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13. ABSTRACT (Maximum 200 words) Significant advances were made in three basic areas: (i) Multiscale flow and deformational of swelling porous media, (ii) nonlocal transport of contaminants in porous media, and (iii) development of a molecular-scale understanding of phase separation in binary fluids in microporous media. Two- and three-scale theories were developed for fluid-flow and chemical transport in expansive media such as natural soils and many biopolymers. The balance laws coupled with novel constitutive theories were implemented computationally and then compared (favorably) to experimental results. The first successful simulation of crust formation was presented. Chemical transport theories for porous media with evolving heterogeneity were developed. The theories were nonlocal in space and time. They were numerically implemented and they compared favorably to field experiments. Numerical statistical mechanical Monte Carlo simulations of binary mixtures in corrugated micropores were reported. Novel examples of strain induced liquifaction, chromatography and phase coexistence were presented. One book and 20 refereed papers were published based on these efforts.				
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**TOWARD A MOLECULAR-SCALE
UNDERSTANDING OF CHEMICAL ADSORPTION
AND FROST HEAVING: PHASE II**

FINAL REPORT

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(1/31/98)
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I. Statement of Problem Studied

Understanding and predicting the deformation of swelling or frost heaving porous media and predicting the evolution of chemicals in such media.

II. Summary of Important Findings

1. Multiscale flow and deformation of hydrophilic swelling porous media.

A three-scale theory of swelling porous media was developed. The colloidal or polymeric sized fraction and vicinal water (water next to colloids) are considered on the microscale. Hybrid mixture theory is used to upscale the colloids with the vicinal water to the mesoscale. The particles and bulk water (water next to the swelling particles) are then homogenized via an asymptotic expansion technique to form a swelling mixture on the macroscale. The solid phase on the macroscale can be viewed as a porous matrix consisting of swelling porous particles. Two Darcy-type laws are developed on the macroscale, each corresponding to a different bulk water connectivity. In one, the bulk water is entrapped by the particles, forming a disconnected system, and in the other the bulk water is connected and flows between particles. In the latter case the homogenized equations give rise to a distributed model with microstructure in which the vicinal water is represented by sources/sinks at the macroscale. The theory is used to construct a three-dimensional model for consolidation of swelling clay soils and new constitutive relations for the stress tensor of the swelling particles are developed. Several heuristic modifications to the classical Terzaghi effective stress principle for granular (non-swelling) media which account for the hydration forces in swelling clay soils recently appeared in the literature. A notable consequence of the theory we developed is that it provides a rational basis for these modified Terzaghi stresses.

2. Multiscale, hybrid mixture theory for swelling systems; a constitutive theory.

The governing field equations and the definitions of all mesoscale and macroscale variables therein were defined in terms of microscale variables. Explicit dependence on transport in interfaces was accounted for. Independent variables were chosen to represent the physics of a multiscale swelling system and used to derive constitutive restrictions for two cases of a dual-porosity multi-component swelling media: one which assumes no interfacial effects, and one which includes interfacial effects. For each case, the entropy inequality is fully expressed using a Lagrange multiplier technique. Novel definitions for macroscopic pressures and chemical potentials were given, and generalized Darcy's and Fick's laws were presented.

3. Moisture transport in shrinking gels during drying.

The transport of moisture in shrinking colloids during drying was studied based on a novel thermomechanical theory developed previously by the author under ARO support. The drying theory accounts for a structural transition in the material during drying. This inherent characteristic is expressed using a term involving the nonequilibrium deformation viscosity property of soils, and is a strong function of the difference between the glass-transition temperature of the material and the temperature of drying.

The theory was applied to the drying of a model cylindrical colloidal system and the equations were solved using a lagrangian FD technique. The predicted drying characteristics depend on the Deborah number, a ratio of the characteristic relaxation time to the characteristic diffusion time. At low Deborah numbers, drying is Darcian. At intermediate and high Deborah numbers, however, drying is non-Darcian. Non-Darcian drying leads to

drying shut-off, a result of surface dry-out and shell/crust formation. Based on a time-dependent surface boundary condition, the model proposes that surface drying is not only a function of the Deborah and Biot numbers, but also a function of the "Achanta" number, a ratio between the Deborah and Biot numbers. The Achanta number accounts for the presence of three resistances (diffusion, deformation and external) to drying or shrinking systems.

The model was verified by comparing its predictions with experimental data from drying gels at several temperatures. The model parameters were estimated by conducting self-diffusion experiments, measuring moisture sorption isotherms, and measuring the moisture dependence of the bending modulus. The model predictions show reasonable agreement with experimental data and they capture the essential sigmoidal shape of the experimentally obtained drying curves. The predicted moisture profiles show crust formation and growth during drying, in-tune with the experimentally obtained moisture profiles. The model provides the basis for further investigations into such phenomena as case-hardening and stress-cracking during drying.

4. Higher-order corrections to the mean dispersive flux.

A nonlocal, eulerian transport model that is second-order accurate (in the variance of the fluctuating log-conducting, σ_f^2) in both flow and transport was developed. Numerical implementation of the theory shows that the flow correction (to the usual first-order flow models) has a profound effect on transverse chemical transport, but the transport correction (to the usual first-order transport models) has little effect. The second-order flow correction moderately decreases the longitudinal second moment, but significantly increases the transverse second moment. This model allows us to significantly increase the degree of heterogeneity in soils and yet maintain accurate simulations.

5. Nonlocal reactive transport with physical and chemical heterogeneity; linear nonequilibrium sorption with random rate coefficients.

A nonlocal, first-order, eulerian stochastic perturbation theory was developed with linear nonequilibrium sorption and random rate coefficients. Nonlocality was manifest in the dispersive and convective fluxes as well as sources and sinks. The mean concentration balance law was solved exactly in Laplace-Fourier space and numerically inverted to real space. The results indicate that there are gaps in existing data sets at major reactive-chemical study sites. The model also suggests the need to design new experiments and it further suggests a number of novel correlation functions should be obtained.

6. Comparison of eulerian to lagrangian expected spatial moments for transport in a heterogeneous porous medium with deterministic linear nonequilibrium sorption.

When a natural porous formation is viewed from an eulerian perspective, incomplete characterization of the hydraulic conductivity leads to nonlocality in the dispersive flux, irrespective of whether the medium has evolving heterogeneity with velocity fluctuations over all scales. Within this framework, we developed a first-order perturbation scheme which gave rise to a nonlocal dispersive flux for a reactive chemical experiencing linear nonequilibrium sorption with deterministic rate constants in a heterogeneous porous medium. Exact solutions for the mean concentration in Fourier-Laplace space were used to obtain mean values of spatial moments through the third. Comparisons were made with results obtained

through a lagrangian approach to the same problem. If local-scale dispersion is neglected in the eulerian analysis and the fully nonlocal flux is retained, then the eulerian and lagrangian moments agree. However, if either 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. The significance of this result is that it states the most commonly used models to simulate mean transport are in error.

7. Modified Darcy's law, Terzaghi's effective stress principle, and Fick's law for swelling clay soils.

Governing equations often used in soil mechanics and hydrology include the classical Darcy's law, Terzaghi's effective stress principle, and the classical Fick's first law. It is known that the classical forms of these relations apply only to non-swelling, granular materials. We summarized recent generalizations of these results for swelling porous media obtained using hybrid mixture theory (HMT) by the authors. HMT is a methodical procedure for obtaining macroscopic constitutive restrictions which are thermodynamically admissible by exploiting the entropy inequality for spatially-averaged properties. HMT applied to the modeling of swelling clay particles, viewed as clusters of adsorbed water and clay minerals, produces additional terms necessary to account for the physico-chemical forces between the adsorbed water and clay minerals or, more generally, for swelling colloids. New directions for modeling consolidation of swelling clays were proposed based on our view of clay particles as a two-phase system.

8. A multiscale theory of swelling porous media, with dual porosity, for consolidation of clays incorporating physical chemical effects.

A three-scale theory of swelling clay soils was developed which incorporates physico-chemical effects and delayed adsorbed water flow during secondary consolidation. Following earlier work, at the microscale the clay platelets and adsorbed water (water between the platelets) are considered as distinct nonoverlying continua. At the intermedia (meso) scale the clay platelets and the adsorbed water are homogenized in the spirit of hybrid mixture theory, so that, at the mesoscale they may be thought of as two overlaying continua, each having a well defined mass density. Within this framework the swelling pressure is defined thermodynamically and it is shown to govern the effect of physico-chemical forces in a modified Terzaghi's effective stress principle. A homogenization procedure is used to upscale the mesoscale mixture of clay particles and bulk water (water next to the swelling mesoscale particles) to the macroscale. The resultant model is of dual porosity type where the clay particles act as sources/sinks of water to the macroscale bulk phase flow. The dual porosity model can be reduced to a single porosity model with long term memory by using Green's functions. The resultant theory provides a rational basis for some viscoelastic models of secondary consolidation.

9. Macroscale thermodynamics and the chemical potential for swelling porous media.

The thermodynamical relations for a two-phase, N -constituent, swelling porous medium are derived using a hybridization of the mixture-theoretic approach and the Coleman and Noll method. Examples of such media include 2-1 lattice clays and hydrophilic polymers. The field equations are obtained by volume averaging microscale field equations so that

explicit relationships between the macroscale field variables and their microscale counterparts are obtained. The system of equations is closed by assuming the rate of change of the volume fraction is a dependent constitutive variable, resulting in viscoelastic behavior of the porous medium. A novel, scalar definition for the macroscale chemical potential for porous media is introduced, and it is shown how the properties of this chemical potential can be derived by slightly expanding the usual Coleman and Noll approach for exploiting the entropy inequality to obtain near-equilibrium results. Within this approach, we use Lagrange multipliers to weakly enforce the continuity equations as well as the relationship between the gradients of the diffusive velocities. The relationship between this novel scalar chemical potential and the tensorial chemical potential of Bowen is discussed. The tensorial chemical potential may be discontinuous between the solid and fluid phases at equilibrium; a result in clear contrast to Gibbsian theories. This discontinuity in the potential is due to an "effective" external field (e.g., the effective stress induced by a load in the solid phase). It is shown that the macroscopic scalar chemical potential is completely analogous with the Gibbsian chemical potential. The relation between the two potentials is illustrated in three examples.

10. New directions for modeling consolidation of swelling clay soils.

Governing equations often used in consolidation theories include Darcy's law for flow and Terzaghi's effective stress principle for deformation. It is known that the classical forms of these relations apply only to non-swelling, granular materials. Swelling clay soils require modifications to incorporate physico-chemical effects and intra-particle adsorbed water flow. We summarized recent generalizations of these results for swelling porous media which are obtained within the framework of "upscaling techniques". The proposed approach consists of a three-scale picture of swelling clays which incorporates physico-chemical effects and delayed adsorbed water flow during consolidation. At the microscale, the clay platelets and adsorbed water (water between the platelets) are considered as distinct nonoverlying continua. At the intermediate (meso) scale the clay platelets and the adsorbed water are homogenized in the spirit of the hybrid mixture theory so that they may be thought of as two overlaying continua, each having a well defined mass density. By viewing the adsorbed water as a thin liquid film averaged over the clay particles, the disjoining or swelling pressure may be defined thermodynamically and shown to be consistent with experiments. This framework yields a rigorous derivation of some modified Terzaghi's effective stress principle for clays which account for physico-chemical forces within and between clay particles. A homogenization procedure is used to upscale the mesoscale mixture of clay particles and bulk water (water next to the swelling mesoscale particles) to the macroscale. The resultant model is of dual porosity type where the clay particles act as sources/sinks to the macroscale bulk phase. A notable consequence of this approach is a macroscopic adsorbed-bulk water mass exchange which appears as a source term in the fluid mass balances. Based on our view of clay particles as a two phase system new directions for modeling consolidation of swelling clays are proposed.

11. Diffusive transport of volatile pollutants in nonaqueous-phase liquid contaminated soils using a fractal model.

Volatile organic chemicals from nonaqueous-phase liquids trapped in soil spread quickly both into the atmosphere and the groundwater system, resulting in long-lasting pollution of the environment. The extent and speed of spread is strongly influenced by the hetero-

geneities present in the soil, which interact with the various mechanisms of transport in a complex manner. A semi-analytical model was developed to investigate the effect of soil-heterogeneities on the spreading of pollutants from a nonaqueous-phase liquid trapped in a soil. Based on field evidence, soil-heterogeneities are modeled as a self-similar fractal process, and diffusive transport of organic chemicals in such a substrate was studied. Various mechanisms of, and resistance, to transport of these contaminants were considered, and it was illustrated how each of these are altered by the presence of heterogeneities. More specifically, it is shown that, while the transport processes at early time are governed by volatilization and dissolution and are quite unaffected by the heterogeneities, the transport processes at late time are strongly dependent on the heterogeneities of the soil and its sorption characteristics. In addition, how failure to recognize these heterogeneities in the soil may result in unsuccessful design of appropriate remediation techniques is discussed.

12. Phase separation in binary simple fluids.

One to three layer cyclohexane and octamethyltetra-cyclosiloxane (OMCTS) films confined between mica-like surfaces were studied to elucidate changes in the films' lattice-type and composition. Grand canonical ensemble Monte Carlo computer simulations were used to study the laterally confined film. 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 of the pore fluid 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 not does cause the sudden shear melting transition associated with epitaxial alignment of the fluid atoms with the surface.

13. The significance of porosity variability to flow and transport in randomly heterogeneous media.

We employed Monte Carlo simulations of flow and transport in random conductivity, porosity to and geochemistry fields to explore the influence of their spatial variability on flow and transport processes for both conservative and reactive chemicals. For conservative transport, results show that when the porosity is correlated to the hydraulic conductivity (which is often the case in geologic formations), the dispersion process is significantly affected. Positive cross-correlation between the porosity and the conductivity decreases dispersion, while a negative correlation tends to increase dispersion in the longitudinal direction. For reactive transport in physically and chemically heterogeneous media, the geochemical variability alone yields results that are significantly different than when both geochemistry and porosity are random space variables correlated to the conductivity field. These results suggest that it is necessary to examine the role porosity variability and its correlation to the conductivity play in flow and transport. Modification of the second-order velocity covariance result, previously obtained by our group, was made to account for the correlation of porosity to the hydraulic conductivity. For the cases studied herein, with a selected form of this cross-correlation, there is a significant difference between deterministic and random porosity. Further, the effect of porous variability on the velocity covariance is much more important than the higher-order head and velocity corrections to it.

14. Laboratory observation of nonlocal dispersion.

Experiments were performed to investigate dispersion between miscible fluids in a heterogeneous porous medium composed of homogeneous layers. The specific questions addressed included:

- 1) Can mixing be adequately modeled with Fick's first law in scale dependent porous media?
- 2) When and where does mixing behave asymptotically? and
- 3) How is the mixing behavior affected by sharp discontinuities in conductivity?

The experiments were performed in cylindrical Lucite columns packed with layers of spherical glass beads. Flow direction was perpendicular to the layers. Concentration profiles of a chloride tracer was measured at numerous locations along the column length. Each media was built at three lengths and replicated in a mirror image of the heterogeneity, giving six models in total. In each model the scale of measurement was finer than the scale of the conductivity heterogeneity. Results show mixing between miscible fluids was affected by transitions in permeability before the transition was reached. This phenomena has been interpreted as a non-local effect, and it is not predicted by theories based on the usual form of Fick's law. The results also show that the rate at which the mixing stabilizes after a transition is dependent on the Darcy velocity.

15. Comparison of nonlocal-eulerian to lagrangian moments for transport in an anisotropic heterogeneous aquifer with deterministic linear nonequilibrium sorption.

An eulerian perturbation scheme was applied to study transport of a reactive chemical experiencing linear nonequilibrium sorption with deterministic rate constants in a heterogeneous porous medium. Exact solutions for the mean concentrations are used to obtain mean values of spatial moments through the third. Comparisons are made with results obtained for the identical problem in a lagrangian frame (Dagan and Cvetkovic, 1993). If local scale dispersion is neglected in the eulerian analysis and the fully nonlocal flux is retained, then the eulerian and lagrangian moments agree. However, if either 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. If local scale dispersion is included in the first-order lagrangian analysis, then one anticipates agreement through the third moments between the two approaches.

16. Nonlocal reactive transport with physical, chemical, and biological heterogeneity.

When a natural porous medium is viewed from an eulerian perspective, incomplete characterization of the hydraulic conductivity, chemical reactivity, and biological activity leads to nonlocal constitutive theories, irrespective of whether the medium has evolving heterogeneity with fluctuations over all scales. Within this framework a constitutive theory involving nonlocal dispersive and convective fluxes and nonlocal sources/sinks is developed for chemicals undergoing random linear nonequilibrium reactions and random equilibrium first-order decay in a random conductivity field. The resulting transport equations are solved exactly in Fourier-Laplace space and then numerically inverted to real space. Mean concentration contours and various spatial moments are presented graphically for several covariance structures.

III. Publications

1) Books:

"The Physics of Fluids in Hierarchical Porous Media: Angstroms to Miles",
J. H. Cushman, Kluwer Academic, NY, 1997.

2) Journal Articles:

- 1) A. E. Hassan and J. H. Cushman (1998) *Thermomechanical theories for swelling porous media with microstructure*. Water Resour. Res. (submitted).
- 2) L. S. Bennethum, M. A. Murad, and J. H. Cushman (1997) *Macroscale thermodynamics and the chemical potential for swelling porous media*. J. Continuum Mechanics and Thermodynamics (submitted).
- 3) S. Mukhopadhyay and J. H. Cushman (1997) *Diffusive transport of organic vapors in nonaqueous-phase liquid contaminated soil: A fractal model*. Trans. Por. Media (in press).
- 4) M. A. Murad and J. H. Cushman (1997) *New directions for modeling consolidation of swelling clay soils*. Trends in Soil Science 2:1-35.
- 5) X. Hu, V. W. Deng, and J. H. Cushman (1997) *Nonlocal reactive transport with physical and chemical heterogeneity: Linear nonequilibrium sorption with random rate coefficients*. In "Subsurface Flow and Transport: A Stochastic Approach", G. Dagan and S. P. Neuman, eds., Cambridge Press, 146-156.
- 6) J. E. Curry and J. H. Cushman (1997) *Normal-strain induced change in lattice-type for confined cyclohexane films*. In "Dynamics in Small Confined Systems III", 115-120.
- 7) S. M. Achanta, M. Okos, J. H. Cushman, and D. Kessler (1997) *Moisture transport in shrinking gels during saturated drying*. AIChE J. 43(8):2112-2122.
- 8) M. A. Murad and J. H. Cushman (1997) *A multiscale theory of swelling porous media: II. Dual porosity models for consolidation of clays incorporating physical chemical effects*. Trans. Por. Media 28(1):69-108.
- 9) L. S. Bennethum, M. Murad, and J. H. Cushman (1997) *Modified Darcy's law, Fick's law, and Terzaghi's effective stress principle for swelling clay soils*. J. Computers in Geotechniques 20(3/4):245-266.
- 10) X. Hu and J. H. Cushman (1997) *Comparison of nonlocal-eulerian to lagrangian moments for transport in an anisotropic heterogeneous aquifer with deterministic linear nonequilibrium sorption*. Water Resour. Res. 33(4):891-896.
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- 12) X. Hu, J. H. Cushman, and F. W. Deng (1997) *Nonlocal theory of reactive transport with physical, chemical and biological heterogeneity*. Adv. Water Resour. Res. 20:298-308.
- 13) J. H. Cushman, X. Hu, and F. W. Deng (1996) *Comparison of Eulerian to Lagrangian expected spatial moments for transport in a heterogeneous porous medium with deterministic linear nonequilibrium adsorption*. Chem. Eng. Com. 148-150:5-21.

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