

# COMPUTATIONAL METHODS FOR MULTIPHASE FLOW AND REACTIVE TRANSPORT PROBLEMS ARISING IN SUBSURFACE CONTAMINANT REMEDIATION

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## **Abstract:**

A mathematical formulation and some numerical approximation techniques are described for a system of coupled partial differential and algebraic equations describing multiphase flow, transport and interactions of chemical species in the subsurface. A parallel simulator PARSSIM has been developed based on these approximation techniques and is being used to study contaminant remediation strategies. Numerical results for a highly complex geochemistry problem involving strontium disposal in a pit at Oak Ridge National Laboratory are presented.

## **1 Introduction**

Mathematical and numerical modeling of the fate and transport of chemical species in the subsurface has become a critical area of research over the past several years. Spills, improper disposal, and leaking storage tanks are but a few of the ways that chemicals infiltrate the subsurface. Chemicals entering the subsurface can spread downward and laterally, contaminating a large volume of soil, and may reach the groundwater or degrade pipe and utility lines. A major concern is how and to what extent these contaminants effect the drinking water supply.

Much of the modeling effort has been directed at devising remediation strategies for contaminated subsurface environments. There are several remediation strategies being studied, depending on the type and location of the contaminants and whether they are in the groundwater or trapped in partially saturated soils.

One strategy being studied for cleaning up contaminated groundwater is microbial biodegradation, which involves the decomposition of contaminants by microorganisms. Microbial biodegradation is a natural process that can be accelerated to protect a potable water supply. U.S. Environmental Protection Agency studies [28] have shown that this strategy can result in almost complete removal of contaminants, whereas many alternative restoration strategies have not proven

as effective. Biodegradation technologies are being employed at several U.S. Department of Energy Laboratories in an effort to remove or contain volatile organic compounds [2, 6, 11, 17, 20, 21, 23, 26, 27, 28, 31].

To remove contaminants contained in unsaturated soils, methods such as flushing, incineration, and excavation have been employed. These methods have proven costly and inefficient. Recently, remediation by *in-situ* soil venting has been proposed to remove contaminants in the soil through volatilization into an induced air flow stream through the porous medium. Air flow can be induced by the appropriate placement of air injection wells and pumps. Fall and Picken [18] reported in a case study that the cost of soil venting was only 25% of the estimated cost of excavation and removal, and allowed continuous operation of the business located at the site. The effectiveness of soil venting has been demonstrated in laboratory studies [29, 9] and in the field [13, 22].

*In-situ* vitrification has been employed at some sites in an attempt to indefinitely contain contaminants in one location and keep them from spreading. Vitrification creates a low permeability waste form (essentially glass), but with significant numbers of small fractures as a result of cooling. As water reacts with the glass, secondary minerals will form relatively rapidly that may act to reduce contaminant mobility by inhibiting glass dissolution and sorbing contaminants.

At the Center for Subsurface Modeling at the University of Texas, we are developing parallel simulators for modeling multiphase flow and multicomponent reactive transport, and applying these simulators to the types of problems just outlined. In attempting to model these remediation and containment strategies, one encounters numerous difficulties. The physical, chemical and geological definition of the problem is always incomplete and imprecise. In addition, the chemical processes involve interphase mass transfer as well as a host of chemical reactions, including dissolution, aqueous phase complexation, ion exchange, adsorption, precipitation, oxidation/reduction, and biological degradation kinetics. The extent of mass transfer and chemical reaction is ultimately limited by thermodynamic equilibrium, but compositions far from equilibrium often arise locally because of kinetic and surface area constraints. First generation models of flow through porous media with general aqueous reactions (e.g., [30]) showed the importance of developing a theoretical understanding of the dynamics of concentration fronts [10, 16]. The ability to account simultaneously for fluid flow and chemical reactions is essential for evaluating many groundwater contamination problems. Additional complexities arise in scaling since parameters derived in laboratory experiments are not always applicable to the field scale aquifer.

Parallel computing offers an opportunity for building detailed models of the chemical and physical processes and in providing the capability of solving larger, more realistic and practical problems faster and more economically. This includes

the ability to use an adequately refined discretization mesh, to incorporate complex chemical and physical effects associated with the transport of contaminants in porous media, and to employ stochastic or conditional simulation. The latter is essential for simulating a realistic geologic aquifer, since much of the data needed to characterize it cannot be quantified accurately.

This paper is outlined as follows. In the next section, we describe a model for two-phase flow with multicomponent transport and aqueous geochemical reactions. This formulation is prototypical of the types of models which arise in these problems. In Section 3, we discuss the numerical algorithms which we use to approximate the solutions to this model, and describe a parallel simulator PARSSIM, developed by the authors and others at the Center for Subsurface Modeling. In Section 4, numerical results from some recent geochemistry studies are presented.

## 2 The Mathematical Model

In this section, we present a model based on two flowing phases, an air or gas phase and an aqueous (water) phase. Coupled to these equations are a reactive transport system involving the chemical species.

We first present the flow equations. They are very similar to the well known black oil model from petroleum engineering as described by Peaceman [25] and to the formulation presented by Parker [24]. The coupled equations are:

*Water(Aqueous) Phase:*

$$\frac{\partial(\phi\rho_w s_w)}{\partial t} + \nabla \cdot (\rho_w u_w) = Q_w + \gamma_w. \quad (1)$$

*Air Phase:*

$$\frac{\partial(\phi\rho_a s_a)}{\partial t} + \nabla \cdot (\rho_a u_a) = Q_a + \gamma_a. \quad (2)$$

*Equations of State:*

$$\rho_w = \rho_w^0 e^{c_w p_w}, \quad \rho_a = \rho_a^0 e^{c_a p_a}. \quad (3)$$

*Darcy's Law:*

$$u_w = -\frac{K k_{rw}(s_w)}{\mu_w} (\nabla p_w - \rho_w g \nabla z), \quad (4)$$

$$u_a = -\frac{K k_{ra}(s_a)}{\mu_a} (\nabla p_a - \rho_a g \nabla z). \quad (5)$$

*Capillary Pressure:*

$$p_c(s_w) = p_a - p_w. \quad (6)$$

*Volume Balance:*

$$s_w + s_a = 1. \quad (7)$$

Here  $\phi$  is porosity,  $p$  phase pressure,  $\rho$  phase density,  $K$  absolute permeability,  $k$  phase relative permeability,  $\mu$  phase viscosity,  $s$  phase saturation,  $c$  phase compressibility,  $g$  gravitational constant,  $z$  depth,  $Q$  an external phase source or sink, and  $\gamma$  are source or sink terms due to mass transfer between phases (subscripts have been omitted).

Multicomponent transport, geochemistry and biochemistry of chemical species are governed by a system of advection-diffusion-reaction equations coupled with ordinary differential or algebraic equations. Consider a system comprised of  $N$  species, and for the moment assume they are distributed only over the aqueous phase and one or possibly more solid phases. For convenience, the name (or chemical formula) of a species is designated  $\hat{X}$ , whereas the concentration of that species (in some convenient set of units) will be given the symbol  $X$ . As an example, we may have that  $\hat{X} = H_2O$  and  $X =$  moles of water per unit volume.

Assume that any of the above constituents can be expressed in terms of a minimal, basic set of species, referred to as *components*, so that any species is either itself a component, or the result of a combination (chemical reaction) of components. It is helpful to think of the components as being simply *elements* (with fixed attributes such as charge and number of elementary particles). This is always a valid set of components, but other choices are possible and sometimes convenient.

We will assume that there exists a set of  $N_s$  components  $\hat{s}_1, \dots, \hat{s}_{N_s}$  associated with the solid matrix of the porous medium (i.e. a set of components that is sufficient to describe the composition of the actual rock). Similarly, the aqueous phase is described by a set of  $N_a$  aqueous components,  $\hat{c}_1, \dots, \hat{c}_{N_a}$ .

We consider two kinds of *product species* that can form as a result of reactions between components:

- $N_x$  aqueous complexed species,  $\hat{x}_1, \dots, \hat{x}_{N_x}$ ,
- $N_y$  solid-phase complexed species,  $\hat{y}_1, \dots, \hat{y}_{N_y}$ .

The aqueous complexed species are participants in the aqueous phase that form from components in the aqueous phase only. The solid phase complexed species are of two kinds: either they are a part of the porous medium and result from

reactions between water-borne components and solid components, or they exist in single-species solid phases and result from reactions only within the aqueous phase. Examples of the former kind include ion-exchange and adsorption; the latter kind is the important case of precipitation/dissolution. The reactions are written:

$$\sum_{j=1}^{N_a} q_{ij}^x \hat{c}_j \rightleftharpoons \hat{x}_i, \quad i = 1, \dots, N_x, \quad (8)$$

$$\sum_{j=1}^{N_a} q_{ij}^y \hat{c}_j + \sum_{j=1}^{N_s} r_{ij} \hat{s}_j \rightleftharpoons \hat{y}_i, \quad i = 1, \dots, N_y. \quad (9)$$

In the above expressions the  $q_{ij}^x$ ,  $q_{ij}^y$  and  $r_{ij}$  are the *stoichiometric coefficients* of the reactive system. Since not all solid product species require the interaction with the porous medium to form, we allow the second term in reaction (9) to be zero.

Relations involving reactive systems are conveniently expressed using linear algebra. Consequently, we represent the composition in terms of species vectors. With the above definitions, and letting  $\hat{x}_i \equiv (\hat{\mathbf{x}})_i$  etc. we let  $\hat{\mathbf{c}} \in \mathbb{R}^{N_a}$ ,  $\hat{\mathbf{s}} \in \mathbb{R}^{N_s}$ ,  $\hat{\mathbf{x}} \in \mathbb{R}^{N_x}$  and  $\hat{\mathbf{y}} \in \mathbb{R}^{N_y}$  denote the vectors of aqueous component species, solid component species, aqueous complexed species and solid complexed species, respectively. The total number of species thus defined is  $N = N_a + N_s + N_x + N_y$ . The stoichiometric data in (8)-(9) are represented in matrix form by  $Q_x \in \mathbb{R}^{N_x \times N_a}$ ,  $Q_y \in \mathbb{R}^{N_y \times N_a}$  and  $R \in \mathbb{R}^{N_y \times N_s}$ . Thus the reactions become

$$Q_x \hat{\mathbf{c}} \rightleftharpoons \hat{\mathbf{x}},$$

$$Q_y \hat{\mathbf{c}} + R \hat{\mathbf{s}} \rightleftharpoons \hat{\mathbf{y}}.$$

The reactive transport system of equations can be described by:

$$\frac{\partial \phi \mathbf{c}}{\partial t} + \mathcal{L}(\mathbf{c}) = \phi \mathbf{r}_c, \quad (10)$$

$$\frac{\partial \phi \mathbf{x}}{\partial t} + \mathcal{L}(\mathbf{x}) = \phi \mathbf{r}_x(\mathbf{c}, \mathbf{x}), \quad (11)$$

$$\frac{\partial \mathbf{s}}{\partial t} = \mathbf{r}_s, \quad (12)$$

$$\frac{\partial \mathbf{y}}{\partial t} = \mathbf{r}_y(\mathbf{c}, \mathbf{s}, \mathbf{y}), \quad (13)$$

with appropriate initial and boundary conditions. Here

$$\mathcal{L}(f) = \nabla \cdot (u_w f - D_w \nabla f), \quad (14)$$

$D_w = D_w(u_w)$  is the hydrodynamic diffusion/dispersion tensor, and the reaction rates are related by

$$\begin{aligned} \mathbf{r}_c &= -(Q_x)^T \mathbf{r}_x - (Q_y)^T \mathbf{r}_y, \\ \mathbf{r}_s &= -R^T \mathbf{r}_y. \end{aligned}$$

Biodegradation reactions can be included in the above model if one further distinguishes the aqueous components as electron donors or electron acceptors. Moreover, microbial mass can also be included as a component. The interaction between donors, acceptors, and microbes are usually described by kinetic expressions, see, for example [2].

Transport of species in the air phase and mass transfer of species between air, water, and solid phases can be incorporated by introducing species concentrations in the air phase similar to those described above in the water phase. Transport equations for components in the air phase similar to (10) can be derived, and mass transfer between air/water and air/solid can be described by chemical reaction equations similar to those outlined above.

### **3 Description of PARSSIM**

Our flow and reactive transport simulator PARSSIM involves the coupling of parallel flow and transport/reaction modules. The latter module was developed to simulate the transport and reactions of dissolved chemical species in the groundwater. This code is based on time splitting for advection, diffusion, and reactions. Either the method of characteristics or a higher order Godunov method is employed for treating advection. The mixed finite element method is used to treat diffusion. Reactions are handled separately as a differential algebraic system. The Godunov scheme is especially useful when the reactive time steps are on the order of a CFL time step. The characteristics-mixed method allows for much larger time steps, since no CFL restriction is needed for stability. The Godunov mixed finite element scheme and the characteristic-mixed method for advection/diffusion were introduced and analyzed by Dawson [14, 15] and Arbogast and Wheeler [1, 5, 6], respectively.

The transport/reaction module handles an arbitrary number of component chemical species, as well as microbial mass and radionuclide decay. The code also incorporates equilibrium and nonequilibrium biological and geochemical kinetics and treats an arbitrary number of phases including the solid phase (adsorption). Each component is dissolved in one or more of these phases. The distribution of mass in the phases is assumed to follow the linear Raoult's or Henry's Law. This code achieves almost linear parallel scaling [6, 4]; thus, it is highly effective when run on a parallel machine. Applications to contaminant transport in single phase groundwater flow can be found in [1] and [6], and to two-phase flow in [2].

To ensure that our code is applicable to as wide a set of geochemical applications as possible, it has been integrated with the general aqueous chemistry package KEMOD (Kinetic and Equilibrium Model [32]). KEMOD handles an ar-

bitrary number of chemical species and considers aqueous phase complexation, ion exchange, adsorption, precipitation/dissolution and oxidation/reduction reactions. The extent of each reaction can be calculated from user-defined kinetic expressions or from considerations of thermodynamic equilibrium. KEMOD thus has the flexibility to handle the aqueous chemistry encountered in most practical applications.

Several modifications were carried out to transform KEMOD from a stand-alone code into a subroutine, called to update the chemical composition at an arbitrary grid location. Currently we assume the reactions occur in the solid phase(s) and a single fluid (aqueous) phase only. Time-step splitting between the advection and chemical reaction routines provides greater accuracy when some of the reactions are kinetically controlled. The equations are solved by the Newton-Raphson iterative method.

The code has two options for flow modules, a single phase module and a two-phase module. The single phase flow module is based on an expanded mixed finite element method with the Raviart Thomas lowest order approximating spaces. Using the trapezoidal quadrature rule the scheme reduces to a cell centered finite difference method [3, 7, 8]. To solve the linear system that arises in the discretization a substructuring or domain decomposition algorithm introduced by Glowinski and Wheeler [19] is employed. The method requires solving only local problems and is in fact a hybrid mixed formulation over subdomains. In addition to its advantage on parallel machines, this method allows one to handle more accurately problems with discontinuous permeability tensors. In such cases the gradient of the pressure is also discontinuous. Approximating it with a function in  $H(\Omega; \text{div})$ , as is done in the cell-centered finite difference method mentioned above, does not give good results. Accuracy is retained, however, if the hybrid form of the expanded mixed method is used. In that case the pressure is also computed on the faces of the elements and its gradient is approximated in an element by element discontinuous space. The domain decomposition method introduces pressure unknowns (Lagrange multipliers) along the subdomain interface and is equivalent to a partial hybridization of the original method. Therefore it is very accurate if the discontinuity of the coefficient lies along a subdomain boundary. To efficiently solve the interface problem on a distributed parallel system, the balancing preconditioner defined by Cowsar, Mandel, and Wheeler [12] has been employed; this preconditioner scales almost linearly for parallel machines.

The two-phase flow module is implicit with fully coupled wells. Capillary pressure and relative permeability are functions of water saturation and formation type. Functional forms can be defined by tables or by definition as piecewise  $C^2$  splines. Equations (1)–(2) and (4)–(5) are discretized using an expanded mixed finite element method with the Raviart Thomas lowest order approximating spaces. The trapezoidal quadrature rule is used to obtain a finite difference scheme for

the unknowns. As mentioned above, this expanded mixed finite element method with quadrature was developed and analyzed in [7, 8, 3] (for single phase flow). Constitutive laws (3), (6) and (7) are used to close the system. The resulting nonlinear equations are treated by Newtonian iteration. Here  $p_a$  and  $s_a$  are chosen as primary variables. A preconditioned domain decomposition GMRES procedure has been developed for treating the nonsymmetric system.

We now describe briefly how the combined modules solve the model (1)-(7) and (10)-(13). The flow module first approximates (1)-(7). Given the saturations and phase velocities the transport module is called. In the transport module, given approximate solutions at time  $t^n$ , we advance to time  $t^{n+1}$  by first solving the following set of un-coupled partial differential equations (with appropriate boundary and initial conditions):

$$\frac{\partial(\phi c_i)}{\partial t} + \mathcal{L}(c_i) = 0, \quad i = 1, \dots, N_a, \quad (15)$$

$$\frac{\partial(\phi x_i)}{\partial t} + \mathcal{L}(x_i) = 0, \quad i = 1, \dots, N_x, \quad (16)$$

$$(17)$$

where  $\mathcal{L}(c_i)$  and  $\mathcal{L}(x_i)$  are the advection and diffusion operators applied to  $c_i$  and  $x_i$ , respectively. This produces a vector of transported but unreacted concentrations,  $[\tilde{\mathbf{c}}, \tilde{\mathbf{x}}]^{n+1}$ , which we distinguish from the final solution at  $t = t^{n+1}$  by the appended tilde.

Incorporating the reactions requires the solution of a mixed algebraic-differential problem. The two major classes of chemical reactions are *equilibrium* and *kinetic*, or *rate* controlled. An equilibrium-controlled reaction occurs instantaneously and adjusts concentrations in such a way that a stable thermodynamic equilibrium is attained. A kinetic reaction, on the other hand, proceeds at a finite rate specified by an appropriate rate expression.

It is convenient to be able to group the species  $\hat{\mathbf{x}}$  and  $\hat{\mathbf{y}}$  according to whether the reactions (8)-(9) through which they form are of equilibrium or kinetic type. To this end, we order the concentrations in such a way that we can write

$$\mathbf{x} = \begin{pmatrix} \mathbf{x}_k \\ \mathbf{x}_e \end{pmatrix} \quad (18)$$

$$\mathbf{y} = \begin{pmatrix} \mathbf{y}_k \\ \mathbf{y}_e \end{pmatrix}, \quad (19)$$

where  $\mathbf{x}_k \in \mathbb{R}^{N_{x,k}}$ ,  $\mathbf{x}_e \in \mathbb{R}^{N_{x,e}}$ ,  $\mathbf{y}_k \in \mathbb{R}^{N_{y,k}}$ ,  $\mathbf{y}_e \in \mathbb{R}^{N_{y,e}}$  and

$$N_x = N_{x,k} + N_{x,e}, \quad (20)$$

$$N_y = N_{y,k} + N_{y,e}. \quad (21)$$



A reaction step involves solving the following system over the time interval  $[t^n, t^{n+1}]$ : First, compute the total aqueous component vector

$$\mathbf{T}^{n+1} = \tilde{\mathbf{c}}^{n+1} + Q_x^T \tilde{\mathbf{x}}^{n+1} + Q_y^T \mathbf{y}^n \quad (22)$$

at  $t^{n+1}$ . Note that  $\mathbf{y}^n$  is unchanged as a result of flow. Then solve

$$\frac{d\mathbf{x}_k}{dt} = \mathbf{r}_x(\mathbf{c}, \mathbf{x}_k), \quad (23)$$

$$\mathbf{x}_k(t^n) = \tilde{\mathbf{x}}_k^{n+1}, \quad (24)$$

$$\frac{d\mathbf{y}_k}{dt} = \mathbf{r}_y(\mathbf{c}, \mathbf{s}, \mathbf{y}_k), \quad (25)$$

$$\mathbf{y}_k(t^n) = \mathbf{y}_k^n, \quad (26)$$

$$\mathbf{f}^x(\mathbf{c}, \mathbf{x}_e) = \mathbf{0}, \quad (27)$$

$$\mathbf{f}^y(\mathbf{c}, \mathbf{s}, \mathbf{y}_e) = \mathbf{0}, \quad (28)$$

$$\mathbf{T}^{n+1} = \mathbf{c} + Q_x^T \begin{pmatrix} \mathbf{x}_k \\ \mathbf{x}_e \end{pmatrix} + Q_y^T \begin{pmatrix} \mathbf{y}_k \\ \mathbf{y}_e \end{pmatrix} \quad (29)$$

$$\mathbf{W} = \mathbf{s} + R^T \mathbf{y}. \quad (30)$$

Here  $\mathbf{W}$  is the vector of total concentrations of solid components. This is a known, time-invariant quantity since the solid matrix, although it undergoes composition changes, does not lose any mass to the flowing phase. However,  $\mathbf{W}$  is spatially varying because of the changing lithotype within a reservoir. The functions  $\mathbf{r}_x : \mathbb{R}^{N_c+N_{x,k}} \rightarrow \mathbb{R}^{N_{x,k}}$  and  $\mathbf{r}_y : \mathbb{R}^{N_s+N_{y,k}} \rightarrow \mathbb{R}^{N_{y,k}}$  are known rate-functions for the aqueous and solid phase complexation reactions, respectively. The equilibrium conditions are expressed in terms of generic, non-linear functions  $\mathbf{f}^x : \mathbb{R}^{N_c+N_{x,e}} \rightarrow \mathbb{R}^{N_{x,e}}$  and  $\mathbf{f}^y : \mathbb{R}^{N_c+N_s+N_{y,e}} \rightarrow \mathbb{R}^{N_{y,e}}$ . These function, known as mass-action equations, can be shown to have the form

$$f_i^x = a_i^x - K_i^x \prod_{j=1}^{N_a} (a_j^a)^{q_{i,j}^x}, \quad i = 1, \dots, N_x, \quad (31)$$

$$f_i^y = a_i^y - K_i^y \prod_{j=1}^{N_a} (a_j^a)^{q_{i,j}^y} \prod_{j=1}^{N_s} (a_j^s)^{r_{i,j}^y}, \quad i = 1, \dots, N_y, \quad (32)$$

where  $a_i^x$  and  $a_i^y$  are the *activities*; either known functions of composition (non-ideal case) or equal to the concentrations (ideal case)

Note that the ODE's require initial conditions which are obtained from the transported species (for the  $\tilde{\mathbf{x}}_k$ ) or from the previous time-step (for the  $\hat{\mathbf{y}}_k$ ).

In the current formulation, the reaction-step equations (23)-(30) above are solved using a fully implicit non-linear equations (NLEQ) approach, which results by simply discretizing the ODE's using the Backward Euler method. Letting the

superscript  $n$  on concentration variables denote approximate solutions at time-level  $t^n$  and setting  $\Delta t \equiv t^{n+1} - t^n$ , the discretized system of non-linear equations is

$$\frac{\mathbf{x}_k^{n+1} - \mathbf{x}_k^n}{\Delta t} = \mathbf{r}_x(\mathbf{c}^{n+1}, \mathbf{x}_k^{n+1}) \quad (33)$$

$$\mathbf{x}_k^n = \tilde{\mathbf{x}}_k^{n+1} \quad (34)$$

$$\frac{\mathbf{y}_k^{n+1} - \mathbf{y}_k^n}{\Delta t} = \mathbf{r}_y(\mathbf{c}^{n+1}, \mathbf{s}^{n+1}, \mathbf{y}_k^{n+1}) \quad (35)$$

$$\mathbf{f}^x(\mathbf{c}^{n+1}, \mathbf{x}_e^{n+1}) = \mathbf{0} \quad (36)$$

$$\mathbf{f}^y(\mathbf{c}^{n+1}, \mathbf{s}^{n+1}, \mathbf{y}_e^{n+1}) = \mathbf{0} \quad (37)$$

$$\mathbf{T}^{n+1} = \mathbf{c}^{n+1} + Q_x^T \begin{pmatrix} \mathbf{x}_k \\ \mathbf{x}_e \end{pmatrix}^{n+1} + Q_y^T \begin{pmatrix} \mathbf{y}_k \\ \mathbf{y}_e \end{pmatrix}^{n+1} \quad (38)$$

$$\mathbf{W} = \mathbf{s}^{n+1} + R^T \mathbf{y}^{n+1}. \quad (39)$$

The discrete equations above can immediately be cast in the standard non-linear equation form

**NLEQ problem:** Find  $\mathbf{U}_* \in \mathbb{R}^{N_{eq}}$  such that

$$\mathcal{F}(\mathbf{U}_*) = \mathbf{0}. \quad (40)$$

Here we have introduced the function  $\mathcal{F} : \mathbb{R}^{N_{eq}} \rightarrow \mathbb{R}^{N_{eq}}$  and the augmented vector of concentrations  $\mathbf{U} = [\mathbf{c}, \mathbf{s}, \mathbf{x}, \mathbf{y}] \in \mathbb{R}^{N_{eq}}$ .

After having completed the transport and reactive step, mass transfer source and sink terms  $\gamma_w$  and  $\gamma_a$  are computed if necessary. The time step is then incremented and the flow subroutine is called to obtain new saturations and phase velocities.

## 4 Geochemistry Modeling—The Oak Ridge Trench Problem

### 4.1 A brief description

Research is currently underway at the Oak Ridge National Laboratory (ORNL) concerning the clean-up and monitoring of certain ORNL waste-sites.

A component in this effort is understanding the effect of sorption on the spreading of radio-nuclide contaminants, such as strontium and cobalt. Simulation can be a useful tool in developing such an understanding, and also in studying the effects of varying geological and chemical parameters.

The site selected for this study is a waste-pit which has been in operation from 1951 to the present. The waste has a reasonably well defined composition, and it is generally agreed that strontium is the major contaminant. It is also known that the pit-sludge was made highly basic ( $pH \sim 12$ ) through the addition of sodium hydroxide, in an attempt to immobilize the waste.

## 4.2 A one-dimensional core test

Here, we will be concerned with a very simple geometrical arrangement, a one-dimensional core of unit length and uniform properties, but a fairly complete model for the chemistry. The first 10 percent of the length of the core will serve as the pit: the pH is high here (12), as is the level of the main contaminants, (notably strontium and cobalt). The rest of the core is at a uniform background concentration, as established by field-work at ORNL. Initial pH and strontium distributions are given in Figures 1 and 2. The core is flooded with an incoming stream of background composition for a time period corresponding to 0.5 pore-volumes injected (PVI).

The chemistry model accounts for aquatic complexation, surface complexation and precipitation/dissolution. A total of 74 species are included in the calculation, and the adsorption model used accounts for electrostatic interactions between the surface and aqueous species. In this simulation, the assumption was made that all reactions are equilibrium controlled (i.e. a *state of local equilibrium* is assumed to prevail at all times.)

The simulation used  $nx = 100$  grid-blocks, and a time-step of  $\Delta t = 0.0025$  PVI. In Figures 3 and 4 the pH and the total strontium distributions are plotted at  $t=0.5$  PVI. The distribution of strontium is broken down into two components: solid phase species, as would result from adsorption or precipitation, and dissolved species, such as free strontium or any of its many aqueous complexed species. The solid line simply indicates the total analytical concentration in both solid and aqueous phases.

It is interesting to note that for this selection of parameters, the contaminant was quite mobile and not very strongly retarded by adsorption. It should be pointed out, however, that the plots shown here do not represent an accurate selection of all the physical parameters. Therefore, the results here are only examples of possible scenarios—further data-acquisition activities will be necessary before a critical simulation can be carried out.

## 5 Conclusions and Current Research

Computational algorithms have been formulated and implemented on distributed memory computer platforms for modeling multiphase flow and reactive transport problems in porous media. The code PARSSIM has been successfully applied to both laboratory and field sites. In addition, optimal *a priori* error estimates have been obtained for many practical applications.

The researchers are presently formulating and implementing several major additions to PARSSIM. These include the addition of more physics such as adding a third phase and the ability to handle horizontal wells. Efforts are also underway for the development of more robust GMRES/Newton preconditioners for solving the fully implicit nonlinear system arising from the discretization of the multiphase flow equations. Further research includes the development of error estimators and adaptive mesh for more accurate treatment of sharp fronts arising in the chemical reactions and flow around wells. This work also involves substantial efforts in analysis of the algorithms.

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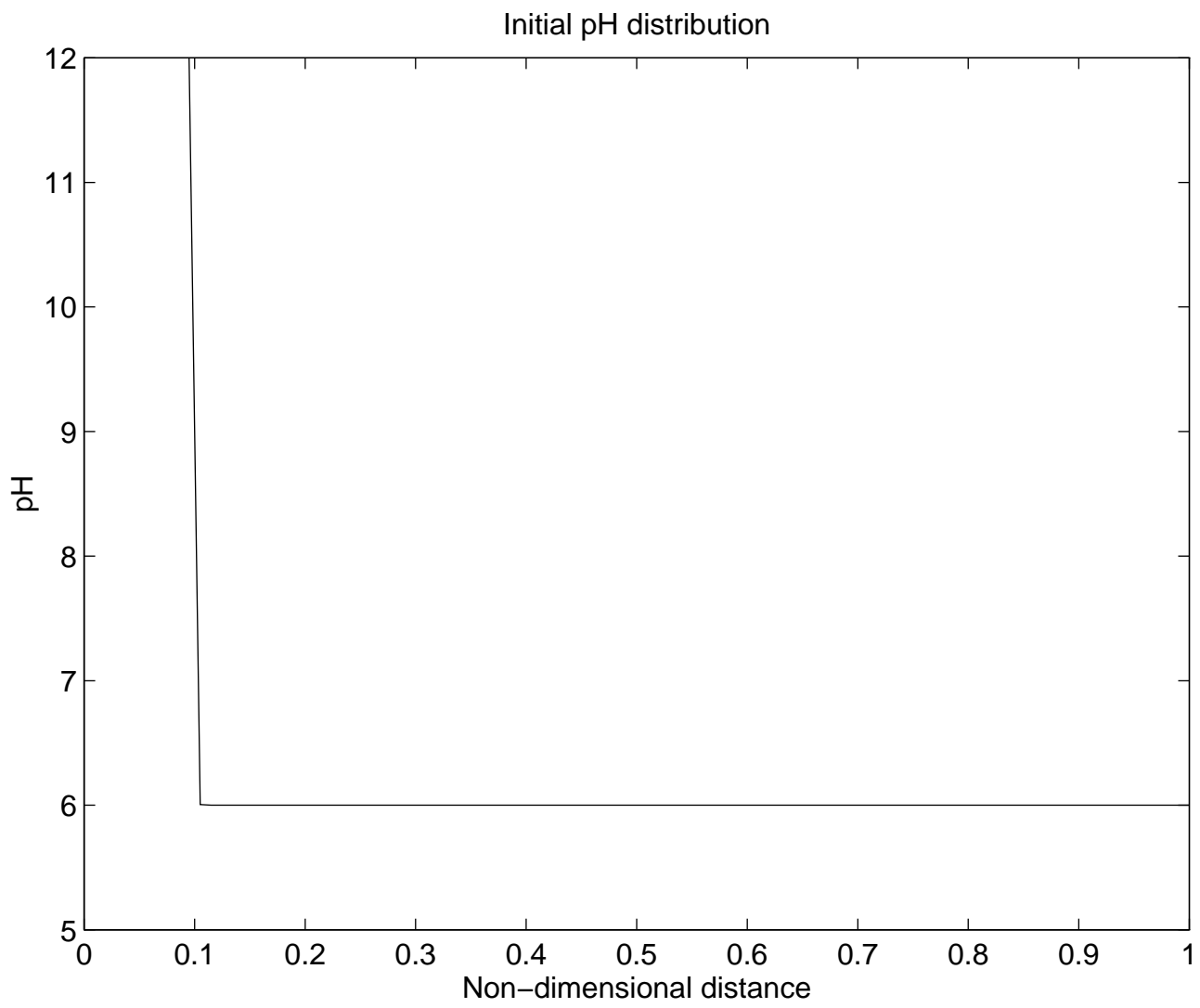


Figure 1: Initial Ph Distribution



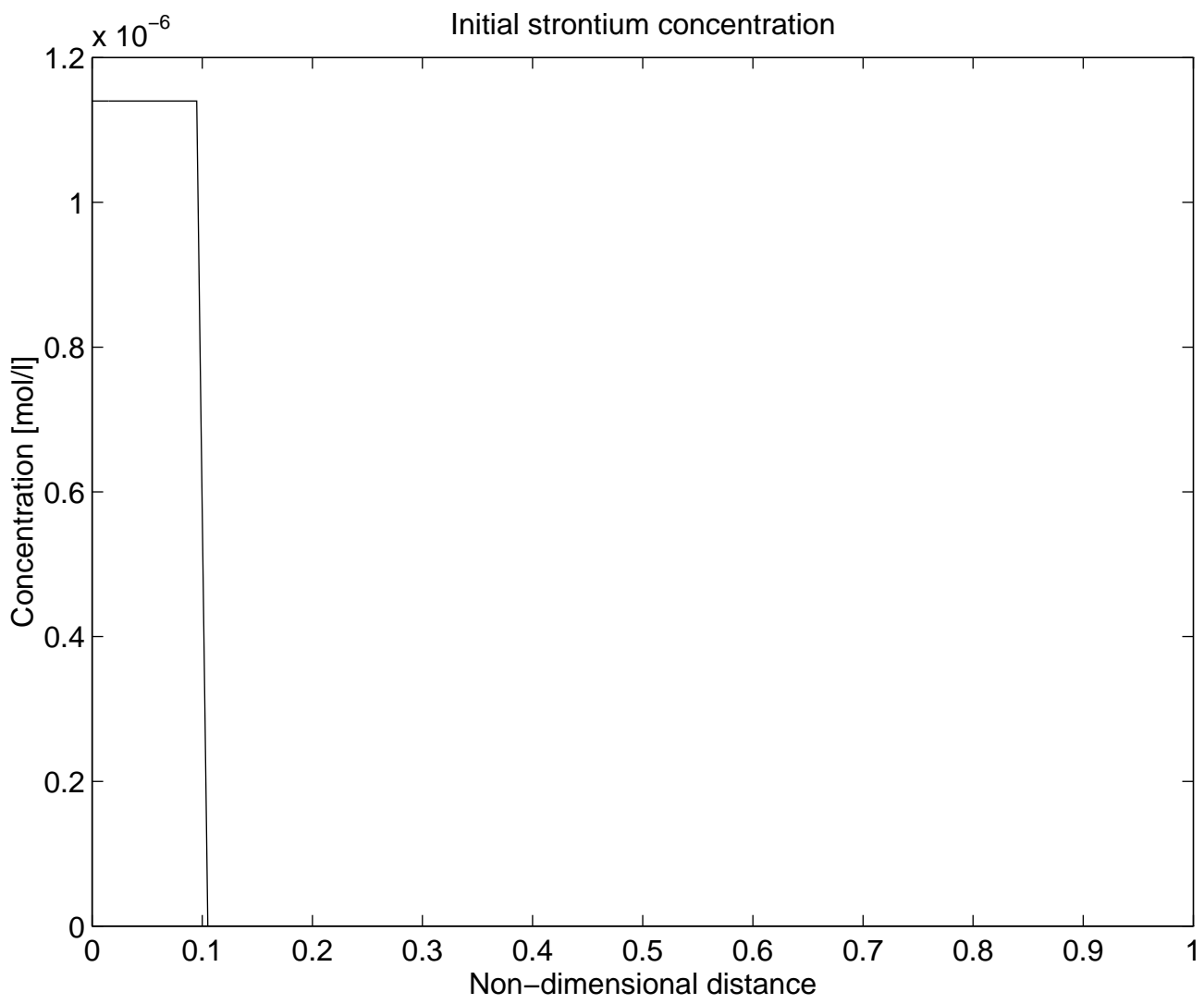


Figure 2: Initial Strontium Distribution

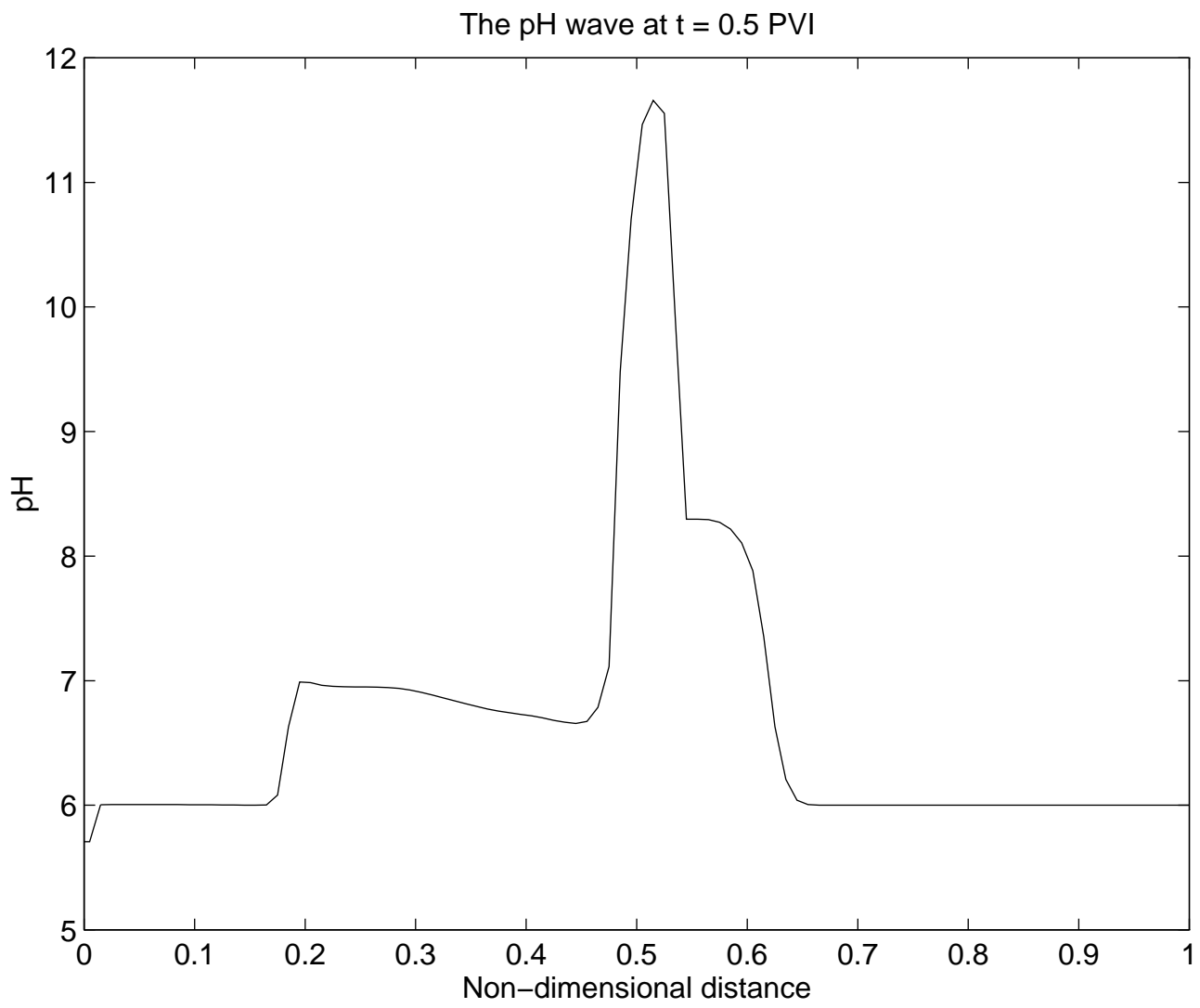


Figure 3: Ph wave at .5 PVI

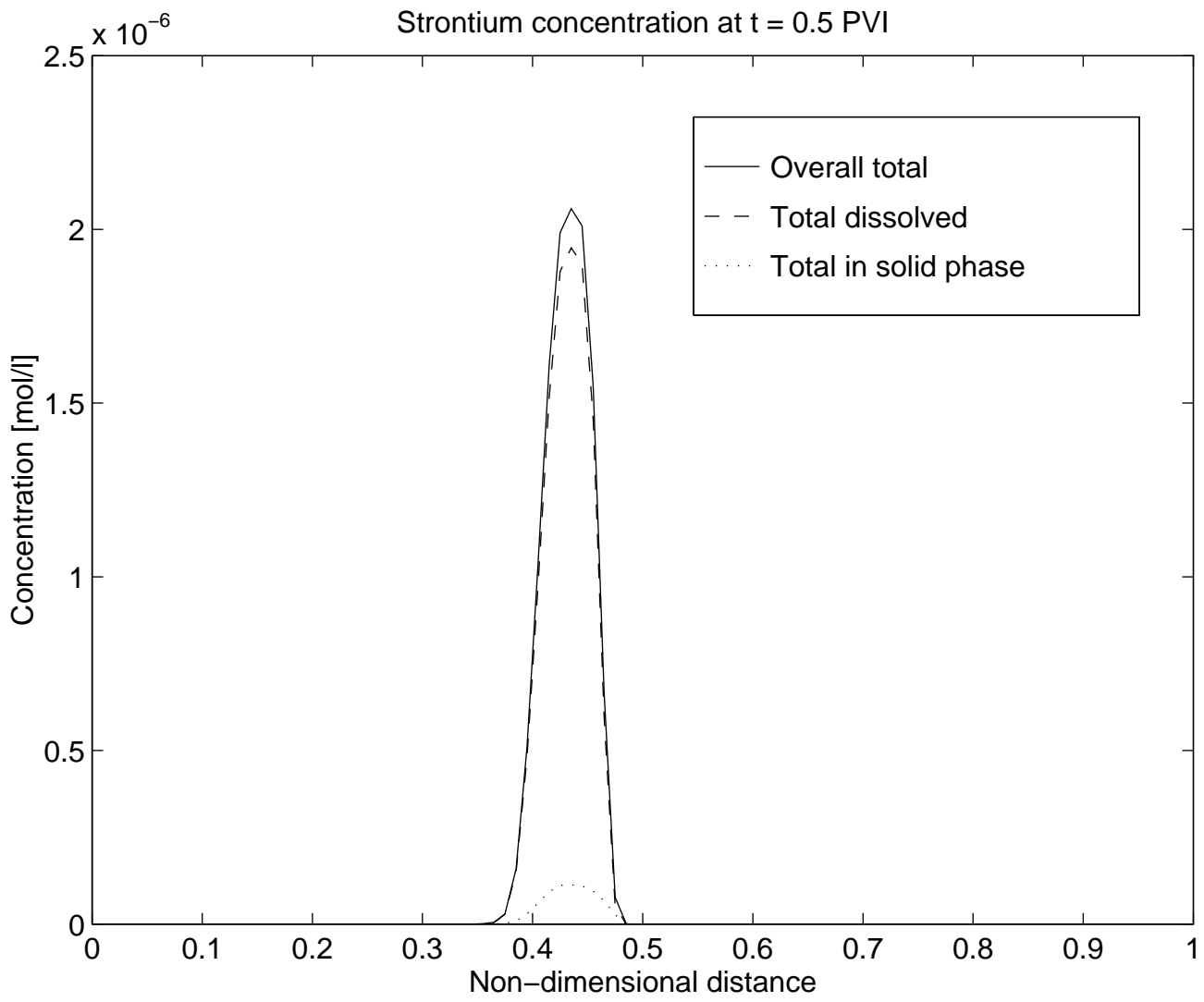


Figure 4: Strontium distribution at t = .5 PVI