EMSP Project 86981
Progress Report, FY 2004

Transport, Targeting, and Applications of Metallic Functional Nanoparticles for Degradation of DNAPL Chlorinated Organic solvents

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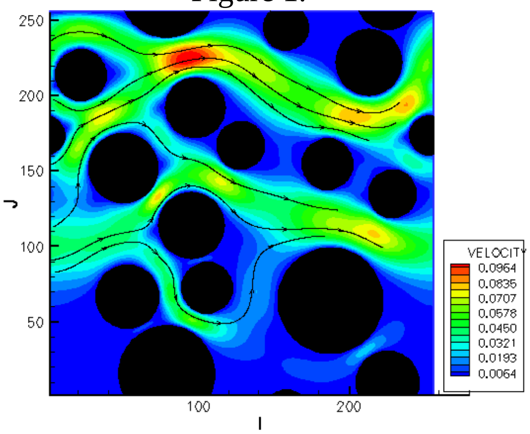
Research Objectives: The goals of this project have been to synthesize reactive metal colloids capable of: 1) reductively degrading chlorinated solvents, 2) being transported in porous media, and 3) partitioning from aqueous to non-aqueous solvents or accumulating at water/organic solvent interfaces. This project addresses the need for methods to efficiently remove or degrade dense non-aqueous phase liquid (DNAPL) contaminants, and that act as long-term sources of groundwater contamination through slow solubilization. This project builds on a general particle-based approach to subsurface contaminant remediation that has been demonstrated by others in the successful degradation of chlorinated compounds dissolved in groundwater using Fe(0) colloids. Delivering reactive particles directly to the surface of the DNAPL will decompose the pollutant into benign materials, reduce the migration of pollutant during treatment, possibly lead to encapsulation of the DNAPL, and reduce the time needed to remove residual pollution by other means, such as natural attenuation. Specific research challenges include: Synthesis of reactive particles that can be deployed in aqueous environments, modification of the particle surfaces, and modeling the transport behavior in porous media containing pendant chlorinated solvent.

Research Progress and Implications: This project is being conducted in collaboration with Carnegie Mellon University (CMU). Rapid progress has been made with respect to the polymer-based modification of particle surface properties and development of a model to describe particle transport behavior at CMU. This has been summarized in a report submitted separately by CMU. The INL responsibilities are in particle synthesis, the development of a complimentary, pore-scale model to describe particle transport and partitioning, and experimental testing using micromodels of porous media.

Model development using the lattice-Boltzmann method (LBM): We have developed a numerical code based on the lattice-Boltzmann method (LBM) (Rothman and Zaleski, 1997; Succi, 2002) to simulate two- and three-dimensional transient flow and two-dimensional colloidal transport through non-uniform granular porous systems. The numerical code is also capable of simulating multiphase and multicomponent transport in two and three-dimensional granular porous systems. This component has not yet been integrated with the colloidal transport component.

The model results for simple flow geometries (e.g., Poiseuille flow between stationary parallel vertical walls) have been compared against analytical solutions available in the scientific literature to evaluate the accuracy of the model results. The agreement between the analytical and numerical results was satisfactory for our applications. The LBM was then used to simulate gravity driven flow in physically heterogeneous 2D and 3D synthetic granular porous systems with non-uniform obstacles. An example is shown in Fig. 1.

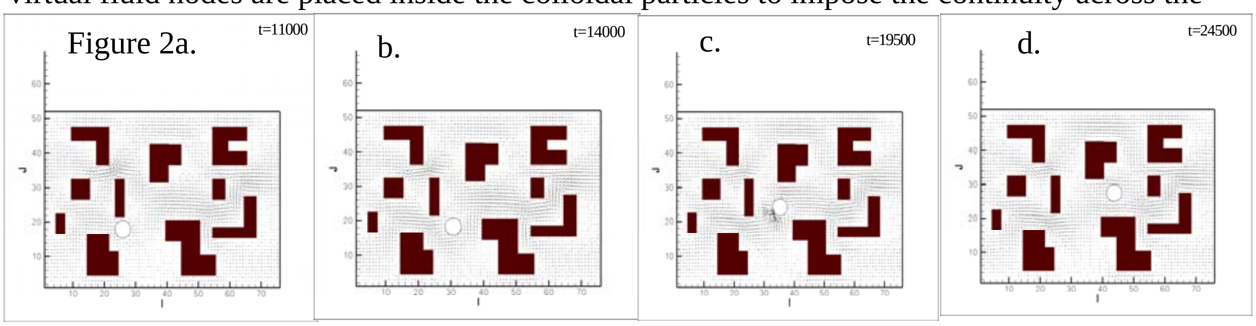
Figure 1.



Solid black objects in these figures represent solid grains and the color scale indicates the steady-state velocities. Periodic boundary conditions were imposed along all boundaries and a no-slip boundary condition was specified at the edge of soil grains. The simulated results are physically reasonable, and conserve mass and momentum exactly.

Next, we focused on the colloidal transport component (see procedure described in Ladd (1994) and Nguyen and Ladd (2002)). In the latter approach, the fluid is assumed to occupy the flow domain outside the colloidal particles. Although this procedure has simulated particle trajectories reasonably well, it gave rise to strong sudden pressure pulses across the flow domain occasionally as the colloidal particle moved through (Fig. 2c). These physically unrealistic pulses died out with time (Fig. 2d).

In the next step, we modified our model in accordance by Ding and Aidun (2003) in which virtual fluid nodes are placed inside the colloidal particles to impose the continuity across the



entire flow field, inside and outside the colloidal particles. We observed from our simulations that inclusion of virtual fluid nodes circumvents the unphysical strong sudden pressure pulses in the flow field. This approach seems to be more appropriate for our simulation objectives and thus it was adopted in our subsequent work.

We have also used the colloidal transport model to simulate settling of a particle through a vertical channel initially placed along and off the

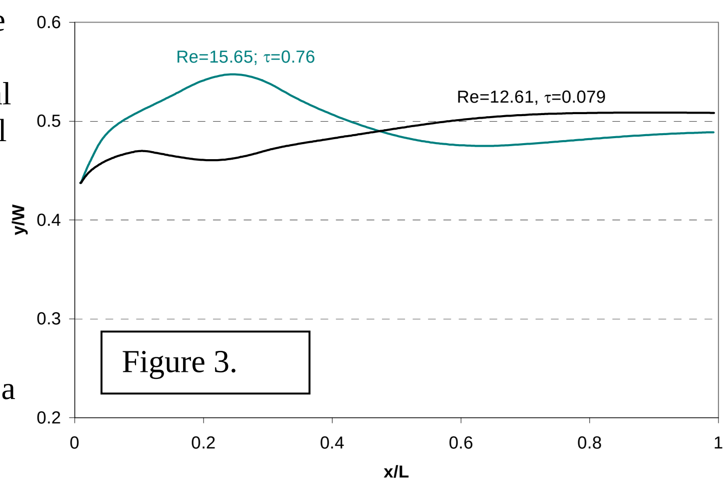


Figure 3.

centerline. According to previously published experimental and numerical experiments, if a colloidal particle is placed off the centerline initially, it will drift towards the centerline due to inertial effects. The particle can undergo oscillatory motion about the centerline if the Reynolds number is large enough, but eventually it will approach its equilibrium position at or near the centerline. The overall dynamics is greatly determined by the Reynolds number, and the relative size of the particle diameter with respect to the channel width. We have captured these dynamics qualitatively, as shown in Fig. 3.

Experimental Micromodels: An initial 2-D representation of porous media with contrasting flow regimes has been fabricated on a silicon wafer (Figure 4). We are currently completing construction of the micromodel with a glass cover, ports for injection of fluids and colloids, and imaging using a particle velicometry imaging system developed at the INEEL. Additional models with larger dimensions are currently being fabricated. These models will be used to track particle advection and diffusion in aqueous systems, and in systems with residual non-aqueous solvents (tri-chloroethylene).

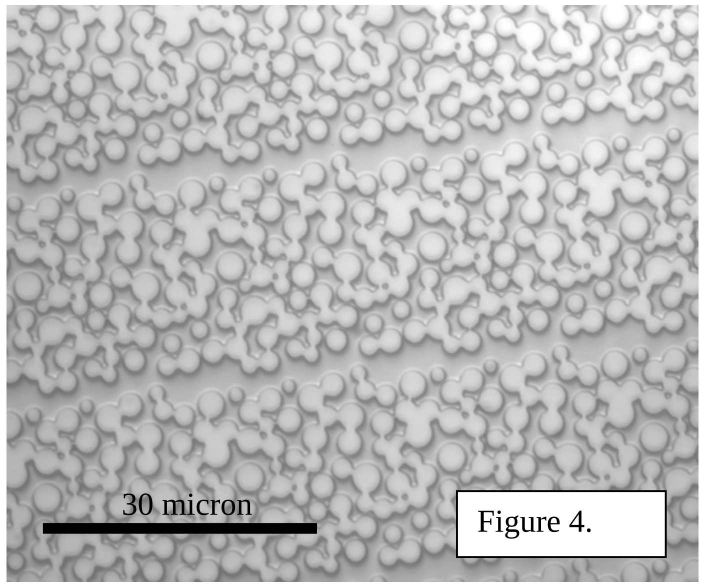


Figure 4.

Planned Activities:

Model development using the lattice-Boltzmann method (LBM): For future work, detailed quantitative comparisons of our colloidal simulation results against the previously published numerical solutions and experimental data will be conducted to develop a better understanding of the model performance and limitations. Brownian motion of colloidal particles has not been included in the current model, and Brownian motion will be added in the next stage. The colloidal transport module will be integrated with the multicomponent/multiphase module to simulate flow and transport processes from our micromodel experiments in analyzing and quantifying pore scale colloidal transport and biodegradation processes. A new version of the overall model will be developed for implementation on parallel computers using MPI (message passing interface) to enhance the efficiency of the code reduce the model run time and allow us to work with larger systems. We also plan on using dissipative particle dynamics methods as an alternative tool to model colloidal transport.

Experimental Micromodels: The first physical micromodel should be completed within the month and will be followed by the set of experiments outlined in the original proposal. Two additional models will be fabricated; one with larger pore and grain dimensions, and one with discrete grains (absence of dead-end pores). The dimensions of these models will be verified using digitized images from SEM and optical microscopy, and the digitized images will then be used in conjunction with the LBM models in order to compare predicted and actual particle migration behavior.

References:

Ding E.J. and Aidun C.K. (2003). Extension of the lattice-Boltzmann method for direct simulation of suspended particles near contact. Journal of Statistical Physics 112(3-4): 685-708.
Ladd A.J.C. (1994). Numerical simulations of particulate suspensions via a discretized Boltzmann equation. 1. Theoretical foundation. Journal of Fluid Mechanics 271:285-309.
Nguyen N.Q. and Ladd A.J.C. (2002). Lubrication corrections for lattice-Boltzmann simulations of particle suspensions. Physical Review E 66, 046708.
Rothman D.H. and Zaleski S. Lattice-gas cellular automata. Cambridge University Press; 1997.
Succi S. The lattice Boltzmann Equation for fluid dynamics and beyond. Oxford University Press; 2001.

Plublications and Presentations:

- Basagaoglu H., Meakin P, Succi S., Rotondi R. "On the compressibility error in two-phase flow simulation using the LBM." Submitted to Advances in Water Resources on 5/11/04.
- Basagaoglu H., Green TC, Meakin P, McCoy BJ. "Lattice-Boltzmann simulation of coalescence-driven island coarsening." Submitted to Journal of Chemical Physics on 6/21/04.
- Basagaoglu H., Meakin P. “Application of the lattice Boltzmann model to two-phase fluid flows and Ostwald ripening process.” (to be presented at the 13rh International Conference on the Discrete Simulation of Fluid Dynamics in Massachusetts, USA , August 2004).
- Basagaoglu H., Meakin P. “Simulation of Colloidal Transport via the Lattice Boltzmann Method.” Presented at INRA 2003 Subsurface Science Symposium, "Advances in Understanding and Modeling Subsurface Processes" in Salt Lake, UT, October 2003.