Supplementary files:

Appendix A: Reactive solute transport in a filled single fracture-matrix system under the unilateral flow.

The governing equations of reactive solute transport in the mobile and immobile domains of filled fracture and rock matrix in Eqs.2.1-2.3 should be transformed in dimensionless formats. The dimensionless variables used in the study of the unilateral flow model are as follows:

$$\mathrm{C_{mD}} = \frac{C_m}{C_0};\ \ \mathrm{C_{imD}} = \frac{C_{im}}{C_0};\ \mathrm{C_{kD}} = \frac{C_k}{C_0};\ \mathrm{x_D} = \frac{x}{b};\ \mathrm{z_D} = \frac{z}{b}\sqrt{\frac{R_3 D_m}{R_1 D_d}};\ \mathrm{t_D} = \frac{D_m}{R_1 b^2}t;\ \mathrm{Pe} = \frac{v_m b}{D_m}$$

$$\theta_1 = \theta_{im}/\theta_m;\ \theta_2 = \theta_k/\theta_m;\ \alpha = \frac{R_1 b^2}{D_m};\ \alpha_1 = \theta_2\sqrt{\frac{R_3 D_d}{R_1 D_m}};\ M'_{fmD} = \frac{M'_{fm}}{C_0 b^2\sqrt{\frac{R_1 D_d}{R_3 D_m}}};\ M'_{fimD} = \frac{M'_{fim}}{C_0 b^2\sqrt{\frac{R_1 D_d}{R_3 D_m}}};\ M'_{kD} = \frac{M'_k}{C_0 b^2\sqrt{\frac{R_1 D_d}{R_3 D_m}}}.$$

In the unilateral flow model, the non-dimensional governing equations (Eqs. (2.1)-(2.3)) now are transformed to their dimensionless formats of Eqs. (A1)-(A3):

$$\frac{\partial C_{mD}}{\partial t_D} + \frac{\theta_1 R_2}{R_1}\frac{\partial C_{imD}}{\partial t_D} = \frac{\partial^2 C_{mD}}{\partial x_D^2} - Pe\frac{\partial C_{mD}}{\partial x_D} - \lambda_1 \alpha C_{mD} - \lambda_2 \theta_1 \alpha \frac{R_2}{R_1} C_{im} + \alpha_1 \left.\frac{\partial C_{kD}}{\partial z_D}\right|_{z_D=\sqrt{\frac{R_3 D_m}{R_1 D_d}}}, \quad \text{(A.1)}$$

$$\frac{\partial C_{imD}}{\partial t_D} = \frac{\omega\alpha}{\theta_{im} R_2}\left(C_{mD} - C_{imD}\right) - \lambda_2 \alpha C_{imD}, \quad \text{(A.2)}$$

$$\frac{\partial C_{kD}}{\partial t_D} = \frac{\partial^2 C_{kD}}{\partial z_D^2} - \lambda_3 \alpha C_{kD}. \quad \text{(A.3)}$$

Applying Laplace transform to Eqs. (A.1)-(A.3) would lead to the following equations:

$$p\overline{C_{mD}} + p\frac{\theta_1 R_2}{R_1}\overline{C_{imD}} = \frac{d^2\overline{C_{mD}}}{dx_D^2} - Pe\frac{d\overline{C_{mD}}}{dx_D} - \lambda_1\alpha\overline{C_{mD}} - \lambda_2\theta_1\alpha\frac{R_2}{R_1}\overline{C_{imD}} + \alpha_1\left.\frac{d\overline{C_{kD}}}{dz_D}\right|_{z_D=\sqrt{\frac{R_3 D_m}{R_1 D_d}}} ,$$

(A.4)

$$p\overline{C_{imD}} = \frac{\omega\alpha}{\theta_{im}R_2}\left(\overline{C_{mD}} - \overline{C_{imD}}\right) - \lambda_2\alpha\overline{C_{imD}} , \tag{A.5}$$

$$p\overline{C_{kD}} = \frac{d^2\overline{C_{kD}}}{dz_D^2} - \lambda_3\alpha\overline{C_{kD}} , \tag{A.6}$$

where p is the Laplace transform parameter in respect to the dimensionless time, t_D and overbar means the term in Laplace domain. From Eq. (A.6), one has

$$\frac{d^2\overline{C_{kD}}}{dz_D^2} = \left(\lambda_3\alpha + p\right)\overline{C_{kD}} \quad , \tag{A.7}$$

The general solution of Eq. (A7) is

$$\overline{C_{kD}} = Ae^{wz_D} + Be^{-wz_D} , \tag{A.8}$$

where $w = \sqrt{\lambda_3\alpha + p}$.

Recalling boundary condition of rock matrix at infinity (Eq. (2.11)), Eq. (A.8) can be simplified as:

$$\overline{C_{kD}} = Be^{-wz_D} \quad . \tag{A.9}$$

Substituting Eq. (A.9) to Eq. (A.6), one can get the following relation:

$$\overline{C_{mD}} = \left.\overline{C_{kD}}\right|_{z_D=\sqrt{\frac{R_3 D_m}{R_1 D_d}}} , \tag{A.10}$$

$$B = \overline{C_{mD}}e^{\sqrt{\lambda_3\alpha+p}\sqrt{\frac{R_3 D_m}{R_1 D_d}}} . \tag{A.11}$$

Now one has the relation between $\overline{C_{kD}}$ and $\overline{C_{mD}}$:

$$\overline{C_{kD}} = \overline{C_{mD}} e^{\sqrt{\lambda_3 \alpha + p}\left(\sqrt{\frac{R_3 D_m}{R_1 D_d}} - z_D\right)}. \tag{A.12}$$

Based on Eq. (A.5), the relation between $\overline{C_{mD}}$ and $\overline{C_{imD}}$ is demonstrated:

$$\overline{C_{imD}} = \frac{\omega}{\frac{\theta_{im} R_2 p}{\alpha} + \omega + \lambda_2 \theta_{im} R_2} \overline{C_{mD}}. \tag{A.13}$$

Substituting Eqs. (A.12)-(A.13) into Eq. (A.4), the final solutions will be reached in the Laplace domain.

Converting M'_{fm}, M'_{fim} and M'_{k} in Eqs. (2.30)-(2.32) into their dimensionless forms defined above, the dimensionless mass per unit width stored in the fracture-rock matrix system of unilateral flow is given as:

$$M'_{fmD} = 2\theta_m \sqrt{\frac{R_3 D_m}{R_1 D_d}} \int_0^\infty C_{mD}\, dx_D \ , \tag{A.14}$$

$$M'_{fimD} = 2\theta_{im} \sqrt{\frac{R_3 D_m}{R_1 D_d}} \int_0^\infty C_{imD} dx_D \ , \tag{A.15}$$

$$M'_{kD} = 2\theta_k \int_{\sqrt{\frac{R_3 D_m}{R_1 D_d}}}^\infty \int_0^\infty C_{kD}\, dx_D\, dz_D \tag{A.16}$$

Appendix B: Reactive solute transport in a filled single fracture-matrix system under the radial flow.

The governing equations (Eqs. (2.20)-(2.21)) are transformed to dimensionless formats. The dimensionless variables used in the study of the radial flow model are defined as follows:

$C_{mD} = \frac{C_m}{C_0}$; $C_{imD} = \frac{C_{im}}{C_0}$; $C_{kD} = \frac{C_k}{C_0}$; $t_D = \frac{At}{R_1 d^2}$; $r_D = \frac{r}{d}$; $z_D = \left(\frac{z}{d}\right)\sqrt{\frac{R_3 A}{R_1 D_d}}$; $\tau_1 = \frac{\theta_2 d}{b}\sqrt{\frac{R_3 D_d}{R_1 A}}$; $\tau = \frac{d^2 R_1}{A}$; $\theta_1 = \theta_{im}/\theta_m$; $\theta_2 = \theta_k/\theta_m$; $M_{fmD} = \frac{M_{fm}}{C_0 d^3 \sqrt{\frac{R_1 D_d}{R_3 A}}}$; $M_{fimD} = \frac{M_{fim}}{C_0 d^3 \sqrt{\frac{R_1 D_d}{R_3 A}}}$; $M_{kD} = \frac{M_k}{C_0 d^3 \sqrt{\frac{R_1 D_d}{R_3 A}}}$.

Converting the system into the dimensionless format, as done for the unilateral flow model, with details provided above, one has:

$$\frac{\partial C_{mD}}{\partial t_D} + \frac{\theta_1 R_2}{R_1}\left(\frac{\partial C_{imD}}{\partial t_D}\right) = \frac{1}{r_D}\left(\frac{\partial^2 C_{mD}}{\partial r_D^2}\right) - \frac{1}{r_D}\left(\frac{\partial C_{mD}}{\partial r_D}\right) - \lambda_1 \tau C_{mD} - \theta_1 \lambda_2 \frac{R_2}{R_1}\tau C_{imD} + \tau_1 \left(\frac{\partial C_{kD}}{\partial z_D}\right)\Bigg|_{z_D = b/d\sqrt{\frac{R_3 A}{R_1 D_d}}}, \tag{B.1}$$

$$\frac{\partial C_{imD}}{\partial t_D} = \frac{\omega \tau}{\theta_{im} R_2}\left(C_{mD} - C_{imD}\right) - \lambda_2 \tau C_{imD}, \tag{B.2}$$

$$\frac{\partial^2 C_{kD}}{\partial z_D^2} - \frac{\partial C_{kD}}{\partial t_D} - \tau \lambda_3 C_{kD} = 0. \tag{B.3}$$

Applying the Laplace transform to Eqs. (B.1)-(B.3) would yield to the following equations in the Laplace domain:

$$p\overline{C_{mD}}+\theta_1\lambda_2\frac{R_2}{R_1}\tau\overline{C_{imD}}+\frac{\theta_1 pR_2}{R_1}\overline{C_{imD}}=\frac{1}{r_D}\left(\frac{d^2\overline{C_{mD}}}{dr_D^2}\right)-\frac{1}{r_D}\left(\frac{d\overline{C_{mD}}}{dr_D}\right)-\lambda_1\tau\overline{C_{mD}}+\tau_1\left(\frac{\partial\overline{C_{kD}}}{\partial z_D}\right)\Bigg|_{z_D=b/d\sqrt{\frac{R_3A}{R_1D_d}}} \tag{B.4}$$

$$p\overline{C_{imD}}=\frac{\omega\tau}{\theta_{im}R_2}\left(\overline{C_{mD}}-\overline{C_{imD}}\right)-\lambda_2\tau\overline{C_{imD}}\ , \tag{B.5}$$

$$\frac{\partial^2\overline{C_{kD}}}{\partial z_D^2}-\overline{C}_{kD}\,p-\tau\lambda_3\overline{C_{kD}}=0\ . \tag{B.6}$$

From Eq. (B.6), we have:

$$\overline{C_{kD}}=a\times exp\left(-\sqrt{\tau\lambda_3+p}\,z_D\right)\quad . \tag{B.7}$$

At the interacting surface between the rock matrix and fracture:

$$\overline{C_{mD}}\left(r_D,p\right)=\overline{C_{kD}}\left(z_D=b/d\sqrt{\frac{R_3A}{R_1D_d}},p\right)=a\times\exp\left(-\sqrt{\tau\lambda_3+p}\times b/d\sqrt{\frac{R_3A}{R_1D_d}}\right). \tag{B.8}$$

So a can be solved as follow:

$$a=\overline{C_{mD}}exp\left(\sqrt{\tau\lambda_3+p}\times b/d\sqrt{\frac{R_3A}{R_1D_d}}\right)\quad . \tag{B.9}$$

Substituting Eq. (B.9) into Eq. (B.7), the relationship between $\overline{C_{kD}}$ and $\overline{C_{mD}}$ can be reached:

$$\overline{C_{kD}}=\overline{C_{mD}}\exp\left[-\sqrt{\tau\lambda_3+p}\left(z_D-b/d\sqrt{\frac{R_3A}{R_1D_d}}\right)\right]\ . \tag{B.10}$$

From Eq. (B.5), the relation between $\overline{C_{imD}}$ and $\overline{C_{mD}}$ is as follow:

$$\overline{C_{imD}} = \frac{\omega}{\frac{\theta_{im} p R_2}{\tau} + \omega + \lambda_2 \theta_{im} R_2} \overline{C_{mD}} \quad . \tag{B.11}$$

Substituting Eqs. (B.10)-(B.11) to Eq. (B.4):

$$\frac{\partial^2 \overline{C_{mD}}}{\partial r_D^2} - \frac{\partial \overline{C_{mD}}}{\partial r_D} - r_D \beta \overline{C_{mD}} = 0 , \tag{B.12}$$

where $\beta = \left(\tau\lambda_1 + \tau_1\sqrt{\tau\lambda_3 + p} + p + \frac{R_2}{R_1} \times \frac{(p + \lambda_2\tau)\theta_1\omega}{\frac{\theta_{im} p R_2}{\tau} + \omega + \lambda_2 \theta_{im} R_2} \right)$.

The Eq. (B.12) is an inhomogeneous differential equation. The general solution is

$$\overline{C_{mD}} = A_1 \times \exp\left(\frac{y}{2}\right) Ai\left(\beta^{\frac{1}{3}} y\right) + A_2 \times \exp\left(\frac{y}{2}\right) Bi\left(\beta^{\frac{1}{3}} y\right), \tag{B.13}$$

where $y = r_D + (4\beta)^{-1}$.

Since $Bi(\infty) \to \infty$, to fulfill the boundary condition below:

$$\overline{C_{mD}}\left(r_D \to \infty, p\right) = 0 . \tag{B.14}$$

A_2 has to be zero. Now Eq. (B.13) is

$$\overline{C_{mD}} = A_1 \exp\left(\frac{y}{2}\right) Ai(\beta^{\frac{1}{3}} y) . \tag{B.15}$$

The boundary condition at the interacting surface of the injection well is given as:

$$\overline{C_{mD}}\left(r_{oD} = \frac{r_0}{d}, p \right) = \frac{1}{p} \quad . \tag{B.16}$$

The parameter A_1 can be expressed:

$$A_1 = \frac{1}{p} \exp\left(-\frac{1}{2} r_{0D} - \frac{1}{2}(4\beta)^{-1} \right) Ai^{-1}\left[\beta^{\frac{1}{3}}\left(r_D + (4\beta)^{-1} \right) \right] . \tag{B.17}$$

Now, the solutions in the Laplace domain could be reached.

By using the dimensionless parameters above, the dimensionless masses stored in the fracture-rock matrix system of radial flow are given as:

$$M_{fmD} = \int_{r_{0D}}^{\infty} \frac{4\pi b\theta_m \sqrt{R_3 A}}{d\sqrt{R_1 D_d}} r_D C_{mD} dr_D \ , \tag{B.18}$$

$$M_{fimD} = \int_{r_{0D}}^{\infty} \frac{4\pi b\theta_{im} \sqrt{R_3 A}}{d\sqrt{R_1 D_d}} r_D C_{imD} dr_D \ , \tag{B.19}$$

$$M_{kD} = \int_{\frac{b}{d\sqrt{\frac{R_1 D_d}{R_3 A}}}}^{\infty} \int_{r_{0D}}^{\infty} 4\pi\theta_k r_D C_{kD} \ dr_D dz_D \ . \tag{B.20}$$

Appendix C: Reactive solute transport in an asymmetrical fracture-rock matrix system.

The dimensionless variables used in this study are defied as follows:

$$C_D = C / C_0 \ , \quad C_{1D} = C_1 / C_0 \ , \quad C_{2D} = C_2 / C_0 \ , \quad x_D = x / b \ , \quad z_D = \frac{z}{b}\sqrt{\frac{R_2 D}{R D_1}} \ , \quad t_D = \frac{D}{Rb^2} t \ ,$$

$$Pe = \frac{vb}{D} \quad , \quad \alpha = \frac{Rb^2}{D} \quad , \quad M_D = \frac{M}{C_0 \times \mathrm{b}^2 \times \sqrt{\frac{RD_1}{R_2 D}}} \quad , \quad M_{1D} = \frac{M_1}{C_0 \times \mathrm{b}^2 \times \sqrt{\frac{RD_1}{R_2 D}}} \quad ,$$

$$M_{2D} = \frac{M_2}{C_0 \times \mathrm{b}^2 \times \sqrt{\frac{RD_1}{R_2 D}}}$$

With the help of those dimensionless parameters above, the non-dimensional governing equations (Eqs. (3.1)-(3.3)) are transformed to the dimensionless formats:

$$\frac{\partial C_D}{\partial t_D} = \frac{\partial^2 C_D}{\partial x_D^2} - Pe\frac{\partial C_D}{\partial x_D} - \lambda \alpha C_D + \frac{\theta_1}{2\theta}\sqrt{\frac{R_2 D_1}{RD}}\left.\frac{\partial C_{1D}}{\partial z_D}\right|_{z_D = z_{0D}} - \frac{\theta_2}{2\theta}\sqrt{\frac{R_2 D_2^2}{RD_1 D}}\left.\frac{\partial C_{2D}}{\partial z_D}\right|_{z_D = -z_{0D}} , \quad \text{(C.1)}$$

$$\frac{\partial C_{1D}}{\partial t_D} = \frac{R_2}{R_1}\frac{\partial^2 C_{1D}}{\partial z_D^2} - \lambda_1 \alpha C_{1D} , \quad \text{(C.2)}$$

$$\frac{\partial C_{2D}}{\partial t_D} = \frac{D_2}{D_1}\frac{\partial^2 C_{2D}}{\partial z_D^2} - \lambda_2 \alpha C_{2D} . \quad \text{(C.3)}$$

After applying Laplace transform to Eqs. (C.1)-(C.3), the following equations would be obtained:

$$p\overline{C_D} = \frac{d^2 \overline{C_D}}{dx_D^2} - Pe\frac{d\overline{C_D}}{dx_D} - \lambda \alpha \overline{C_D} + \frac{\theta_1}{2\theta}\sqrt{\frac{R_2 D_1}{RD}}\left.\frac{\partial \overline{C_{1D}}}{\partial z_D}\right|_{z_D = z_{0D}} - \frac{\theta_2}{2\theta}\sqrt{\frac{R_2 D_2^2}{RD_1 D}}\left.\frac{\partial \overline{C_{2D}}}{\partial z_D}\right|_{z_D = -z_{0D}} , \quad \text{(C.4)}$$

$$p\overline{C_{1D}} = \frac{R_2}{R_1}\frac{\partial^2 \overline{C_{1D}}}{\partial z_D^2} - \lambda_1 \alpha \overline{C_{1D}}, \tag{C.5}$$

$$p\overline{C_{2D}} = \frac{D_2}{D_1}\frac{\partial^2 \overline{C_{2D}}}{\partial z_D^2} - \lambda_2 \alpha \overline{C_{2D}}, \tag{C.6}$$

where p is the Laplace transform parameter in respect to the dimensionless time, t_D and overbar means the term in Laplace domain. From Eqs. (C.5)-(C.6), one has:

$$\frac{\partial^2 \overline{C_{1D}}}{\partial z_D^2} = \frac{R_1}{R_2}(\lambda_1 \alpha + p)\overline{C_{1D}}, \tag{C.7}$$

$$\frac{\partial^2 \overline{C_{2D}}}{\partial z_D^2} = \frac{D_1}{D_2}(\lambda_2 \alpha + p)\overline{C_{2D}}. \tag{C.8}$$

The general solutions of the Eqs. (C.7)-(C.8) are:

$$\overline{C_{1D}} = A_1 e^{w_1 z_D} + B_1 e^{-w_1 z_D}, \tag{C.9}$$

$$\overline{C_{2D}} = A_2 e^{w_2 z_D} + B_2 e^{-w_2 z_D}, \tag{C.10}$$

Where $w_1 = \sqrt{\frac{R_1}{R_2}(\lambda_1 \alpha + p)}$, $w_2 = \sqrt{\frac{D_1}{D_2}(\lambda_2 \alpha + p)}$.

Recalling the boundary conditions of rock matrix at infinity (Eq. (3.9)), Eqs. (C.9)-(C.10) can be further simplified as:

$$\overline{C_{1D}} = B_1 e^{-w_1 z_D}, \tag{C.11}$$

$$\overline{C_{2D}} = A_2 e^{w_2 z_D}. \tag{C.12}$$

After substituting in boundary conditions (Eqs. (3.6)-(3.8)), one can acquire:

$$\overline{C_{1D}} = \overline{C_D} \times \exp\left[-\sqrt{\frac{R_1}{R_2}\left(p + \lambda_1 \alpha\right)}\left(z_D - \sqrt{\frac{R_2 D}{R D_1}}\right)\right], \tag{C.13}$$

$$\overline{C_{2D}} = \overline{C_D} \times \exp\left[\sqrt{\frac{D_1}{D_2}(p+\lambda_2\alpha)}\left(z_D + \sqrt{\frac{R_2 D}{R D_1}}\right)\right] \quad , \tag{C.14}$$

where $k_1 = \lambda\alpha + p + \frac{\theta_1}{2\theta}\sqrt{\frac{R_1 D_1}{RD}(p+\lambda_1\alpha)} + \frac{\theta_2}{2\theta}\sqrt{\frac{R_2 D_2}{RD}(p+\lambda_2\alpha)}$.

Substituting Eqs. (C.13)-(C.14) and the first-type boundary condition Eq. (3.10) into Eq. (C.4), the final solutions and the diffusion loss under the first-type condition can be reached:

$$\overline{C_D} = \frac{1}{p}\exp\left(\frac{Pe - \sqrt{Pe^2 + 4k_1}}{2} x_D\right) \quad , \tag{C.15}$$

$$\overline{C_{1D}} = \frac{1}{p}\exp\left[\frac{Pe - \sqrt{Pe^2 + 4k_1}}{2} x_D - \sqrt{\frac{R_1}{R_2}(p+\lambda_1\alpha)}\left(z_D - \sqrt{\frac{R_2 D}{R D_1}}\right)\right], \tag{C.16}$$

$$\overline{C_{2D}} = \frac{1}{p}\exp\left[\frac{Pe - \sqrt{Pe^2 + 4k_1}}{2} x_D + \sqrt{\frac{D_1}{D_2}(p+\lambda_2\alpha)}\left(z_D + \sqrt{\frac{R_2 D}{R D_1}}\right)\right], \tag{C.17}$$

$$\overline{q_1} = \frac{1}{p}\frac{\theta_1 D_1}{b}\sqrt{\frac{R_1 D}{R D_1}(p+\lambda_1\alpha)}\exp\left[\frac{Pe - \sqrt{Pe^2 + 4k_1}}{2} x_D\right], \tag{C.18}$$

$$\overline{q_2} = \frac{1}{p}\frac{\theta_2 D_2}{b}\sqrt{\frac{R_2 D}{R D_2}(p+\lambda_2\alpha)}\exp\left[\frac{Pe - \sqrt{Pe^2 + 4k_1}}{2} x_D\right]. \tag{C.19}$$

It is the similar method to solve the problem under the third-type boundary condition Eq. (3.11), the final solutions are:

$$\overline{C_D} = \frac{1}{p} \times \frac{2}{1 + \sqrt{1 + 4k_1 / Pe^2}}\exp\left(\frac{Pe - \sqrt{Pe^2 + 4k_1}}{2} x_D\right), \tag{C.20}$$

$$\overline{C_{1D}} = \frac{1}{p} \times \frac{2}{1+\sqrt{1+4k_1/Pe^2}} \exp\left[\frac{Pe-\sqrt{Pe^2+4k_1}}{2} x_D - \sqrt{\frac{R_1}{R_2}\left(p+\lambda_1\alpha\right)} \left(z_D - \sqrt{\frac{R_2 D}{RD_1}} \right) \right], \tag{C.21}$$

$$\overline{C_{2D}} = \frac{1}{p} \times \frac{2}{1+\sqrt{1+4k_1/Pe^2}} \exp\left[\frac{Pe-\sqrt{Pe^2+4k_1}}{2} x_D + \sqrt{\frac{D_1}{D_2}\left(p+\lambda_2\alpha\right)} \left(z_D + \sqrt{\frac{R_2 D}{RD_1}} \right) \right]. \tag{C.22}$$

Converting the mass stored in each domain (Eqs. (3.32)-(3.34)) into corresponding dimensionless formats defined above, the dimensionless mass per unit width stored in each domain is given as:

$$M_D = 2\theta \sqrt{\frac{R_2 D}{RD_1}} \int_0^\infty C_D dx_D , \tag{C.23}$$

$$M_{1D} = \int_{\sqrt{\frac{R_2 D}{RD_1}}}^\infty \int_0^\infty C_{1D} \times \theta_1 dx_D dz_D , \tag{C.24}$$

$$M_{2D} = \int_{-\infty}^{-\sqrt{\frac{R_2 D}{RD_1}}} \int_0^\infty C_{2D} \theta_2 dx_D dz_D . \tag{C.25}$$

For the back-diffusion problem, the water starts flushing the system after t_0. The diffusion coefficients after water flushing may change to D_{1b}, D_{2b}, D_b:

$$D_{1b} = a_1 D_1 ,\quad D_{2b} = a_2 D_2 , D_b = aD . \tag{C.26}$$

For the back-diffusion process, the governing equations are similar as:

$$\frac{\partial C_D}{\partial t_D} = a \frac{\partial^2 C_D}{\partial x_D^2} - Pe \frac{\partial C_D}{\partial x_D} - \lambda \alpha C_D + \frac{\theta_1 a_1}{2\theta} \sqrt{\frac{R_2 D_1}{RD}} \left. \frac{\partial C_{1D}}{\partial z_D} \right|_{z_D = z_{0D}} - \frac{\theta_2 a_2}{2\theta} \sqrt{\frac{R_2 D_2^2}{RD_1 D}} \left. \frac{\partial C_{2D}}{\partial z_D} \right|_{z_D = -z_{0D}} , \tag{C.27}$$

$$\frac{\partial C_{1D}}{\partial t_D} = a_1 \frac{R_2}{R_1} \frac{\partial^2 C_{1D}}{\partial z_D^2} - \lambda_1 \alpha C_{1D}, \tag{C.28}$$

$$\frac{\partial C_{2D}}{\partial t_D} = a_2 \frac{D_2}{D_1} \frac{\partial^2 C_{2D}}{\partial z_D^2} - \lambda_2 \alpha C_{2D}. \tag{C.29}$$

Following the similar method, the solutions during back diffusion are:

$$\overline{C_D}' = -\frac{1}{p} \exp\left(\frac{Pe - \sqrt{Pe^2 + 4k_2 a}}{2a} x_D \right) , \tag{C.30}$$

$$\overline{C_{1D}}' = -\frac{1}{p} \exp\left[\frac{Pe - \sqrt{Pe^2 + 4k_2 a}}{2a} x_D - \sqrt{\frac{R_1}{a_1 R_2}(p + \lambda_1 \alpha)} \left(z_D - \sqrt{\frac{R_2 D}{R D_1}} \right) \right], \tag{C.31}$$

$$\overline{C_{2D}}' = -\frac{1}{p} \exp\left[\frac{Pe - \sqrt{Pe^2 + 4k_2 a}}{2a} x_D + \sqrt{\frac{D_1}{a_2 D_2}(p + \lambda_2 \alpha)} \left(z_D + \sqrt{\frac{R_2 D}{R D_1}} \right) \right], \tag{C.32}$$

where $k_2 = \lambda\alpha + p + \frac{\theta_1}{2\theta} \sqrt{\frac{R_1 D_1 a_1}{RD}(p + \lambda_1 \alpha)} + \frac{\theta_2}{2\theta} \sqrt{\frac{R_2 D_2 a_2}{RD}(p + \lambda_2 \alpha)}$.

The overall final solutions are:

$$C = \begin{cases} f(x,z,t) & t \le t_0 \\ f(x,z,t) + g(x,z,t - t_0) & t > t_0 \end{cases} , \tag{C.33}$$

where $f\,(x,z,t)$ is the solution (Eqs. (C.15)-(C.17)) before water flushing, $g\,(x,z,t)$ is the solution (Eqs. (3.30)-(3.31)) during water flushing time period.

Appendix D: Reactive solute transport in a fully coupled asymmetric stratified system, comparison of scale dependent and independent dispersion schemes.

The governing equation of solute transport in the permeable layer is as follow:

$$\theta R\frac{\partial C}{\partial t}=\theta\frac{\partial}{\partial x}\left[D(x)\frac{\partial C}{\partial x}\right]-\theta v\frac{\partial C}{\partial x}-\theta\lambda RC-\frac{q_1}{2b}-\frac{q_2}{2b}. \quad \text{(D.1)}$$

The terms q_1 and q_2 refer to the diffusive mass entering the less permeable layers, which are expressed as:

$$q_1=-\theta_1 D_1\left.\frac{\partial C_1}{\partial z}\right|_{z=b}, \quad \text{(D.2)}$$

$$q_2=\theta_2 D_2\left.\frac{\partial C_2}{\partial z}\right|_{z=-b}. \quad \text{(D.3)}$$

A contaminant source at constant concentration is placed at the left boundary condition, which is also called the first type boundary condition and is expressed as:

$$C(x=0,t)=C_0. \quad \text{(D.4)}$$

The governing equations of solute transport in the upper layer (layer 1) and lower layer (layer 2) are respectively:

$$R_1\frac{\partial C_1}{\partial t}=D_1\frac{\partial^2 C_1}{\partial z^2}-\lambda_1 R_1 C_1, \quad \text{(D.5)}$$

$$R_2\frac{\partial C_2}{\partial t}=D_2\frac{\partial^2 C_2}{\partial z^2}-\lambda_2 R_2 C_2. \quad \text{(D.6)}$$

The entire system is free of solute at beginning:

$$C(x,t=0)=C_1(x,z,t=0)=C_2(x,z,t=0)=0. \quad \text{(D.7)}$$

The permeable layer is considered as infinitely long and the less permeable layers are considered as infinity thick. Thus, we have:

$$C(x \to \infty, t) = 0,\ \ C_1(x, z \to \infty, t) = 0, C_2(x, z \to -\infty, t) = 0. \tag{D.8}$$

The concentrations at the interfaces of different layers are continuous:

$$C_1(x, z = b, t) = C(x,t),\ \ C_2(x, z = -b, t) = C(x,t). \tag{D.9}$$

The technique of Laplace transform is adopted here. Eqs. (D.1), (D.5) and (D.6) are then transformed into Laplace domain as:

$$D(x)\frac{d^2\overline{C}}{dx^2} + \left[\frac{dD(x)}{dx} - v\right]\frac{d\overline{C}}{dx} - \Psi\overline{C} = 0, \tag{D.10}$$

$$R_1\overline{C_1} = D_1\frac{\partial^2\overline{C_1}}{\partial z^2} - \lambda_1 R_1\overline{C_1}, \tag{D.11}$$

$$R_2\overline{C_2} = D_2\frac{\partial^2\overline{C_2}}{\partial z^2} - \lambda_2 R_2\overline{C_2}, \tag{D.12}$$

where $\Psi = pR + \lambda R + \frac{\theta_1}{2b\theta}\sqrt{(p+\lambda_1)R_1D_1} + \frac{\theta_2}{2b\theta}\sqrt{(p+\lambda_2)R_2D_2}$, p is the Laplace transform parameter and the over bar means the terms in Laplace domain.

With the consideration of continuous concentration at interfaces of layers (Eq. (D.9)), Eqs. (D.11)-(D.12) can be solved as follows:

$$\overline{C_1} = \overline{C} \times \exp\left[-\sqrt{\frac{pR_1 + \lambda_1 R_1}{D_1}}(z-b)\right], \tag{D.13}$$

$$\overline{C_2} = \overline{C} \times \exp\left[\sqrt{\frac{pR_2 + \lambda_2 R_2}{D_2}}(z+b)\right]. \tag{D.14}$$

For the case of a linear scale-dependent dispersivity, one has: $D(x) = \alpha(x) \times v + D_0$, where $\alpha(x) = kx$. Substituting this relationship into Eq. (D.10), we have:

$$(kvx + D_0)\frac{d^2\overline{C}}{dx^2} + [kv - v]\frac{d\overline{C}}{dx} - \Psi\overline{C} = 0. \tag{D.15}$$

Defining a new variable $\xi_1 = \sqrt{kvx + D_0}$, then the equation above turns to:

$$\xi_1^{\,2}\frac{d^2\overline{C}}{d\xi_1^{\,2}} + \left[1 - \frac{2}{k}\right]\xi_1\frac{d\overline{C}}{d\xi_1} - \left(\frac{2}{kv}\right)^2 \xi_1^{\,2}\Psi\overline{C} = 0. \tag{D.16}$$

This equation has the form of the following Bessel equation:

$$\xi_1^{\,2}\frac{d^2\overline{C}}{d\xi^2} + [1 - 2\gamma]\xi_1\frac{d\overline{C}}{d\xi_1} + \left(-\delta^2\eta^2\xi_1^{\,2n} + \gamma^2 - \gamma^2\eta^2\right)\overline{C} = 0, \tag{D.17}$$

where $\gamma = \frac{1}{k}$, $\delta = \frac{2}{kv}\sqrt{\Psi}$, $\eta = 1$. It have been proven that $\xi_1^{\gamma} I_\gamma(\delta\xi_1^{\eta})$ and $\xi_1^{\gamma} K_\gamma(\delta\xi_1^{\eta})$ are two independent special solutions of the equation, where $I_\gamma(x)$ and $K_\gamma(x)$ are the first and second kinds of modified Bessel functions with the order γ. Therefore, the general solution of this equation is:

$$\overline{C} = \xi_1^{\gamma}\left\{A_1 K_\gamma(\delta\xi_1) + B_1 I_\gamma(\delta\xi_1)\right\}, \tag{D.18}$$

where A_1 and B_1 are two constants. According to the boundary condition (Eq. (D.8)), when $\xi_1 \to \infty$, $\overline{C}$ is finite. Thus, B_1 equals to zero. The solution could be simplified as:

$$\overline{C} = \xi_1^{\gamma} A_1 K_\gamma(\delta\xi_1). \tag{D.19}$$

After substituting in boundary condition $\overline{C}(x = 0, p) = \frac{C_0}{p}$, one can acquire:

$$A_1 = \frac{1}{p} \frac{C_0}{\left(\sqrt{D_0}\right)^{\gamma} K_{\gamma}(\delta\sqrt{D_0})} . \quad \text{(D.20)}$$

The final solution in Laplace domain can be derived now as:

$$\overline{C} = \xi_1^{\gamma} \frac{1}{p} \frac{C_0}{\left(\sqrt{D_0}\right)^{\gamma} K_{\gamma}(\delta\sqrt{D_0})} K_{\gamma}(\delta\xi_1) . \quad \text{(D.21)}$$

For the case of an exponential scale-dependent dispersivity, the dispersivity can be expressed as: $\alpha(x) = a(1-e^{-k_1 x})$. Thus, the governing equation could be rewritten as:

$$\left[a(1-e^{-k_1 x})\times v + D_0\right]\frac{d^2\overline{C}}{dx^2} + \left[ak_1 v e^{-k_1 x} - v\right]\frac{d\overline{C}}{dx} - \Psi\overline{C} = 0 . \quad \text{(D.22)}$$

Defining two variables: $\xi_2 = He^{k_1 x}$, $H = 1 + D_0 / (av)$, Eq. (D.22) can be expressed as:

$$\xi_2(1-\xi_2)\frac{d^2\overline{C}}{d\xi_2^{\ 2}} - \left(1 - \frac{1}{ak_1 H}\right)\xi_2 \frac{d\overline{C}}{d\xi_2} + \frac{1}{Havk_1^2}\psi\overline{C} = 0 . \quad \text{(D.23)}$$

The above equation has the form of the following Gauss hypergeometric equation:

$$\xi_2(1-\xi_2)\frac{d^2\overline{C}}{d\xi_2^{\ 2}} + \left[Q - \left(1+m+n\right)\right]\xi_2 \frac{d\overline{C}}{d\xi_2} - mn\overline{C} = 0 , \quad \text{(D.24)}$$

where $Q = 0$, $m = \frac{1}{2ak_1 H}\left[-1 + \sqrt{1 + \frac{4aH}{v}\psi}\right]$, and $n = \frac{1}{2ak_1 H}\left[-1 - \sqrt{1 + \frac{4aH}{v}\psi}\right]$.

As $1 \le \xi_2 \le \infty$, the solution can be written in terms of the hypergeometric function as follows:

$$\overline{C} = A_2 \xi_2^{\ -m} F\left(m, m+1; m-n+1; \xi_2^{\ -1}\right) + B_2 \xi_2^{\ -n} F\left(n, n+1; n-m+1; \xi_2^{\ -1}\right), \quad \text{(D.25)}$$

where $F\left(m, m+1; m-n+1; \xi_2^{-1}\right)$ and $F\left(n, n+1; n-m+1; \xi_2^{-1}\right)$ are the Gauss hypergeometric functions.

In terms of the outlet boundary condition (Eq. (D.8)), the concentration remain finite when $\xi_2 \to \infty$. Thus, the B_2 must equal zero as n is less than zero. The solution can be simplified as:

$$\overline{C} = A_2 \xi_2^{-m} F\left(m, m+1; m-n+1; \xi_2^{-1}\right). \tag{D.26}$$

After substituting $\overline{C}(x=0, p) = \frac{C_0}{p}$, A_2 could be solved as:

$$A_2 = \frac{C_0 \left(1 + \frac{D_0}{av}\right)^m}{pF\left(m, m+1; m-n+1; \left(1 + \frac{D_0}{av}\right)^{-1}\right)} . \tag{D.27}$$

The final solution is then derived as:

$$\overline{C} = \frac{C_0 \left(1 + \frac{D_0}{av}\right)^m}{pF\left(m, m+1; m-n+1; \left(1 + \frac{D_0}{av}\right)^{-1}\right)} \xi_2^{-m} F\left(m, m+1; m-n+1; \xi_2^{-1}\right). \tag{D.28}$$