FINAL REPORT: DOE DE-FG02-07ER64417

Mechanistically-Base Field Scale Models of Uranium Biogeochemistry from Upscaling Pore-Scale Experiments and Models

Oregon State University
Principal Investigator: Brian Wood
Subtask Lead: Task 3
Key Contributors: Brian Wood's expertise is in transport theory and experimental methods for studying transport in biological systems and in multiphase media. His research has been centered around engineering problems that require the upscaling of interacting physical, biological, and chemical systems; particular focus has been on problems involving solute transport in porous media. He has experience with a variety of theoretical techniques including classical ensemble averaging, field-theoretical methods for upscaling, and volume averaging. Wood will have lead responsibility for application of volume averaging and other upscaling methods (Task 3).

Consortium Arrangements

Pacific Northwest National Laboratory
Principal Investigator: Tim Scheibe (Collaborator: Alexander Tartakovsky)
Subtask Lead: Tasks 2 and 4
Key Contributors: Tim Scheibe is experienced in field-scale simulation of subsurface flow and transport in heterogeneous media, and in geostatistical and other methods for generating heterogeneous model systems. Scheibe will lead efforts of field-scale reactive transport modeling (Task 4) as well as serve as overall project manager. Alexander Tartakovskys areas of expertise include uncertainty quantification, stochastic differential equations and ensemble averaging methods, and subsurface flow and transport and multiscale computational fluid dynamics. Tartakovsky will lead efforts of pore-scale model development and application (Task 2).

Montana State University
Principal Investigator: Joseph Seymour
Subtask Lead: Task 1
Key Contributors: Joseph Seymour is affiliated with the Center for Biofilm Engineering at Montana State University. His primary expertise is in magnetic resonance imaging methods as applied to biofilm characterization. Seymour will have lead responsibility for the experimental characterization of pore geometry and biofilm development (Task 1).

1 Executive Summary

This final report summarizes the research done by the PI at Oregon State University for the collaborative research described in Task 3 of the proposal for DOE project DE-FG02-07ER64417.

1.1 Problem Statement

Biogeochemical reactive transport processes in the subsurface environment are important to many contemporary environmental issues of significance to DOE. Quantification of risks and impacts associated with environmental management options, and design of remediation systems where needed, require that we have at our disposal reliable predictive tools (usually in the form of numerical simulation models). However, it is well known that even the most sophisticated reactive transport models available today have poor predictive power, particularly when applied at the field scale. Although the lack of predictive ability is associated in part with our inability to characterize the subsurface and limitations in computational power, significant advances have been made in both of these areas in recent decades and can be expected to continue.

We assert that the greater limitation in application of predictive models to field problems lies in our lack of understanding of the impacts of 1) complex spatial variability (heterogeneity) and 2) temporal dynamics (physical and biogeochemical non-equilibrium). Both of these factors give rise to effects that have as yet poorly understood manifestations at the field scale.

1.2 Results and Technical Effectiveness

In Task 3 of this research, we were given the objective of "upscaling pore-scale results to obtain continuum models and parameters" for the problem of bioremediation via biofilms in porous media. The principle idea was to start with a conceptual description of the bioremediation process at the pore scale, and apply upscaling methods to formally develop the appropriate upscaled model at the so-called Darcy scale (i.e., the scale that represents a representative volume of porous medium). A graphical illustration of the scales of interest for bioremediation appears as Fig. 1.

The purpose was to determine (1) what forms the upscaled models would take, and (2) how one might parameterize such upscaled models for applications to bioremediation in the field. We were able to effectively upscale the bioremediation process to explain how the pore-scale phenomena were linked to the field scale. The end product of this research was to produce a set of upscaled models that could be used to help predict field-scale bioremediation. These models were mechanistic, in the sense that they directly incorporated pore-scale information, but upscaled so that only the essential features of the process were needed to predict the effective parameters that appear in the model. In this way, a direct

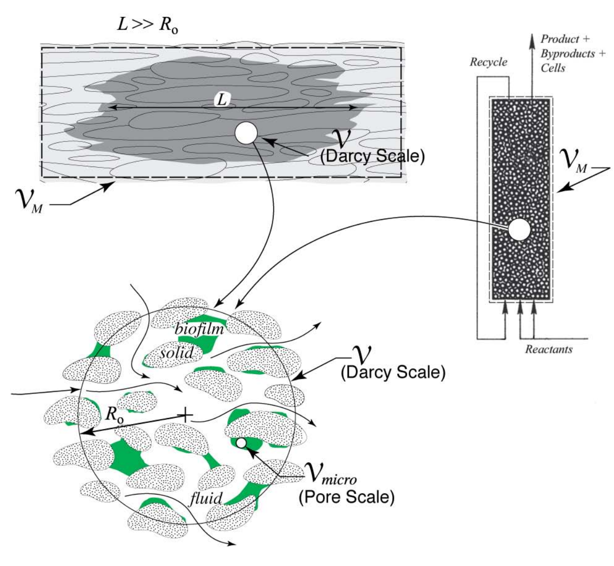

Figure 1: Hierarchy of scales in bioremediation in porous media.

link between the microscale and the field scale was made, but the upscaling process helped inform potential users of the model what kinds of information would be needed to accurately characterize the system.

Eight publications related to upscaling biofilms and subsurface processes relevant to bioremediation were generated on this project (Davit *et al.*, 2012, 2010; Ginn *et al.*, 2009; Golfier *et al.*, 2009, 2011; Porter *et al.*, 2011, 2010; Valdes-Parada *et al.*, 2011).

2 Comparison of Proposed and Actual Accomplishments

As initially envisioned, the proposed research stated the following set of goals for Task 3.

1. Year 1: Apply volume averaging to initial model porous medium simulations (see Tasks 1 and 2) and evaluate associated model errors and uncertainties. Develop (i) the one-equation, effectiveness factor model, and (ii) the two-equation model.

2. Year 1: Define alternative approaches to upscaling and test using initial model porous medium simulations.

3. Years 2 and 3: Apply volume averaging to simulated flow and transport results for a limited number of textural classes to derive upscaled (field-scale) models and parameters. Closure problems will be solved in three-dimensional media, with solid, fluid, and biofilm phases as determined under Task 1. Image segmentation and mesh generation will be done for a fully 3- dimensional, representative volume of porous media containing a well-developed biofilm. The solution to the closure problems will be conducted using the software STAR-CD on a parallel computing platform.

4. Years 2 and 3: Apply alternative approaches to upscaling (e.g., random-walk particle state transition probability model).

Goals 1 through 3 were attained largely as stated. A brief description of actual versus achieved goals for each item is summarized below.

Results for Goal 1. In Goal 1, the development of both one- and two-equation upscaled models was undertaken, and both of these models were developed. The upscaling effort was focused on the pore to Darcy level of descriptions (i.e., our goal was to start with a model that presumed pore-scale knowledge of the distribution of biofilms and solids defining the porous medium; the upscaled model that resulted was homogenized over a representative volume of that medium) as illustrated in Fig. 1. One equation models result from the approximation of local mass equilibrium between the biofilm and the fluid-phase. One-equation models are simple because separate equations for the mass of chemical species (e.g., a contaminant) contained in the fluid and biofilm phases are unnecessary. However, assuming local mass equilibrium also requires that some very stringent constraints be met (specifically, the time scales for transport via convection in the fluid phase and diffusion in the biofilm phase must be of a similar order). When these constraints are not met, then more complex two equation models are needed. Upscaling efforts for both the one- and two-equation modeling perspectives were completed during this research. Results from the research associated with this goal are summarized in project publications Davit *et al.* (2012), and Golfier *et al.* (2009).

Results for Goal 2. For goal 2, a method where non-equilibrium mass transfer between the biofilm and fluid phases was examined as an alternative to the one-equation equilibrium model was investigated. For this model, we examined the conditions for which a one-equation model could be used under non-equilibrium conditions. This approach has the advantages of a one-equation model (i.e., it is simple), but allows for some representation of the complex influence that mass-transfer can have on the field-scale transport process. Results from this research are reported in Davit *et al.* (2010).

Results for Goal 3. Goal 3 involved providing example applications of the models derived under Goals 1 and 2. Examples of computations for the one- and two-equation models were presented in the associated publications (Davit *et al.*, 2010; Golfier *et al.*, 2009). We made direct comparisons of theory and experiment by comparing the results of the upscaled theory with transport experiments done in model porous media created in micro-flowcells. In these experiments, we focussed on (1) the pure hydrodynamic dispersion process (in the absence of biofilms), and (2) the process of dispersion and chemotaxis of microbial cells as they move through a porous medium. Results related to this component of Goal 3 are reported in Porter *et al.* (2011), Porter *et al.* (2010), and Valdes-Parada *et al.* (2011).

A secondary component of this goal was to examine the upscaling for field-scale heterogeneities that might influence the process of bioremediation. These heterogeneities would be manifest at the largest scale illustrated on Fig. 1. Essentially, at this scale, the pore-scale has been entirely homogenized so that it is no longer resolved. However, there may still be fluctuations of the physical properties of the porous material within a representative volume. We also examined how physical heterogeneity can influence transport of aqueous species in systems with heterogenity. We reported the results of upscaling Darcy-scale heterogeneities, and their influence on the effective dispersion observed, in (Golfier *et al.*, 2011). In this work, there was a direct comparison of theory and experiment for a set of transport experiments that had been conducted previously at PNNL. In this work, we showed an excellent agreement between theory and experiment, suggesting that the volume averaging method was an effective approach for representing field-scale transport under conditions of statistically characterizable subsurface heterogeneities.

Results for Goal 4. The goal stated in item 4 was investigated, in part, as follow-on research to work conducted by two of the PIs (Scheibe & Wood, 2003). Although research toward this goal was initiated in the project, it was determined early on that these methods would not add additional benefit to the upscaling approach. Efforts were re-focussed on the existing (non-particle-based) methods for upscaling, as described above. No further results were pursued for this goal.

3 Summary of Project Activities

3.1 Research Hypotheses

The research hypotheses stated in the original proposal were as follows.

Global Hypothesis. In natural porous media, pore-scale flow and transport processes lead to incomplete mixing that cause anomalous (non-classical) reactive transport behavior to be manifested at larger scales. Explicit simulation of pore-scale processes provides a means of developing sound conceptual models of continuum-scale reactions that properly account for small-scale features.

Although the above statement accurately describes the underlying concept behind the proposed research, the validity of this general hypothesis is to some extent self-evident while at the same time difficult to test in a generalized manner. Therefore, of greater importance are the specific sub-hypotheses that arise from application of this general hypothesis to the specific reactive transport systems on which we have chosen to focus. These can be stated as follows.

Specific Hypotheses.

1. Effective reaction rates in granular porous media will generally be smaller than the associated fundamental rates derived from well-mixed batch experiments because of incomplete mixing associated with pore-scale heterogeneity.

2. In systems with significant biofilms, mass-transfer rate limitations imposed by the biofilm itself will further reduce effective reaction rates.

3. Localized biofilm growth and pore clogging are coupled to changes in flow patterns that significantly impact local mass transfer rates and reaction rates.

4. Anomalies in effective reaction and transport processes (e.g., non-linearity, multiplicity of parameter values, hysteresis) arise in part from variations in local boundary conditions associated with large-scale heterogeneity and flow patterns, such that a given pore geometry can manifest a variety of different macroscopic behaviors.

The specific sub-hypotheses related to Task 3 were primarily items 1 through 3.

The research performed for Task 3 on this project was primarily focussed on two areas (1) development of an appropriate microscale / macroscale system and subsequent upscaling for conditions that represented one of the conditions associated with the hypotheses, and (2) numerical modeling to solve the so-called "closure" problems that define the macroscale effective parameters that were identified during the upscaling process.

For the upscaling efforts, the method of volume averaging (**?**) was the primary upscaling tool adopted. For this method, the microscale balance equations are averaged over a compact averaging volume. Interchange of spatial differentiation and integration are done through the spatial averaging theorem, a three-dimensional analogue to the Leibniz rule for integration. This process generates integrals of functions of the dependent variables, and these integrals are determined by solution to a set of ancillary equations known as the "closure" problem. The process is very similar to the Reynolds decomposition process used in the study of turbulence, except the decompositions are in space, and the problems are usually linear.

In our work, we used the method of volume averaging to develop a number of upscaled representations of cases relevant to the hypotheses. These included the following.

1. **One-equation local mass equilibrium convection dispersion equation for systems with biofilms.** For this work, the microscale is initially given by two separate balance equations- one for the fluid, and one for the biofilm. Under local mass equilibrium conditions, we show how this can be reduced to a one-equation model, which is more convenient for applications when the restrictions for assuming local mass equilibrium are valid. The effective parameters were determined using simple unit cells with varying amounts of biofilm. A complex unit cell with the structure of an actual porous medium (extracted from an magnetic resonance image collected previously by the PI) was also used to compute the effective parameters. The results showed (1) There exists a domain of validity for the one-equation model requiring that both the Péclet (Pe) and Damköhler (Da) numbers be less than unity, and (2) the volume averaging method provided a good means for predicting the effective dispersion tensor for such systems.

2. **Two-equation and one-equation nonequilibrium convection dispersion relations for systems with biofilms.** In this work, we compared the result of one-equation nonequilibrium models with those of two-equation models. Fro the one-equation nonequilibrium model, one requires that, at sufficiently long times, anomalous behaviors of the third and higher spatial moments can be neglected; this, in turn, implies that the macroscopic model is well represented by a convection-dispersion-reaction type

equation. We completed the upscaling for this problem, and examined the influence of the microstructure through the closure problem in simple unit cells. The dispersion exhibits the classical form, and increases mainly with the Péclet number as the hydrodynamic dispersion becomes predominant. The effective reaction rate depends almost only on Da because the mass transfer through the boundary is mainly driven by diffusion. For low Da, the reaction rate is maximum and decreases when the consumption is large compared to diffusion. This suggests that the reaction rate could be written under the conventional "effectiveness factor" form ηR_{max} with $\eta \leq 1$ being a function of Da.

3. **Dispersion in weakly heterogeneous media.** In this work, we capitalized on the availability of an existing data set for dispersion in a porous medium with Darcy-scale heterogeneities. These data were collected previouisly by PNNL researchers (**?**). We computed the effective large-scale (field-scale) dispersion tensor that would apply to a heterogeneous system of inclusions in a matrix, with a ratio of the hydraulic conductivities on the order of $1 : 7.5$. Our results from this work were as follows.
   - A relatively low permeability contrast is not a sufficient criterion to establish whether the system behavior is driven by a one-equation or two-equation description.
   - in the case of a continuous injection, as long as the characteristic timescale associated with convection in the matrix is greater than the characteristic time for convection within the inclusions, the system can be represented by a one-equation equilibrium model.
   - If the characteristic time for injection is less than the characteristic time for convection through the inclusions, a two-equation model must be used to correctly capture early-time behavior.

4. **Comparison of one-equation nonequilibrium and two-equation models for solute transport.** In this work, we compared the long-time limit of one-equation nonequilibrium models, and two-equation models. In principle, one would expect the results of these two models to converge as time grows arbitrarily large. The main result of this paper is to show that there is only a weak asymptotic convergence of the solution of the two-equation model towards the solution of the one-equation nonequilibrium model in terms of standardized moments but, interestingly, not in terms of centered moments. The physical interpretation of this result is that deviations from the Fickian situation persist in the limit of long times but that the spreading of the solute is eventually dominating these higher order effects.

5. **Microscale dispersion in porous media.** For this work, our objective was to validate the upscaled transverse dispersion tensor component obtained via volume averaging. To do this, we examined concentration profiles of experimental data reported in the literature, and to compared the results of the upscaling approach tthe measured data. This work is unique in that the exact microscale geometry is available; thus, no simplifying assumptions regarding the geometry are required to predict the effective dispersion coefficients directly from theory. Transport of both an inert tracer and nonchemotactic bacteria were investigated for an experimental system that was designed to promote transverse dispersion. Overall, the upscaled dispersion coefficients and concentration profiles were not appreciably different than those obtained from inverse modeling procedure; this suggests that the volume averaging procedure may be a useful method for estimating the hydrodynamic dispersion tensor.

In addition to these primary results directly related to the hypotheses, we also generated some results of "opportunity" on the topics of (1) the role of tortuosity in describing diffusion and dispersion in porous media, and (2) the use of volume averaging in describing the process of chemotaxis in porous media.

4 Products

The research products from this work are exclusively the refereed journal articles that have been produced. Seven articles were published in association with this research. The references are Davit *et al.* (2012, 2010); Ginn *et al.* (2009); Golfier *et al.* (2009, 2011); Porter *et al.* (2011, 2010); and Valdes-Parada *et al.* (2011). Full bibliographic information appears in the "References" section at the end of the document.

References

DAVIT, YOHAN, DEBENEST, GERALD, WOOD, BRIAN D. & QUINTARD, MICHEL 2010 Modeling non-equilibrium mass transport in biologically reactive porous media. *Advances in Water Resources* **33** (9), 1075–1093 (doi:10.1016/j.advwatres.2010.06.013).

DAVIT, Y., WOOD, B. D., DEBENEST, G. & QUINTARD, M. 2012 Correspondence between one- and two-equation models for solute transport in two-region heterogeneous porous media. *Transport in Porous Media* **95** (1), 213–238 (DOI 10.1007/s11242–012–0040–y).

GINN, T. R., TARTAKOVSKY, D. M. & WOOD, B. D. 2009 Preface: Special issue on fundamental advances in modeling dispersion in porous media. *Advances in Water Resources* **32**, 633–634 (doi:10.1016/j.advwatres.2009.02.002).

GOLFIER, FABRICE, QUINTARD, MICHEL & WOOD, BRIAN D. 2011 Comparison of theory and experiment for solute transport in weakly heterogeneous bimodal porous media. *Advances in Water Resources* **34** (7), 899–914 (doi:10.1016/j.advwatres.2011.04.019).

GOLFIER, FABRICE, WOOD, BRIAN D., ORGOGOZO, LAURENT, QUINTARD, MICHEL & BUES, MICHEL 2009 Biofilms in porous media: Development of macroscopic transport equations via volume averaging with closure for local mass equilibrium conditions. *Advances in Water Resources* **32** (3), 463–485 (doi:10.1016/j.advwatres.2008.11.012).

PORTER, M. J., VALDÉS-PARADA, F.J. & WOOD, B.D. 2011 Multiscale modeling of chemotaxis in porous media. *Water Resources Research* **47**, W06518–1 to W06518–13 (doi:10.1029/2010WR009646).

PORTER, MARK L., VALDES-PARADA, FRANCISCO J. & WOOD, BRIAN D. 2010 Comparison of theory and experiments for dispersion in homogeneous porous media. *Advances in Water Resources* **33** (9), 1043–1052 (doi:10.1016/j.advwatres.2010.06.007).

SCHEIBE, T. D. & WOOD, B. D. 2003 A particle-based model of size or anion exclusion with application to microbial transport in porous media. *Water Resources Research* **39** (4), SBH 3–1 to 3–10 (doi:10.1029/2001WR001223).

VALDES-PARADA, FRANCISCO J., PORTER, MARK L. & WOOD, BRIAN D. 2011 The role of tortuosity in upscaling. *Transport in Porous Media* **88** (1), 1–30 (DOI 10.1007/s11242–010–9613–9).