

October 28, 2015

NOTE TO: James Rubenstone, Acting Director NMSS/YMD  
FROM: Tianqing Cao /RA/  
SUBJECT: MASS BALANCE EQUATIONS FOR A SINGLE FRACTURE,  
DECOVALEX-2015 Task C1

This intra-office note describes the reformulation of a mass balance approach used by Yasuhara, et al. (2004) to simulate observations and estimate changes in fracture aperture for laboratory experiments performed under elevated mechanical stress and temperature conditions. The novaculite laboratory experiment, along with a similar experiment on a fractured granite core sample (Yasuhara, et al., 2011), were the main components of a thermal-hydrological-mechanical-chemical (THMC) modeling exercise for DECOVALEX-2015 Task C1. DEvelopment of COupled models and their VALidation against EXperiments (DECOVALEX) is an international collaboration focusing on the simulation of large underground experiments related to disposal of radioactive waste; see <http://www.decovalex.org/>. Because coupled THMC processes in fractured rocks are complex, simplified and well-constrained conditions in laboratory experiments can be used to better understand important processes before attempting less well-constrained conditions in field experiments.

This intra-office note (i) describes the development of the mass balance equations, (iii) identifies a missing term in the mass balance formulation published by Yasuhara, et al. (2004), and, (iii) provides the solution approach for the reformulated mass balance equations. Because the estimate of aperture change is dependent on the formulation, the results of the reformulated mass balance are compared with Yasuhara et al.'s (2004) modeling results directly, and not the experimental results for the fractured novaculite sample. The appendix to this note includes the time discretization scheme used to solve the mass balance equation and estimate the change in aperture.

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## Introduction

Laboratory scale flow-through experiments on a natural fracture under controlled effective stresses and temperatures are useful for examining the effect of the coupled processes on flow and transport characteristics in fractures. Experiments performed by Polak, et al. (2003) and Yasuhara, et al. (2006a,b, 2011) studied the transport parameter changes for natural fractures in novaculite and granite subjected to temperatures between 20 and 120 °C [68 and 248 °F] and differential water pressure applied to the different ends of the core samples. Novaculite is a low-grade metamorphic rock composed of microcrystalline or cryptocrystalline quartz. The measurements of efflux of fluid and dissolved minerals, and the post-experiment X-ray computed tomography imaging of the fracture provide constraints to the evolution of fracture structure and changes in permeability that resulted from stress and temperature dependent dissolution (Yasuhara, et al., 2006a,b).

Yasuhara, et al. (2004) proposed a conceptual mechanistic model to describe the stress and dissolution dependent closure of a fracture in rock that has been simulated with laboratory experiments on a natural fracture. The fracture is idealized as two rough surfaces held apart by bridging asperities. Where the asperities come in contact, the stress on the minerals is enhanced and dissolution more readily occurs (compared to a non-stressed condition), which is referred to as pressure dissolution. Dissolved minerals are transported to open pore spaces by diffusion through the thin water film separating the contacting asperities. In addition to pressure dissolution at contacting areas and diffusion through the water film, a third process of precipitation or free-face dissolution may occur at open pore space walls. These three processes are coupled to define the mass transport through the system and the reduction of fracture aperture. Intensive modeling of the experimental results has been performed by Yasuhara, et al. (2003, 2004, 2006a,b, 2011), in which each process contributes to the mass transport and the whole fracture system follows a mass balance equation. By solving the mass balance equation, the time changes of the simulated dissolved mineral concentrations in the effluent may be compared with the experimental measurements. Estimates of aperture can be obtained using the hydrologic conditions of the experiment. The aperture recovered from the flow-through experiment is derived using the cubic law (Piggott and Elsworth, 1993; Polak, et al., 2003), and thus is a hydraulic aperture. Yasuhara, et al. (2004) considered this to be approximately equivalent to the mechanical aperture.

Following Yasuhara's conceptual model, a revised mass balance equation is derived. This revised mass balance equation contains additional terms that account for the volumetric changes of the interface region and the pore region. The numerical simulation using the reformulated mass balance equation shows that the pressure dissolution mass flux is balanced with the diffusion mass flux. Without including these volumetric changes the aperture reduction is overestimated when the diffusion mass flux is used for the aperture reduction calculation.

## Reformulation of Mass Balance Equation

The fracture is conceptualized as two rough surfaces held apart by bridging asperities (Yasuhara, et al., 2004) with a thin water film between the contacting surfaces. The pressure acting on the contacting area causes increased, or pressure, dissolution of the minerals possibly due to distortions in the mineral structure. The dissolved mineral mass in the water film can be transported to the pore void through the diffusion process. In the open pore space between contacting asperities, precipitation of minerals to the pore walls (free-face) or free-face dissolution can occur depending on the saturation state of the fluid. Similar to modeling of their experiments (Yasuhara, et al., 2004, 2006a,b), the reformulated mass balance modeling also includes the above three processes: (i) the dissolution at highly stressed mineral contact of the fracture, (ii) the diffusive transport of the dissolved mass through the contact boundaries, and (iii) the precipitation or dissolution of the mineral mass on free surfaces of the fracture. For these three processes, the following formulations from Yasuhara, et al. (2004, 2011) are adopted.

$$dM_{diss}^{PS} / dt = \frac{3V_m^2 (\sigma_a - \sigma_c) k_+ \rho_g A_c}{RT} \quad (1)$$

$$dM_{diff} / dt = 8\pi D_b \omega (C_{int} - C_{pore}) \quad (2)$$

$$dM_{diss}^{FF} / dt = k_+ A_{pore} \rho_g V_m \quad (3)$$

where  $dM_{diss}^{PS} / dt$ ,  $dM_{diff} / dt$ , and  $dM_{diss}^{FF} / dt$  are the mass fluxes for the contacting area pressure dissolution, diffusion from contacting area to the void, and free-face dissolution, respectively. As defined in Yasuhara, et al. (2011),  $V_m [m^3 mol^{-1}]$  is the molar volume,  $\sigma_a [Pa]$  is the pressure acting at a contact area exceeding the hydrostatic pore pressure,  $\sigma_c$  is the critical stress at which the compaction of the indenting asperity contacts will halt,  $k_+ [mol m^{-2} s^{-1}]$  is the dissolution rate constant of the fracture solid,  $\rho_g [kg m^{-3}]$  is the solid density,  $A_c [m^2]$  is the contact area,  $R [J K^{-1} mol^{-1}]$  is the gas constant,  $D_b [m^2 s^{-1}]$  is the diffusion coefficient,  $C_{int} [kg m^{-3}]$ , and  $C_{pore}$ , the mineral concentrations in the interface fluid and pore space respectively,  $A_{pore} [m^2]$ , the nominal geometric surface area of the void (pore space), and  $\omega [m]$  is the thickness of the interface water film between contacting asperities. Following Yasuhara, et al. (2004, 2006, 2011),  $\omega$  is assumed to be a constant 4 nm. Equation (3) only includes the free-face dissolution and ignores the effect of precipitation, which is a reasonable assumption for a system undersaturated with respect to silica and far from equilibrium.

The above relations interacting together define a thermal-hydrological-mechanical-chemical coupled process, which controls the aperture reduction or fracture closure. Using the measured fracture surface profiles to define a simple relation between fracture wall contact area ratio and fracture aperture, a mechanical model can be derived to predict the aperture reduction. The

aperture reduction will be a function of time for given driving stress, rock temperature, and fluid flow rate going through the system.

### Mass balance Equations of the System

The mass (conservation) balance equation for the interface volume  $V_{int}$  (the product of contacting area and the water film thickness) is:

$$\int_0^t \frac{dM_{diss}^{PS}}{dt} dt = \int_0^t \frac{dM_{diff}}{dt} dt + V_{int}(t)C_{int}(t) - V_{int}(0)C_{int}(0)$$

The time derivative of this equation is

$$dM_{diss}^{PS} / dt = dM_{diff} / dt + V_{int}(t)dC_{int}(t) / dt + C_{int}(t)dV_{int}(t) / dt \quad (4)$$

The last term on the right side of Equation (4) is not included in Yasuhara, et al.'s (2003, 2004, 2006a,b, 2011) formulation. This equation shows the pressure dissolution mass flux on the left side is balanced with the diffusion mass flux, the mass fluxes due to the mineral concentration change and the interface volume change on the right side. Similarly, the mass balance equation for the pore volume  $V_{pore}$  ( $Q$  is the flow rate) is:

$$dM_{diss}^{FF} / dt - C_{pore}(t)Q + dM_{diff} / dt = V_{pore}(t)dC_{pore}(t) / dt + C_{pore}(t)dV_{pore}(t) / dt \quad (5)$$

Setting  $q_1 = dM_{diss}^{PS} / dt$ ,  $q_2 = dM_{diss}^{FF} / dt - C_{pore}(t)Q$ , and using Equation (2) for the diffusion term  $dM_{diff} / dt = 8\pi\omega D_b (C_{int}(t) - C_{pore}(t)) = D_1 (C_{int}(t) - C_{pore}(t))$ , which follows Yasuhara, et al. (2011), Equations (4) and (5) can be combined to get the matrix equations for the mass balance of the whole fracture system (the notation of time dependence for  $C_{int}$ ,  $C_{pore}$ ,  $V_{int}$ , and  $V_{pore}$  has been omitted in the following):

$$\begin{pmatrix} q_1 \\ q_2 \end{pmatrix} = D_1 \begin{pmatrix} 1 & -1 \\ -1 & 1 \end{pmatrix} \begin{pmatrix} C_{int} \\ C_{pore} \end{pmatrix} + \begin{pmatrix} V_{int} & 0 \\ 0 & V_{pore} \end{pmatrix} \begin{pmatrix} dC_{int} / dt \\ dC_{pore} / dt \end{pmatrix} + \begin{pmatrix} C_{int} & 0 \\ 0 & C_{pore} \end{pmatrix} \begin{pmatrix} dV_{int} / dt \\ dV_{pore} / dt \end{pmatrix} \quad (6)$$

Compared to Yasuhara et al.'s (2011) Equation (26), the third term on the right side of Equation (6) accounts for the mass fluxes due to interface volume change and pore volume change. For a short time step  $\Delta t$ , the approximations  $dC_{int} / dt \approx (C_{int}^{t+\Delta t} - C_{int}^t) / \Delta t$  and similar expressions for  $dC_{pore} / dt$ ,  $dV_{pore} / dt$ , and  $dV_{int} / dt$  are applied. Replacement of the time derivatives in Equation (6) by these expressions leads to the mass balance solution for the updated mineral concentrations  $C_{int}$  and  $C_{pore}$  at  $t + \Delta t$  (see appendix). These concentrations are used in an iteration process to calculate the aperture reduction as a function of time, as described below.

## Aperture Reduction Calculation

For the aperture calculation, the iteration process follows that described in Yasuhara, et al. (2003, 2004, 2006a,b, and 2011). The following are some highlights of the iteration steps. The mechanical mean aperture  $\langle b \rangle$  is assumed to be the function of the contacting area ratio  $R_c$  (Yasuhara, et al., 2011):

$$\langle b \rangle = b_r + (b_0 - b_r) \exp(-(R_c - R_0)/a) \quad (7)$$

where  $b_r$ ,  $b_0$ , and  $a$  are constant and  $R_0$  is the initial contacting area ratio. The cumulative volume removed from the contacting area as a function of contacting ratio can be derived by the following integration [see Equation (10) of Yasuhara, et al., 2006b]

$$V_t^c = -WL \int_{R_0}^{R_c} \frac{R_c}{1 - R_c} \frac{d\langle b \rangle}{dR_c} dR_c = F(R_c) \quad (8)$$

Where  $W$  and  $L$  are the width and length of the fracture,  $F(R_c)$  denotes the integrated function of  $R_c$ , which is expressed with exponential integral functions [see Equation (22) of Yasuhara, et al. (2011) for the details of  $F(R_c)$ ]. The exponential integral functions must be numerically evaluated.

Evaluation of the aperture reduction as a function of time follows Equations (1), (7), and (8). Integration of Equation (1) to any time  $t$  through an iteration process with time step  $\Delta t$  is used to obtain the cumulative mass removed from contacting area (dissolved), which is divided by the density to convert the mass to a volume, and then equated to the volume at any time  $t$  in Equation (8) to solve for the contacting ratio  $R_c$  at time  $t$ . Using this updated ratio, the mean aperture  $\langle b \rangle$  can be updated to time  $t$ . With this approach, the aperture reduction can be calculated without solving the mass balance Equation (6) because the pressure dissolution process defined by Equation (1) is not affected by the diffusion process [Equation (2)] and free-face dissolution process [Equation (3)]. Using this solution approach for the mass balance equations, there is no upper limit for the mineral concentration  $C_{int}$  (H. Yasuhara, personal communication); i.e., there is no feedback from the diffusion process to the pressure dissolution process.

Yasuhara, et al. (2011) chose the mass flux through diffusion process to calculate the mass volume removed for the mean aperture reduction evaluation, which is to integrate Equation (2) to get the removed volume [Equation (21) of Yasuhara, et al. 2011]:

$$V_t^c = \int ((dM_{diff} / dt) / \rho_g) dt$$

in which we have simplified their equation from multi-mineral form to single-mineral form for novaculite. Because this approach needs updated mineral concentrations to update  $dM_{diff} / dt$  [see Equation (2)], mass balance equation has to be solved for the purpose of aperture reduction calculation.

## Comparison

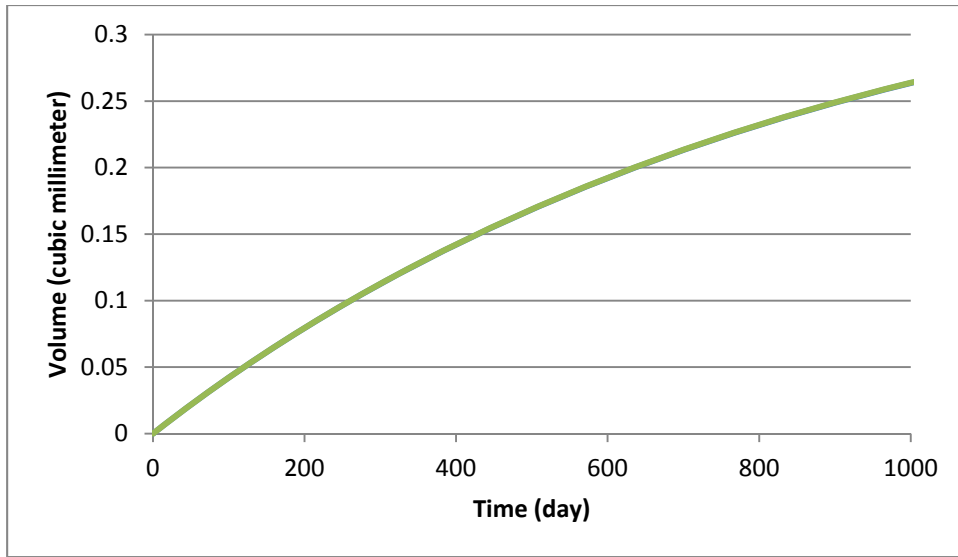
Figure 1 shows the two mass flux integrations using Equations (1) and (2) combined with the reformulated mass balance Equation (6) derived in this intra-office note. The figure shows that the two integrations provide the same mass volume, which is physically reasonable for the balance between the mass removed by pressure dissolution and the mass transferred from the contacting interface to the pore space through diffusion. This figure also indicates that the mass flux due to dissolved mineral concentration change is balanced with the mass flux due to interface volume change.

A numerical test shows that the first time step  $\Delta t$  creates a high value of  $C_{int}$  regardless of the initial concentrations used, and then  $C_{int}$  slowly decreases ( $dC_{int}/dt < 0$ ). The mass flux term due to mineral concentration change in Equation (4) is always negative and the mass flux term due to interface volume change is always positive. Without this volume change term in the balance equation, the diffusion term becomes larger than the pressure dissolution term ( $dM_{diss}^{PS}/dt < dM_{diff}/dt$ ) as suggested by Figure 2.

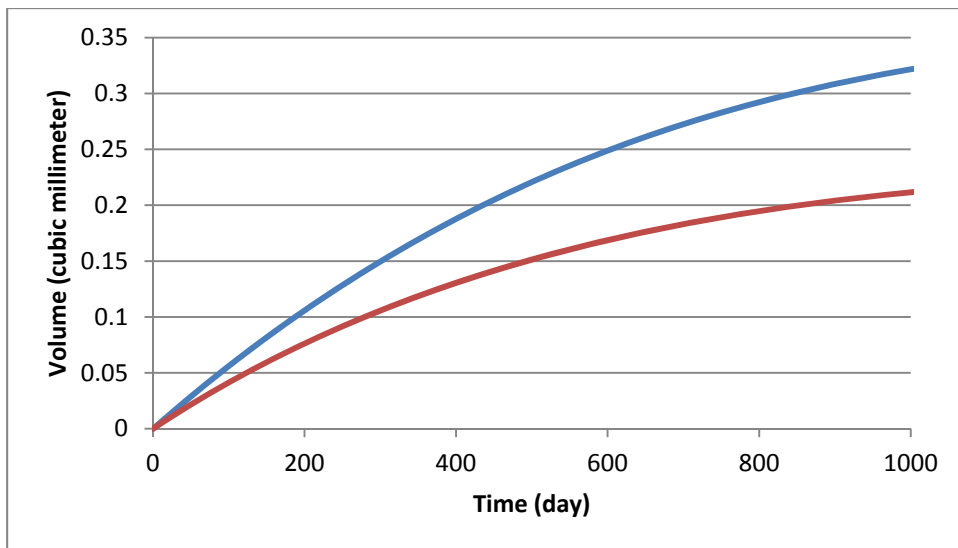
Figure 2 shows the two mass flux integrations but using the Yasuhara, et al. (2003, 2004, and 2011) mass balance equation, in which the interface volume change and the pore volume change [see the third term on the right side of Equation (6)] are not considered. When the mass balance is used without the volume changes, the diffused mass flux is more than the pressure dissolution mass flux, which is physically unreasonable. Due to the indicated missing volume term in the mass balance equation, the diffusion mass flux becomes higher than the pressure dissolution mass flux. At 1000 days, the difference in cumulative mass volume reaches approximately 50%. Note also that the red curve in Figure 2 is close to the curves of Figure 1. The slight difference is due to the difference in the contacting ratio, which is updated using pressure dissolution mass volume in Figure 1 and diffusion mass volume in Figure 2.

Figure 3 shows the difference in aperture reduction estimated using the mass balance formulation of Yasuhara et al.'s (2003, 2004, and 2011) and using the reformulated mass balance approach of this intra-office note. This figure shows that using diffusion mass flux to update the area contacting ratio when the volume change term is not included in the mass balance equation leads to overestimates of the aperture reduction. The overestimate in the Yasuhara mass balance approach causes the diffusion mass flux to be higher than the pressure dissolution mass flux as shown in Figure 2.

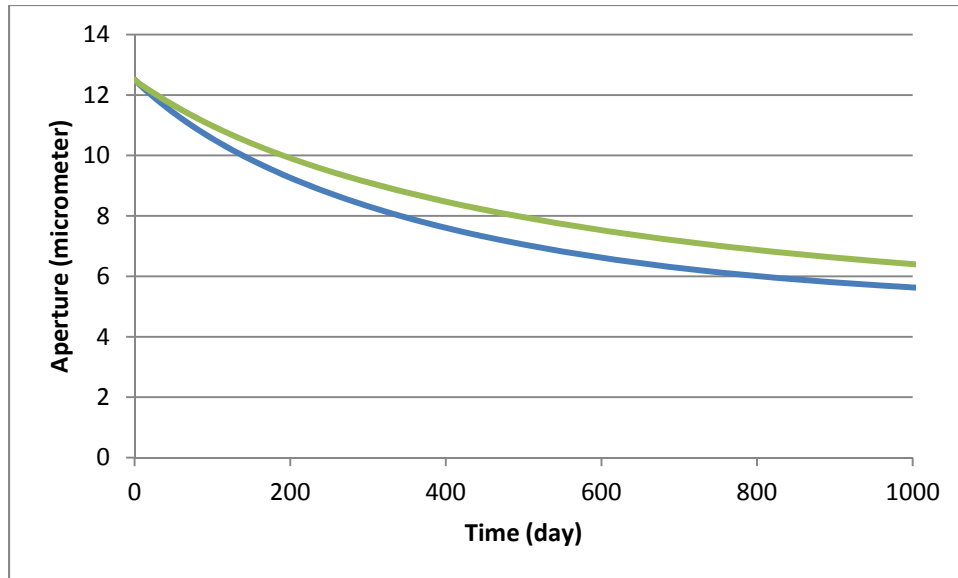
The parameters used in the above calculations to produce Figures 1, 2, and 3 are chosen to be the same as in Yasuhara et al. (2004). These parameter values are:  $V_m = 2.27 \times 10^{-5} \text{ m}^{-3} \text{ mol}^{-1}$  and  $\rho_g = 2650 \text{ kg m}^{-3}$  for quartz,  $D_b = 1.12 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ ,  $k_+ = 2.51 \times 10^{-9} \text{ mol m}^{-2} \text{ s}^{-1}$ ,  $\sigma_c = 73.2 \text{ MPa}$ ,  $WxL = 2.36 \times 10^{-3} \text{ m}^2$  for the total fracture area,  $R = 8.317 \text{ J mol}^{-1} \text{ K}^{-1}$ ,  $T = 150^\circ \text{C}$ , and  $Q = 3.75 \times 10^{-9} \text{ m}^3 \text{ s}^{-1}$ . The constants used in Equation (7) are  $b_r = 2.5 \mu\text{m}$  and  $b_0 - b_r = 10 \mu\text{m}$ , which leads to an initial aperture of  $12.5 \mu\text{m}$  and an initial contacting ratio 0.01.



**Figure 1.** Volume of the cumulative mass obtained by integrating the mass fluxes of pressure dissolution at interface and diffusion between interface and pore, respectively. The two curves overlies when the reformulated mass balance [Equation (6)] is used.



**Figure 2.** Volume obtained from each of the two mass flux integrations using Yasuhara's mass balance equation. The blue curve is for the diffusion mass flux and the red curve is for the pressure dissolution mass flux.



**Figure 2.** Aperture reduction estimated using Yasuhara's (blue) and the reformulated mass balance equations (green), respectively. The red curve for the reformulated mass balance equations uses pressure dissolution mass removal and the blue curve from Yasuhara's mass balance equations uses diffusion mass removal.

## Conclusion and Discussion

Yasuhara, et al.'s (2004) conceptual mechanistic model for a fracture in rock is idealized as two rough surfaces held apart by bridging asperities where stress at contacts enhances mineral dissolution. Transport of dissolved mineral species is approximated as diffusion through a thin water film to open pores. A reformulated mass balance equation for the fracture includes the volume changes of the contacting interface region and the pore space. In the reformulated mass balance approach, the pressure dissolution mass flux is balanced with the diffusion mass flux. The mass flux due to change in dissolved mineral concentration (decrease) and the mass flux due to volume change (increase) offset each other. When the mass fluxes due to volume changes are not included in the mass balance equations, the diffusion mass flux term is larger than the pressure dissolution mass flux, which is not physically possible. Using Yasuhara's approach, it is shown that the aperture reduction is overestimated when the diffusion mass flux is used for the contacting area ratio update in the aperture reduction calculation.

In this conceptual mechanistic model, the pressure dissolution is not affected by the diffusion in the thin film of water at contact areas nor by free-surface dissolution or precipitation processes in the open pores. Additional experiments would be needed to verify this assumption.



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## Appendix

This appendix provides the discretized version of the reformulated mass balance equation that is used for the computations.

Replacement of  $dC_{\text{int}} / dt$  by  $(C_{\text{int}}^{t+\Delta t} - C_{\text{int}}^t) / \Delta t$  and the similar expression for  $dC_{\text{pore}} / dt$  in

Equation (6) leads to the matrix equation

$$\begin{pmatrix} dM_{\text{diss}}^{PS} / dt \\ dM_{\text{diss}}^{FF} / dt \end{pmatrix}_{t+\Delta t} = \begin{pmatrix} D_1 & -D_1 \\ -D_1 & D_1 + Q \end{pmatrix} \begin{pmatrix} C_{\text{int}}^{t+\Delta t} \\ C_{\text{pore}}^{t+\Delta t} \end{pmatrix} + \begin{pmatrix} V_{\text{int}}^{t+\Delta t} / \Delta t & 0 \\ 0 & V_{\text{pore}}^{t+\Delta t} / \Delta t \end{pmatrix} \begin{pmatrix} C_{\text{int}}^{t+\Delta t} \\ C_{\text{pore}}^{t+\Delta t} \end{pmatrix} - \begin{pmatrix} V_{\text{int}}^{t+\Delta t} / \Delta t & 0 \\ 0 & V_{\text{pore}}^{t+\Delta t} / \Delta t \end{pmatrix} \begin{pmatrix} C_{\text{int}}^t \\ C_{\text{pore}}^t \end{pmatrix} + \begin{pmatrix} dV_{\text{int}} / dt & 0 \\ 0 & dV_{\text{pore}} / dt \end{pmatrix} \begin{pmatrix} C_{\text{int}}^{t+\Delta t} \\ C_{\text{pore}}^{t+\Delta t} \end{pmatrix}$$

Combining the terms evaluated at  $t + \Delta t$  and  $t$ , separately, leads to the matrix equation

$$\begin{pmatrix} D_1 + V_{\text{int}}^{t+\Delta t} / \Delta t + dV_{\text{int}} / dt & -D_1 \\ -D_1 & D_1 + Q + V_{\text{pore}}^{t+\Delta t} / \Delta t + dV_{\text{pore}} / dt \end{pmatrix} \begin{pmatrix} C_{\text{int}}^{t+\Delta t} \\ C_{\text{pore}}^{t+\Delta t} \end{pmatrix} = \begin{pmatrix} dM_{\text{diss}}^{PS} / dt \\ dM_{\text{diss}}^{FF} / dt \end{pmatrix}_{t+\Delta t} + \begin{pmatrix} V_{\text{int}}^{t+\Delta t} / \Delta t & 0 \\ 0 & V_{\text{pore}}^{t+\Delta t} / \Delta t \end{pmatrix} \begin{pmatrix} C_{\text{int}}^t \\ C_{\text{pore}}^t \end{pmatrix} = \begin{pmatrix} dM_{\text{diss}}^{PS} / dt + C_{\text{int}}^t V_{\text{int}}^{t+\Delta t} / \Delta t \\ dM_{\text{diss}}^{FF} / dt + C_{\text{pore}}^t V_{\text{pore}}^{t+\Delta t} / \Delta t \end{pmatrix} \quad (\text{A1})$$

Solving the inverse matrix of the left side and replacing  $dV_{\text{int}} / dt$  by  $(V_{\text{int}}^{t+\Delta t} - V_{\text{int}}^t) / \Delta t$ , and  $dV_{\text{pore}} / dt$  by  $(V_{\text{pore}}^{t+\Delta t} - V_{\text{pore}}^t) / \Delta t$  leads to the matrix equation

$$\begin{pmatrix} D_1 + (2V_{\text{int}}^{t+\Delta t} - V_{\text{int}}^t) / \Delta t & -D_1 \\ -D_1 & D_1 + Q + (2V_{\text{pore}}^{t+\Delta t} - V_{\text{pore}}^t) / \Delta t \end{pmatrix}^{-1} = \frac{1}{A} \begin{pmatrix} D_1 + Q + (2V_{\text{pore}}^{t+\Delta t} - V_{\text{pore}}^t) / \Delta t & D_1 \\ D_1 & D_1 + (2V_{\text{int}}^{t+\Delta t} - V_{\text{int}}^t) / \Delta t \end{pmatrix} \quad (\text{A2})$$

where  $A = [D_1 + (2V_{\text{int}}^{t+\Delta t} - V_{\text{int}}^t) / \Delta t][D_1 + Q + (2V_{\text{pore}}^{t+\Delta t} - V_{\text{pore}}^t) / \Delta t] - D_1^2$ .

Multiplying Equations (A1) by (A2) leads to the matrix equation

$$\begin{pmatrix} C_{\text{int}}^{t+\Delta t} \\ C_{\text{pore}}^{t+\Delta t} \end{pmatrix} = \frac{1}{A} \begin{pmatrix} D_1 + Q + (2V_{\text{pore}}^{t+\Delta t} - V_{\text{pore}}^t) / \Delta t & D_1 \\ D_1 & D_1 + (2V_{\text{int}}^{t+\Delta t} - V_{\text{int}}^t) / \Delta t \end{pmatrix} \begin{pmatrix} dM_{\text{diss}}^{PS} / dt + C_{\text{int}}^t V_{\text{int}}^{t+\Delta t} / \Delta t \\ dM_{\text{diss}}^{FF} / dt + C_{\text{pore}}^t V_{\text{pore}}^{t+\Delta t} / \Delta t \end{pmatrix} \quad (\text{A3})$$

The first row of (A3) is

$$C_{\text{int}}^{t+\Delta t} = \frac{1}{A} \left\{ [D_1 + Q + (2V_{\text{pore}}^{t+\Delta t} - V_{\text{pore}}^t) / \Delta t] (dM_{\text{diss}}^{PS} / dt + C_{\text{int}}^t V_{\text{int}}^{t+\Delta t} / \Delta t) + D_1 (dM_{\text{diss}}^{FF} / dt + C_{\text{pore}}^t V_{\text{pore}}^{t+\Delta t} / \Delta t) \right\} \quad (\text{A4})$$

and the second row is

$$C_{pore}^{t+\Delta t} = \frac{1}{A} \left\{ \begin{array}{l} [D_1 + (2V_{int}^{t+\Delta t} - V_{int}^t) / \Delta t] (dM_{diss}^{FF} / dt + C_{pore}^t V_{pore}^{t+\Delta t} / \Delta t) + \\ D_1 (dM_{diss}^{PS} / dt + C_{int}^t V_{int}^{t+\Delta t} / \Delta t) \end{array} \right\} \quad (A5)$$

These are the solutions for updating the concentrations at each time step forward in the iterative numerical calculation. Multiplying the denominator and numerator in (A4) and (A5) by  $(\Delta t)^2$  leads to

$$C_{int}^{t+\Delta t} = \frac{[(D_1 + Q)\Delta t + (2V_{pore}^{t+\Delta t} - V_{pore}^t)](\Delta t dM_{diss}^{PS} / dt + C_{int}^t V_{int}^{t+\Delta t}) + D_1 \Delta t (\Delta t dM_{diss}^{FF} / dt + C_{pore}^t V_{pore}^{t+\Delta t})}{D_1 \Delta t [Q\Delta t + (2V_{pore}^{t+\Delta t} - V_{pore}^t)] + (D_1 + Q)\Delta t (2V_{int}^{t+\Delta t} - V_{int}^t) + (2V_{int}^{t+\Delta t} - V_{int}^t)(2V_{pore}^{t+\Delta t} - V_{pore}^t)} \quad (A6)$$

$$C_{pore}^{t+\Delta t} = \frac{[D_1 \Delta t + (2V_{int}^{t+\Delta t} - V_{int}^t)](\Delta t dM_{diss}^{FF} / dt + C_{pore}^t V_{pore}^{t+\Delta t}) + D_1 \Delta t (\Delta t dM_{diss}^{PS} / dt + C_{int}^t V_{int}^{t+\Delta t})}{D_1 \Delta t [Q\Delta t + (2V_{pore}^{t+\Delta t} - V_{pore}^t)] + (D_1 + Q)\Delta t (2V_{int}^{t+\Delta t} - V_{int}^t) + (2V_{int}^{t+\Delta t} - V_{int}^t)(2V_{pore}^{t+\Delta t} - V_{pore}^t)} \quad (A7)$$

When the extra term in the reformulated mass balance Equation (6) is eliminated, the corresponding solution of (A6) will reduce to the form provided in Yasuhara, et al. [2004, Equation (19)].

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