



Benchmark
Reactive Transport

http://www.gdrmommas.org/ex_qualifications.html

Committee

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Table of Contents

Introduction	3
Presentation of the flow, transport and chemical phenomena:	4
Flow phenomena	4
Transport equations	4
General description for chemistry	5
Geometry	7
Characteristics of the media	7
Geometry for 1D problem	8
Geometry for 2D problem	9
Easy test case	11
Medium test case	13
Instantaneous equilibrium reactions:	13
Kinetic reaction:	13
Hard test case	15
Instantaneous equilibrium reactions:	15
Kinetic reactions:.....	15
CPU evaluation	17
Expected results	18
Results for 1D flow	18
Results for 2D flow	18

Introduction

The objective of this benchmark is to compare the numerical methods used for solving a reactive transport problem in porous media. According to the interests of GdR MoMaS, the reactive transport problem should be representative of the problems encountered in nuclear waste disposal simulations. We want to interest a community as large as possible: geochemistry, hydro geology, numerical methods, applied mathematics... Nevertheless, the high complexity of both transport and chemical phenomena occurring in such a system may be an obstacle for some researcher who may not be familiar with hydro-geological and geochemical concepts. The problems proposed here are built on the same mathematical concepts as real hydro-geochemical problems, but their description has been simplified. The difficulty for building this benchmark was also to provide a sufficient simple problem without loss of mathematical and numerical difficulties.

This benchmark consists in three independent parts, ranked by complexity:

Easy

Medium

Hard

Each part consists of a 1D and a 2D reactive transport problem. The flow and transport phenomena are the same for the three parts. From one part to the other, some chemical phenomena are added increasing the difficulties.

Presentation of the flow, transport and chemical phenomena:

Flow phenomena

Darcy's law and the continuity equation give the relations between pressure (h) and pore velocity (u).

$$\begin{cases} \omega \mathbf{u} = -K \nabla(h) \\ \nabla(\omega \mathbf{u}) = 0 \end{cases}$$

Note that for 1D problem, the continuity equation leads to:

$$\omega \mathbf{u} = \text{cste}$$

The flow field is not affected by chemical phenomena and is then unchanged during all the experiment.

Transport equations

$$\omega \frac{\partial (T_{M_j} + T_{F_j})}{\partial t} = -\nabla(\omega \mathbf{u} T_{M_j}) + \nabla(\bar{\mathbf{D}} \cdot \nabla T_{M_j}) - \omega \sum_k [\mathbf{a}c_{k,j} \cdot f_k(C_i, Cc_k)]$$

The dispersion tensor D is given by:

$$\bar{\mathbf{D}} = \begin{bmatrix} \alpha_T \cdot \omega \cdot |\mathbf{u}| + (\alpha_L - \alpha_T) \cdot \omega \frac{u_x^2}{|\mathbf{u}|} & (\alpha_L - \alpha_T) \cdot \omega \frac{u_x \cdot u_y}{|\mathbf{u}|} \\ (\alpha_L - \alpha_T) \cdot \omega \frac{u_x \cdot u_y}{|\mathbf{u}|} & \alpha_T \cdot \omega \cdot |\mathbf{u}| + (\alpha_L - \alpha_T) \cdot \omega \frac{u_y^2}{|\mathbf{u}|} \end{bmatrix}$$

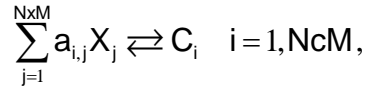
$$\bar{\mathbf{D}} = \alpha_T \cdot \omega \cdot |\mathbf{u}| \mathbf{I} + (\alpha_L - \alpha_T) \cdot \omega \frac{\mathbf{u} \otimes \mathbf{u}}{|\mathbf{u}|}$$

where T_{M_j} is the total mobile concentration for each component and T_{F_j} is the total immobile concentration. $\sum_k [\mathbf{a}c_{k,j} \cdot f_k(C_i, Cc_k)]$ is the source-sink term for chemical phenomena described with a kinetic approach. $\mathbf{a}c_{k,j}$ are stoichiometric coefficient of component X_j for the formation of the kinetic species Cc_k ; $f_k(C_i, Cc_k)$ is the rate of the reaction of formation of Cc_k .

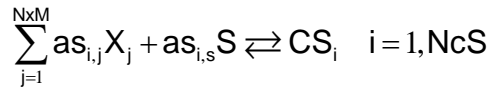
General description for chemistry

Instantaneous equilibrium

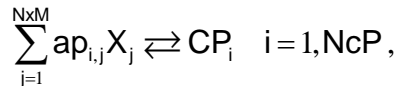
We consider a set of chemical reactions among several species. After relabeling, we assume that each reaction may be written so that a set of *components* gives rise to a single product. We also distinguish between *mobile* (in solution) and *immobile* (on the solid matrix) species. Reactions among mobile species are written as



where the X_j , $j=1, \dots, NxM$ are the (mobile) components, and the C_i are the secondary species, and reactions between mobile and immobile species are written as (we assume a single immobile component S)



Mobile components may react each other to form some precipitated species which are non mobile:



Each chemical reaction gives rise to a mass action law, and we have a conservation law for each component.

Conservation laws used for transport equations are:

$$T_{M_j} = X_j + \sum_{i=1}^{NcM} a_{i,j} C_i \quad \text{and} \quad T_{F_j} = \sum_{i=1}^{NcS} as_{i,j} \cdot CS_i + \sum_{i=1}^{NcP} ap_{i,j} \cdot CP_i \quad j=1, \dots, NxM$$

$$T_{M_S} = 0 \quad \text{and} \quad T_{F_S} = S + \sum_{i=1}^{NcS} as_{i,s} \cdot CS_i$$

For each component, conservation laws are:

$$T_j = X_j + \sum_{i=1}^{NcM} a_{i,j} \cdot C_i + \sum_{i=1}^{NcS} as_{i,j} \cdot CS_i + \sum_{i=1}^{NcP} ap_{i,j} \cdot CP_i$$

$$TS = S + \sum_{i=1}^{NcS} as_{i,s} \cdot CS_i$$

For each aqueous species C_i , the mass action law is:

$$C_i = K_i \cdot \prod_{j=1}^{NxM} X_j^{a_{i,j}}$$

For each fixed species CS_i , the mass action law is:

$$CS_i = K_{s_i} \cdot \prod_{j=1}^{NxM} X_j^{as_{i,j}} \cdot S^{as_{i,s}}$$

For each precipitated species CP_i , a solubility product must be respected:

$$\text{if } 1 > Kp_i \cdot \prod_{j=1}^{N \times M} X_j^{ap_{i,j}} \text{ then } CP_i = 0$$

$$\text{else } Kp_i \cdot \prod_{j=1}^{N \times M} X_j^{ap_{i,j}} = 1$$

Kinetic description

For both medium and hard test cases, chemical phenomena are described using a combination of instantaneous equilibrium and kinetic formulation. In this benchmark, chemical species described by a kinetic approach are not mobile. The formation for the majority of species is described using the instantaneous formulation presented previously. The formation of some species is described using a kinetic formulation. The reaction rate for these species leads to an ordinary differential equation:

$$\frac{dC_{C_k}}{dt} = f_k(C_i, C_{C_k})$$

The specific formulations of the reaction rates and the source sink term will be given for each test case.

Geometry

Characteristics of the media

Each problem, 1D or 2D is made using two media, A and B. Medium A is a highly permeable medium, with low porosity and low reactivity. Medium B is a low permeability medium with high porosity and high reactivity.



Medium A



Medium B



Impermeable boundary



Inflow zone



Outflow zone

Figure 1: Legend of the schemes for 1D and 2D problem

Table 1 : Characteristics of the media

	Medium A	Medium B
Porosity ω (-)	0,25	0.5
Permeability K ($L.T^{-1}$)	10^{-2}	10^{-5}
Concentration $[T_S]$	1	10

Two values of dispersivity are proposed in order to test the codes both under advective (Table 2) and dispersive transport (Table 3) conditions.

Table 2 : Dispersivity of the media – Advective case

	Medium A	Medium B
Dispersivity α_L (L)	10^{-2}	$6 \cdot 10^{-2}$
Dispersivity α_T (L)	10^{-3}	$6 \cdot 10^{-3}$

Table 3 : Dispersivity of the media – Dispersive Case

	Medium A	Medium B
Dispersivity α_L (L)	10	60
Dispersivity α_T (L)	1	6

Geometry for 1D problem

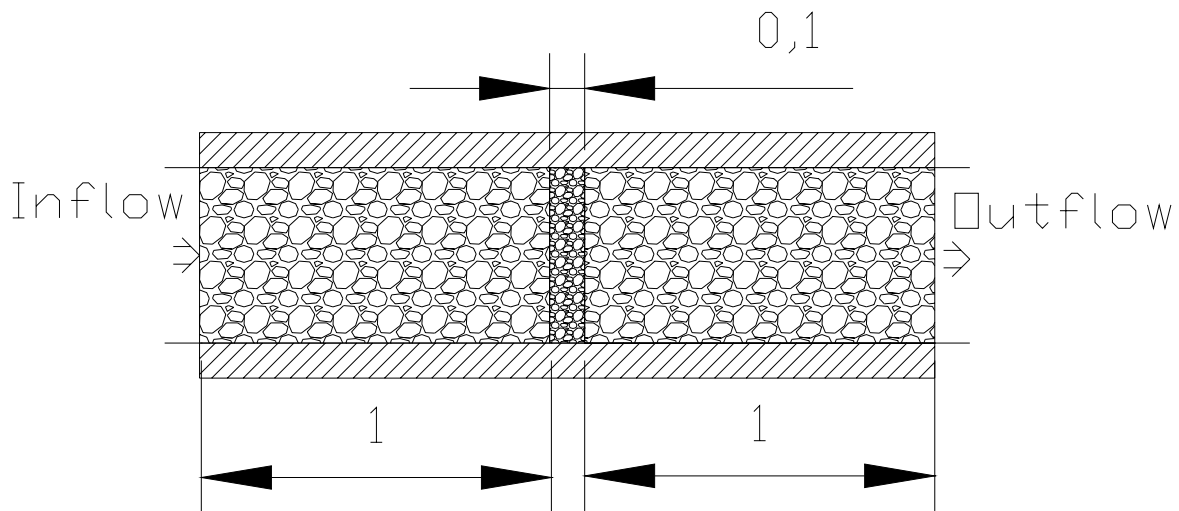


Figure 2: Scheme of the 1D problem

Flow conditions:

For the 1D problem, the pore velocity is given by:

$$\omega \cdot \mathbf{u} = 5.5 \cdot 10^{-3} \text{ L} \cdot \text{T}^{-1} \text{ over all the domain}$$

Boundary conditions:

In order to be close of realistic cases, boundary and initial conditions are not expressed for fundamental variables *i.e.* component concentrations. Indeed, chemical analysis can provide quite easily a measure of the total concentration or of the total dissolved concentration of each component.

Imposed concentrations for the inflow boundary:

$$T_j(x=0, t) = T_j^{\text{inj}} \text{ or } T_j(x=0, t) = T_j^{\text{less}}$$

Zero concentration gradient at outflow boundary

$$\nabla(Td_j)_{x=2,1,t} = 0 \quad \forall [j \in \{1, \dots, N \times A\}]$$

Injection period correspond to specific inflow concentrations depending on the test case. All the injection periods are 5000 T long.

Leaching period correspond to specific inflow concentrations depending on the test case. Leaching periods are more than 1000 T long. If needed, leaching periods can be prolonged after 1000 T to reach the following condition: the end of the leaching period, 99.9% of the injected pollutant (X_1 , X_3 and X_5 depending on the test case) as been removed out of the domain.

Geometry for 2D problem

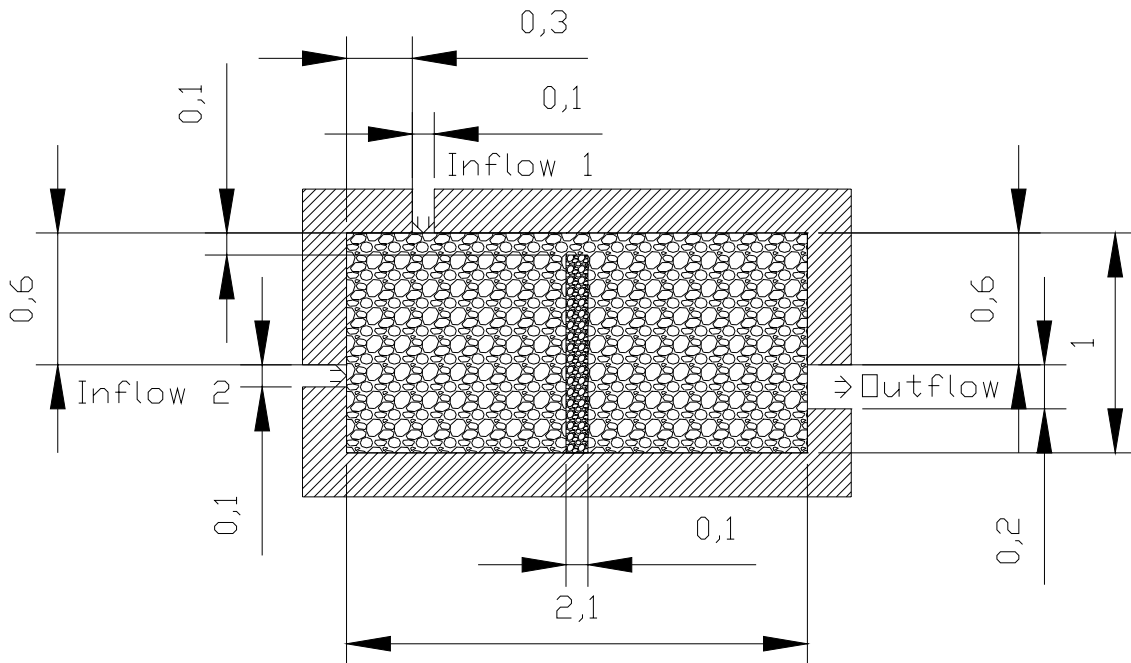


Figure 3: Scheme of the 2D problem

Point $x = 0.0$; $y = 0.0$ is at left bottom corner of the flow domain

In order to show more clearly the flow in the 2D domain, we give an illustration of the velocity field (Figure 4).

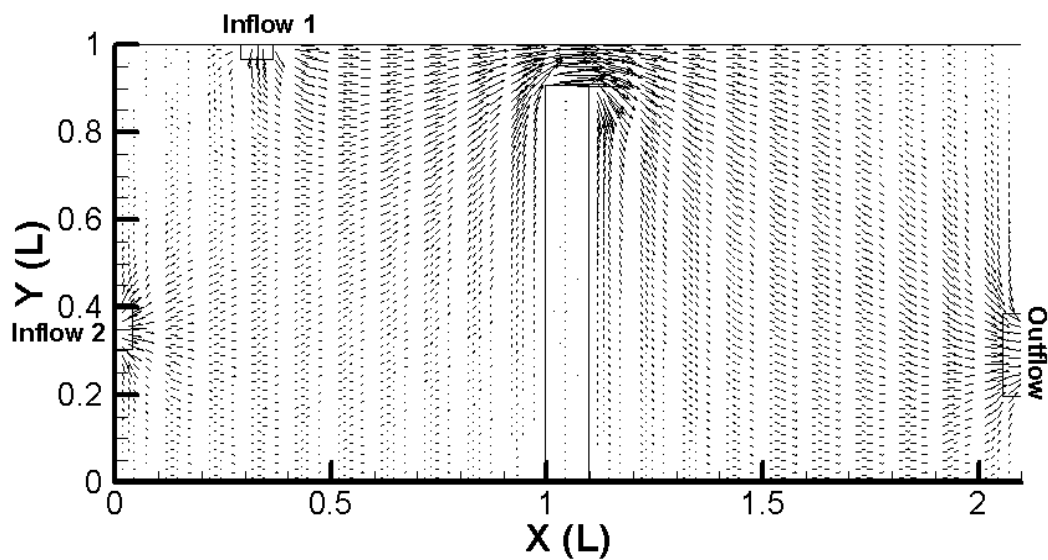


Figure 4 : Illustration of the velocity field

Boundary conditions for flow:

Flow velocities at inflow 1 and 2 are equal:

$$\omega \cdot u_1 = \omega \cdot u_2 = 2.25 \cdot 10^{-2} \text{ L} \cdot \text{T}^{-1}$$

Pressure head is imposed at outflow:

$$H_{\text{Outflow}} = 1 \text{ L}$$

All other boundary conditions are “no flow”: $\omega \cdot u \cdot n_{\text{Impermeable}} = 0$

Boundary conditions for transport

Imposed concentrations for the inflow boundary:

$$T_j(\text{Inflow}_i, t) = T_j^{\text{inj}} \text{ or } T_j(\text{Inflow}_i, t) = T_j^{\text{less}}$$

Injection concentration can differ for inflow zone 1 and 2, and will be given in the description of the 3 different cases.

Zero concentration gradient at outflow boundary:

$$\nabla(Td_j)_{\text{Outflow},t} = 0 \quad \forall [j \in \{1, \dots, N \times A\}]$$

Zero total flux for impermeable boundary:

$$\text{No convective flux because } \omega \cdot u \cdot n_{\text{Impermeable}} = 0$$

$$\text{No diffusive flux: } \nabla(Td_j)_{\text{Impermeable},t} = 0 \quad \forall [j \in \{1, \dots, N \times A\}]$$

The injection period correspond to specific inflow concentrations depending on the test case. All the injection periods are 5000 T long. Component X_2 is always injected at the Inflow zone 1. Depending on the test case, some component (X_1 , X_3 or X_5) are injected at the Inflow zone 2.

Leaching period correspond to specific inflow concentrations depending on the test case. Leaching periods are more than 1000 T long. If needed, leaching periods can be prolonged after 1000 T to reach the following condition: the end of the leaching period, 99.9% of the injected pollutant (X_1 , X_3 and X_5 depending on the test case) as been removed out of the domain.

Easy test case

The chemical phenomena for the easy test case are described using instantaneous equilibrium only. Table 4 shows the stoichiometric coefficients and equilibrium constants for this test case.

Table 4 : Equilibrium for easy test case

	X ₁	X ₂	X ₃	X ₄	S	K
C ₁	0	-1	0	0	0	1.00E-12
C ₂	0	1	1	0	0	1
C ₃	0	-1	0	1	0	1
C ₄	0	-4	1	3	0	0.1
C ₅	0	4	3	1	0	1.00E+35
CS ₁	0	3	1	0	1	1.00E+6
CS ₂	0	-3	0	1	2	1.00E-01
Total (m.L⁻³)	T ₁	T ₂	T ₃	T ₄	TS	
Initial for medium A	0	-2	0	2	1	
Initial for medium B	0	-2	0	2	10	
Injection t ∈ [0,5000]	Imposed total concentration at inflow boundary					
Inflow for 1D	0.3	0.3	0.3	0		
Zone 1 for 2D	0.3	0.3	0.3	0		
Zone 2 for 2D	0.3	0.3	0.3	0		
Leaching t ∈ [5000,...]	Imposed total concentration at inflow boundary					
Inflow for 1D	0	-2	0	2		
Zone 1 for 2D	0	-2	0	2		
Zone 2 for 2D	0	-2	0	2		

How to read the equilibrium Tables?

These tables give the stoichiometric coefficients for mass action laws and conservation equation. Mass action laws are given for row and conservations for column.

Mass action law for the formation of species C₄ is:

$$C_4 = K_4 \cdot \prod_{j=1}^{N \times M} X_j^{a_{4,j}} = 0.1 \cdot X_1^0 \cdot X_2^{-4} \cdot X_3^3 \cdot X_4^1$$

Conservation equation for component X₃ is:

$$T_3 = X_3 + \sum_{i=1}^{NcM} a_{i,3} \cdot C_i + \sum_{i=1}^{NcS} as_{i,3} \cdot CS_i + \sum_{i=1}^{NcP} ap_{i,3} \cdot CP_i = X_3 + 1 \cdot C_2 + 1 \cdot C_4 + 3 \cdot C_5 + 1 \cdot CS_1$$

The domain, 1D or 2D, is initially at local equilibrium with the surface component **S** in the presence of aqueous components X_2 and X_4 .

During injection, component X_4 will be removed. Component X_1 is a perfect tracer, X_2 and X_3 will react together, with the surface **S** and with X_4 still present.

During leaching, X_1 and X_3 will be removed. X_2 and X_4 will react with the surface and with X_3 still present.

Medium test case

Instantaneous equilibrium reactions:

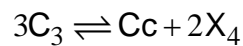
Some reactions are described under the instantaneous equilibrium assumption as described in Table 5:

Table 5 : Equilibrium for medium test case

	X ₁	X ₂	X ₃	X ₄	S	K
C ₁	0	-1	0	0	0	1.00E-12
C ₂	0	1	1	0	0	1
C ₃	0	-1	0	1	0	1
C ₄	0	-4	1	3	0	0.1
C ₅	0	4	3	1	0	1.00E+35
C ₆	0	10	3	0	0	1,00E+32
C ₇	0	-8	0	2	0	1,00E-04
CS ₁	0	3	1	0	1	1.00E+6
CS ₂	0	-3	0	1	2	1.00E-01
Total (m.L ⁻³)	T ₁	T ₂	T ₃	T ₄	TS	
Initial for media A	0	-3	0	1	1	
Initial for media B	0	-9	0	3	10	
Injection t ∈ [0,5000]	Imposed total concentration at inflow boundary					
Inflow for 1D	0.3	0.3	0.3	0		
Zone 1 for 2D	0.3	0.3	0.3	0		
Zone 2 for 2D	0.3	0.3	0.3	0		
Leaching t ∈ [5000,...]	Imposed total concentration at inflow boundary					
Inflow for 1D	0	-3	0	1.5		
Zone 1 for 2D	0	-3	0	1.5		
Zone 2 for 2D	0	-3	0	1.5		

Kinetic reaction:

A non mobile species Cc is formed:



This reaction is described using a kinetic formulation:

$$\frac{dCc}{dt} = \left(0.2 \frac{C_3^3}{X_4^2} - 1 \right) k \quad \text{with } Cc \geq 0$$

$$\text{if } 0.2 \frac{C_3^3}{X_4^2} \geq 1 \text{ then } k = 10^{-2} \text{ else } k = 10$$

Because stoichiometry of species C_3 is:

$$C_3 = -X_2 + X_4$$

we can express the stoichiometry of Cc as a combination of components X_2 and X_4 :

$$Cc = 3C_3 - 2X_4 = -3X_2 + X_4$$

This leads to the following kinetic source sink terms to be introduced into reactive transport equations for components X_2 and X_4 :

$$\text{For } X_2: \sum_k [ac_{k,2} \cdot f_k(C_i, Cc_k)] = -3 \frac{dCc}{dt}$$

$$\text{For } X_4: \sum_k [ac_{k,4} \cdot f_k(C_i, Cc_k)] = \frac{dCc}{dt}$$

Initial concentration is for all the domains:

$$Cc(z, t = 0) = 5.00$$

The domain, 1D or 2D, is initially at disequilibrium between components X_2 and X_4 , and species Cc . The surface component S is at equilibrium with aqueous components X_2 and X_4 , and related other species.

During injection, component X_4 will be removed. This leads to the dissolution of species Cc . Component X_1 is a perfect tracer, X_2 and X_3 will react together, with the surface S and with component X_4 still present.

During leaching, X_1 and X_3 will be removed. Injected X_2 and X_4 will react with the surface and with X_3 still present. Species CF will be formed when concentrations of X_2 and X_4 become high enough.

Hard test case

Instantaneous equilibrium reactions:

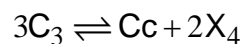
Some reactions are described under the instantaneous equilibrium assumption as described in Table 6:

Table 6 : Equilibrium for hard test case

	X ₁	X ₂	X ₃	X ₄	X ₅	S	K
C ₁	0	-1	0	0	0	0	1.00E-12
C ₂	0	1	1	0	0	0	1
C ₃	0	-1	0	1	0	0	1
C ₄	0	-4	1	3	0	0	0.1
C ₅	0	4	3	1	0	0	1.00E+35
C ₆	0	10	3	0	0	0	1,00E+32
C ₇	0	-8	0	2	0	0	1,00E-04
CS ₁	0	3	1	0	0	1	1.00E+6
CS ₂	0	-3	0	1	0	2	1.00E-01
CP ₁	0	3	1	0	0	0	8.00E+10
CP ₂	0	1	0	0	1	0	20
Total (m.L ⁻³)	T ₁	T ₂	T ₃	T ₄	T ₅	TS	
Initial for media A	0	-30	0	10	0	1	
Initial for media B	0	-90	0	30	0	10	
Injection t ∈ [0,5000]	Imposed total concentration at inflow boundary						
Inflow for 1D	0.3	0.3	0	0	0.3		
Zone 1 for 2D	0.3	0.3	0	0	0.3		
Zone 2 for 2D	0.3	0.3	0	0	0.3		
Leaching t ∈ [5000,...]	Imposed total concentration at inflow boundary						
Inflow for 1D	0	-3	0	1.5	0		
Zone 1 for 2D	0	-3	0	1.5	0		
Zone 2 for 2D	0	-3	0	1.5	0		

Kinetic reactions:

A non mobile species Cc is formed:



This reaction is described using a kinetic formulation:

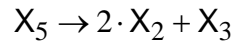
$$\frac{dCc}{dt} = \left(0.2 \frac{C_3^3}{X_4^2} - 1 \right) k \quad \text{with } Cc \geq 0$$

$$\text{if } 0.2 \frac{C_3^3}{X_4^2} \geq 1 \text{ then } k = 10^{-2} \text{ else } k = 10$$

Initial concentration is for all the domains:

$$C_c(z, t = 0) = 5.00$$

Component X_5 is not stable and dissociates to give 2 X_2 and X_3 as shown:



The reaction rate V_{X_5} for this dissociation of X_5 depends on the CP_2 concentration:

$$v_{X_5} = 0.05 \cdot X_5 + 5 \cdot CP_2$$

This leads to the following kinetic source-sink terms to be introduced into reactive transport equations:

$$\text{For } X_2: \sum_k [a_{c_{k,2}} \cdot f_k(C_i, C_{c_k})] = -3 \frac{dC_c}{dt} - 2(0.05 \cdot X_5 + 5 \cdot CP_2)$$

$$\text{For } X_3: \sum_k [a_{c_{k,3}} \cdot f_k(C_i, C_{c_k})] = -(0.05 \cdot X_5 + 5 \cdot CP_2)$$

$$\text{For } X_4: \sum_k [a_{c_{k,4}} \cdot f_k(C_i, C_{c_k})] = \frac{dC_c}{dt}$$

$$\text{For } X_5: \sum_k [a_{c_{k,5}} \cdot f_k(C_i, C_{c_k})] = (0.05 \cdot X_5 + 5 \cdot CP_2)$$

CPU evaluation

In order to compare the efficiency of the proposed method, we suggest that the participants give an evaluation of the CPU time needed to solve the test cases. To reduce the influence of different hardware, the CPU time unit will be defined as the time needed to compute the product of two (1000 x 1000) real matrix.

A is a matrix, real double precision, size 1000x1000

B is a matrix, real double precision, size 1000x1000

C is a matrix, real double precision, size 1000x1000

A = random (1000x1000) with $0 < A(i,j) < 1$

B = random (1000x1000) with $0 < B(i,j) < 1$

Time 1

C = matrix product (A,B)

Time 2

CPU unit = Time 2 – Time 1

The CPU unit is the time needed to run this program

Expected results

Each test case can be solved independently, for a 1D or a 2D flow or for both. The convergence for space mesh and time step refinement should be given.

Results for 1D flow

Plot the concentration of each species and component, and the total dissolved concentration of each component at the output of the domain ($x = 2.1$) versus the time.

Plot the concentration of each species and component, and the total dissolved concentration of each component, over the entire domain at different time:

$t = 10$
 $t = 1000$
 $t = 2000$

For the leaching period:

$t = 5010$
 $t = 5050$
 $t = 5100$

Gives the estimation of the CPU time needed to compute from $t = 0$ to $t = 6000$

Results for 2D flow

Plot the concentration of each species and component versus the time:

at the centre of the output zone ($x = 2.1; y = 0.3$)

at the centre of the fast velocity zone ($x = 1.05; y = 0.95$).

Plot the concentration of each species and component, and the total dissolved concentration of each component, over the entire domain at different time:

For injection period:

$t = 10$
 $t = 1000$
 $t = 2000$

For the leaching period:

$t = 5010$
 $t = 5050$
 $t = 5100$

Gives the estimation of the CPU time needed to compute from $t = 0$ to $t = 6000$