**INTRODUCTION**

- Chemical reactions in porous media are often limited by mixing. Local concentration fluctuations occur at multiple scales [1,2].

- Consequently, the classical advection-dispersion-reaction equation (ADRE) typically over-predicts mixing and reaction.

- Thus, a formulation that accounts for the generation, transport and decay of local concentration fluctuations is needed to correctly model reactions in porous media.

- We propose a Lagrangian formulation [3] that is able to simultaneously reproduce the coarse-scale transport [e.g., advection-dispersion] of the averaged concentrations (spreading) as well as the evolution of the sub-scale fluctuations [mixing].

**MATHMATICAL FORMULATION**

- The motion equation governs coarse-scale paths of fluid particles, which drive solute spreading. Classical Brownian motion (8):

\[ x_c(\tau + \Delta \tau) = x_c(\tau) + \mathbf{v}_A \Delta \tau + \mathbf{D} \mathbf{v}_A \Delta \tau \]

with \( \mathbf{D} = \mathbf{D}(\mathbf{v}) \) and \( E \rightarrow 0(1) \). In this case, in the absence of chemical reactions, averaged concentrations \( c_A \) follow the ADRE.

\[ \frac{dc_A(t)}{dt} = D \cdot (\nabla c_A) + \alpha A \]

(2)

- The choice of Relaxation equation drives the local-scale mixing state. We propose the following general Multi-Rate Interaction by Exchange with the Mean (MRIEM):

\[ c_{A,s}(t) = \sum \alpha_{A,i} c_{A,i}(t) \]

(3)

\[ \frac{dc_{A,s}(t)}{dt} = \frac{1}{\tau_1} \left( c_{A,s}(t) - c_{A,s}(t - \tau_1) \right) \]

(4)

where \( \tau_1 \) and \( \tau_2 \) one can emulate a mixing process subject to aging. A simple parameter choice (DR) is:

\[ \tau_1 = \tau_2 = \eta \]

Then,

\[ \frac{dc_{A,s}(t)}{dt} = \frac{1}{\tau_1} \left( c_{A,s}(t) - c_{A,s}(t - \tau_1) \right) \]

(5)

**COVARIANCE AND MIXING STATE**

- DR case (5). Let \( c_{A,s}(t) = c_{A,s}(t) - c_{A,s}(t) \). The concentration covariance \( \Sigma_{AB} = \langle c_A c_B \rangle \) evolves as:

\[ \frac{\partial \Sigma_{AB}}{\partial t} = 2 \alpha \nabla \cdot \nabla \Sigma_{AB} - \Delta \Sigma_{AB} \]

(7)

For other parameterizations than (5), decay term becomes more complicated (see [3]).

- Analyt. solutions for the mixing state \( \langle x_{AB} \rangle \)

**SUMMARY AND CONCLUSIONS**

- A Lagrangian mathematical and numerical model of reactive transport that accounts for the effect of local concentration fluctuations on chemical reactions.

- Transp. of average concentrations depends on stochastic fluid-particle motion (1), while local concentrations are subject to MRIEM (4).

- The differential equation describing the evolution of the local concentration variance can be derived (7). The mixing state shows temporal scaling that is consistent with the typically observed behaviors [e.g. [4]]

- The proposed approach can reproduce experimental results that could not be explained by the upscaled ADRE [3] alone.

**CURRENT AND FUTURE WORK**

- CFD pore-scale simulations with OpenFOAM at the MareNostrum supercomputer*

- Identify and validate MRIEM parameter sets that faithfully emulate mixing in granular media (sph.) with varying grain-size heterogeneity & Pe number.

**REFERENCES**


