Multicomponent reactive transport under thermodynamics equilibrium in porous media

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Thermal retardation and analytical solutions

De Simoni et al. (2005) have developed the analytical solution of reactive transport by decoupling speciation from transport, yielding the general expression for the reaction rate

$$\mathbf{r_e} = \left(\mathbf{S}_{\mathrm{e2}}^{\mathrm{T}}\right)^{-1}\frac{1}{\phi}\left[\frac{\partial(\phi \mathbf{c}_2)}{\partial t} - L_t(\mathbf{c}_2)\right]$$

$$= \left(\mathbf{S}_{\mathrm{e2}}^{\mathrm{T}}\right)^{-1}\left\{\sum_{p=1}^{N_r}\frac{\partial \mathbf{c}_2}{\partial K_p}\left[\frac{\partial K_p}{\partial t} - \left(-\mathbf{v}\cdot\nabla K_p + \nabla\cdot(\mathbf{D}\nabla K_p)\right)\right] - \sum_{i=1}^{N_u}\sum_{j=1}^{N_u}\left(\frac{\partial^2 \mathbf{c}_2}{\partial u_i \partial u_j}\nabla^T u_j \mathbf{D}\nabla u_i\right) - 2\sum_{i=1}^{N_u}\sum_{q=1}^{N_r}\left(\frac{\partial^2 \mathbf{c}_2}{\partial u_i \partial K_q}\nabla^T K_q \mathbf{D}\nabla u_i\right) - \sum_{p=1}^{N_r}\sum_{q=1}^{N_r}\left(\frac{\partial^2 \mathbf{c}_2}{\partial K_p \partial K_q}\nabla^T K_q \mathbf{D}\nabla K_p\right)\right\}$$

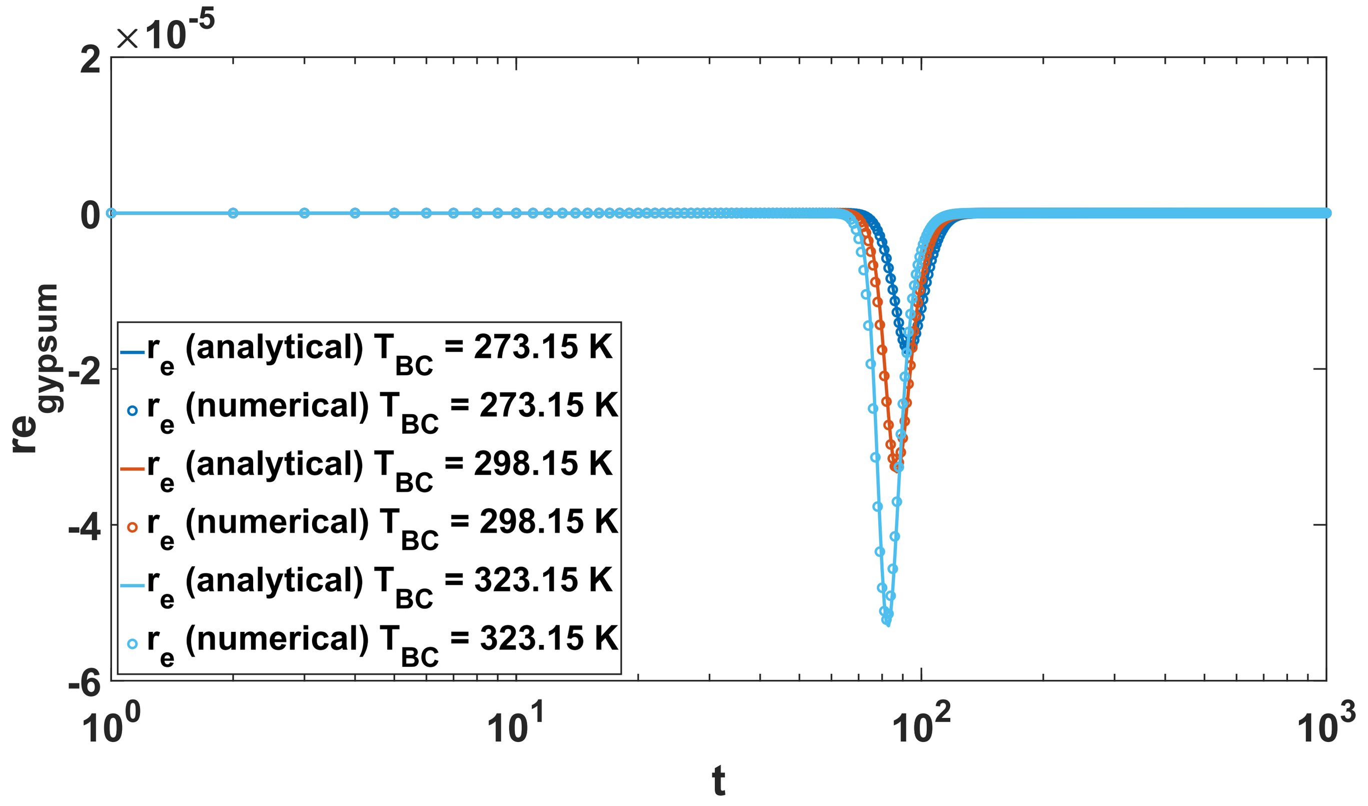
In case of constant K, the reaction rate is proportional to the mixing rate and chemical derivatives of concentrations

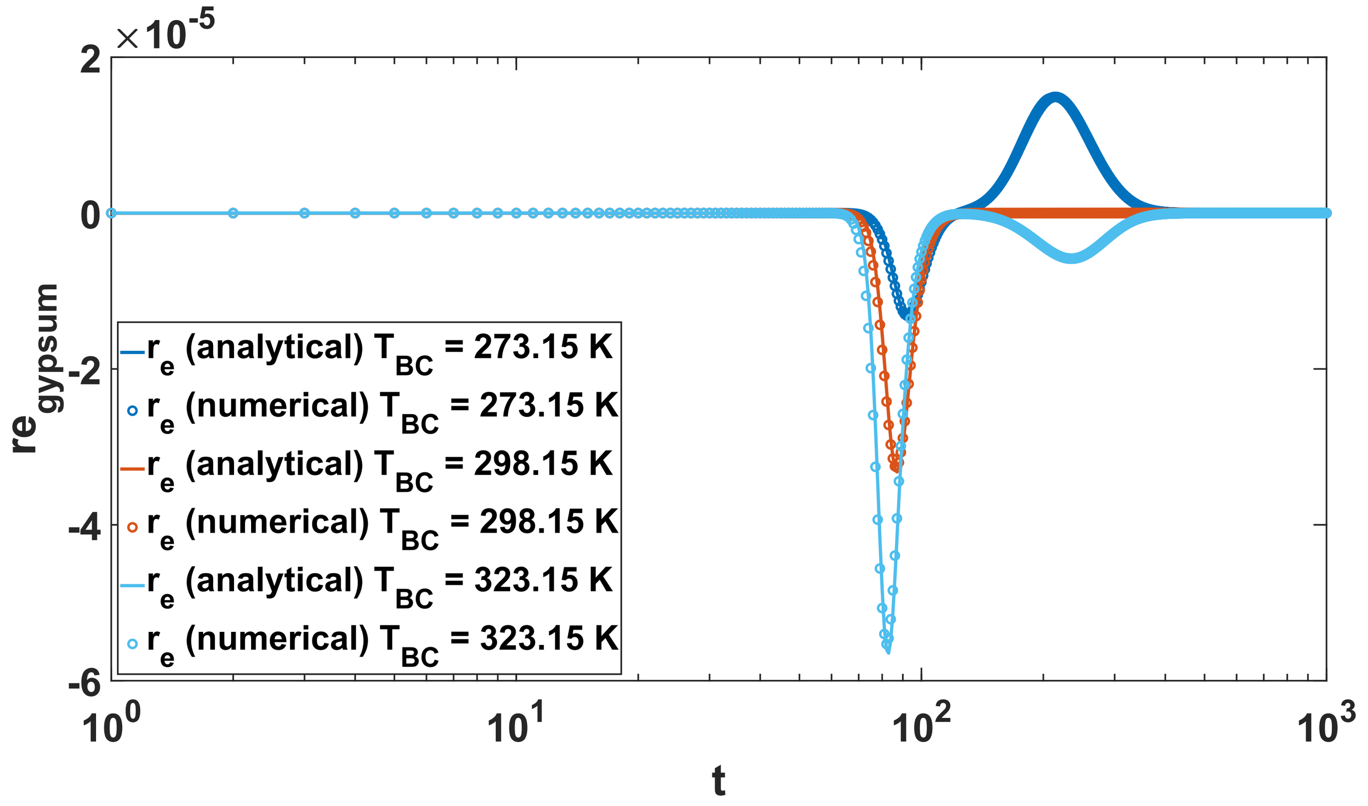
$$\mathbf{r_e} = \left(\mathbf{S}_{\mathrm{e2}}^{\mathrm{T}}\right)^{-1}\sum_{i=1}^{N_u}\sum_{j=1}^{N_u}\left(\frac{\partial^2 \mathbf{c}_2}{\partial u_i \partial u_j}\nabla^T u_j \mathbf{D}\nabla u_i\right)$$

Analytical solution for Thermal-Hydraulic-Chemical (THC) processes considering aqueous species transport and precipitation/dissolution affected by temperature has been deduced by extending the procedure of De Simoni et al. (2005) for conservative quantities, temperature.

When K as a function of temperature T, the reactions rate becomes

$$\mathbf{r_e} = \left(\mathbf{S}_{\mathrm{e2}}^{\mathrm{T}}\right)^{-1}\left\{\sum_{p=1}^{N_r}\frac{\partial \mathbf{c}_2}{\partial K_p}\frac{\partial K_p}{\partial T}\left[\frac{\partial T}{\partial t} - \left(-\mathbf{v}\cdot\nabla T + \nabla\cdot(\mathbf{D}\nabla T)\right)\right] - \sum_{i=1}^{N_u}\sum_{j=1}^{N_u}\left(\frac{\partial^2 \mathbf{c}_2}{\partial u_i \partial u_j}\nabla^T u_j \mathbf{D}\nabla u_i\right) - 2\sum_{i=1}^{N_u}\frac{\partial^2 \mathbf{c}_2}{\partial T \partial u_i}\nabla^T T \mathbf{D}\nabla u_i - \frac{\partial^2 \mathbf{c}_2}{\partial T^2}\nabla^T T \mathbf{D}\nabla T\right\}$$





In porous and fractured media, heat transport through advection and dispersion is retarded compared to components transport, due to the heat capacity of the solid. Thus, the reaction rate is retarded. First, solute mixing front, then thermal front. The separation can be magnified by reducing porosity. Due to the thermal retardation, the precipitation of gypsum turns into the dissolution with time.

Impact on mobile-Immobile transport mechanisms

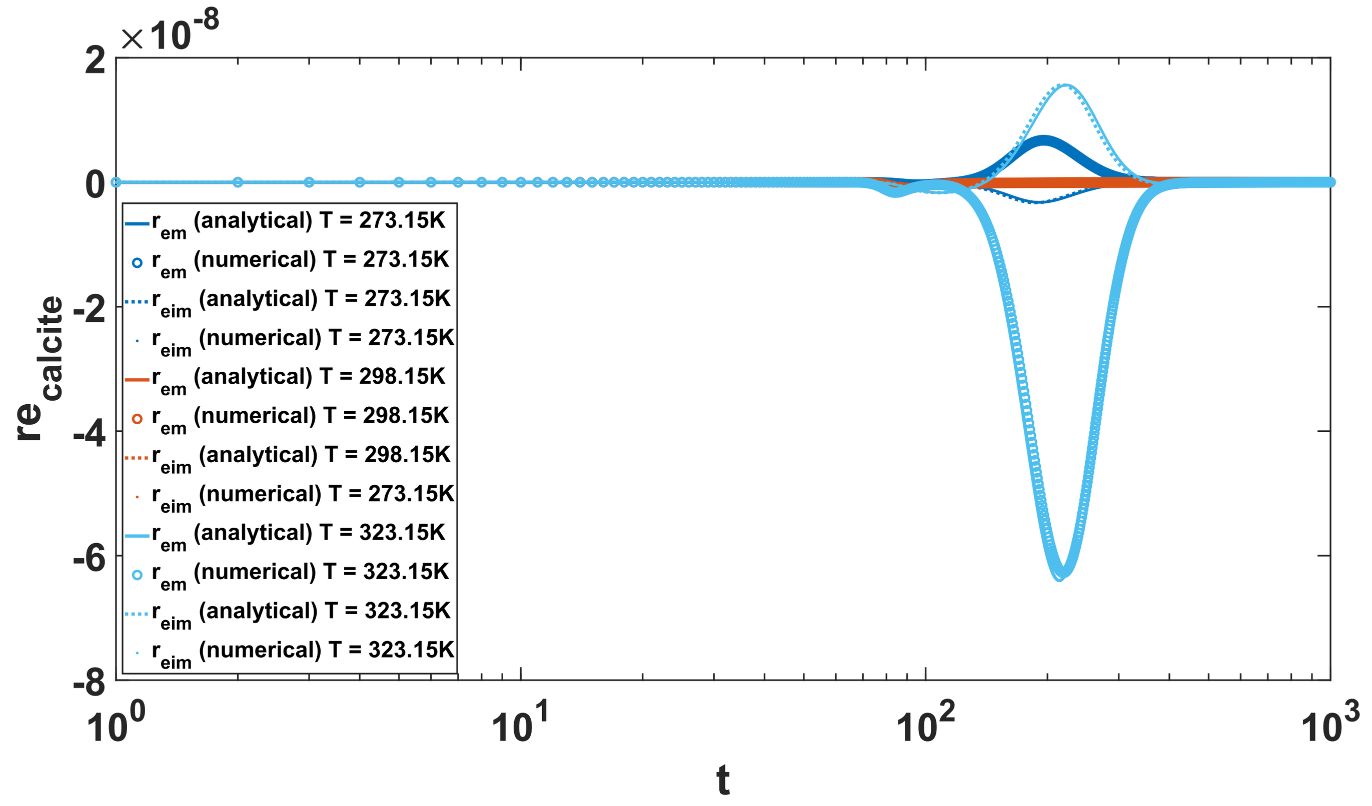
Analytical solution of reactive transport in multicontinuum media has been deduced by Donado et al. (2009). When the equilibrium constant does not vary in space and time, the total reaction rate is the sum of dispersion induced mixing and species enhanced mixing due to mass transfer between mobile and immobile zones.

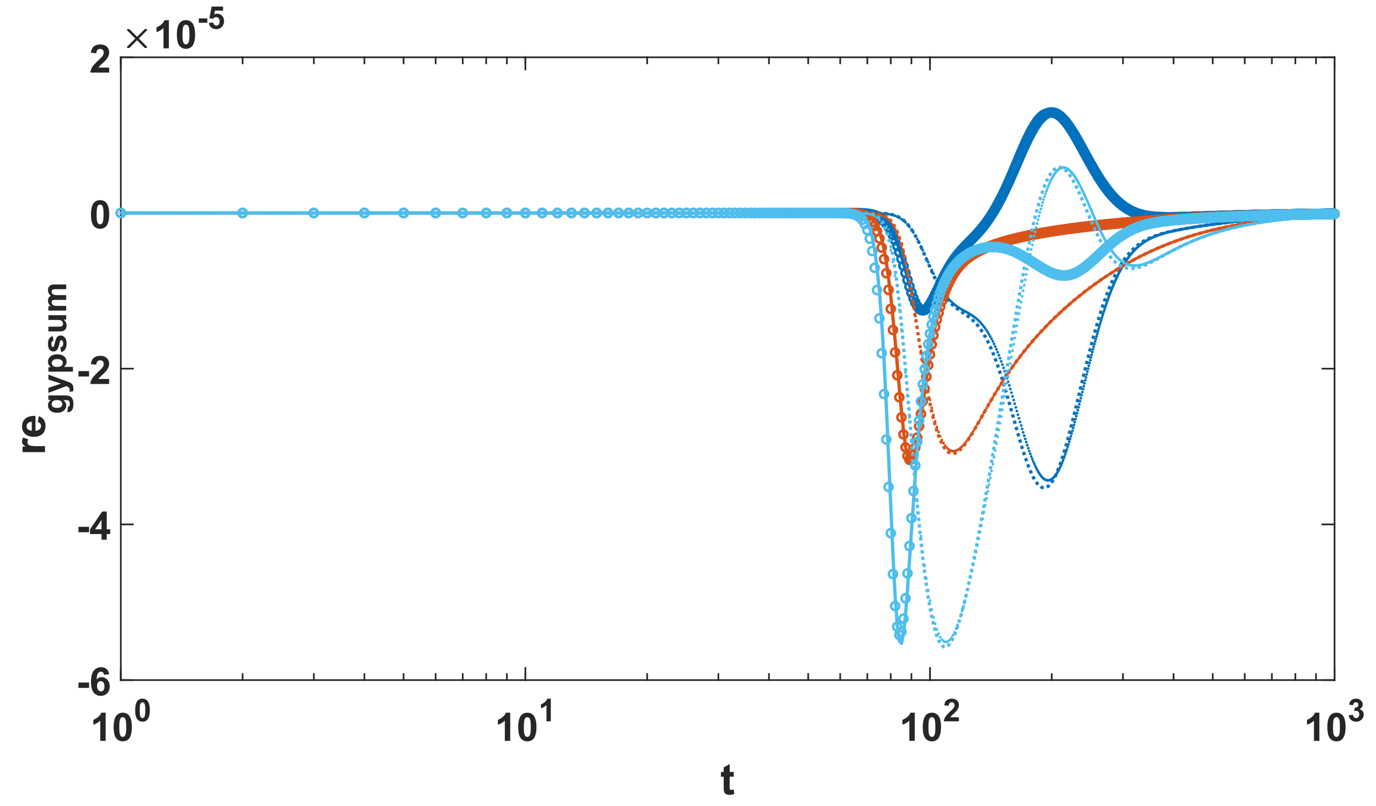
$$\mathbf{r_e} = \left(\mathbf{S}_{\mathrm{ea2}}^{\mathrm{T}}\right)^{-1}\left(-\frac{\partial^2 \mathbf{c}_{2,m}}{\partial \mathbf{u}_m^2}\nabla^T \mathbf{u}_m \mathbf{D}\nabla \mathbf{u}_m\right) + \left(\mathbf{S}_{\mathrm{ea2}}^{\mathrm{T}}\right)^{-1}\left[\frac{\partial \mathbf{c}_{2,m}}{\partial \mathbf{u}_m}\left(-\frac{\phi_{im}}{\phi_m}\sum_{j=1}^{N} p_j \frac{\partial \mathbf{u}_{im,j}}{\partial t}\right) + \frac{\phi_{im}}{\phi_m}\sum_{j=1}^{N} p_j\left(\frac{\partial \mathbf{c}_{2,im,j}}{\partial \mathbf{u}_{im,j}}\frac{\partial \mathbf{u}_{im,j}}{\partial t}\right)\right]$$

When the equilibrium constant is a function of temperature, it yields

$$\mathbf{r_e} = \left(\mathbf{S}_{\mathrm{ea2}}^{\mathrm{T}}\right)^{-1}\left\{\sum_{p=1}^{N_r}\frac{\partial \mathbf{c}_{2,m}}{\partial K_p}\frac{\partial K_p}{\partial T}\left[\frac{\partial T}{\partial t} - \left(-\mathbf{v}\cdot\nabla T + \nabla\cdot(\mathbf{D}\nabla T)\right)\right] - \sum_{i=1}^{N_u}\sum_{j=1}^{N_u}\left(\frac{\partial^2 \mathbf{c}_{2,m}}{\partial u_{i,m}\partial u_{j,m}}\nabla^T u_{j,m}\mathbf{D}\nabla u_{i,m}\right) - 2\sum_{i=1}^{N_u}\frac{\partial^2 \mathbf{c}_{2,m}}{\partial T \partial u_{i,m}}\nabla^T T \mathbf{D}\nabla u_{i,m} - \frac{\partial^2 \mathbf{c}_{2,m}}{\partial T^2}\nabla^T T \mathbf{D}\nabla T\right\} + \left(\mathbf{S}_{\mathrm{ea2}}^{\mathrm{T}}\right)^{-1}\left[\frac{\partial \mathbf{c}_{2,m}}{\partial \mathbf{u}_m}\left(-\frac{\phi_{im}}{\phi_m}\sum_{j=1}^{N} p_j\frac{\partial \mathbf{u}_{im,j}}{\partial t}\right) + \frac{\phi_{im}}{\phi_m}\sum_{j=1}^{N} p_j\left(\frac{\partial \mathbf{c}_{2,im,j}}{\partial \mathbf{u}_{im,j}}\frac{\partial \mathbf{u}_{im,j}}{\partial t} + \sum_{p=1}^{N_r}\frac{\partial \mathbf{c}_{2,im,j}}{\partial K_p}\frac{\partial K_p}{\partial T}\frac{\partial T}{\partial t}\right)\right]$$

The over all reaction rate is retarded and enhanced by temperature. Notice that the first term is identical to the one in homogeneous media.





In mobile-immobile transport, temperature retardation may cause different behaviors in mobile and immobile zones, which allows precipitation and dissolution to coincide spatially, producing an additional localization effect.

References

https://github.com/Jingjingwangxiang/THC

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