

SIMULATION OF ENHANCED REDUCTIVE DECHLORINATION FOR REMEDIATION OF TCE IN A FRACTURED CLAY SYSTEM: A NEW MODEL APPROACH AND APPLICATION TO FIELD SITE

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Summary. An innovative model is developed for Enhanced Reductive Dechlorination (ERD) of chlorinated solvents in a fractured glacial till. The model consists of three components: hydraulics, transport and degradation. The hydraulic component calculates the flow of water through a fractured clay till with interspersed sand lenses and stringers. The transport model couples diffusion dominated transport in the clay matrix, with advective-dispersive transport in the fractures and higher permeability sand lenses. The reactive model calculates sequential reductive dechlorination of TCE (trichloroethylene) to its daughter products DCE (dichloroethylene), VC (vinyl chloride) and ethene. The model employs a Monod kinetic description, with two degrading bacterial populations, and competitive inhibition. The model is applied to a field site located in Tommerup, Denmark, where ERD has been used to remediate a contamination of trichloroethylene located in a fractured clay till. The site is simulated using the model developed. Fracture geometry, site parameters and degradation rates are based on observations from the site and lab studies. The risk for drinking water is assessed and cleanup times are simulated using model results. The spatial extent of remediation and downstream impact of the technology is evaluated. Perspectives for enhanced bioremediation technologies in fractured clay systems are discussed.

1 INTRODUCTION

Chlorinated solvents are common subsurface contaminants and they represent a threat to groundwater. Contaminated sites are frequently located in fractured aquitards where contaminants slowly diffuse in the clay matrix and rapidly migrate through the fracture network. The presence of fractures creates preferential pathways for flow and transport and the contamination can impact an underlying aquifer for hundreds of years¹.

Because of the mass transfer limitation and the complexity of the processes involved in a clay/sand system, remediation of chlorinated solvents in low permeability porous media is challenging. The *Enhanced Reductive Dechlorination* (ERD) has been successfully applied in sandy aquifers for the degradation of dissolved phase TCE but the performance of the technology has not yet been fully investigated in fractured clay tills. For this reason a better

understanding of the processes governing the fate and transport of contaminants in such a geological setting both in natural and enhanced conditions is required.

Modelling flow and transport in discretely fractured porous media is quite complex and significant work has been done in this area over the last 20 years (e.g. Sudicky and McLaren², Slough *et al.*³). However none of these studies has addressed the issue of how degradation occurs in a fractured system and there is a lack of information on the development of efficient remediation strategies.

A Monod kinetic biodegradation model has been included in a fracture-matrix transport model in Chambon *et al.*⁴ to simulate the depletion of TCE by anaerobic dechlorination. In order to overcome the limitations associated with the simplified single fracture-matrix system considered in Chambon *et al.*⁴ an innovative modelling approach is presented here. A more sophisticated model has been developed for the simulation of flow, transport and degradation in a complex network of vertical and horizontal fractures.

The model is applied to a field site located in Tommerup, Denmark, where a full scale remediation by ERD has been conducted from 2006. The site is contaminated by approximately 25kg of trichloroethylene (TCE) located between 13 and 22m below ground surface in a fractured clay till. The contaminant is slowly leaching out of the clay into the underlying sandy aquifer where concentrations up to 350µg/l have been measured. The hot-spot is situated around 180m south-west of the Tommerup waterworks and monitoring at the site showed the migration of contaminants towards the water supply wells. In order to prevent an unacceptable impact on drinking water, specific degraders (*Dehalococcoides* bacteria) and electron donors (EOS[®] emulsion) were injected in 40 boreholes in the clay layer to facilitate the degradation of the contaminants. The model is applied to the field site using a detailed description of the subsurface and is used for risk assessment and ERD performance evaluation. Risk is assessed by evaluating the flux of contaminants reaching the aquifer and the transient impact on drinking water is estimated considering dilution in the water supply wells.

2 MATHEMATICAL FORMULATION

2.1 Groundwater flow

Assuming two-dimensional steady flow, incompressible fluid and saturated non-deformable fractured medium, the general equation for groundwater flow is⁵:

$$\frac{\partial}{\partial x_i} \left[K_{i,j} \frac{\partial h}{\partial x_j} \right] = 0 \quad i, j = 1, 2 \quad (1)$$

where h is the groundwater potential and $K_{i,j}$ is the hydraulic conductivity. Applying the Darcy equation the groundwater flux \mathbf{q} can be calculated at any point as $\mathbf{q} = -\mathbf{K} \cdot \nabla h$.

According to Berkowitz *et al.*⁶ if the fractures are assumed to be planar with aperture $2b$ and the hydraulic conductivity is supposed constant along the fractures, the steady state groundwater flow within a fracture can be described by the following equation:

$$\hat{K} \frac{d^2 \hat{h}}{dl^2} \cdot (2b) - q_n|_{I^-} + q_n|_{I^+} = 0 \quad (2)$$

where $\hat{h} = \hat{h}(l)$ is the hydraulic head in a fracture along the distance l and q_n is the normal flux across the fracture/matrix interfaces (I^- and I^+) assuming continuity with the groundwater head in the matrix. According to Bear⁵ the fracture hydraulic conductivity \hat{K} can be defined as $\hat{K} = \rho g (2b)^2 / (12\mu)$ where ρ , μ and g are, respectively, the fluid density, the fluid viscosity and the acceleration due to gravity.

2.2 Solute transport

In this work a late-time scenario is considered. The system is modeled long after contamination, the residual phase of contaminants is neglected and only dissolved and sorbed phases are taken into account. Two equations are used to model the solute transport in the fractured porous medium (one for the matrix and one for fractures) and coupled by the continuity of concentration at the fracture/matrix interface. Assuming linear sorption, the general reactive advection-dispersion equation for a porous medium is written as:

$$R_k \cdot \vartheta \frac{\partial C_k}{\partial t} = \nabla(\mathbf{D}_k \cdot \vartheta \cdot \nabla C_k) - \mathbf{q} \cdot \nabla C_k + \left(\frac{\partial C_k}{\partial t} \right)_{\text{deg}} \quad (3)$$

where C_k is the concentration of the compound k in the porous matrix, ϑ is the porosity and \mathbf{D}_k is the dispersion tensor. The retardation factor of compound k is defined as $R_k = 1 + \rho_b / \vartheta \cdot K_d$ where ρ_b is the bulk density and K_d is the equilibrium partition coefficient⁷. The hydrodynamic dispersion is described by⁵:

$$D_{i,j} \cdot \vartheta = (\alpha_l - \alpha_t) \cdot \frac{q_i \cdot q_j}{|q|} + \alpha_t \cdot |q| \cdot \delta_{i,j} + \tau \cdot \vartheta \cdot D_d \cdot \delta_{i,j} \quad i, j = 1, 2 \quad (4)$$

where α_l and α_t are, respectively, the longitudinal and transverse dispersivities, τ is the matrix tortuosity, D_d is the molecular diffusion coefficient and $\delta_{i,j}$ is the Kronecker delta.

The mass balance for the solute transport in a fluid-filled fracture is written as²:

$$\hat{R}_k \cdot \frac{\partial \hat{C}_k}{\partial t} = \frac{\partial}{\partial l} \left[\hat{D}_k \cdot \frac{\partial \hat{C}_k}{\partial l} \right] - \hat{q} \cdot \frac{\partial \hat{C}_k}{\partial l} + \frac{\Gamma_n|_{I^-}}{2b} - \frac{\Gamma_n|_{I^+}}{2b} + \left(\frac{\partial \hat{C}_k}{\partial t} \right)_{\text{deg}} \quad (5)$$

where $\hat{C}_k = \hat{C}_k(l, t)$ is the concentration of compound k in a fracture, \hat{R}_k is the retardation factor describing linear sorption onto the fracture surface and \hat{D}_k is the hydrodynamic dispersion coefficient for the fractures. The retardation factor in a fracture is defined as $\hat{R} = 1 + 2 \cdot \hat{K}_d / (2b)$, where \hat{K}_d is a fracture/surface distribution coefficient⁷. The dispersion coefficient for fractures is estimated as $\hat{D}_k = \hat{\alpha}_l \cdot \hat{q} + D_d$ where $\hat{\alpha}_l$ is the longitudinal dispersivity value defined for a fracture². The total flux across the matrix/fracture interface is calculated

according to Sudicky and MacLaren². For example, across the interface I , the flux of contaminant k is:

$$\Gamma_n|_{I^-} = \left[\mathbf{q}_n \cdot C_k - \mathbf{D}_n \cdot \mathcal{G} \frac{\partial C_k}{\partial n} \right]_{I^-} \quad (6)$$

where \mathbf{q}_n is the normal flux across the fracture walls and \mathbf{D}_n and $\partial C_k / \partial n$ are, respectively, the hydrodynamic dispersion and the concentration gradient perpendicular to the matrix/fracture interface.

2.3 Degradation

In the presence of specific degraders, an electron donor and anaerobic conditions, dissolved phase TCE is sequentially degraded to DCE, VC and ethene. This process is modelled using Monod kinetics considering inhibition between chlorinated ethenes⁴. Two groups of bacteria are taken into account: one group is able to degrade TCE (X_1) and one (*Dehalococcoides*) is responsible for the conversion of DCE to ethene (X_2). The degradation of the compound k generated as daughter product of the chlorinated ethene $k-1$ is described by the following equation:

$$\left(\frac{\partial C_k}{\partial t} \right)_{\text{deg}} = - \frac{\mu_k}{Y} \cdot \frac{C_k}{C_k + K_k \left(1 + \sum_{e \neq k} \frac{C_e}{K_{i,e}} \right)} \cdot X_i + \frac{\mu_{k-1}}{Y} \cdot \frac{C_{k-1}}{C_{k-1} + K_{k-1} \left(1 + \sum_{e \neq k-1} \frac{C_e}{K_{i,e}} \right)} \cdot X_j \quad (7)$$

where μ_k is the maximum growth rate of k [d^{-1}], X_i is the concentration of dechlorinating biomass [mg/l], Y is the specific yield [$\text{mg biomass/mg substrate}$], K_k is the half velocity coefficient of k [mg/l], and $K_{i,e}$ is the inhibition constant describing the competition between the chlorinated ethenes e and k . The degradation model parameters are based on the experimental results presented in Chambon *et al.*⁴.

As discussed in Lima and Sleep⁸ migration and growth of bacteria in the clay matrix may be limited by the small pore size. Limited field data from the site shows that degradation is highly variable, occurring mostly in the sand lenses, in fractures and in a narrow zone around them⁴. In this work degradation is limited to fractures and a reactive zone located in the clay matrix according to the scenarios described in the next section.

2.4 Numerical formulation

As presented in Sudicky and MacLaren², the fracture network is designed by superimposing one-dimensional line elements onto the triangular element mesh. Line elements and triangular elements share common nodes and the continuity of potential head and concentration at the fracture-matrix interface is automatically satisfied. As a consequence the fluxes across the fracture/matrix interface are accounted for naturally and the calculation of the terms $q_n|_I$ and $\Gamma_n|_I$ in equations (2) and (5), respectively, are unnecessary.

The model is solved using COMSOL Multiphysics, a generic partial differential equation solver based on the finite element method. The model discretization consists of 339214 triangular elements with localized mesh refinement at the fracture/matrix interface.

3 RESULTS AND DISCUSSIONS

The numerical model presented above has been applied to the Tommerup site using a cross section of the contaminated area. As shown in **Figure 1** the subsurface is divided into five hydrostratigraphic units. The geological setting is characterized by two fractured clay layers (middle clay and lower clay) divided by a hummocky sandy layer (middle sand). The regional groundwater is flowing towards north-east in the primary aquifer located around 40m below ground surface. The hot spot is located in the middle clay where a concentration of TCE up to 16000 $\mu\text{g/l}$ has been measured. Because the contamination is situated in the middle clay the unsaturated zone is neglected in the simulation. Fracture geometry and hydraulic parameters (porosity, hydraulic conductivity, etc.) are based on observations from the site.

The hydraulic model shows that the groundwater flow is essentially horizontal in the sandy layers while the vertical component of flow is dominant in the low permeability layers. The system is controlled by the regional groundwater: the flux entering the system in the primary aquifer is 96% of the total inflow, recharge at the top of the middle clay represents the remaining 4%. Secondary groundwater flows in the middle sand and amounts to only 1% meaning that most of the water infiltrating from the top reaches the primary aquifer. As expected fractures are preferential conduits for flow and 75% of the water infiltrating in the middle clay reaches the layer below through the fractures network. The permeability contrast between the fractures and the clay matrix is five orders of magnitude (the permeabilities being $3.75 \times 10^{-4} \text{ m/s}$ and $1.98 \times 10^{-9} \text{ m/s}$, respectively) and the fully penetrating fractures act as a collector of groundwater and a preferential pathway for contaminant transport.

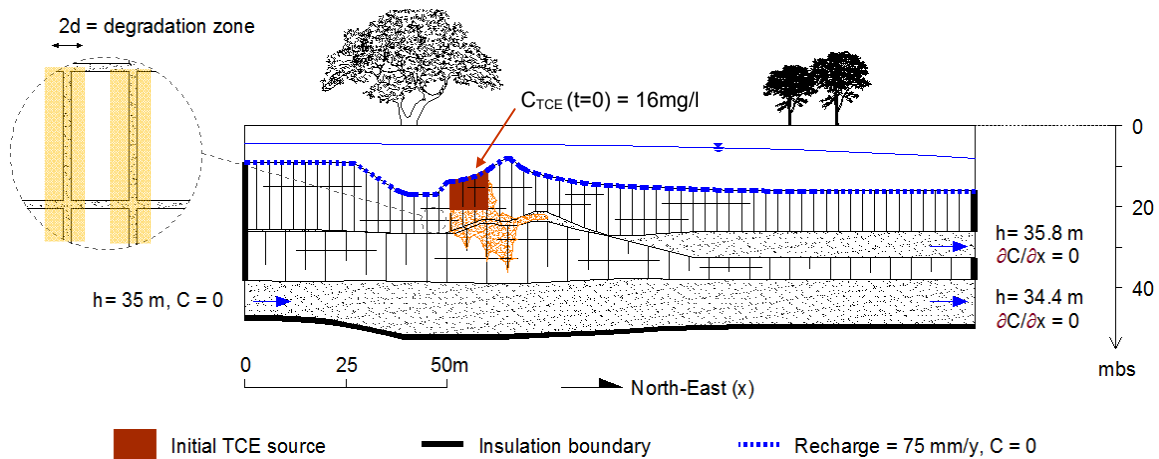


Figure 1: Conceptual model. The model includes, from top to bottom, five geological units: upper glacial till, middle clay (MC), middle sand (MS), lower clay (LC) and primary aquifer (PA).

The development of the TCE concentration with time is illustrated in **Figure 2**. Clay layers are diffusion controlled and contaminants slowly migrate towards the primary aquifer. The TCE contamination trapped in the middle clay is channeled into fractures where the high pore water velocity rapidly transports contaminants by advection. High concentration gradients develop at the fracture/matrix interface increasing the diffusive flux and speed up the spreading of TCE. The simulated plume of TCE at 30 years is comparable with the field measurements before remediation and it is used as initial condition for applying degradation to the transport model.

Degradation is assumed to occur only in the fractures in the middle clay where substrate and specific degraders were injected. In order to include the presence of a reactive zone surrounding the fractures and investigate the influence of possible high permeability regions in the clay matrix, a degradation zone of variable width around each fracture is included in the model. Different scenarios are considered: scenario *a* examines the spreading of contaminants in the absence of degradation (natural conditions), scenario *b* includes degradation in the fractures and in a degradation zone 20cm wide and scenarios *c* and *d* consider dechlorination occurring in a degradation zone 2 and 3m wide, respectively. In scenario *d* the reactive zone width is equal to the fracture spacing and degradation takes place in the whole clay matrix. This assumption is in contrast with the field data but it allows consideration of a “best-case” scenario.

The model is used to evaluate the performance of remediation and assess the risk posed to drinking water in natural and enhanced conditions. In **Figure 3a** the mass reduction of chlorinated ethenes for the different scenarios is presented. The results show that in natural conditions it takes more than 100 years for contaminants to leach out of the middle clay.

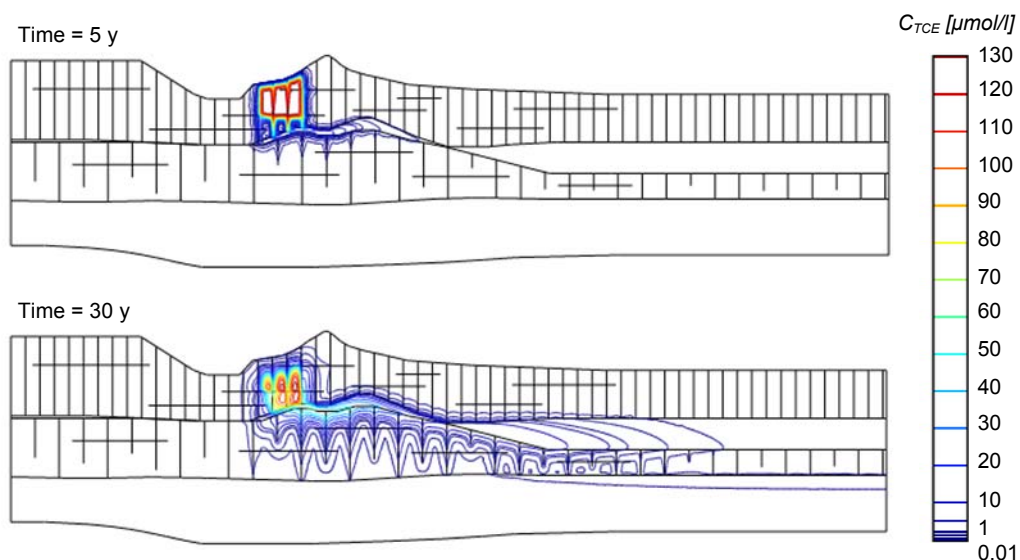


Figure 2: Change in trichloroethene distribution (aqueous concentration in $\mu\text{mol/l}$) with time.

The simulations reveal that a large amount of contaminants has already spread in the middle sand and lower clay before the start of remediation (around 45%). Then, in the “best-case” scenario, remediation cuts the leaching time from 70 years down to 20 years: TCE is degraded but leaching of contaminants still occurs because of the formation of its daughter products (DCE and VC). This means that dechlorination actually remediates the hot spot in the middle clay but the lower clay may act as a new source of contamination.

The downstream impact of the contamination is evaluated by estimating the concentration of chlorinated ethenes impacting the Tommerup waterworks. The fluxes of contaminants leaving the system are calculated by integrating the total flux across the north-east boundary. The downstream waterworks is modelled as a single pumping well and the flux of contaminant reaching the well J_{well} [kg/y] is assumed equal to the flux leaving the system. The predicted concentration at the water supply well is subsequently calculated as $C_{well} = J_{well}/Q_{well}$ where Q_{well} is the pumping rate of the waterworks [m^3/y]. The simulations show that the contamination would pose a risk to the water supply wells if remediation had not been started in 2006 with the guideline concentration for chlorinated ethenes being exceeded both in scenario *a* (Natural conditions) and *b*. Remediation decreases contaminant impact only in scenario *c* and *d*: the guideline values are not exceeded but contaminants are not fully degraded. **Figure 3b** illustrates that even in the “best-case scenario” the contamination will impact the water supply well for more than 100 years. The use of bioremediation results in incomplete dechlorination which causes a plume of VC that can pose an increased risk to the drinking water. The VC never exceeds the guideline values but concentrations up to 0.1 $\mu\text{g/l}$ are expected. These results suggest that anaerobic dechlorination is a feasible remediation strategy only if degradation can occur in the clay matrix. The efficiency of remediation is affected by the formation of daughter products and the complete dechlorination of TCE to ethene is found to be a key issue for an efficient clean-up.

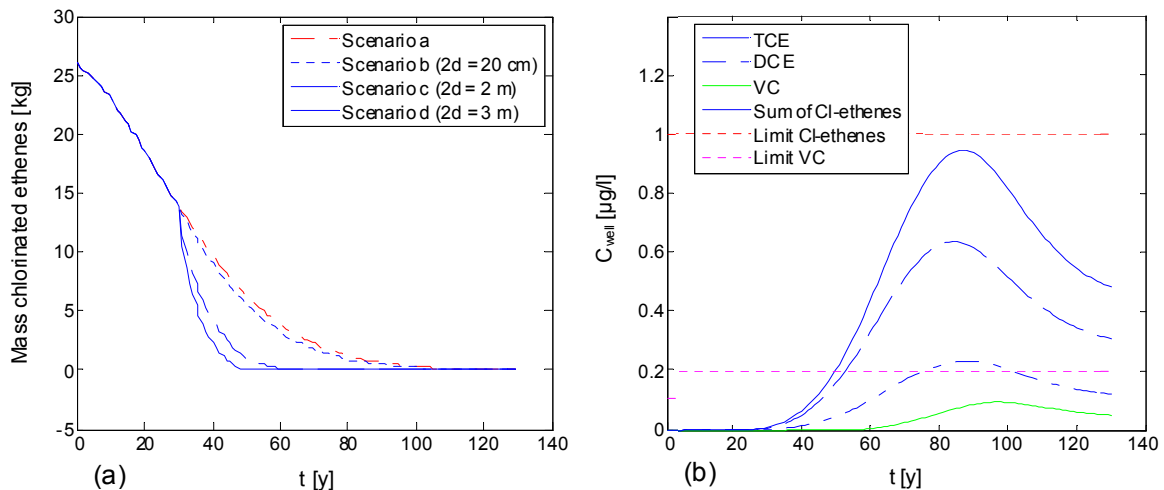


Figure 3: Mass reduction of chlorinated ethenes in the middle clay for the different simulated scenarios (a). Estimated concentration [$\mu\text{g/l}$] of chlorinated ethenes at the water supply wells in scenario *d* (b).

4 CONCLUSIONS

A comprehensive modelling tool has been developed for the simulation of groundwater flow, contaminant transport and reductive dechlorination in a fractured clay/sand system. The model overcomes the limitations associated with the modelling approach presented in Chambon *et al.*⁴ and the dechlorination processes are coupled for the first time with flow and transport in a complex network of fractures.

The model is shown to be a useful tool for risk assessment and remediation performance evaluation in fractured clay tills. The model shows that reductive dechlorination may greatly reduce the mass of contaminants if acting in the whole matrix but the impact of remediation is small if degradation is limited to narrow reactive zones. At the Tommerup site incomplete dechlorination is observed. Model results show that contaminants are not completely degraded and VC reaches the water supply wells in concentrations up to 0.1µg/l as a consequence of the remedial action. Note however that the fracture network considered in this work is a model simplification. Heterogeneities existing at the site such as sand lenses and stringers are expected to play a key role in the remediation process and they should be included in the model. A deeper understanding of the interaction between the geological setting and the degradation processes is required to design an efficient remediation strategy.

Further development of the model will focus on modelling biomass injection and spreading in order to better understand the spatial extent of dechlorination. Future research should focus on the characterization of complex network of fractures and sand stringers.

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