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Author(s): D. R. Janecky, S. Chen, S. Dawson, K. C. Eggert, B. J. Travis

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D. R. Jonecky, S. Chen, S. Dawson, K. C. Eggert, B. J. Travis
Los Alamos National Laboratory, USA

ABSTRACT: Lattice gas automata models are described, which couple solute transport with chemical reactions at mineral surfaces within pore networks. Diffusion in a box calculations are illustrated, which compare directly with Fickian diffusion. Chemical reactions at solid surfaces, including precipitation/dissolution, sorption, and catalytic reaction, can be examined with the model because hydrodynamic transport, solute diffusion and mineral surface processes are all treated explicitly. The simplicity and flexibility of the approach provides the ability to study the interrelationship between fluid flow and chemical reactions in porous materials, at a level of complexity that has not previously been computationally possible.

1 INTRODUCTION

Chemical reaction processes are often spatially distributed in both geologic and engineered systems. Intrinsically coupled flow and chemical reaction processes are also a common factor. In geologic systems, a detailed description and simulation capability for mineral-fluid interaction as a function of time is critical to our understanding of a wide variety of geochemical processes, including weathering, diagenesis, and hydrothermal alteration. There are also a variety of practical applications which demand sophisticated modeling capabilities. In petroleum reservoirs, applications of interest include coupling between oil migration, secondary recovery processes, and the evolution and/or manipulation of porosity. Similarly, reactions coupled to ground water flow and contaminant migration are important in environmental systems.

As chemical reaction models have become increasingly comprehensive to include such complexities, it has been recognized that new modeling approaches are required to better understand many pressing issues. Interrelated factors such as rock texture, mineral distribution, multiphase flow, and pore or fracture network geometry all affect the simultaneously interrelated processes of mineral dissolution, deposition, and mass transport. In addition, reaction kinetics can significantly affect the integrated results of such processes (e.g. Wells and Goringo, 1991). For bulk reactions on large scales of tens to thousands of meters, models of geochemical processes have provided significant insights using averaged or phenomenological descriptions of the permeability, fluid flow fields, mineral distributions, and fluid composition (Bassett and Melchior, 1990; Lichtner, 1988; Ague and Brimhall, 1989; and references therein). There are also models for reactions on the molecular scale (e.g. Lasaga and Gibbs, 1987). Between these two scales, however, there is a paucity of general and flexible models of fluid-rock interaction. This intermediate scale is particularly important to a quantitative understanding of both geochemical and flow processes in

natural porous media because it is precisely the scale at which most detailed analytical, experimental, and descriptive methods provide information.

Rothman (1988) and Chen and others (1991) examined applications of lattice gas automata (LGA) methods to geological problems by formulating models to simulate flow through complex porous media. Wells and others (1991) examined coupling to the LGA models both surface reactions and fluid transport through flow and diffusion for a single solute. These studies demonstrated the potential of this class of models for examining complex pore network processes explicitly. In this paper, we report further developments and refinements of the techniques.

2 LATTICE-BASED HYDRODYNAMIC MODELS

The core of these models is streaming and collision of "particles" on a lattice. The lattice can be developed in a variety of structures to represent two or three dimensional flow systems (see examples in Diemer and others, 1990). A hexagonal symmetric lattice has been shown to provide a numerical solution to the two-dimensional Navier-Stokes equations (Frisch and others, 1986, 1987; Wolfram, 1986), and thus is capable of modeling real systems. Hydrodynamic operation of the model is divided into two processes: streaming of "particles" from one node to the next during each time step, and calculation of collision results at the new nodes. Constraining the "particles" to single node streaming results in an isothermal model.

The calculations of Wells and others (1991) used the minimal collision 2-D FHP-I model of Frisch and others (1986) in which each lattice node can contain up to six solvent "particles". Exclusion rules allow only one "particle" traveling in any one direction to occupy a node. This model was subsequently upgraded to include a full set of collisions and the possibility of a rest "particle" at each node, which results in more physically reasonable viscosity (Chen and

thers 1991). The binary basis of these approaches (a "particle" either exists or is absent at each of the six or seven possible states of a node) results in very fast parallel computations. However, the models intrinsically are noisy due to short term fluctuations of density on individual nodes caused by the limited number of accessible states.

To eliminate most of the noise of the LGA systems, lattice Boltzmann equation (LBE) approaches have recently been developed (Chen and others 1992). In LBE models real numbers are used instead of bits to represent "particle" distributions. Thus, the LBE method is a finite-difference approach to solving a set of kinetic equations in discrete space and discrete time.

3 CHEMICAL REACTION SLB-MODELS

The simplest models for chemical processes in a porous media involve diffusion in the solvent-occupying pores and reactions at solid surfaces. Our initial interest is in systems involving solutes in an aqueous solvent. Thus, the distinction here between "particles" in the LGA or LBE sense and the chemical perspective of units of solution containing both solvent and solutes. Homogeneous solution transport is commonly assumed for geochemical calculations (e.g. Helgeson and others 1984) and will be used here. However, such single fluid phase systems are only part of the range of interest with respect to chemical interactions to which these methods are being examined, including oil or gas saturated systems or even two-phase systems (Rochman and Keller 1989; Somers and Rem 1991; Chen and others 1991).

In a geologic pore network, chemical reactions at surfaces may take several forms. Surface reactions may involve significant mass transfer via dissolution and/or precipitation which modifies the pore network structure and thus the hydrodynamic environment. When the components of interest are at much higher concentrations, sorption and desorption reactions become important and the pore network may be either fixed or variable. Catalytic reactions of solutes at solid surfaces could also be modeled using this approach.

3.1 Diffusion

Solutes are transported down a concentration gradient by diffusion. To simulate diffusion in an LGA model, a concentration of a solute is assigned to each open space node (Wells and others 1991). If the mass of solute or changes in the mass of solute is small relative to the total mass of solution, only minor perturbations of momentum for the lattice "particles" are involved which can be ignored. This approach to solution composition tracking is similar to the energy tracking approach of Serravallo and Hermann (1990). In LGA models, each "particle" is assigned a concentration equal to that of the node at which it is residing. During each time step, "particles" travel to new nodes and the concentration of those nodes is assigned the concentration of the arriving "particle". If more than one "particle" arrives at a node during a time step, the resulting concentration at that node becomes the mean concentration of all "particles". During the next time step, all "particles" arrive the mean concentration to their next destination. This method of simulating diffusion contrasts with models for pure diffusion

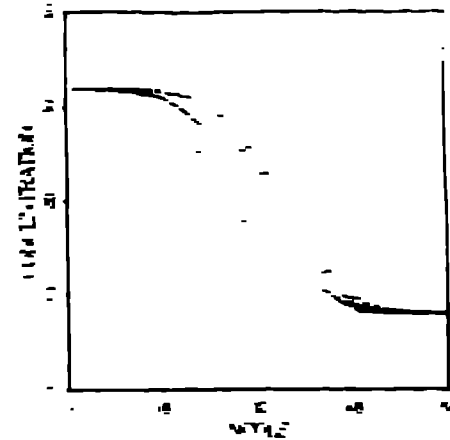


Figure 1. Diffusion profiles calculated by LGA method at 60 steps for a 640 node with initial concentration step of 30 units. Shown are the average profile (solid line), the standard deviation from average for each node (dotted lines), and extrema for each node (dashed lines).

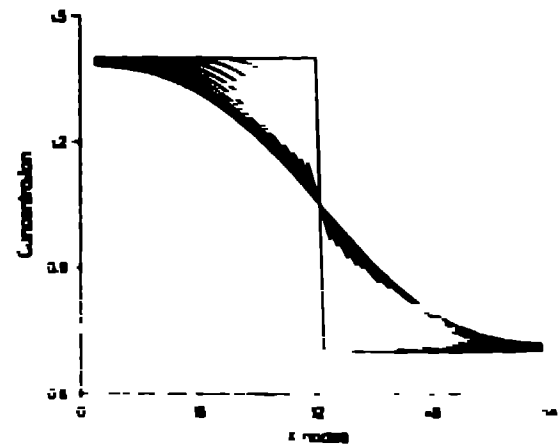


Figure 2. Diffusion profiles calculated using the LBE method for a 640 node and initial concentration step of 4 units. Shown are concentration profiles for initial conditions and nine subsequent conditions (10-step intervals).

of different types of species of "particles" primarily by considering solvent flow separately from solute diffusion and transport. This distinction between the solvent flow in the form of "particles" and solutes as variable terms attached to the "particles" results in considerable flexibility for the models including multi-component systems. This approach was examined by performing a set of calculations of diffusion in a closed box (Figure 1). The initial concentration field consists of a step function in which the concentration equals 32 arbitrary units in the left half of the box and 8 units in the right half. Mean concentration profiles at different time steps for the LGA calculation are in good agreement with the high diffusion profiles calculated using a finite difference technique. Each point on the observed profiles constitute the average value of each domain in the box. This calculation also illustrates the level of noise inherent in LGA calculations (as discussed above) and the average (and completely smooth) for a 640 node box. The rate of diffusion may be used to delineate the space-time relationships of models that are being applied to a specific

problems. For instance, Wells and others (1991) calculated a space to time ratio of 0.002 (nodal spacing in meters per second), using a diffusion coefficient of 10^{-9} m²sec⁻¹.

In comparison to the LGA results, the LBE diffusion calculation produces smooth profiles (Figure 2) with no variations along the diffusion front. Extension of these models to multi-component-multiphase systems with independent diffusion behavior is relatively straight forward. In fact, the present LBE model includes potential for up to 200 solute components and binary solute reactions (Dawson and Chen, unpublished).

3.0 Surface reactions

Surface reactions involving dissolution and precipitation are simulated by allowing wall nodes to serve as sources or sinks for mass of a dissolved component (Wells and others, 1991). Whenever a "particle" collides with a wall, mass may be exchanged, thus increasing or decreasing the local concentration in solution depending upon the saturation state of the fluid. Any kinetic reaction model can be integrated into the lattice models and for this work, a representation of a transition state rate law was applied (Helgeson and others, 1984). In addition, pressure dependent effects on surface reactions as a function of spatial distribution in the pore network are included in the method.

After some number of mass transfer events in an undersaturated fluid, a wall node becomes an open space node simulating dissolution. Similarly, after some number of supersaturated mass transfer events, an open space node becomes a wall node simulating mineral precipitation. The number of events required to create or destroy a wall node depends on the relative concentrations of solute species per unit volume in the solvent and solid phases.

Many mineral dissolution reactions are spatially heterogeneous. For example, crystallographic defects are sites of excess strain energy which constitute regions especially favorable to dissolution (Lasaga and Blum, 1986). Such heterogeneous surface reactions can be simulated with a lattice model by defining zones of higher solubility (Figure 1). Over the course of this simulation the entire wall recedes slightly, but the central region dissolves more readily resulting in an etch pit. The lattice models can effectively model transport-controlled dissolution in which a significant rate-limiting step is the diffusion of the dissolved component away from a mineral surface. This is possible because the model explicitly treats both the fluid and the mineral surface. In this example, the local solution concentrations within an etch pit are much higher than the concentration in the bulk fluid. With increasing diffusion control in the etch pit, the local concentration approaches saturation. Thus, the local probability of mass transfer decreases and transport-controlled dissolution relies on the ability of the solute to diffuse out of the etch pit.

COUPLED FLOW AND CHEMICAL REACTIONS

An example of a simple, chemically reactive porous flow model is shown in Figure 3. The concentration field that

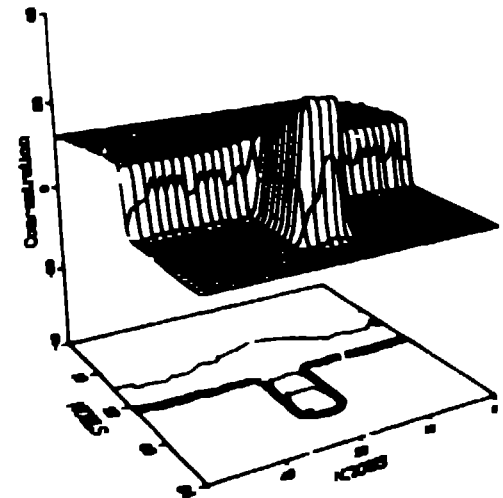


Figure 3. Static dissolution LGA experiment for a hypothetical single component solid into a solution. An 8 node wide line defect in the center of the solid phase dissolves more rapidly to create an etch pit (after Wells and others, 1991).

results from the reaction of a wall mineral with an initially undersaturated fluid is clearly inhomogeneous. The concentration within the principle flow channel is relatively low whereas the concentration in dead-end pores and around obstructions is relatively high. This type of simulation has important implications for increasing our understanding of the relationship between porosity and permeability in dynamic systems in which the porous structure of a rock is altered by mineral dissolution and growth. The effect of reaction and transport heterogeneities on the overall evolution of fluid composition and rock porosity and permeability is not well understood at this time, but is certainly a function of fluid velocity, rock composition, and the geometry of the porous network. The lattice approach has great potential for aid in investigations of these phenomena.

5. SUMMARY

We have presented a general approach to lattice models (LGA and LBE) which couple solute transport with chemical reactions at mineral surfaces and in pore networks. The models treat both surface-controlled and transport-controlled mineral reactions because solute diffusion, fluid flow, and mineral surface detachment processes are all treated explicitly. This will be particularly useful for the analysis of diagenetic and alteration processes observed in thin sections and hand specimen samples in which fluid flow and mineral reaction processes are heterogeneous in space and time. The simplicity and flexibility of this lattice approach provides the ability to study the interrelationship between fluid flow and chemical reactions in porous materials at a level of complexity that has not been computationally possible in the past.

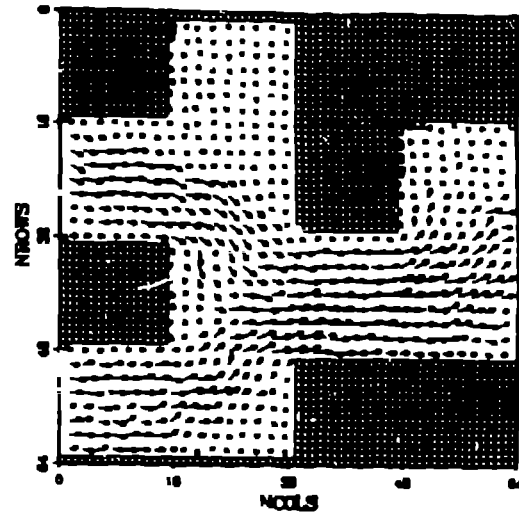
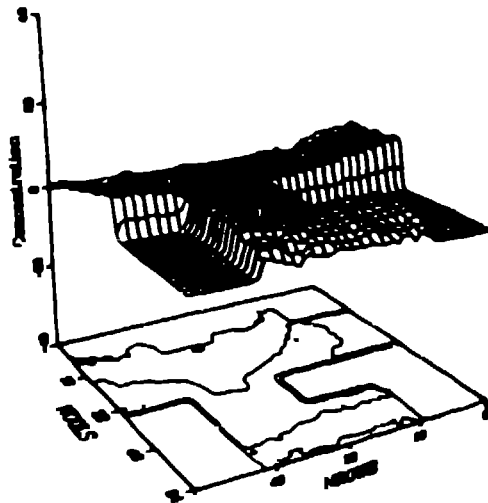


Figure 4. An example of kinetically controlled dissolution reactions in a pore network with flowing solution. Heterogeneous concentration field (a) in a simple structure (b) in which initial and input concentration is zero units with soluble walls (after Wells and others (1991)). In this figure the vectors represent the local fluid velocity.

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