Denitrification example

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1 Introduction

We consider a simplified denitrification process in a clean aquifer, where polluted water enters through the inflow. The aqueous species are $H^+, Cl^-, N_{2(aq)}, CH_2O_{(aq)}, HCO_3^-, O_{2(aq)}, NO_3^-, CO_3^{2-}$, and the gases are $CO_{2(g)}, O_{2(g)}$ and $N_{2(g)}$.

We consider the following equilibrium reactions.

- Bicarbonate dissociation:

$$HCO_3^- = CO_3^{2-} + H^+$$

- Atmospheric CO_2:

$$H^+ + HCO_3^- = CO_{2(g)} + H_2O$$

- Atmospheric O_2:

$$O_{2(aq)} = O_{2(g)}$$

and kinetic reactions:

- Aerobic oxidation of DOC:

$$CH_2O_{(aq)} + O_{2(aq)} \rightarrow H^+ + HCO_3^-$$

- Denitrification ($NO_3^- \rightarrow N_2$):

$$CH_2O_{(aq)} + 0.8NO_3^- \rightarrow HCO_3^- + 0.2H^+ + 0.4N_2 + 0.4H_2O$$

The kinetic reaction rates are governed by the Monod formula (Monod (2012)):

$$r_{K,1} = \mu_1 \frac{[CH_2O_{(aq)}]}{k_{DOC} + [CH_2O_{(aq)}]} \frac{[O_{2(aq)}]}{k_{O_2} + [O_{2(aq)}]}$$

$$r_{K,2} = \mu_2 \frac{I_{O_2}}{I_{O_2} + [O_{2(aq)}]} \frac{[CH_2O_{(aq)}]}{k_{DOC} + [CH_2O_{(aq)}]} \frac{[NO_3^-]}{k_{NO_3^-} + [NO_3^-]}$$

The boundary water is in equilibrium with atmospheric O_2 and CO_2, therefore the stoichiometric matrix at the inflow is

$$\mathbf{S}_e^{inf} = \begin{pmatrix} H^+ & Cl^- & N_{2(aq)} & CH_2O_{(aq)} & HCO_3^- & O_{2(aq)} & NO_3^- & CO_3^{2-} & H_2O & CO_{2(g)} & O_{2(g)} \\ -1 & 0 & 0 & 0 & -1 & 0 & 0 & 0 & 1 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 & -1 & 0 & 0 & 1 & 0 & 0 & 0 \end{pmatrix}$$

since there are no kinetic reactions. In the domain, there are only aqueous reactions, therefore the equilibrium stoichiometric matrix in the domain is

$$\mathbf{S}_e^{dom} = \begin{pmatrix} H^+ & Cl^- & N_{2(aq)} & CH_2O_{(aq)} & HCO_3^- & O_{2(aq)} & NO_3^- & CO_3^{2-} & H_2O \\ 1 & 0 & 0 & 0 & -1 & 0 & 0 & 1 & 0 \end{pmatrix}$$

and the kinetic stoichiometric matrix in the domain is

$$\mathbf{S}_K = \begin{pmatrix} H^+ & Cl^- & N_{2(aq)} & CH_2O_{(aq)} & HCO_3^- & O_{2(aq)} & NO_3^- & CO_3^{2-} & H_2O \\ 1 & 0 & 0 & -1 & 1 & -1 & 0 & 0 & 0 \\ 0.2 & 0 & 0.4 & -1 & 1 & 0 & -0.8 & 0 & 0.4 \end{pmatrix}.$$

There are 7 primary species; therefore, the component matrix is

$$\mathbf{U} = (\mathbf{I} \mid \mathbf{U}_2)$$

where

$$\mathbf{U}_2 = \begin{pmatrix} CO_3^{2-} \\ -1 \\ 0 \\ 0 \\ 0 \\ 1 \\ 0 \\ 0 \end{pmatrix}.$$

We choose a mesh made of 11 nodes with a separation of $0.1m$ between them. The time step (in days) is 10^{-1}. To solve transport, we consider $\phi = 0.5, q = 5m/d, D = 0.25m^2/d$. Regarding the boundary conditions, we prescribe the mass flux at the inflow and we assume no dispersive flux at the outflow. Moreover, we have considered 1 initial water ("clean" aquifer) and 1 inflow water ("polluted" water in equilibrium with atmospheric CO_2 and atmospheric O_2). The initial and boundary concentrations are in Table 1.

	initial	inflow
H^+	10^{-7}	10^{-8}
Cl^-	10^{-16}	10^{-3}
$N_{2(aq)}$	$5 \cdot 10^{-4}$	$5 \cdot 10^{-4}$
$CH_2O_{(aq)}$	10^{-5}	$2 \cdot 10^{-3}$
HCO_3^-	10^{-3}	$5.3761 \cdot 10^{-4}$
$O_{2(aq)}$	10^{-6}	$2.5295 \cdot 10^{-4}$
NO_3^-	10^{-5}	10^{-3}

Table 1: Primary species concentrations of initial and boundary waters (in molalities)

2 Data Input

```
'TITLE OF THE PROBLEM: Denitrification with 2 reactions'
'-------------------------------------------------------------------------------------------------'
'DEFINITION OF THE GEOCHEMICAL SYSTEM'
'PRIMARY AQUEOUS SPECIES'
'h2o(p)'
'h+'
'cl-'
'n2(aq)(p)'
'ch2o(aq)'
'hco3-'
'o2(aq)'
'no3-'
'*'
'AQUEOUS COMPLEXES'
'co3-2'
'*'
'MINERALS'
'*' .true. .true.
'GASES'
'co2(g)' .true. .true.                  ! name of gas, flag equilibrium, flag constant activity
'o2(g)' .true. .true.
'n2(g)' .true. .true.
'*' .false. .false.
'REDOX REACTIONS'
'aerobic oxidation of DOC' .false.      ! name of redox reaction, flag equilibrium
'denitrification' .false.
'*' .false.
'-------------------------------------------------------------------------------------------------'
'end'
```

Figure 1: Chemical system file

3 Pseudocode

1. Define path to databases
2. Define path to input files for denitrification problem
3. Choose option for transport: either compute or read lambdas.
   If option is to compute lambdas:
   - Read transport data: call subroutine *initialise_transport_1D_transient_RT*
   - Allocate transport arrays: call subroutines *allocate_arrays_PDE_1D* and *allocate_conc*
   - Compute lambdas: call *compute_mixing_ratios_Delta_t_homog*
   - Set transport attribute in reactive transport object: call *set_transport_trans*

   If option is to read lambdas:
   - Set transport attribute in reactive transport object: call *set_transport_trans*
   - Read time discretisation: call *read_time_discretisation*
   - Read transport data to apply WMA: call *read_transport_data_WMA*
4. Read chemistry: call *read_chemistry*
5. Call reactive mixing solver: there will be different solvers depending on the model for activity coefficients (ideal or not) and the WMA method (lumped or consistent):
   - If lumped and ideal: call *solve_reactive_mixing_ideal_lump*
   - If consistent and ideal: call *solve_reactive_mixing_ideal_cons*
   - If lumped and non-ideal: call *solve_reactive_mixing_lump*
   - If consistent and non-ideal: call *solve_reactive_mixing_cons*
6. Set chemistry attribute in reactive transport object: call *set_chemistry*
7. Write data and results: call *write_RT_1D*

```
'TITLE OF THE PROBLEM: Denitrification with 2 reactions'
'-------------------------------------------------------------------------------'
'INITIAL AND BOUNDARY WATER TYPES'
0                                ! activity coefficients model
2                                ! n° water types
1     25.0                       ! iwtype initial, temp (C)
'entrada'                        ! name
'       icon        guess         ctot          constrain'
'h+'             1     1d-8       1d-8       ''
'cl-'            1     1d-3       1d-3       ''
'hco3-'          4     1d-6       3.5d-4     'co2(g)'
'o2(aq)'         4     1d-4       2d-1       'o2(g)'
'ch2o(aq)'       1     2d-3       2d-3       ''
'h2o(p)'         1     1d-9       1d-9       ''
'no3-'           1     1d-3       1d-3       ''
'n2(aq)(p)'      1     5d-4       5d-4       ''
'*'       0         0.0           0.0        ''
2     25.0                       !iwtype initial, temp (C)
'dominio'                        ! name
'       icon        guess         ctot          constrain'
'h+'             1     1d-7       1d-7       ''
'cl-'            1     1d-16      1d-16      ''
'hco3-'          1     1d-3       1d-3       ''
'o2(aq)'         1     1d-6       1d-6       ''
'ch2o(aq)'       1     1d-5       1d-5       ''
'h2o(p)'         1     1d-9       1d-9       ''
'no3-'           1     1d-5       1d-5       ''
'n2(aq)(p)'      1     5d-4       5d-4       ''
'*'       0         0.0           0.0             ''
'-------------------------------------------------------------------------------'
'INITIAL AND BOUNDARY GAS ZONES'
1                                          !ngtype= number of gas zones
1     25   1d9                             !igtype, temp (°C), volume
'atmosphere'                               ! name of gas zone
'gas                  partial pressure'    ! pressure in atm
'co2(g)'                   3.5d-4
'o2(g)'                    2d-1
'n2(g)'                    7.99965d-1
'*'                   0.00
'-------------------------------------------------------------------------------'
'end'
```

Figure 2: Local chemistry file

References

Monod, J. (2012). The growth of bacterial cultures. *Selected Papers in Molecular Biology by Jacques Monod*, 139:606.

```
'TITLE OF THE PROBLEM: Denitrification with 2 reactions'
'-------------------------------------------------------------------------------'
'CHEMICAL OPTIONS'
1           ! Chemical input data option (1: CHEPROO-based, 2: PHREEQC, 3:PFLOTRAN)
1           ! Option to compute Jacobians (0:incremental coefficients, 1:analytically)
.true.      ! Lumping flag
2           ! Consistent WMA option (1: explicit, 2: upstream to downstream)
2           ! Estimation of downstream waters reaction amounts
2           ! Average of reaction rates option (1: concentrations, 2: reaction rates)
'-------------------------------------------------------------------------------'
'end'
```

Figure 3: Chemical options