

Interpretation of column experiments of transport of solutes undergoing an irreversible bimolecular reaction using a continuum approximation

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[1] We provide a quantitative interpretation of the column experiment reported by Gramling et al. (2002). The experiment involves advection-dominated transport in porous media of three dissolved species, i.e., two reactants undergoing a fast irreversible reaction and the resulting product. The authors found that their observations could not be properly fitted with a model based on an advection-dispersion-reaction equation (ADRE) assuming the reaction was instantaneous, the actual measured total reaction product being lower than predictions for all times. The data have been recently well reproduced by Edery et al. (2009, 2010) by means of a particle tracking approach in a continuous time random walk framework. These and other authors have questioned the use of partial differential equation (PDE)-based approaches to quantify reactive transport because of the difficulty in capturing local-scale mixing and reaction. We take precisely this approach and interpret the experiments mentioned by means of a continuum-scale model based on the ADRE. Our approach differs from previous modeling attempts in that we imbue effects of incomplete mixing at the pore scale in a time-dependent 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. The time dependence of the kinetic term presented accounts for the progressive effects of incomplete mixing due to pore-scale rate-limited mass transfer, and follows a power law, which is consistent with the compilation of existing experiments reported by Haggerty et al. (2004). Our interpretation can form the basis for further research to assess the potential use of PDE approaches for the interpretation of reactive transport problems in moderately heterogeneous media.

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1. Introduction

[2] Transport of reactive species in porous systems is characterized by a combination of chemical and physical processes. These occur on a multiplicity of space and time scales which should be properly considered within a conceptual and mathematical modeling framework. Among the various types of processes which might occur in these complex porous media, we focus on homogeneous irreversible reactions which are driven by mixing of two waters with different chemical signatures. More specifically, we consider the dynamics of bimolecular reactions taking place in a laboratory-scale column filled with granular material that we model as uniform in terms of hydraulic conductivity and porosity distributions.

[3] A modeling approach which is typically used to interpret reactive transport is based on the conceptualization of the porous system as an equivalent macroscopic continuum. Mass conservation of the transported species is then formulated in terms of a partial differential equation. A common model is based on the advection-dispersion-reaction equation (ADRE). A bimolecular irreversible chemical reaction $aA + bB \rightarrow cC$, occurring during a laboratory-scale column (i.e., one-dimensional) experiment is then described by the following model:

$$\frac{\partial c_i}{\partial t} = -v \frac{\partial c_i}{\partial x} + D \frac{\partial^2 c_i}{\partial x^2} + M_i r_i. \quad (1)$$

Here, c_i is the aqueous concentration of chemical species i ($i = A, B, C$), v is velocity, D is the dispersion coefficient, and M_i is a stoichiometric coefficient, directly related to coefficients a , b , and c . Finally, r_i represents the space-time-dependent rate at which species i is produced (or removed) by the reaction. Appropriate initial and boundary conditions complete the mathematical description of the problem.

[4] The theoretical framework based on the ADRE assumes that two scale-separation conditions are maintained:

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(1) the characteristic length associated with the pore space geometry should be much smaller than that of the averaging volume, and (2) solutes undergo instantaneous and complete mixing within a control volume. These two conditions are often violated in reactive transport processes that involve mixing [e.g., *Jose and Cirpka*, 2004; *Tartakovsky et al.*, 2008, 2009], suggesting the need for a different macroscopic description of the underlying processes. Along these lines, it has been observed [*Rashidi et al.*, 1996; *Cao and Kitanidis*, 1998; *Raje and Kapoor*, 2000; *Gramling et al.*, 2002; *Li et al.*, 2006; *Palanichamy et al.*, 2009; *Ederly et al.*, 2009, 2010] that the concentration of chemical species can display significant variations within a given pore. Thus, it will be different to compute total reaction rates from pore-averaged concentrations or from averaging pore-scale rates within the pore.

[5] An additional limitation of the ADRE is that it assumes that transport can be depicted as a Fickian process, thus giving rise to interpretation problems associated with the observation of non-Fickian or anomalous transport (see the recent review by *Berkowitz et al.* [2006, and references therein]). These observations have motivated intense research toward alternative modeling schemes. Among these, particle tracking (PT) methodologies are considered to be effective techniques to provide appropriate depictions of some of the salient features of reactive transport scenarios [*Gillespie*, 1977; *Fabriol et al.*, 1993; *Cao et al.*, 2005; *Romero et al.*, 2007; *Palanichamy et al.*, 2009; *Ederly et al.*, 2009].

[6] Regardless of the above mentioned limitations, a continuous formulation based on the ADRE is still used as a basis modeling tool for reactive transport problems [see, e.g., *Fernández-García et al.*, 2008; *Sanchez-Vila et al.*, 2009, and references therein]. As such, it is embedded in a variety of codes [e.g., *Cederberg et al.*, 1985; *Mangold and Tsang*, 1991; *Yeh and Tripathi*, 1991; *Steeffel and Lasaga*, 1994; *Walter et al.*, 1994; *Saaltink et al.*, 2004; *De Simoni et al.*, 2005; *Bea et al.*, 2009 and references therein] and is at the core of benchmark problems comparing the results provided by different numerical models to identify their similarities and critical differences [e.g., *Cochepein et al.*, 2008]. In the context of a transport scenario involving a precipitation reaction, *Tartakovsky et al.* [2008] and *Katz et al.* [2010] observed that a very fine grid discretization could capture some of the features of the investigated process, albeit an accurate quantitative description was not obtained.

[7] In this scenario, pore-scale modeling techniques can be extremely important in assessing the validity of continuum approximations in reactive transport modeling, and establishing links between microscale processes and macroscale effective parameters [*Zhang et al.*, 2008; *Tartakovsky et al.* 2008]. *Meile and Tunçay* [2006] employ pore-scale modeling to investigate the effect of small-scale heterogeneity on estimates of reaction rates for diffusion-controlled heterogeneous and homogeneous reactions. They use high-resolution computational models that explicitly resolve small-scale heterogeneity in synthetically generated porous media and upscale the pore-scale simulation results of reactive transport to obtain effective diffusion coefficients and volume averaged reaction rates. The latter were then compared against results obtained by a continuum model based on the diffusion-reaction equation. Their findings indicated that, while pore-scale heterogeneity can substantially affect estimates of heterogeneous reactions, a macroscopic description of the

homogeneous reactions could lead to interpretative errors of a few percent. Recently, *Battiato et al.* [2009] illustrate a set of sufficient conditions under which macroscopic reaction-diffusion equations can provide an adequate averaged description of pore-scale processes in the presence of heterogeneous reactions.

[8] Experimental work is useful to validate existing methodologies for reactive transport modeling. *Gramling et al.* [2002] used data from bimolecular reactive transport column experiments to claim the inadequacy of the ADRE model. In their reactive transport experiments, the cryolite-filled column was saturated with EDTA⁴⁻, and then CuSO₄ was injected as a step input. The colorimetric reaction $\text{Cu}^{2+} + \text{EDTA}^{4-} \rightarrow \text{CuEDTA}^{2-}$ was measured in the mixing zone. The experiment was repeated with three different inlet flow rates. The authors report the concentration profiles of CuEDTA²⁻ at four different times for the lowest flow rate. They then report the concentration of total product generated as a function of time. The measured produced CuEDTA²⁻ was compared to an analytical solution of the ADRE. The latter was derived upon the assumption that the concentration of the limiting reactant was instantaneously and completely consumed in the reaction. The authors observed that the analytical solution of the ADRE significantly over-predicted the space-time evolution (in particular, the total rate) of CuEDTA²⁻ in the system.

[9] *Ederly et al.* [2009, 2010] developed and implemented a particle tracking (PT) approach to describe bimolecular reactions under both Fickian and non-Fickian transport regimes. They compared the results of their approach against the data of the lowest flow rate experiment of *Gramling et al.* [2002], and concluded that a stochastic PT technique including local-scale dynamics through the incorporation of the joint probability density function (*pdf*) of particles' transition rates could successfully describe the experiments, while an ADRE-based analytical solution could not capture the actual local-scale dynamics (degree of mixing).

[10] Here, we reinterpret that same experiment of *Gramling et al.* [2002] on the basis of an ADRE formulation. As opposed to the methodology of *Gramling et al.* [2002], we describe the macroscopic chemical behavior of the system by means of a kinetic reaction rate. In our model, the latter is proportional to the local concentrations of the reactants, with an evolving (time-dependent) coefficient of proportionality that accounts for the progressive evolution of imperfect mixing at the pore scale. The proposed model is consistent with the reported experiments collected by *Haggerty et al.* [2004]. We numerically solve the resulting system of partial differential equations and show that they provide a viable mean to interpret the experiments.

2. Modeling Assumptions

[11] We start by assuming that the system can be modeled by means of the ADRE described by equation (1). At the molecular level, the rate of the reaction of Cu²⁺ with EDTA⁴⁻ has been described as linearly proportional to the concentration of each of the reactants [*Hering and Morel*, 1988],

$$r = \beta c_A c_B, \quad (2)$$

where c_A and c_B are the aqueous concentrations of species A and B , identifying Cu²⁺ and EDTA⁴⁻, respectively, and

β [$\text{m}^3/(\text{mol} \cdot \text{s})$] is a first-order reaction rate constant. For the reactive tracer experimental conditions of *Gramling et al.* [2002], the observed β value reported in the literature [*Hering and Morel*, 1988] leads to a characteristic reaction time of fractions of milliseconds, thus suggesting the use of instantaneous reaction for the observation times of the experiment. As stated before, when dealing with porous media, this approach proved to be inadequate to model the experiments of *Gramling et al.* [2002]. Another point to make is that these experiments show tailing in the concentration curves. This observation can be associated with the presence of slow advection zones, where displacement is mainly controlled by diffusive processes. As shown in section 3, these tails are associated with a very small contribution to the total mass of the reaction product. Yet, they are conceptually very significant, since the presence of pore-scale immobile zones has a large impact in the fate of reactants and reaction product. Species A which is injected in the column cannot completely and instantaneously react with an already existing species B , as part of the pore water is not instantaneously accessible. This results in slow and incomplete mixing at a macroscale.

[12] In short, a kinetic model for the reaction should incorporate the availability of the two reactants at a given location (this is a necessary, albeit not sufficient, condition for a reaction to take place). We contend that, since occurring of the reaction would depend on the concentration of the two species, one can assume a model similar to equation (2). Here, the β coefficient should be considered as a lumped parameter including both pore-scale mixing and chemistry-related effects. Equation (2) would be equivalent to a two-region mass transfer model regulating the rate of change of dissolved species concentration in the immobile zones [see, e.g., *Kechagia et al.*, 2002; *Lichtner and Kang*, 2007; *Donado et al.*, 2009], so that β is closely related to the first-order mass transfer rate coefficient appearing in a two-region mass transfer model and regulating the rate of change of dissolved species concentration in the immobile zones. From a physical standpoint immobile zones can represent sequences of micropore conduits with relatively slow pore velocities as compared to the mean water velocity (i.e., water does not need to be totally “immobile”). These conduits are randomly distributed in the system and mass transfer between them and the main flowing conduits depends upon advective and diffusive processes. Each of these regions has different mass transfer properties so that the total solute mass exchange represented in the macroscopic system takes place over various time scales. *Haggerty et al.* [2004] present a review of more than 300 solute transport experiments and suggest that mass transfer coefficients found in typical porous media with a variety of occurring pore-scale mass transfer processes are mostly correlated to residence times and experiment durations. Adopting the concepts suggested by *Haggerty et al.* [2004] and on the basis of the analogy between equation (2) and a two-region mass transfer scheme, we model β as a time-dependent term, with the form $\beta = \beta_0 t^{-m}$. The coefficient β_0 and the exponent m need to be calibrated against time-dependent experimental observations.

[13] The reaction here studied has stoichiometric coefficients $M = -1$ for reactants and $M = +1$ for the reaction product. Regardless the reaction model proposed, either equation (2) or any other alternative constitutive transport model, one can derive two independent quantities, e.g., $A_0 = c_A + c_C$, and $B_0 = c_B + c_C$, that satisfy a conservative

equation (in our model, the ADE). Any linear combination of these two quantities (e.g., $M_0 = c_A + c_B + 2c_C$ or $M_1 = c_A - c_B$) also satisfies an ADE. In particular, A_0 satisfies the following PDE (it follows directly from the manipulation of equation (1) written in terms of species A and C)

$$\frac{\partial A_0}{\partial t} = -v \frac{\partial A_0}{\partial x} + D \frac{\partial^2 A_0}{\partial x^2}, \quad (3)$$

with the corresponding initial and boundary conditions

$$\begin{aligned} A_0 &= C_0(1 - H(x)) \text{ at } t = 0 \\ A_0 &= C_0 \text{ at } x \rightarrow -\infty; A_0 = 0 \text{ at } x \rightarrow +\infty \end{aligned} \quad (4)$$

H and C_0 being the Heavyside function and the concentration of species A at the column inlet, respectively. An analogous equation is satisfied by B_0 with different initial and boundary conditions. It then follows that $M_0 = C_0 = \text{constant}$. The analytical solutions for A_0 and B_0 are well known and have also been provided by *Gramling et al.* [2002]. From the definitions above, $A_0(x,t) - B_0(x,t) = c_A(x,t) - c_B(x,t)$, and it can then be shown that the concentration of the aqueous species B is governed by

$$\frac{\partial c_B}{\partial t} = -v \frac{\partial c_B}{\partial x} + D \frac{\partial^2 c_B}{\partial x^2} - \beta c_B (c_B + A_0 - B_0). \quad (5)$$

This nonlinear partial differential equation can be solved by a simple explicit scheme. Finally, at any given point in space and time one can obtain the concentration of reaction product, c_C , as

$$c_C(x,t) = B_0(x,t) - c_B(x,t). \quad (6)$$

3. Interpretation of the Experiments and Discussion

[14] The main interest of our work lies in the assessment of the ability of our proposed modeling strategy to capture the time-dependent behavior of the system, in terms of the evolution of (1) the space-time distribution and (2) the cumulative mass of the reaction product, CuEDTA^{2-} . We focus on the first experiment performed by *Gramling et al.* [2002]. Four space distributions of concentrations recorded at different observation times have been documented for this experiment [*Gramling et al.*, 2002], providing the amount of information needed for the calibration of the parameters included in our model. The other two experiments only show the concentration profiles in the column for one observation time and provided little information on the time-dependent behavior of the system. Thus, they were excluded from this study. The works of *Ederly et al.* [2009, 2010] analyze the same experiment, thus allowing for a comparison of the general modeling strategy and results. We assume that the inlet flow rate and medium porosity are only minimally affected by measurement uncertainty and set them to the values reported by *Gramling et al.* [2002], i.e., 2.67 mL/min and 0.36, respectively.

[15] Sensitivity analysis reveals that the amount of information available allows a reliable calibration of the three parameters D , β_0 , and m . A small β value indicates that no reaction is taking place, so that c_A approaches A_0 , c_B approaches B_0 , and c_C approaches 0. Very large β values (i.e.,

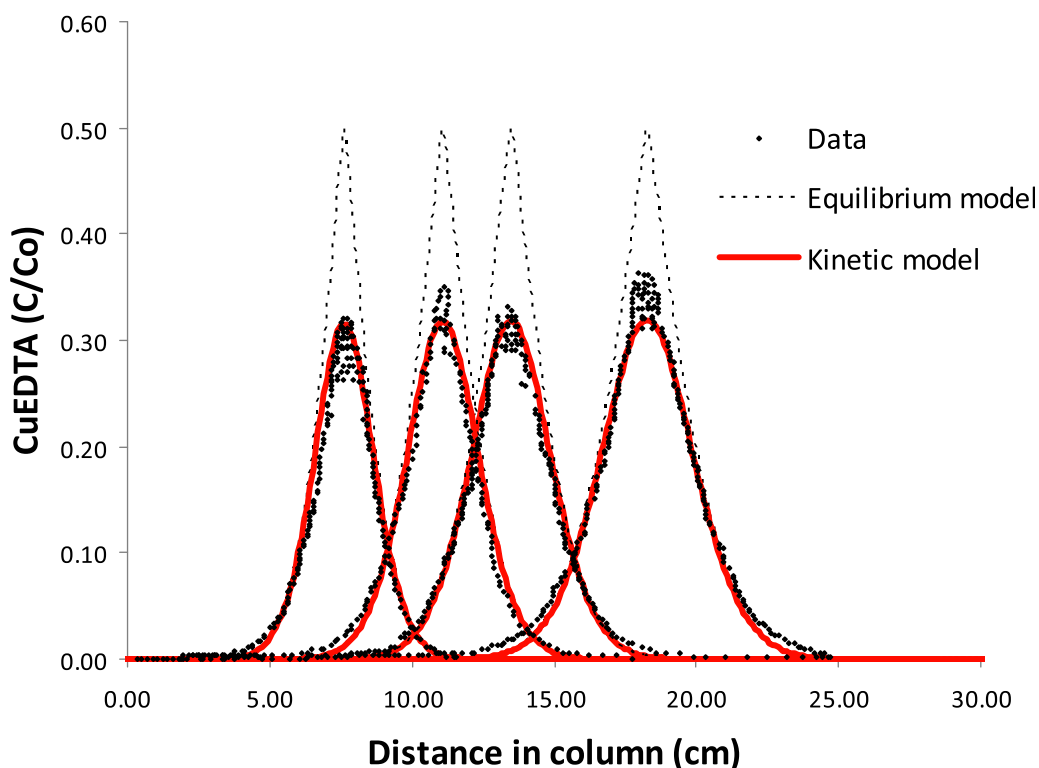


Figure 1. Best fit obtained with the kinetic reactive transport model for four different times (610, 916, 1114, and 1510 s). CuEDTA^{2-} concentrations for the experiment conducted with a flow rate of 2.67 mL/min. The first and the third curves starting from the left are used for calibration. The remaining two curves are predictions, used for model validation. The curves corresponding to the ADRE model considering instantaneous equilibrium is reported for comparative purposes.

corresponding to small times) result in an instantaneous reaction, so that c_C converges to the solution presented by *Gramling et al.* [2002]. The shape of the concentration curves is also very sensitive to the choice of the hydrodynamic dispersion coefficient (D).

[16] Calibration of the ADRE model is performed upon considering three adjustable parameters, D , β_0 , and m . Calibration is performed manually against the data associated with sampling times 610 and 1114 s jointly (one single individual curve could not be used since the m parameter characterizes the temporal behavior of reaction rates). The best fit between experimental observations and modeling results is obtained for $D = 1.30 \times 10^{-3} \text{ cm}^2/\text{s}$ (which is slightly lower than the value calibrated by *Gramling et al.* [2002] for their nonreactive transport experiment), $\beta_0 = 240 \text{ L}/(\text{mol s}^{1-m})$, and $m = 0.93$. The calibrated parameters are then used to provide predictions associated with the remaining two sampling times corresponding to 916 and 1510 s, respectively. Figure 1 compares the spatial distribution of the (normalized) reaction product, the results obtained with our proposed kinetic reactive transport model for all four sampling times, and the analytical solution obtained by assuming instantaneous reaction with complete pore-scale mixing. The agreement between our model and the experimental data is quite remarkable.

[17] A most significant result of our model is the evolution of β with time. The analysis of *Haggerty et al.* [2004] suggests that the mass transfer time, which is inversely proportional to the first-order transfer rate coefficient, scales as

a power law of the advective and experimental observation times (t_{adv} and t_{exp} , respectively). These authors derive the corresponding scaling exponents by a linear regression between the log-transformed diffusion time and t_{adv} and t_{exp} . In our context we can assume that t_{adv} corresponds approximately to the location of the observed peak concentration of the reaction product (the actual experimental curve is virtually symmetric), while t_{exp} is the time at which a given profile of the reaction product concentration is reported. *Haggerty et al.* [2004] find that the first-order mass transfer rate coefficient scales as $\bar{t}_{adv}^{-0.85}$, or else as $\bar{t}_{exp}^{-0.88}$, with correlation coefficients $r^2 = 0.62$ and 0.71 , respectively. Our calibrated value of m ($= 0.93$) is remarkably close to these two exponents. This supports our idea that the failure of the modeling attempt of *Gramling et al.* [2002] is related to their disregarding of incomplete mixing effects associated with delayed pore-scale diffusion. Incorporating such effects in the way we propose has a strong impact on the model calibration and predictive capabilities.

[18] Our results should be contrasted with those of *Ederly et al.* [2009, 2010] who showed that a particle tracking scheme in conjunction with an ADE-based depiction of transport could not reproduce the concentration profiles of the product, neither at the peak, nor at the tails. The agreement observed in Figure 1 is of similar quality to that obtained by *Ederly et al.* [2010; their Figure 1a] when their PT scheme is implemented within a non-Fickian model based on a CTRW approach. They simulated the bimolecular reaction by introducing two types of particles (marked “A” and “B”)

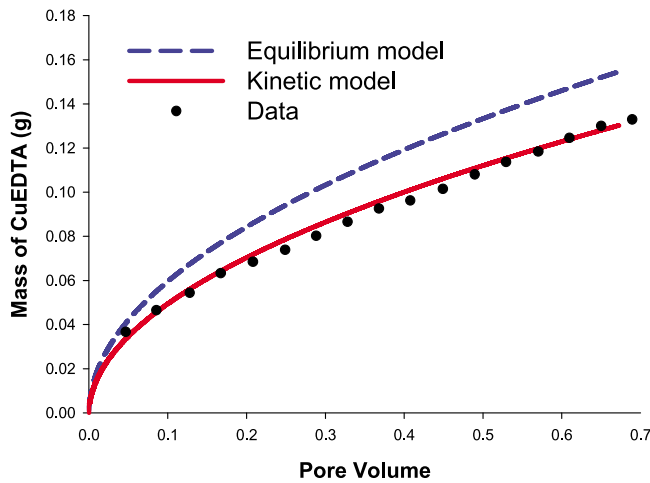


Figure 2. Total mass of CuEDTA^{2-} produced as a function of time compared to that predicted by our model for a flow rate of 2.7 mL/min. The curve corresponding to the ADRE model considering instantaneous equilibrium is reported for comparative purposes.

into the simulation domain and then letting them migrate within the system until the relative distance between two given A and B particles was smaller than a prescribed value, R . When this happens, the two particles are replaced by a “C” particle, mimicking the occurrence of a reaction. Therefore, the model of *Ederly et al.* [2009, 2010] has essentially two key adjustable parameters, one governing the probabilistic distribution of the particles transitions times, and a second one being the “effective” reaction radius, R . The latter is found to be orders of magnitude larger than the molecular interaction radius, which specifies the capability of two molecules to react and is usually in the order of nanometers. Establishing a relationship between these two parameters and those appearing in our model is not trivial and needs to be further investigated.

[19] We next consider the integrated reaction rate as a function of time, $R(t) = \int_{-\infty}^{+\infty} r(x,t)dx$, and the corresponding cumulative mass of CuEDTA^{2-} produced, $M(t) = \int_0^t R(\tau)d\tau$. Figure 2 depicts the time evolution of measured M together with that determined by our model on the basis of the calibrated parameters. As a term of comparison, the produced mass estimated on the basis of an ADRE model assuming instantaneous equilibrium is also reported. At early times, the reaction is relatively fast, because solutes move mainly in the mobile zone. The immobile zones have not yet been accessed by the solute, and thus mixing can almost be considered complete. The rate of growth of $M(t)$ then decreases with time, being mostly controlled by the slow diffusion of the reacting species into and out of the immobile regions of the system, causing incomplete (delayed) mixing. Extrapolating the data reported in the experiment to large times, results in $M(t)$ being (approximately) proportional to $t^{0.53}$. Our ADRE kinetic model shows that $M(t)$ is asymptotically proportional to $t^{0.5}$. This is equivalent to having $R(t) = dM/dt$ to scale as $t^{-0.5}$ for large times, without ever stabilizing to a nonzero value (notice that the same behavior for dM/dt would also be obtained with an ADRE model assuming instantaneous equilibrium). As a consequence, we find

that diffusion becomes the only relevant process at large times.

[20] Among the predictive capabilities of the kinetic ADRE model proposed, it is worth mentioning that the model is capable of capturing the observed temporal increase of the height of the peak of CuEDTA^{2-} . This feature can be observed in Figure 1, despite the large error associated to the measurements at such high concentration values. Our kinetic model indicates that two competing processes affecting the peak of the reaction product are simultaneously taking place in the column. While hydrodynamic dispersion is reducing the peak of the reaction product due to dilution, the rate-limited mass transfer process taking place between mobile and immobile water causes an increase of the reaction product due to the late occurrence of local reactions in the immobile water (delayed mixing). This interplay between dispersive and reactive processes was already discussed by *Ederly et al.* [2009, 2010]. Notice that the peak concentration values obtained with the analytical solution of the ADRE assuming instantaneous equilibrium (also reported in Figure 1) not only overestimate of about 40% the peak concentration, but also display a constant height of the peak (due to the instantaneous total local consumption of the species with lowest concentration).

[21] The evolution of the peak concentration of CuEDTA^{2-} with time is very sensitive to the actual choice of parameters, indicating that calibration is indeed possible. The sensitivity analysis on the relevant model parameters describing the kinetic term is shown in Figure 3. For the conditions of Gramling’s experiment, our model shows that the evolution of the simulated peak value with time is very sensitive to the m and β_0 values (Figures 3a and 3b, respectively) but not to hydrodynamic dispersion (not shown). The curve for peak concentration versus log-time seems to display a straight line for large times, where the slope is governed by m , and for a given slope, the intercept is dictated by the β_0 value. Irrespectively of the actual values of the parameters, all curves show that dispersion is the dominant factor for very small times (residence time in the column on the order of 10^{-3} pore volumes) and the height of the peak of the reaction product decreases with time. Then, the late occurrence of local reactions associated with the effects of the immobile water regions becomes increasingly important and the peak height increases with time. Since the time that is required for the system to experience the above mentioned transition in the relative strength of dominant processes is extremely small and the residence times in the column range between 0.1 and 1 pore volumes, this feature cannot be used to validate or reject the kinetic model presented.

[22] Our model does not provide a very good reproduction of the tails of the concentration profiles, the agreement between observed and modeled tails slightly deteriorating for the largest observation time reported. This is not a surprising feature. Tails are associated with low values of either species A or B . Under these conditions, the reaction rate is close to 0 (see equation (2)), and the transport equations of the species A and B basically reduce to the ADE. The fact that an ADE-based transport model cannot properly reproduce such tails is a well-known feature that has been extensively discussed in the literature [e.g., *Berkowitz et al.*, 2006]. However, this discrepancy did not influence significantly the ability of the model to capture the remaining salient features of the experiment, in particular the total rate of

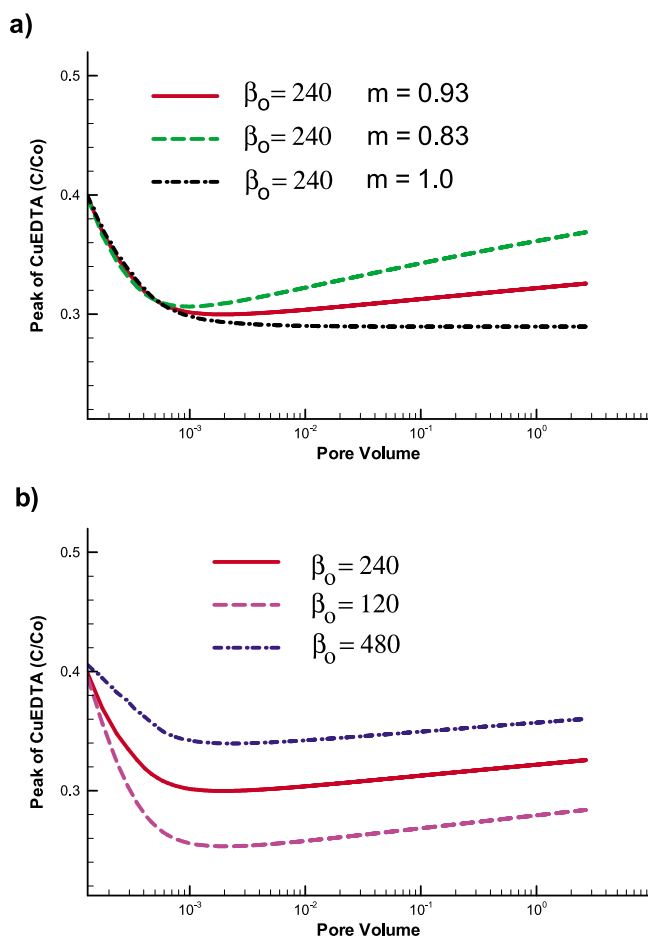


Figure 3. Sensitivity analysis of the peak concentration of CuEDTA²⁻ produced as a function of time: (a) sensitivity to the power law exponent m (dimensionless) and (b) sensitivity to the coefficient β_0 (all reported values in L/(mol s^{1-m})). The best fit used throughout the text was obtained with $m = 0.93$, $\beta_0 = 240$ L/(mol s^{1-m}).

production, since the tails do not contribute much to the total mass.

[23] Finally, we note that, in principle, the coefficient β appearing in equation (2) is also related to the chemistry of the system under study. For the purpose of this analysis we have assumed that this dependence is absorbed by β_0 . Further work is needed to fully explore this dependence and to discern the various contributions to the system dynamics.

4. Concluding Remarks

[24] We have provided an interpretation of some of the experimental results of Gramling *et al.* [2002] by means of a modeling approach based on the formulation of the reactive transport problem in terms of a set of PDEs and conceptualizing the porous system as an equivalent continuum. The salient feature is the introduction of an effective kinetic reaction term whose forward rate coefficient is linear in the concentration of both reactants. This term is included in the model as a way to account for incomplete mixing. The same experiments were recently modeled by Ederly *et al.* [2009, 2010] on the basis of a stochastic particle tracking methodology, upon including pore-scale dynamics via a solute

particles displacement *pdf* and the introduction of an effective reaction distance.

[25] Our modeling approach is based on the idea that microscale heterogeneity of the pore space causes the reactive solutes to experience differential diffusion, developing on different time scales, so that reactants cannot interact instantaneously and are controlled by mass transfer between regions associated with different pore velocities. The agreement between the observed experimental concentration profiles and our modeling results suggests that the reactive transport scenario analyzed can be modeled by means of a continuum-scale representation, when an appropriate effective first-order kinetic term for the reaction rate is considered. Essentially, this term is included in the model as a way to account for incomplete mixing. On the contrary, modeling the analyzed experiments on the assumption that the system attains instantaneously local equilibrium conditions (assuming complete mixing locally) provides an overestimate of the observed reaction product.

[26] Our modeling approach requires the calibration of three parameters. These include (1) the impact of dispersive processes, as imbued in the dispersion coefficient and (2) effects of diffusion between zones associated with different fluid velocity, as reflected by the dependence of the reaction rate coefficient on observation time. This dependence is generally nonlinear and is consistent with observed dependencies of mass transfer rates on residence/observation times in dual porosity media. Our results also suggest that the data we analyze can be interpreted with similar high quality agreement by adopting the hydrodynamic dispersion coefficient calibrated by Gramling *et al.* [2002] in the context of nonreactive transport experiments.

[27] The assessment of the format of the functional dependence of the reaction rate coefficient on both the microscale properties of the porous medium and the system chemistry is still an open issue. Further developments might include, for instance, the assessment of the potential of upscaling methodologies to provide further insights on the physics underpinning the experimental observations. The analysis of the relationships between the parameters appearing in our model and those adopted in the stochastic particle tracking simulations by Ederly *et al.* [2009, 2010] can provide relevant information and a solid basis upon which one can understand how the information content of parameters defined on different scales can be transferred. Nevertheless, we believe that our interpretation can form the basis to spark further research to assess the potential use of continuum approaches for the quantitative interpretation of reactive transport problems at different scales.

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