ORNL/TM-2004/107

HYDROGEOCHEM 5.0

A Three-Dimensional Model of Coupled Fluid Flows, Thermal Transport, and HYDROGEOCHEMical Transport under Variably Saturated Conditions: Version 5.0

Gour-Tsyh Yeh, Jiangtao Sun, Philip M. Jardine, William D. Burgos, Yilin Fang, Min-Hsu Li, and Malcolm D. Siegel

Presented at

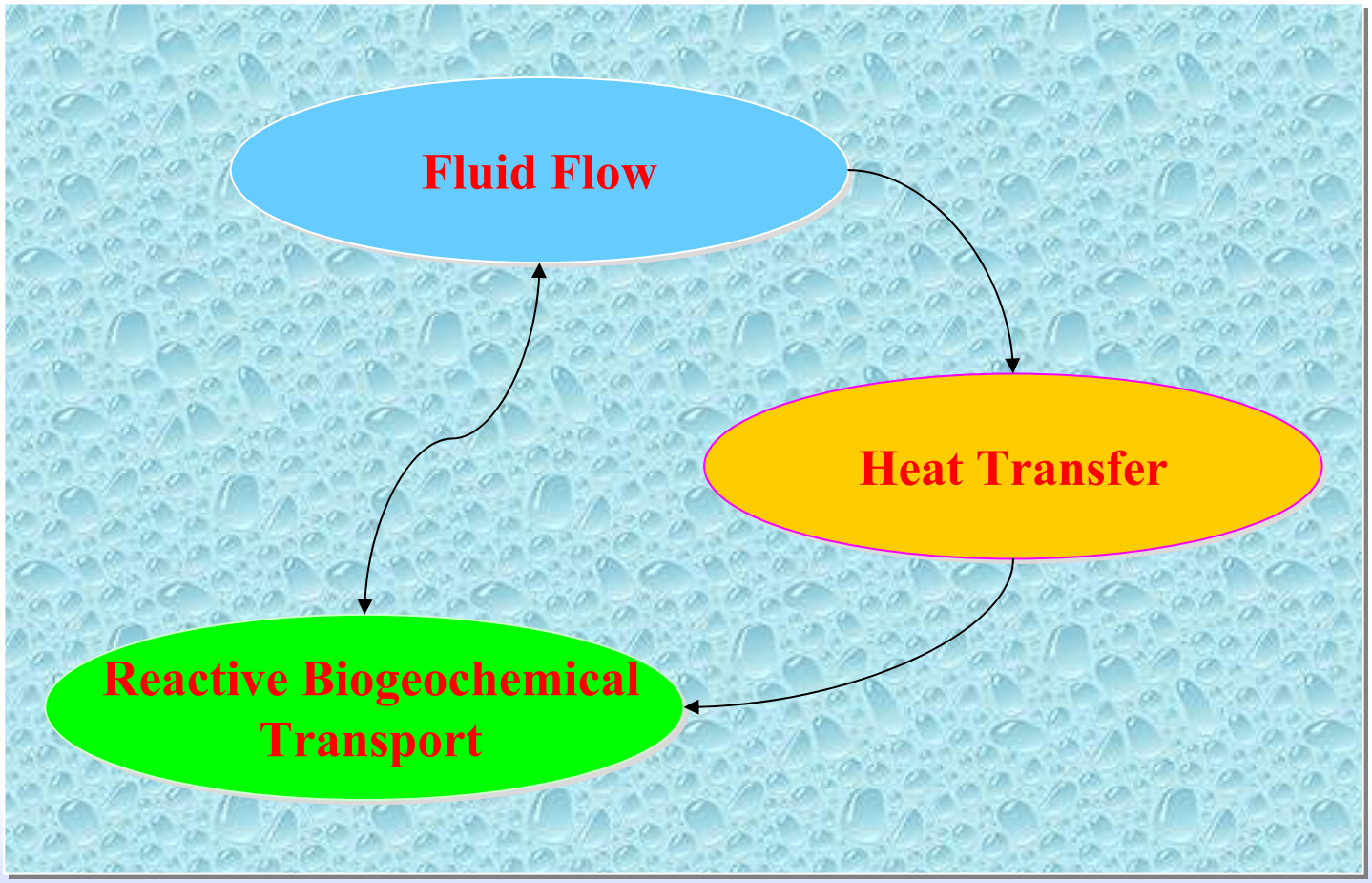
FRC Workshop, Oak Ridge Tennessee

October 18-20, 2004

OUTLINE

- What Dose HYDROGEOCHEM 5.0 DO?
- Demonstrative Examples
- General Paradigm for Biogeochemistry
- Discussions

What Dose HYDROGEOCHEM 5.0 Do?



Demonstrative Examples

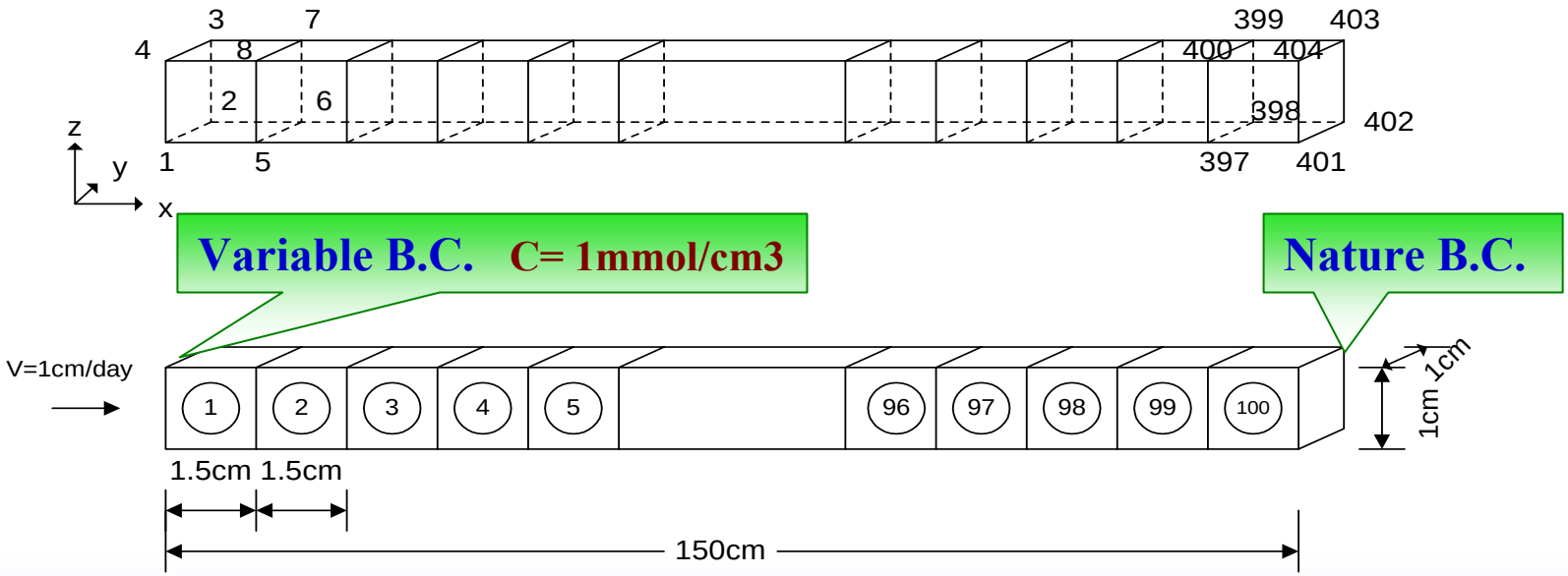
- **Example 1: Adapted from Fan Zhang's Dissertation**
  - ✓ Use a simple 1-D reactive transport problem to show the need of various numerical options and coupling strategies for both research and practical applications.
- **Example 2**
  - ✓ Use a 3-D flow and reactive transport problem to illustrate the design capability of the model to deal with geochemical processes controlled by comprehensive reaction networks
- **Example 3**
  - ✓ Use a 3-D flow and reactive transport problem to illustrate the design capability of the model to deal with geochemical processes governed by comprehensive reaction networks under non-isothermal conditions

Example 1: 1-D Simple Reactive Transport Problems

$C \leftrightarrow S,\ K_d = 1.0$

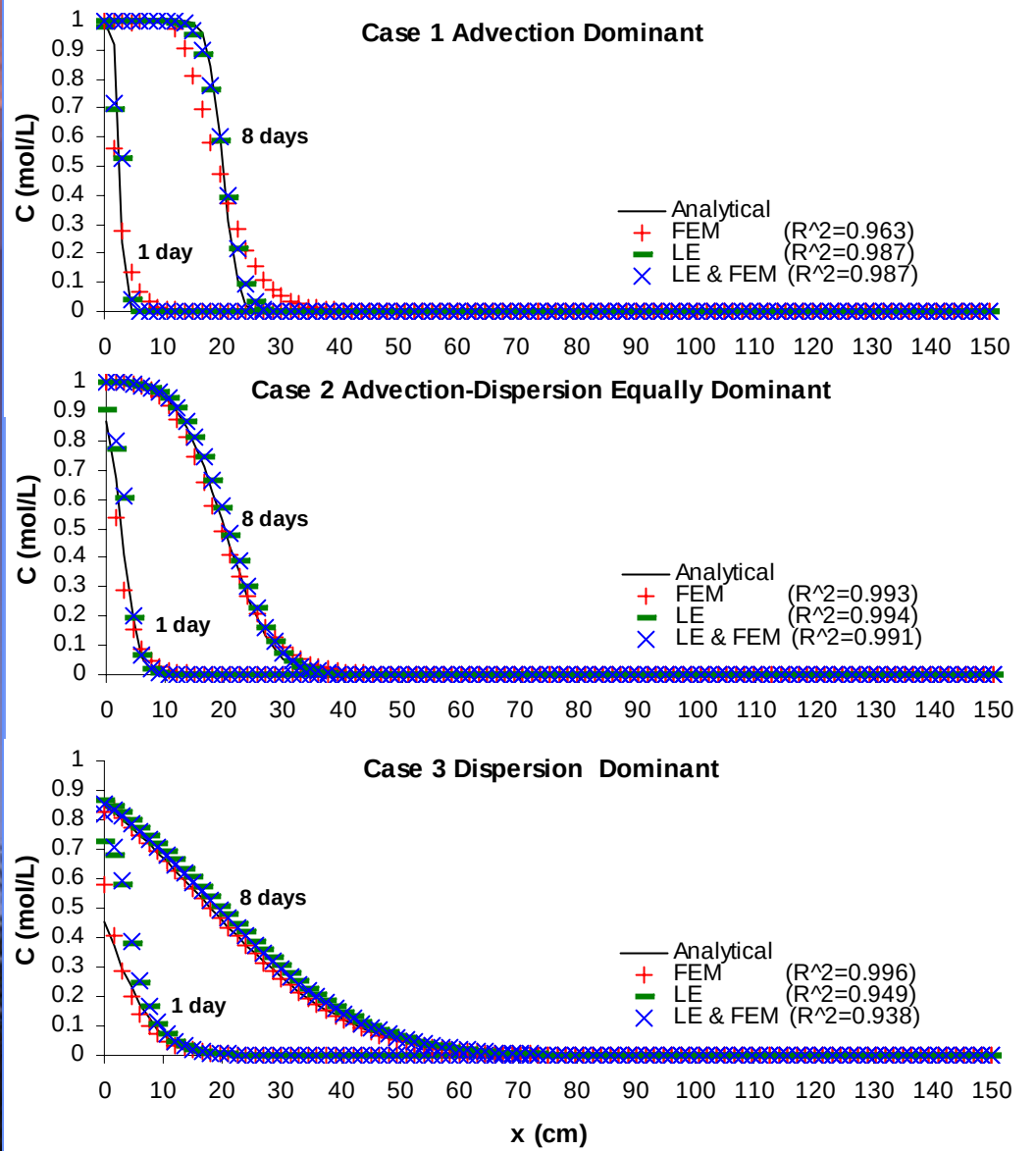
$C \leftrightarrow S,\ K_d = 1.0$

$C \leftrightarrow S,\ K_f = K_b = 10^{-3}$



Problem Definition and Boundary Conditions for Example 1

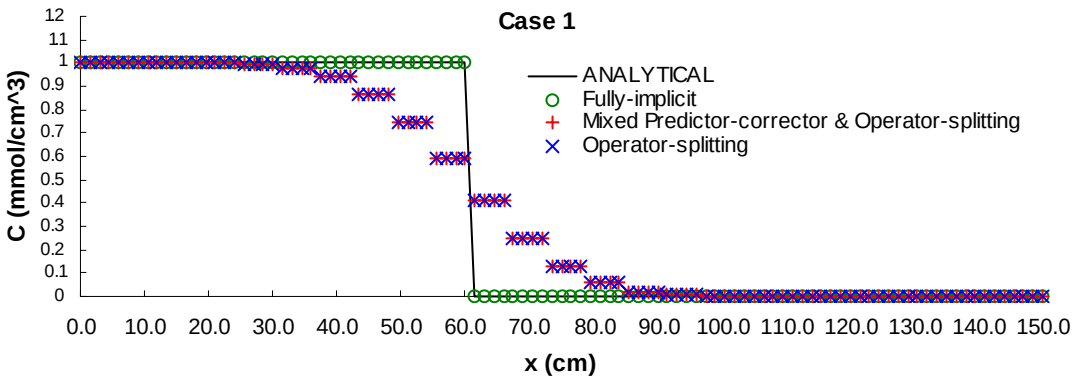
Comparison of Three Numerical Options

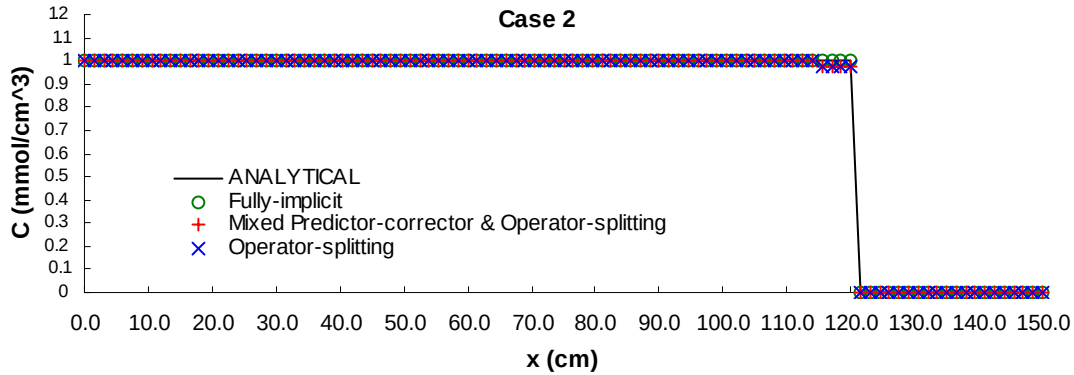


It is seen that: (1) for advection dominant, LE and LE-FEM give more accurate simulation than FEM; (2) for advection-dispersion equally-dominant, all three options yield almost same accurate results with LE giving slightly better results than FEM, and FEM yielding slightly better results than LE/FEM; (3) for dispersion dominant, all three options give approximately the same accurate simulation at time = 8 days but with FEM giving better results than the LE and LE/FEM at time = 1 day.

Therefore, for research applications, when accuracy is the primary concerns, LE and LE/FEM are preferred for advection dominant transport problems, but FEM is preferred for dispersion dominant transport problems. For practical applications, when the efficiency is the primary concern, LE is preferred under all transport conditions because it gives the most efficient computation in term of CPU time.

Comparison of three coupling strategies



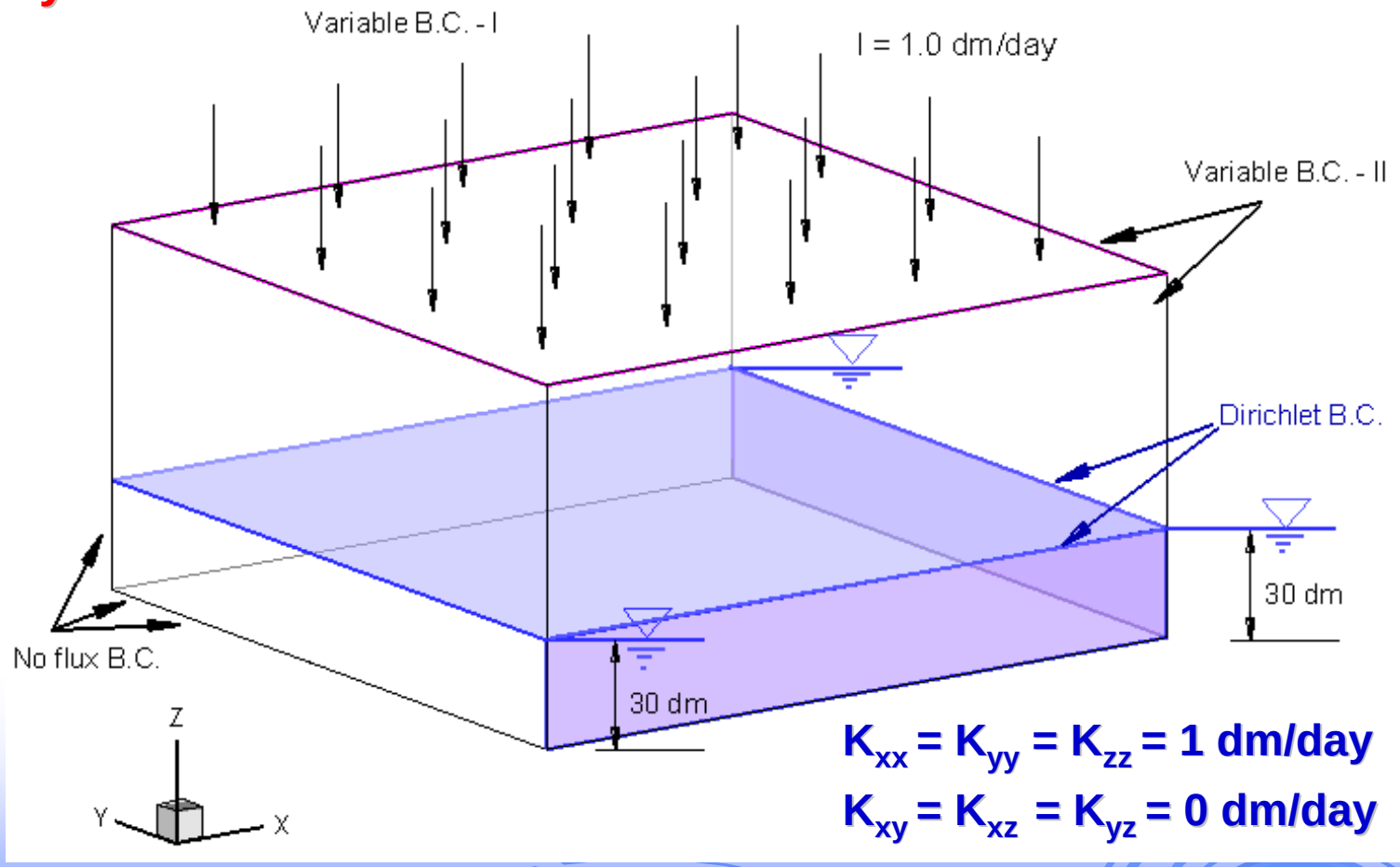


It is seen that the FI gives accurate solution for both cases. However, simulation accuracy using the mixed PC/OP and OP varies. For Case 1 fast equilibrium reaction, PC/OP and OP are not accurate. For Case 2 slow kinetic PC/OP and OP are nearly as accurate as FI.

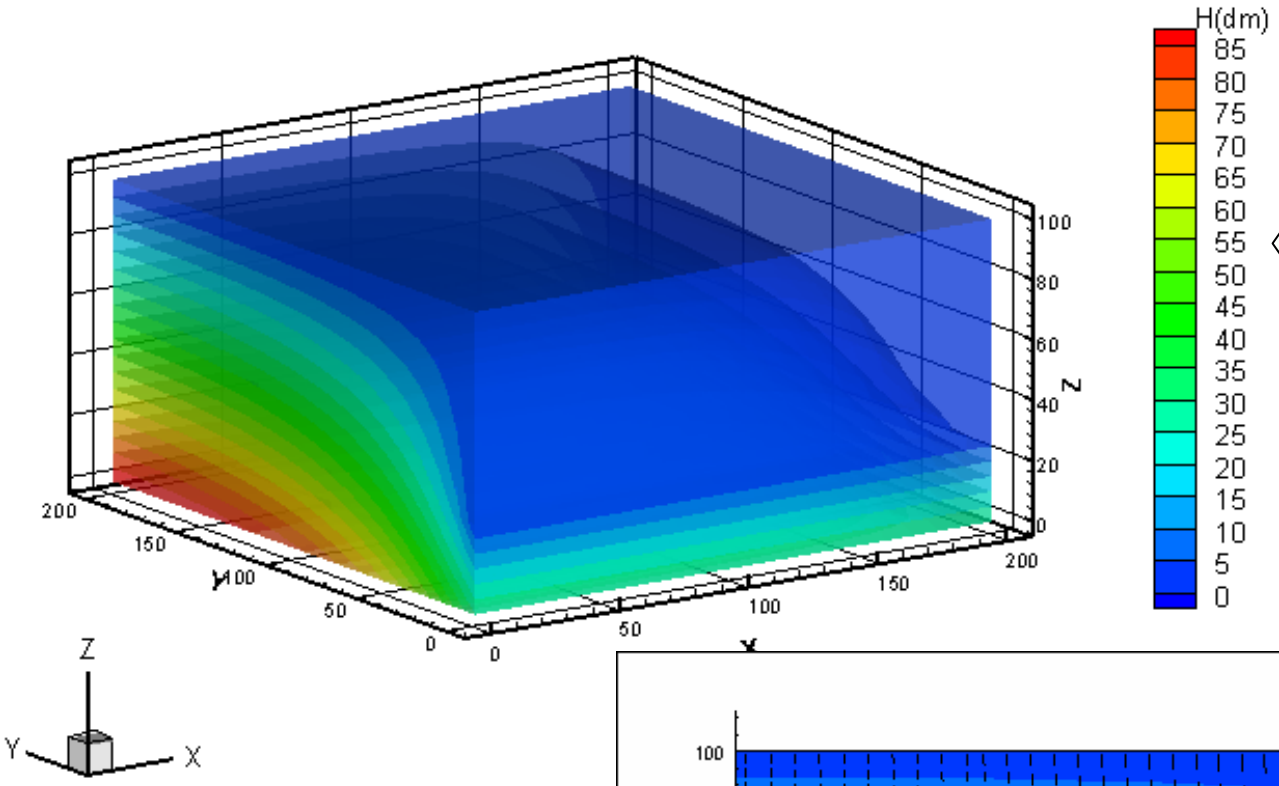
For research applications when accuracy is the primary concern, FI is recommended for problems with any rate of reactions, especially for fast equilibrium reactions. Fro practical applications, because the FI is computationally more demanding, PC/OP and OP are recommended for problems with slow kinetic reactions, but FI is preferred for problems with fast equilibrium reactions because PC/OP and OP simply cannot give enough accurate simulations.

Example 2: 3-D Flow and Chemical Transport with Complexation, Adsorption, Ion-Exchange and Mineral Dissolution Reactions

Steady-state Flow

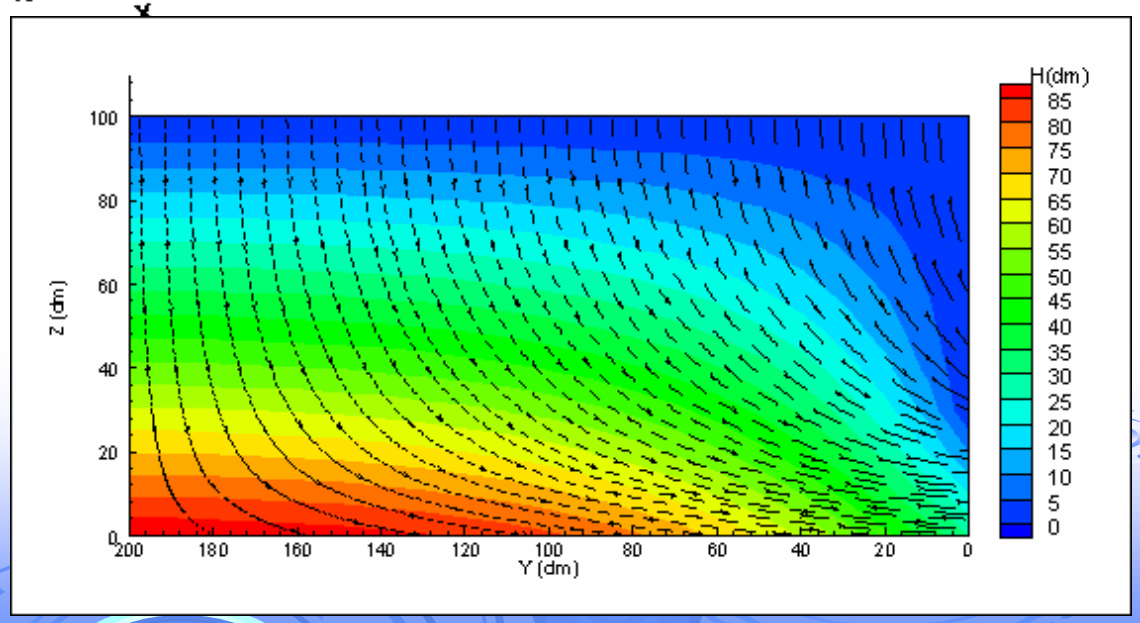


Flow Boundary Conditions and Initial Condition for Example 2



Steady-State Pressure Head

Velocity Fields along Cross-Section x = 0 and Its animation (velocity.avi)

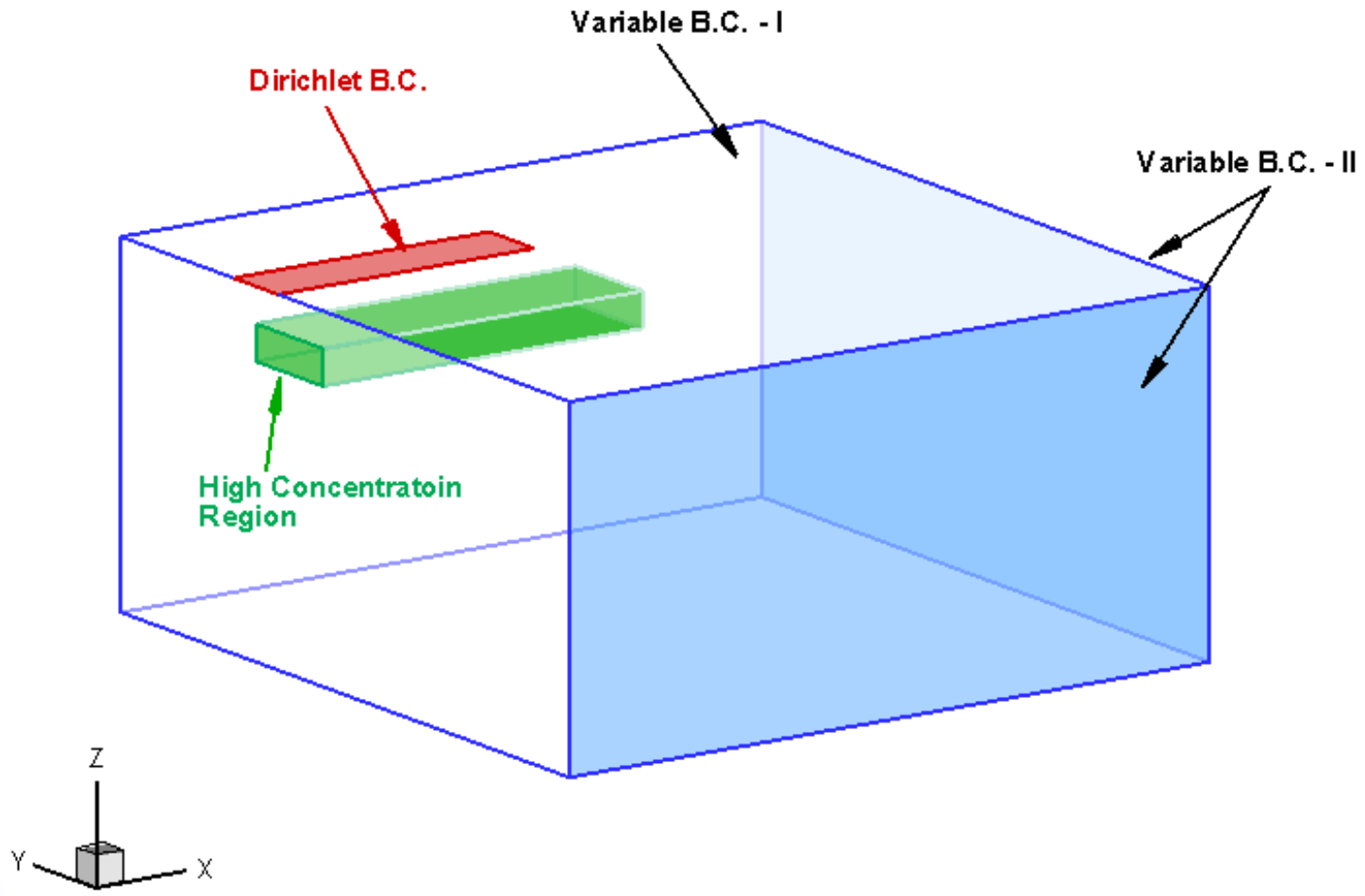


Transient Reactive Biogeochemical Transport

Reaction	#	Reaction Constants
Mineral Dissolution and Surface Site Formation Reactions		
$M \leftrightarrow C_1 - 3C_2$	(R1)	$k_1^f = 0.05$
$M \leftrightarrow S_1$	(R2)	User specified partition between bulk and surface metal ions as expressed by equation (M1)
Aqueous Complexation Reactions		
$C_3 \leftrightarrow C_4 + C_5$	(R3)	$\text{Log } k_3^f = 2.03$, $\text{Log } k_3^b = 20.00$
$C_6 + C_5 \leftrightarrow C_7$	(R4)	$\text{Log } K_4^e = 12.32$
…	…	…
$4C_2 + C_5 \leftrightarrow C_{26}$	(R23)	$\text{Log } K_{23}^e = 23.10$
$C_2 + C_{27} \leftrightarrow C_{28}$	(R24)	$\text{Log } K_{24}^e = 14.00$
Adsorption-Desorption Reactions		
$S_1 \leftrightarrow S_2 + C_2$	(R25)	$\text{Log } K_{25}^e = -11.60$
…	…	…
$S_1 - C_2 + C_4 \leftrightarrow S_7$	(R30)	$\text{Log } k_{30}^f = -0.99$, $\text{Log } k_{30}^b = 1.70$
$S_1 + C_2 + C_5 + C_6 \leftrightarrow S_8$	(R31)	$\text{Log } k_{31}^f = 25.0$, $\text{Log } k_{31}^b = 1.19$
Ion-Exchange Reactions		
$C_{29} + 2\ \text{site-}C_{30} \leftrightarrow \text{site-}C_{29} + 2C_{30}$	(R32)	$\text{Log } k_{32}^f = -0.75$, $\text{Log } k_{32}^b = -0.5$
$C_6 + 2\ \text{site-}C_{30} \leftrightarrow \text{site-}C_6 + 2C_{30}$	(R33)	$\text{Log } k_{33}^e = 0.6$

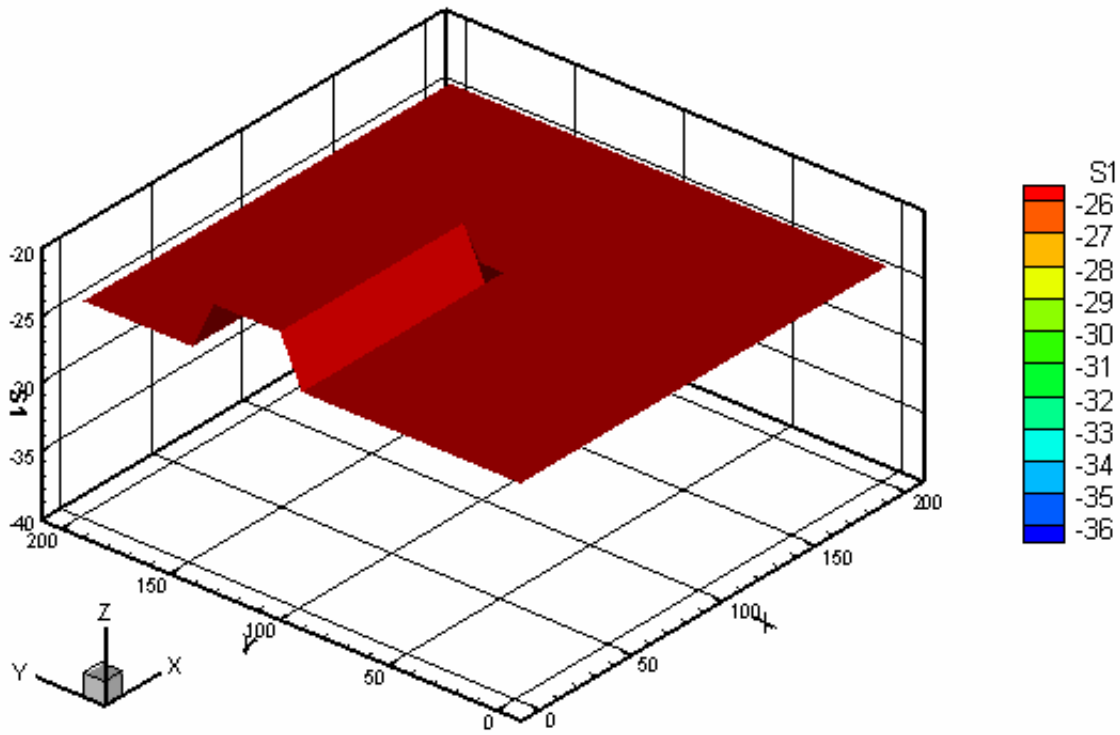
A Comprehensive Reaction Network

- **Reactions: 33**
  - ✓ 25 fast equilibrium reactions
  - ✓ 8 slow kinetic reactions
- **Species: 42**
  - ✓ 29 dissolved species plus H_2O
  - ✓ 8 adsorbed
  - ✓ 3 ion-exchanged
  - ✓ 1 mineral
- **Governing Equations**
  - ✓ A total of 42 species, thus need 42 equations
  - ✓ The activity of H_2O is assumed 1.0 and its concentration is approximately 55 M, thus only need 41 equations
  - ✓ 29 of the 41 equations are transport equations for 29 dissolved species

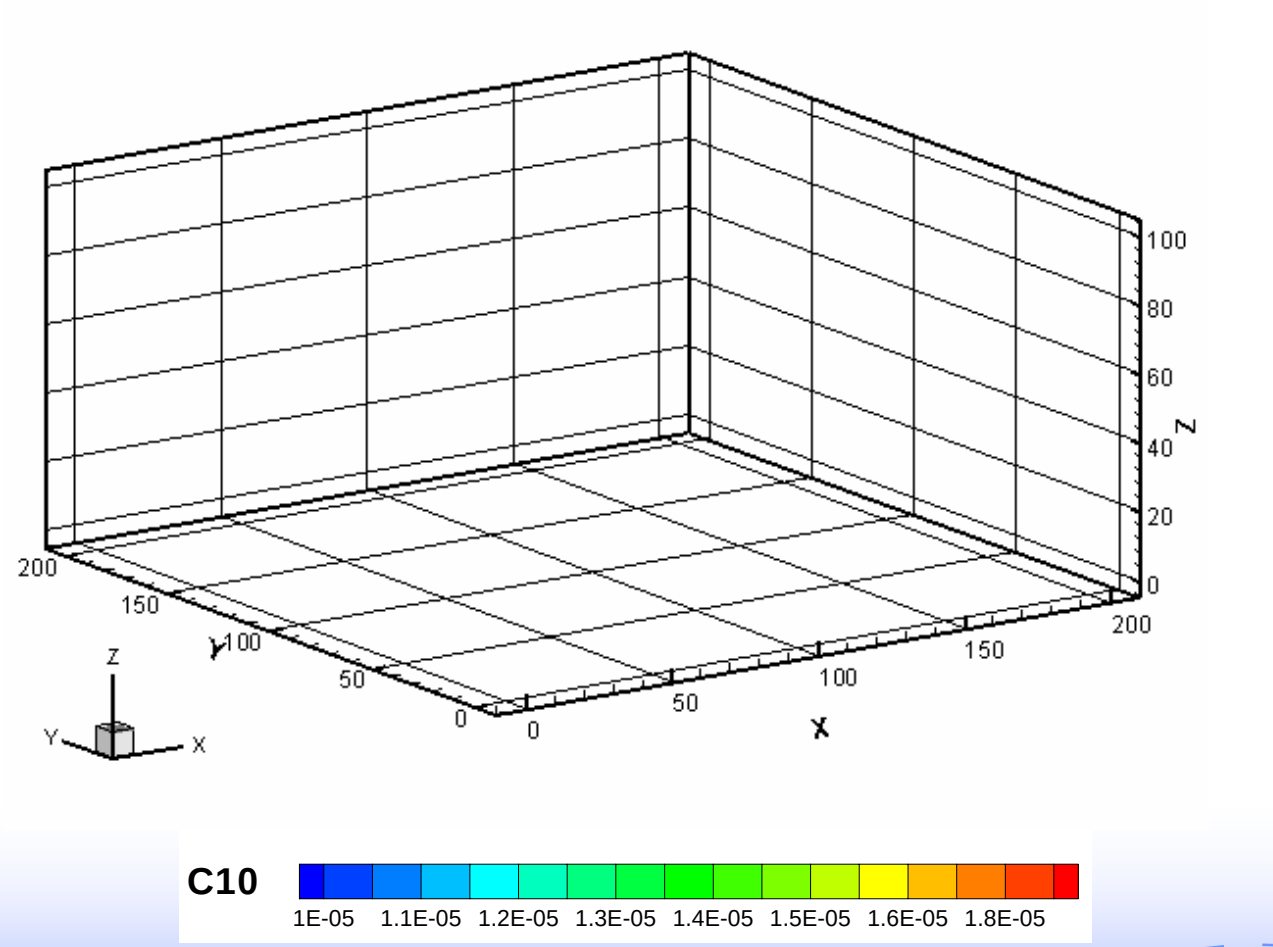


Transport Boundary Conditions and Initial Condition for Example 2

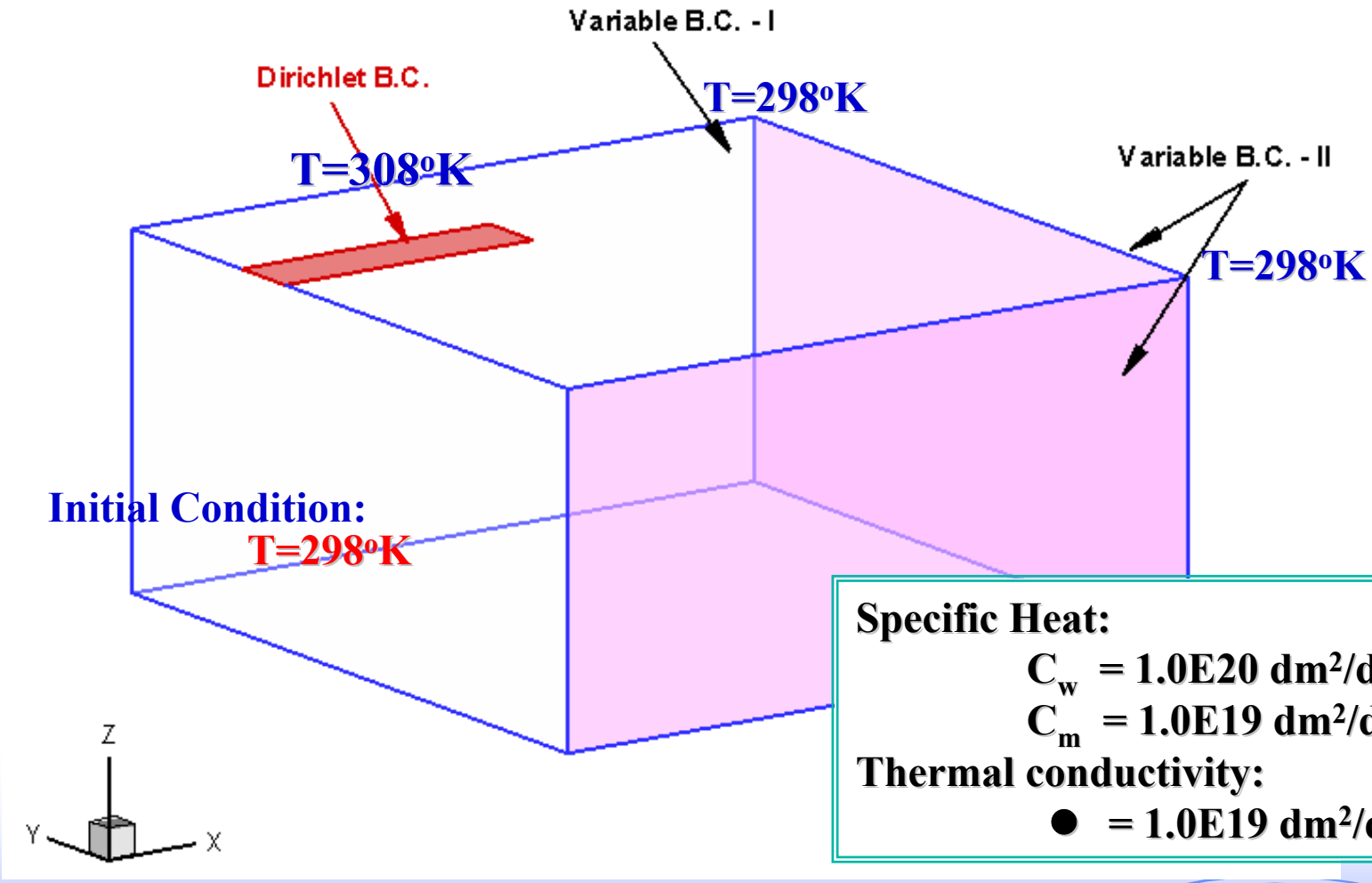
Animation of Concentration Contours of Logarithm value for Sorbed Species S_1 along Cross-Section z = 90dm of the Domain at Various Time Steps for Example 2 (S1.AVI)



Animation of Concentration Contours for Species C10 at Various Time Steps for Example 2 (C10.avi)



Example 3: Same as Example 2 except with Heat Transfer



Specific Heat:

C_w = 1.0E20 $dm^2/day^2/K$

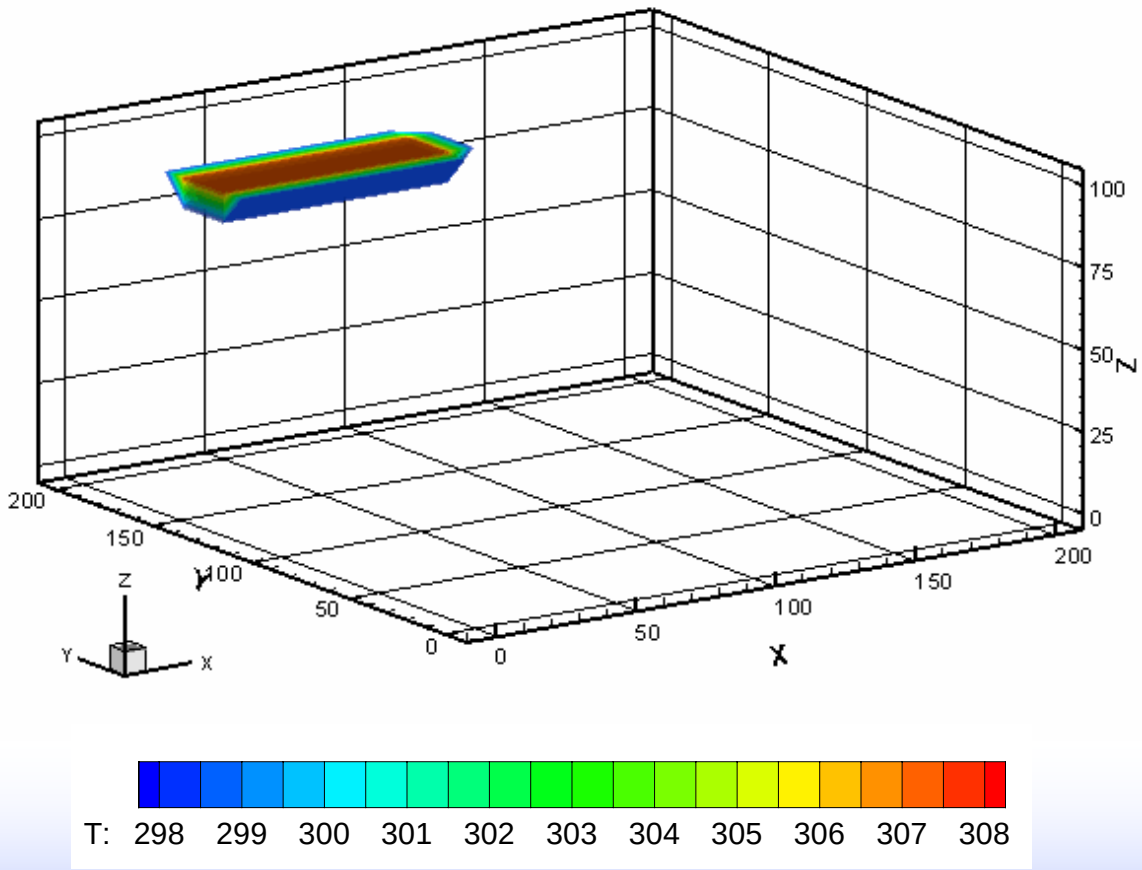
C_m = 1.0E19 $dm^2/day^2/K$

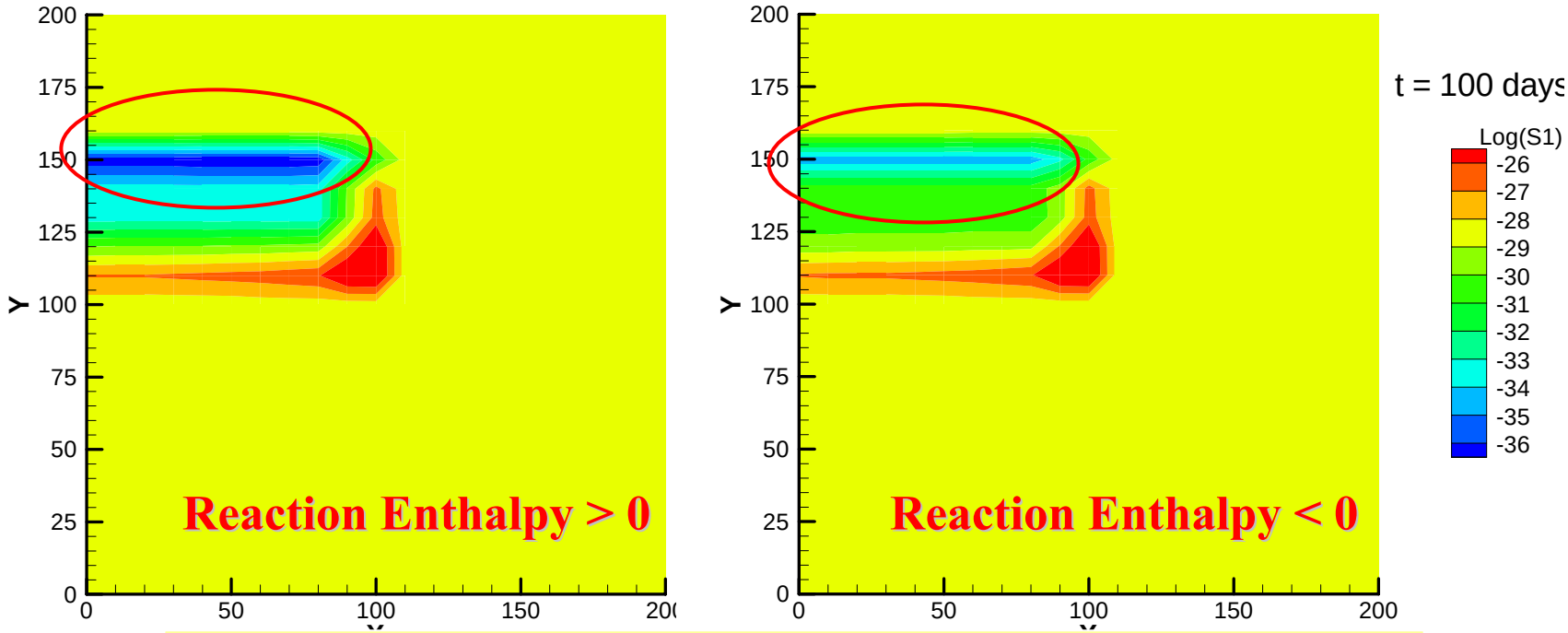
Thermal conductivity:

- = 1.0E19 $dm^2/day^2/K$

Heat Transfer Initial and Boundary Conditions for Example 3

Animation of Temperature Contours for Heat Transfer for Example 3 (Temperature.avi)





$$S1 + 3C2 + C5 \leftrightarrow S4 \quad ; \quad \text{Log } K_{27}^{e} = 30.48 \qquad (R27)$$

Since a high temperature increases reaction extent with a positive enthalpy and vice versa, the concentration of reactant S1 decreases faster with positive enthalpy than that with negative enthalpy.

General Paradigm for Biogeochemistry

- **Reaction-based approaches in which biogeochemical processes are modeled with reaction networks** (physical processes such as a mass transfer can also be conceptualized as a reaction, e.g. $C_m \leftrightarrow C_{im}$)
- **Fast equilibrium reactions are described with**
  - ✓ Mass action or
  - ✓ Users' specified algebraic equations in SUBROUTINE USERMA
    - Reaction sites
    - ----
    - Langmuir nonlinear isotherm
    - Your own algebraic equations
- **Slow kinetic reactions are described with**
  - ✓ Elementary rate or
  - ✓ User' specified rate equations in SUBROUTINE RUSRLW
    - Monod kinetic – single, dual, or triple Monod kinetics with and/or without time lag and inhibition
    - -----
    - N-th order
    - Your own rate equations

Users' Algebraic Equations and Rate Equations

SUBROUTINE USRMA

```
    ----
   ELSEIF(ITYPE.EQ.-9)THEN
C *** Langmuir isotherm 1
      A1=ACTIV(1)
      A2=ACTIV(2)
      A3=ACTIV(3)
      P1=PARUS(1,IES)
      P2=PARUS(2,IES)
      RE=A3-P1*A1*A2/(P2+A1)
    ELSEIF(ITYPE.EQ.-10)THEN
C ***  Your first algebraic equation
            -----
      RE=---
    ELSEIF(ITYPE.EQ.-11)THEN
C*** Your second algebraic equation
            -----
      RE=----
    ENDIF
```

SUBROUTINE RUSRLW

```
    ----
   ELSEIF(KRTYPK.EQ.13) then
C  ***   n-th order
      P1=PARLAW(1,K)
      PN=PARLAW(2,K)
      A1=ACTIV(1)
      RRATE(K)=P1*A1**PN
   ELSEIF(krtypk.eq.14) THEN
C *** Your first rate equation
         ----
         ----
      RRATE(K)=---
   ELSEIF(krtypk.eq.15) THEN
C *** Your second rate equation
         -----
         -----
      RRATE(K)=---
   ENDIF
```

➢ Diagonalization of Reaction Network

- ✓ **Greatly reduce transport equations**
- ❖ **For the demonstrative example, reduce from 29 to 11: 8 for non-conservative components and 3 for mobile kinetic-variables**
- ✓ **The other 30 equations are: 25 mass action or algebraic equations for 25 equilibrium reactions and 5 ordinary differential equation for 5 immobile kinetic-variable**
- ✓ **Each kinetic-variable measures one slow kinetic reaction if all kinetic reactions are linearly independent**
- ❖ **Reaction rates can be formulated and parameterized one by one.**

Discussions

- The inclusion of three numerical options and three coupling strategies enables the application of the model to both research and practical problems under different transport conditions and various rates of reaction.

- The general paradigm for geochemistry makes it possible to model problems with comprehensive reaction networks composing of both
  - ✓ fast equilibrium reactions: (i) mass actions and (ii) users' specified algebraic equations and
  - ✓ slow kinetic reactions: (i) elementary rates, (ii) Monod kinetics, (iii) dual Monod kinetics, (iv) triple Monod kinetics, (v) n-th order rate, and (vi) users' specified rate equations.

- Reaction-based approaches: The rate equations are descriptive of reactions, which is potentially more universal, rather then descriptive of species rates, which is by natural problem specific.
- Diagonalization approaches greatly reduce the number of transport equations and enable the formulation of rate equations, one reaction at a time.
- The model is designed for modeling coupled fluid flow, thermal transport, and reactive biogeochemical transport.

- The caveat is: we must transform our understanding and hypotheses into reaction networks. This is by no means easy. However, if we don't or can't, our understanding is incomplete or false.

Thank You