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Using streamlines to simulate stochastic reactive transport in heterogeneous aquifers: Kinetic metal release and transport in CO_2 impacted drinking water aquifers

Adam L. Atchley *, Reed M. Maxwell, Alexis K. Navarre-Sitchler

Hydrological Science & Engineering Program, Department of Geology and Geological Engineering, Colorado School of Mines, Golden, CO 80401, USA

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ABSTRACT

A Lagrangian streamline approach that stochastically represents uncertainty in spatial hydraulic conductivity distribution is coupled to kinetic reactive transport in a heterogeneous 3-D domain. This methodology is designed to efficiently account for uncertainties inherent in subsurface reactive transport while maintaining hydro-geochemical processes. A hypothetical CO_2 leak from a geological carbon storage site into an overlying aquifer is used to simulate reactive transport where contamination may occur. Uncertainty in subsurface hydraulic conductivity is accounted for using correlated, Gaussian random fields in a Monte Carlo approach. In this approach 100 realizations of each ensemble were simulated with variances of the natural log of hydraulic conductivity (σ^2_{lnK}) of 1, 3.61, and 16. Peak ensemble lead concentrations were found at σ^2_{lnK} of 3.61, the middle of the variances simulated. σ^2_{lnK} within an aquifer was found to influence chemical residence time, which in turn determined the equilibrium state of the plume along the flow path and at the pumping well thus driving geochemical conditions. However, macrodispersion due to heterogeneous flow paths caused lower contaminant concentrations at the pumping well due to dilution with uncontaminated water. Furthermore, a strong link between σ^2_{lnK} and the probability of well-capture was found, suggesting that proper characterization of the σ^2_{lnK} within an aquifer will help to quantify the impact of uncertainty on risks of groundwater contamination.

1. Introduction

Groundwater constitutes a reliable source of clean drinking water worldwide and provides a substantial portion of drinking water in the Unities States [1]. Carbon capture and storage projects (CCS), a technique under consideration to offset anthropogenic causes of climate change, may adversely affect groundwater quality if the CO_2 injected into deep formations were to leak into overlying drinking water aquifers. If leakage occurs, geochemical reaction between CO_2, groundwater and aquifer minerals will alter the groundwater chemistry [2–10] and aquifer heterogeneity will control the shape and extent of the plume of impacted groundwater [11–14]. However, characterization of subsurface heterogeneity is imperfect, which then requires modeling approaches designed to assess impacts of CO_2 leakage on groundwater to account for uncertainty [15,16]. Stochastic approaches typically used to account for uncertainty are often computationally expensive and compel simplifications of geochemical reactive transport. These simplifications may result in the loss of important hydro-geochemical mechanisms. Still, proper quantification of potential impacts of CCS on aquifers suitable for drinking water requires an approach that maintains both geochemical and hydrological complexity found in natural systems and accounts for subsurface uncertainty.

Reduced pH and increased alkalinity resulting from CO_2 leakage have been shown to drive kinetic mineral dissolution and precipitation reactions and metal sorption and desorption from mineral surfaces [2–7,17]. Aquifer properties such as buffering capacity (for example the presence of calcite) and metal-containing minerals or metals on mineral surfaces have been shown to control the release of metals into the groundwater after CO_2 leakage [4,7]. The kinetic rates of these processes along with hydrological flow further dictate the extent and solution make-up of a geochemically reactive plume [3,4]. These interacting reactions and hydrological processes motivate the development of coupled hydro-geochemical transport methods [1,18] capable of representing finely resolved plume spreading and residence times that influence kinetic reactions.

Heterogeneities in permeability control the spreading of a reactive plume. Plume fingering and spreading can then regulate reactive plume lengths [3,19–21], even at fine scales [18], and result in a distribution of fluid residence times within an aquifer [11–14,23]. In a reactive system, such as a CO_2 leak, fluid residence time is directly related to the amount of time available for the

* Corresponding author. Tel.: +1 303 384 2456; fax: +1 303 273 3859.
E-mail addresses: aatchley@mymail.mines.edu (A.L. Atchley), rmaxwell@mines.edu (R.M. Maxwell), asitchle@mines.edu (A.K. Navarre-Sitchler).

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impacted water to react with the aquifer minerals. Given sufficient time and sufficiently fast reactions, the water and minerals will reach a new geochemical equilibrium, after which no additional change to groundwater chemistry is expected [24]. The result is a spatially complex geochemical response to uncertain subsurface heterogeneity.

The inability to fully characterize subsurface heterogeneity requires approaches that incorporate uncertainty, with a primary driver often being hydraulic conductivity [15,26]. Stochastic methods are commonly used to capture the bounds of probable outcomes and propagate these uncertainties to model predictions e.g. [13,15,25–27]. Stochastically accounting for the uncertainty in physical heterogeneity provides insight into the probabilistic outcomes of contaminant transport in heterogeneous aquifers and quantifies the uncertainty in human health risk assessment e.g. [16,26–28]. Likewise, ensemble techniques to capture subsurface uncertainty in hydro-geochemical transport has the potential to improve reactive transport assessment, especially with regards to evaluating CCS impacts to groundwater [9]. For these reasons groundwater risk assessment and management studies are often required to use stochastic methods that characterize probabilistic outcomes by regulatory agencies [29–33].

A stochastic method investigating CCS risk to groundwater would ideally employ a fully coupled hydrological and geochemical model. However, simulations of fully-kinetic hydro-geochemical transport on a large 3-D heterogeneous domain require utilization of super computing facilities that employ thousands to upwards of 100 K CPU cores via sophisticated parallel codes [10,34,35]. While these resources can model complex hydro-geochemical transport such as transient conditions [35], they are often out of reach for management agencies needing to assess contamination scenarios that capture uncertainty. Therefore, it is often necessary to use model simplifications when stochastically representing reactive transport. However, chemical simplifications used to predict plume migration in heterogeneous aquifers may not adequately capture the solute make-up of a reactive CO_2 plume, which is a product of complex carbonate buffering and oxidation-reduction processes [3,4,6,7,36]. On the other hand modeling efforts that maintain full geochemical processes on modest computational resources are forced to simplify hydrogeological properties, such as fine scale heterogeneity which impacts plume spreading e.g. [2,14,22,37,38]. As a result relatively few hydro-geochemical studies have used stochastic techniques e.g. [9,39].

This paper presents a computationally efficient streamline methodology, which can be used to evaluate coupled hydro-geochemical problems where uncertainty in subsurface properties necessitates an ensemble approach. Fine-scale heterogeneity and thus macrodispersion and kinetic geochemistry are represented to account for complex hydrological and geochemical processes. Ensemble simulations allow the interaction of hydrological and geochemical processes to propagate into probabilistic results. The efficient ensemble approach presented here does not account for local transverse mixing at the sub-grid scale but does directly simulate macrodispersion and reactive transport processes, which has been shown to be in agreement with approaches that include transverse dispersion [40]. The streamline method is then used to investigate how subsurface heterogeneity affects geochemical conditions from a hypothetical CCS leakage scenario into an aquifer. Spatially homogenous geochemical conditions are used to illicit a simple reaction path towards equilibrium in relation to complex solute residence times due to heterogeneous permeabilities. An investigation of how the coupled hydro-geochemical processes propagate through ensemble statistics is made. Specifically, the goals of this work are to study how these coupled processes (1) control geochemical response in kinetic reactive transport, and (2) influence ensemble predictions using Monte Carlo methods to account for uncertainty in an aquifer hydraulic conductivity field.

2. Methods

2.1. Streamline model

Streamlines are one-dimensional (1D) flow paths traced within a divergence-free three or two-dimensional flow field e.g. [17,21,40–53]. The nature of a divergence-free flow field dictates that streamlines follow a unique path and cannot intercept or cross other streamlines. In order to maintain a 3-D description, multiple 1-D streamlines are used to capture all the flow paths that occur in a 3-D heterogeneous flow domain. The principle advance to this approach is the ability to solve 1-D reactive transport models on multiple, deconvolved streamlines in parallel [21,42–47].

The streamline method presented here builds upon the approach of Thiele et al. [41], Crane and Blunt [44], and Maxwell et al. [47]. Streamlines are traced in a 3-D, steady-state, single phase flow-field that is described by:

$$\nabla \bullet q = \pm q_s \tag{1a}$$

$$v = \frac{q}{\phi} = \frac{-K\nabla H}{\phi} \tag{1b}$$

where q_s is the source/sink term [1/T], q is the total Darcy flux [L/T], K is the hydraulic conductivity tensor [L/T], H is the head potential [L], v is the groundwater velocity [L/T], and ϕ is porosity [–]. The Darcy velocity at each cell face is calculated on a finite difference grid, velocities within each grid cell are assumed to vary linearly in each coordinate direction based of the velocity values of each grid cell face. Streamlines are mapped through the flow field by tracing particles in an advective only regime. The particle tracking technique [54,55] and the streamline transform e.g. [41,44,47,49,51] are described in Appendix A. Each streamline retains spatial (x, y, z) and temporal data in the form of residence time or time of flight, $\tau[T]$, as the trajectory is traced through domain grid cells. τ can be used in place of spatial coordinates and velocity in the advection equation. Thus transport along a streamline from source zone to capture zone for a reactive species C_i, [Mol/L^3] can be expressed as

$$\frac{\partial C_i}{\partial t} + \frac{\partial C_i}{\partial \tau} + R_i = 0 \tag{2}$$

where R_i is the total reaction rate of species i in solution [Mol/L^3 T]. Maintaining a one to one link between spatial coordinates and τ results in 1-D transport along cells of assorted τ lengths and allows for the reactive transport to solve efficiently while maintaining a level of τ discretization needed to represent the spatial domain.

2.2. Basic structure & methodology

The streamline methodology is implemented in four distinct steps (Fig. 1): (I)) create a flow domain, (II) trace streamlines via advective transport within the flow domain, (III) transform streamline spatial coordinates to time of flight, and (IV) simulate geochemical reactions along each streamline using a reactive transport code. Established codes were used to perform steps I, II, and IV. Heterogeneous subsurface properties were created using turning-bands, a method found to be free of computational bias that accurately produces Gaussian random fields [56–60] in ParFlow. ParFlow is a parallel, 3-D groundwater flow model [61–63] that is also used to solve groundwater flow in the heterogeneous domain. In step II, streamlines were defined by tracking particles through an advective flow field using SLIM-FAST, a Lagrangian contaminant transport model [47,64–67]. CrunchFlow, a