Hyperbolic Structure of Reaction Fronts in Porous Media

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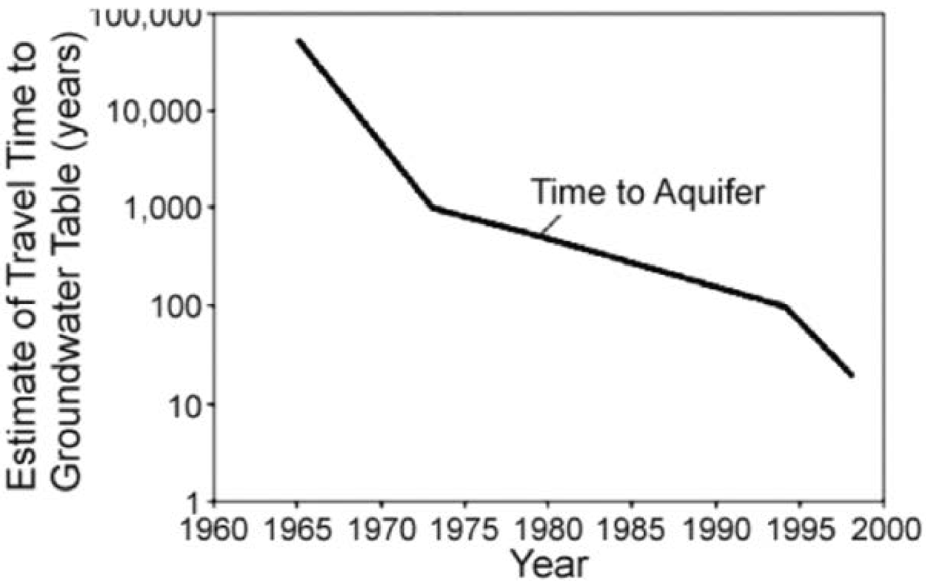
Outline

- Introduction & Examples
- Governing equations
- Classical chromatography
- Extensions to geochemistry
- Anomalous waves

MOTIVATION

Idaho Waste “Management” Complex

Research Needs in Subsurface Science, The National Academies Press, 2000.



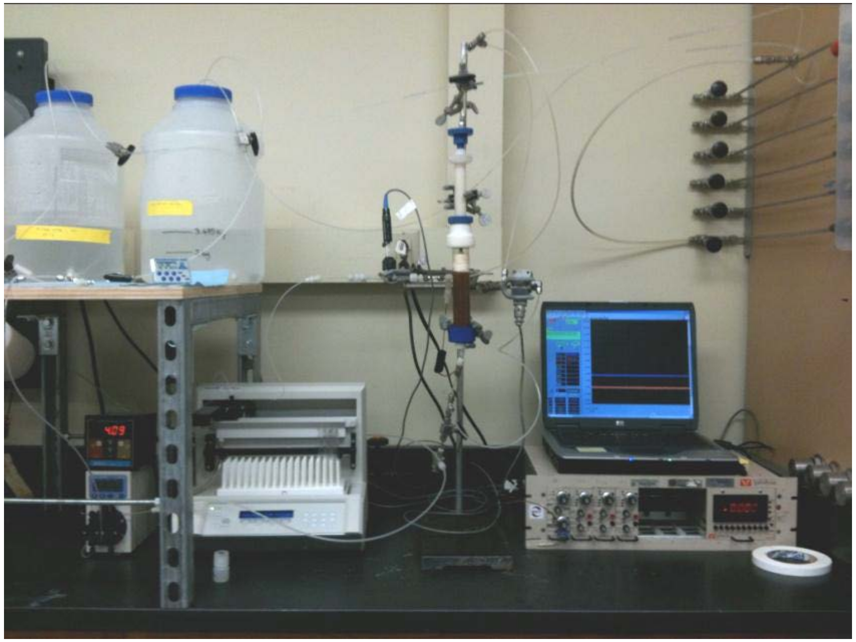
(Source: Idaho Natl. Engineering & Environmental Laboratory)

cerns. As shown in the figure, travel time estimates have decreased from tens of thousands to a few tens of years. The uncertainty of these estimates is attributed to several factors, including incorrect conceptualizations of the hydrogeologic system, improper simplifying assumptions, incorrect transport parameters, and overlooked transport phenomena.

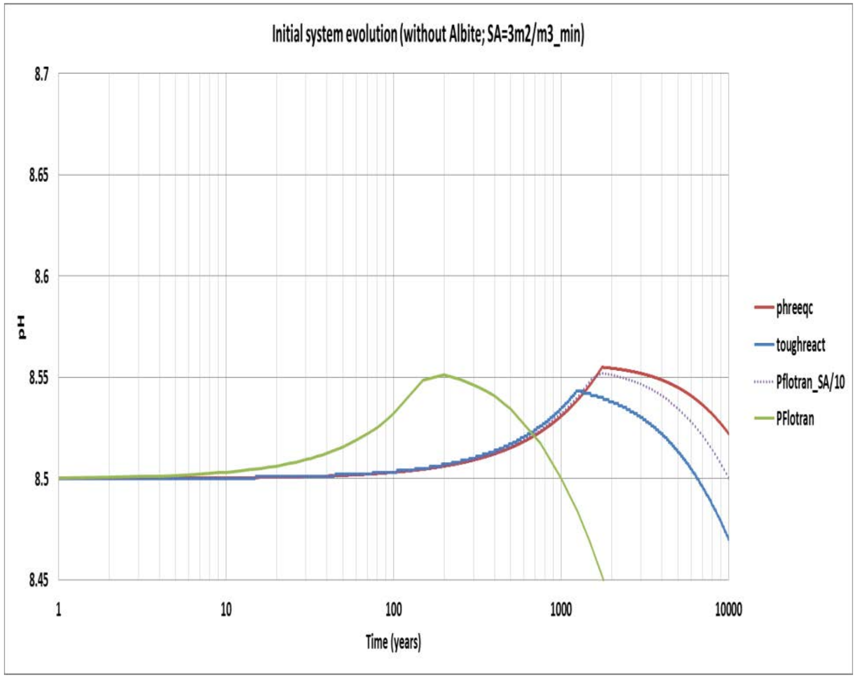
$\Rightarrow$ It is all about wave/front speeds, i.e. hyperbolic part

Immediate motivation

Planning Experiments



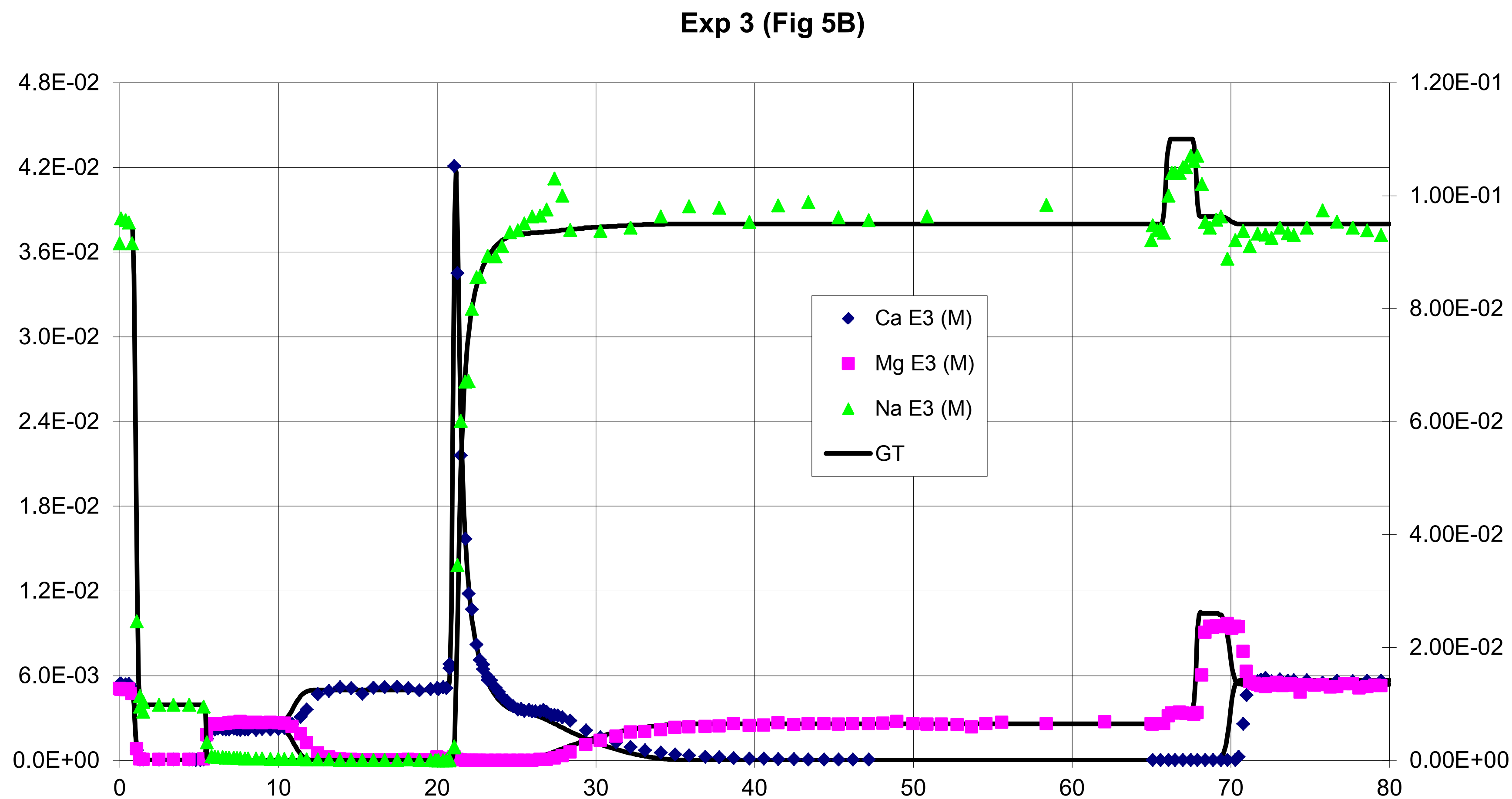
Benchmarking codes



EXAMPLE

4 components: Ca, Mg, Na, Cl

Voeglin et al. (2000) JCH 48



GOVERNING EQUATIONS

n_c component Solid-fluid system

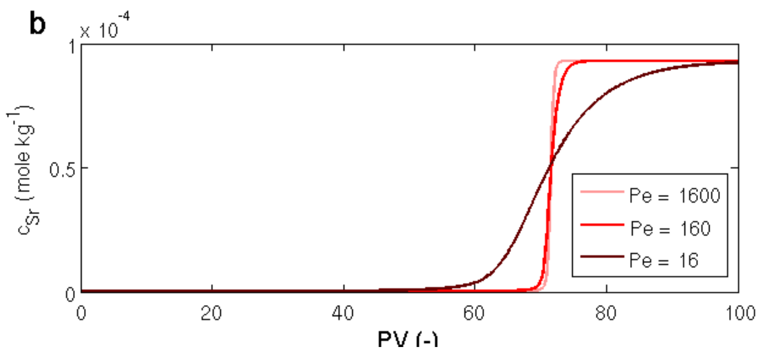
$$\frac{\partial}{\partial t}\left(\phi c_{f,c}\right) + \nabla \cdot \left(\vec{q} c_{f,c} - \phi \boldsymbol{D} \nabla c_{f,c}\right) = kS\left(c_{s,c}^{eq} - c_{s,c}\right)$$

$$\frac{\partial}{\partial t}\left((1-\phi) c_{s,c}\right) = -kS\left(c_{s,c}^{eq} - c_{s,c}\right)$$

- $c_{f,c}$ & $c_{s,c}$: total concentrations in fluid & solid
- $c_{s,c}^{eq}$: equilibrium concentration in/on solid
- ϕ: porosity, $\vec{q}$: Darcy flux, $\boldsymbol{D}$: hydro. Dispersion
- k: reaction rate, S: surface area,

Hyperbolic limit - small Pe

Effect of “dispersion”



- $Pe = \frac{|\vec{v}|L}{D} \gg 1$
- **Lab**: L is small
  $|\vec{v}|$ is large
  D is small
  $\Rightarrow Pe \approx 160 - 400$
- **Field**: L is very large
  $|\vec{v}|$ is small
  D is debated
  $\Rightarrow Pe \approx 200 - 40{,}000$

Local Chemical Equilibrium (LCE)

In limit of $Da = \frac{kSL}{\phi|\vec{v}|} \gg 1$ then $c_{s,c} \rightarrow c_{s,c}^{eq}$

Equilibrium constraint: $c_{s,Ca}^{eq} = c_{s,Ca}^{eq}\left(c_{f,Ca}, c_{f,Mg}, c_{f,Na}\right)$

Sum the fluid and solid equations:

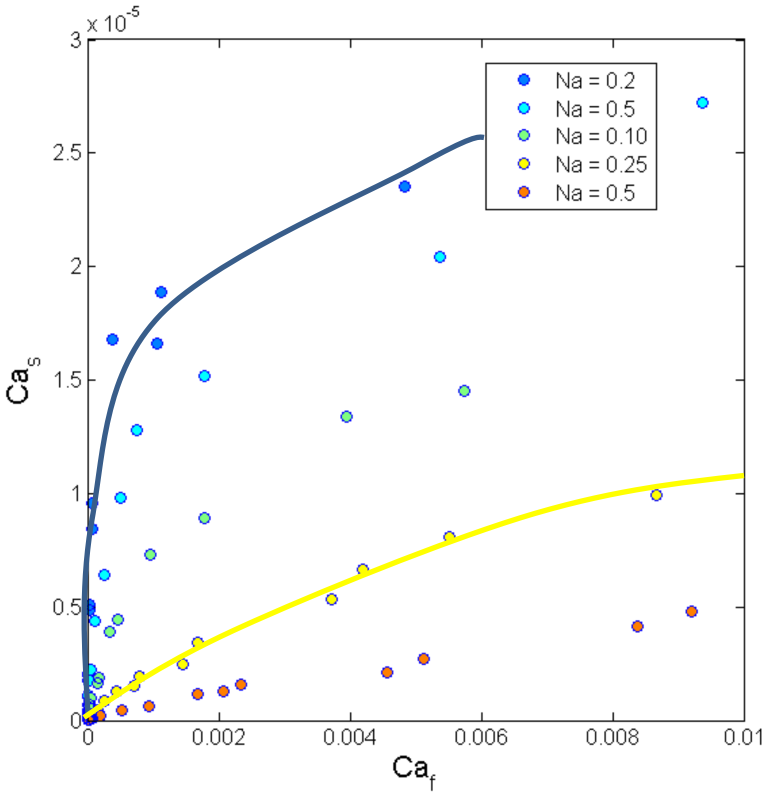
$$\frac{\partial}{\partial t}\left(\phi c_{f,c} + (1-\phi)c_{s,c}^{eq}\left(c_{f,c}\right)\right) + \nabla \cdot \left(\vec{q} c_{f,c}\right) = 0$$

Or in almost standard hyperbolic notation:

$$\boxed{\boldsymbol{a}(\boldsymbol{c})_t + \boldsymbol{c}_x = 0} \quad \text{or} \quad \boldsymbol{c}_t + (\nabla_c \boldsymbol{a})^{-1}\boldsymbol{c}_x = 0$$

Langmuir Isotherm: $c_{s,Ca}^{eq}(c_{f,Ca}, c_{f,Na})$

Voeglin et al. (2000) JCH 48



Langmuir Isotherm:

$$c_{s,i}^{eq} = \frac{NK_i c_{f,i}}{1 + \sum_j K_j c_{f,j}}$$

Couples all variables

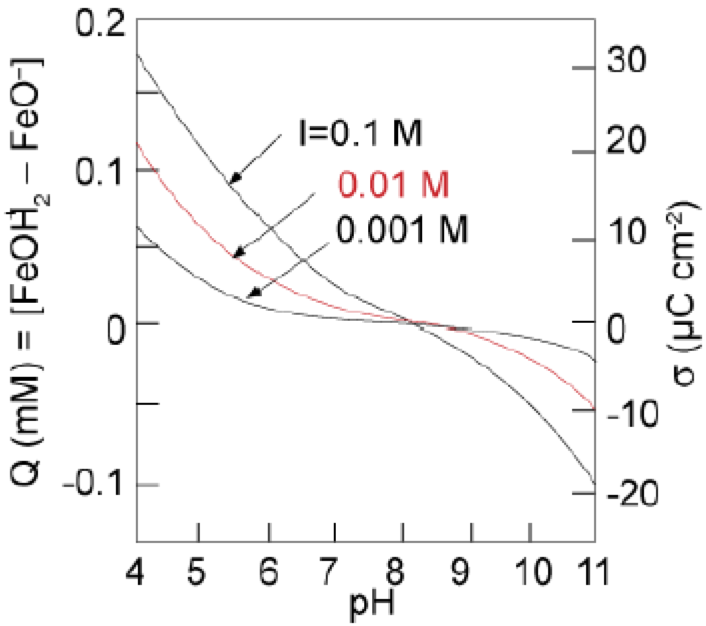
Langmuir properties:

Monotone: $\frac{\partial c_{s,i}^{eq}}{\partial c_{f,j}} \geq 0$

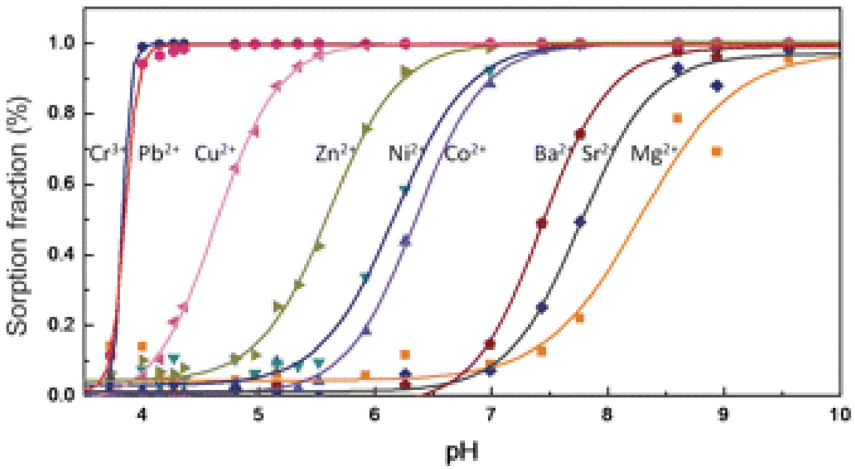
Convex: $\frac{\partial^2 c_{s,i}^{eq}}{\partial c_{f,j} \partial c_{f,k}} \leq 0$

Surface complexation

- Amphoteric surfaces

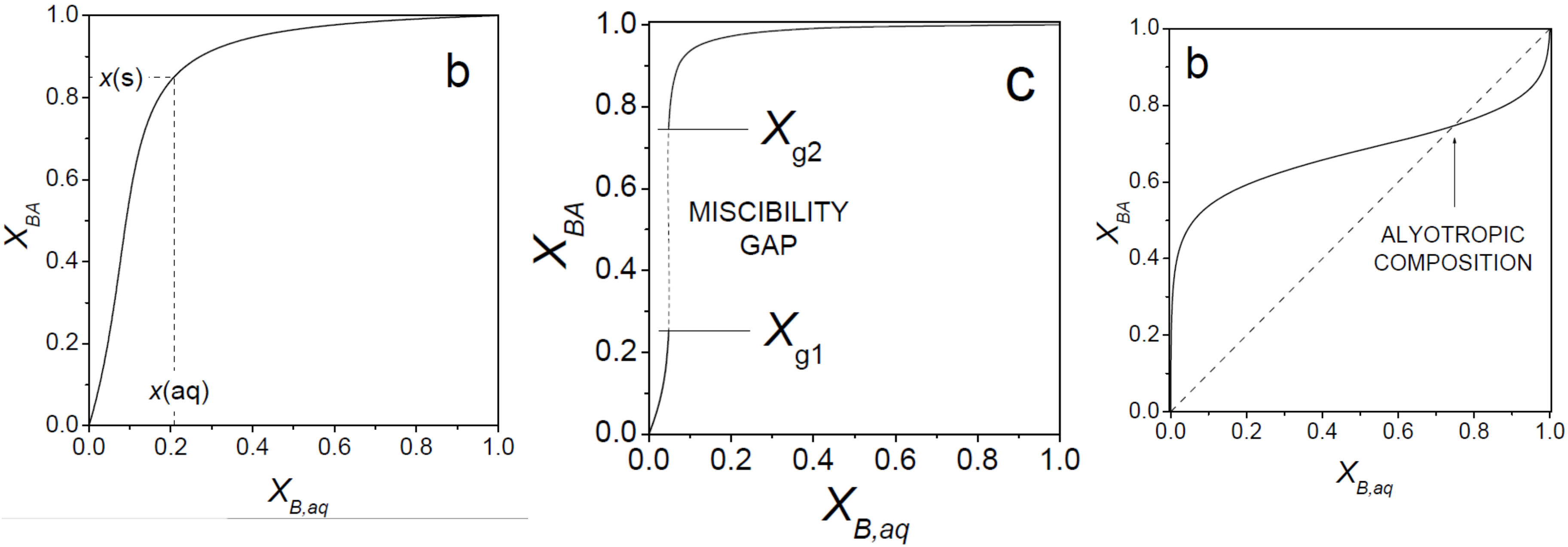


Heavy metals show "Sorption edges"



⇒ inflection points?

Precipitation/Dissolution



$\Rightarrow$ Many types of nonlinear constitutive functions!

Comparison with standard form

Chromatography

$$\boldsymbol{a}(\boldsymbol{c})_t + \boldsymbol{c}_x = 0$$
$$\boldsymbol{c}(x,0) = \boldsymbol{c}_0(x)$$

Nonlinear accumulation: $\boldsymbol{a}(\boldsymbol{c})$

$\boldsymbol{c}$ not conserved quantities

Self-similar solution:

$$\left(\nabla_c \boldsymbol{a} - \frac{1}{\lambda}\boldsymbol{I}\right)\frac{d\boldsymbol{c}}{d\xi} = 0$$

$\sigma = \frac{1}{\lambda} = \frac{t}{x} \quad \Rightarrow \quad$ retardation

Jump condition: $\Sigma_p = \frac{[a_p]}{[c_p]}$

Standard conservation law

$$\boldsymbol{q}_t + \boldsymbol{f}(\boldsymbol{q})_x = 0$$
$$\boldsymbol{q}(x,0) = \boldsymbol{q}_0(x)$$

Nonlinear flux: $\boldsymbol{f}(\boldsymbol{q})$

$\boldsymbol{q}$ conserved quantities

Self-similar solution:

$$(\nabla_q \boldsymbol{f} - \lambda\boldsymbol{I})\frac{d\boldsymbol{q}}{d\lambda} = 0$$

$\lambda = \frac{x}{t} \quad \Rightarrow \quad$ velocity

Jump condition: $\Lambda_p = \frac{[f_p]}{[q_p]}$

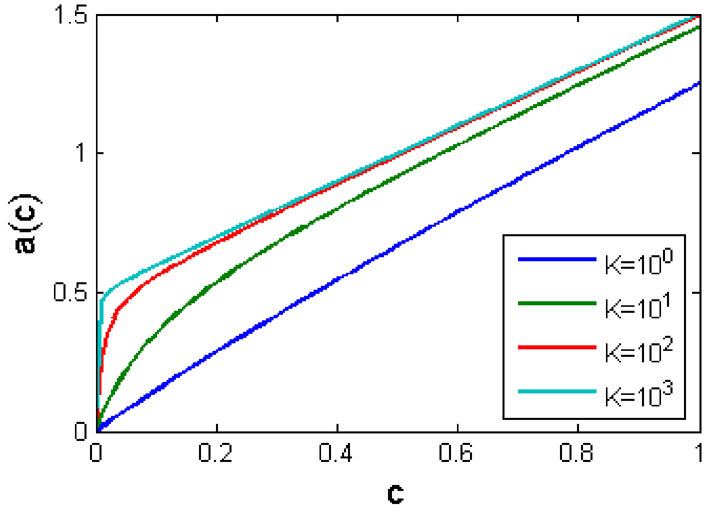
Rewrite in standard form

Chromatography

$\boldsymbol{c} = \boldsymbol{c_f}$ = fluid concentration

$$\boldsymbol{c}_t + (\nabla_c \boldsymbol{a})^{-1} \boldsymbol{c}_x = 0$$

$$a = c + \varphi \frac{NKc}{1 + Kc}$$

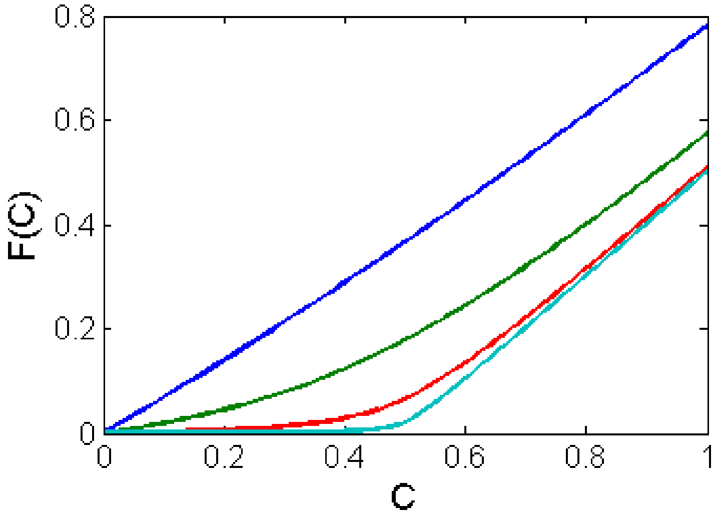


Total concentration

$$\boldsymbol{C} = \boldsymbol{a}(\boldsymbol{c}) = \phi \boldsymbol{c}_f + (1 - \phi)\boldsymbol{c}_s$$

$$\boldsymbol{C}_t + \boldsymbol{F}(\boldsymbol{C})_x = 0$$

$$F = \frac{(1 + \varphi NK - KC) + \sqrt{(1 + \varphi NK - KC)^2 + 4KC}}{2K}$$



Classical chromatography

Glueckauf (1949)
Rhee et al. (1970)

2 x 2 Langmuir adsorption

$$c_{s,i} = \frac{NK_i c_{f,i}}{1+\sum_j K_j c_{f,j}}$$

Integral curves of eigenvectors

$$\frac{d^2 c_1}{dc_2^2}\left[2c_2 \frac{dc_1}{dc_2} - (k + c_1 - hc_2)\right] = 0$$

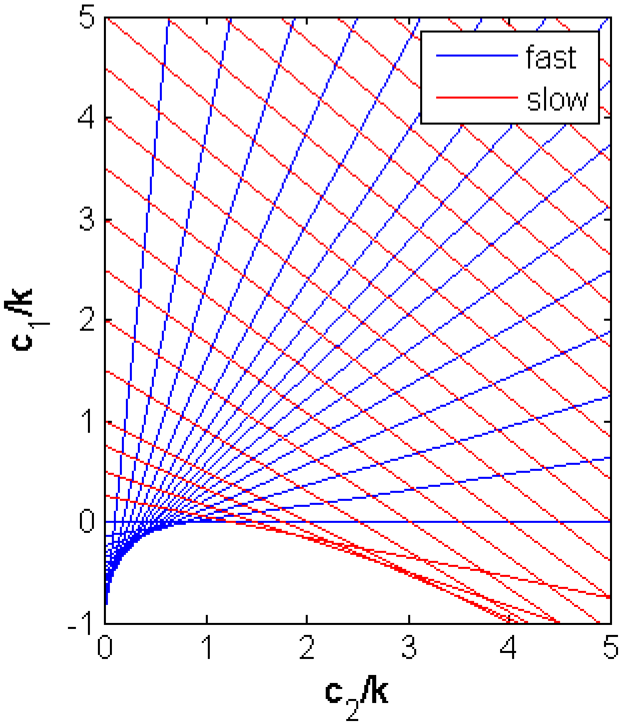
Which has the family of solutions

$$c_1 = \beta c_2 - \frac{k\beta}{\beta + h}$$

$\beta > 0$: fast paths

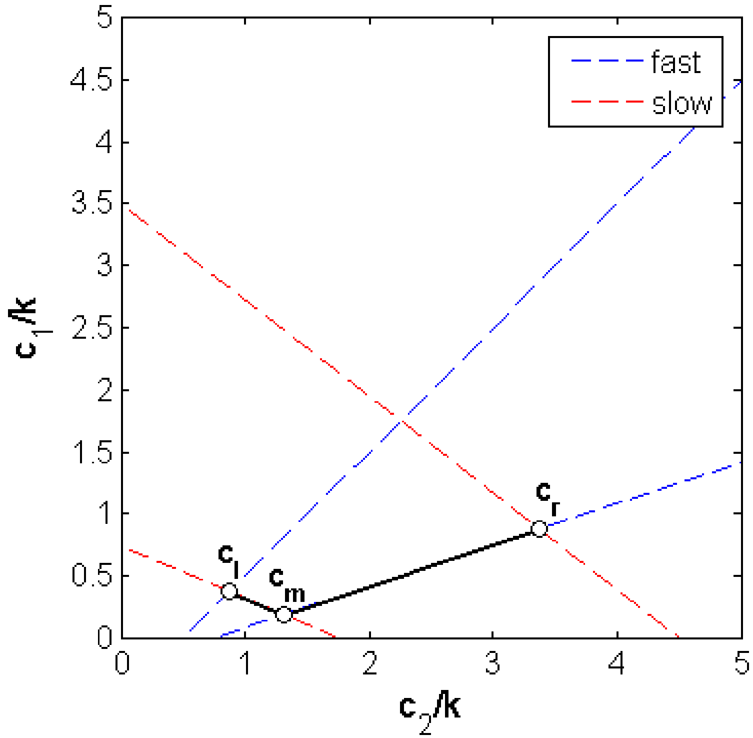
$\beta > 0$: slow paths

Hodograph plane

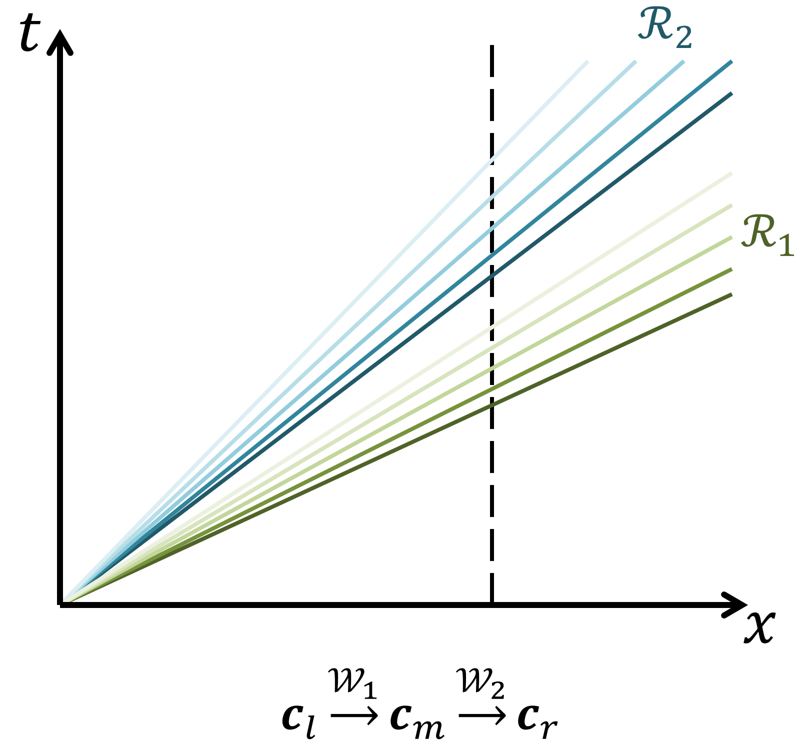


Solution construction

Hodograph plane



xt - plane



Environmental reactive transport

System: Sr^{2+}, H^+, OH^-, Cl^-

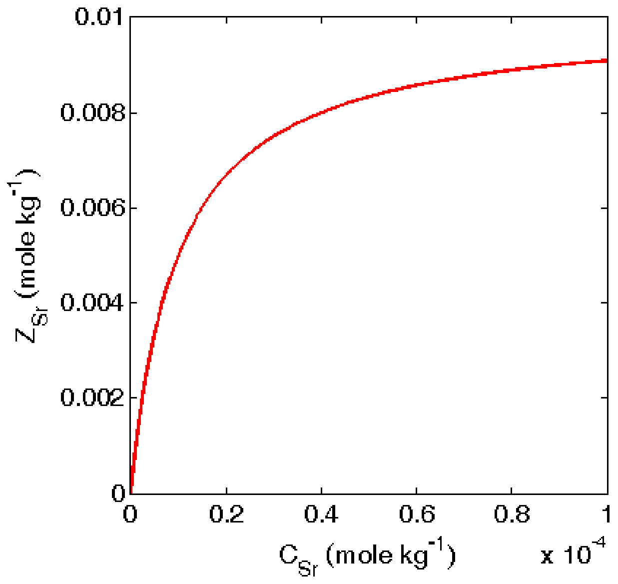
- In chromatography coupling is through competition for sorption sites!
- Charges species: electro-neutrality constraint $\Rightarrow$ strong coupling
- Dissociation of water:

$$K_w = c_H c_{OH}$$

- 2 x 2 system for Sr^{2+} and Cl^-

Isotherm:

$$Z_{Sr} = \frac{Z_t C_{Sr} K_{Sr}}{1 + C_H K_H + C_{Sr} K_{Sr}}$$



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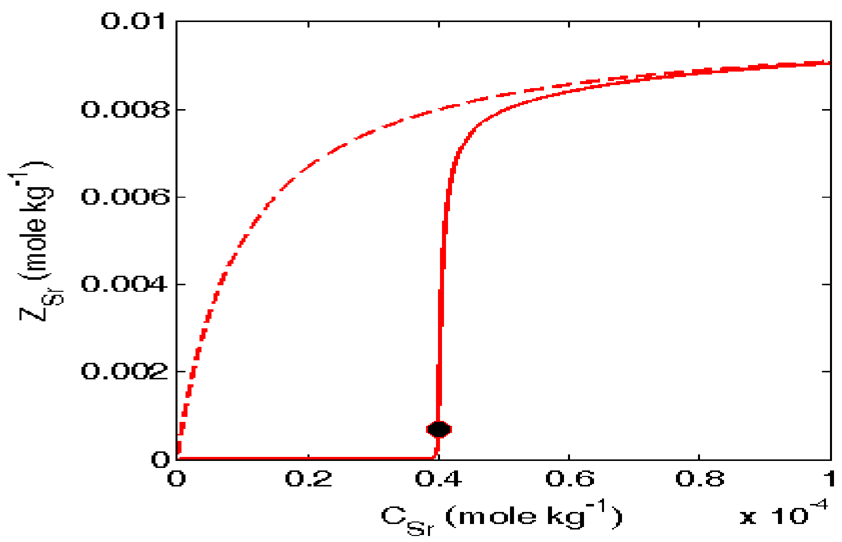
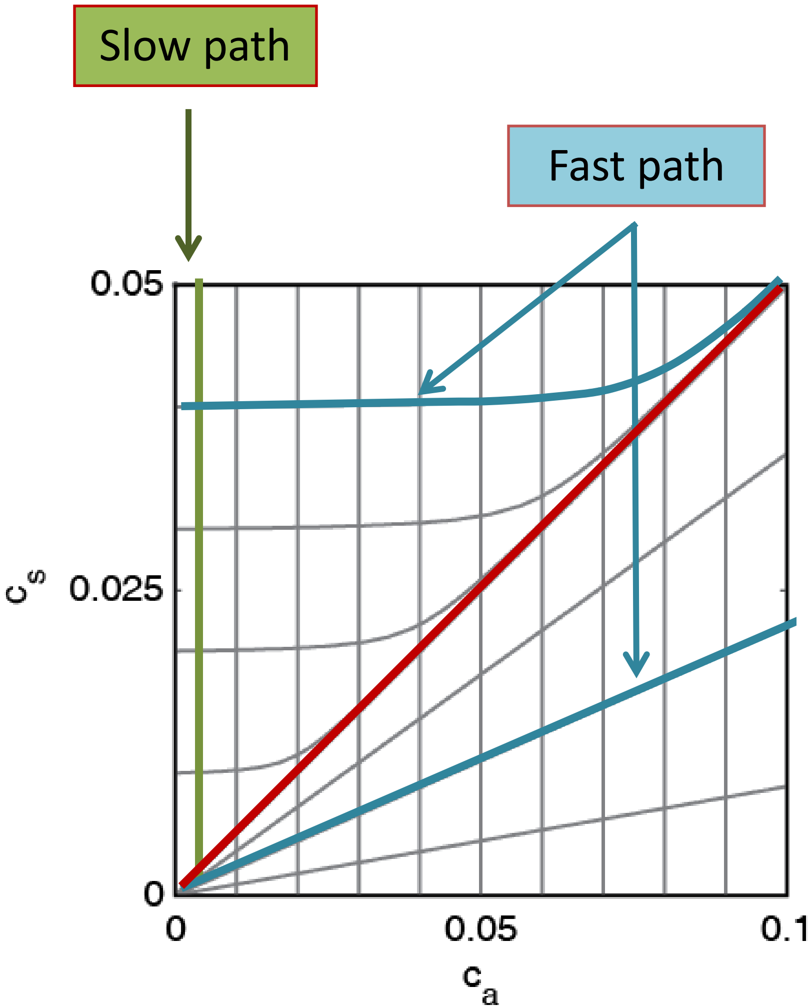
- Dissosiation of water:
  $$K_w = c_H c_{OH}$$
- 2 x 2 system for Sr^{2+} and Cl^-

Isotherm:

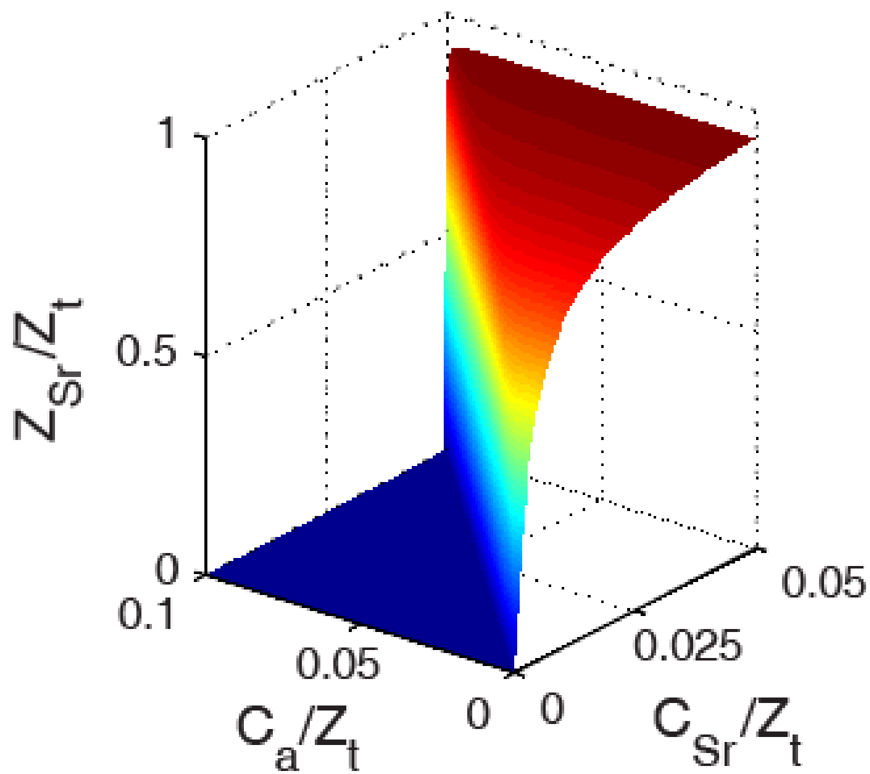
$$Z_{Sr} = \frac{Z_t C_{Sr} K_{Sr}}{1 + 0.5\left[-C_{Sr} + C_a + \sqrt{(C_{Sr} - C_a)^2 + 4K_w}\right] K_H + C_{Sr} K_{Sr}}$$



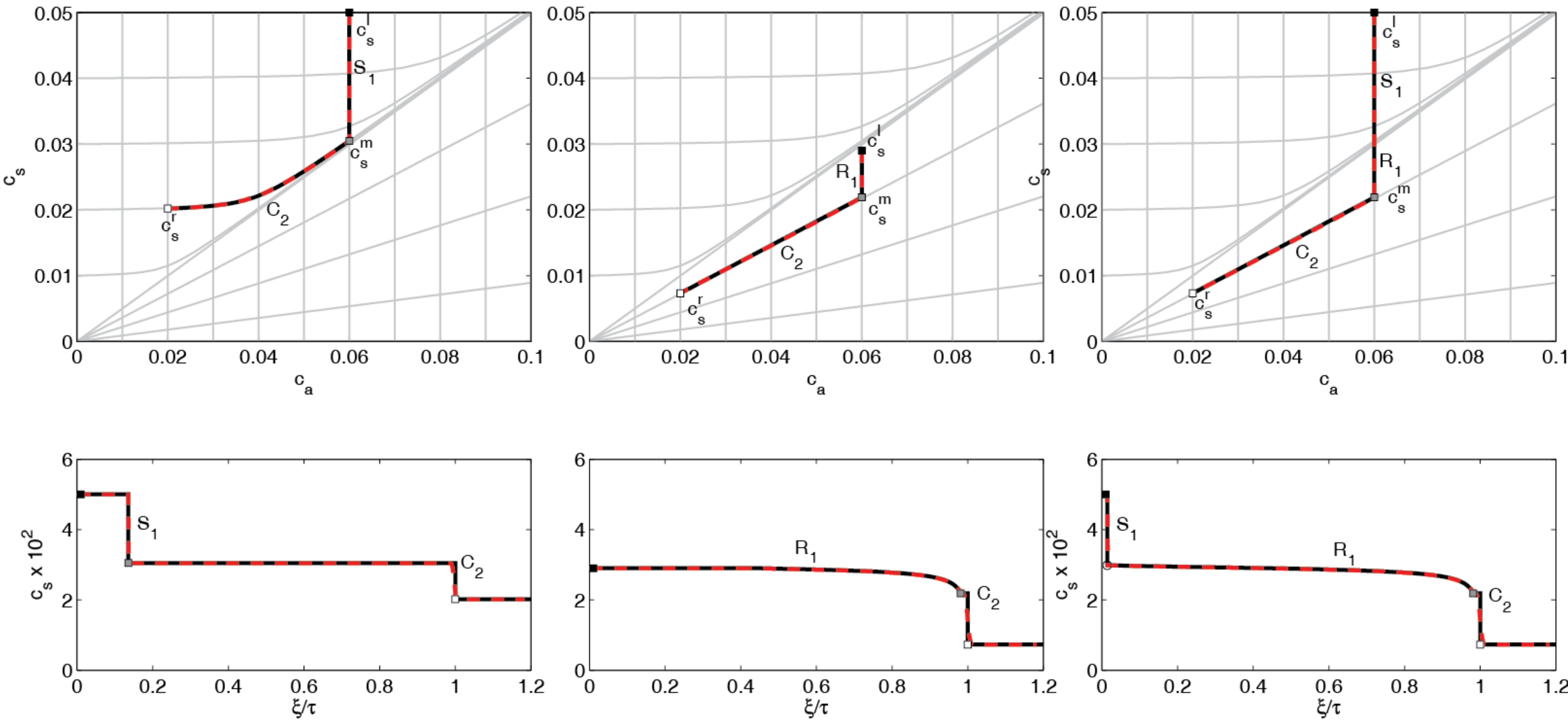
Hodograph plane



Fast path = isotherm contours



Enumerate the types of solution

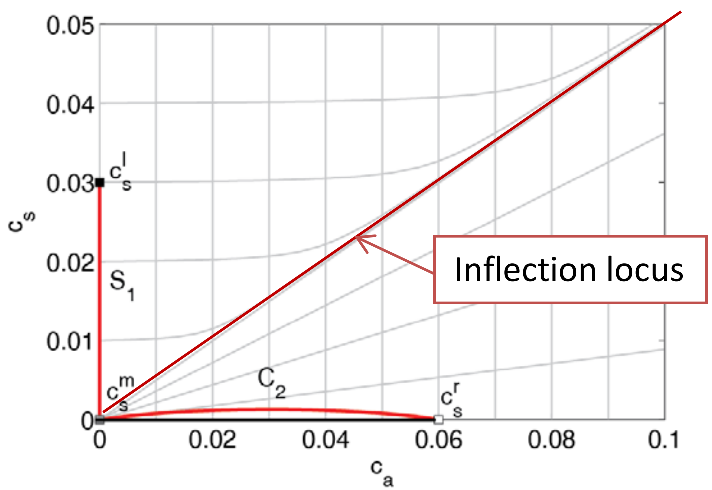


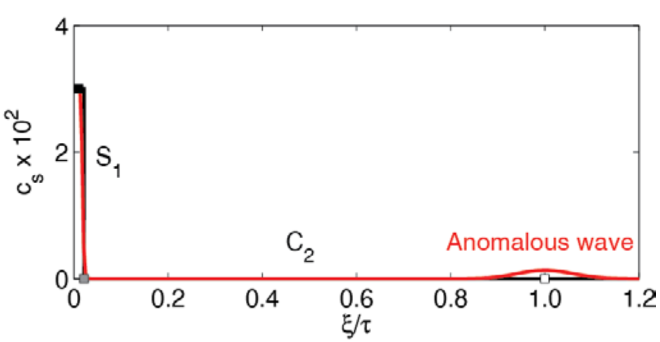
Analytical solution

Numerical solution assuming large *Pe*

Anomalous wave

Theory & Simulation

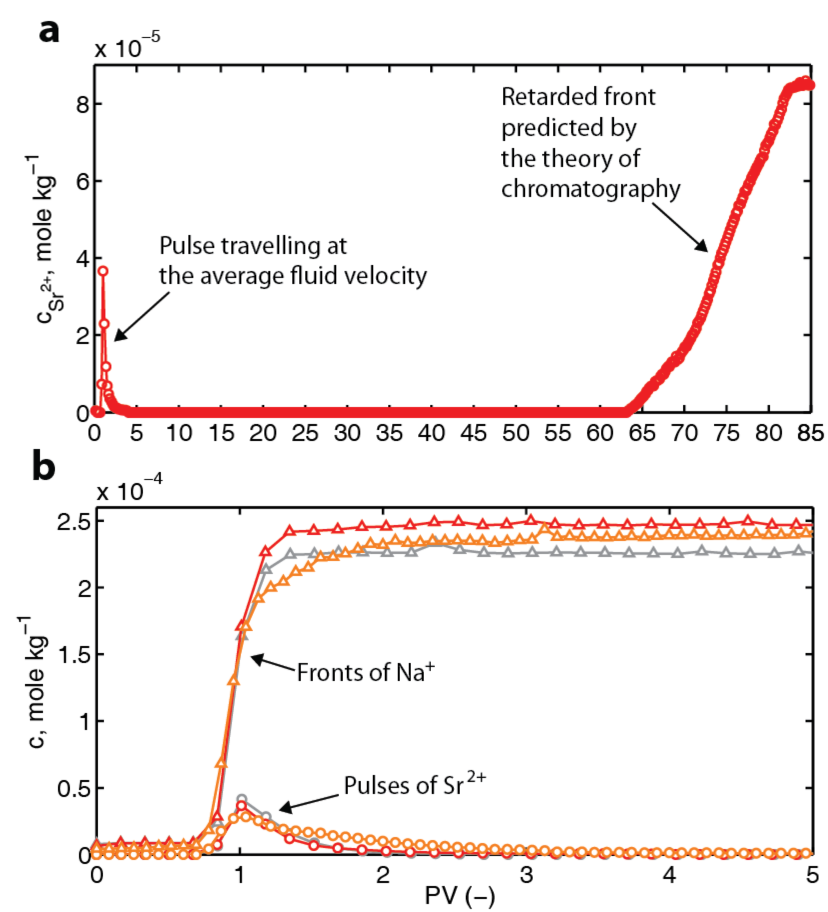




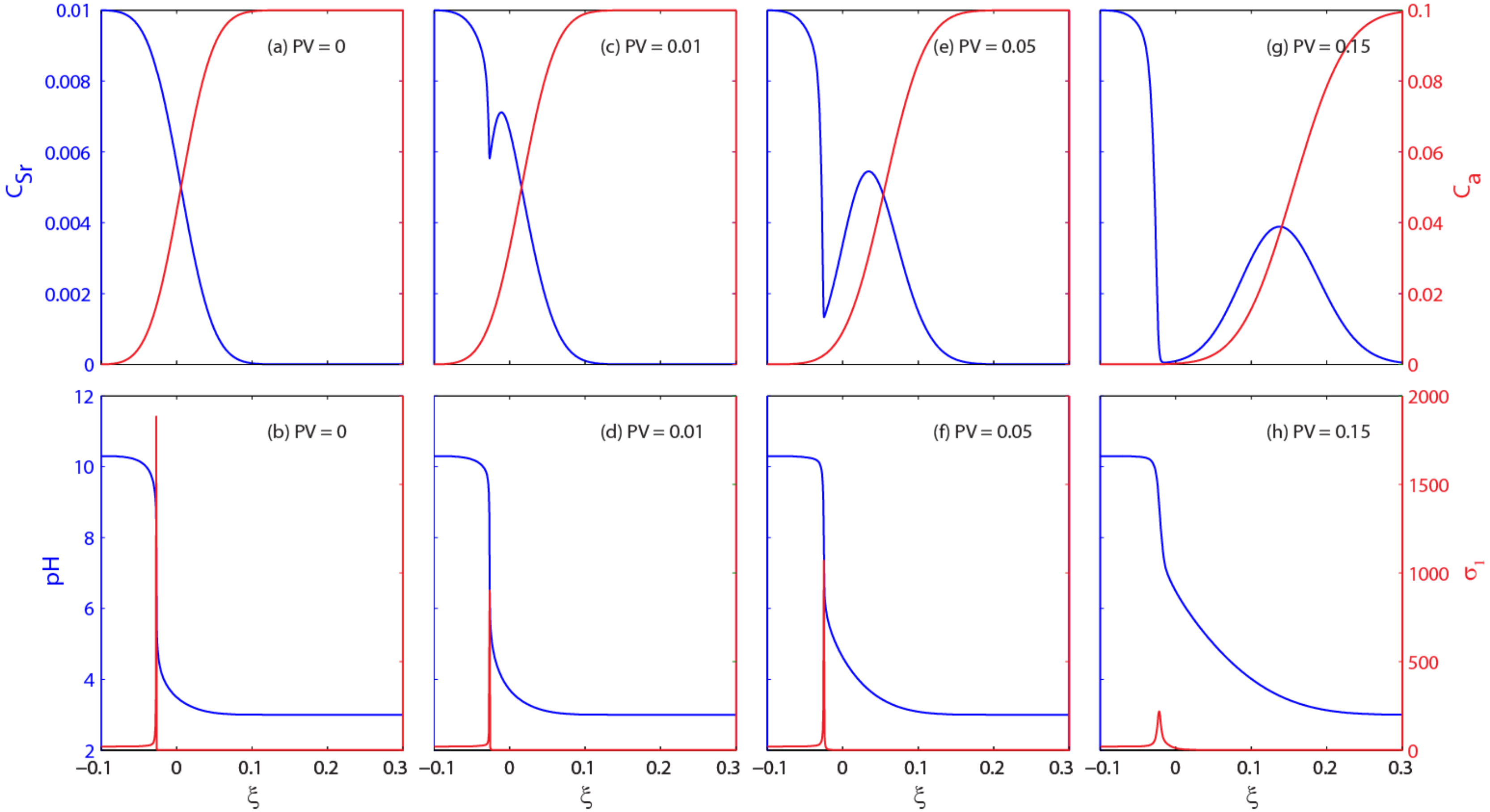
Analytical solution

Numerical solution assuming **small** *Pe*

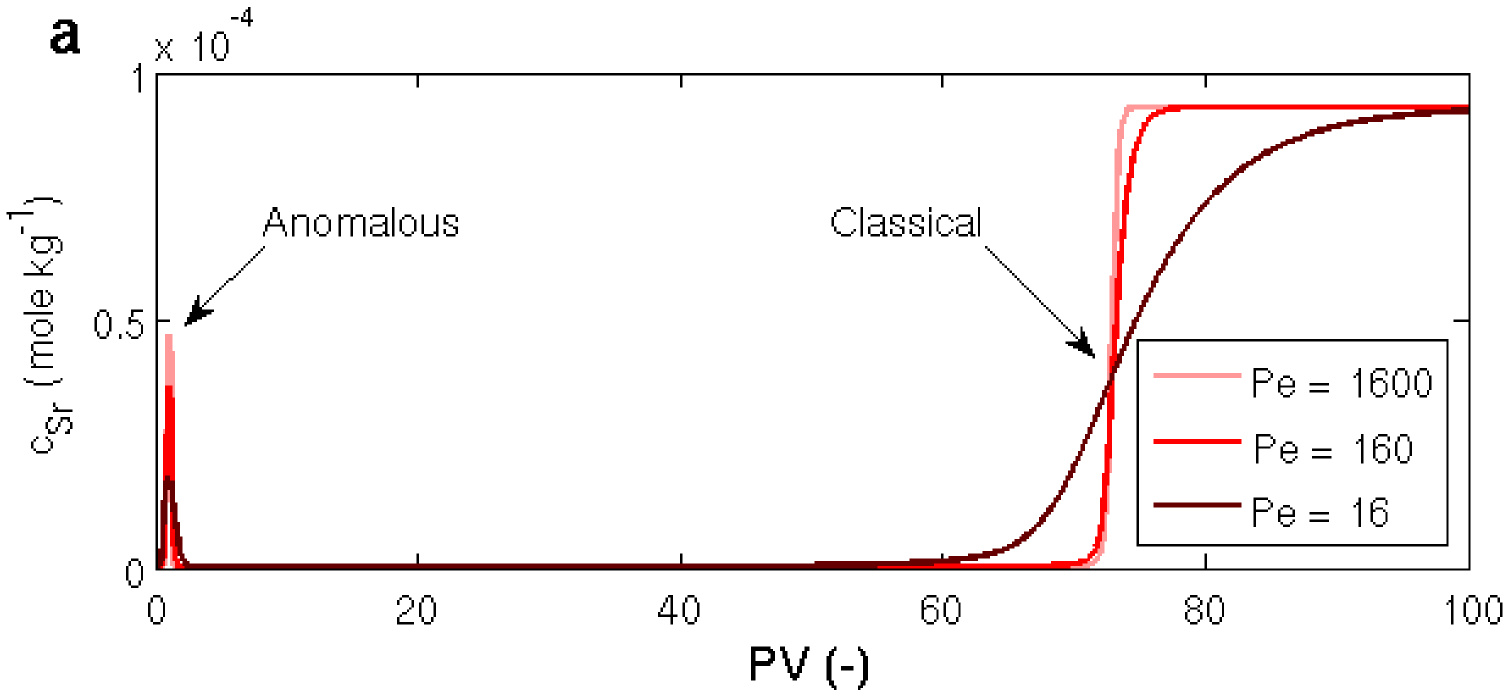
Experiments



Formation of anomalous wave



Not limiting to the hyperbolic solution in the expected way



Summary

- Theory of hyperbolic eqns. can help us understand reactive transport in the environment.
- Provides useful benchmarks for numerical solutions.
- Helps us identify unusual behavior.
- May eventually help improve robustness of numerical solutions