Modeling reactive transport with local mixing limitation via random walk particle tracking

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Non-reactive transport of solutes in porous media can be described (at least for low to moderate degrees of sub-scale heterogeneities) by the classical advection-dispersion-equation (ADE), with an upscaled dispersion coefficient that accounts for hydrodynamic dispersion due to the local variability of fluid velocities.

However, when chemical reactions are involved, reaction rates tend to be over-predicted [1,2]. This is mainly due to the inability of the upscaled dispersion term in the ADE to treat spreading and mixing separately. In other words, the implicit assumption of full-mixing at all scales below the scale of interest is, in most cases, erroneous.

We propose a particle-based method to simulate transport of solutes with mixing-limitation at the sub-scale. In our method, besides solute mass, numerical particles also carry a local perturbation relative to the volume-averaged concentration. The perturbations are naturally generated by the random displacements of particles, and relax in time by local mixing. Therefore, the local concentrations, which ultimately control the chemical reactions, are not defined in the Eulerian space, but on particles instead. On the other hand, the volume-averaged concentrations are explicitly defined in space and controlled by the ADE. We show that, in its simplest form, the proposed model relates to *Kapoor and Gelhar*'s [3] concentration variance conservation equation.

The proposed method is implemented to reproduce the experiments of *Gramling et al.* [1]. Our numerical results show close agreement with the experimental measurements for physically meaningful values of the parameters.

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