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APPLICATION OF A LUMPED-PROCESS MATHEMATICAL MODEL TO DISSOLUTION OF NON-UNIFORMLY DISTRIBUTED IMMISCIBLE LIQUID IN HETEROGENEOUS POROUS MEDIA

J. C. Marble¹, E. L. DiFilippo¹, Z. Zhang², G. R. Tick³, and M. L. Brusseau^{1,2,*}

¹Hydrology and Water Resources University of Arizona 429 Shantz Tucson, Arizona 85721

²Soil, Water, and Environmental Science University of Arizona 429 Shantz Tucson, Arizona 85721

³University of Alabama Tuscaloosa, AL

Abstract

The use of a lumped-process mathematical model to simulate the complete dissolution of immiscible liquid non-uniformly distributed in physically heterogeneous porous-media systems was investigated. The study focused specifically on systems wherein immiscible liquid was poorly accessible to flowing water. Two representative, idealized scenarios were examined, one wherein immiscible liquid at residual saturation exists within a lower-permeability unit residing in a higher-permeability matrix, and one wherein immiscible liquid at higher saturation (a pool) exists within a higher-permeability unit adjacent to a lower-permeability unit. As expected, effluent concentrations were significantly less than aqueous solubility due to dilution and by-pass flow effects. The measured data were simulated with two mathematical models, one based on a simple description of the system and one based on a more complex description. The permeability field and the distribution of the immiscible-liquid zones were represented explicitly in the more complex, distributed-process model. The dissolution rate coefficient in this case represents only the impact of local-scale (and smaller) processes on dissolution, and the parameter values were accordingly obtained from the results of experiments conducted with one-dimensional, homogeneously-packed columns. In contrast, the system was conceptualized as a pseudo-homogeneous medium with immiscible liquid uniformly distributed throughout the system for the simpler, lumped-process model. With this approach, all factors that influence immiscible-liquid dissolution are incorporated into the calibrated dissolution rate coefficient, which in such cases serves as a composite or lumped term. The calibrated dissolution rate coefficients obtained from the simulations conducted with the lumped-process model were approximately two to three orders of magnitude smaller than the independently-determined values used for the simulations conducted with the distributed-process model. This disparity reflects the difference in implicit versus explicit consideration of the larger-scale factors influencing immiscible-liquid dissolution in the systems.

Keywords

DNAPL; dissolution; modeling

*Corresponding author brusseau@ag.arizona.edu.

INTRODUCTION

Mathematical modeling has become a critical component of risk assessment, characterization, and remediation-system development efforts for hazardous-waste sites. Unfortunately, the application of advanced mathematical models is often greatly constrained by insufficient knowledge of subsurface properties and contaminant distributions. This is particularly the case for immiscible-liquid contaminated sites, for which the location and architecture of the source zones is rarely known in detail. Thus, the use of simpler models for simulating immiscible-liquid dissolution at larger scales, particularly the field scale, has become of great interest. A focus of this interest has been the issue of the scalability of the first-order mass transfer approach typically used to represent immiscible-liquid dissolution (e.g., Zhang and Brusseau, 1999; Saba and Illangasekare, 2000; Brusseau et al., 2002; Parker and Park, 2004; Park and Parker, 2005; Christ et al., 2006). When applied to a column system for example, the mass-transfer term clearly represents the pore-scale mechanisms mediating dissolution at the local scale. However, when this approach is applied to larger-scale systems, the mass-transfer term represents all factors influencing dissolution that are not otherwise explicitly represented in the model. In such cases, the mass-transfer rate coefficient becomes in essence a macro-scale model-calibration parameter. This situation is especially apparent for heterogeneous systems comprising non-uniform immiscible liquid distributions.

The subsurface environment is heterogeneous across a multitude of scales, and this heterogeneity has a profound impact on the movement, retention, and distribution of immiscible liquids. In fact, porous-medium heterogeneity is generally considered to be the predominant factor governing the distribution of immiscible liquid in subsurface systems (e.g., NRC, 1999,2000,2004;EPA, 2003). This has been illustrated by the results of laboratory experiments conducted with well-defined heterogeneous systems (e.g., Schwillie, 1988;Kueper et al., 1989; Illangasekare et al., 1995a,b;Oostrom et al., 1999), as well as by detailed examination of soil cores and excavation profiles for actual immiscible-liquid-contaminated source zones (e.g., Poulsen and Kueper, 1992;Kueper et al., 1993;Jawitz et al., 2000;Parker et al., 2003). The impact of porous-medium heterogeneity and/or non-uniform immiscible-liquid distribution on immiscible-liquid dissolution behavior and associated aqueous-concentration profiles has been examined for some time through laboratory, modeling, and field studies (e.g., Schwillie, 1988;Anderson et al., 1992;Mayer and Miller, 1996;Berglund, 1997;Powers et al., 1998;Unger et al. 1998;Broholm et al., 1999; Brusseau et al., 1999,2000,2002;Zhang and Brusseau, 1999;Frind et al., 1999;Nambi and Powers, 2000;Saba and Illangasekare, 2000;Sale and McWhorter, 2001;Lemke et al., 2004;Parker and Park, 2004;Phelan et al., 2004;Soga et al., 2004;Rivett and Feenstra, 2005;Fure et al., 2006;Lemke and Abriola, 2006; Brusseau et al., 2007,2008). An expert-panel workshop was convened recently to discuss the research needs for characterization and remediation of immiscible-liquid contaminated source zones (SERDP, 2006). One issue that was particularly emphasized was the behavior of systems in which immiscible liquid is associated with regions of the subsurface that are poorly accessible to flowing groundwater (i.e., that are “flow limited”), such as immiscible liquid located within or adjacent to lower-permeability zones.

The purpose of this study was to investigate the use of a lumped-process mathematical model to simulate the complete dissolution of immiscible liquid non-uniformly distributed in physically heterogeneous porous-media systems. The study focused on idealized systems in which immiscible liquid is hydraulically poorly accessible, wherein immiscible liquid was located within (residual saturation) or adjacent to (pool) lower-permeability matrices. The data were analyzed with both distributed-process and lumped-process mathematical models.

MATERIALS AND METHODS

Systems Investigated

As noted above, the objective of the study was to investigate the use of mathematical models for simulating immiscible-liquid dissolution in systems wherein immiscible liquid is poorly accessible to flowing water. As such, the flow-cell systems were designed to represent, in an idealized manner, source zones that have aged to an extent such that contaminant mass associated with hydraulically accessible domains (e.g., so-called residual or ganglia immiscible liquid within higher-permeability units) has been removed, and immiscible liquid associated with flow-limited regions remains. Two representative, idealized scenarios were examined, one wherein immiscible liquid at residual saturation exists within a lower-permeability unit residing in a higher-permeability matrix, and one wherein immiscible liquid at higher saturation (a pool) exists within a higher-permeability unit adjacent to a lower-permeability unit.

The flow-cell systems were prepared in such a manner to focus specifically on the issue of poorly accessible immiscible liquid. Thus, the immiscible liquid was emplaced only in the target zones, rather than being “spilled” into the system. In addition, an idealized permeability distribution was used to eliminate the impact of non-uniform flow associated with permeability variability in regions upgradient and downgradient of the source zone on mass removal and mass flux. It should be emphasized that the systems are designed to represent the specific idealized scenarios noted above, and that the immiscible-liquid distributions employed are not necessarily those that would occur if immiscible liquid were spilled into the top of a water-saturated flow cell with these particular permeability configurations. This is particularly true for the systems with lower-permeability units residing in a matrix of higher-permeability material (e.g., Kueper et al., 1989; Kueper and Frind, 1991a,b; Oostrom et al., 1999). However, these configurations comprising immiscible liquid emplaced within a lower-permeability zone represent systems wherein site conditions promoted penetration of immiscible liquid into lower-permeability layers (in this case a fine sand). This might occur for example, when immiscible liquid enters a variably saturated (e.g. vadose zone) profile, which afterwards becomes water saturated due to a rise in the water table. The trapping of immiscible liquid in lower-permeability units under such conditions has been demonstrated in prior laboratory and modeling studies (e.g., Illangasekare et al., 1995a,b; Brusseau and Oostrom, 2001; Oostrom et al., 2003).

The results of six sets of dissolution experiments were used in this study, designated as Lower-K-1, Lower-K-2, Lower-K-3, Pool, Control, and Column. The first three data sets were obtained for systems wherein immiscible liquid was located within a lower-permeability unit. For the first experiment (Lower-K-1), two rectangular lower-permeability zones, composed of 360- μm diameter and 172- μm diameter sand, respectively, were emplaced within a higher-permeability (724- μm diameter sand) matrix (see Figure 1a). For the second experiment (Lower-K-2), immiscible liquid was located within three lenticular lower-permeability zones (360- μm) packed within a higher-permeability matrix (724- μm) (see Figure 1b). For the third experiment (Lower-K-3), a single cubic (2.5-cm each side) lower-permeability zone (360- μm) was placed within a uniform packing of higher-permeability (724- μm) sand. A fourth experiment (Pool) was conducted to examine the case wherein pools of immiscible liquid reside within higher-permeability units adjacent to a lower-permeability unit. For this case, three lenticular higher-permeability zones, composed of 724- μm diameter sand, were emplaced within a lower-permeability (360- μm) matrix. The configuration was similar to that used for experiment Lower-K-2, except the two media types were reversed. For this system, the immiscible liquid was injected into the designated zones during packing. A control experiment was conducted to characterize dissolution of immiscible liquid non-uniformly distributed in a homogeneous porous medium. Finally, a set of ancillary column-scale dissolution experiments was conducted under conditions wherein dissolution was as ideal as possible to evaluate

system-scale effects and to determine local-scale dissolution rate coefficients. The first four experiment sets (Lower-K-1,2,3, and Pool) were first reported in Brusseau et al. (2008). The Control and Column experiments are newly reported herein.

Materials

The porous media used in the experiments are commercially available, natural sands obtained from Unimin Corporation (Le Sueur, MN). Three media with different median particle diameters were used, 724 μm (20-30 mesh), 360 μm (40-50 mesh), and 172 μm (70-100 mesh). Relevant properties of the media are reported in Table 1. Trichloroethene and carbon tetrachloride, ACS grade (Aldrich Chemical Co, Inc., Milwaukee, WI), were used as the immiscible liquids. They were dyed with certified Sudan IV (Aldrich Chemical Co, Inc., Milwaukee, WI) at a concentration of 100 mg/L, which has been shown to have minimal impact on fluid properties and behavior (e.g., Schuille, 1988; Kennedy and Lennox, 1997). Dichloromethane (DCM) used in extractions was ACS/HPLC certified solvent (Burdick and Jackson, Muskegon, MI). The flow cells used in the study were constructed of stainless steel and tempered glass, with approximate dimensions of 50 cm long by 40 cm high by 5 cm wide (except as noted below). The flow cells were equipped with multiple, evenly spaced injection/extraction ports, the latter of which could be used to collect discrete aqueous samples and flow-rate measurements.

Methods

The flow cells were packed under saturated conditions (ponded water). The flow cell was packed to a height coincident with the top boundary of each of the planned inclusions. The matrix was then excavated to the lower boundary of the planned immiscible-liquid zone, and the selected source-zone material was added. For the Lower-K experiments, the medium for each source zone was prepared by thoroughly mixing a pre-determined amount of damp sand (moisture content of ~20%) with an amount of immiscible liquid that would yield a saturation close to residual. This material was then packed into each designated location. Subsamples of the contaminated media were collected during packing and subjected to solvent extraction to determine actual saturations, which were approximately 14% for all experiments (except the Pool experiment). For the “pool” experiment, the water table was raised above the top boundary after excavation, and the zone was packed with 724- μm diameter sand. The water table was then lowered to 1 cm below the bottom of the zone, and immiscible liquid was injected into the top of the zone at a rate of 1.0 ml/min using a syringe pump. After emplacement of the zones, the water table was slowly raised and the matrix sand was packed above the zone. Dye and non-reactive tracer tests were conducted for each of the source-zone configurations to characterize the associated flow fields.

A smaller, cylindrical stainless steel flow cell was used for experiment Lower-K-3 and the control experiment. For these two experiments, the source zone, containing a residual saturation of immiscible liquid, was placed in the center (both radially and longitudinally) of the flow cell. The only difference between the two experiments was that the immiscible liquid resided in a finer-grained sand for experiment Lower-K-3, while the control experiment comprised a homogeneous pack of the same coarser-grained sand used as the matrix for experiment Lower-K-3.

A set of ancillary one-dimensional column experiments was conducted under conditions wherein dissolution was as ideal as possible to evaluate system-scale effects and to determine local-scale dissolution rate coefficients. These experiments were conducted with stainless steel columns (lengths ranging from 5 to 80 cm). A residual saturation of immiscible liquid was established throughout the column using standard procedures wherein the immiscible liquid is injected and then displaced with water (e.g., Imhoff et al., 1994; Powers et al., 1994; Johnson

et al., 2003). A subset of experiments was conducted wherein the immiscible liquid was mixed with damp porous media prior to packing the column (similarly to the manner in which immiscible liquid was emplaced for the Lower-K flow-cell experiments). The results of the two sets of experiments were essentially identical, indicating the procedure used to emplace the immiscible liquid had no measurable impact on dissolution behavior.

The flow rates for the experiments were equivalent to an average pore-water velocity of approximately 20 cm/hr. For all experiments, effluent samples were collected with a glass syringe and either analyzed immediately with an ultraviolet-visible (UV-VIS) spectrophotometer (Shimadzu 1601) or injected into glass autosampler vials. The latter samples were stored at 4°C until analyzed using a gas chromatograph (Shimadzu 14A or 17A) with a flame ionization detector (FID) and electron capture detector (ECD). The quantifiable detection limits were approximately 1 mg/L (UV-VIS), 0.1 mg/L (FID), and 0.0001 mg/L (ECD). Upon completion of all experiments (except for which the dual-energy gamma system was used as discussed below), the flow-cell was opened and sub-samples of the porous media were collected for solvent-extraction analysis. The sub-samples were added to vials containing DCM. The samples were then sealed and shaken. Aliquots of the extractant were removed and analyzed using a gas chromatograph (FID). These analyses revealed that all immiscible-liquid mass was removed to the limit of detection.

The initial immiscible-liquid saturation was known a priori for all experiments except for the pool experiment. Thus, a fully automated dual-energy (280 mCi Americium and 100 mCi Cesium) gamma radiation system was used to measure immiscible-liquid saturations within the flow cell for this experiment (see Figure 1c), following procedures used in prior experiments (e.g., Oostrom et al., 1999; Brusseau et al., 2000; 2002). The spatial resolution was approximately 0.25 cm², with a saturation measurement sensitivity of approximately 0.003. The scans required 60 seconds per location, for a total of approximately 12 hours for the entire flow cell.

DATA ANALYSIS

Three-dimensional Distributed-Process Model

A three-dimensional distributed-process mathematical model based on that presented by Zhang and Brusseau (1999) was used to simulate flow, immiscible-liquid dissolution, and solute transport in the flow cells following the methods employed by Brusseau et al. (2002). The governing equation for solute transport in the flow cells with dissolution of immiscible liquid is described by:

$$\theta_a \frac{\partial C}{\partial t} + \rho_N \frac{\partial \theta_N}{\partial t} = \frac{\partial}{\partial x_i} \left(\theta_a D_{ij} \frac{\partial C}{\partial x_j} \right) - q_i \frac{\partial C}{\partial x_i} \quad (1)$$

where C is the aqueous concentration of solute; θ_a is the fractional volumetric water content; θ_N is the fractional volumetric content of the immiscible liquid; ρ_N is density of the immiscible liquid; q_i is Darcy velocity; D_{ij} is the dispersion coefficient tensor; x_i is cartesian coordinates; $i, j = 1, 2, 3$ and conforms to the summation convention; and t is time. Sorption of the organic compounds by the media used in these experiments is minimal, and is therefore ignored.

The spatial distribution of θ_N is represented explicitly, and the initial distribution was based on the measurements made during flow-cell preparation. Immiscible-liquid dissolution is described with the widely used first-order mass transfer equation:

$$\rho_N \frac{\partial \theta_N}{\partial t} = k_{La} (C - C_s) \quad (2)$$

where k_{La} is a lumped mass transfer coefficient for dissolution, and C_s is the aqueous solubility of the immiscible liquid. The magnitude of k_{La} will decrease with time given that it incorporates the global specific immiscible-liquid/water interfacial area, which decreases as dissolution proceeds. The time dependency of k_{La} is represented by:

$$k_{La}(t) = k_{La0} \left[\frac{Re(t)}{Re_0} \right]^{\beta_1} \left[\frac{\theta_N(t)}{\theta_{N0}} \right]^{\beta_4} \quad (3)$$

where k_{La0} and Re_0 are the initial local (nodal) values, and Re is the Reynolds number [$v \rho_w d_{50} / \mu_w$].

As shown by several investigators (e.g., Miller et al., 1990; Powers et al., 1992, 1994; Imhoff et al., 1994), the magnitude of k_{La} is dependent on many factors, including pore-water velocity and porous media properties. Thus, the local (i.e., nodal) value of k_{La} is expected to vary spatially for a heterogeneous system such as used herein. An empirical relationship, in conjunction with the independently measured initial k_{La} value, is used to account for these effects. The correlation used is the one presented by Powers et al. (1994):

$$Sh = \alpha_N Re^{\beta_1} \delta^{\beta_2} U_i^{\beta_3} \left(\frac{\theta_N}{\theta_{N0}} \right)^{\beta_4} \quad (4)$$

where Sh is the modified Sherwood number [$k_{La} d_{50}^2 / D_m$]; $\delta = d_{50} / d_M$ is a normalized grain size; $U_i = d_{60} / d_{10}$ is the uniformity index for the porous medium; α_N and β are coefficients; θ_{N0} is the initial volumetric fraction of immiscible liquid in the source zone; d_i is the diameter of the media grains, % of which in weight are smaller than d_i ; $d_M (=0.05 \text{ cm})$ is taken as the reference diameter; D_m is the aqueous-phase molecular diffusion coefficient of the solute; v is pore-water velocity (q/θ_a); ρ_w and μ_w are density and dynamic viscosity of water, respectively. The values of coefficients β_1 (0.598), β_2 (0.673), β_3 (0.369), and β_4 ($0.518 + 0.114\delta + 0.10U_i$) were obtained from Powers et al. (1994). The α_N term is calculated with equation 4 using the laboratory-measured value for initial k_{La} .

To summarize, equation 4 is not used to solve the inverse problem (i.e., to obtain calibrated estimates of initial k_{La} values). Rather, equation 4 is used to convert the initial k_{La} values obtained independently from the column experiments to discrete nodal values for use in modeling the flow-cell systems, thereby accounting for the spatial differences in physical properties that exist in the flow cells. Specifically, the local (nodal), initial k_{La} values are calculated from the initial column-obtained value (designated as k_{La}') as follows:

$$k_{La} = k_{La}' \left(\frac{d_{50}'}{d_{50}} \right)^2 \left(\frac{Re'}{Re} \right)^{\beta_1} \left(\frac{\delta'}{\delta} \right)^{\beta_2} \left(\frac{U_i'}{U_i} \right)^{\beta_3} \quad (5)$$

where primed variables are representative of the conditions used to obtain the measured k_{La} value for the column experiments. This procedure allows us to produce simulations that are independent predictions of the measured data, which is a more robust test of model performance compared to the often-used calibration approach. The impact of uncertainty in parameter values

and the sensitivity of simulations to the parameters for this approach are discussed in Brusseau et al. (2002).

The permeability fields were developed using the measured intrinsic permeabilities and calculated relative permeabilities. Initial aqueous-phase relative permeabilities were calculated using relationships based on the Mualem pore-size distribution model (Mualem, 1976), as discussed by Lenhard and Parker (1987). A primary assumption associated with the calculations is that the entrapped immiscible liquid is uniformly distributed over the entire pore space. Considering that the immiscible liquid was mixed into the sand for the lower-K experiments, this is a viable assumption for those experiments. The relative permeabilities were computed using the two-phase model derived by Lenhard and Parker (1987), modified to account for immiscible-liquid/water fluid pairs. The effect of dissolution on reduction of immiscible-liquid saturation and the resultant changes in relative permeability and pore-water velocity is explicitly considered in the model. The change in relative permeability is described using:

$$k_{rw} = 1 - [(1 - k_{ro}) S_N / S_{N0}] \quad (6)$$

where k_{rw} is the relative permeability and k_{ro} is the initial aqueous relative permeability. The change in pore-water velocity is implemented through the equality $v = q/[\theta(1-S_N)]$, where θ is total porosity.

The flow cells were discretized into 0.5-1 cm $\times$ 1 cm elements. For flow calculations, the domain was expanded horizontally to allow the use of constant water-head boundaries at both ends of the model domain, while using no-flow boundaries at the top and bottom. For transport, zero dispersive-flux conditions were used at the boundaries. The numerical methods used to solve the flow and transport equations are described in Zhang and Brusseau (1999).

One-dimensional Lumped-Process Model

A one-dimensional model employing equations 1, 2, and 3 (with the Re term removed from eqn 3) was calibrated to the elution curves for both the flow cell and column experiments. Two parameters were calibrated, k_{La} and β_4 . For these simulations, the system was conceptualized as a pseudo-homogeneous medium, with immiscible liquid uniformly distributed along the entire length and cross section of the system. The porous medium and water flow were assumed to be uniform. Effective immiscible-liquid saturations (S_N) were calculated for these simulations by dividing the known volume of immiscible liquid by the pore volume of the entire flow cell (Table 2). This extremely simplified approach represents a scenario where minimal information is available concerning the distribution of permeability and immiscible liquid. With this approach, the larger-scale factors that influence immiscible-liquid dissolution and transport are not explicitly represented in the model. As a result, their impact is incorporated into the calibrated dissolution rate coefficient, which in such cases serves as a composite, condition-dependent term. The simulations were very sensitive to the magnitude of the calibrated terms, with coefficient of variations of less than approximately 5%. The 1-D model was also calibrated to the data obtained from the column experiments. Given that these systems consisted of uniformly distributed (at the local scale) immiscible liquid in homogeneously packed columns, immiscible-liquid dissolution is assumed to be influenced only by local-scale mass transfer processes.

RESULTS AND DISCUSSION

The contaminant elution curves obtained from the flow-cell experiments are presented in Figure 2. The effluent concentrations are less than aqueous solubility values as expected due

to dilution effects associated with the system configurations. The elution curves exhibit relatively extensive periods wherein the concentrations decrease gradually, reflecting the impacts of mass-removal constraints. Mass removal was constrained primarily by the non-uniform flow fields associated with the systems, wherein most of the water flowed around rather than through the immiscible-liquid contaminated zones, as observed in prior studies (e.g., Frind et al., 1999; Brusseau et al., 2000; Nambi and Powers, 2000). This was true for the pool system as well as the lower-K-zone systems, as confirmed by the results of dye tracer tests (data not shown). The mass removal and mass flux reduction behavior observed for these systems is discussed by Brusseau et al. (2008).

The application of the distributed-process model is illustrated in Figure 3, wherein it is used to independently predict the results of the Lower-K-1 experiment. Recall that the permeability field and the distribution of the immiscible-liquid zones were represented explicitly in this model. Thus, the impact on dissolution behavior of the non-uniform immiscible-liquid distribution is explicitly accounted for in the simulation. The k_{LA} and β_4 values used for the simulation were obtained independently from the column experiments, and thus represent only the impact of local-scale dissolution behavior. Inspection of Figure 3 shows that the predicted simulation provides a good match to the data. The relatively minor differences between measured and predicted behavior may be due in part to nonuniform distribution of immiscible liquid within the inclusions, as discussed by Brusseau et al. (2002). The successful predictions obtained with the model illustrate that local-scale dissolution rate coefficients can be used to simulate immiscible-liquid dissolution at larger scales if the larger-scale factors influencing dissolution are explicitly accounted for in the model, as previously discussed by Brusseau et al. (2002). Unfortunately, as noted above, such information is often lacking, particularly for field applications.

The simulations produced with the simple lumped-process model are presented with the measured data in Figure 4. The simulations adequately match the measured data. The calibrated mass-transfer coefficients for dissolution, k_{LA} and β_4 , are presented in Table 2. The calibrated k_{LA} values obtained for the lumped-process modeling are approximately two to three orders-of-magnitude smaller than the values obtained from the column experiments, and which were used successfully for the simulations conducted with the distributed-process model. The disparity in magnitudes of the values used for the lumped-process and distributed-process modeling reflects the difference in implicit versus explicit consideration of the larger-scale factors influencing immiscible-liquid dissolution in the systems. The k_{LA} value for the control experiment, 0.11 hr^{-1} , is also approximately 100 times smaller than the values obtained from the experiments conducted with the columns. The only difference between the control and column experiments is that immiscible liquid was distributed non-uniformly and did not encompass the entire cross section of flow for the former experiments. The calibrated dissolution rate coefficient is much smaller for the control experiment as would be expected to account for the effects of dilution on effluent concentrations.

The k_{LA} value obtained for experiment Lower-K-3 is approximately 40% smaller than the value obtained for the control experiment. These two experiments have identical system configurations, with the exception that the immiscible liquid resided in a finer-grained sand for experiment Lower-K-3, while the control experiment comprised a homogeneous pack of the same coarser-grained sand used as the matrix for the Lower-K-3 experiment. The difference in dissolution rate coefficient values thus illustrates the impact of by-pass flow effects wherein the immiscible liquid residing within the lower-permeability zone was poorly accessible to flowing water, thereby constraining overall mass removal.

The k_{LA} values for experiments Lower-K-2 and Lower-K-3 are similar, despite there being a significant difference in system lengths (50 cm vs. 10 cm). This apparent insensitivity to system

length was also observed for the results of the column experiments, for which similar k_{LA} values were obtained for experiments conducted with columns ranging from 5 cm to 80 cm long (data not shown). The k_{LA} value obtained for experiment Lower-K-1 is approximately 4 times smaller than the values obtained for experiments Lower-K-2 and Lower-K-3. This is likely due at least in part to the fact that one of the lower-permeability zones used for experiment Lower-K-1 was a finer grained sand than used for the other two experiments (Table 2). Thus, by-pass flow effects would be expected to be of greater significance for the Lower-K-1 system. The k_{LA} value obtained for the experiment conducted with higher saturations of immiscible liquid present (Pool experiment) is similar to those obtained for experiments Lower-K-2 and Lower-K-3. The calibrated values for the β_4 term range from 0.45 to 1.75, and exhibit no correlation to specific system configuration.

SUMMARY AND CONCLUSIONS

Distributed-process and lumped-process mathematical models were used to simulate the dissolution of immiscible liquid non-uniformly distributed in physically heterogeneous porous-media systems. The permeability field and the distribution of the immiscible-liquid zones were represented explicitly in the distributed-process model. Thus, the impact on dissolution behavior of non-uniform immiscible-liquid distributions is explicitly accounted for in the simulation. The dissolution rate coefficient values used for the distributed-process modeling were obtained independently from column experiments, and thus represent only the impact of local-scale dissolution behavior. The predicted simulations provided a good match to the data. This illustrates that local-scale dissolution rate coefficients can be used to simulate immiscible-liquid dissolution at larger scales if the larger-scale factors influencing dissolution are explicitly accounted for in the model.

A simple lumped-process model was also used to simulate the measured data. For these simulations, the system was conceptualized as a pseudo-homogeneous medium, with immiscible liquid uniformly distributed along the entire length and cross section of the system. This extremely simplified approach represents a scenario where minimal information is available concerning the distribution of permeability and immiscible liquid. With this approach, all factors that influence immiscible-liquid dissolution are incorporated into the calibrated dissolution rate coefficient, which in such cases serves as a composite or lumped term. The calibrated dissolution rate coefficients obtained for the lumped-process modeling were approximately two to three orders-of-magnitude smaller than the values obtained from the column experiments, and which were used successfully for the distributed-process modeling. The disparity in magnitudes of the values used for the lumped-process and distributed-process modeling reflect the difference in implicit versus explicit consideration of the larger-scale factors influencing immiscible-liquid dissolution in the systems.

Dilution effects associated with the non-uniform distributions of immiscible liquid were shown to have a significant impact on the magnitude of the calibrated dissolution rate coefficient for the lumped-process modeling, as would be expected. These results suggest that a first step in upscaling dissolution rate coefficients for use in simple models being applied to heterogeneous systems would be to account for dilution effects. This would require knowledge of the general size and location of the source zone. The degree of characterization necessary to obtain this level of information is significantly less than that needed to characterize the specific source-zone architecture, the latter information of which is needed for parameterization of a more complex, distributed-process model. While the simple model was able to produce reasonable simulations of the measured data, the simulations were obtained through calibration. The limitations inherent to model calibration, as well as means by which to independently estimate the macro-scale dissolution rate parameters are important considerations for such an approach.

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Figure 1A.
Schematic of flow-cell configuration for experiment Lower-K-1.

Figure 1B.
Schematic of flow-cell configuration for experiments Lower-K-2 and Pool.

Figure 1C.
Initial distribution of immiscible liquid for the Pool experiment.

Figure 2. Contaminant elution curves for the flow-cell experiments. Effluent concentrations are normalized by the aqueous solubility of the contaminant.

Figure 3. Measured and simulated (predicted) elution curves for experiment Lower-K-1 (flow cell with two lower-K source zones): three-dimensional distributed-process modeling.

Figure 4. Measured and simulated elution curves for the flow-cell experiments: one-dimensional lumped-process modeling.

Table 1

Physical properties of porous media

d ₅₀ (μm)	724	360	172
Hydraulic conductivity (cm/hr)	464.4	72	7.2
Porosity	0.34	0.36	0.38

Table 2

Experiment conditions and calibrated parameters for 1-D lumped-process modeling.

Experiment	Source zone media (μm)	Initial S_N^I (%)	$k_{La}(\text{hr}^{-1})$	β_4
Lower-K-1	360, 172	2	0.014	1.75
Lower-K-2	360	0.9	0.06	0.45
Lower-K-3	360	0.5	0.07	0.8
Pool	724	2	0.05	0.54
Control	724	0.6	0.11	1.3
Column ²	172, 360, 724	11-15	8-15	0.85

¹ S_N is defined as volume of immiscible liquid in pore space divided by total volume of pore space.

² Column experiments conducted with homogeneously packed column and uniform distribution of immiscible liquid.