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Mass Transfer Limitations and Non-Locality for Large Scale Reactive Transport

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The correct characterization of large scale reactive transport dynamics is an important issue for modeling reactive transport on the Darcy scale, specifically in situations in which reactions are localized, that is when different reactions occur in different portions of the porous medium. We consider here reactive transport in a porous medium that is characterized by mass transfer between a mobile and a suite of immobile regions. Chemical and physical heterogeneities are reflected by distributions of kinetic reaction rate constants and residence times in the immobile zones. We derive an effective reactive transport equation for the mobile solute that is characterized by non-local physical mass transfer and reaction terms. Mass transfer limitations due to physical heterogeneity yield effective kinetic rate coefficients that can be much smaller than the volumetric average of the local scale coefficients. These results help to explain and quantify the often reported discrepancy between observed field reaction rate constants and the ones obtained under well mixed laboratory conditions. Furthermore, these results indicate that transport under physical and chemical heterogeneity cannot be upscaled separately.