1
2 **TITLE:** Naturally Occurring Dechlorination
3 Reactions in Rock Matrices: Impacts on
4 TCE Fate and Flux
5
6
7
8
9

10 **AUTHORS:** Charles E. Schaefer*

11
12 **AFFILIATIONS:** CDM Smith
13
14
15
16
17
18
19
20
21

22 ***CORRESPONDING AUTHOR:**
23

24 CDM Smith
25 110 Fieldcrest Avenue, #8
26 6th Floor
27 Edison, NJ 08837
28
29 schaeferce@cdmsmith.com
30
31
32
33
34
35
36
37
38
39

40 **Key Words:** TCE, matrix diffusion, bedrock
41
42
43
44

Abstract

Chlorinated solvents in rock matrices can serve as a long-term contaminant source in fractured bedrock 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 $1 \times 10^{-8} \text{ s}^{-1}$ 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 (at most) if these abiotic reactions are occurring within the rock matrix.

1.0 Introduction

The presence of chlorinated solvents, such as tetrachloroethene (PCE) or trichloroethene (TCE), in fractured bedrock 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 bedrock [1-3]. 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 [4, 5].

Simulation studies performed by West and Kueper [5] 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. [6] showed that naturally dechlorination reactions were occurring in crushed rock samples. Using intact rock cores, Schaefer et al. [7] 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 $4.2 \times 10^{-8} \text{ s}^{-1}$. 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 [8].

1 These recent studies demonstrating the abiotic dechlorination of TCE in rock matrices
2 suggest that naturally occurring dechlorination reactions may substantially mitigate the
3 long back-diffusion timeframes associated with the slow release of chlorinated ethenes
4 from rock matrices. However, quantification of the impacts of these slow dechlorination
5 reactions on contaminant uptake and release into the rock matrix, and ultimately on the
6 contaminant fate in the bedrock aquifer, have yet to be assessed, particularly with respect
7 to reaction rate constants typical of real rock matrix systems. The objective of this paper
8 is to, based on the rock matrix reactivity and diffusion data obtained by Schaefer et al. [7,
9 8], assess the impacts of abiotic TCE dechlorination reactions occurring naturally within
10 the rock matrix on TCE fate in fractured bedrock systems. Specifically, the impacts of
11 these dechlorination reactions on TCE uptake into the rock matrix, the persistence of
12 TCE release from the rock matrix, and net contaminant migration in the aquifer are
13 evaluated and discussed.

16 **2.0 Simulation Approach**

17 One-dimensional simulations were performed to describe the coupled diffusion and
18 reaction of TCE through rock matrices. It is noted that such simulations are intended for
19 screening purposes only, and as a means to assess the relative impacts of TCE
20 dechlorination reactions in rock matrices on TCE uptake and release from/into adjacent
21 hydraulically conductive fractures. The diffusion and reaction model used was developed
22 previously [7]. Briefly, the mass balance for this model is as follows:

$$R \frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - \frac{k'}{\theta} C \quad \text{Eq. 1}$$

$$k' = k K_d \rho \quad \text{Eq. 2}$$

$$R = 1 + \frac{\rho K_d}{\theta} \quad \text{Eq. 3}$$

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 porosity, K_d is the linear adsorption coefficient [L/kg], and ρ is the rock density (2.6 kg/L assumed). Equations 1 through 3 were solved using a finite difference model with operator splitting in a Microsoft Excel[®] spreadsheet-based model [7, 9, 10]. 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 to 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 the unsteady state solution to coupled diffusion and first order reaction processes [9]. Neretnieks (11) 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, amendable 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 (11) 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), causing the diffusive uptake of TCE in the rock matrix. Boundary and initial conditions are summarized in Figure 1, and in the equations below:

$$C(x,t=0) = 0 \quad \text{Eq. 4}$$

$$C(x=0, L \text{ for all } t) = 1 \quad \text{Eq. 5}$$

Where C is the TCE concentration, t is time, and L is the distance between the fractures. A constant concentration (1mM) of TCE in the adjacent fractures is assumed for a 30-year simulation period (serving as the constant concentration boundary condition), as TCE

diffuses into the rock matrix. Table 1 lists the model input parameters. The impacts both matrix dechlorination reaction and matrix porosity are evaluated.

2.2 Case 2: TCE Back-Diffusion Flux from the Rock Matrix

Case 2 evaluates the back-diffusion flux of TCE from the rock matrix following the 30-year loading periods simulated in Case 1. The impacts of both reaction and porosity on back-diffusive flux are examined. Simulation conditions and parameters are presented in Figure 2 and Table 1. The initial condition for this simulation is the TCE concentration profile within the rock matrix obtained from Case 1. For the Case 2 simulations, the TCE concentrations are assumed to rapidly decrease to zero in the fractures at 30 years, and maintained at a TCE concentration of zero for another 30 years as TCE back-diffuses out of the rock matrix (thus, a constant boundary condition of 0 concentration). Thus, boundary and initial conditions for the back-diffusion portion of the simulation are:

$$C(x,t=0) = \text{concentration profile at end of Case 1} \quad \text{Eq. 6}$$

$$C(x=0, L \text{ for all } t) = 0 \quad \text{Eq. 7}$$

These simulations might represent the application of a remedial technology (e.g., *in situ* bioremediation or chemical oxidation) that effectively and rapidly decreases TCE concentration to (or near) analytical detection limits in conductive fractures, followed by longer-term treatment or groundwater extraction to maintain relatively low concentrations in the fractures. In any cases, the simplifying assumption of negligible TCE on the fractures serves to maximize the rate of TCE back-diffusion from the matrix;

relaxing this assumption would primarily serve to increase back-diffusion time frames,
but still demonstrating the relative importance of abiotic reaction on flux from the matrix.

It is recognized that the Case 2 simulations do not describe the impact of the matrix back-diffusion flux on groundwater concentrations in the hydraulically conductive fractures. More complex models, similar to those developed by West and Kueper [5], would be required to simulate these effect. However, the Case 2 simulations described herein provide a means of quantitatively comparing the impacts of matrix porosity and reaction on the back-diffusion flux and timeframes, and therefore serve as a means to highlight the importance of these parameters and mechanisms on bedrock plumes sustained by matrix back-diffusion.

2.3 Case 3: TCE Flux into the Rock Matrix Compared to Flux through Fractures

Case 3 evaluates the flux of TCE into the rock matrix compared to the convective flux of TCE through a single hydraulically conductive fracture plane. The impact of matrix dechlorination reaction on matrix uptake of TCE is evaluated. Simulation conditions and parameters are presented in Figure 3 and Table 1. The simulation distance is performed over a 10 m length (parallel to groundwater flow) assumed to be immediately downgradient of the source. Rock matrix diffusion boundary and initial conditions are the same as in Case 1, except that the boundary conditions vary with time based on the decrease in concentration within the fractures due to diffusive uptake into the rock matrix:

$$C(x=0, L \text{ for all } t) = C(t) \quad \text{Eq. 8}$$

1
2 A fracture aperture of 0.0001 cm, a width (perpendicular to groundwater flow) of 20 m,
3 and a groundwater superficial velocity through the fractures of 2 m/day are assumed. For
4 the Case 3 simulations, a mass balance within the numerical simulation is used to
5 determine the average TCE concentration in the fractures (thus the variable diffusive
6 boundary condition) by calculating the mass of TCE entering the rock matrix during each
7 10 m (5 day) interval. This average fracture concentration is updated in the numerical
8 model, thus simulating a variable surface concentration due to coupled diffusive and
9 reactive uptake within the rock matrix. It is also noted that the Case 3 simulation focuses
10 on a single fracture plane, and plume mitigation due to dispersive forces and/or spreading
11 into multiple fracture planes (with increased surface area for matrix uptake) are not
12 considered. Since a fracture plane is bounded above and below by the rock matrix, the
13 simulated uptake into the rock matrix is multiplied by two.

14 15 **3.0 Results**

16 *3.1 Case 1*

17 Simulation results for Case 1 are shown in Figure 4. For all porosities simulated,
18 inclusion of the abiotic dechlorination reaction in the rock matrix resulted in a notable
19 decrease in the TCE mass residing within the rock matrix compared to the simulation
20 cases where TCE dechlorination reactions were neglected. In addition, decreasing the
21 rock matrix porosity from 0.12 to 0.02 resulted in a substantial decrease in TCE mass
22 within the rock matrix, for both the reactive and non-reactive simulations. Finally, the
23 extent to which TCE mass within the rock matrix was decreased by inclusion of the

dechlorination reaction was related to the rock matrix porosity. For the lowest simulated matrix porosity (0.02), inclusion of the dechlorination reaction within the rock matrix resulted in an 88% decrease in the TCE mass within the rock matrix for the 30-year simulation. In contrast, for the largest simulated rock matrix porosity (0.12), inclusion of the dechlorination reaction within the rock matrix resulted in a 71% decrease in the TCE mass within the rock matrix.

Also shown for Case 1 are the simulated TCE molar concentrations in the matrix porewater as a function of distance from the fracture interface (Figure 5). For the 0.12 matrix porosity simulation without reaction, TCE diffusion into the rock matrix is substantial, with TCE concentrations equal to 40% of the fracture concentration at the midpoint between fractures (i.e., 15 cm into the rock matrix) after 30 years of diffusion. For this simulated matrix porosity, increasing the fracture spacing would substantially increase the TCE uptake into the rock by increasing the effective concentration gradient. For all simulations shown in Figure 5, inclusion of the matrix dechlorination reaction substantially limits the penetration of the TCE concentration profile, with the impacts of reaction more pronounced for the lower matrix porosity systems. Thus, the naturally occurring dechlorination reactions in rock matrices previously observed [7] play an important role with respect to contaminant uptake.

3.2 Case 2

Simulation results for Case 2 are shown in Figure 6. For the simulations without reaction, the TCE back-diffusion flux is greater for the high porosity (0.12) simulation than for the low (0.02) porosity simulation. This is due to both the greater mass uptake of

1 TCE for the high porosity simulation compared to the low porosity simulation (as shown
2 in Figures 4 and 5), and also due to the greater diffusive flux of TCE from the rock
3 matrix (resulting from the elevated effective diffusion coefficient, as shown in Table 1)
4 associated with the high matrix porosity simulation. As the rock matrix becomes slowly
5 depleted of TCE in the high matrix porosity simulation, the flux of TCE in the 0.12
6 matrix porosity simulation decreases; the flux from the 0.12 matrix simulation (without
7 reaction) decreases by nearly an order of magnitude over the 30 year simulation period.
8 In contrast, the back-diffusion TCE flux remains essentially constant for the 0.02 matrix
9 simulation (no reaction) over the 30 year period, as only a very small fraction of the TCE
10 mass leaves the rock matrix.

11 For both simulated matrix porosities, the impact of the matrix reaction on the TCE
12 back-diffusion flux is substantial. For both matrix porosities, inclusion of reaction results
13 in a decrease in back-diffusion flux throughout the 30-year simulation period. By the end
14 of the 30-year simulation period, for both porosities examined, the simulated flux that
15 includes reaction is greater than three orders of magnitude less than the flux simulated
16 without reaction. However, the relative decrease in flux due to reaction (i.e, the relative
17 decrease in flux between the reactive and non-reactive simulations) is approximately 5-
18 times greater for the low porosity simulation than for the high porosity simulation,
19 indicating that the impacts of reaction are more significant in low porosity systems. It is
20 also of note that the maximum simulated concentration of TCE in the rock matrix
21 decreased to 3.8×10^{-5} mM (5 micrograms/L) when reaction is included, which is the
22 drinking water standard set forth by the USEPA, by 24 and 34 years in the 0.02 and 0.12
23 simulations, respectively. If back-diffusion is neglected for the 0.12 simulation by setting

the effective diffusion coefficient to approximately zero, thus forcing all of the TCE removal in the matrix to occur via TCE dechlorination reaction, 39 years are needed for TCE concentrations to decrease to 3.8×10^{-5} mM; thus, TCE attenuation in the rock matrices is largely controlled by reaction. This 39 year period also is virtually independent of the matrix loading time (i.e., Case 1) and the fracture spacing assuming 1 mM of TCE in the conductive fractures (verified by additional simulations where up to 80 years of loading were assumed), as removal in the rock matrix is governed by the first order reaction kinetics of TCE removal in the rock matrix. Again, these results highlight the importance of previously measured TCE dechlorination rate constants [7] in controlling back-diffusion in rock matrices.

3.3 Case 3

Simulation results for Case 3 are shown in Figure 7. TCE migration through the simulated fracture plane (through the first 10 m downgradient of the simulated constant source) is greater than the TCE uptake into the rock matrix for all times, and for both the reactive and non-reactive cases. This indicates that, for the specific conditions simulated, TCE uptake into the rock matrix through the first 10 m downgradient does not prevent the continued migration through a single hydraulically conductive fracture plane in the presence of a sustained source.

The fractional uptake of TCE in the rock matrix is similar for both the reactive and non-reactive simulations at early (< 2 years) times. In absence of reaction, the simulated TCE uptake in the rock matrix slowly decreases over time. When reaction is included, the uptake into the rock matrix decreases over the first five years, but then reaches a steady

1 state value that is approximately one-half that of the TCE migration through the fracture
2 plane. The initial decrease over the first 5 years is due to the decrease in diffusive flux, as
3 diffusion dominates over reaction at early times. However, at longer times, matrix
4 reaction is the controlling mechanism.

5 An additional set of simulations (with and without matrix dechlorination reaction)
6 was performed for Case 3 using a rock matrix porosity of 0.06. The comparison between
7 reactive and non-reactive was similar to that observed for the 0.12 porosity simulation.
8 However, the uptake of TCE into the matrix was substantially less (approximately 2.5-
9 and 6-times less for the non-reactive and reactive cases, respectively).

12 **4.0 Discussion**

13 The simulation results presented in the previous section, using abiotic dechlorination
14 rates previously measured in intact rock cores, all demonstrate the potential importance
15 of relatively slow abiotic reactions in rock matrices. These dechlorination reactions
16 impact both the TCE mass storage as well as the flux (into or out of) the rock matrix.
17 While several simulation and modeling studies have been performed to assess
18 contaminant uptake and/or back-diffusion from rock matrices, the simulation results
19 presented herein focus on demonstrating the impacts of slow abiotic dechlorination
20 reactions in rock matrices.

21 The Case 1 and Case 2 simulations results suggest that, in the long term, the impacts
22 of matrix dechlorination reactions will likely be more pronounced in lower porosity rock
23 matrices compared to higher porosity rock matrices. In low porosity rock matrices,

1 diffusion timeframes are much longer due to the low values of the effective diffusion
2 coefficient; these long time frames allow for a greater extent of dechlorination reaction
3 and thus a greater relative impact of reaction compared to the relatively shorter diffusion
4 timeframes associated with higher matrix porosity systems.

5 The Case 2 simulations demonstrate the importance of matrix dechlorination
6 reactions on back-diffusion flux, and suggest that incorporation of slow dechlorination
7 reactions may be a vital component of natural attenuation at many bedrock sites (or, at
8 least bedrock sites where these reactions are likely to be occurring). The long back-
9 diffusion timeframes observed in this current study in absence of matrix reaction, as well
10 as in simulation efforts performed by others [4, 5], may be substantially mitigated in the
11 presence of rock matrix reactions. The Case 2 simulations, using abiotic TCE
12 dechlorination rates actually measured in intact bedrock samples, demonstrate the
13 importance of these reactions in limiting attenuation timeframes for plumes that
14 otherwise might be sustained by matrix back-diffusion. If such reactions are present in
15 the rock matrix, then remedial efforts targeting sources in hydraulically conductive
16 fractures will likely not be negated by the long term impacts of matrix back-diffusion.
17 The Case 2 simulations further suggest that, assuming rock matrix properties similar to
18 those described in Table 1 (with reaction), the ability of matrix back-diffusion alone to
19 sustain TCE plumes in fractured bedrock likely is limited to 20 to 40 years under worst
20 (i.e., negligible flow in fractures to facilitate dilution from the matrix) conditions.

21 While matrix diffusion typically causes concerns with respect to site remedial and
22 management practices, the simulations performed in Case 3 suggest that matrix diffusion
23 can provide some benefit by limiting the mass discharge through hydraulically

1 conductive fractures, thereby limiting the downgradient migration of contaminant. While
2 the TCE migration through a fracture plane relative to uptake into the rock matrix will be
3 highly dependent on several site-specific conditions (e.g., aperture, velocity, matrix
4 porosity, and dechlorination rate constant), the results shown in Figure 7 indicate that
5 such uptake may need to be considered at many bedrock sites. Furthermore, in fractured
6 bedrock with low flow velocities, small fracture aperture, and/or high fracture density,
7 contaminant uptake into the matrix will likely be an important factor controlling the long-
8 term downgradient flux of contaminants, particularly if dechlorination reactions are
9 occurring at rates previously observed in rock [8]. These observations are consistent with
10 those of Lipson et al. [4], who examined the impacts of rock matrix properties on plume
11 attenuation, but who did not simulate the benefits of slow matrix dechlorination reactions.
12 The simulations shown in Figure 7 suggest that matrix dechlorination reactions can
13 substantially enhance uptake into the rock matrix, thereby serving as an additional
14 mechanism to limit mass discharge and downgradient contaminant migration. With the
15 matrix properties and reaction shown in Table 1, matrix reactions can enhance plume
16 attenuation by approximately a factor of two.

17 While the simulations performed in this study were based on abiotic dechlorination
18 rates observed for TCE, the simulations results can be applied to any first order
19 degradation reactions. Of particular note are slow biotic reactions, many of which are too
20 slow to be typically observed or thought useful in many natural attenuation studies. As
21 shown in the simulation studies presented herein, even very slow reaction rates can be
22 important in rock matrices, where diffusion timescales are very long. Additional research
23 to identify transformation reactions, both biotic and abiotic, under a wide range of

1 mineralogic and geochemical conditions, and for both a wide range of organic and
2 inorganic compounds, is needed to incorporate these slow reaction processes into matrix
3 attenuation models. Most importantly, this study has demonstrated that the rates of
4 reaction previously observed to occur within intact rock core [7, 8] are sufficiently large
5 to make a substantial impact on TCE fate and transport in fractured bedrock systems.

6 7 8 **Acknowledgments**

9 Support for this research was provided in part by the Strategic Environmental
10 Research and Development Program (SERDP) under Project ER-1685. Views, opinions,
11 and/or findings contained in this report are those of the authors and should not be
12 construed as an official Department of Defense position or decision unless so designated
13 by other official documentation.

14 15 16 **References**

- 17
- 18 [1] R.D. Mutch, J.I. Scott, D.J. Wilson, Cleanup of fractured rock aquifers: implications
19 of matrix diffusion, *Environ. Monitor. Assess.* 24 (1993) 45-70.
- 20
- 21 [2] S.N. Sterling, B.L. Parker, J.A. Cherry, J.H. Williams, J.W.; Lane Jr., F.P. Haeni,
22 Vertical cross contamination of trichloroethylene in a borehole in fractured
23 sandstone, *Ground Water* 43 (2005) 557-573.

1

2 [3] B.L. Parker, R.W. Gillham, J.A. Cherry, Diffusive disappearance of immiscible-phase
3 organic liquids in fractured geologic media, Ground Water 32 (1994) 805-820.

4

5 [4] D.S. Lipson, B.H. Kueper, M.J. Gefell, Matrix diffusion-derived plume attenuation
6 in fractured bedrock, Ground Water 43 2005, 30-39.

7

8 [5] M.R. West, B.H. Kueper, Plume detachment and recession times in fractured rock,
9 Ground Water 48 (2010) 416-426.

10

11 [6] R. Darlington, L. Lehmicke, R.G. Andrachek, D. Freedman, Anaerobic abiotic
12 transformations of *cis*-1,2-dichloroethene in fractured sandstone, Chemosphere 90 (2013)
13 2226-2232.

14

15 [7] C.E. Schaefer, R.M. Towne, D.R. Lippincott, V. Lazouskaya, T.B. Fischer, M.E.
16 Bishop, H. Dong, Coupled diffusion and abiotic reaction of trichlorethene in minimally
17 disturbed rock matrices, Environ. Sci. Technol. 47 (2013) 4291-4298.

18

19 [8] C.E. Schaefer, R.M. Towne, D.R. Lippincott, P. Lacombe, M.E. Bishop, H. Dong,
20 Abiotic Dechlorination in Rock Matrices Impacted by Long-Term Exposure to TCE,
21 Chemosphere 119 (2015) 744-749.

22

23 [9] J. Crank, J. The Mathematics of Diffusion, second edition. Oxford Science
24 Publications, 1995.

1

2 [10] D. Lanser, J.G. Verwer, Analysis of operator splitting for advection-diffusion-
3 reaction problems from air pollution modelling, J. Comp. Appl. Math. 111 (1999) 201-
4 216.

5

6 [11] Neretnieks, I., Diffusion in the rock matrix: an important factor in radionuclide
7 migration? J. Geophys. Res. 85 (1980) 4379-4397.

8

9 [12] T.B. Boving, P. Grathwohl, Tracer diffusion coefficients in sedimentary rocks:
10 correlation to porosity and hydraulic conductivity, J. Contam. Hydrol. 53 (2001) 85-100.

11

12

13

14

Tables

Table 1. Rock matrix simulation parameters used for each Case. The TCE sorption coefficient and the abiotic TCE dechlorination rate constant were based on previously measured bedrock parameters [7].

Parameter	Case 1	Case 2	Case 3
Fracture spacing [cm]	30	30	30
Simulation time [yr]	30	60 ¹	30
Constant TCE fracture concentration [mM]	1	1, then 0	NA
Porosity	0.02, 0.06, 0.12	0.02, 0.12	0.06, 0.12
Effective Diffusion Coeff. [cm^2s^{-1}]	5.2×10^{-9} , 6.5×10^{-8} , 2.6×10^{-7}		
TCE Sorption Coeff. [L/kg]	0.12	0.12	0.12
Rate constant [s^{-1}]	0 or 1×10^{-8}		

NOTES:

NA – not applicable, as Case 3 did not have a constant TCE fracture (boundary) condition. The initial TCE in the fracture was 1 mM.

¹ The first 30 years of the simulation was performed during Case 1, as TCE mass was loading within the rock matrix. Starting with initial TCE concentrations in the rock matrix identical to those at the end of the Case 1 simulation, back-diffusion was simulated for the next 30 years (0 concentration boundary condition maintained at fractures).

² Effective diffusion coefficients are shown for rock matrix porosities of 0.02, 0.06, and 0.12, respectively. Effective diffusion coefficients are based on previously reported experimental data [7, 12].

1 **Figures**

3
4
5 **Figure 1.** Conceptual model for the Case 1 simulation.

12
13 **Figure 2.** Conceptual model for the Case 2 simulation. The Case 2 simulation starts at the
14 end of the Case 1 simulation, with TCE mass loaded within the rock matrix at
15 concentrations determined during Case 1. The concentration at each fracture interface is
16 then maintained at zero to promote back-diffusion of the TCE within the rock matrix.

1

2

3

4

5

6

7

8

9

10

11

12

13

14

Figure 3. Conceptual model for the Case 3 simulation. Fracture apertures of 0.0001 cm are assumed, as well as a superficial groundwater velocity (v) of 2 m per day through the fractures. The rate of TCE migration (mmole per day) through a single fracture plane in a 20 m wide zone perpendicular to groundwater flow) is simulated, as well as the TCE uptake into the rock matrix.

Figure 4. Simulation results from Case 1 showing TCE uptake into the rock matrix after 30 years of exposure.

Figure 5. Simulation results for Case 1 showing TCE porewater profiles into the rock matrix after 30 years of exposure. Porosity values are shown adjacent to the corresponding solid lines (no reaction), and the underlying dashed lines represent simulations where matrix reaction was included.

Figure 6. Simulation results for Case 2 showing TCE back-diffusion flux from the rock matrix after 30 years of loading. Simulated matrix porosities are identified, as well as whether matrix reaction was included.

Figure 7. Simulation for Case 3 showing TCE migration through an adjacent fracture plane (topmost solid line) compared to uptake into the overlying and underlying rock matrix. The simulations were performed using a matrix porosity of 0.12, and with (dashed line) and without (solid line) dechlorination reaction.