UPSCALING ACTINIDE SORPTION FOR TRANSPORT MODELING

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ABSTRACT

Sites for remedial action have spatial scale lengths from tens of meters or less to several kilometers or more. For example, assessment models for the Hanford site need to consider radionuclide transport over a 20 km path. In stark contrast, nearly all studies of *processes* controlling the environmental behavior of actinides have been derived from representative scale-lengths of 10^{-3} m or less.

Scaling is the extrapolation of information derived at one scale to another scale of application. The sorption of actinides by geomedia is one of several processes that govern the transport of actinides through environmental flow systems. This paper provides an overview of scaling issues as they relate to sorption and describes the relationship between molecular-level information and sorption models at the field scale.

INTRODUCTION

> *'Although it might seem a paradox, all exact science is dominated by the idea of approximation.'* Bertrand Russell

The coupled physical, chemical and biological processes that control the fate and transport of actinides in natural systems are complex. The processes span a broad spectrum of length scales ranging from molecular to field lengths. For example, the interaction of actinides with dissolved organic ligands (e.g., humic acids, fulvic acids and extracellular microbial ligands) and mineral surfaces (e.g., aluminosilicates and oxides) is controlled, to a large extent, by the strength of the relevant molecular interactions. The interactions of actinides with naturally occurring nanostructures (e.g., dissolved humic acid aggregates), environmental colloids (e.g., humic acid coated inorganic particles) and biological microstructures (e.g., bacterial biofilms) significantly impact actinide mobility and reactivity in natural systems. Microscale and macroscale physico-chemical processes such as Fickian diffusion and hydrodynamic dispersion have also a significant impact on actinide mobility in subsurface formations.

Hydrogeologists, for example, are well aware that macrodispersion at the field scale is determined by the summation of dispersive mixing processes that occur at the micrometer and meter physical scales. However, in practice, it is impractical to consider or characterize these processes in a deterministic manner at the meter scale in order to model flow and transport at the field scale. Instead, it is necessary for hydrogeologists to make simplifying "engineering" assumptions based on various measurements at a specific field site, which then allows a flow model to be calibrated that describes the characteristics of the hydrologic system within a given

tolerance. Such a model is recognized to be imperfect, but it may be technically acceptable to an environmental manager and a regulatory authority. While substantial progress has been made on developing a sound framework for upscaling physical controls on solute transport (e.g., macrodispersivity [1]), little experimental or theoretical guidance exists for upscaling (bio)chemical processes in either spatial or temporal scales or system complexity (e.g., polymineralic system behavior predicted from monomineralic subsystems).

The essential problem in predicting the behavior of actinides in environmental systems is that the scale of interest for model outcomes is rarely, if ever, the scale for which information is available to construct a model. We need to model, in fact, <u>because</u>, we have incomplete access to system information.

The goal of *scaling* is to capture essential system characteristics at a scale of direct observation and to extrapolate to a different scale. Unfortunately, projections in time and space must be made often without confirmation at the target scale. The issue of upscaling information from the molecular level to scales of interest for environmental remediation is increasingly at the center of questions involving resource allocation in research funding. Two recent National Research Council reports [2,3] explicitly cite the need to develop a theoretical basis and methodologies for extending molecular-level information to scales of relevance for applying to management decisions. Although the types of information subject to scaling questions with respect to actinide fate and transport are many (e.g., the length-scale dependence of hydraulic conductivity), this paper will focus on scaling issues associated with actinide sorption.

Sorption included the processes adsorption (surface complex formation), surface precipitation and absorption (the penetration of a solute into a sorptive substrate (i.e., sorbent). Sorption processes contribute to the retardation of solute transport through environmental systems. This paper will primarily consider the process of adsorption in the context of reactive transport models.

In the discussion to follow on the incorporation of sorption into reactive transport models, it is useful to differentiate between processes and physical model structures. Model structures represent geologic, geometric and geochemical characteristics of the medium; processes are physical and chemical phenomena, such as groundwater flow, colloidal transport, dissolution and precipitation [4].

Concerning the physical system, heterogeneous geologic and geometric characteristics of the medium on the large scale, such as faults, layering, and heterogeneity, can strongly affect its hydrologic and hydrodynamic parameters. These parameters have been discussed in literature previously [5] and will not be addressed in this context. However, here we will focus on the variations of mineral phases over space as they affect the overall sorption characteristics of the system and lead to changes in metal transport behavior.

The complexity of the chemical processes involved, such as sorption reactions, strongly depends on the complexity of the solution chemistry of the groundwater system itself. For instance, the presence of organic and inorganic ligands may be relevant to metal sorption processes to mineral surfaces, which may further complicate the modeling approaches for these processes. Spatial and

temporal variations pose additional difficulties, which appropriate models should be able to solve accordingly.

In addition, geochemical and hydrodynamic processes are in many cases coupled [6]. For instance, the characteristics and variations of the minerals composing the rock matrix of the system strongly affect groundwater chemistry and the chemical processes involved. The aqueous chemistry may also depend on the hydrodynamic regime and the average residence time, as geochemical interactions are often kinetically controlled. On the other hand, geochemical reactions may alter the hydrodynamic behavior of the medium, for instance as minerals precipitate or dissolve, and change the permeability of the matrix.

The nature of models

Adsorption takes place at the molecular level through bond making and breaking. However, in transport simulations we need to account for the expression of the molecular-level process at the macroscopic level. Because the scaling of information cannot be separated from the question of models, it is crucial to begin the discussion of scaling by establishing a reference frame on the nature of models when they are developed for the purpose of predicting the fate of actinides at space and time scales of importance for en environmental systems.

Oreskes *et al.,* [7] have provided an analysis of the issues of the validation, verification and confirmation of numerical models in the earth sciences. While the discussion of model attributes is often philosophical in nature, a realistic understanding of what we should expect from modeling is at the core of decision that need to be made regarding the expenditure of time, effort and money in environmental research.

A core characteristic of environmental systems is that it is not possible for models to be an accurate representation of physical and chemical reality: as Oreskes *et al.* [7] point out, it is not even a theoretical possibility. As such, it is not possible to verify, or demonstrate the truth of, models. Because field-scale systems are open (and arguably even bench- and intermediate-scale systems):

- Input parameters for reactive transport models will always be incompletely known (i.e., have varying associated uncertainties including being unknowable);
- They will be mathematically *underdetermined*; and,
- Unique model outcomes for the field scale are not possible.

The consequence of the above is that it is not possible to evaluate models absolutely, but only relative to each other: the most appropriate use of models is as heuristic devices for exploring our understanding of systems; they are 'useful for guiding future study but '*are not susceptible to proof*' [8]. For any model and process of interest, there should exist a point of "optimum complexity" that would correspond to the minimum set of equations and parameters for which the addition of extra feedbacks, processes, or parameters produces negligible influence on the behavior of interest [9]. Disagreements between simulation results and experimental data are generally attributed to neglected processes [6], and recent publications show a trend towards increased model complexity. However, to quote Oreskes [8]:

'The heterogeneity of the natural world ensures that any model that strives for realistic representation must contain a large quantity of empirical input. This returns us to the complexity paradox: the more data we have, the more likely our model is to capture nature's diversity and richness. However, the more data we have, the more complex the model becomes and the less likely it is to be unique- another model of equal complexity but with a different mix of empirical input could have produced the same result'.

Because truth is not possible with models, van Fraassen [10] argues that the goal of models should be 'empirical adequacy'.

Complexity in systems evaluated by environmental experimentalists and modelers

Figure 1 compares attributes of physical, chemical and modeling environmental at different scale lengths. In recent years, a number of important advances have been made in surface analysis that have allowed the acquisition of information of portions of systems at the nanometer scale (10^{-9} m), where analytical techniques may integrate information from a few hundred to a few thousand sites (e.g., [11]). For example, consider the environment of uranium within a small volume (nanometer scale) of contaminated aquifer at a given field site. Current spectroscopic techniques allow the characterization of the oxidation state and coordination environment of the uranium in a sample containing a nanometer scale volume (within certain detection limits). At such a small physical scales it can be expected that the coordination of actinides would be dominated by only a small number (possibly one) of bond types, depending on the chemical environment, e.g., ternary uranyl-carbonate-iron oxide surface bonds or uranium(IV) precipitated as uraninite.

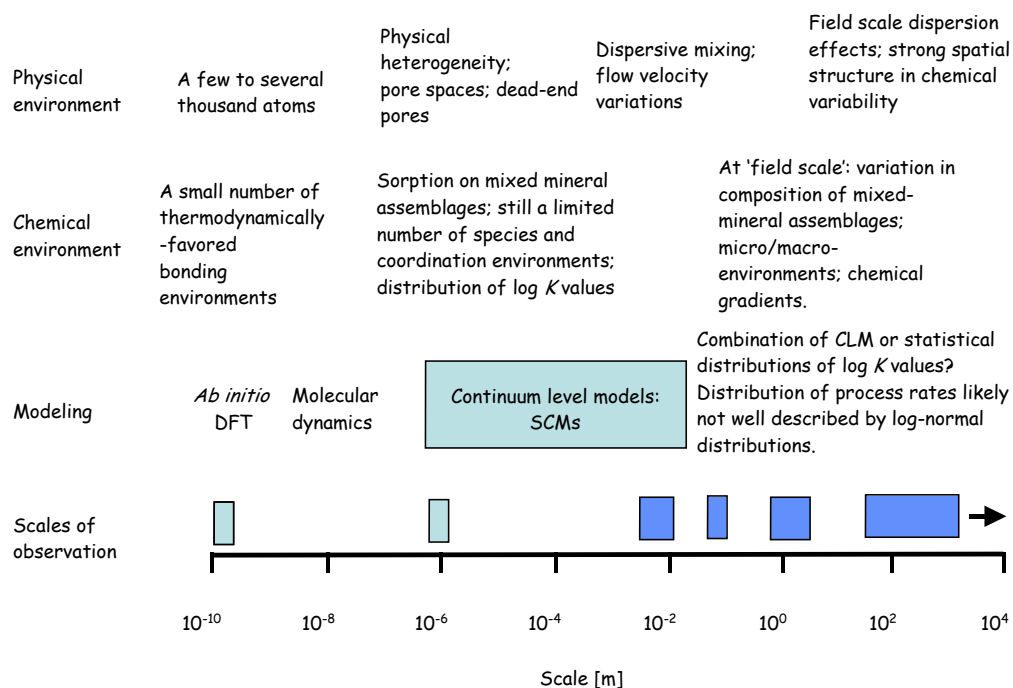## Scale Issues for Metal-ion Sorption/Transport

Fig. 1. Attributes of physical, chemical and modeling environments at different scale lengths. The approximate number of actinide binding sites at each scale length can be approximated by assuming that the volume corresponding to the scale is composed of a fine-grained porous media with a site concentration of 0.1 moles sites m^3. Thus, the nanometer scale consists of a few thousand site; field scales of interest may contain 10^{30} sites or more.

As the physical scale increases to the micrometer scale, a larger number of bond types and a larger distribution of effective binding strengths for a given bond type can be expected (Fig. 1). This variability is due, in part, to the increase in the number and type of minerals present. For example, in the case of sorbed U(VI), in addition to the ternary uranyl-carbonate-iron oxide surface bonds mentioned above, one might also find ternary uranyl-phosphate-aluminum oxide surface bonds, uranyl-phthalate bonds, and uranyl bound within bacterial exopolymeric material. Even for a given bond type, such as ternary uranyl-carbonate-iron oxide surface bonds, one can expect to find a larger distribution of effective binding strengths as the size of the sample analyzed becomes larger, because of the variability of the iron oxide surfaces in terms of surface defects, distribution of exposed crystal faces, variable crystal chemistries, degrees of crystallinity, and other factors. At the micrometer scale, the number of surface functional groups available for binding actinides is on the order of 10^{10}. In addition to chemical heterogeneity, physical heterogeneity become important, with the existence of microenvironments and dead-end pores.

Most laboratory experiments take place on the 'grain' or cm scale. At this scale, even in the case of monominealic systems, the number of actinide binding sites that is available is quite large and models invoked to explain actinide sorption data typically must include multiple-site types. In typical bench-scale experiments, site / actinide ratios are on the order of 10^3 or greater.

At the meter scale, the number of bond types expected may grow even larger (e.g., 10^{20} sites). For example, at this scale both oxidizing and reducing environments can exist in close proximity because of heterogeneities in the permeability and composition of the porous medium, and variable groundwater flow velocities. Microenvironments can differ substantially in chemical conditions and microbial populations, causing very different nanoscale bonding environments for actinides to exist within close physical proximity. Although it has not been well studied as a function of physical scale, it is expected that the distribution of binding strength for certain bond types (e.g., sorbed actinide species) can be described by a normal distribution. For example, in performance assessment modeling for nuclear waste repositories, uranium(VI) sorption is sometimes described by a normal distribution or randomly sampled distribution of partitioning coefficients (e.g., K_d values) determined on selected environmental samples.

At scales important for remediation (kilometer scale lengths; 10^{30} or more sites), models that are 'predictive' of actinide transport need to be based on an understanding of the chemistry, physics and biology of the system. The distribution of K_d values used to describe actinide transport over a range of system conditions, for example, may be explained in terms of underlying system chemistry (e.g., increased solubility of U(VI) in the presence of aqueous carbonate and the resulting smaller K_d values) but the K_d values themselves are not calculated (i.e., upscaled') from a knowledge of the underlying chemical processes. The end result is that most predictions of transport behavior are intended to describe averaged system behavior that is most likely far from the set of conditions used to calibrate the model, particularly with respect to extrapolating to large time scales.

In fact, at field scales, the interplay between physical and chemical processes becomes crucial. Figure 2 [1] shows a relationship between hydraulic conductivity and sorption distribution coefficient, K_d, for a weakly sorbing ion. The K_d was calculated from the retardation factor for the species for a field-scale transport experiment. Note that hydraulic conductivity can correlate with length scales.
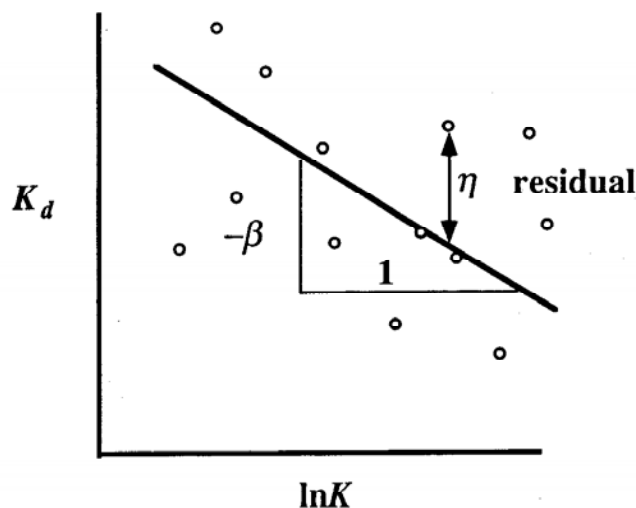
Fig. 2. Distribution coefficient (L kg^{-1}) v. ln k (hydraulic conductivity). From Gelhar [1].

The figure shows that that there is a correlated part between K_d and ln K (β), and an uncorrelated part, η. The data suggests that different macrodispersivities belong to different transported species, and that the macrodispersivity itself will have a dependence on scale.

Modeling actinide sorption at different scales

For simulations at the molecular- to nanometer-level scales, *ab initio* density functional theory (DFT) and molecular dynamics (MD) simulations provide the most fundamental description of a molecular system in terms of terms of its atomic nuclei and the distribution of electrons around them [12].

For the most part, simulations of actinide binding that are applicable for reactive transport modeling are continuum-level models, which, by their very nature, entail a loss of information relative to molecular-level processes. Continuum-level models include isotherms and surface complexation models. Linear (e.g., K_d) and non-linear isotherms are often employed for mathematical tractability provide no direct linking between the chemistry of the system and the process being simulated. Surface complexation models (SCM) (e.g., the Diffuse Double Layer Model [13]) represents particular molecular hypotheses of the surface and provide the ability to link solution- and surface-phase reactions. Information from surface spectroscopy (e.g., EXAFS) can provide a starting point for simulations of sorption data using SCMs but, in practice, postulated reactions invoked to explain sorption data typically extend beyond the molecular-level data.

In the following sections, two illustrations of the interplay of scale and sorption are presented.

Distribution of heterogeneity.
It is clear that the subsurface is heterogeneous. It is also known that the transport of an actinide through the subsurface depends on the nature of the immobile phase and therefore the

heterogeneity. However, less well understood is the effect of the distribution of heterogeneity on actinide transport.

In this modeling exercise [14], the effects of the distribution of two types of sorbent materials in a hypothetical, heterogeneous aquifer on metal sorption and transport behavior are examined. For comparison, linear (K_d value) and Freundlich isotherms are invoked. The linear isotherm might be characteristic of a system in which the actinide binds to a single site type; the Freundlich isotherm captures multiple site type behavior. As the main interest here is in the effects of system heterogeneity on chemical processes, we excluded any possible variation of hydrodynamic properties over the length of the aquifer; and the two mineral phases are only distinguished by their sorption properties. In each distribution scenario, 32 cells of a hypothetical 1-dimensional aquifer are filled differently, according to the solid phase: 2 blocks of weak and strong site types (16 cells each), alternating cells of strong and weak, or randomly distributed cells of strong and weak sorbing materials. In all three scenarios, the overall mass of each fraction is kept constant, and the model was implemented as implicit finite difference scheme.

The first conclusion from the modeling is that the distribution of different sorbent materials shows no effect on transport if actinide sorption is modeled as a linear relationship between solute and sorbate activities (K_d value). The reason for this is that the incorporation of a linear isotherm into the 1-dimensional advection-dispersion (A-D) equation in the form of a retardation factor still results in a linear differential equation, assuming that all other parameters of the equation are kept constant. The results indicate that if actinide binding to the various sorbents in a flow system is such that the sorption is characteristic of binding to only high-energy site types, then the distributing of the heterogeneity is not important.

In contrast, if actinide sorption is incorporated as nonlinear behavior (e.g., as in a Freundlich isotherm), the model predicts different breakthrough curves (BTCs) depending on the distribution of surface-active materials (Fig. 3). As a consequence, knowing the distribution of the heterogeneity becomes critical.
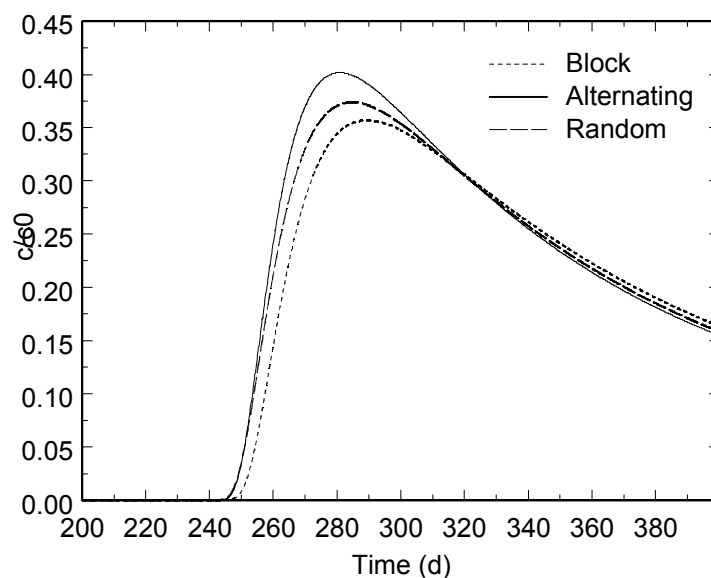
Fig. 3 Breakthrough curves from three scenarios of sorbent
material distribution using Freundlich isotherms [14].

Accounting for heterogeneity in surface complexation modeling of composite geomedia.
Surface complexation models, developed in the early 1970's, have a common set of characteristics [13]: 1) sorption takes place at specific surface coordination sites; 2) sorption reactions can be described by mass law equations; 3) surface charge results from the sorption reaction itself; and 4) the effect of surface charge on sorption can be taken into account by applying a correction factor derived from electrical double layer (EDL) theory to the mass law constants for surface reactions. In some cases (e.g., [15]) the EDL term is implicitly included in a conditional surface complex formation 'constant'.

The difference between the various SCMs is the way in which the free energy of sorption is distributed between $\Delta G_{chemical}$ and $\Delta G_{electrostatic}$, which is a consequence of the molecular hypothesis of the interface that is invoked. A practical effect of the adoption of a particular molecular hypothesis is the number of parameters that either need to be known or 'fit' to simulate the experimental data. Of the surface complexation models, the number of fitting parameters ranges from 3 for the Diffuse Double Layer [13] and Generalized Composite [15] models to 12 for the CD-MUSIC model [16]. Model parameters include surface site types and densities, interfacial region capacitances (1 – 2), the acidity of surface groups, among others depending on the nature of the model. Because SCMs use postulated reactions of molecular-level interactions, information from high-energy spectroscopy on molecular-level speciation is necessary, but not sufficient, for the construction of defensible models.

To account for the heterogeneity of mineral phases in SCMs two approaches have been proposed: 1) the component additivity (CA) approach (e.g. [17]), in which it is assumed that the

overall sorption to the mineral surface can be modeled as the sum of adsorption to each specific sorbent, and 2) the generalized composite approach (GC) [15], which describes the surface sites as "generic" sites regardless of the specific chemical characteristics of the sorbent.

In the CA approach, composite geomedia is directly 'upscaled' as a system whose complexity is simply the summation of component 'building blocks'. Geomedia component submodels are constructed from bench-scale studies of monomineralic systems. The molecular hypothesis selected for the models must be consistent. The GC approach is typically manifested as a non-electrostatic model, although that is not a requirement of the approach. As with the CA, postulated reactions are based when possible on information from molecular level studies. However, with the GC approach, postulated reactions and equilibrium constants are simultaneously optimized for a parsimonious fit to the data.

In this example, the sorption behavior of U(VI) to carbonate-free sorbent prepared from a natural composite material from the Naturita, CO, UMTRA site. U(VI) sorption to the material was investigated via laboratory batch experiments [18], and modeled using surface complexation models (SCMs).

Table I contains the mineral composition if the Naturita geomedia. Figure 4 shows the results of simulations of U(VI) sorption data using the CA and GC approaches. The CA model shown represents the summation of the submodels for ferrihydrite, Gibbsite and quartz. The proportion of the sites for each submodel in the overall model was determined by surface analysis of the geomedia. Site densities (e.g., sites nm^{-2}) were taken from literature values.

Table I   Mineralogical composition of aquifer material
from the Naturita, CO, UMTRA Site

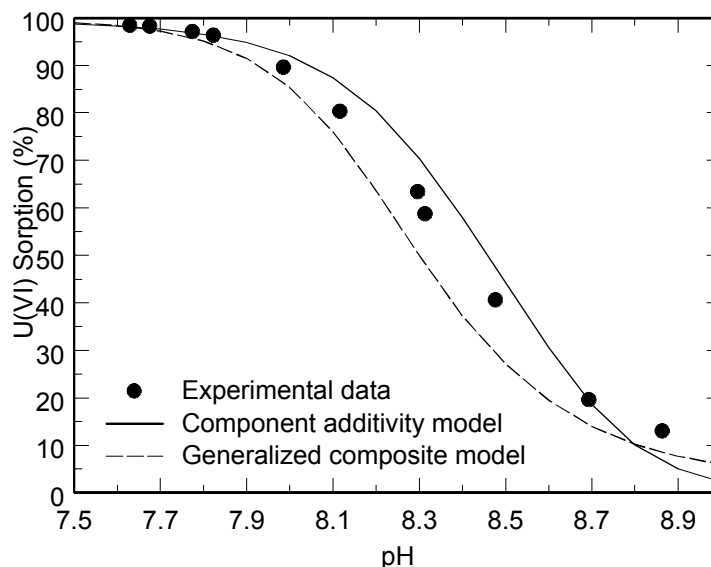| Oxide	Percent Composition
SiO_2	81.6
Al_2O_3	6.8
Fe_2O_3	3.8
CaO	1.5
K_2O	1.2
Na_2O	1.2
MgO	1.0
TiO_2	0.4
MnO	0.1

Fig. 4   Comparison of CA and GC models to simulate U(VI) sorption onto carbonate-free Naturita material. Solid concentration = 100 g/L, $U(VI)_{TOT} = 10^{-6}$ M, $P_{CO2} = 10^{-3.4}$ atm, Ionic strength = 0.02 M (artificial groundwater). (from Sanpawanitchakit [18]).

The GC model were derived though inverse modeling a subset of the sorption data set. Postulated reactions included strong and weak surface site types with the formation of bi-dentate surface complexes. While both modeling approaches resulted in equally good fits to the data, and similar predictive capacity, the GC approach, required considerably less effort for the model development. The CA method is clearly an upscaling exercise in the application of information from the micrometer scale (i.e., the size of mineral grains in the composite material) to the centimeter scale simulations.

Modeling at the field scale
Of course, the objective of upcaling is to predict the behavior of the contaminant of interest at the target scale. As noted above in the discussion of Fig. 1, field systems contain total sorption sites on the order of 10^{30} or more. As systems increase in size, physical and chemical complexity also increases. However, it is not evident that all attributes of complexity manifest themselves at the scale of interest such that they need to be explicitly included in model development. Recently, studies of the application of the surface complexation approach to kilometer-scale systems suggests that large systems may have the sorptive characteristics that can be captured in model construction in relatively straightforward ways. For example, Kent et al. [19] showed that the transport of Zn through a sandy aquifer at Cape Cod, MA, could be simulated using a two-site Generalized Composite model for the Zn sorption. Reaction written were consistent with

spectroscopic information on the sorption of metal-ions to mineral surfaces but the model itself was generic with respect to the sorbent type.

SUMMARY

Expectations for upscaling of sorption processes in intimately tied to the nature of models. Because the 'truth' of environmental systems can never be known, the appropriate goals of reactive transport modeling are the development of the model as a heuristic device and the attainment of 'empirical adequacy'.

Molecular-level information is an important starting point for the construction of continuum-level models. However, upscaling by necessity requires the loss of information relative to the molecular scale. The value of studies at scales other that the scale of direct application (i.e., the 'field scale') is that they provide the user of the model with some confidence that the appropriate *processes* have been captured in the model formulation.

REFERENCES

1   Gelhar, L.W. (1997). Perspectives on Field-Scale Application of Stochastic Subsurface Hydrology. *In* Subsurface Flow and Transport: The Stochastic Approach. G. Dagen and S.P. Neuman, eds. Cambridge University Press/UNESCO.

2   National Research Council (2001). *Science and Technology for Environmental cleanup at Hanford*. National Academy Press (Washington, D.C.). 180 p.

3   National Research Council (2000). *Research Needs in Subsurface Science.* National Academy Press (Washington, D.C.: (2000). 159 p.

4   Mangold, D.C. and Tsang Ch. (1991). A summary of subsurface hydrological and hydrochemical models. *Review of Geophysics* 29(1): 51-79.

5   Thompson, A. and Jackson, K. (1996). Reactive transport in heterogeneous systems. In P. Lichtner, C. Steefel, E. Oelkers (eds), *Reactive transport in porous media, Rev. Mineral.* 34: 269-310. Washington, DC: Mineral. Soc. of Am.

6   Van der Lee, J. and De Windt, L. (2001). Present state and future directions of modeling of geochemistry in hydrogeological systems. *Journal of Contaminant Hydrology* 47: 265-282.

7   Oreskes, N. K. Shrader-Frechette and K. Belitz (1994). Science, **263**, 641-646.

8   Oreskes, N. (2000). Why Believe a Computer? Models, Measures and Meaning in the Natural World. In The Earth Around Us: Maintaining a Livable Planet. Edited by Jill. S. Schneiderman (W.H. Freeman and Co., New York).

9   Bras, R.L., Tucker, G.E. and Teles, V. (2003). *Six myths about mathematical modeling in geomorphology.* In P.R. Wilcock & R.M. Iverson (eds), Geophysical Monograph 135: Predictions in Geomorphology: 63-79. Washington, DC: American Geophysical Union.

10   van fraassen, B. (1980). *The Scientific Image* (Oxford University Press, New York).

11   Sylwester, E.R., Hudson, E. A. and Allen P.G. (2000). The Structure of Uranium (VI) Sorption Complexes on Silica, Alumina, and Montmorillonite. *Geochim. et Cosmochim. Acta*, **64**, 2431-2438.

12   Leach, A. R. (1996). *Molecular Modeling: Principles and Applications*, Addison Wesley Longman Limited, 1996.

13   Dzombak, D.A. and FM.M. Morel (1990). *Surface Complexation Modeling: Hydrous Ferric Oxide.* Wiley-Interscience (New York).

14   Tinnacher, R. and B.D. Honeyman, unpublished.

15   Davis, J.A., Coston, J.A., Kent, D.B. and Fuller, C.C. (1998). Application of the surface complexation concept to complex mineral assemblages. *Environ. Sci. Technol.*, **32**, 2820-2828.

16   Heimstra, T, W.H. van Reimsdijk (1996). A surface structural approach to ion adsorption: the charge distribution model. *J. Coll. Interf. Sci.,* 179, 488.

17   Honeyman, B.D. 1984. *Cation and anion adsorption at the oxide/solution interface in systems containing binary mixtures of adsorbents: An investigation of the concept of adsorptive additivity.* Ph.D. Dissertation, Stanford University.

18   Sanpawanitchakit, Ch. (2001). *The application of surface complexation modeling to the adsorption of uranium(VI) on natural composite materials.* PhD Dissertation, Colorado School of Mines, Colorado.

19   Kent, D.B. *et al.* (2000). Wat. Res. Res., **36**, 3411-3425

20   Analysis of the geomedia included x-ray diffraction (XRD), x-ray photoelectron specrtroscopy (XPS), micro synchrotron x-ray fluorescence (micro-SXRF), micro x-ray absorbance near edge fine structure (micro-XANES) and high resolution transmission electron microscopy (HTEM).