

¹ **On the Transport of Emulsions in Porous**

² **Media**

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⁶ **Abstract**

⁷ Emulsions appear in many subsurface applications including bioremediation, surfactant-
⁸ enhanced remediation, and enhanced oil-recovery. Modeling emulsion transport in
⁹ porous media is particularly challenging because the rheological and physical prop-
¹⁰ erties of emulsions are different from averages of the components. Current modeling
¹¹ approaches are based on filtration theories, which are not suited to adequately ad-
¹² dress the pore-scale permeability fluctuations and reduction of absolute permeabil-
¹³ ity that are often encountered during emulsion transport. In this communication,
¹⁴ we introduce a Continuous Time Random Walk based alternative approach that
¹⁵ captures these unique features of emulsion transport. Calculations based on the
¹⁶ proposed approach resulted in excellent match with experimental observations of
¹⁷ emulsion breakthrough from the literature. Specifically, the new approach explains
¹⁸ the slow late-time tailing behavior that could not be fitted using the standard ap-
¹⁹ proach. The theory presented in this paper also provides an important stepping
²⁰ stone towards a generalized self-consistent modeling of multiphase flow.

²¹ *Key words:* emulsion, porous media, colloidal transport, memory effects

²² **1 Motivation**

²³ Transport [1] of (micro)emulsions in porous media is relevant to several subsur-
²⁴ face applications. Nearly all enhanced oil recovery processes involve emulsion
²⁵ formation and flow in some form or other [1]. Recently, it has been shown
²⁶ that emulsification of edible oils prior to injection into groundwater (as a
²⁷ substrate for enhanced bioremediation) improves its spatial distribution in
²⁸ the contaminated zone [2,3]. Subsurface uses of microemulsions, which posses
²⁹ large interfacial area and have the ability to solubilize otherwise immiscible
³⁰ liquids [4], include cleanup of chlorinated solvents from groundwater [5] and
³¹ enhanced oil-recovery [6–8].

³² Emulsion transport in porous media can be broadly classified according to
³³ (a) the stability of the emulsion and (b) the drop size of the dispersed phase
³⁴ relative to the pore size of the medium [9]. One class involves dilute, rela-
³⁵ tively unstable emulsion with very small average drop-size to pore-size ratio.
³⁶ A second class involves relatively stable emulsions with drop-size to average
³⁷ pore-size ratio on the order of unity. A third class, which is the subject of
³⁸ this paper, involves stable emulsions with relatively small drop-size to average
³⁹ pore-size ratio.

⁴⁰ Current approaches of modeling the latter class of emulsions capitalize on
⁴¹ the similarity of the transport and attachment-detachment processes of the
⁴² dispersed-phase droplets with those of colloids [10,3]. In general, most col-
⁴³ loidal transport models are extensions of the advection-dispersion equation
⁴⁴ (ADE), which assumes colloid and grain size homogeneity at all scales. As

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45 a result, these models predict a fast exponential concentration decay and do
 46 not capture slow late-time elution of colloids satisfactorily. Recently, we intro-
 47 duced a Continuous Time Random Walk (CTRW) based filtration model for
 48 biocolloid transport [11] that captures small-scale heterogeneity in an effective
 49 stochastic framework. The proposed approach provided excellent match with
 50 experimental breakthrough curves, including the late-time slow tailing. The
 51 objective of this communication is to extend the CTRW based approach to
 52 the transport of emulsions.

53 **2 Theoretical Considerations**

54 Soo and Radke [10] described the transport of emulsion in porous media as
 55 analogous to transport of a colloidal phase. Transport of colloids is commonly
 56 modeled by colloid filtration theory (CFT) [12] as an extension of the ADE

$$57 \frac{\partial c}{\partial t} + \frac{\rho_b}{\theta} \frac{\partial s}{\partial t} = \mathbb{F}[c(x, t)], \quad (1)$$

58 where lengths are made non-dimensional with respect to the column length L ,

$$59 \mathbb{F}[c(x, t)] \equiv -v \left[\lambda c + \frac{\partial c}{\partial x} - \alpha \frac{\partial^2 c}{\partial x^2} \right] \quad (2)$$

60 is the classical filtration operator (with v the pore velocity and α the disper-
 61 sivity) acting on the colloid concentration $c(x, t)$, and

$$62 \frac{\partial s}{\partial t} = \frac{\theta}{\rho_b} k_f c - k_r s \quad (3)$$

63 where θ is the porosity, ρ_b is the colloid density, s is the colloid concentration
 64 adsorbed reversibly on solid surfaces, k_f , and k_r are the forward and reverse
 65 sorption rates, respectively. The parameter λ is the filtration coefficient, the

66 fraction of irreversibly sorbed dispersed phase, which can be calculated as

67
$$\lambda = -\ln(f) + \alpha \ln(f^2) \quad (4)$$

68 where f is the eluted fraction [13]. An extensive review of the filtration coef-
69 ficient λ and its parameters can be found in [14] and [15]. Eq. (3) adequately
70 describe the initial advection-dispersion dominated breakthrough, but not the
71 late-time elution of the dispersed phase. Laboratory and field experiments of-
72 ten display power-law decaying of the breakthrough curve tails, which cannot
73 be captured by the ADE-based filtration models that predict an exponen-
74 tial decay of the dispersed-phase concentration. The misrepresentation of the
75 tails is rooted in the definition of the forward and reverse sorption rates in
76 (3) as mean values over some volume. The inherent heterogeneity of natural
77 porous materials, however, induces a wide spectrum of rates, which can only
78 be represented by some probabilistic distribution function (pdf).

79 Physico-chemical attachment and detachment of the dispersed phase can be
80 attributed to small scale heterogeneities of the pore-surface dispersed-phase
81 properties. In particular, surface charge heterogeneities on both, the dispersed
82 and solid phases play a fundamental role in the transport of the dispersed
83 phase. Furthermore, the dispersed-phase droplets can vary in shape, size,
84 and surface heterogeneity. These multiscale heterogeneities, which are diffi-
85 cult to characterize in a fully deterministic way, call for an ensemble averaged
86 stochastic treatment of the unresolved level of heterogeneity. In order to ac-
87 count for these heterogeneities, we propose a conceptual model that is similar
88 to the filtration model described in (1) to the extent that it decouples the
89 transport of the dispersed phase into advective and dispersive fluxes, and
90 sorption and desorption mechanisms. Whereas the ADE approach ignores the

91 small heterogeneities, our proposed model treats these in terms of probabilistic
 92 distributions. We have shown elsewhere [11] that a CTRW based filtration-
 93 model provides excellent description of both the advection-dispersion domi-
 94 nated early breakthrough and the late time elution of colloids. CTRW is an
 95 effective stochastic transport theory based on local-scale ensemble averages.
 96 At the core of the CTRW formulation is $\psi(t)$, the waiting time pdf for a
 97 single droplet transition over time t . This function implicitly accounts for all
 98 transport mechanisms (e.g., advection, dispersion, sorption, and desorption)
 99 that displace a particle from one spatial location to another. For an extensive
 100 review of the CTRW in hydrogeological applications see [16] and references
 101 therein. The CTRW filtration equation can be written as

$$102 \quad u\tilde{c}(x, u) - c_0(x) = \tilde{M}(u)\mathbb{F}[\tilde{c}(x, u)]. \quad (5)$$

103 The tilde \sim in Eq. 5 indicates Laplace transformed quantities with respect to
 104 time t , and u is the Laplace variable. The quantity $\tilde{M}(u)$ is defined as

$$105 \quad \tilde{M}(u) = \bar{t}u \frac{\tilde{\psi}(u)}{1 - \tilde{\psi}(u)} \quad (6)$$

106 and plays the role of a memory function, which convolutes the classical filtra-
 107 tion operator, $\mathbb{F}[\tilde{c}(x, u)]$.

108 Considering the similarity in ζ -potentials between bio-colloids and oil droplets
 109 in emulsions, we propose that (5) can be used to effectively describe emulsion
 110 transport in porous media.

111 Following Margolin et al. [17], we define the waiting time pdf $\psi(t)$ (which
 112 describes how the droplets in the dispersed phase are temporarily trapped
 113 and then released after some time t) as a generalized convolution integral of
 114 two contributions: $\psi_0(t)$, which is related to the complexity of the pore space

115 geometry, and $\phi(t|\tau)$ (with $\tau = (t - t')/T$), which defines the retention of
 116 the dispersed droplets, $\psi(\mathbf{s}, \tau) = \int_0^\tau \psi_0(\mathbf{s}, \tau - \tau')\phi(\tau'|\tau - \tau')d\tau'$. In the limit
 117 $\phi(t|\tau) \equiv \delta(t' - \Lambda\tau)$, Eq. 5 is reduced to an ADE with simple retardation
 118 $R = (1 + \Lambda)$. More generally, $\phi(t|\tau)$ accounts for multiple attachment and
 119 detachment events of a droplet in the time interval τ , and as such can be
 120 defined by means of multiple convolutions of a large number of single “sticking
 121 time” pdfs, $\varphi(t)$, (compound Poisson process). Denoting by Λ the average free
 122 state sticking rate, it is possible to write $\tilde{\varphi}(u) \equiv \exp(\Lambda\tau(\tilde{\varphi}(u) - 1))$. With
 123 these definitions, $\tilde{\psi}(u)$ reads as $\tilde{\psi}(u) = \tilde{\psi}_0(u + \Lambda(1 - \tilde{\varphi}(u)))$. When $\tilde{M}(u) = 1$,
 124 and $\Lambda = 0$ the CTRW filtration PDE reduces to the classical filtration theory.
 125 If $\Lambda > 0$, the memory $\tilde{M}(u) \neq 1$, i.e., the model exhibits memory effects as a
 126 result of the time convolution. A detailed account of these developments can
 127 be found in [17] and [11].

128 At this point we introduce some assumptions on the functional forms of
 129 $\psi_0(t)$ and $\varphi(t)$. The $\psi_0(t)$ models the impact of pore space heterogeneity
 130 on the anomalous tailing of the dispersed phase due to pore shape hetero-
 131 geneity and accounts for the anomalous tailing in the breakthrough of con-
 132 servative tracers in homogeneously packed soil columns. To account for pore-
 133 level geometric heterogeneity of a passive tracer experiments, it is sufficient
 134 to adopt an asymptotic power-law model of the form $\tilde{\psi}_0(u) = 1/(1 + u^\gamma)$
 135 (with $0 < \gamma < 1$), which yields a power law tailing [18]. For homogeneous
 136 porous structures, γ approaches 1, and the waiting time pdf tends towards an
 137 exponential, $\psi_0(t) \sim \exp(-t/\bar{t})$, i.e., passive tracer transport tends toward a
 138 Fickian-behavior limit.

139 Small-scale heterogeneities in physico-chemical interactions can also be repre-
 140 sented by a sticking time pdf of the form $\tilde{\varphi}(u) \equiv 1/(1 + u^\beta)$, where $0 < \beta < 1$

¹⁴¹ [11]. From a physical point of view, this means that there is no single charac-
¹⁴² teristic filtration time scale for this problem.

¹⁴³ **3 Illustrative Example**

¹⁴⁴ The experimental results used to illustrate the proposed theory were derived
¹⁴⁵ from Coulibaly et al. [3] (experiment FS-7%-#2). The experiment was con-
¹⁴⁶ ducted using a PVC column of length $L = 0.8$ m and diameter $D = 0.029$ m.
¹⁴⁷ The column was filled with medium to fine sand ($D_{10} = 0.10$ mm, $D_{50} =$
¹⁴⁸ 0.38 mm, $D_{60} = 0.45$ mm, and 6.9% by weight is finer than 75μ m) dry packed
¹⁴⁹ to achieve bulk density of 1.44kg/m^3 , equivalent to a porosity of $\theta = 0.46$. The
¹⁵⁰ emulsions used in this experiment were prepared by blending 33% by volume
¹⁵¹ soybean oil, 62% tap water, and 5% premixed surfactant (38% polysorbate
¹⁵² 80, 56% glycerol monooleate from Lambent Technologies and 6% water) in a
¹⁵³ commercial blender at high speed for 5 min. The mean droplet size was $1.2\mu\text{m}$
¹⁵⁴ (standard deviation $1.3\mu\text{m}$). The ζ potential of the oil droplets and sand in
¹⁵⁵ tap water ($\text{pH} = 8.2$ and specific conductance = $190\mu\text{S/cm}$) were -18 mV
¹⁵⁶ and -24 mV, respectively, indicating unfavorable conditions for the negatively
¹⁵⁷ charged oil droplets to stick to the negatively charged sand [3].

¹⁵⁸ The column was first evacuated and then saturated by flowing de-aerated wa-
¹⁵⁹ ter upwards at 2.5 mL/min for 2 hours. Subsequently, a nonreactive transport
¹⁶⁰ test was conducted by injecting 25 mL (~ 0.1 PV) of 175 mg/L NaBr solution
¹⁶¹ through the column followed by 1000 mL of deaired water. Effluent samples
¹⁶² were analyzed for Br by ion chromatography. The emulsion flow test was con-
¹⁶³ ducted by injecting 25 mL of 11% oil by volume emulsion (~ 0.05 PV of pure
¹⁶⁴ oil) followed by 1000 mL of deaired water. The effluent was collected every 30

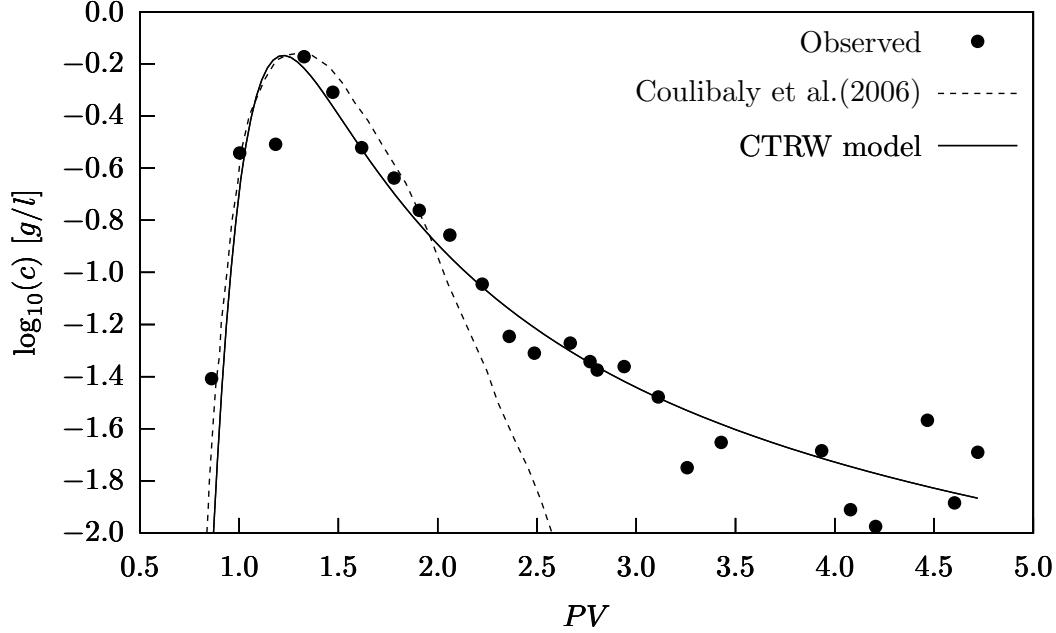


Fig. 1. Comparison of experimental results with model fits

165 mL and analyzed for oil content by volatile solids method.

166 The experimental oil BTC was fitted by means of (5). The time has been
 167 rescaled in such a way that the BTC is plotted in pore-volumes. Lengths have
 168 been rescaled by the column length L . The value of the filtration coefficient
 169 $\lambda = 2.72$, was obtained from (4) with the reported eluted fraction, $f = 0.065$
 170 and the value of the dispersivity $\alpha = 0.1$ was obtained from the NaBr tracer
 171 test [3]. This non-dimensional value of the dispersivity clearly indicates a scale
 172 effect [19]. Considering that the porous medium used in the experiments was
 173 made of sand grains of different sizes, it is legitimate to expect significant
 174 small-scale heterogeneity of flow and transport properties. Long tailing in the
 175 passive tracer BTC, which is typical in such porous media [2], might have been
 176 misinterpreted as elevated dispersivity. Therefore, we introduce a model for the
 177 $\psi_0(t)$ which assumes a long tailing, i.e., $\gamma < 1$ and a value of the dispersivity
 178 of the same order of magnitude of the the median grain diameter-to-column
 179 length ratio, $D_{50}/L = 4.75 \times 10^{-4}$. Given the distribution of diameter size

180 typical of the sand used in the experiment, we selected a value of $\alpha = 1.5 \times$
181 $10^{-3} \sim 3D_{50}/L$. A sensitivity analysis indicates the appropriateness of this
182 choice of α . In contrast, using the value of $\alpha = 0.1$ reported by Coulibaly
183 et al. [3] and a value of $\gamma = 1$ (Gaussian transport for the passive tracer),
184 results in unsatisfactory CTRW model fit of the experimental BTC. The best
185 fit values of the free parameters are $\Lambda = 0.58$, $\beta = 0.4$, and $\gamma = 0.9$. The
186 relatively high value for γ indicates that some geometrical disorder is present
187 in the experimental column, as one would expect for natural soils. The small
188 value of β is in agreement with that of transport of bio-colloids [18]. This value
189 for β indicates a very high degree of phsycico-chemical disorder of the surface
190 heterogeneity and a corresponding broad sticking time pdf $\varphi(t)$.

191 The best fit value for the transport velocity v indicates a retardation factor
192 $R = (1 + \Lambda) = 1.58$, in accordance to the sharply peaked $\phi(t, t-t') \sim \delta(t'-\Lambda\tau)$
193 analyzed earlier. The results are, thus, pointing towards a bi-modal type of
194 transport for the dispersed phase: the first mode explains the attachment
195 and detachment of the oil droplets to the pore walls and is characterized by
196 a power law dominated sticking time pdf, whereas the second mode, clearly
197 indicated by the overall retardation, can be attributed to a film-like flow along
198 the surface of the pores.

199 4 Open Research Questions

200 The CTRW based model for emulsion transport introduced in this paper pro-
201 vided an excellent match to the experimental oil BTC of Coulibaly et al.
202 [3]. In particular, the late-time long tailing was shown to be in remarkable
203 agreement with a power-law dominated pdf for attachment and detachment

204 of the dispersed-phase (oil). This finding leads to interesting research ques-
205 tions related to multiphase flow in porous media. We have shown here that
206 the long time correlations underlying the power-law dominated pdfs need to
207 be taken into account for a correct description of emulsion transport. The
208 consequences of this microscopic behavior on other measurable macroscopic
209 parameters needs further exploration.

210 We also recognize that the permeable pore space available for water flow is
211 continuously changed as oil-droplets are lodged in pore-throats and pore-walls,
212 resulting in transient effects in the small scale permeability to water. This ef-
213 fect is different from straining of rigid colloids because the capillary forces
214 that keep emulsion droplets in place can be readily overcome by hydrody-
215 namic stresses. Moreover, the oil droplets in the dispersed phase inside the
216 pore space are continuously moving giving the water phase a moving bound-
217 ary for its flow. Recalling that the permeability of a porous medium at Darcy
218 scale (k_0) is defined as the volume average of the Stokes velocity flow field
219 in the pore space available to the water phase, it becomes evident that when
220 the fluctuation of the local k value (with respect to k_0) are correlated in time,
221 can induce macroscopically measurable changes in the effective permeability.
222 Elsewhere, we have shown that long-range correlations in the spatial distribu-
223 tions of diffusivity can induce memory effects and that these can be captured
224 in the transient behavior of the effective permeability [20]. We argue that sim-
225 ilar transient effects in the deviations from k_0 are responsible for the changes
226 in effective transient permeability observed in the emulsion transport exper-
227 iments. Hence, the parameters of the CTRW filtration such as the free state
228 sticking rate Λ , may be correlated to the observed drops in permeability. If we
229 consider that a drop in permeability affects the velocity of the carrying fluid

230 (the water), and that the dispersed phase moves advectively with the water,
231 it is plausible to draw a connection between the retardation factor observed
232 in the oil BTC experiments and the drop in permeability. Assuming that this
233 working hypothesis holds, the corresponding drop in the permeability should
234 be given by $k/k_0 \approx 1/R$. For the experimental results reported in figure 1 this
235 corresponds to $k/k_0 = 0.63$, which is of the order of magnitude of permeabil-
236 ity drops observed in literature for this kind of porous media (e.g., [2]). This
237 conjecture can be tested in multiple-column laboratory experiments.

238 The relation of the β exponent with the rheology of the emulsion remains
239 poorly understood. Emulsion flow under simple experimental conditions ex-
240 hibits non-Newtonian behavior such as aging and memory [21]. Further ex-
241 ploration is needed to test whether these non-Newtonian characteristics
242 are also responsible for the memory effects observed in the more complicated
243 geometries of porous media.

244 Finally, the importance of microscopic transitions in emulsion transport high-
245 lighted in this communication is likely to be important in other multiphase
246 flow problems. Therefore, future research in multiphase flow theory need to
247 address these effects in a self-consistent manner.

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