



## Modeling of bimolecular irreversible reactive transport in column experiments

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We studied an irreversible bi-molecular reactive transport experiment performed by Gramling et al. [2002]. In this experiment, colorimetric reactions between  $\text{CuSO}_4$  and  $\text{EDTA}^{4-}$  were measured in a laboratory column filled with cryolite. After pre-saturating the system with  $\text{EDTA}^{4-}$  (denoted as species B),  $\text{CuSO}_4$  (denoted as A) was injected as a step input. Mixing of the injected species and the reaction region where the product  $\text{CuEDTA}^{4-}$  (denoted as C) formed were measured and concentration profiles of species A, B, and C were offered at four observation times. The concentration of total product generated was measured as a function of displaced pore volumes.

The authors then found that their observations could not be properly interpreted with an advection dispersion reaction equation (ADRE) assuming that the reaction was instantaneous, the actual measured total reaction rate being lower than predictions for all times. Data have been recently well reproduced by means of a particle tracking approach in a Continuous Time Random Walk framework [Edery et al., 2009, 2010]. These authors have questioned the use of partial differential equation (PDE) approaches to quantify reactive transport, because of the difficulty in capturing local scale mixing and reaction. Here, we interpret these experiments by means of a continuum-scale model based on the ADRE. Our modeling approach is based on the idea that micro-scale heterogeneity of the pore space causes the reactive solutes to experience differential diffusion. The latter develops on different time scales so that reactants cannot interact instantaneously and are controlled by mass transfer between regions associated with different pore velocities. We assume that the effects of incomplete mixing at the pore-scale can be embedded in a first-order kinetic reaction term and show that this model allows quantitative interpretation of the experiments in terms of both reaction product profiles and time-dependent global production rate. A salient result is that the key model parameters display a time-dependent behavior. This dependence is generally non-linear and is consistent with published relationships between mass transfer rates and residence / observation times of mass transfer experiments in dual porosity media.