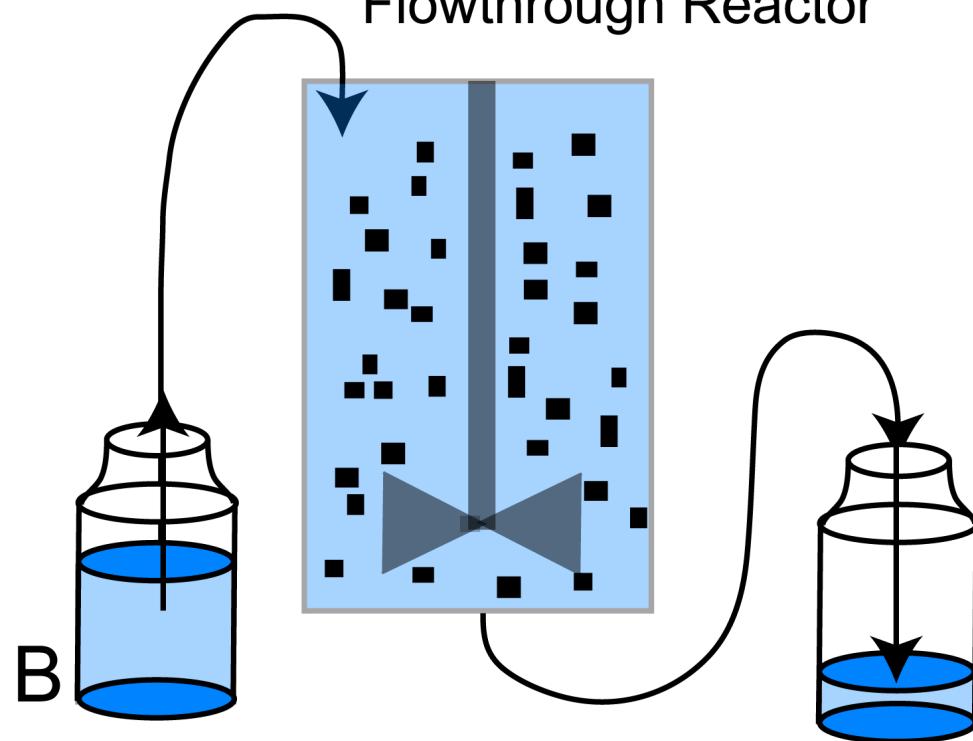
Closed versus Open Systems

Batch Reactor



A

Flowthrough Reactor



B

C

Characteristic Reaction and Transport Times

Conservation Equation

$$\frac{dM}{dt} = J_{in} - J_{out} - R = C_{in}Q_{in} - C_{out}Q_{out} - R$$

Steady State

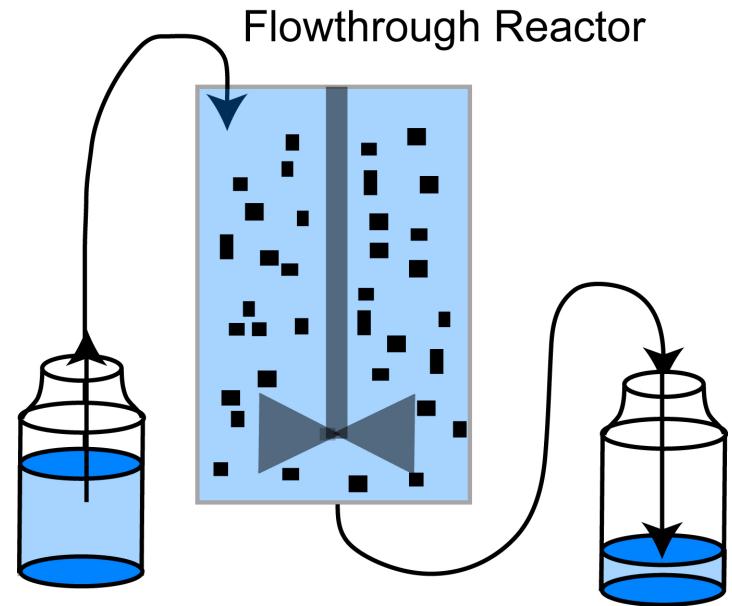
$$R = kC_{out}V = C_{in}Q_{in} - C_{out}Q_{out}$$

Residence Time

$$\tau_{res} = V / Q$$

Ratio of Characteristic Times

$$\frac{k}{\tau_{res}} = \frac{kV}{Q} = \frac{(C_{in} - C_{out})}{C_{out}}$$



t = time

M = mass of solute

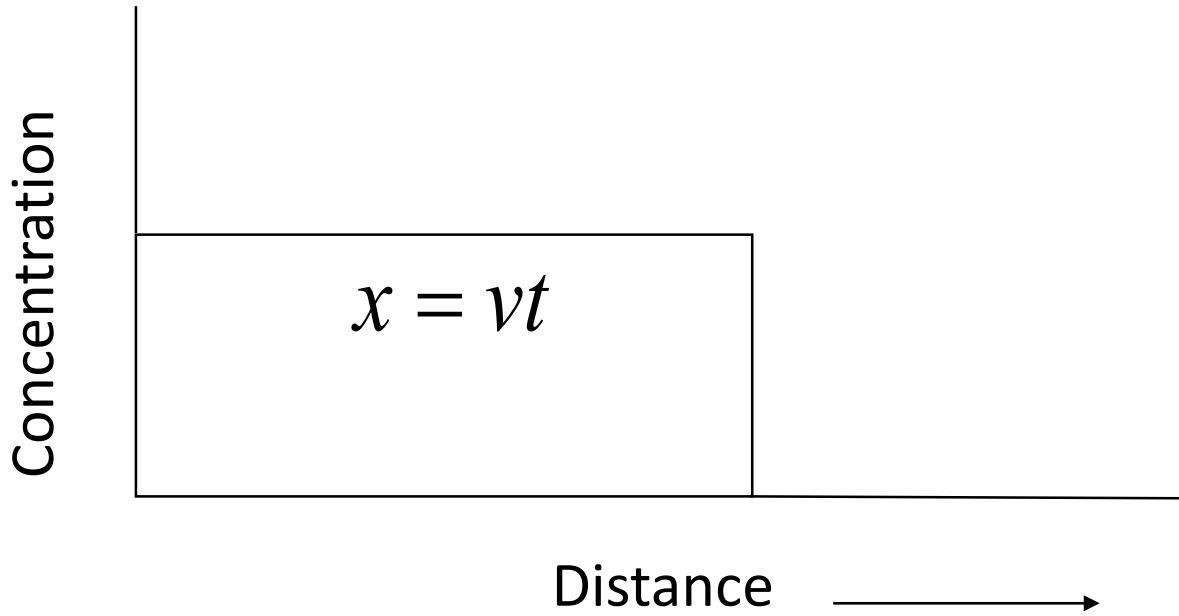
Q = volumetric flow rate

V = volume of reactor

C = concentration of solute

R = reaction rate

Advective Transport



$$J_{adv} = \phi v C_i$$

Diffusive Transport

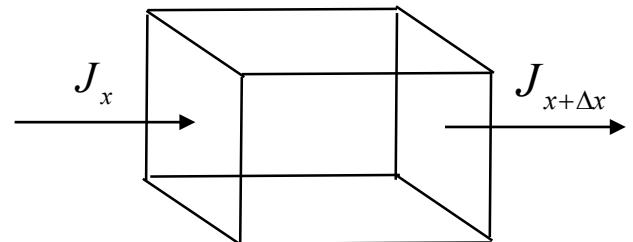
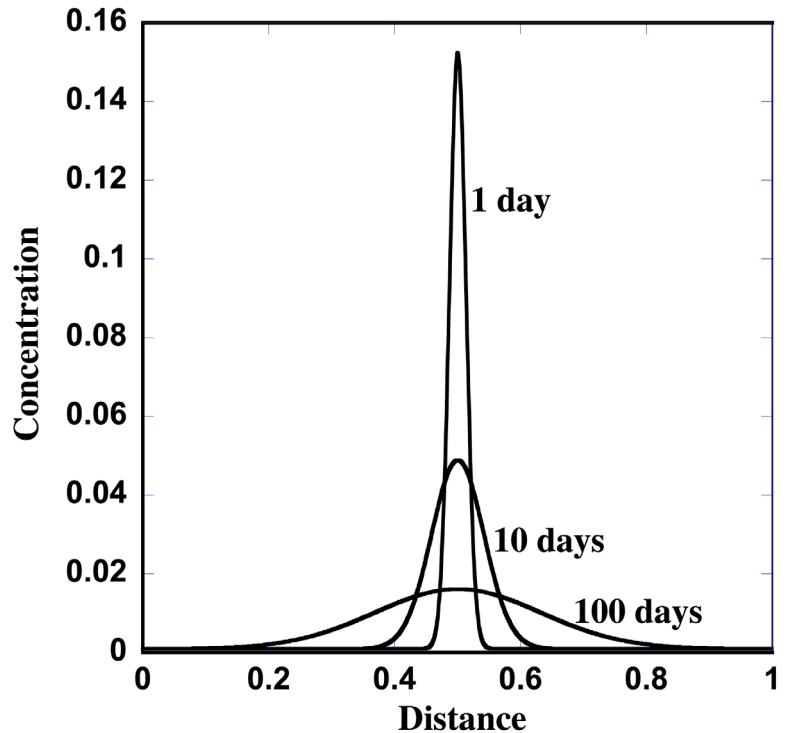
Fick's 1st Law

$$J_i = -D_i \frac{\partial C_i}{\partial x}$$

Diffusive flux is proportional to the concentration gradient

Fick's 2nd Law

$$\frac{\partial C_i}{\partial t} = \frac{\partial}{\partial x} [J_i] = -D_i \frac{\partial^2 C_i}{\partial x^2}$$



Hydrodynamic Dispersion

Treatment of dispersive flux as a Fickian process

$$J_i^{disp} = -D_h \frac{\partial C_i}{\partial x}$$

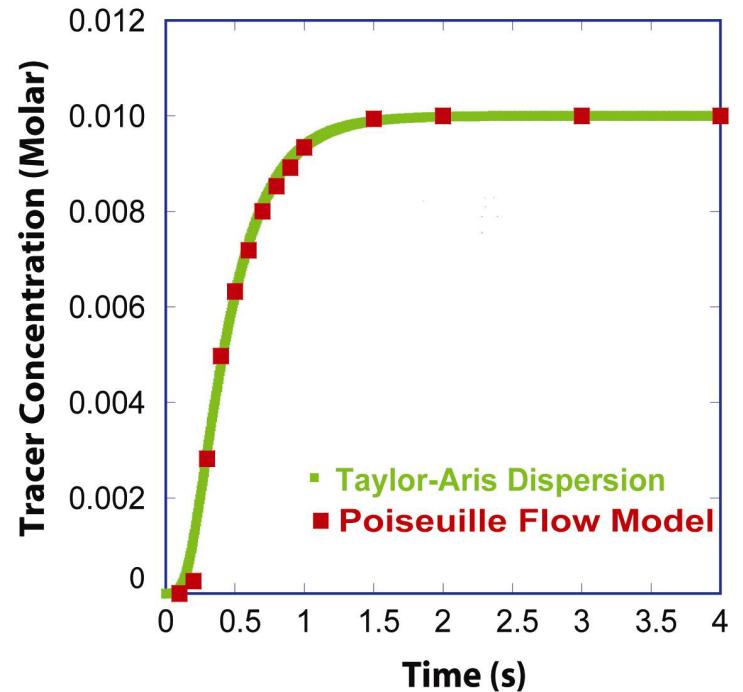
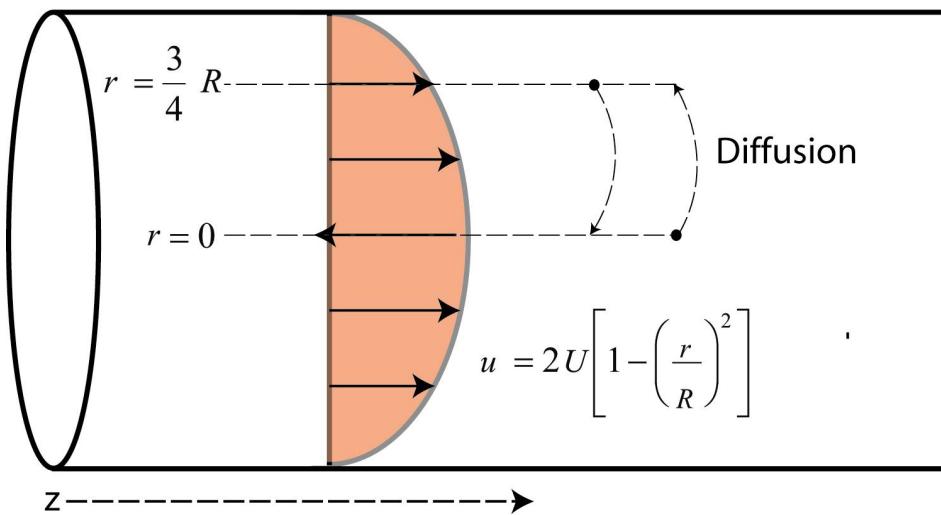
Dispersion coefficient

$$D_L = \alpha_L V_i; D_T = \alpha_T V_i$$

Does not capture the time dependence of the dispersion coefficient, which grows as the plume advances

Overestimates mixing and its effect on reactions

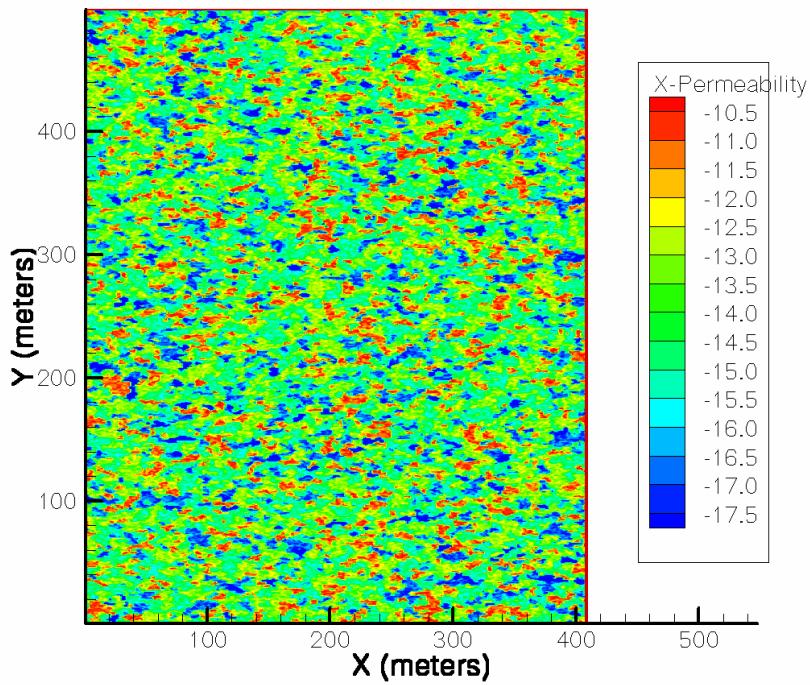
Taylor-Aris Dispersion



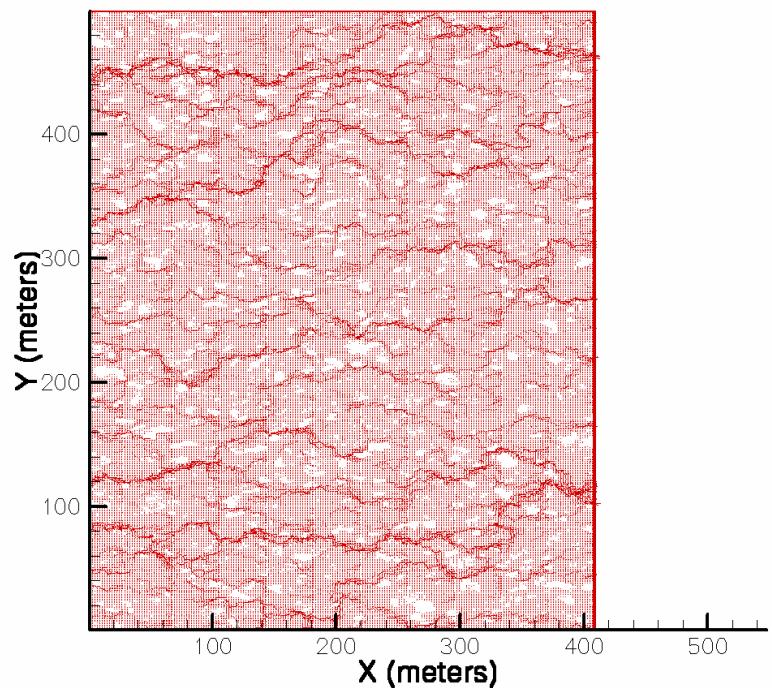
$$D_{Tay}^* = D + \frac{U^2 R^2}{48D}$$

Macrodispersion

Permeability Field



Velocity Field

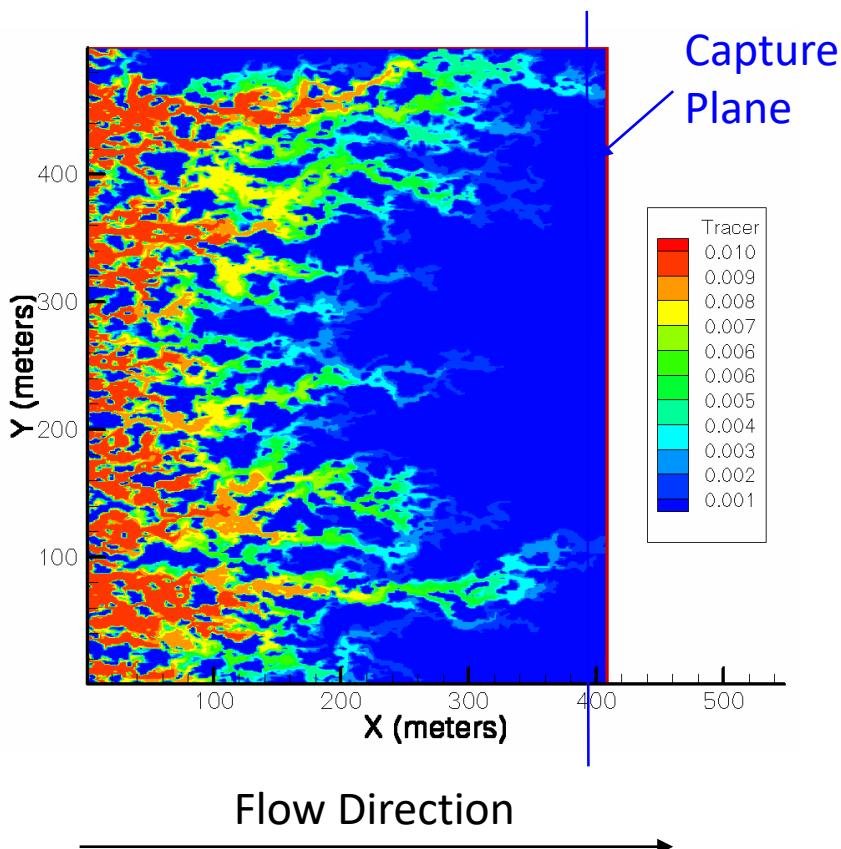


Flow Direction

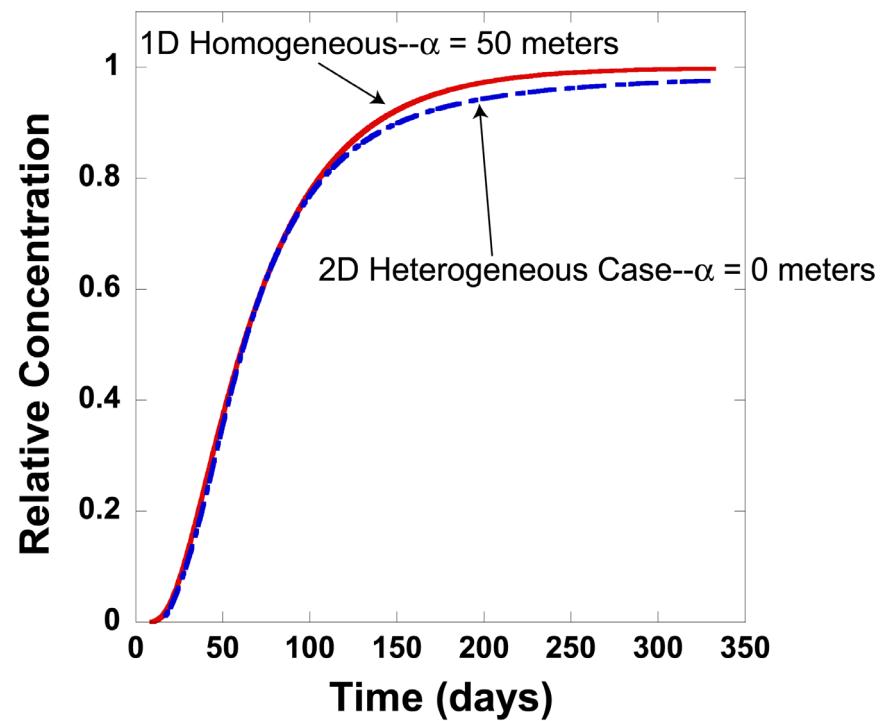


Macrodispersion

Tracer Concentration Field



Comparison of 2D Heterogeneous Case and 1D Homogeneous Case



Non-Dimensional Numbers

Péclet and Damköhler

Advection-dispersion-reaction equation

$$\frac{\partial C_i}{\partial t} = -v \frac{\partial C_i}{\partial x} + D^* \frac{\partial^2 C_i}{\partial x^2} - Ak(C - C_{eq})$$

Non-dimensional form of advection-dispersion-reaction equation

$$\frac{\partial C_i}{\partial t'} = \frac{1}{Pe} \frac{\partial^2 C_i}{\partial x'^2} - \frac{\partial C_i}{\partial x'} - Da_I(C - C_{eq})$$

Péclet number

$$Pe = \frac{t'_A}{t'_D} = \frac{vl}{D^*}$$

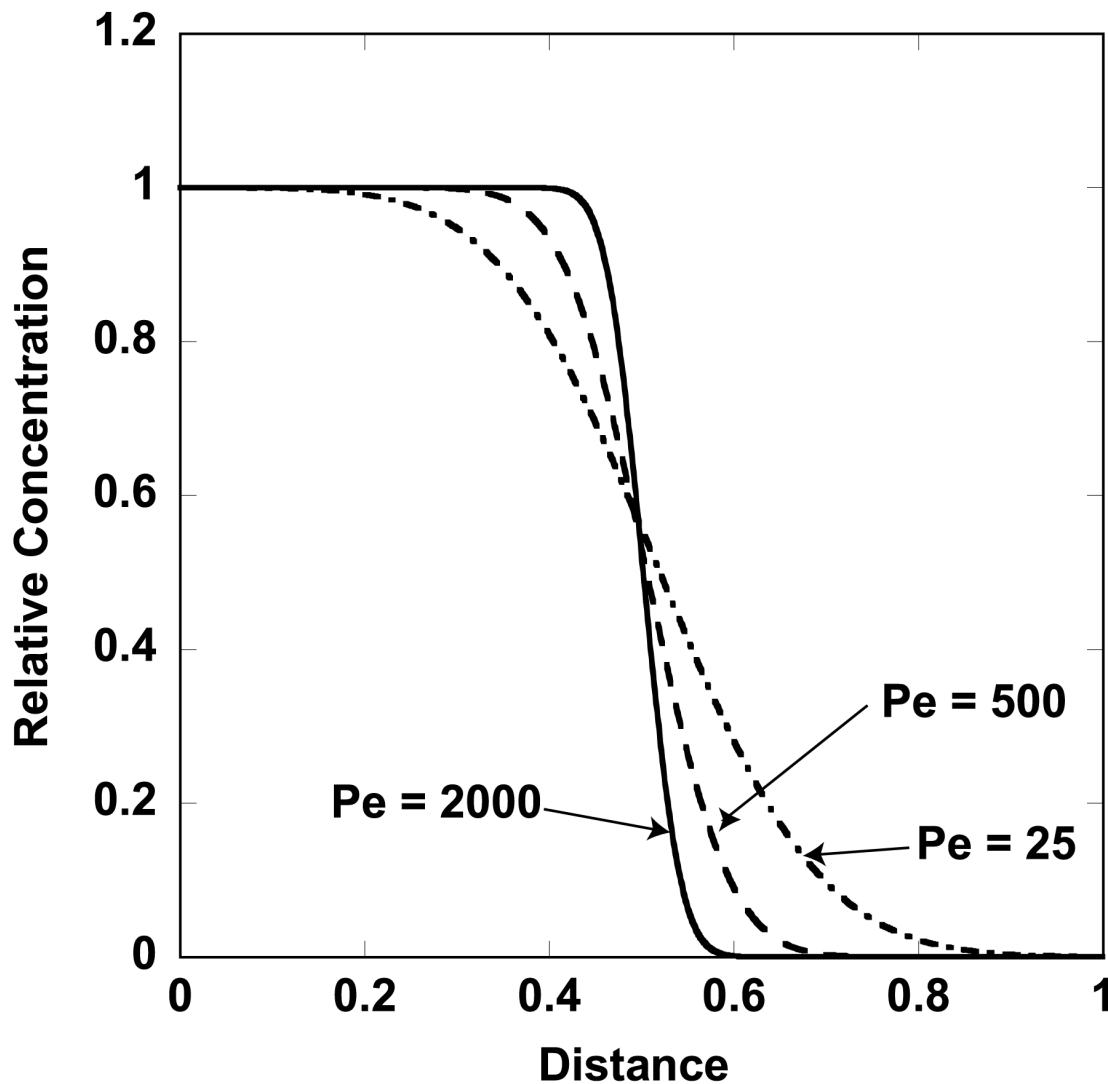
Damköhler I number

$$Da_I = \frac{t'_R}{t'_A} = \frac{Akl}{v}$$

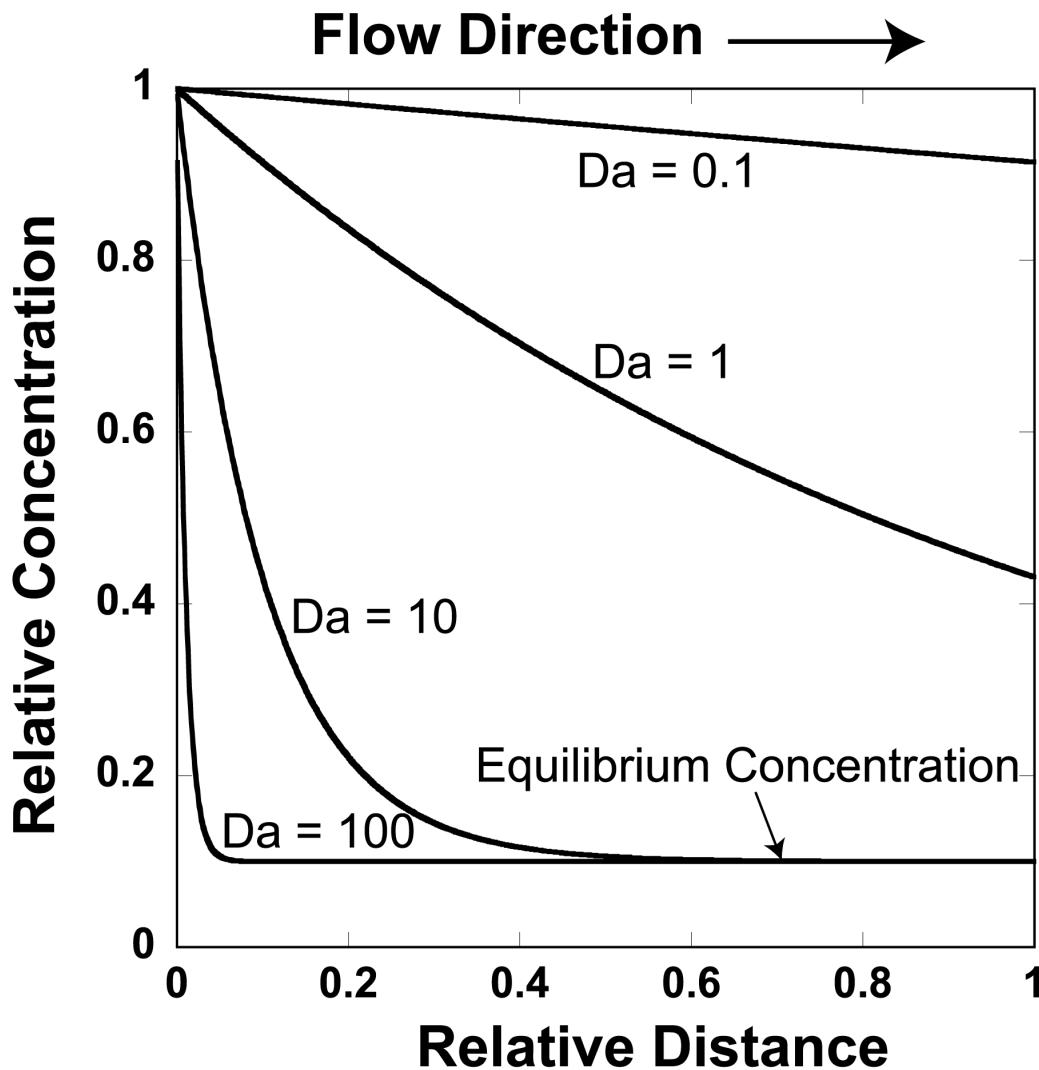
Damköhler II number

$$Da_{II} = \frac{t'_R}{t'_D} = \frac{Akl^2}{D^*}$$

Effect of Peclet Number



Effect of Damköhler Number



Analytical Solutions to ADR Equation

Solutions in one dimension for linear kinetics take the form

$$C' = e^{-\alpha' x'}$$

Pure advective transport

$$\alpha' = Da_I = \frac{Akl}{v}$$

Pure diffusive transport

$$\alpha' = Da_{II} = \frac{Akl^2}{D^*}$$

Mixed advective and diffusive transport

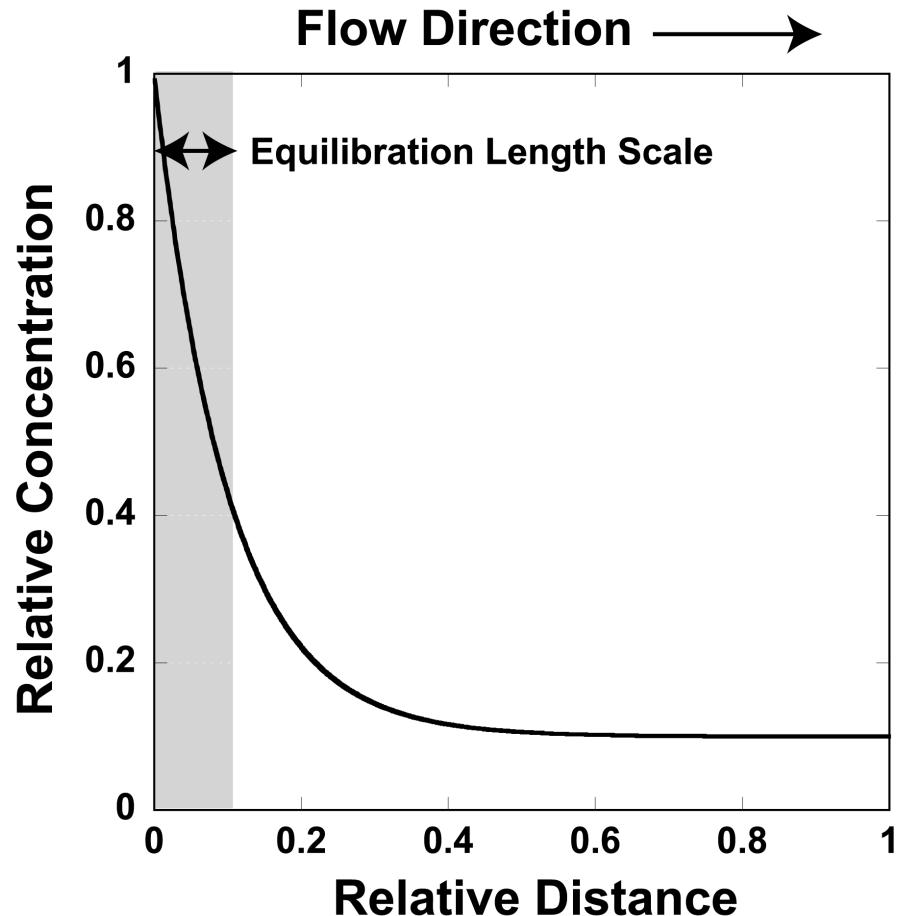
$$\alpha' = \frac{1}{2} \left(\sqrt{Pe^2 + 4Da_I \cdot Pe} - Pe \right) = \frac{1}{2} \left(\sqrt{Pe^2 + 4Da_{II}} - Pe \right) = \frac{1}{2} \left[\sqrt{\left(\frac{vl}{D}\right)^2 + 4 \frac{Akl^2}{D}} - \frac{vl}{D} \right]$$

Equilibration Length Scales

$$C' = e^{-\alpha' x'}$$

Equilibration length = λ

$$\lambda' = \frac{\lambda}{l} = \frac{1}{\alpha'}$$



Multicomponent Geochemistry

Aqueous Speciation

Canonical Form



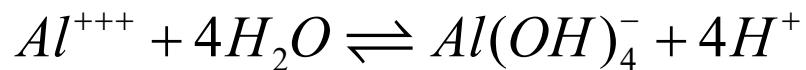
$$K_{eq} = \frac{[CO_3^{2-}][H^+]}{[HCO_3^-]}$$

$$[HCO_3^-] = \frac{[CO_3^{2-}][H^+]}{K_{eq}}$$

$$X_i = K_i^{-1} \gamma_i^{-1} \prod_{j=1}^{N_c} (\gamma_j C_j)^{\nu_{ij}} \quad (i = 1, \dots, N_x),$$

Total Concentration

$$T_j = C_j + \sum_{i=1}^{N_x} v_{ij} X_i,$$



Primary Species

$$\begin{bmatrix} 4 & -4 & 1 \\ 1 & -1 & 0 \end{bmatrix} \begin{bmatrix} H_2O \\ H^+ \\ Al^{+++} \end{bmatrix} = \begin{bmatrix} Al(OH)_4^- \\ OH^- \end{bmatrix}$$

Secondary Species

$$T_{H_2O} = C_{H_2O} + 4C_{Al(OH)_4^-} + C_{OH^-}$$

$$T_{H^+} = C_{H^+} - 4C_{Al(OH)_4^-} - C_{OH^-}$$

$$T_{Al^{+++}} = C_{Al^{+++}} + C_{Al(OH)_4^-}.$$

Michaelis-Menten (Monod) Kinetics

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

Inhibition Term

$$I_m = \left(\frac{[C_{in}] + K_{in}}{K_{in}} \right)$$

Mineral Dissolution/Precipitation Rate Laws

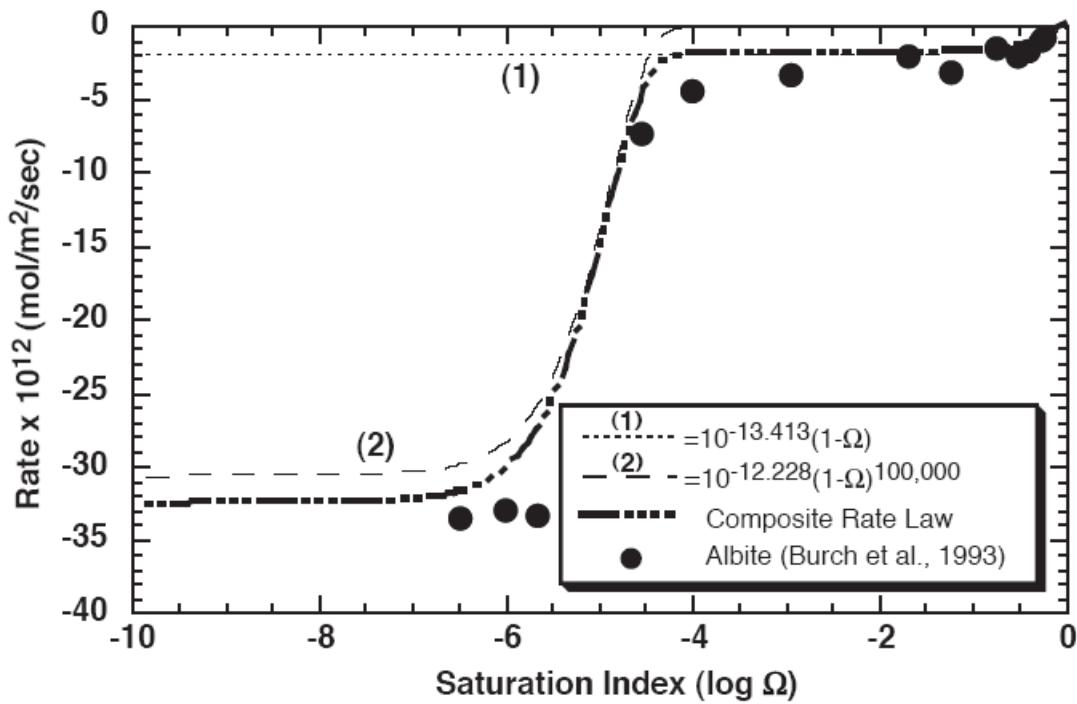
General Form

$$r_s = -A_s \left\{ \sum_{l=1}^{N_{rs}} k_l \left(\prod_{i=1}^{N_c+N_x} a_i^{p_{il}^s} \right) \right\} \left[1 - \left(\frac{Q_s}{K_s} \right)^M \right]^n,$$

Burch et al., 1993

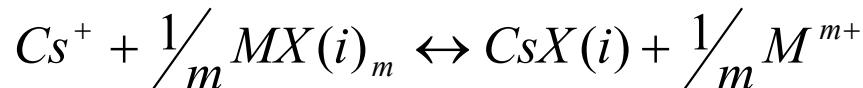
$$R_1 = RSA \cdot k_1 (1 - Q / K_{eq})^1$$

$$R_2 = RSA \cdot k_2 (1 - Q / K_{eq})^{100,000}$$



Cation Exchange

Exchange reaction involving Cs^+ and a competing cation



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

Selectivity Coefficient

$$K_{M/Cs} = \frac{\beta(i)_M^{1/m} [\text{Cs}^+]}{\beta(i)_{Cs} [\text{M}^{m+}]^{1/m}}$$

Cation Exchange Capacity

Single exchange site

$$CEC = \sum_M z_M q_M$$

Multiple exchange sites

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

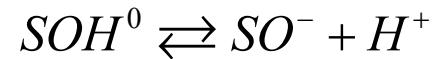
Surface Complexation

Protonation-deprotonation reactions controlling surface charge



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

First Acidity Constant



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

Second Acidity Constant

Electrostatic Effects

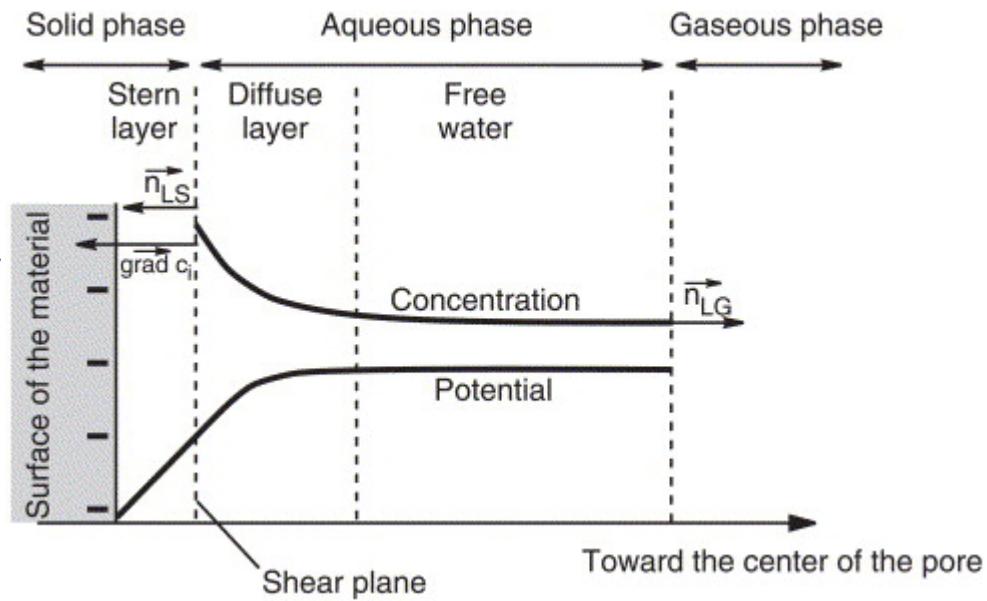
$$W = (+)_{\text{surface sites}} - (-)_{\text{surface sites}}$$

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

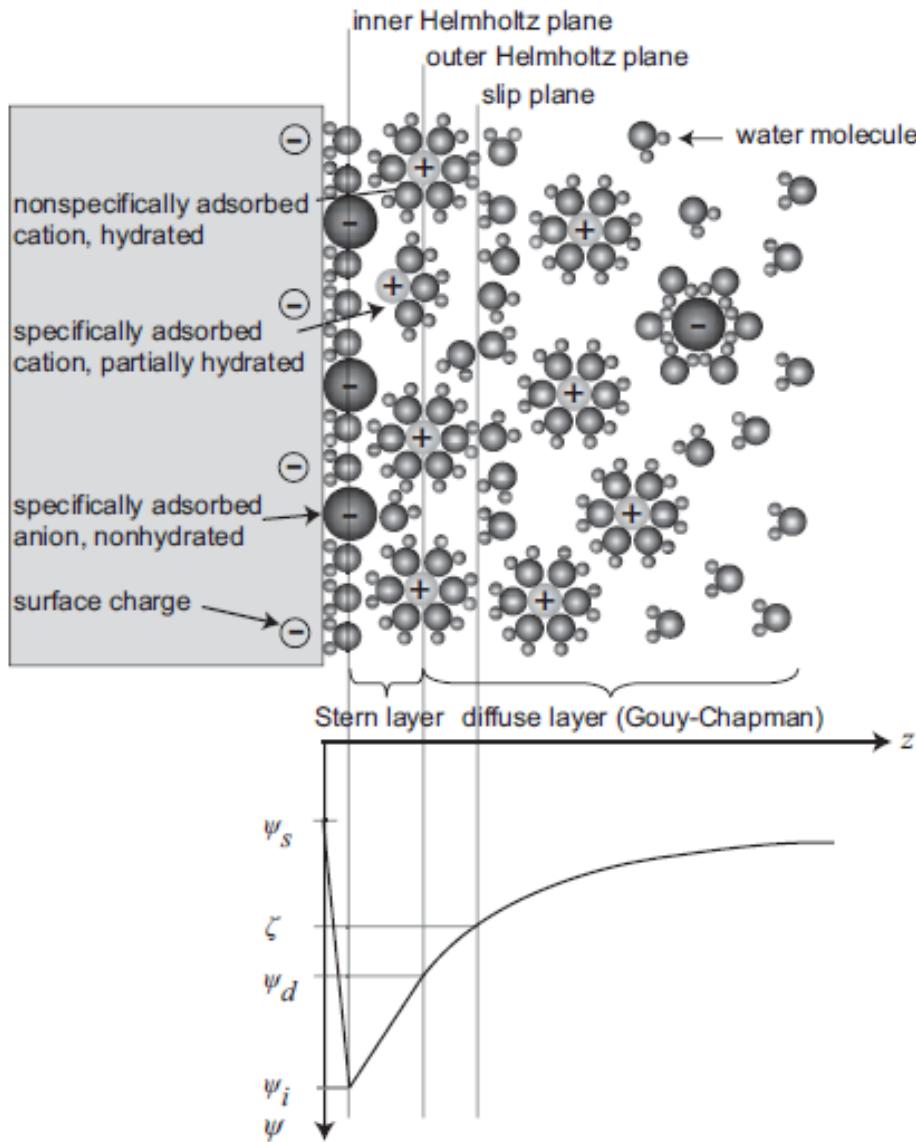
$$\sigma(C/m^2) = \frac{QF}{A} \leftarrow \text{Surface charge density}$$

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

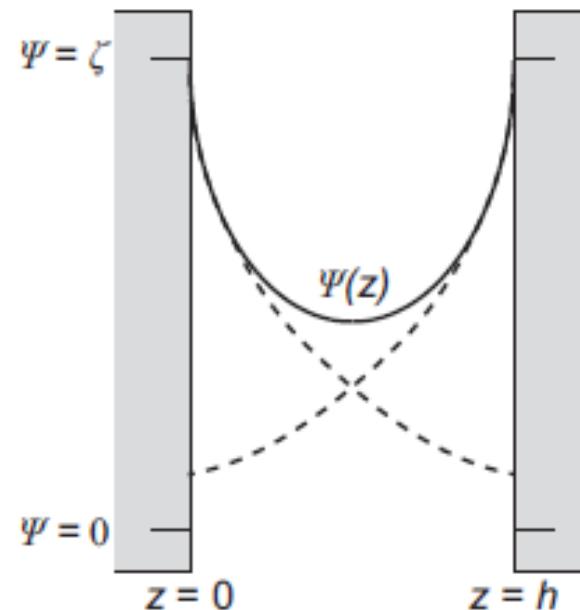
$$K_a = K_{\text{intrinsic}} \exp \left[\frac{\Delta z F \Psi}{RT} \right]$$



Electrical Double Layer



Double Layers between Charged Surfaces



Solid line: Overlapping double layers
Dashed line: No opposite wall present

After Schoch et al, 2008

Nernst-Planck Equation

$$\mu_j = \mu_j^0 + RT \ln a_j + z_j F \psi = \mu_j^0 + RT \ln(\gamma_j C_j) + z_j F \psi$$

Chemical
Potential Electrostatic
Potential

$$J_j = -u_j C_j \frac{\partial \mu_j}{\partial x} = -\frac{D_j C_j}{RT} \frac{\partial \mu_j}{\partial x}$$

Mobility

$$J_j = -D_j \nabla C_j - \frac{z_i F}{RT} D_i C_i \nabla \psi - D_j C_j \nabla \ln \gamma_j$$

Fickian Electrochemical Activity Coefficient
Diffusion Migration Gradient

$$J_j = -D_j \nabla C_j - \frac{z_i F}{RT} D_i C_i \nabla \psi$$

Nernst-Planck Equation

Left Boundary

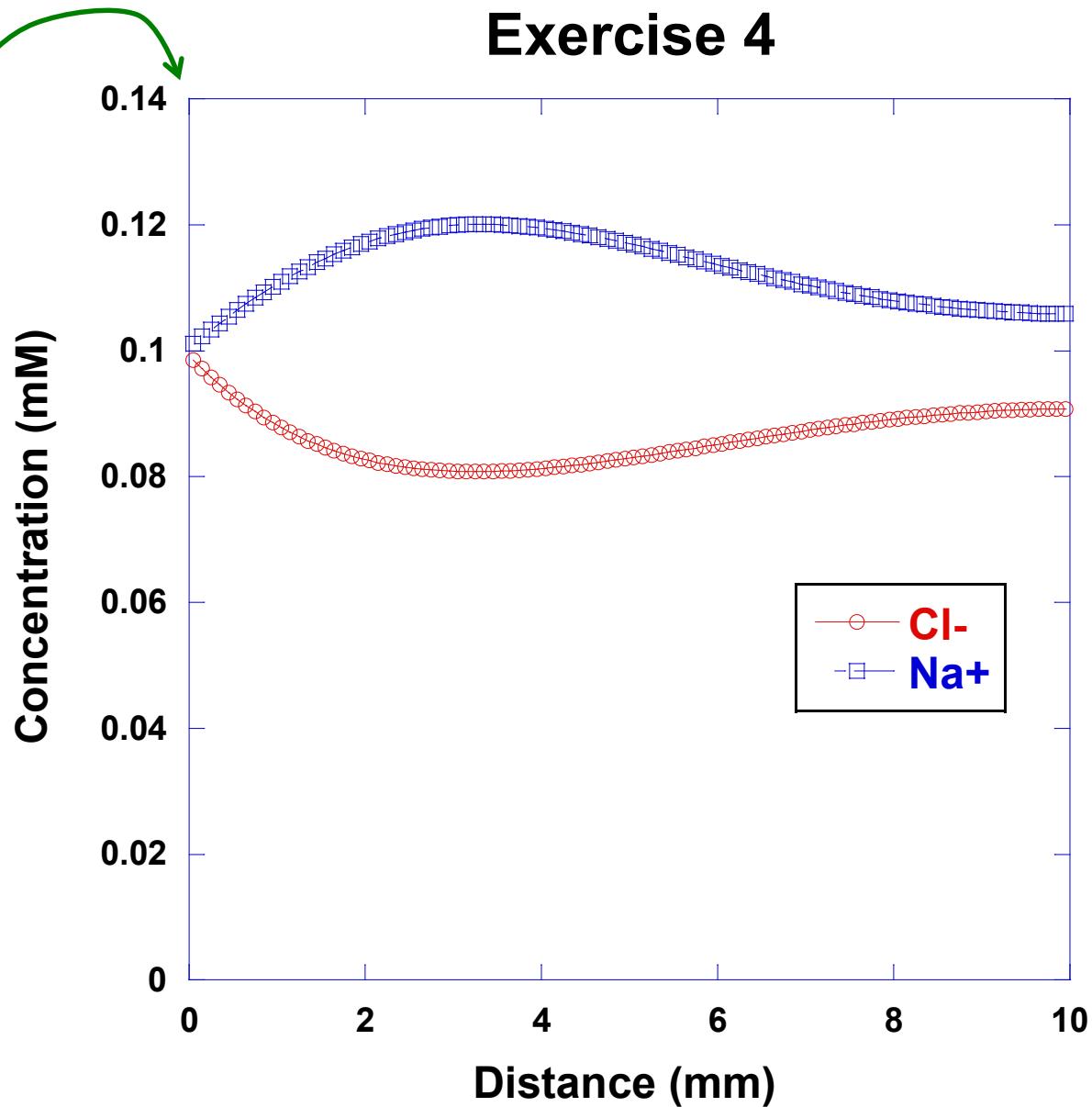
pH 6.0
Cl⁻ 0.1 mM
Na⁺ 0.1 mM
NO₃⁻ 0.001 mM

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

Initial Condition

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

Exercise 4



Reactive Transport Equations

Fully Kinetic Approach

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

Accumulation
Term

Dispersion-
Diffusion

Advection

Aqueous
Reactions

Mineral
Reactions

Gas
Reactions

Partial Equilibrium Approach

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

Total
Concentration

Secondary
Species

Rewritten with
Primary Species

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

Reactive Transport Equations: Numerical



Accumulation
Term

Dispersion-
Diffusion

Advection

Aqueous
Reactions

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

Rewrite Ψ in terms of primary species concentrations

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

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

Advection 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-Hückel adh' 0.4939 0.5114 0.5465 0.5995 0.6855 0.7994 0.9593 1.2180
'Debye-Hückel bdh' 0.3253 0.3288 0.3346 0.3421 0.3525 0.3639 0.3766 0.3925
'Debye-Hückel 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

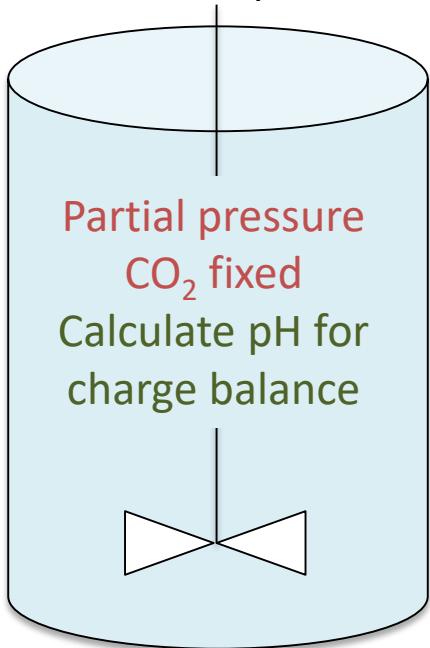
Spatial profile files include:

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 (m³/m²/yr)
9. toperatio_aq#.out per mil
10. toperatio_min#.out per mil

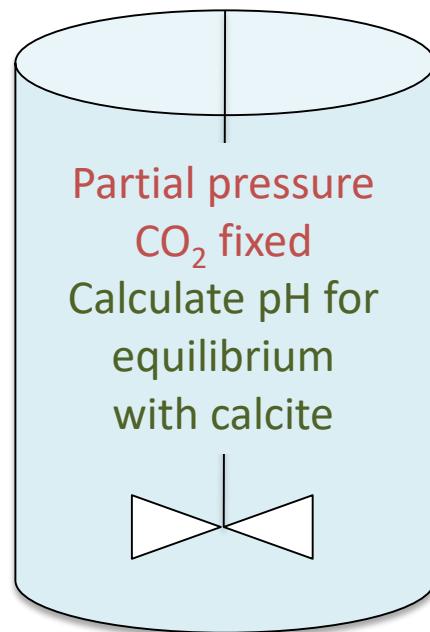
SPECIATION

Exercise 1: Carbonate Speciation

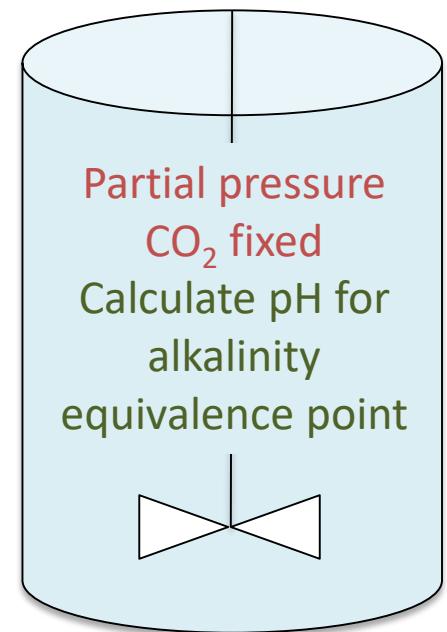
Condition: speciate 1



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
```

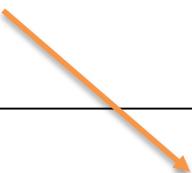
GASES

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

MINERALS

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

Log rate (mol/m²/s)



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-
HC03-	6.3414E+00	-1.00	1.00	0.00	0.00	0.00	0.00
H13C03-	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
C03--	1.6666E+01	-2.00	1.00	0.00	0.00	0.00	0.00
13C03--	1.6664E+01	-2.00	0.00	1.00	0.00	0.00	0.00
CaC03(aq)	1.3350E+01	-2.00	1.00	0.00	1.00	0.00	0.00
Ca13C03(aq)	1.3348E+01	-2.00	0.00	1.00	1.00	0.00	0.00
CaHC03+	5.2986E+00	-1.00	1.00	0.00	1.00	0.00	0.00
CaH13C03+	5.2961E+00	-1.00	0.00	1.00	1.00	0.00	0.00
NaC03-	1.6157E+01	-2.00	1.00	0.00	0.00	1.00	0.00
Na13C03-	1.6155E+01	-2.00	0.00	1.00	0.00	1.00	0.00
NaHC03(aq)	6.1857E+00	-1.00	1.00	0.00	0.00	1.00	0.00
NaH13C03(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

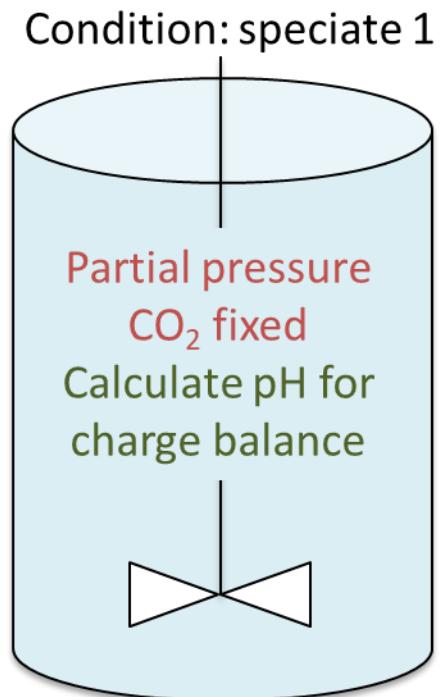
Gases	log K	Stoichiometric Coefficients					
		H+	CO2(aq)	13CO2(Ca++	Na+	Cl-
CO2(g)	-1.4677E+00	0.00	1.00	0.00	0.00	0.00	0.00
13CO2(g)	-1.4680E+00	0.00	0.00	1.00	0.00	0.00	0.00

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
```

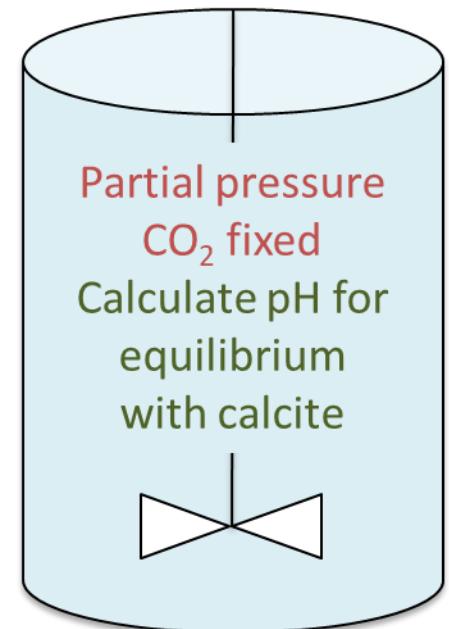
Gas partial pressure in bars



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: speciate 2



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
```

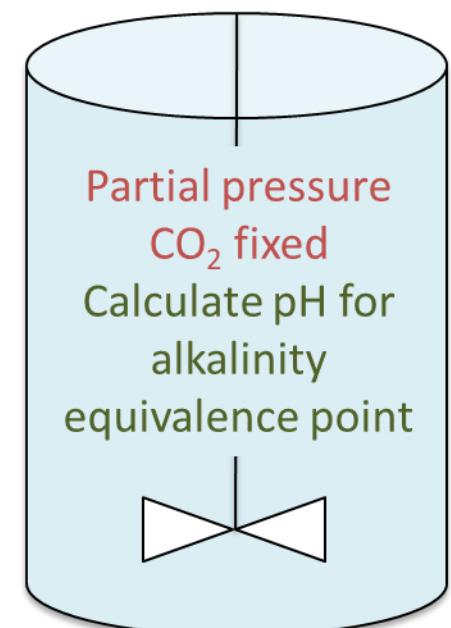
```
Na+          0.01
```

```
Cl-          0.01
```

```
Ca++         0.00
```

```
END
```

Condition: speciate 3



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
		Charge	
H+	-6.4078E-19		
CO2(aq)	1.3074E-05	Gas	CO2(g)
13C02(aq)	1.3206E-07	Gas	13C02(g)
Ca++	1.0326E-30	Total	
Na+	1.0000E-02	Total	
Cl-	1.0000E-02	Total	

$$\delta^{13}\text{C} = 0\text{\textperthousand}$$

Concentrations of Individual Species, Exchangers, and Surface Complex

Species	Log Molality	Log Activity	Log 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
13C02(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
HC03-	-5.612	-5.657	2.443E-06	2.204E-06
H13C03-	-7.606	-7.650	2.479E-08	2.236E-08

$$\delta^{13}\text{C} = 4.6\text{\textperthousand}$$

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
HC03-	-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]) *****

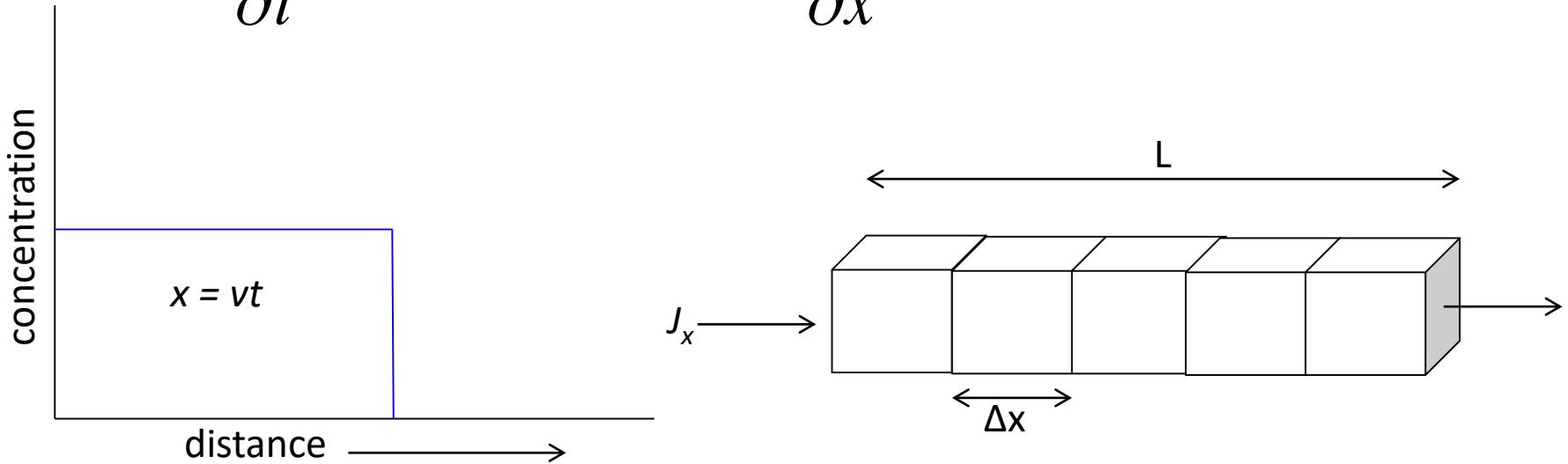
Calcite -32.0097

ADVECTION

Exercise 2: Advection 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-Lowy Condition

Numerical Dispersion

$$\frac{[C_i^{n+1} - C_i^n]}{\Delta t} = -v \frac{[C_i^n - C_i^n]}{\Delta x}$$

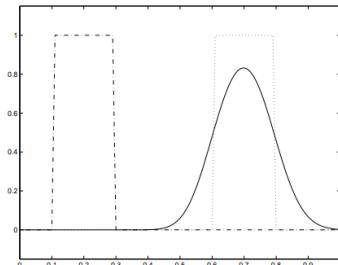
Upwind Scheme

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

Taylor Series Expansions

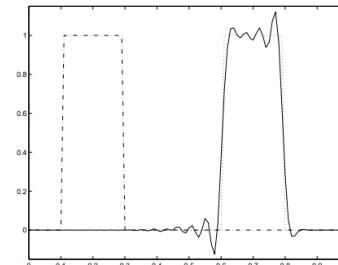
$$C_i^{n+1} = C_i^n - \Delta x \left[\frac{\partial C}{\partial x} \right]_i^n + \frac{(\Delta x)^2}{2} \left[\frac{\partial^2 C}{\partial x^2} \right]_i^n + \dots$$

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



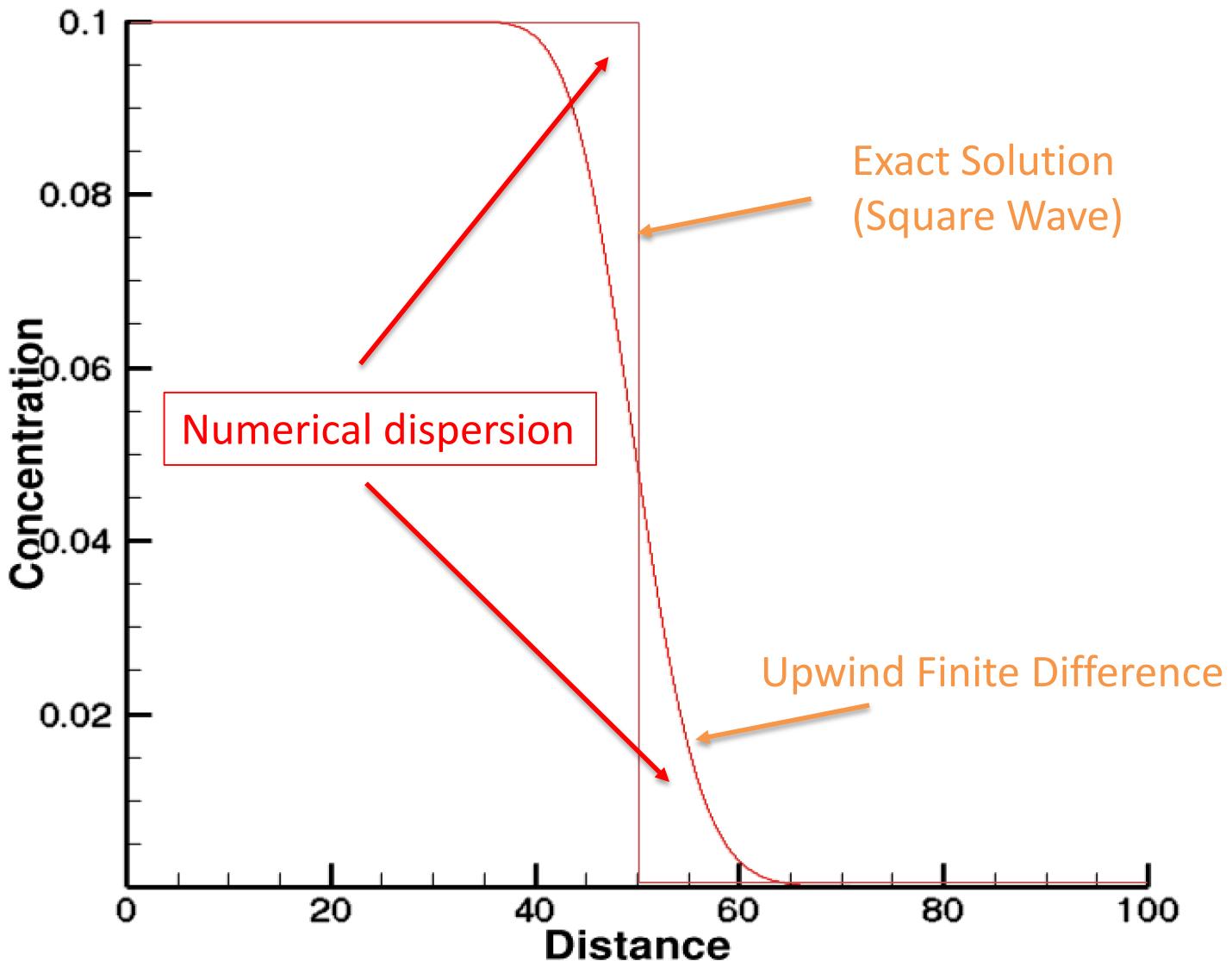
smearing (amplitude errors)

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



wiggles (phase errors)

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 1-1 1-1
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 Units of meters
END
```

Gradually increase until you have a match

What dispersivity do you need to match?

FICKIAN DIFFUSION

Exercise 3: Fickian Diffusion



(a) early

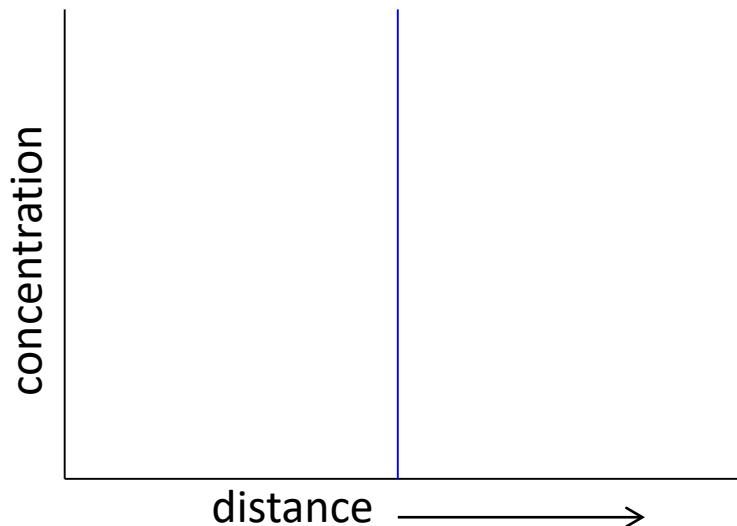


(b) intermediate



(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  
junk 1-501 1-1 1-1  
boundary 251-251 1-1 1-1  
END
```

Writes over earlier
specified initial
condition

```
BOUNDARY_CONDITIONS  
x_begin junk flux  
x_end junk 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

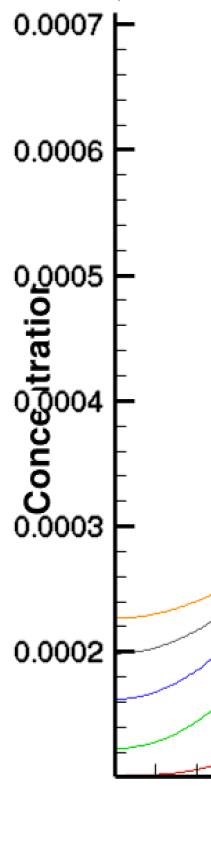
Condition junk
units mol/kg
temperature 25.0
Tracer 0.0001
END

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

```
BOUNDARY_CONDITIONS  
x_begin junk Dirichlet  
x_end junk Dirichlet  
END
```

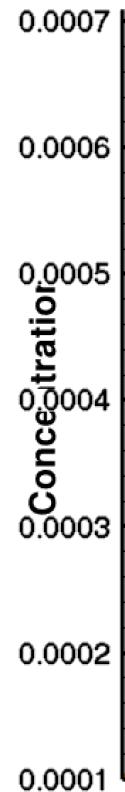
Exercise 3: Fickian Diffusion

Flux boundary



Flux boundary

Dirichlet boundary



Dirichlet boundary



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

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

Fickian

Electrical
Potential

Activity
Coefficient

Nernst-Planck Equation

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

Diffusion Potential

$$\nabla \psi = -\frac{RT}{F} \frac{\sum_j z_j D_j [\nabla C_j + C_j \nabla \ln \gamma_j]}{\sum_j z_j^2 D_j C_j}$$

Term vanishes if diffusion
coefficients are all the same

CrunchTope Equation

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

Fick's Law

Diffusion Potential

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

BOUNDARY CONDITIONS

```
X_begin inlet      Dirichlet
X_end   initial    flux
END
```

Refers to Condition
“inlet” and “initial”

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
```

Species-specific
diffusion coefficients

```
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
```

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
```

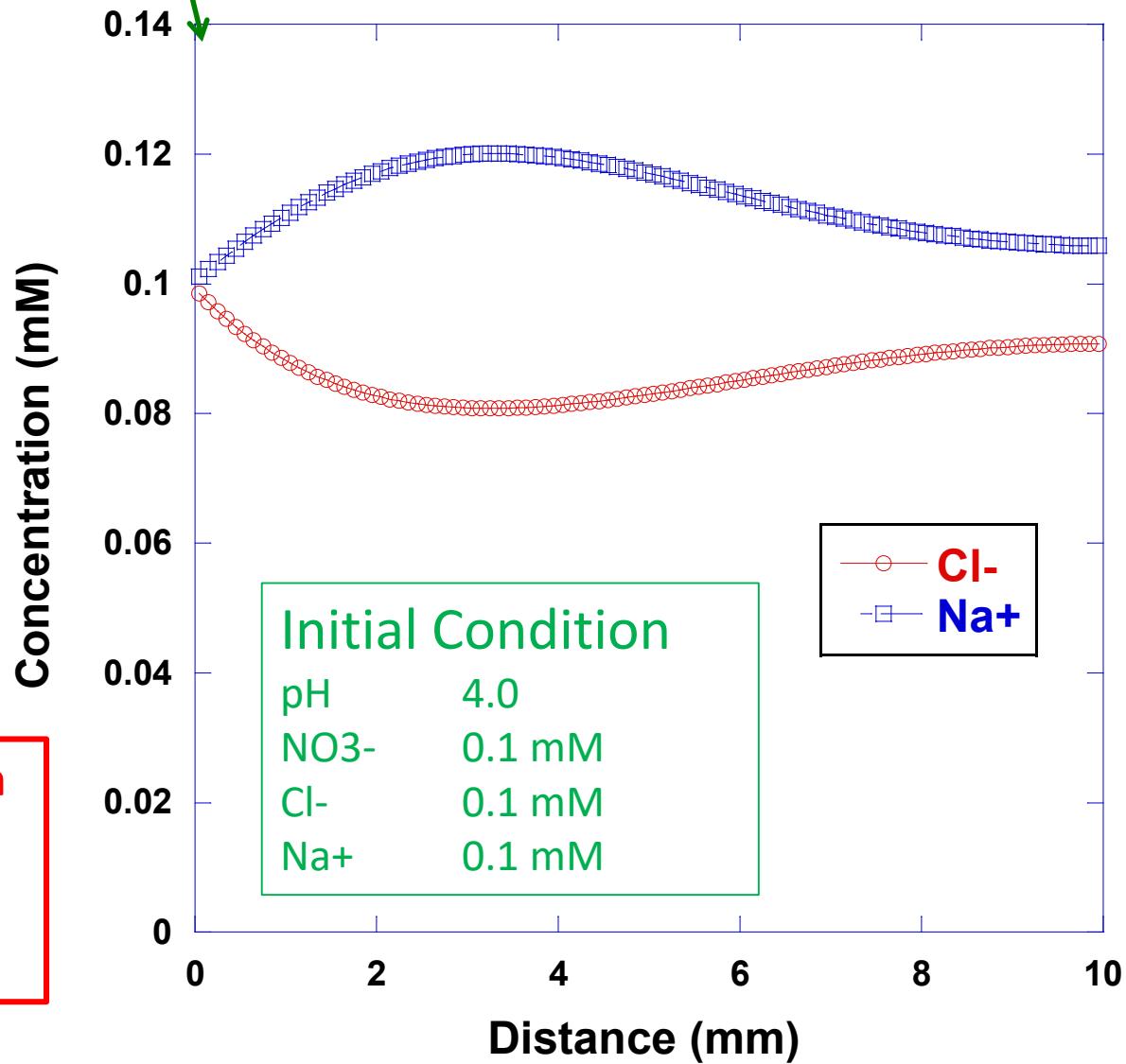
Exercise 4: Nernst-Planck Equation

Exercise 4

Left Boundary

pH	6.0
NO ₃ ⁻	0.001 mM
Cl ⁻	0.1 mM
Na ⁺	0.1 mM

Concentration (mM)



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

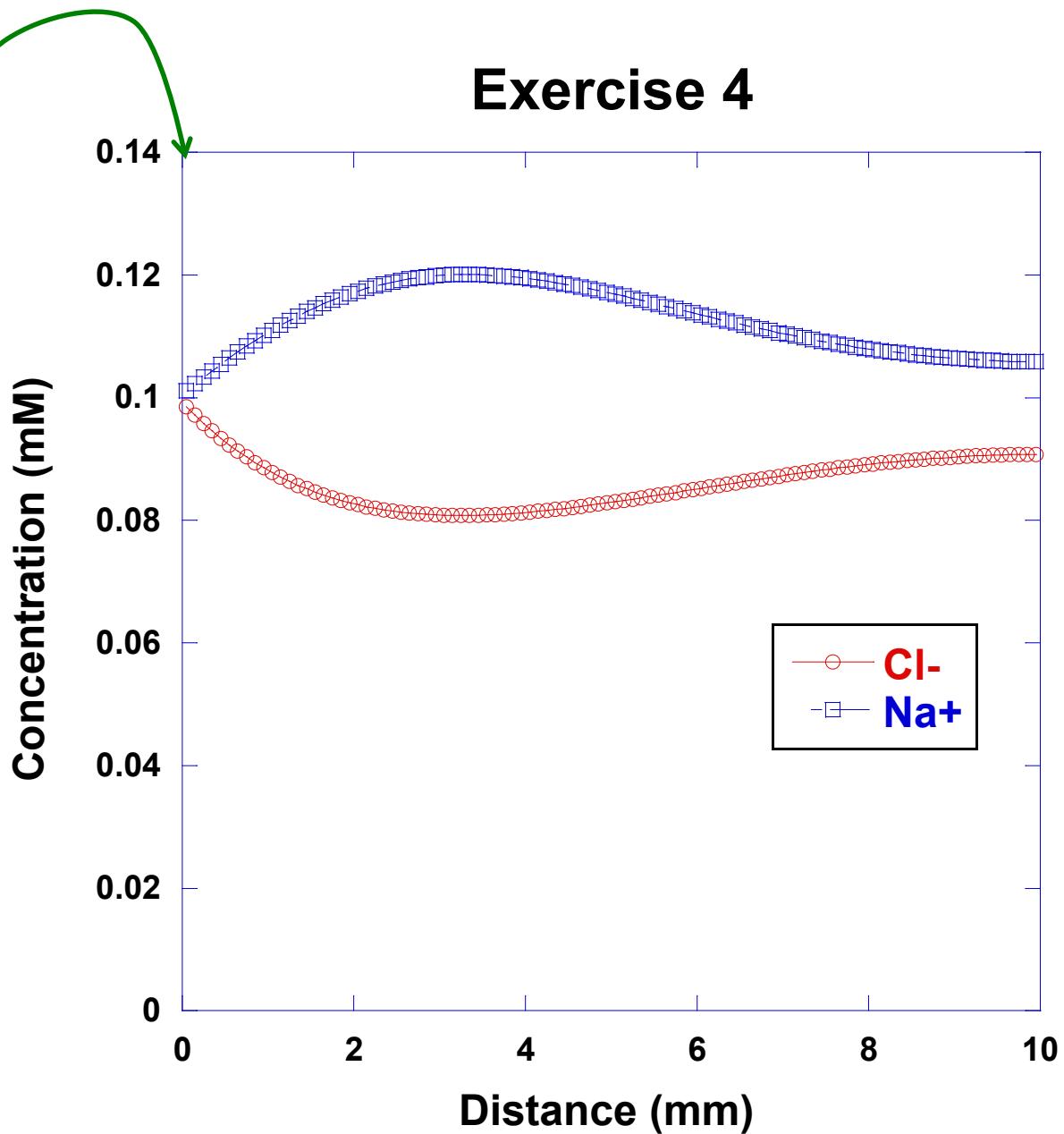
Exercise 4

Left Boundary

pH	6.0
NO_3^-	0.001 mM
Cl^-	0.1 mM
Na^+	0.1 mM

Initial Condition

pH	4.0
NO_3^-	0.1 mM
Cl^-	0.1 mM
Na^+	0.1 mM



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

ISOTOPES
primary 37Cl- Cl- 0.333
END

Rare Isotope Common Isotope

Isotopic fractionation
expressed in per mil

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

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)

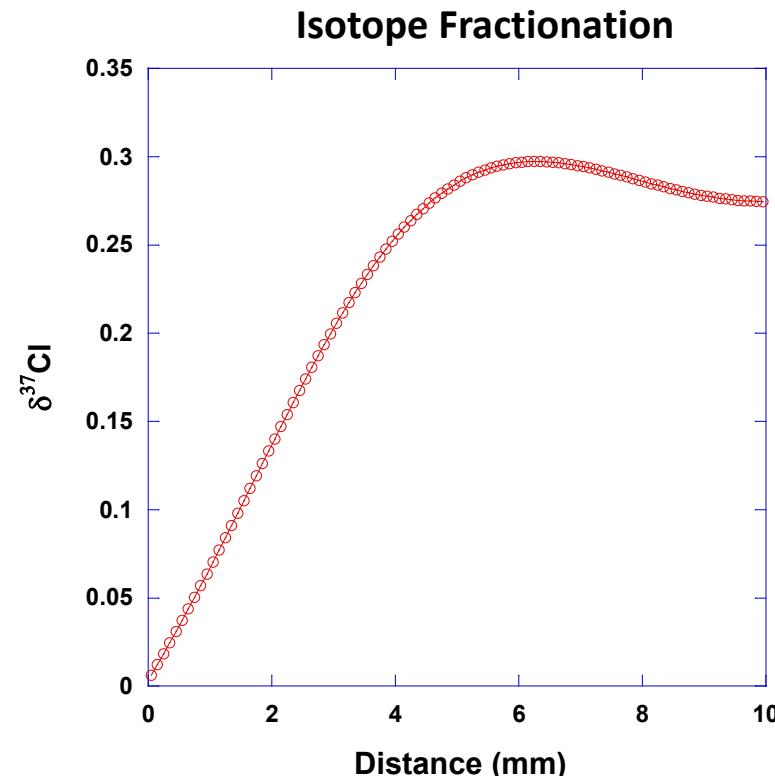
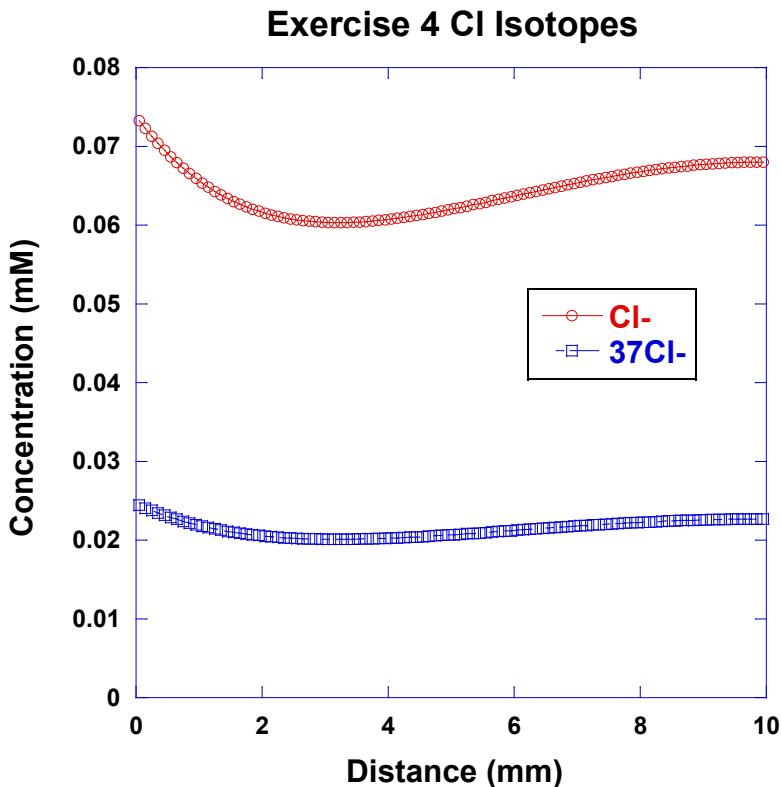
Find isotopic ratios in **toperatio_aq1.out**

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

Left Boundary		
pH	6.0	
Cl-	0.075	
^{37}Cl -	0.025	
Na+	0.1	
NO ₃ -	0.001	

D_25 Cl- 2.032E-5
D_25 ^{37}Cl - 2.028E-5

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



Plot isotopic ratios in [toperatio_aq1.out](#)

SORPTION

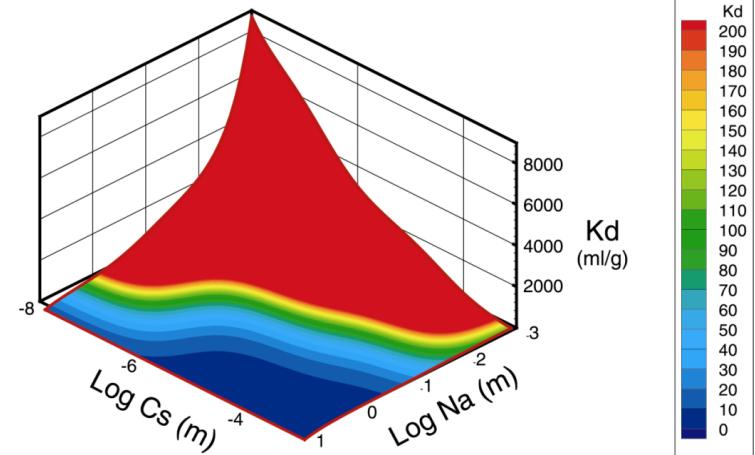
Contaminant Retardation

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

ρ_B : bulk density (g/ml)

K_d : distribution coefficient (ml/g)

ϕ : porosity



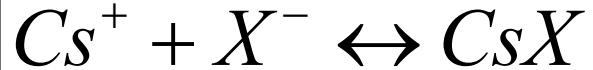
$$R \frac{\partial C}{\partial t} = \frac{\partial}{\partial x_i} \left[D_{ij} \frac{\partial C}{\partial x_j} \right] - \frac{\partial}{\partial x_i} [v_i C]$$

Contaminant
Velocity v_c

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

Exercise 6a: Cesium Ion Exchange

Exchange reaction involving Cs^+ and a competing 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

Single exchange site

$$CEC = \sum_M z_M q_M$$

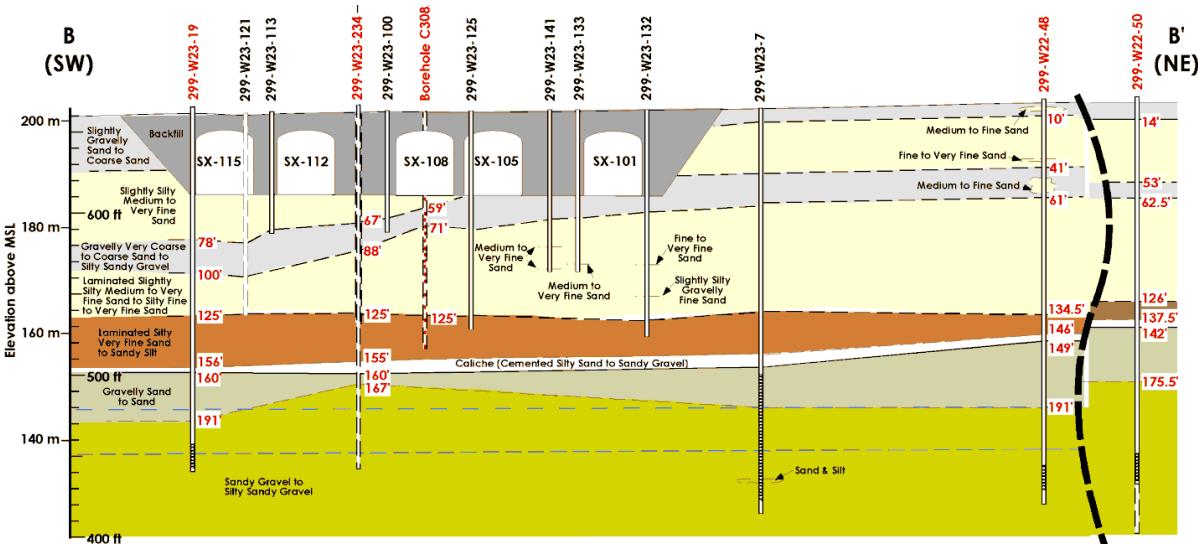
Multiple exchange sites

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

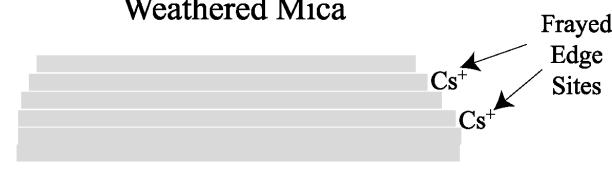
Cation Exchange Capacity:

Real World Example for ^{137}Cs Cation Exchange

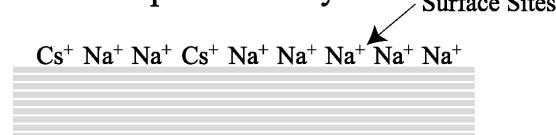
Leaking high ionic strength waste tanks led to contamination of the deep Hanford Vadose Zone



Weathered Mica

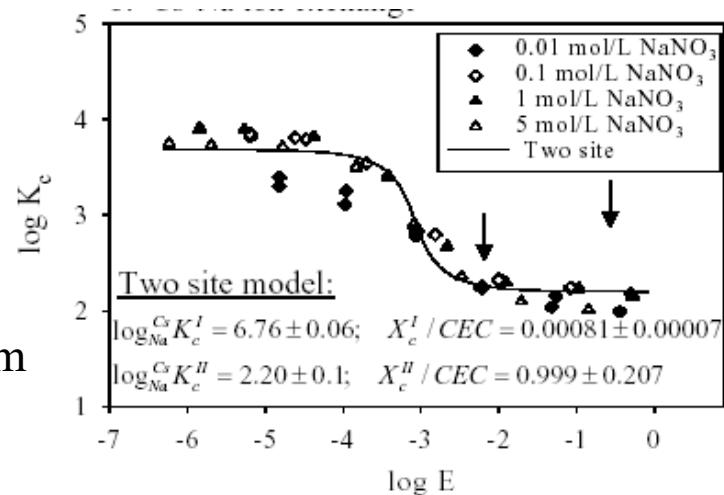


Expansible Clays



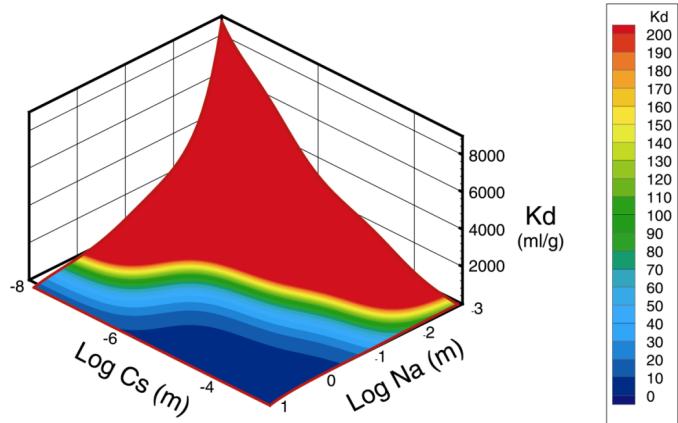
Failure of K_d models spawned a major Science and Technology Program at Hanford funded by the U.S. DOE

Binary exchange data from
Zachara et al. (2002)



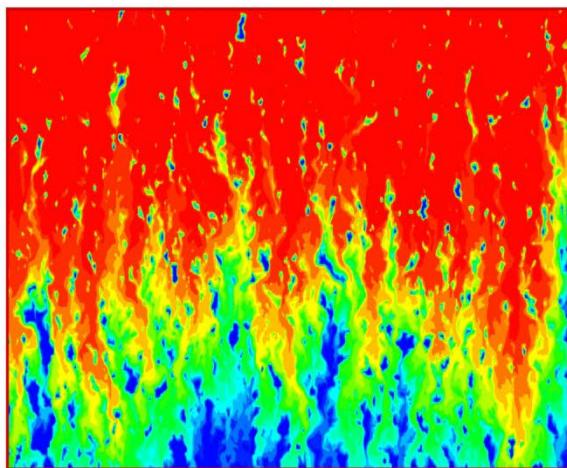
Cs Mobility in High Ionic Strength Solutions

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



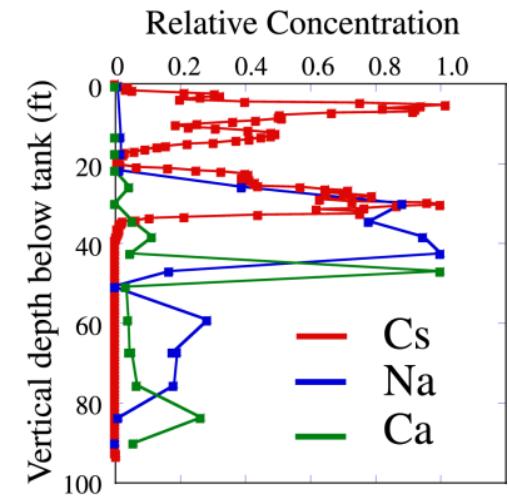
Cesium K_d in Hanford Sediments

Relative Distance



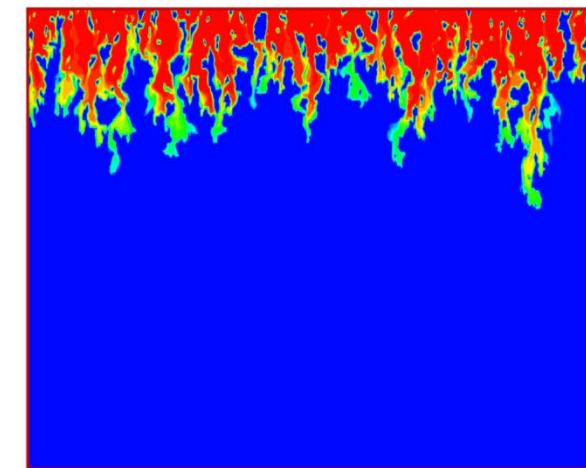
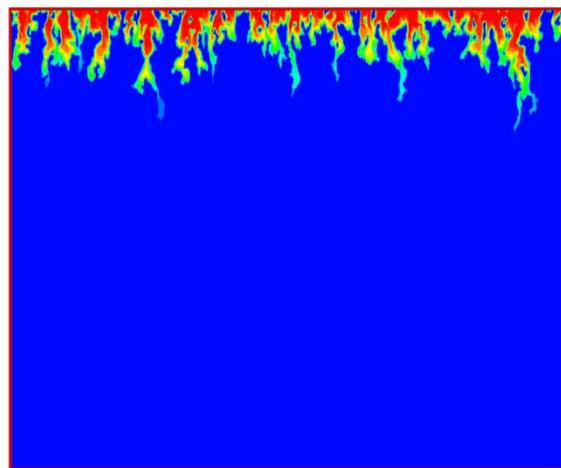
Nitrate

Steefel et al., 2003;
2005



Cesium
(1M NaNO_3)

Cesium
(5M NaNO_3)



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)

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
```

BOUNDARY_CONDITIONS

```
x_begin nano3flush      flux
x_end   initial_condition flux
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

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

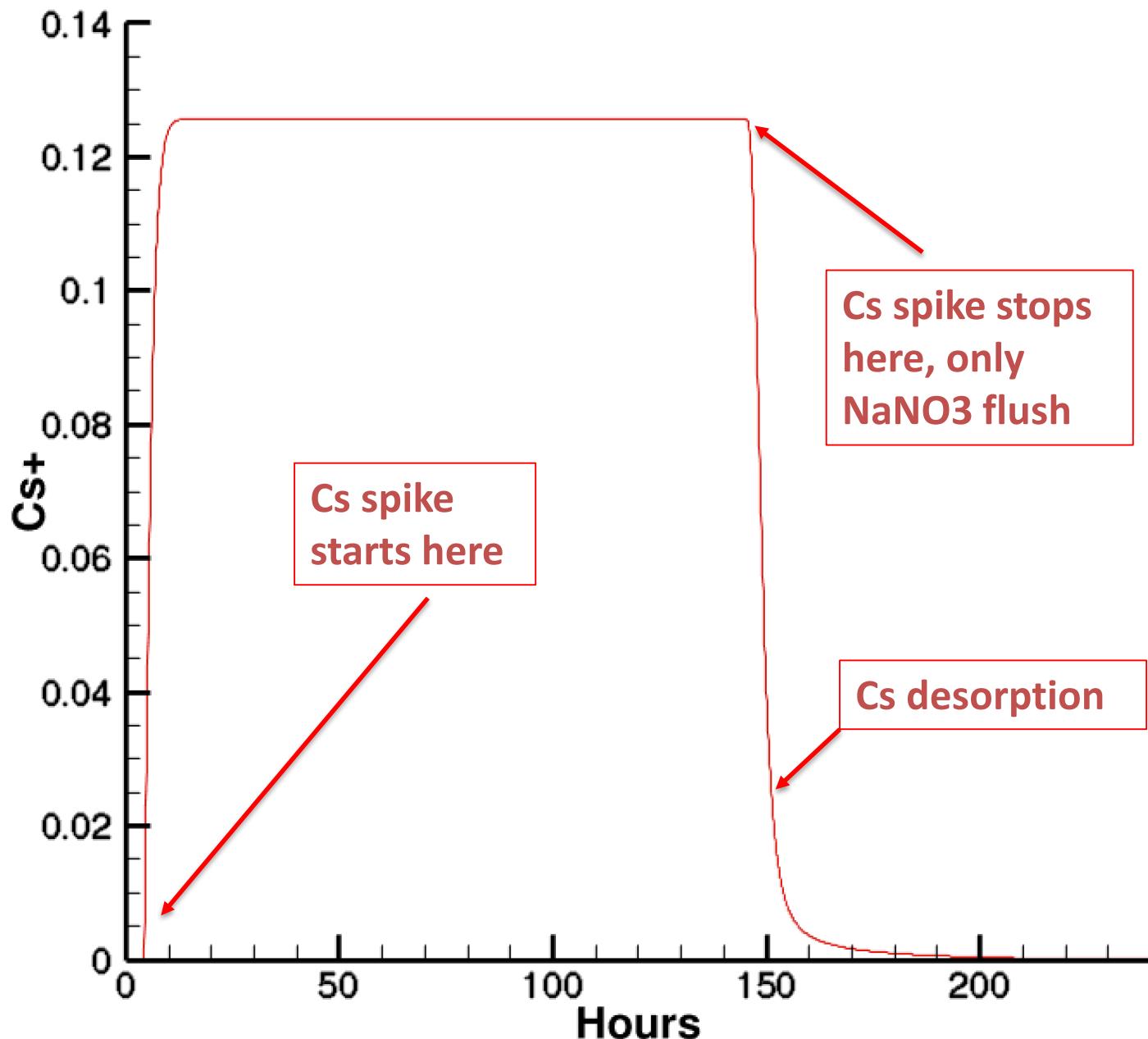
```
x_begin cesiumflush      flux
x_end   initial_condition flux
END
```

BOUNDARY_CONDITIONS

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

Exercise 6a: Cesium Ion Exchange

Column effluent breakthrough curve



Exercise 6b: Surface Complexation

Protonation-deprotonation reactions controlling surface charge

Electrostatic Effects

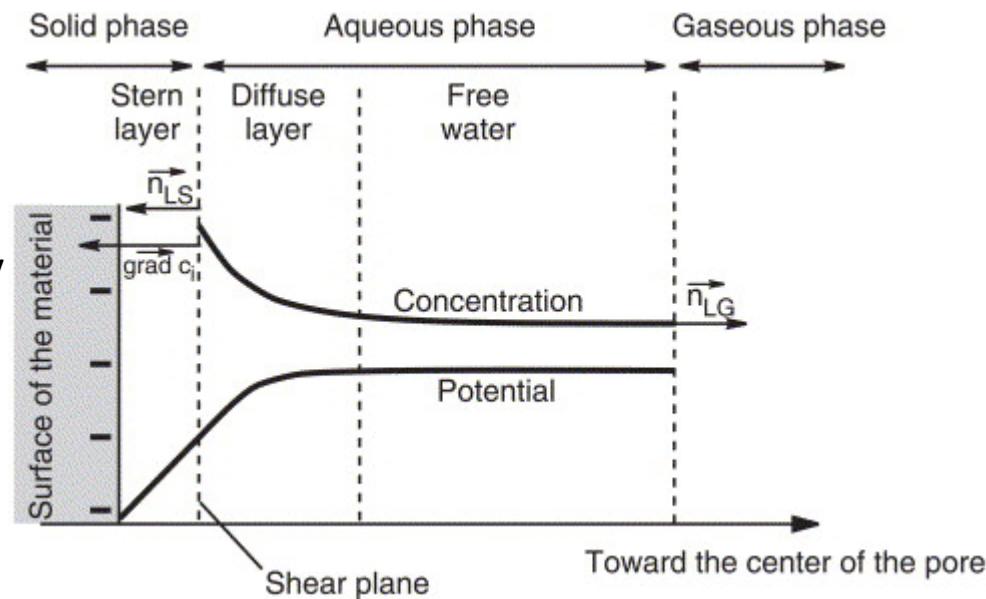
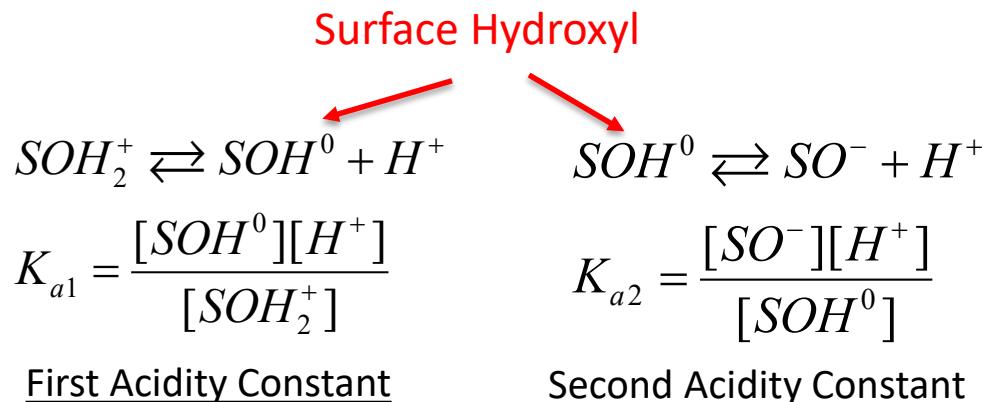
$$W = (+)_{\text{surface sites}} - (-)_{\text{surface sites}}$$

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

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

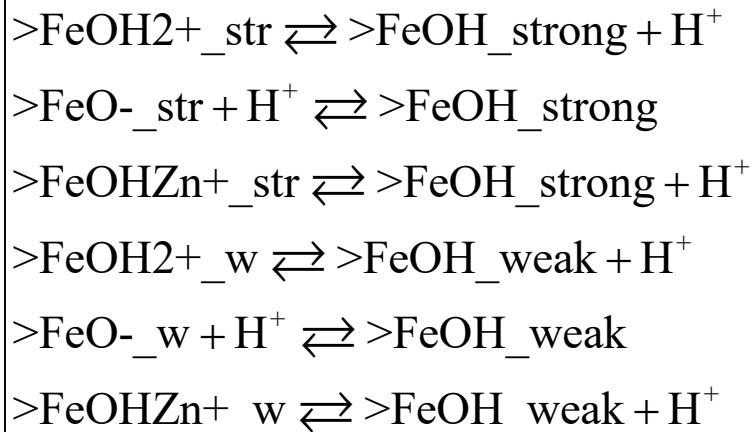
$$\Delta G_{ads} = \Delta G_{chem} + \Delta G_{coul}$$

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



Exercise 6b: Surface Complexation

Surface Complexation of Zn⁺² on Fe(OH)₃



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

!!!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

Partitions total concentration between surface and aqueous

Site densities for weak and strong sites

!! Note: Gives 0.09 g/kgw water Fe(OH)3, 54 m**2 surface

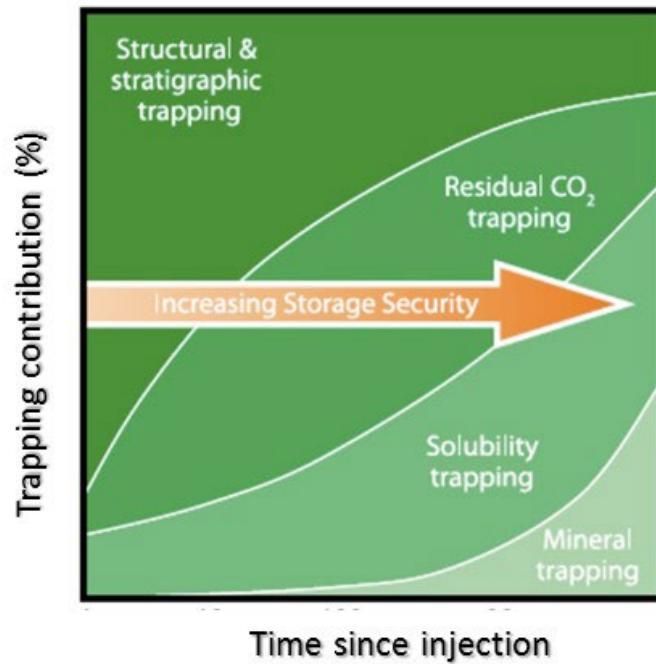
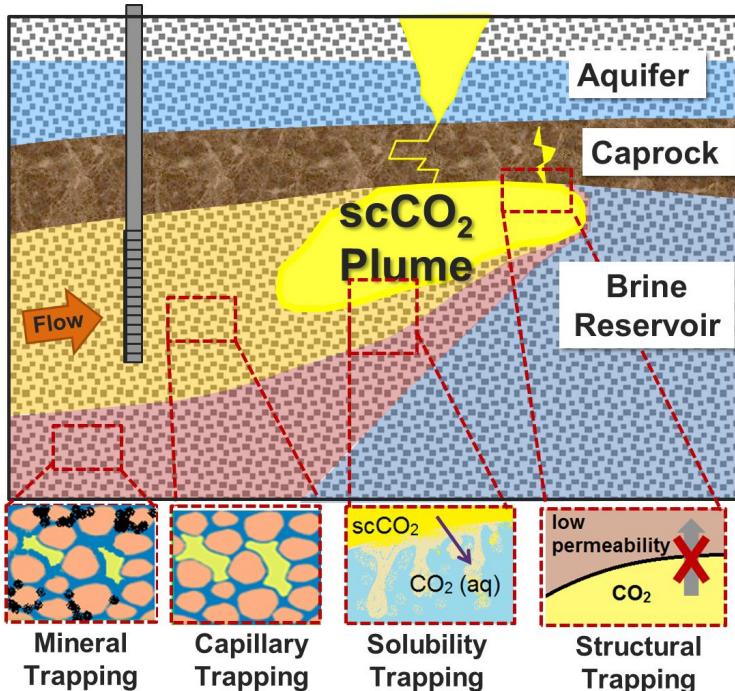
!! Based on a density of 1017 kg/m**3, 1.017 g/cm**3

!! 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

CO₂ ATTACK ON CEMENT

Exercise 7: CO₂ Attack on Cement



Dirichlet
Boundary:
Supercritical
CO₂ at 100 bars

Diffusion-Reaction System



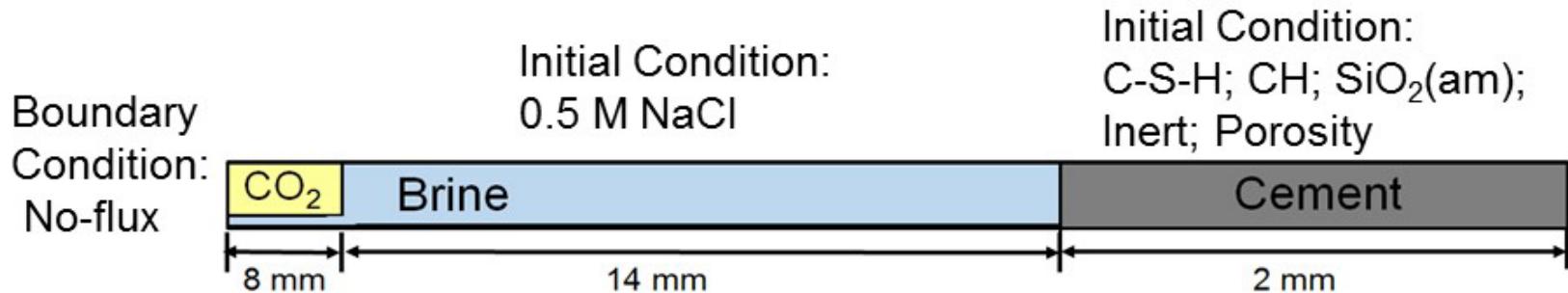
Mineralogy:

1. Portlandite

2. Calcium-silica hydrate (CSH)

3. Calcite precipitates

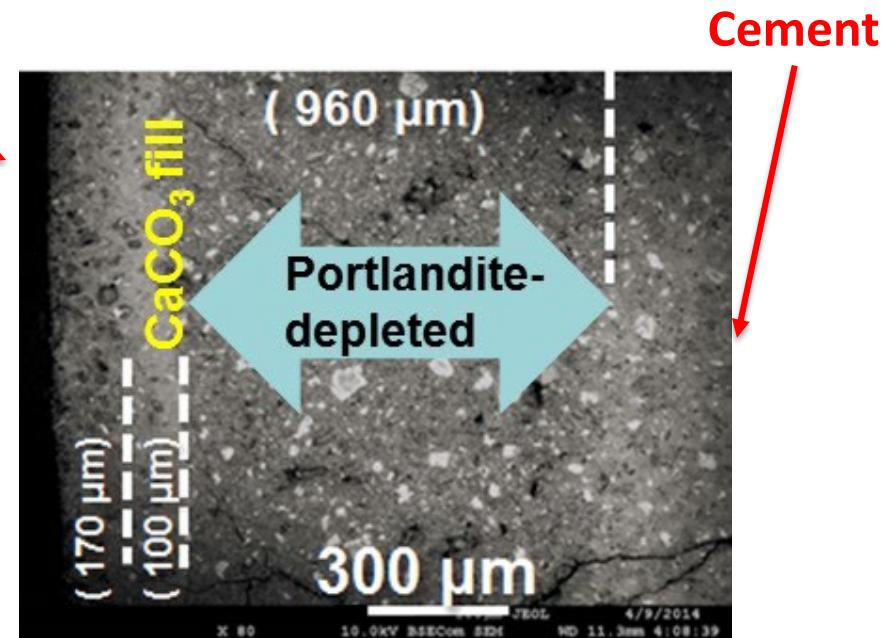
Exercise 7: CO₂ Attack on Cement



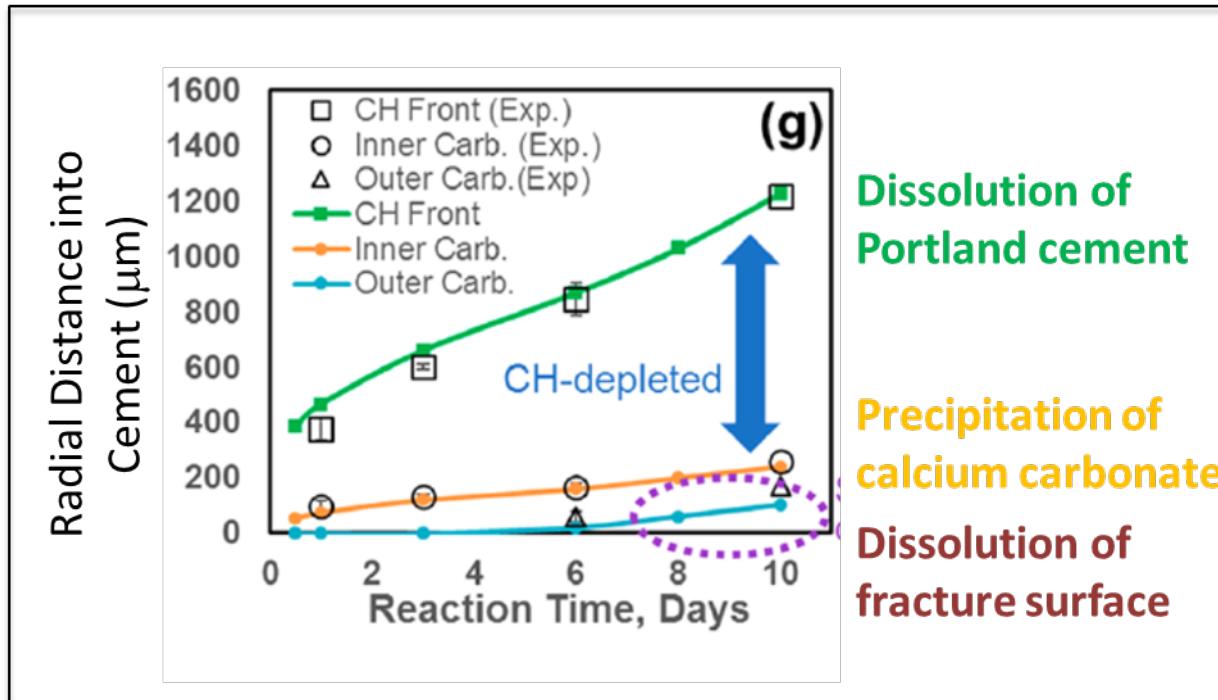
Super-critical CO₂

Based on:

Li, Q., C.I. Steefel, Y-S Jun (2017) Deciphering calcium carbonate precipitation associated with CO₂ attack on cement using reactive transport modeling. *Environmental Science and Technology* 51: 10861-10871, doi: 10.1021/acs.est.7b00594.



Exercise 7: CO₂ Attack on Cement



Li, Q., C.I. Steefel, Y-S Jun (2017) Deciphering calcium carbonate precipitation associated with CO₂ attack on cement using reactive transport modeling. *Environmental Science and Technology* **51**: 10861-10871, doi: 10.1021/acs.est.7b00594.

Exercise 7: CO₂ 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

Pre-exponential J_0

Constant terms

Interfacial free energy

Specific surface area of nucleated phase

Template for 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
```

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

Exercise 7: CO₂ 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 320 100 200 100

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: CO₂ Attack on Cement

Reactive Surface Area Options

Condition Cement

temperature	95.0
pH	Portlandite
CO ₂ (aq)	1.E-10
Ca++	0.001
Na+	charge
Cl-	0.500
SiO ₂ (aq)	0.0000001
Calcite	0.00001
CSH(1.6)	0.35
SiO ₂ (am)	0.10
Portlandite	0.20
Bogusite	0.20
Teflon	0.0
set_porosity	0.15
END	

Specific Surface
Area (m²/g)

ssa 1
ssa 1
ssa 1
ssa 0.01

Bulk Surface
Area (m²/m³)

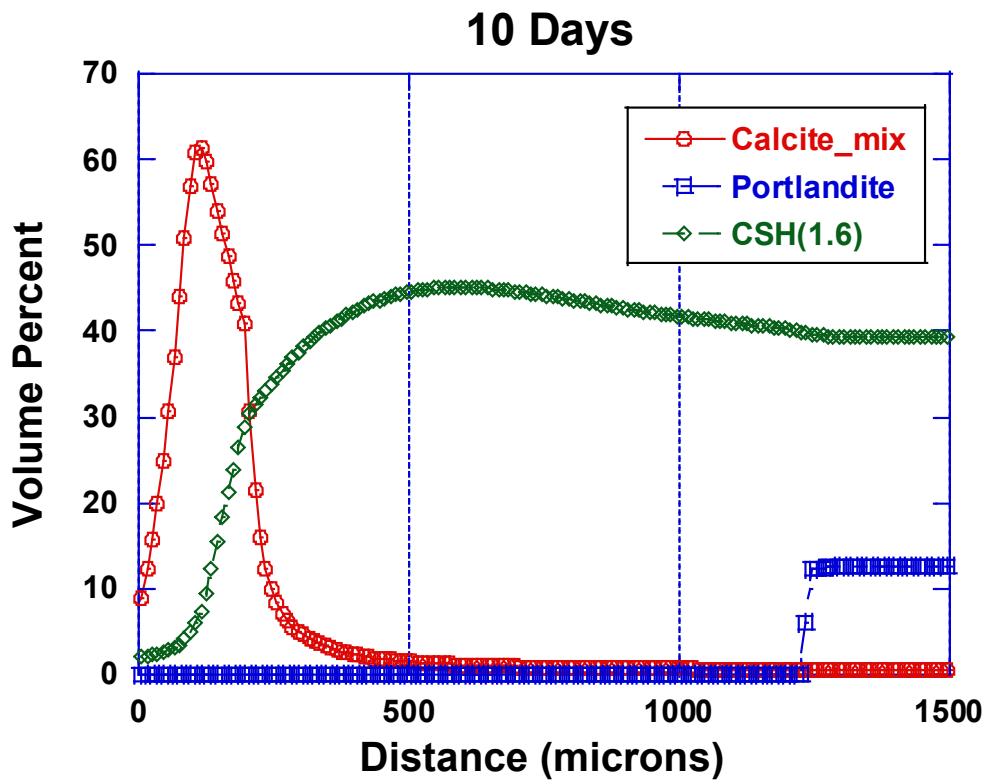
1.0
1.0

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

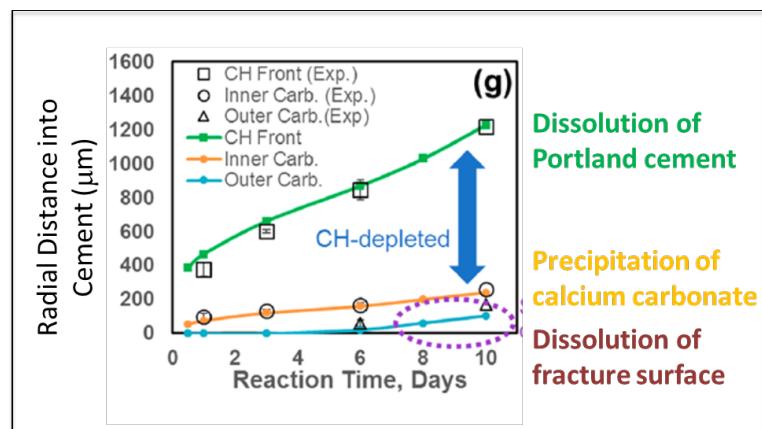
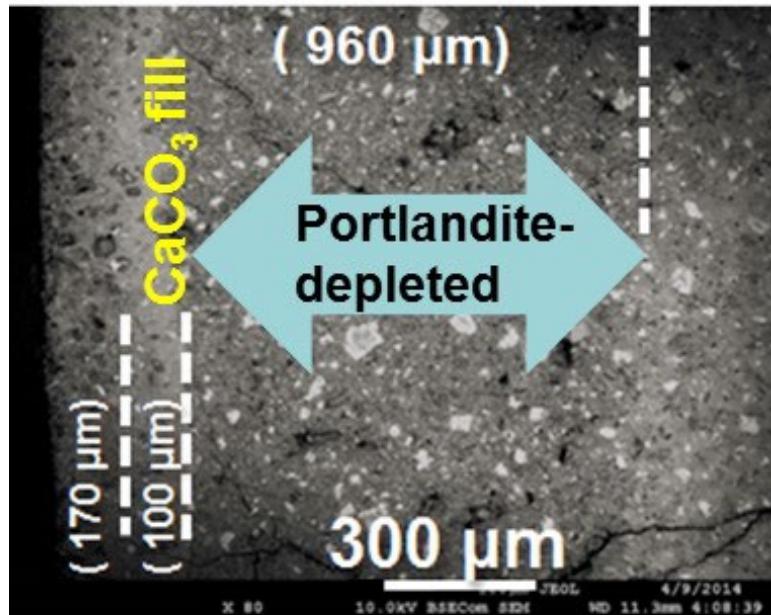
1st four grid cells are
unsaturated (10%)

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

Exercise 7: CO₂ Attack on Cement

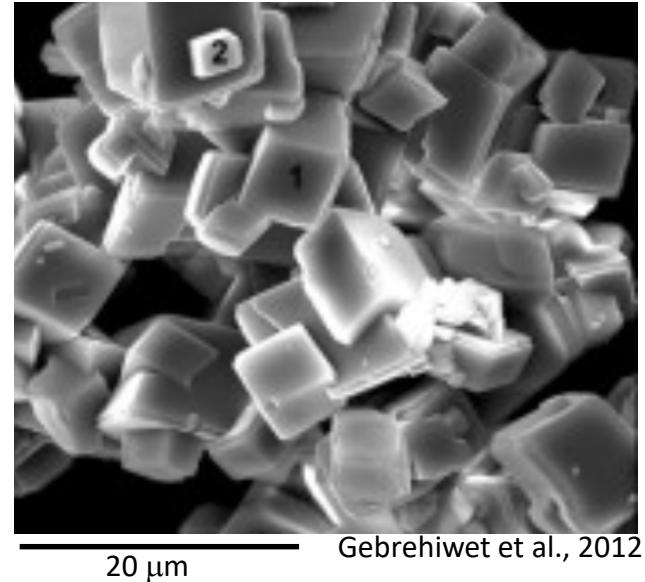
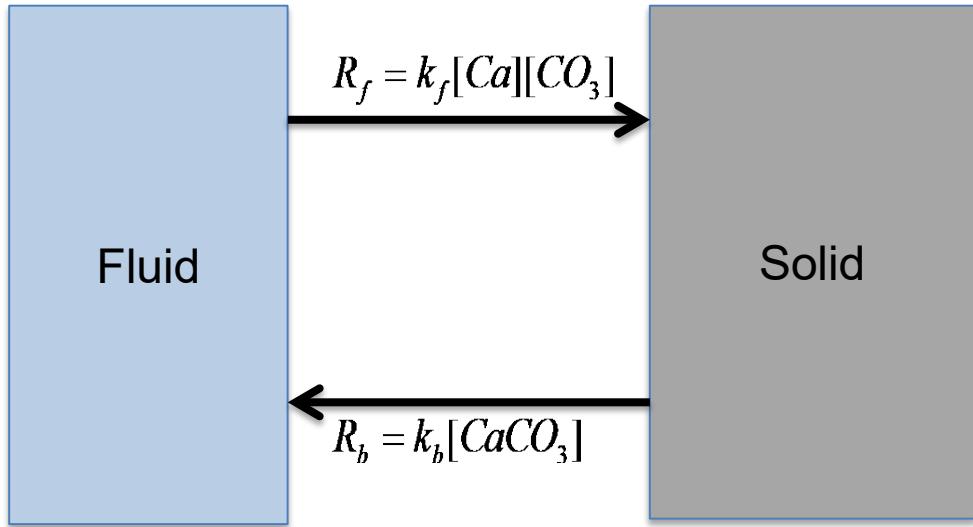


Li et al, ES&T, 2017



ISOTOPIC FRACTIONATION

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



$$R_{net} = R_f - R_b = k_f[\text{Ca}][\text{CO}_3] - k_f[\text{CaCO}_{3(s)}]$$

$$R_{net} = [\text{CaCO}_{3(s)}]k \left[\frac{[\text{Ca}^{2+}][\text{CO}_3^{2-}]}{[\text{CaCO}_{3(s)}]} \frac{1}{K_{eq}} - 1 \right]$$

At equilibrium, $R_{net} = 0$

$$R_f = R_b$$

$$k_f[\text{Ca}^{2+}][\text{CO}_3^{2-}] = k_b[\text{CaCO}_{3(s)}]$$

$$\frac{k_b}{k_f} = \frac{[\text{Ca}^{2+}][\text{CO}_3^{2-}]}{[\text{CaCO}_{3(s)}]} = K_{eq}$$

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

Isotope activities based on mole fractions

$${}^{44}X = \frac{[{}^{44}\text{CaCO}_3]}{[\text{CaCO}_3]}$$

$$R_{net} = [\text{CaCO}_{3(s)}] k \left[\frac{[\text{Ca}^{2+}][\text{CO}_3^{2-}]}{[\text{CaCO}_{3(s)}]} \frac{1}{K_{eq}} - 1 \right]$$

\downarrow

$$[{}^{40}\text{CaCO}_3] + [{}^{44}\text{CaCO}_3] = [\text{CaCO}_3]$$

$${}^{40}R_N = {}^{40}k_b {}^{40}X \left(\frac{[{}^{40}\text{Ca}][\text{CO}_3]}{K_{sp} {}^{40}X} - 1 \right)$$

$${}^{44}R_N = {}^{44}k_b {}^{44}X \left(\frac{[{}^{44}\text{Ca}][\text{CO}_3]}{K_{sp} {}^{44}X} - 1 \right)$$

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

```
INITIAL_CONDITIONS  
amendment 1-1 1-1 1-1  
END
```

```
DISCRETIZATION  
distance_units centimeters  
xzones 1 1.0  
END
```

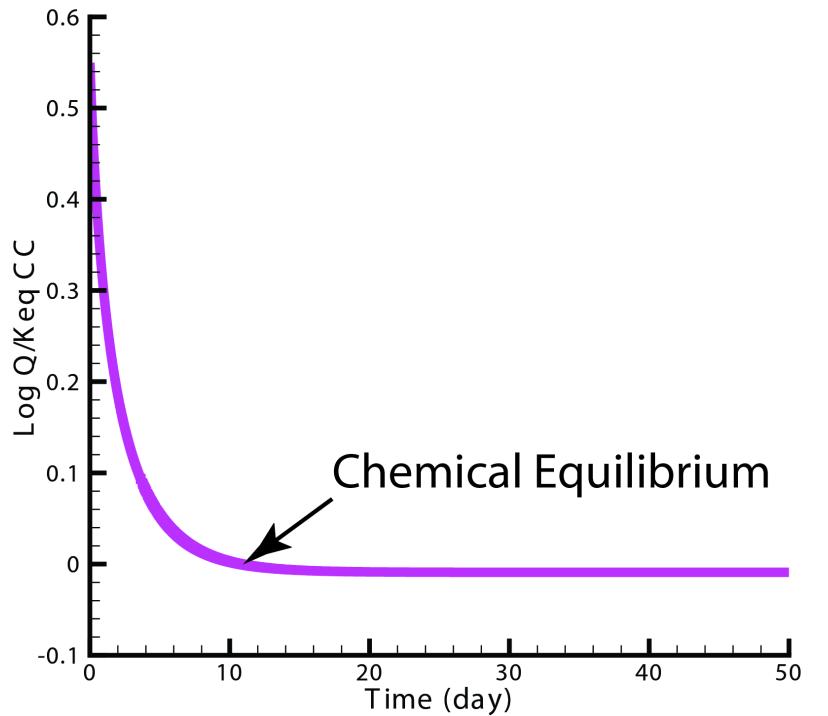
```
condition amendment  
units mmol/kg  
temperature 25.0  
H+ 0.11544  
Ca++ 5.28  
Ca44++ 0.111997921  
HCO3- 10.0  
!! Mineral name <volume fraction m3/m3>  
CalciteRifle 0.7833831 bsa 1.33E-02  
Calcite44Rifle 0.0166170 bsa 1.33E-02  
END
```

```
MINERALS  
CalciteRifle -label default -rate -4.10000000  
!!! 2 per mil kinetic fractionation Kinetic fractionation  
Calcite44Rifle -label default -rate -4.10217692  
END  
  
ISOTOPES  
primary Ca44++ Ca++ 0.021667  
mineral Calcite44Rifle CalciteRifle bulk  
isotope_time_series BatchExperiment.out 1 1  
1  
END
```

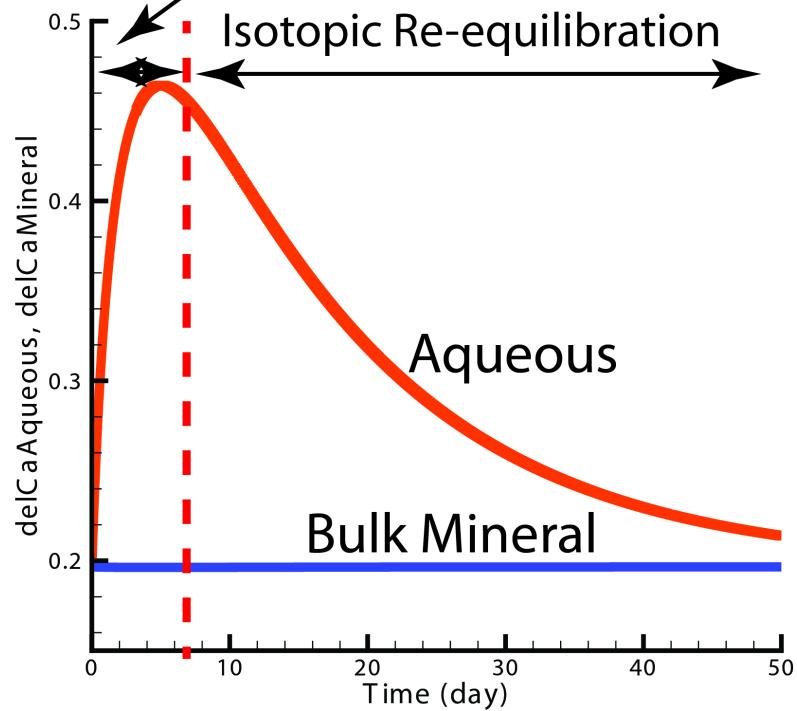
- Isotopic back-reaction with**
- Bulk
 - Surface
 - None

Output isotope time series to file at grid cell

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

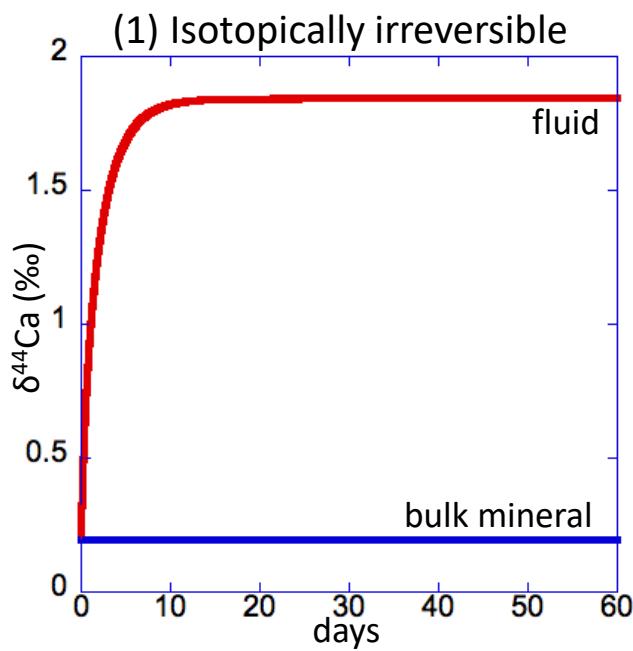


Kinetic Fractionation
due to Precipitation

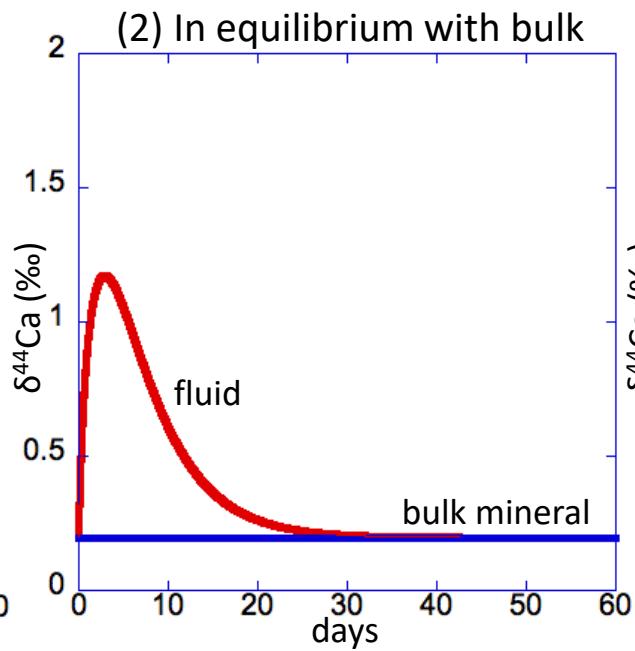


Exercise 8: Calcite precipitation with $\delta^{44}\text{Ca}$

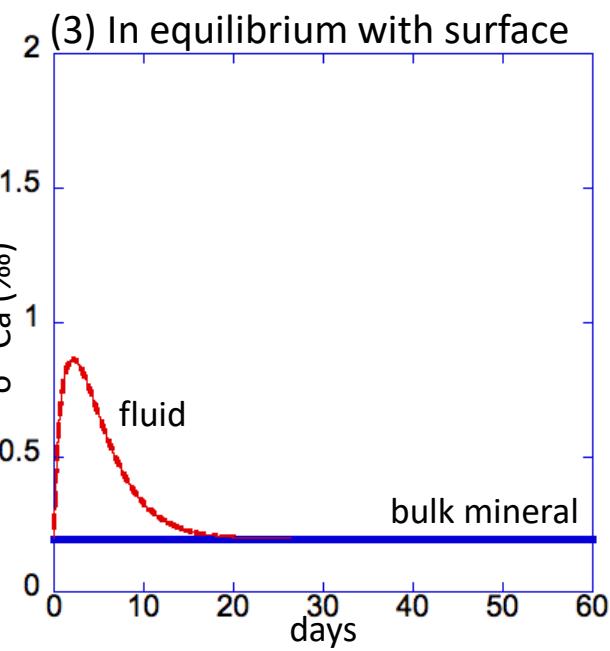
“None”



“Bulk”



“Surface”



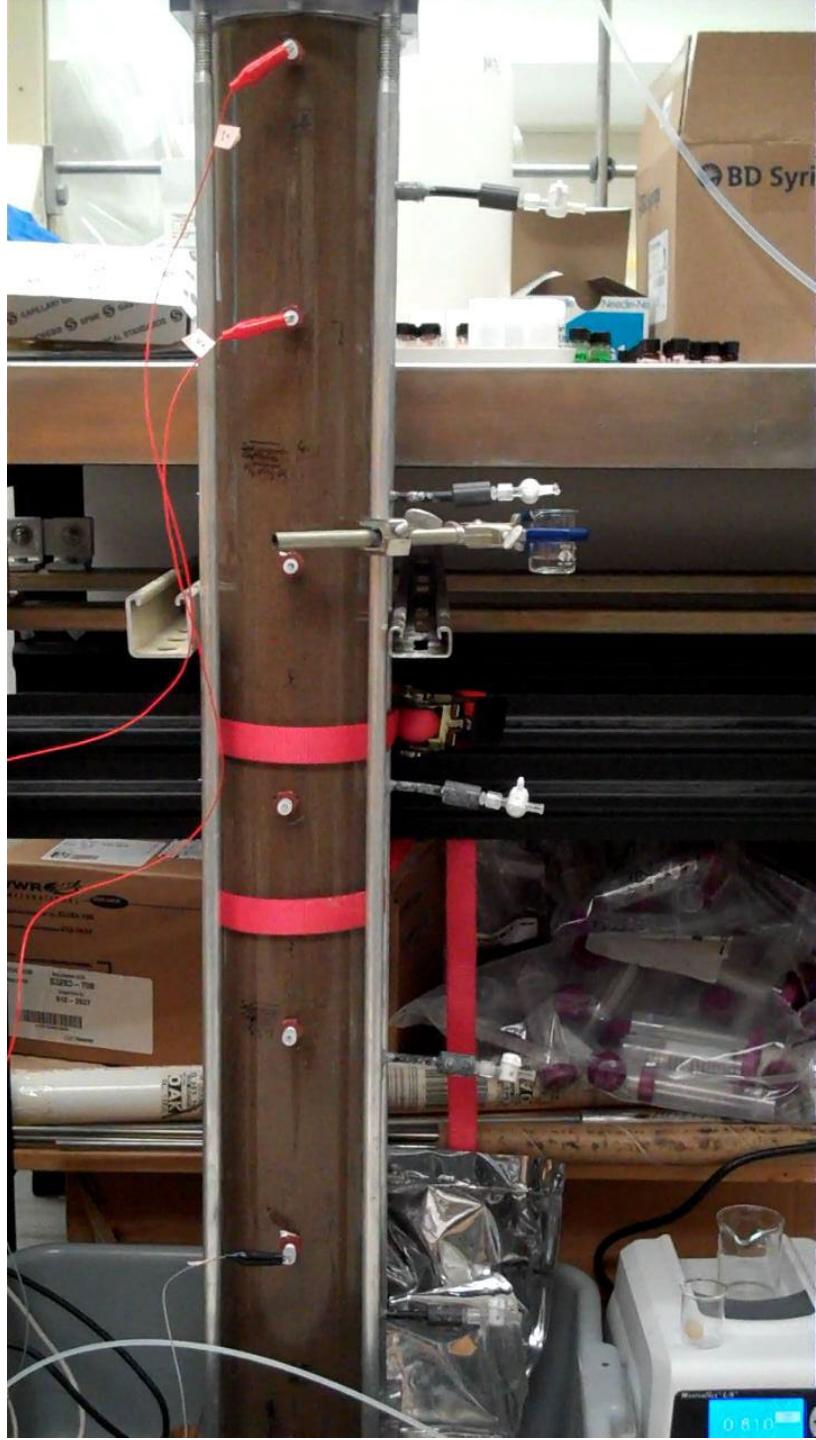
Exercise 9: Microbial Redox

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



Exercise 9: Microbial Redox



$\text{CH}_3\text{COO}^-_{(\text{aq})}$
+ Rifle groundwater:

Uranium 0.7 – 1.5 μM

pH 7.0 – 7.2

Alkalinity 7 – 10 meq/L

Eh -150 to 240 mV

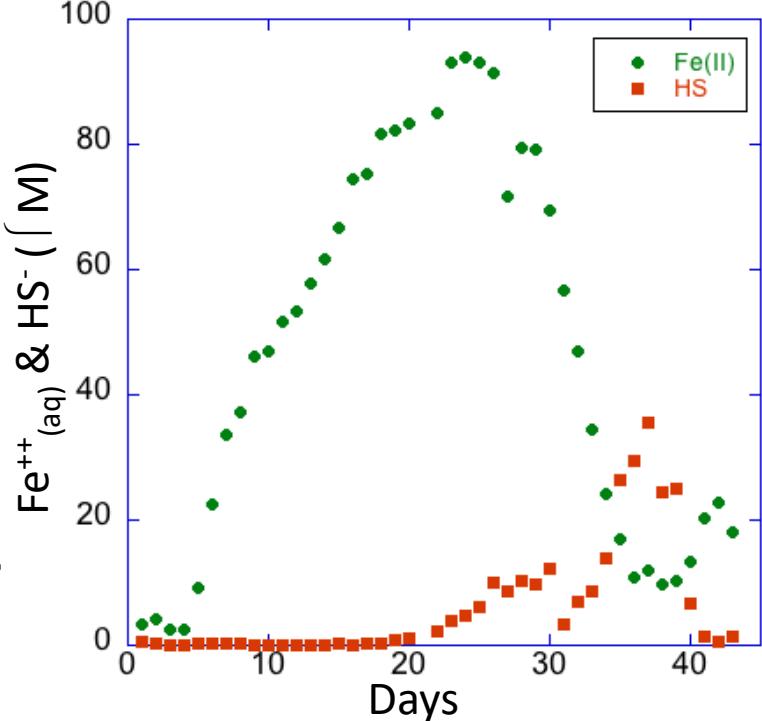
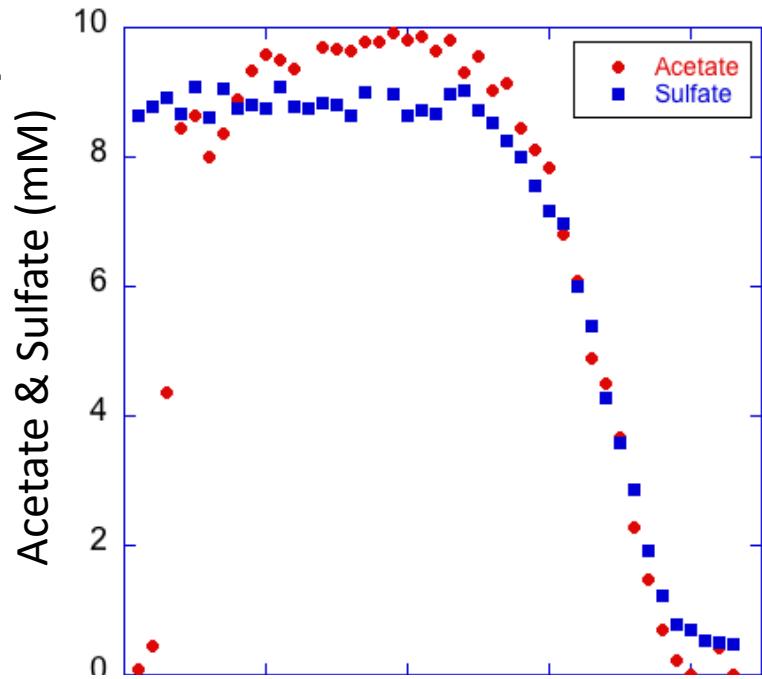
DO 3 – 20 μM

Fe(II) 15 – 50 μM

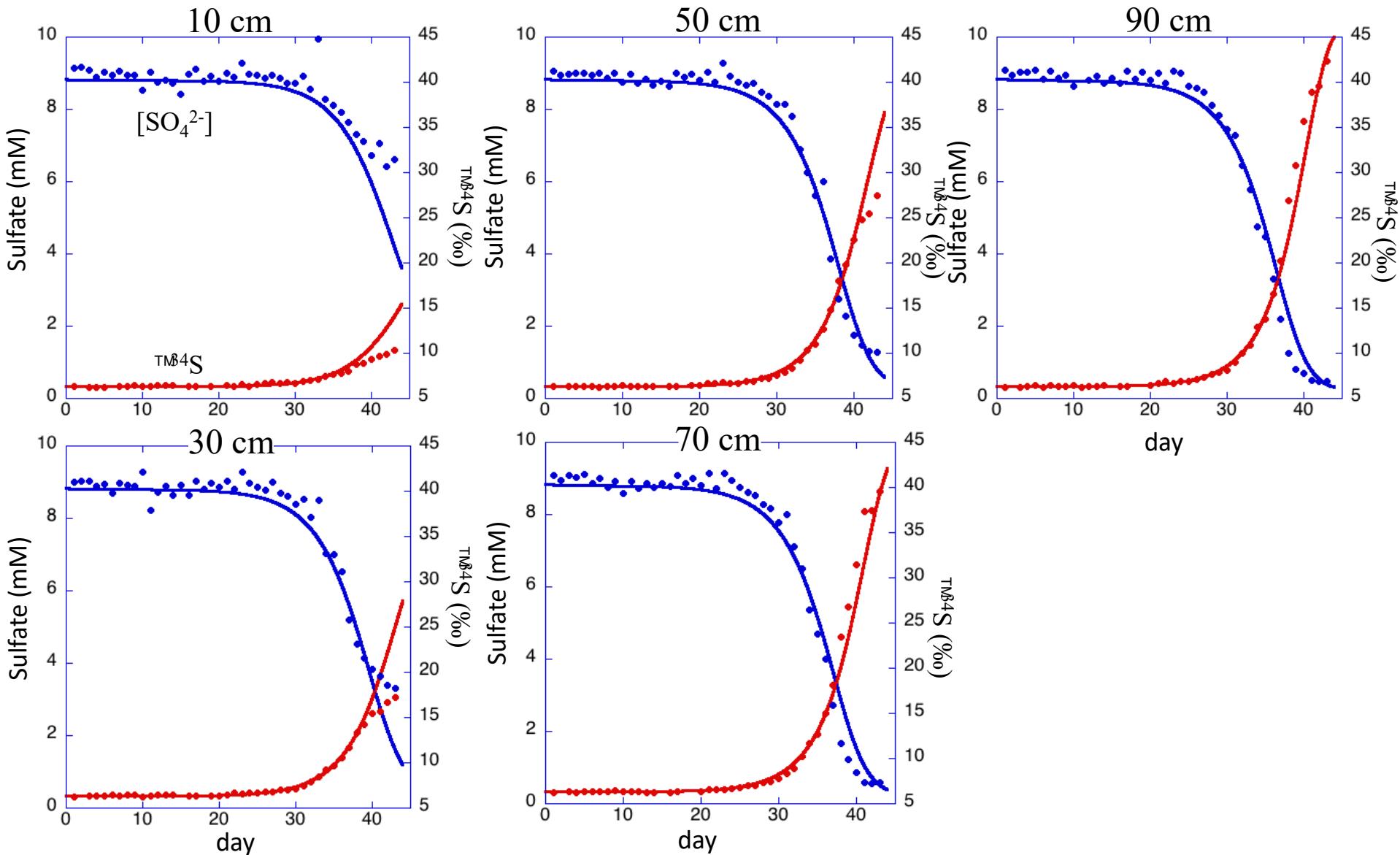
Nitrate 2 – 3 μM

Sulfate 8 – 11 mM

Sulfide 0.03 – 0.5 μM



Exercise 9: Microbial Redox



POROSITY-PERMEABILITY CHANGE

Exercise 10: Porosity-Permeability

Mineral	Reaction	$\log K_{25}$
Calcite	$\text{Ca}^{2+} + \text{CO}_3^{2-} \leftrightarrow \text{CaCO}_3$	8.4750
Gypsum	$\text{Ca}^{2+} + \text{SO}_4^{2-} + 2\text{H}_2\text{O} \leftrightarrow \text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	4.5800
Ferrihydrite	$\text{Fe}^{3+} + 3\text{H}_2\text{O} \leftrightarrow \text{Fe(OH)}_3 + 3\text{H}^+$	-4.8910
Jarosite	$\text{K}^+ + 3\text{Fe}^{3+} + 2\text{SO}_4^{2-} + 6\text{H}_2\text{O} \leftrightarrow \text{KFe}_3(\text{SO}_4)_2(\text{OH})_6 + 6\text{H}^+$	9.2100
Gibbsite	$\text{Al}^{3+} + 3\text{H}_2\text{O} \leftrightarrow \text{Al(OH)}_3 + 3\text{H}^+$	-8.1100
Siderite	$\text{Fe}^{2+} + \text{CO}_3^{2-} \leftrightarrow \text{FeCO}_3$	10.4500

Primary components	Unit	Initial condition	Boundary condition
pH	—	9.38	3.0
Ca^{2+}	$\text{mol l}^{-1} \text{ H}_2\text{O}$	1.57×10^{-4}	1.00×10^{-4}
CO_3^{2-}	$\text{mol l}^{-1} \text{ H}_2\text{O}$	2.57×10^{-4}	1.0×10^{-2}
SO_4^{2-}	$\text{mol l}^{-1} \text{ H}_2\text{O}$	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

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
```

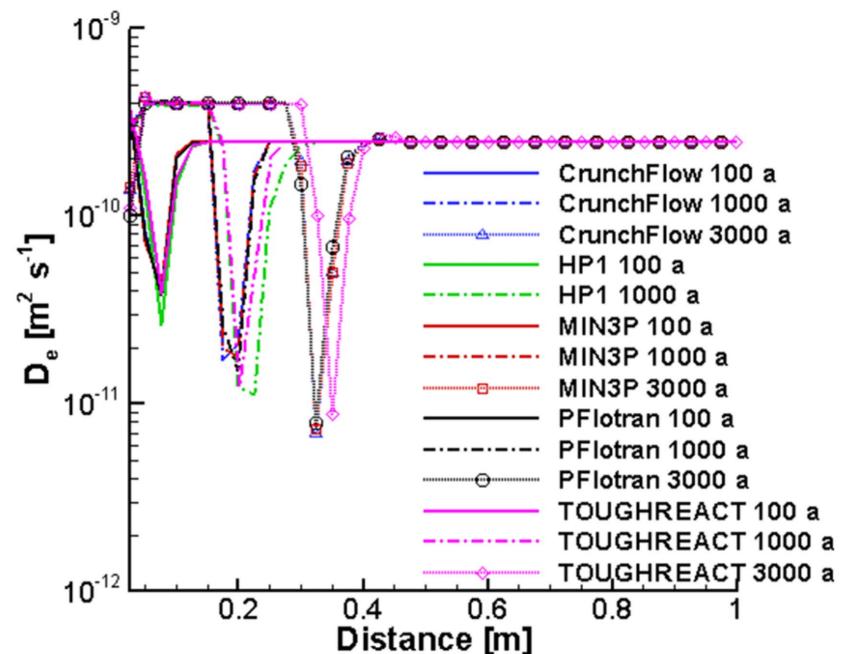
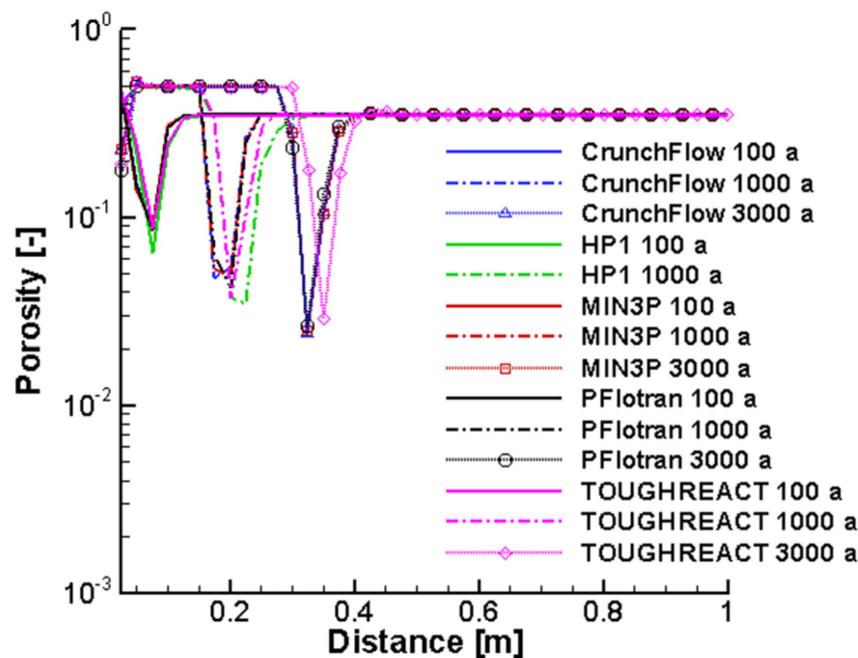
DISCRETIZATION

```
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

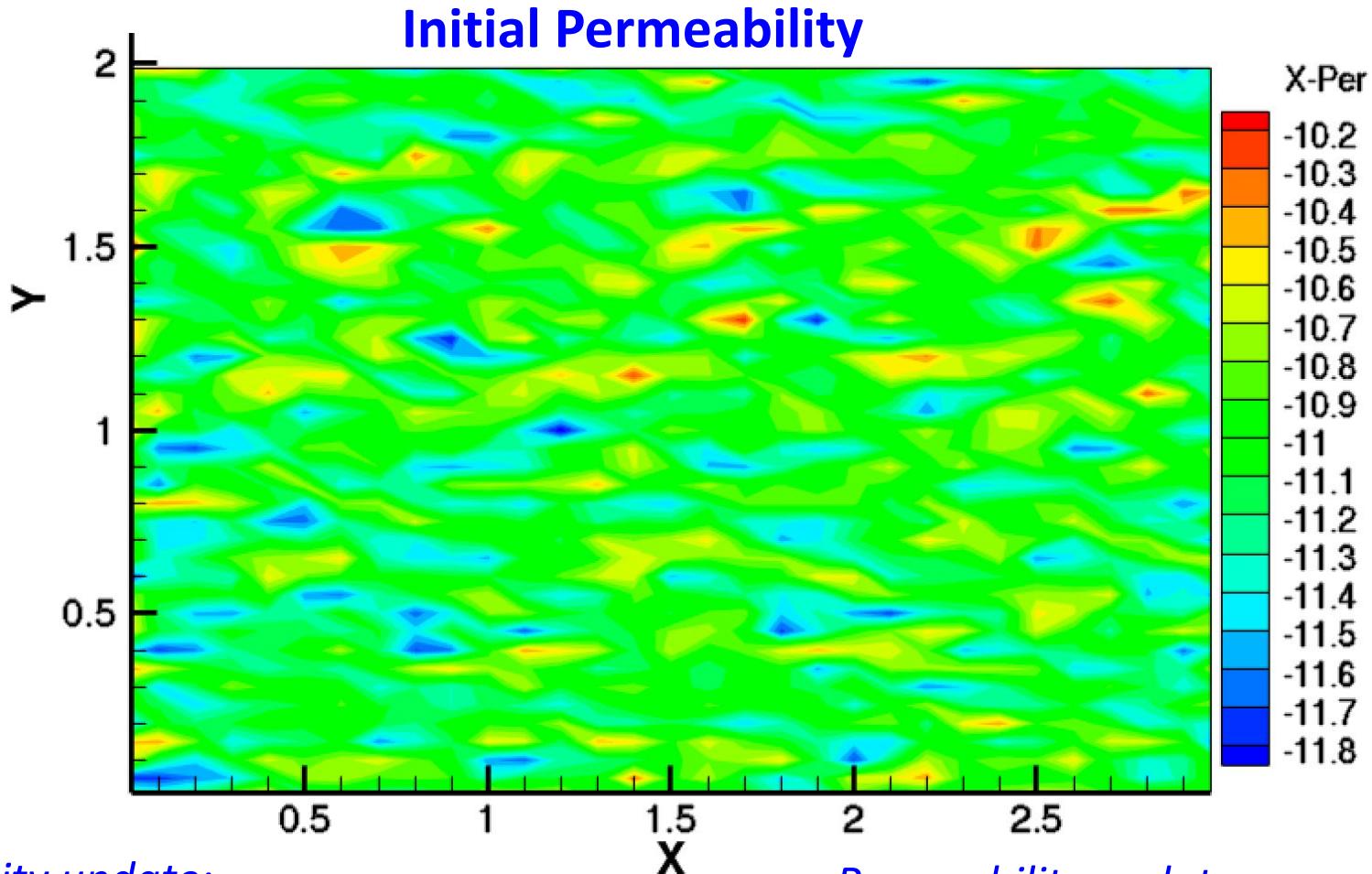
```
!! Standard linear TST calcite
Calcite        -label default    -rate -4.301029996
Gypsum         -label default    -rate -4.301029996
Ferrihydrite   -label default    -rate -5.301029996
Jarosite       -label default    -rate -5.301029996
Gibbsite       -label default    -rate -6.301029996
Siderite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



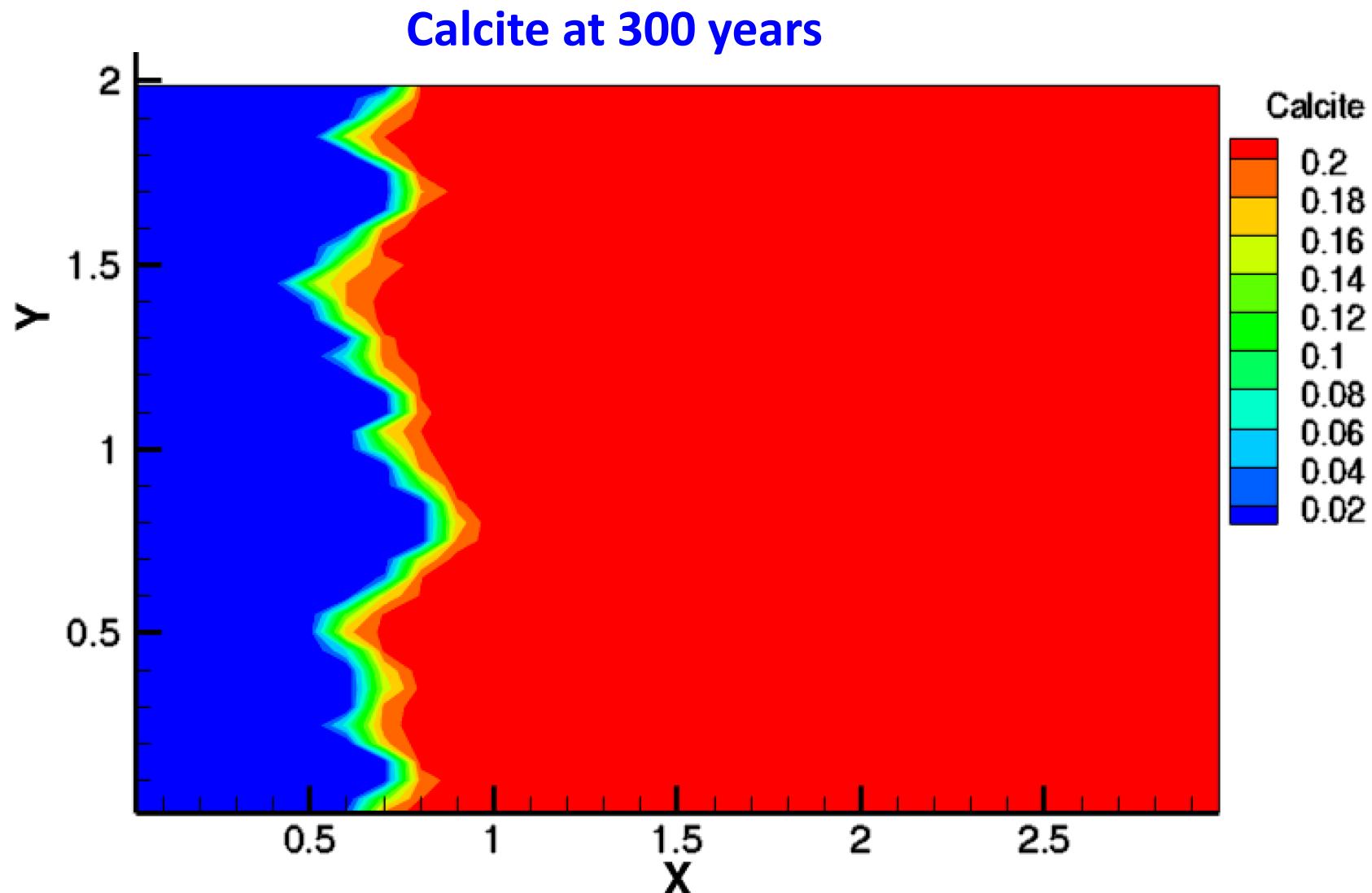
Porosity update:

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

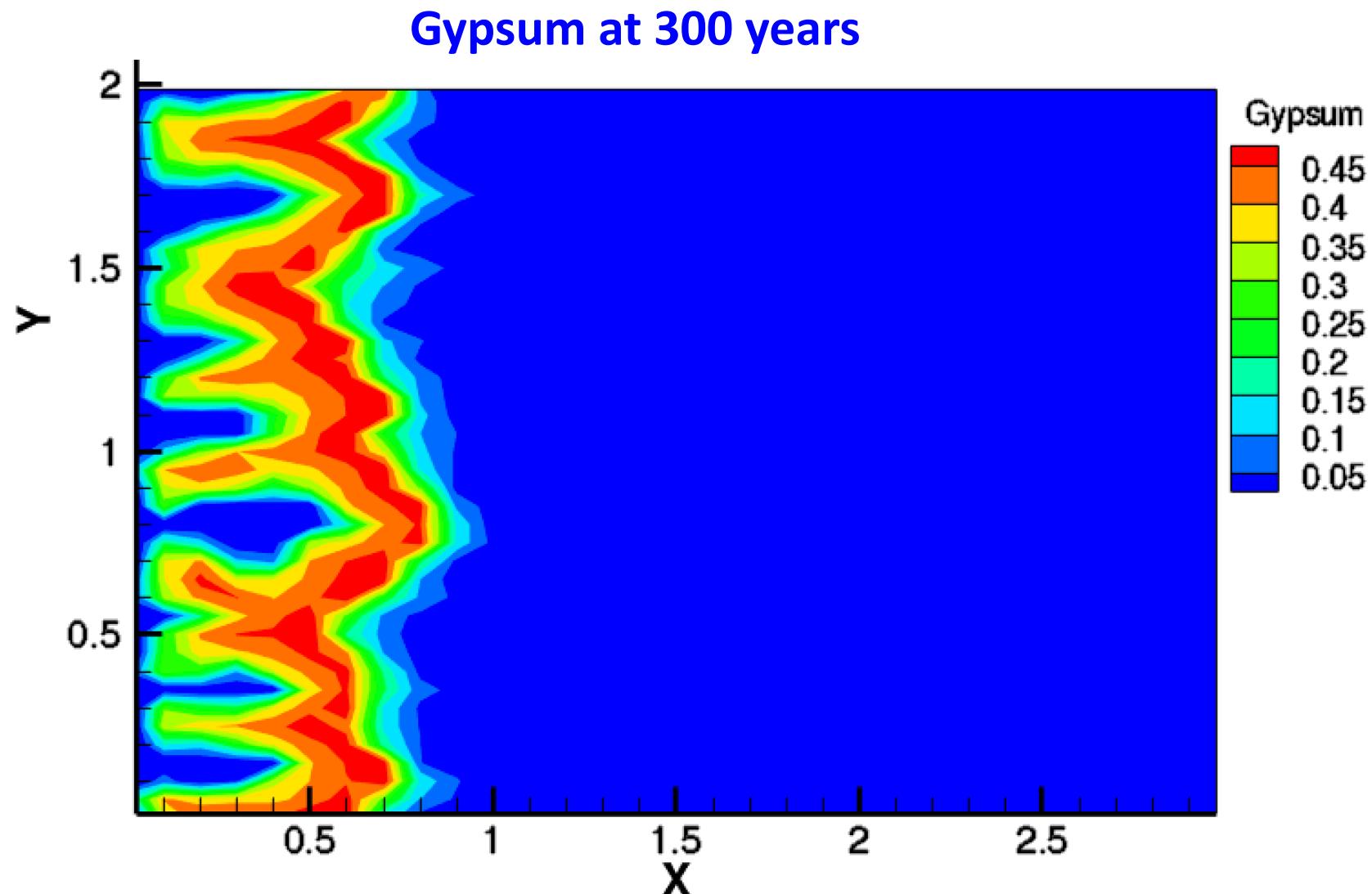
Permeability update:

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

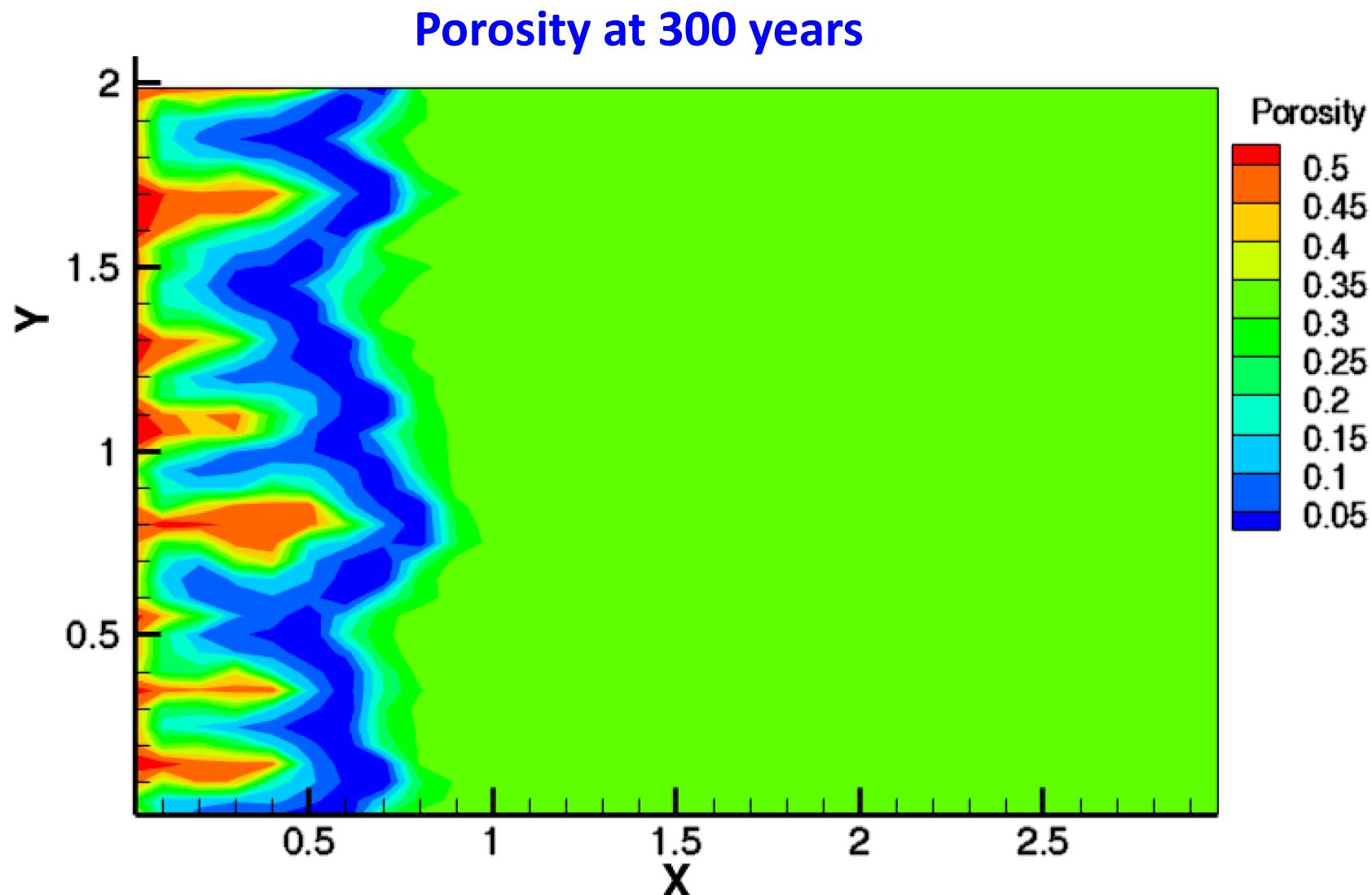
Exercise 10: 2D Porosity-Permeability



Exercise 10: 2D Porosity-Permeability



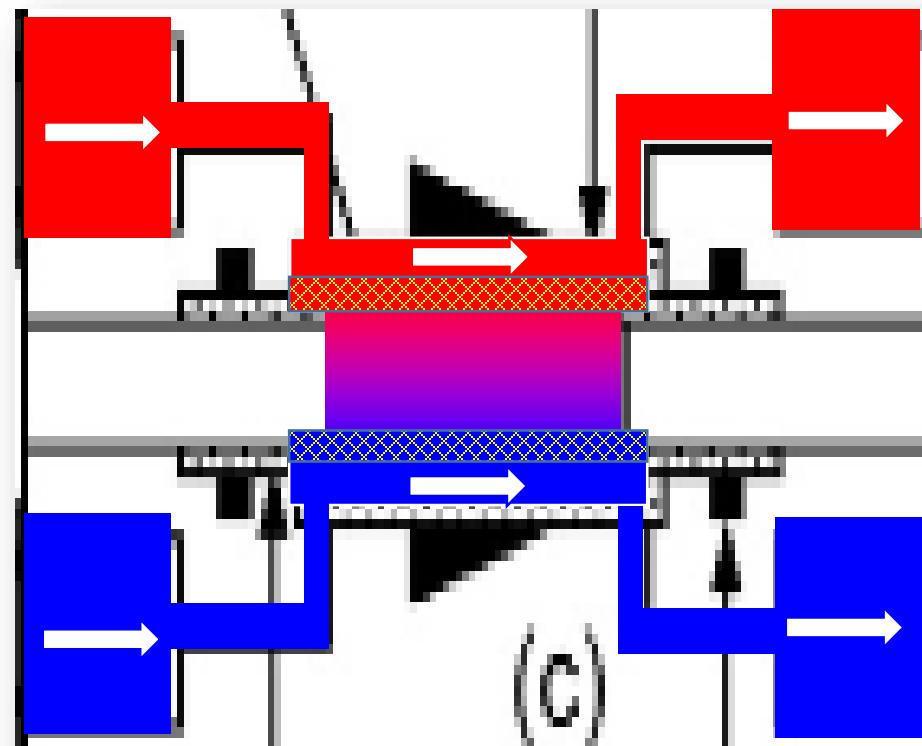
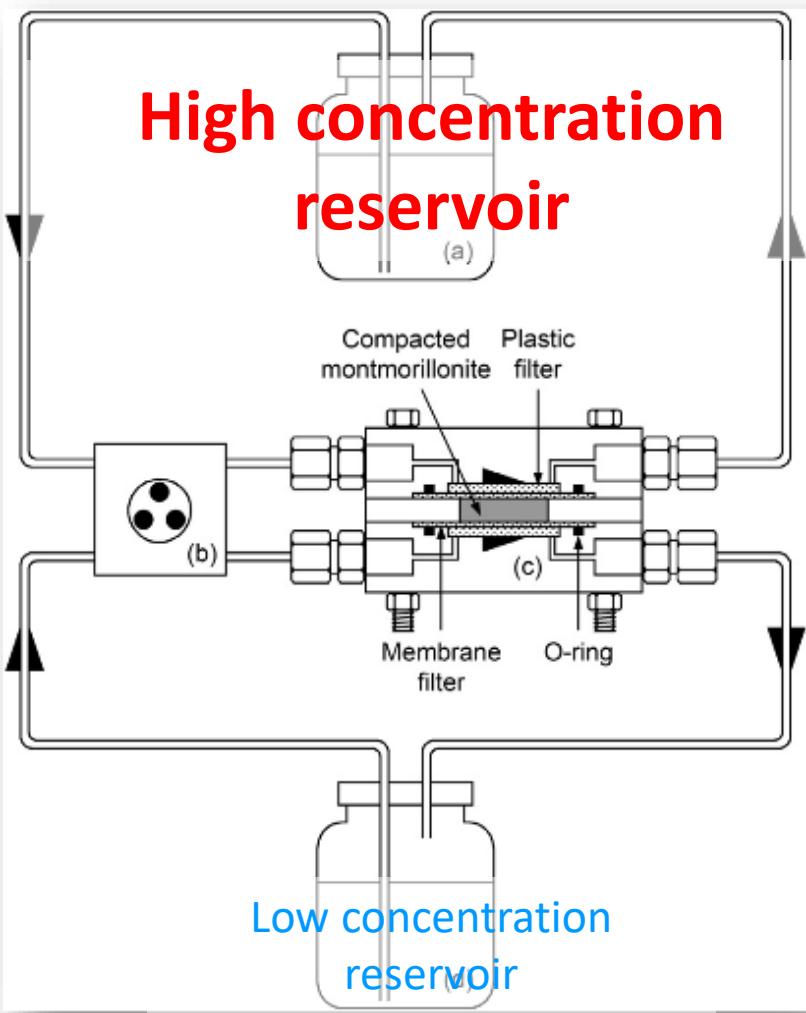
Exercise 10: 2D Porosity-Permeability



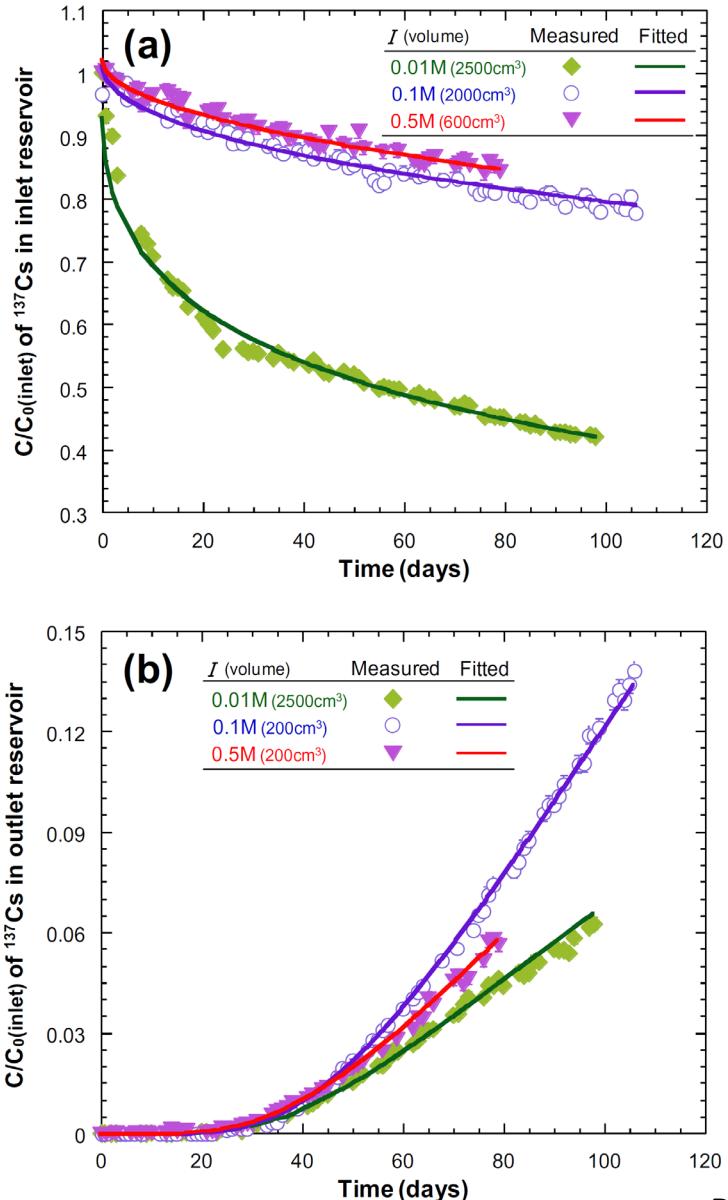
DIFFUSION IN CLAY

Exercise 11: Diffusion in Clay

Experimental setup



Example of results

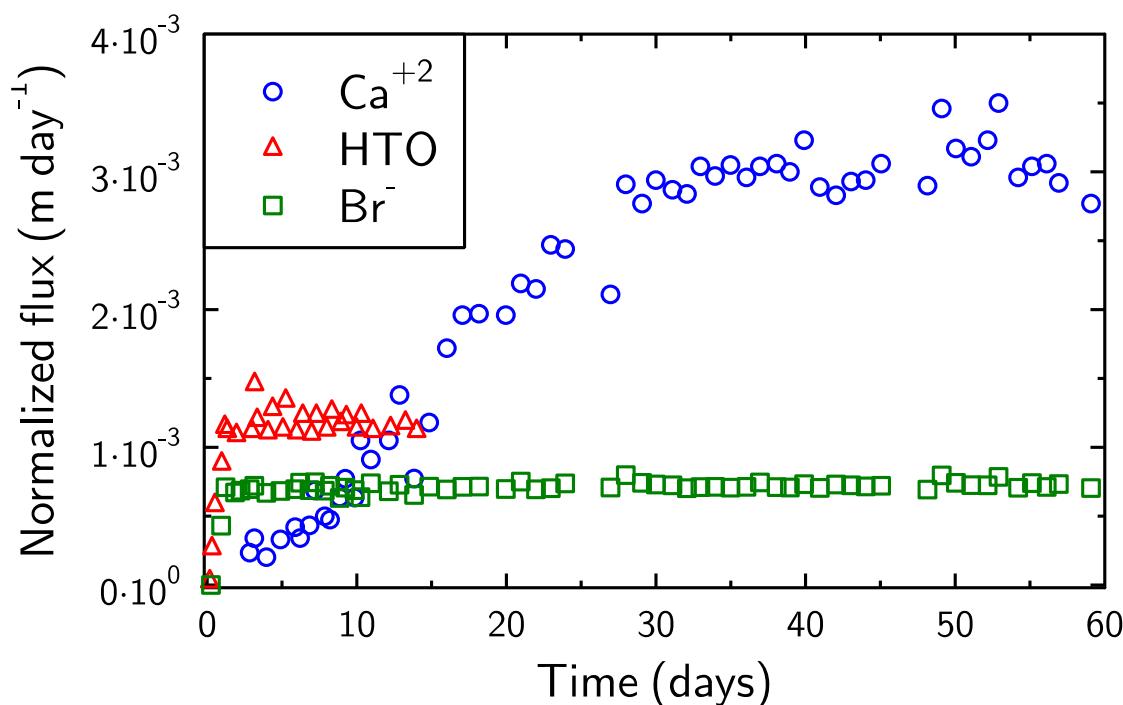


$$Flux_{outlet} = \frac{\partial C}{\partial t} \Big|_{outlet} \times \frac{V_{outlet}}{S_{outlet}}$$

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
```

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

INITIAL_CONDITIONS

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

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

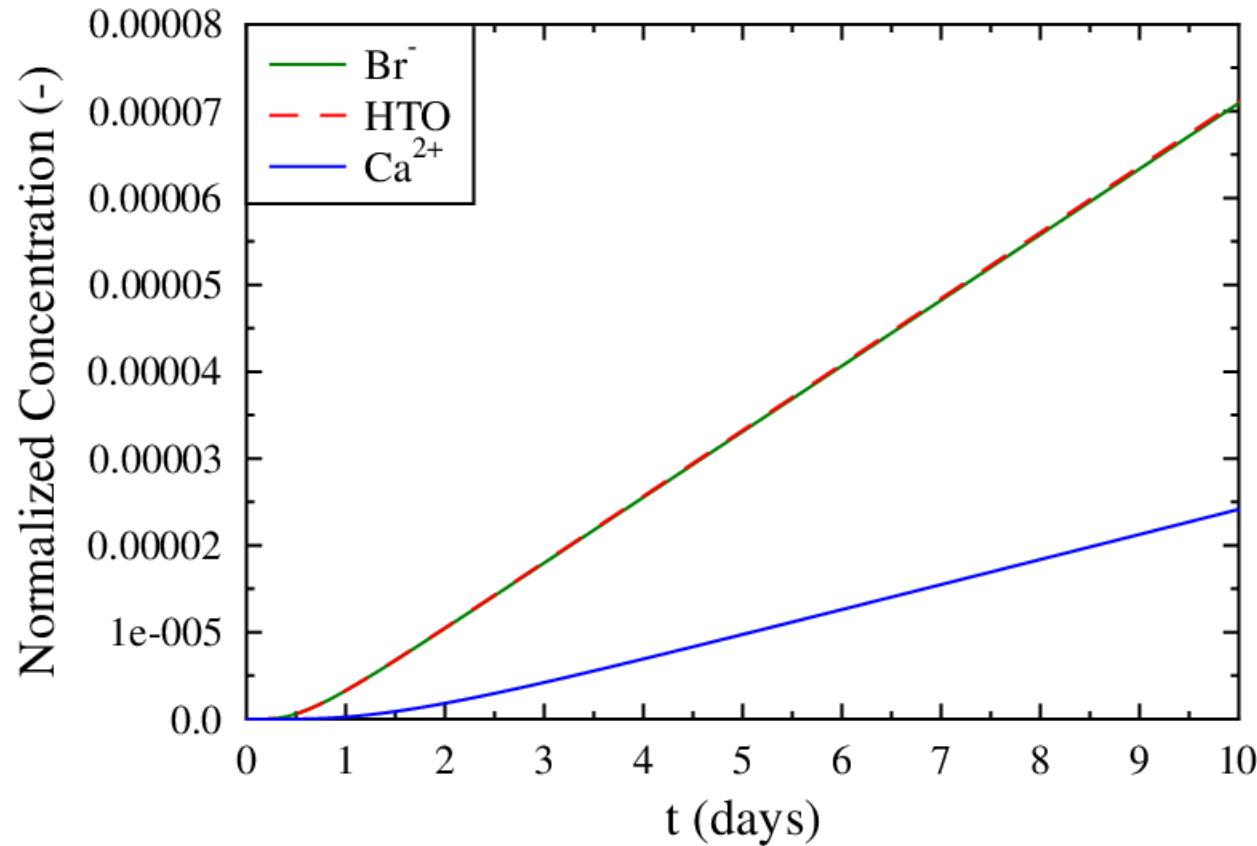
Redefinition of the the bulk vs DL porosity for each of the domains

See explanation in input files for calculation of these values

Here bulk porosity is 10 % of the total porosity

Results

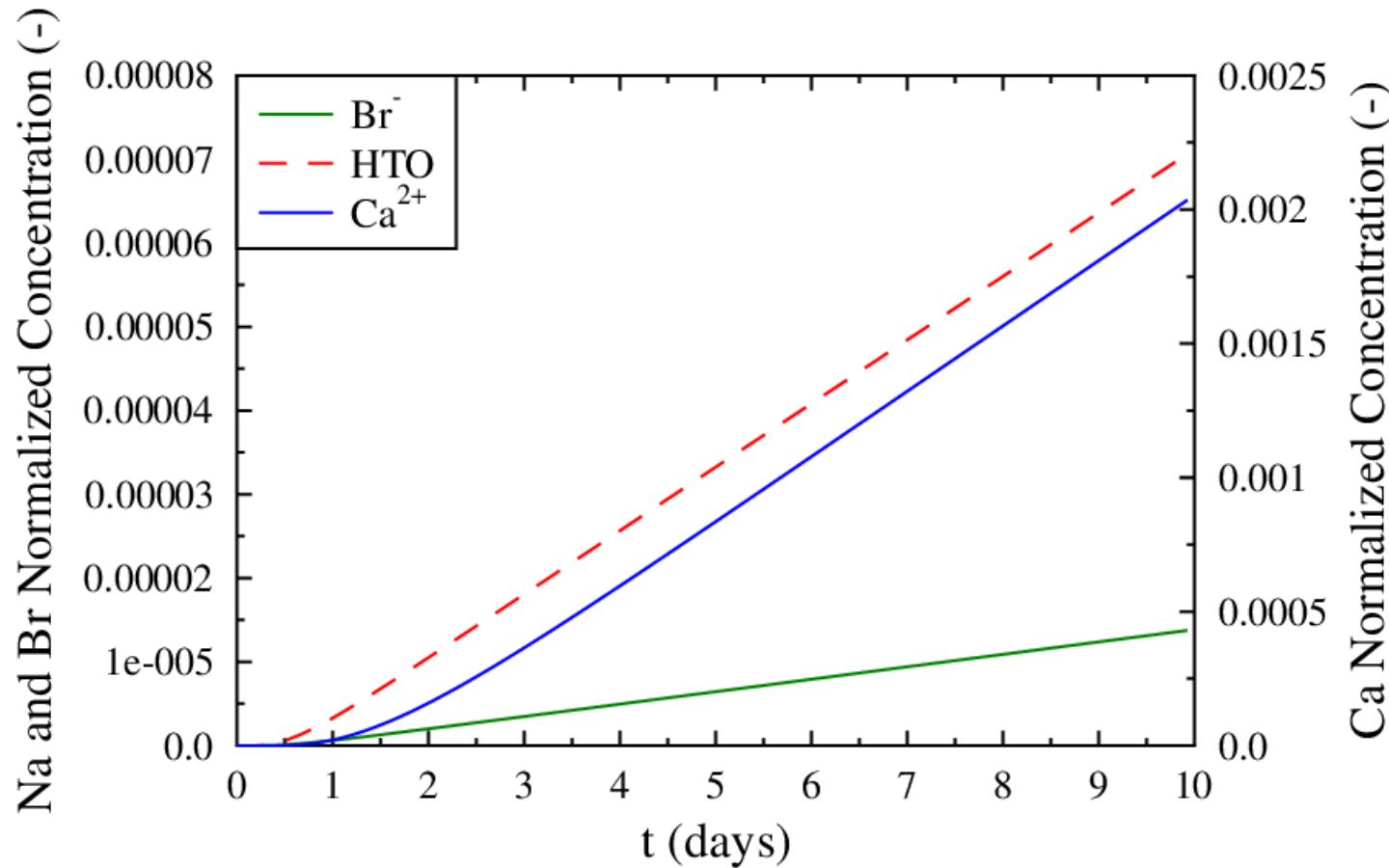
Concentration in the outlet reservoir



Why do the Br^- and HTO concentrations increase faster than the Ca^{2+} concentration?

Results

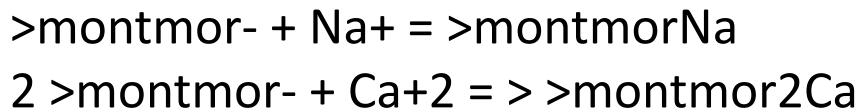
Increase the surface charge in the clay plug to 0.9 mol charge/kg clay



What is the species that diffuse the fastest now ?

Results

Add surface complexation reactions:



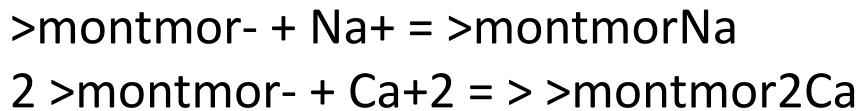
In database:

```
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
```

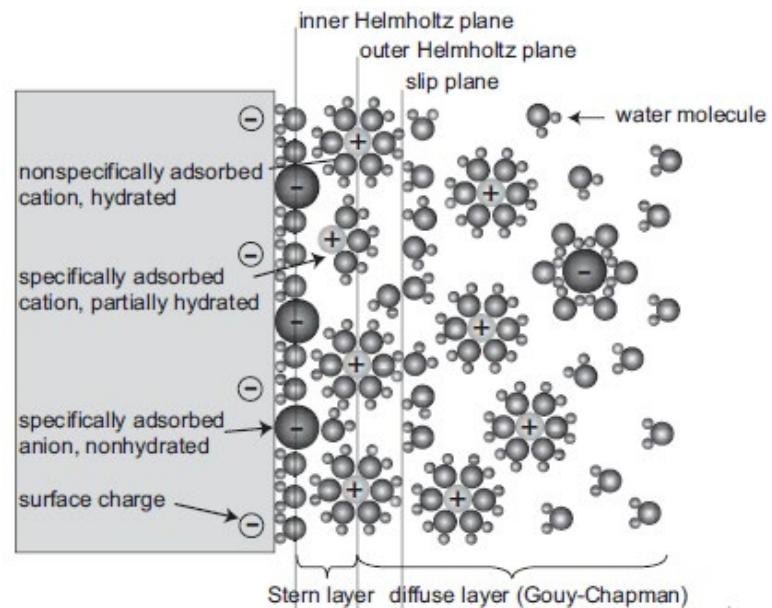
```
Begin surface complexation parameters
>montmor-    -1.0
>montmorNa   0.0
>montmor2Ca  0.0
End surface complexation parameters
```

Results

Add surface complexation reactions:



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/m³) = 5.6548800E-04
Total Fixed Charge (mol/m³) = -5.6548800E-04

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

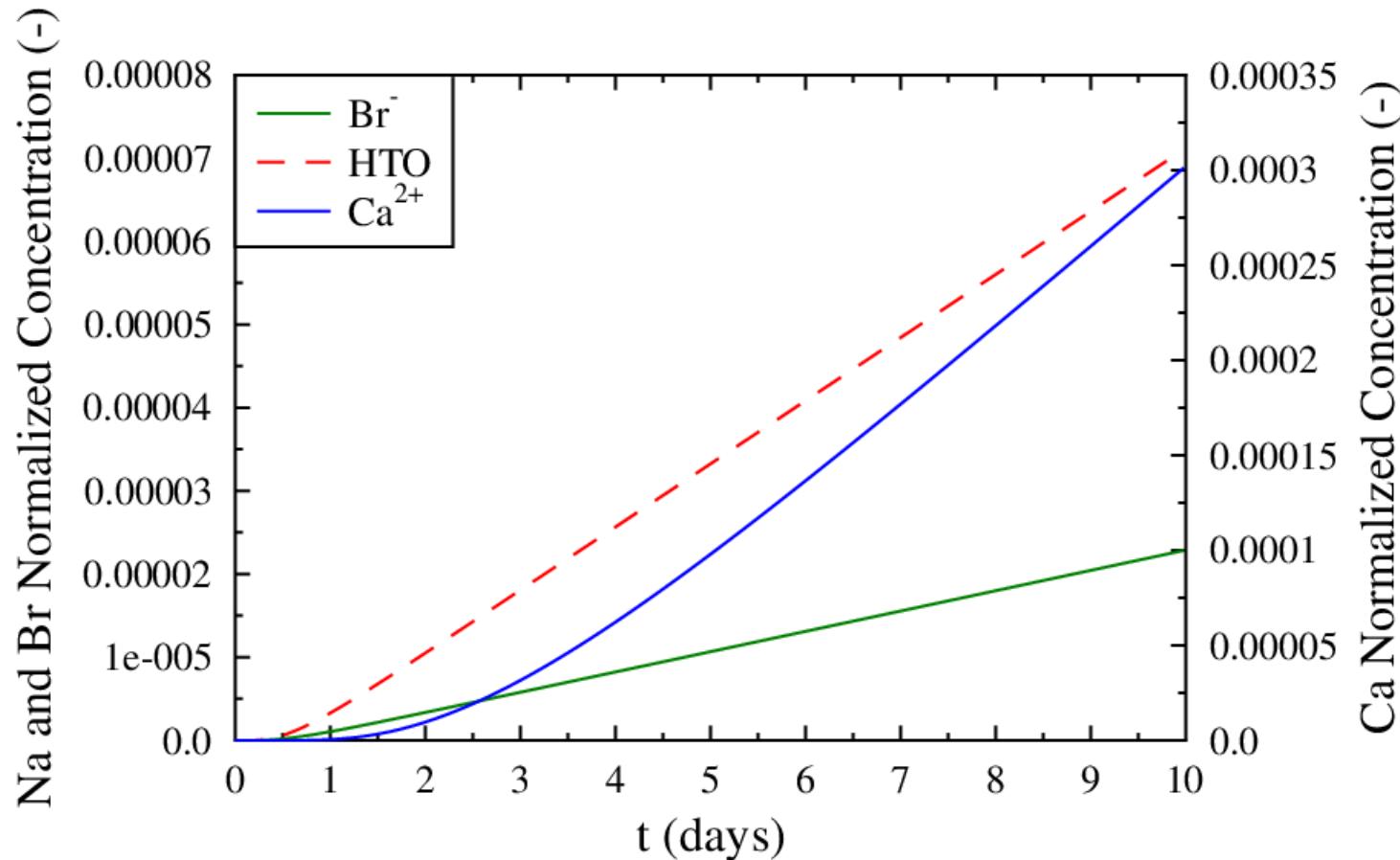
With surface complexes

Total Charge in DDL (mol/m³) = 2.8973120E-04
Total Fixed Charge (mol/m³) = -2.8973120E-04

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

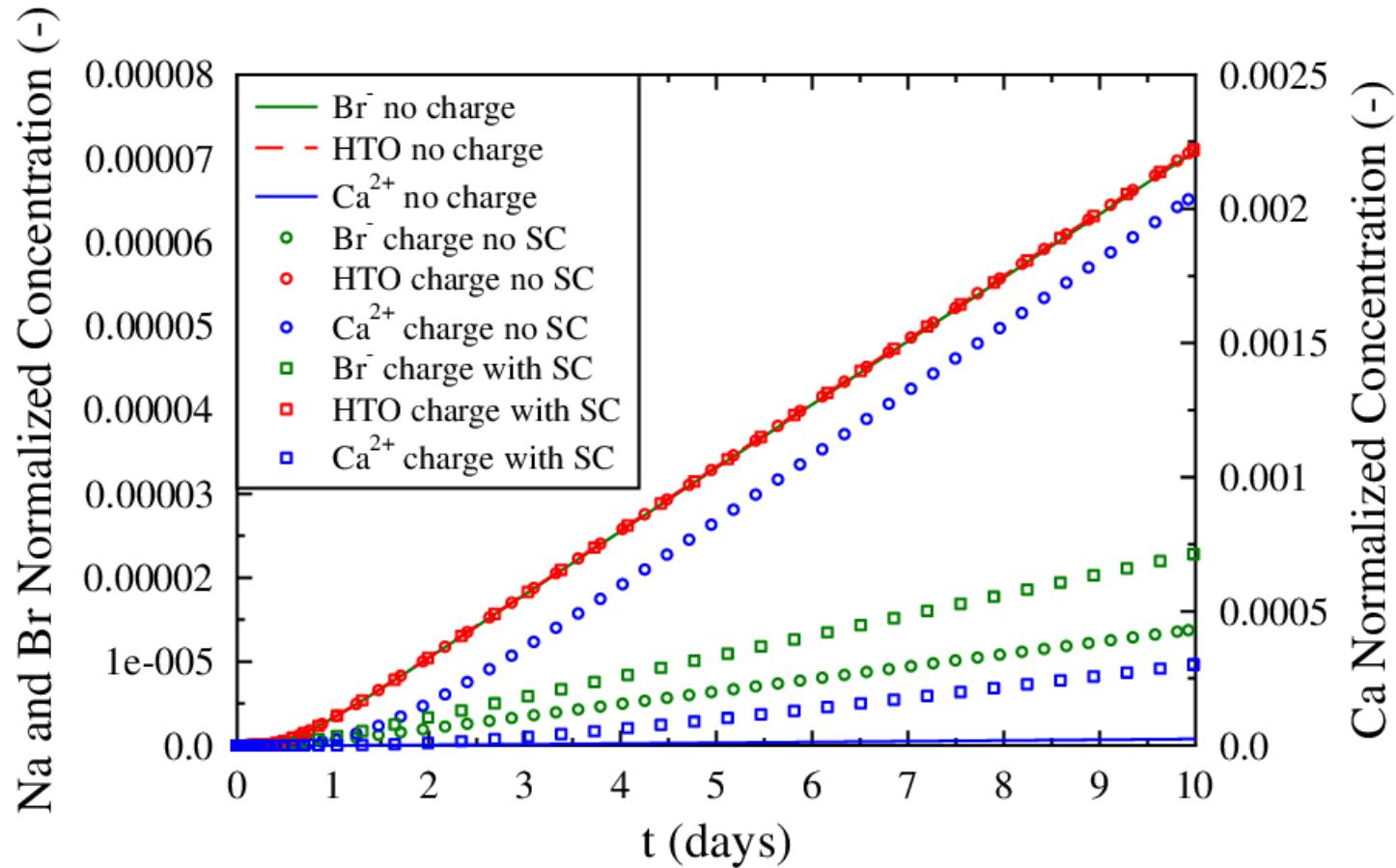
Results

Add surface complexation reactions:



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

Summary

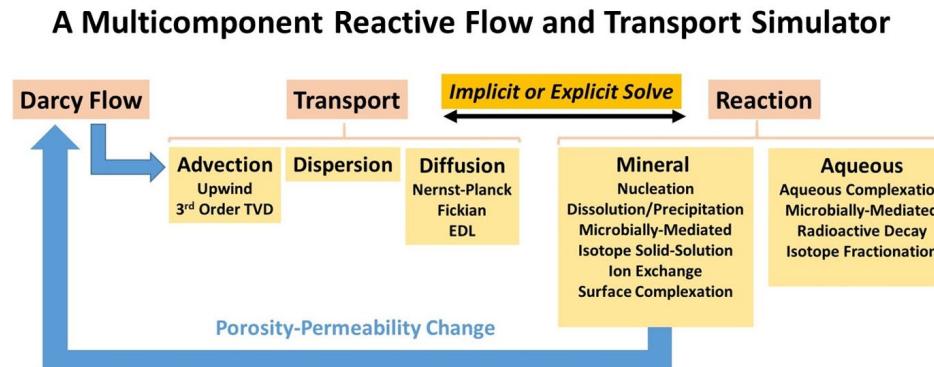
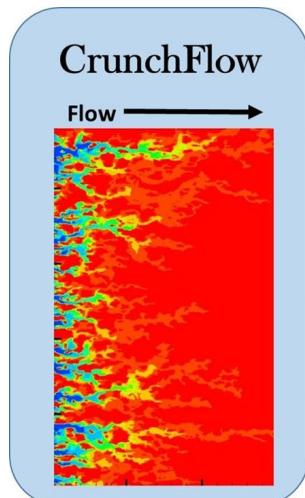


INVERSE MODELING WITH PEST-CRUNCH

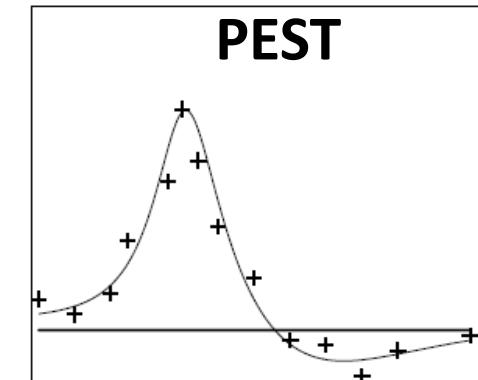
Exercise 12: Inverse Modeling with PEST-CrunchTope

Use PEST together with CrunchTope for inverse modeling and sensitivity analysis

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



<https://bitbucket.org/CrunchFlow/>



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      Parameters  
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
```

```
* 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	Calculated	Residual	Weight
	value	value		
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

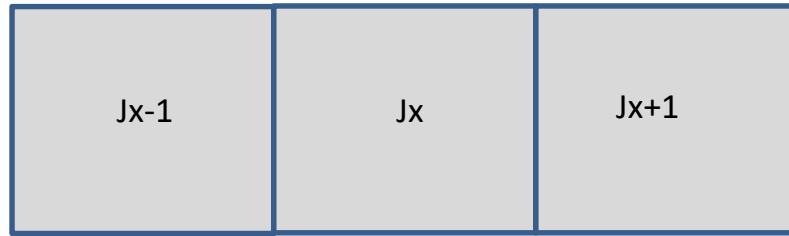
$$\frac{\partial}{\partial C_k} \left\{ \left[\psi_{i,jx}^{n+1} \right] \right\} = \frac{\partial}{\partial C_k} \left\{ C_i + \sum_{l=1}^{N_s} \nu_{i,l} C_l \right\} = \delta_{i,k} + \sum_{l=1}^{N_s} \left(\frac{\nu_{k,l}}{C_k} \right) \nu_{i,l} \left[\prod C_p^{\nu_{p,l}} K_{eq}^{-1} \right]$$

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



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

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

Jx

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

Jx+1

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

Newton's Method for Global Implicit Method

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

Nc x Nc Jacobian Submatrix

Nc Residual Vectors

Newton's Method for Global Implicit

For JX = 2

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

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

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

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

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