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Naturally occurring dechlorination reactions in rock matrices: Impacts on TCE fate and flux

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HIGHLIGHTS

- Abiotic dechlorination reactions in rock matrices are simulated.
- Back-diffusion timeframes can be greatly reduced due to abiotic dechlorination.
- Downgradient migration can be mitigated due to dechlorination in the rock matrix.

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ABSTRACT

Chlorinated solvents in rock matrices can serve as a long-term contaminant source in fractured rock aquifers, sustaining groundwater plumes for extended periods of time. The intensity and longevity of the groundwater plume will be impacted by the diffusional flux between the rock matrix and adjacent conductive fractures, as well as the fate of contaminants residing within the rock matrix itself. In this study, 1-dimensional numerical simulations are performed to assess the impacts of slow naturally occurring abiotic dechlorination reactions on TCE fate and transport in rock matrices. Simulation parameters for the rock matrix, including effective diffusion coefficients and trichloroethene (TCE) first order dechlorination rate constants, are derived from experimental data from intact rock cores. Simulations show that a TCE dechlorination rate constant of 1×10^{-8} s^{-1} can have a substantial impact on TCE uptake and release from the rock matrix. In addition, varying the simulated matrix porosity indicates that the impacts of matrix reactions are exacerbated in low porosity matrices. Overall, simulation results show that contaminant removal from rock matrices can be dominated by abiotic reaction, and that the back-diffusion timeframes for sustaining bedrock plumes above regulatory levels may be limited to a few decades if these abiotic reactions are occurring within the rock matrix.

1. Introduction

The presence of chlorinated solvents, such as tetrachloroethene (PCE) or trichloroethene (TCE), in fractured rock poses a significant challenge to the environmental industry. As shown in many studies, diffusive uptake into and the subsequent back-diffusion of contaminants from the rock matrix are the primary challenges facing the environmental industry in fractured rock (Mutch et al., 1993; Sterling et al., 2005; Parker et al., 1994). Not only does the rock matrix often serve as the primary reservoir for contaminant mass, but the slow release of contaminants from the rock matrix can sustain contaminant plumes in bedrock aquifers for decades to centuries (Lipson et al., 2005; West and Kueper, 2010).

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Simulation studies performed by West and Kueper (2010) showed that contaminant degradation within the matrix can reduce the timeframes associated with matrix back-diffusion. However, until recently, few studies have been performed to closely examine the potential for slow dechlorination reactions of chlorinated ethenes in rock matrices. Darlington et al. (2013) showed that naturally dechlorination reactions were occurring in crushed rock samples. Using intact rock cores, Schaefer et al. (2013) showed that the complete dechlorination of TCE occurred abiotically in multiple rock types, and that the observed rates of reaction were related to the ferrous iron that was adjacent to the wetted rock porosity; TCE complete dechlorination was shown to be reasonably described by first order rate constants ranging from 8.3×10^{-10} to 4.2×10^{-8} s^{-1}. Furthermore, it was shown that these abiotic reactions persisted despite decades of exposure to TCE in a TCE-contaminated fractured bedrock aquifer, and that the abiotic dechlorination rates observed were sufficiently large to impact TCE migration within the rock matrix (Schaefer et al., 2015).

These recent studies demonstrating the abiotic dechlorination of TCE in rock matrices suggest that naturally occurring dechlorination reactions may substantially mitigate the long back-diffusion timeframes associated with the slow release of chlorinated ethenes from rock matrices. However, quantification of the impacts of these slow dechlorination reactions on contaminant uptake and release into the rock matrix, and ultimately on the contaminant fate in the bedrock aquifer, have yet to be assessed, particularly with respect to reaction rate constants typical of real rock matrix systems. The objective of this paper is to, based on the rock matrix reactivity and diffusion data obtained by Schaefer et al. (2013, 2015), assess the impacts of abiotic TCE dechlorination reactions occurring naturally within the rock matrix on TCE fate in fractured rock systems. Specifically, the impacts of these dechlorination reactions on TCE uptake into the rock matrix, the persistence of TCE release from the rock matrix, and net contaminant migration in the aquifer are evaluated and discussed.

2. Simulation approach

One-dimensional simulations were performed to describe the coupled diffusion and reaction of TCE through rock matrices. It is noted that such simulations are intended for screening purposes only, and as a means to assess the relative impacts of TCE dechlorination reactions in rock matrices on TCE uptake and release from/into adjacent hydraulically conductive fractures. The diffusion and reaction model used was developed previously (Schaefer et al., 2013). Briefly, the mass balance for this model is as follows:

$$R\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} - \frac{k'}{\theta}C \tag{1}$$

$$k' = k\,K_\mathrm{d}\,\rho \tag{2}$$

$$R = 1 + \frac{\rho K_\mathrm{d}}{\theta} \tag{3}$$

where R is the retardation factor, C is the aqueous molar concentration of TCE [M], k' is the bulk first order degradation rate coefficient, and k is the first order reaction rate constant describing the complete dechlorination of TCE [s^{-1}], D is the effective aqueous diffusion coefficient [cm^2/s], t is the time [s], θ is the matrix porosity, K_d is the linear adsorption coefficient [L/kg], and ρ is the rock density (2.6 kg/L assumed). Eqs. (1) through (3) were solved using a finite difference model with operator splitting in a Microsoft Excel® spreadsheet-based model (Schaefer et al., 2013; Crank, 1995; Lanser and Verwer, 1999). The finite difference model used a distance step of 5 cm and a time step of 5×10^5 s, was performed over a duration of 30–60 years (one simulation was performed for up to 80 years), and a total length of 30 cm.

The model was used to simulate the one-dimensional diffusion of TCE from the fracture interface into the rock matrix, or the back-diffusion of TCE from the rock matrix into an adjacent fracture. In all simulations, adjacent fracture concentrations were used as concentration boundary conditions. Simulation cases, as well as key assumptions and boundary/initial conditions used in the model, are provided in the following subsections.

It is recognized that analytical solutions exist for unsteady state coupled diffusion and first order reaction processes (Crank, 1995). Neretnieks (1980) also presents a solution for coupled diffusion and reaction, and even provides a solution for variable surface concentration. However, simulating the diffusive uptake followed by the diffusive release of TCE from the rock matrix (where the initial condition for the diffusive release is based on the diffusion profile of TCE in the rock matrix) is not, to the best of our knowledge, amenable to an analytical solution. In addition, as discussed for Case 3 below, the variable concentration boundary condition applied is not conducive to an analytical solution. Analytical solutions presented by Neretnieks (1980) provide solutions for diffusive uptake into rock with first-order reaction and variable surface concentration, but the solution is based on a semi-infinite medium assumption, which is not valid for the simulations presented herein. The variable surface concentration presented by Neretnieks also is described by a first order decay, which (as described below) is not appropriate for the Case 3 simulation.

2.1. Case 1: TCE uptake into the rock matrix

Case 1 evaluates the impact of matrix dechlorination reactions on TCE uptake into the rock matrix. Case 1 simulates the case where a persistent and constant source is present in the fractures (either from upgradient, or from DNAPL sources),