Final Report (7/30/98) #DOE/ER/60310-1 (7/98)

on

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Grant DE-FG-02-86ER-60310

between

Subsurface Science Program of OHER/DOE

and

Purdue University

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Titled

Nonlocal Transport of Chemically Reactive,
Degradable Species in Heterogeneous Porous Media

by

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Summary

The project had a three-fold focus:

- (i) To develop a probabilistic framework for simulation of degradable chemicals in a heterogeneous subsurface environment
- (ii) To develop a quantitative understanding of fluid mixtures in micropores; and
- (iii) To develop multiscale constitutive models for swelling soils.

Chemical transport in a heterogeneous subsurface is notoriously difficult to simulate. Two approaches are generally viable, perturbation and Monte Carlo, and we have applied both. Perturbation theory shows the evolution of the contaminants' moments is both spatially and temporally nonlocal, i.e., past history and large spatial neighborhood of the contaminant are required to describe its statistics. We have developed a wide class of nonlocal models for both flow and contaminant transport in a chemically, physically, and biologically heterogeneous subsurface and we have successfully tested these models against Monte Carlo simulators, which also were developed within our group.

Clays and organic matter are the two most chemically reactive components of the subsurface. To a large extent these two substances govern the retardation of chemicals when they traverse geologic formations. We have spent considerable effort in developing a rational framework for simulating on the molecular scale the sorption of fluid mixtures to plate-like structures. Specifically, we have pioneered the use of isostress-isostrain grand-canonical Monte Carlo simulators. This included developing the thermodynamics and stability criteria for the sorptive process, and developing the simulators themselves.

In addition to our molecular scale simulation capability for clays, we have also developed a large scale simulation capability. Specifically we have developed theories for swelling particles (which consist of clay platelets and adsorbed fluid) and mixtures of swelling particles with bulk fluid. These theories have also been applied to swelling polymers. The theories were implemented in radially symmetric coordinates to simulate the formation of crusts upon drying.

This grant resulted in the publication of two books and 26 journal articles.

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1 Introduction

One of the most significant challenges facing environmental engineers and scientists is predicting the movement and degradation of chemicals in hierarchical porous media. The distribution of subsurface properties is poorly known because of the inaccessibility of the subsurface environment and the random nature of the geologic deposition process. In addition, the subsurface often possesses distinct physical, chemical and biological hierarchies, which complicates our ability to successfully characterize and thus predict property distributions and processes with information from a limited number of sample locations over a limited number of scales.

Knowledge of the spatial structure of microbial populations and activities and the "dynamic" environmental factors that control this spatial structure are important in characterizing sites for remediation and disposal, and for the ability to effectively deliver nutrients to promote degradation and stabilization. To do so effectively requires a correct theoretical formulation of the problem, implementation of this formulation for predictive purposes, and even more importantly knowledge of what should be measured and how and when to measure it. To this end, consider Hu *et al.*, (1997). In that work a chemical undergoing first-order nonequilibrium reactions with first-order degradation in a physically, chemically and geologically heterogeneous environment was studied theoretically. It was found that to predict the evolution of the mean concentration a number of novel correlation functions must be measured. Among these are $\overline{fk_f}$, $\overline{fk_b}$, $\overline{fk_s}$, $\overline{fk_c}$, $\overline{k_fk_f}$, $\overline{k_bk_b}$, $\overline{k_s k_s}$, $\overline{k_b k_s}$, $\overline{k_b k_c}$, and $\overline{k_s k_c}$ where f is the spatially fluctuating log-conductivity, k_f is the fluctuating forward rate coefficient, k_b is the fluctuating backward rate coefficient, and k_s and k_c are the fluctuating sorbed and solution phase degradation rates. The overbar indicates mean value, so for example, $\overline{fk_f}$ is the covariance function between the fluctuating log-conductivity and the fluctuating forward rate coefficient. None of these aforementioned correlation functions have ever been measured experimentally, nor to the author's knowledge has anyone, save us, proposed measuring them. Thus the importance of developing an adequate theoretical formulation for this type of environmental problem cannot be overstated.

The remainder of this report is as follows: (Section 2) statement of goals, (Section 3) development of nonlocal models for chemical transport with uncertainty in biological, physical and chemical data, (Section 4) a discussion of molecular-scale phenomena of relevance to adsorption and flow in nanoporous materials such as clays, (Section 5) meso and macroscale models of flow in, and deformation of, clays, (Section 6) collaborative efforts with DOE labs, (Section 7) P.I. awards, (Section 8) publications resulting from the research efforts supported through this grant, and finally students supported under this grant.

2 Goals

- i. To develop a rational probabilistic framework for predicting the evolution of degradable chemicals in physically, chemically and biologically heterogeneous media with uncertain data at the field scale.
- ii. To develop a quantitative understanding of fluid mixtures in micropores.
- iii. To develop multiscale constitutive models for flow and transport in expansive soils.

3 Chemical Transport in Heterogeneous Media

Listed below are specific areas in which substantial progress has been made.

- i) Mean Spatial Moments for Classical-, Quasi-, and Convolution-Fickian Dispersion of a Conservative Tracer (Deng and Cushman, 1995a)

Mean spatial moments up to the fourth for the concentration with convolution-, quasi-, and classical-Fickian dispersive fluxes for a conservative tracer were developed and compared. Convolution-Fickian dispersion yields a non-Gaussian distribution while quasi- and classical-Fickian dispersion result in a Gaussian type distribution regardless of the distribution of the stationary velocity field. The first- and second-mean central spatial moments are the same for convolution- and quasi-Fickian fluxes, while the third- and fourth-central moments differ. *This is a very important result as it states effective macroscale dispersion coefficients do not work — even for conservative tracers.*

- ii) Comparison of Nonlocal Eulerian to Lagrangian Mean-Spatial Moments for the Concentration in a Heterogeneous Aquifer with Deterministic Linear Nonequilibrium Sorption and Constant K_d (Cushman *et al.*, 1996; Hu and Cushman, 1997)

A framework was developed to study the evolution of mean concentration for a reactive chemical undergoing linear nonequilibrium sorption with deterministic rate constants in a physically heterogeneous medium. The model was nonlocal and eulerian. Exact first-order representations were obtained for the mean concentration and spatial moments through the third. Comparisons were made to results obtained for the identical problem in a lagrangian frame. If local-scale dispersion is neglected in the eulerian frame and the fully nonlocal flux is retained, then the eulerian and lagrangian moments agree. However, if the eulerian model is localized or if local-scale dispersion is retained, then the moments disagree. *This disagreement is especially acute in the asymptotic limits. This point is important as it says lagrangian approaches to study transport do not at present carry the correct physics.*

- iii) Nonlocal reactive Transport with Physical and Chemical Heterogeneity: Linear Nonequilibrium Sorption with Random Rate Coefficients (Hu *et al.*, 1995b; Hu *et al.*, 1996)

Two cases were studied: (i) that with random partition coefficient, K_d , but deterministic reaction rate, K_r , and (ii) that with random forward, K_f , and backward, K_b , reaction rates. In case (i) an important observation was that unlike in Deng *et al.*, (1993), nonlocality is manifest not just in the dispersive flux, but in an effective convective flux and sources as well. The first-order fully nonlocal formulation was solved exactly in Fourier-Laplace space and converted to real space via FFT. Positive,

negative, and uncorrelated models relating the fluctuating partition coefficient to the fluctuating log-conductivity were used to examine the evolution of mean concentration and spatial moments through the third. The initial sorbed concentration and the deterministic reaction rate were shown to have significant effect on the moments, especially the second longitudinal. The first moment was shown to be relatively insensitive to the various correlation structures, but the second and third moments may exhibit a sensitivity. *The importance of this finding is that it tells the experimenter that he must accurately measure the self-correlation of K_d and cross correlation between K_d and the conductivity K — something that has not been done to date.* (ii) These results were extended to account for random forward and backward sorption rates. Again, nonlocal fluxes and sources manifest, and the mean equation was solved as before. *The results indicate (as pointed out in the introduction) that there are serious gaps in existing data sets at major reactive chemical study sites. The formulation also suggests the need to design new experiments and it further suggests a number of novel correlation functions should be obtained.*

iv) Localization Errors (Cushman *et al.*, 1995)

The origin of nonlocality in “macroscale” models for subsurface chemical transport was illustrated. It was argued that media which are either nonperiodic (e.g., media with evolving heterogeneity) or periodic media which are viewed on a scale wherein a unit cell is discernible, must display some nonlocality in the mean. A metaphysical argument suggests that owing to the paucity of information on natural scales-of-heterogeneity and on scales-of-observation associated with an instrument’s window, constitutive theories for the mean concentration should at the outset of any modeling effort always be considered nonlocal. The fully nonlocal (FNL) formulations associated with (1)–(3) were localized in space (NLT, nonlocal in time) and then in time (FL, fully local). For conservative chemical transport there is little difference between the first-order FL and FNL formulations for spatial moments through the second. However, for conservative transport the first-order NLT formulation differs significantly from the FNL formulation in the third spatial moment. For reactive transport all spatial moments differ between the FNL and FL formulations. The second transverse horizontal and third longitudinal horizontal moments for the NLT model differ from the FNL model. *These results suggest the localized first-order models (with effective macroscopic properties) are deficient, and that nonlocal formulations are far superior.*

v) Nonlocal Reactive Transport with Physical, Chemical and Biological Heterogeneity (Hu and Cushman, 1995; Hu *et al.*, 1997)

Our framework for a physically and chemically heterogeneous environment was extended to handle a simplistically heterogeneous biological environment. Again, a nonlocal eulerian framework was established and studied. It was found that relative to the effect of different chemical models on spatial moments, the influence of various biological frameworks on the first and second longitudinal moments and skewness can

be neglected, but the influence on the second transverse moment is significant. With the exception of the zeroeth moment, other spatial moments are not sensitive to the mean degradation rates, but they are sensitive to the mean chemical reaction rates. These conclusions were obtained under the condition that the mean degradation rates were much less than the reaction rates and $\sigma_c^2 \ll \sigma_f^2$. Under these conditions we believe it is not important whether K_c and K_s are treated deterministically or randomly. *This illustrates the power of the approach as it dictates sampling schemes for certain parameters.*

vi) High-Order Corrections to the Flow Formulation (Deng and Cushman, 1995b)

In 1983 Gelhar and Axness developed an expression to relate the fluctuating log-conductivity covariance to the fluctuating velocity covariance which was first-order in the variance of the log-fluctuating conductivity, σ_f^2 . Over the years this expression has been criticized because it is only first-order accurate and as such should break down in more heterogeneous media. This is important because though the fluctuating velocity covariance appears in the equation for the mean concentration, we actually measure the fluctuating conductivity covariance and not the fluctuating velocity covariance. It is the fluctuating velocity covariance that to a large extent governs the dispersion of a chemical. We (Deng and Cushman, 1995b) developed a second-order (in σ_f^2) accurate correction to the flow velocity covariance tensor to help improve its estimate in more heterogeneous media. It was shown that the velocity covariance is insensitive to second-order corrections in the head field, but highly sensitive to second-order corrections in the velocity when the log-fluctuating conductivity variance approaches unity. A closed expression was derived for a second-order correction to the velocity variance when there is no second-order correction to the head field. The longitudinal second-order correction to the velocity covariance is $0.4\sigma_f^2$ different from the first-order approximation in isotropic media, $1.5\sigma_f^2$ different in a highly stratified formation, and no different when the ratio of vertical to horizontal integral scales approaches infinity. The second-order corrections to the horizontal and vertical transverse velocity variances were shown to be $2\sigma_f^2$ different from the first-order approximations for both isotropic and anisotropic systems. *These results are of importance because they allow us to study flows in more heterogeneous media.*

vii) Solutions to the Stochastic Transport Problem of $O(\sigma_v^N)$ for Conservative Solutes (Cushman and Hu, 1997)

The main problem with the models presented in points (1)–(5) above is that the accuracy of the approximation scheme for the transport problem is not known, except through comparison with Monte Carlo experiments. The reason for this is historically we have attempted to solve the equation for the mean concentration. But to do so requires a closure approximation for $\overline{c\mathbf{v}}$, the mean dispersive flux. The authors have gotten around this problem by solving a hierarchical recursive system for the

stochastic concentration, and subsequently using this solution to obtain the mean concentration...the mean equation is never employed. The stochastic concentration is given to arbitrary order in σ_v , the variance of the fluctuating velocity. The result gives the stochastic concentration as a perturbation to the deterministic concentration for constant mean flow. The closed form solution is given recursively in terms of integrals of the Green's function for the deterministic problem and multipoint velocity correlation functions. *The important point to note here is that the order of accuracy of the problem can only be increased by measuring $\overline{v_i v_j}$, $\overline{v_i v_j v_k}$, $\overline{v_i v_j v_k v_l}$, etc.*

viii) Laboratory Observation of Nonlocal Dispersion (Sternberg, *et al.*, 1996a,b)

We undertook a one-dimensional experimental investigation of contaminant transport in a porous medium with heterogeneity on the scale of observation. The purpose was to begin to test the models presented in points (1)–(5). The experimental media were constructed from distinct layers of spherical glass beads packed into cylindrical columns of lucite. Flow was in the direction perpendicular to the layers. Dispersion was measured by recording the concentration of a chloride tracer as a function of time and position. The scale of measurement was finer than the scale of heterogeneity. The results show that the mixing between miscible fluids was affected by transitions in the system parameters, before the transitions were encountered by the mixing zone. *This newly observed phenomenon has been interpreted as a nonlocal effect, and it begins to verify our new models.*

4 Molecular-Scale Phenomena

In saturated flow molecular scale phenomena control adsorption on interfaces. In unsaturated flow molecular scale phenomena control both adsorption on interfaces and the propagation of the fluid phase. The studies reported in this section were designed to elucidate the molecular mechanisms for adsorption, species segregation and interfacial tension in model colloidal systems.

i) Adsorption and Liquifaction

The statistical mechanical Monte Carlo method was employed in a novel ensemble (grand-isostress) to elucidate strain induced liquifaction near surfaces (Schoen *et al.*, 1994a; 1994b; 1994c). The behavior of molecularly thin confined film (between two plane-parallel walls) was studied with controlled state variables, temperature T , chemical potential μ , normal stress (load) applied to the walls τ_{zz} , and crystallographic alignment of the pore walls α (relative registry). A multiplicity of phases is found to comport with a given choice of the parameters. The thermodynamically stable one minimizes the grand isostress potential (free energy). By means of thermodynamic integration the stable phase of the film was determined as a function of α at fixed T , μ , τ_{zz} for given surface area, A . Solid films comprising integral numbers of layers of atoms parallel with the walls are stable when the walls are appropriately aligned. When such films are sheared (α is varied), they undergo drainage (imbibition) transitions at critical strains, whereupon the film loses (gains) whole layers. Depending on the conditions, the solid film may melt just prior to the transition.

ii) Interfacial Tension

The isostrain grand-canonical Monte Carlo method was employed to study the interfacial tension in a film confined to a slit-pore whose plane-parallel walls comprise rigidly fixed similar atoms (Curry *et al.*, 1994a). In narrow pores, where both walls strongly influence the whole film, the interfacial tension is shown to be a highly complex function of pore width and registry. Oscillations in the tension are correlated with the addition of new fluid layers, the most highly structured layers corresponding to maxima in the interfacial tension. Separate interlayer and intralayer contributions to the tension were defined and shown to be useful in explaining the physics of the change in the interfacial tension with addition of new layers to the film.

iii) Fluids in Pores Structured on Both the Molecular and Nanoscales

Grand-canonical Monte Carlo and microcanonical molecular dynamics methods were employed to simulate an ultra thin film confined to a slit-pore. Both pore walls possess molecular structure, but in addition one wall contains nanoscale corrugation (i.e., it is scored with regularly spaced rectilinear grooves one to several nanometers wide) (Curry *et al.*, 1994b). Properties of the film have been

computed as a function of the registry, with temperature, chemical potential, and distance between the walls kept constant. Changing the registry carries the film through a succession of equilibrium states, ranging from all solid at one extreme to all fluid at the other. Over the range of intermediate registries the film consists of fluid and solid portions in equilibrium, that is fluid-filled nanocapillaries separated by solid strips. The range of registries over which such fluid-solid equilibria exist depends upon the width of the grooves and frequency of the corrugation. For grooves of width comparable to the range of the interatomic potential, fluid and solid phases cease to coexist. In the limit of very wide grooves the character of the film is similar to that of the film confined by strictly smooth walls.

iv) Phase Separation in Binary Liquid Mixtures

One-to-five layer cyclohexane and octamethyltetra-cyclosiloxane (OMCTS) films confined between mica-like surfaces were studied to elucidate changes in the lattice type and composition of the films. Grand canonical ensemble Monte Carlo simulations were used to study the laterally confined film (Curry and Cushman, 1995a; 1998). In contrast to previous studies, solid-like order is induced primarily by the strong fluid-solid interaction and is largely a function of pore width. Solid-like order within the layers causes the composition to shift from the bulk composition, favoring either cyclohexane or OMCTS, depending on the pore width. A shift in the relative alignment of the surfaces perturbs the solid-like fluid structure but does not cause the sudden shear melting transition associated with epitaxial alignment of the fluid atoms with the surface.

v) Anomalous Diffusion in Slit-Pores

A monolayer, epitaxially adsorbed film confined to a slit-pore and subjected to shear strain begins to melt and desorb if a critical strain (shear melting point) is exceeded. The resultant "molten" phase exhibits structural disorder characteristic of an adsorbed liquid yet it supports a shear stress. Molecular dynamics and Monte Carlo calculations were used to study diffusion in this molten phase as a function of excess shear strain above the critical value (Schoen *et al.*, 1995). Three distinct diffusion time scales are manifest through plots of the mean-square displacement (MSD). Over the shortest time scale the MSD can be represented by a power-law, $\sim t^d$, where t is time and d is a function of the excess shear strain, varying from 0 for the solid just below the shear melting transition to its Brownian-limit value of 1 for completely liquified film, having the disorder of a bulk fluid and supporting no shear stress. That $d < 1$ indicates anomalous (i.e., fractional Brownian) diffusion. The intermediate time scale is characteristic of a strongly cooperative process that is spatially non-local and gives rise to anomalous diffusion. Both short and intermediate time scales exceed by several orders of magnitude typical times after which Brownian diffusion is observed in dense homogeneous bulk fluids. The persistence of anomalous diffusion is ascribed to severe spatial confinement of the film atoms. The longest time scale corresponds

to asymptotic Brownian diffusion $d = 1$. All results may be explained using an effective porous medium generated by equipotentials associated with wall atoms.

vi) Binary Mixtures in Pores With Both Molecular and Nanoscale Structure

Earlier we discussed binary mixtures in slit pores with molecularly structured walls, subsequently we discussed single species fluids in pores possessing both molecular and nanoscale structured walls. Here we report results for binary mixtures in pores with both molecular and nanostructured walls (Curry and Cushman, 1995b,c). We again used the corrugated pore model, and the binary fluid mixture is in equilibrium with its bulk counterpart. The grooved surface divides the confined fluid into two strip-shaped regions, that inside and that outside the grooves. Transverse solid-like order in the film gives rise to shear stress. Transverse order coupled with packing restrictions gave rise to a difference between the bulk and pore fluid compositions. Solid-like order could appear within the grooves only, outside the grooves only, or in both regions simultaneously. As the relative alignment of the walls was shifted the pore-fluid underwent freeze-thaw cycles in one or both regions with associated changes in the shear stress and pore fluid composition.

5 Flow, Transport and Deformation in Expansive Soils

Flow and transport in expansive (swelling) soils are probably the most difficult subsurface modeling challenges and they are among the least understood subsurface environments. We have made significant progress in advancing our understanding of swelling soils and flow and transport therein (Achanta *et al.*, 1994,1997; Achanta and Cushman, 1994; Murad *et al.*, 1995).

The thermomechanics of a multiphase, multispecies mixture were developed in the spirit of modern continuum physics. A new axiom of constitution, "equipresence of constituents", was stated and employed to obtain macroscale equations of constitution which are consistent with their microscale counterparts. Here we have assumed a scale separation wherein classical microscale theory of mixtures applies within each phase and interface, and a hybrid theory of mixtures, which is a homogenization of the microscale mixture theory over phases and interfaces, applies at the macroscale. We thus postulate the existence of a two-scale hierarchy of overlaying continua. Such scale separation is common to many types of geologic media.

Exploitation of the entropy inequality in the sense of Coleman and Noll and application of equilibrium constraints produced a complex list of functional relations forming a macroscale theory of matter constitution. In a three-phase system linearization of several of these relations produces novel analogs of Fick's first law of dispersion and Darcy's law of fluid flow in deforming soils. These analogs of Fick's and Darcy's laws are significantly different from their traditional forms in that they contain an "interaction potential". We feel that the contribution of the interaction potential to fluid flow dynamics could be of crucial importance in swelling and shrinking colloidal systems. Another especially important consequence of the theory of constitution is the development of the experimentally observed exponential relation between disjoining (swelling) pressure and the pore width in a smectitic clay-water system. This relation could not be developed via classical Gibbsian arguments. In addition, the nonequilibrium swelling pressure relation obtained has had a heretofore theoretically unverified experimental analog in polymer physics. A similar relation is found for the nonequilibrium capillary pressure, and it is quite different from the classical capillary pressure. These results were used to successfully simulate crust formation in drying soils.

The results have been extended to a 3-scale setting by homogenizing (in the sense of matched asymptotics) the 2-scale results. Novel forms of Darcy's, Fick's and Terzaghi's laws were obtained. This theory was successfully applied to flow and transport in a consolidating soil.

6 Collaboration with DOE Labs

The research supported by this grant resulted in numerous collaborations and discussions with other researchers at various DOE labs (PNL, Ginn, Simmons, Murphy; Los Alamos, L. Winter, D. Zhang; Oak Ridge, R. Luxmore; LBNL S. Mukhopadhyah).

7 Awards

Dr. Cushman was presented with the McCoy Award largely for research supported by DOE. He was also named Fellow AGU, Hydrology Section, for work supported by DOE.

8 Publications

a) Books Published:

1. J. H. Cushman (1997) "The Physics of Fluids in Hierarchical Porous Media: Angstroms to Miles". Kluwer Acad., The Netherlands, 485 pp.
2. P. F. Low, J. H. Cushman and C. B. Roth (1999) "The Physical Chemistry of Clay Colloids". To appear, 350 pp.

b) Refereed Publications:

1. S. Achanta and J. H. Cushman (1994) *Nonequilibrium swelling and capillary-pressure relations for colloidal systems*, J. Col. Int. Sci., 168:266–268.
2. S. Achanta, J. H. Cushman, and M. R. Okos (1994) *On multicomponent, multiphase thermodynamics with interfaces*, Int. J. Eng. Sci., 32(11):1717–1738.
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9 Students Partially Supported by D.O.E.

S. Achanta (Chemical Engineering, Ph.D. 1995)
F. W. Deng (Civil Engineering, Post Doc)
B. X. Hu (Agronomy, Ph.D. 1996, Post Doc)
S. P. Sternberg (Chemical Engineering, Ph.D. 1996)
J. E. Curry (Chemistry, Post Doc)
M. Schoen (Physics, Post Doc)
.. L. S. Bennethum (Mathematics, Post Doc)
M. Murad (Mathematics, Post Doc)

10 Appendix

Reprints - removed for separate
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