

# Moffett Field Funnel and Gate TCE Treatment System: Interpretation of Field Performance using Reactive Transport Modeling

Steve Yabusaki, Pacific Northwest National Laboratory  
Kirk Cantrell, Pacific Northwest National Laboratory  
Bruce Sass, Battelle Columbus Laboratories

**Abstract.** *A multicomponent reactive transport simulator was used to understand the behavior of chemical components, including TCE and cis-1,2-DCE, in groundwater transported through the pilot-scale funnel and gate chemical treatment system at Moffett Field, California. Field observations indicated that zero-valent iron emplaced in the gate to effect the destruction of chlorinated hydrocarbons also resulted in increases in pH and hydrocarbons, as well as decreases in  $E_H$ , alkalinity, dissolved  $O_2$  and  $CO_2$ , and major ions (i.e., Ca, Mg, Cl, sulfate, nitrate). Of concern are chemical transformations that may reduce the effectiveness or longevity of the iron cell and/or create secondary contaminants. A coupled model of transport and reaction processes was developed to account for mobile and immobile components undergoing equilibrium and kinetic reactions including TCE degradation, parallel iron dissolution reactions, precipitation of secondary minerals, and complexation reactions. The model reproduced solution chemistry observed in the iron cell using reaction parameters from the literature and laboratory studies. Mineral precipitation in the iron zone, which is critical to correctly predicting the aqueous concentrations, was predicted to account for up to 3 percent additional mineral volume annually. Interplay between rates of transport and rates of reaction in the field was key to understanding system behavior.*

**Description.** A pilot-scale funnel and gate treatment system using zero-valent iron ( $Fe^0$ ) to engineer TCE destruction was installed at Moffett Field, California. While it is clear that  $Fe^0$  can be effective in transforming chlorinated hydrocarbons to benign byproducts, there are many other components in the groundwater that will also be affected by the presence of  $Fe^0$ . Of concern are reactions that could adversely affect the long-term performance of the iron barrier or create secondary contaminants. Since the solution chemistry (e.g., pH,  $E_H$ , alkalinity, dissolved gases, major cations and anions) of groundwater will vary from site to site, the long-term performance of a “standard” implementation of an iron barrier may also be expected to vary. Understanding the impact of the local groundwater chemistry on the performance of the iron barrier provides opportunities to assess the feasibility of the technology and adapt the engineering design to site-specific conditions.

After installation of the funnel and gate in April 1996, a very comprehensive field data collection effort measured chlorinated volatile organic compounds (CVOCs), hydrocarbons, major ions, dissolved gases, temperature,  $E_H$ , pH, and alkalinity. Based on the observed changes to the groundwater chemistry from the aquifer through the iron zone, the following aqueous species were modeled:

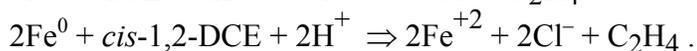
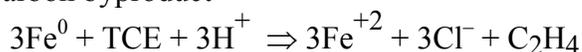
*Organic chemistry:* TCE, cis-1,2-DCE,  $CH_4$ ,  $C_2H_4$ ,  $Cl^-$   
*Carbonate chemistry:*  $H^+$ ,  $OH^-$ ,  $HCO_3^-$ ,  $CO_2(aq)$ ,  $CO_3^{2-}$

Major metal ions:  $\text{Ca}^{+2}$ ,  $\text{Mg}^{+2}$

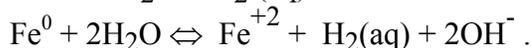
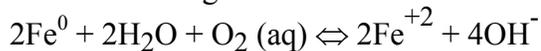
Redox couples:  $\text{Fe}^{+3}/\text{Fe}^{+2}$ ,  $\text{O}_2(\text{aq})/\text{H}_2\text{O}$ ,  $\text{H}_2\text{O}/\text{H}_2(\text{aq})$ ,  $\text{SO}_4^{-2}/\text{HS}^-$ ,  $\text{NO}_3^-/\text{NH}_4^+$

Metal complexes:  $\text{FeOH}^{+2}$ ,  $\text{Fe}(\text{OH})_2^+$ ,  $\text{Fe}(\text{OH})_3(\text{aq})$ ,  $\text{Fe}(\text{OH})_4^-$ ,  $\text{FeOH}^+$ ,  $\text{Fe}(\text{OH})_2(\text{aq})$ ,  $\text{Fe}(\text{OH})_3^-$ ,  $\text{FeCO}_3(\text{aq})$ ,  $\text{FeHCO}_3^+$ ,  $\text{CaHCO}_3^+$ ,  $\text{CaCO}_3(\text{aq})$ ,  $\text{MgHCO}_3^+$ ,  $\text{MgCO}_3(\text{aq})$ ,  $\text{CaSO}_4(\text{aq})$ ,  $\text{MgSO}_4(\text{aq})$ ,  $\text{FeSO}_4(\text{aq})$

Based on equilibrium modeling analyses, the following secondary minerals were included in the model:  $\text{Fe}(\text{OH})_3(\text{am})$ ,  $\text{Fe}(\text{OH})_2(\text{am})$ ,  $\text{FeS}(\text{am})$ , brucite [ $\text{Mg}(\text{OH})_2$ ], siderite ( $\text{FeCO}_3$ ), aragonite ( $\text{CaCO}_3$ ), and green rust [ $\text{Fe}_4^{\text{II}}\text{Fe}_2^{\text{III}}(\text{OH})_{12}[\text{SO}_4\cdot 3\text{H}_2\text{O}]$ ]. We chose to model the degradation of TCE and *cis*-1,2-DCE using the beta elimination pathway as a bulk first-order kinetic reaction that includes the oxidation of iron in addition to the transformation of the chlorinated organics to undifferentiated hydrocarbons and chloride. In this case, we use ethene as the nominal hydrocarbon byproduct



In addition to the CVOC-induced iron oxidation in these reactions, there are two other parallel iron reactions involving the reduction of dissolved oxygen and reduction of water:



The rate constant for the parallel iron dissolution reaction involving the reduction of water was derived from a column study using the granular iron from Peerless Metal Powders, Inc. and Moffett Field groundwater. Rate laws for the seven secondary minerals are based on reversible mineral reaction rates from an earlier study of a reactive iron permeable barrier at the U.S. Coast Guard Support Center near Elizabeth City, North Carolina. Note that we have adopted their respective rates for the calcium, magnesium, and sulfur sinks to the aragonite, brucite, and FeS/green rust minerals used in our model.

The model uses a one-dimensional representation of the gate that includes the upgradient pea gravel zone (0.6 m) and the reactive iron cell (1.8 m). The downgradient pea gravel zone was neglected because of contamination from the downgradient aquifer. The system is discretized into 60 grid cells of uniform size (0.04 m). The estimated range of likely pore velocities was 0.06 – 0.6 meters per day, which is equivalent to a Darcy flux range of 0.04 – 0.4 meters per day (based on iron porosity of 0.66). Dispersion and diffusion were assumed to be negligible. The boundary condition and the initial conditions for the model are based on the April 1997 sampling event.

**Results.** With  $\text{O}_2(\text{aq})$  nearly absent and CVOCs at relatively low concentrations in the background aquifer, the reduction of water by iron oxidation is the dominant iron corrosion reaction as well as the principal mechanism for elevating pH and lowering the redox potential in the iron cell at Moffett Field. pH and redox conditions control the behavior of many of the chemical components in the iron cell; consequently, any attempt to reproduce spatially variable concentrations of chemical components in the iron cell must first consider the interplay between

this relatively slow hydrolysis reaction and the rate of transport, which controls the residence time in the iron cell.

The modeled TCE concentrations reflect the rapid degradation observed in the field, supporting, to some degree, the TCE degradation rate derived in the laboratory. For *cis*-1,2-DCE, the laboratory rate used in the model appears to be high as the *cis*-1,2-DCE is predicted to be eliminated after 0.1 meter in the iron cell compared with 0.5 meters observed in the field. Relative to the overall system of chemical components, the CVOC chemistry has minimal impact.

The Darcy flux of 0.04 meters per day in conjunction with the hydrolysis rate from the laboratory ( $5 \times 10^{-12}$  mol/m<sup>2</sup>/s) was clearly consistent with the observed behavior of pH, alkalinity, Mg, sulfate, and nitrate. However, this should be a concern because the pre-construction Darcy flux in the vicinity of the permeable barrier was estimated to be 0.064 meters per day. The capture zone for the funnel and gate system is likely to be quite small if that is the case.

Mineral precipitation in the iron cell could potentially shorten the longevity of the reactive barrier and thus, is of concern to the future deployment of similar in situ chemical treatment technologies. In the initial part of the iron zone there is a net reduction in porosity of 0.015-0.03 each year, principally due to the precipitation of aragonite and siderite. If the precipitation is confined only to the entrance of the iron zone, there could be significant reduction in porosity and permeability over many years that would result in the buildup of head on the upgradient side of the iron barrier. Furthermore, the predicted volume of outgassed hydrogen is significant and it is possible that hydrogen gas bubbles are occupying a portion of the void space, resulting in a reduction of permeability.

The modeling shows ammonia to be a thermodynamically favored component that is consistent with the disappearance of nitrate in the iron cell and the lack of significant change to the N<sub>2</sub>(aq) concentrations. It should be considered for field sampling analyses at iron barrier sites whenever nitrate is known to be present.

Using 36 chemical components and 8 minerals to model a system may appear to be too complicated for routine engineering of an in situ reactive barrier; however, the model was built up in a straightforward fashion from the observed behavior in the system. Because of the systematic coupling of transport and reactions for multiple chemical components, simply adjusting precipitation rates to match the disappearance of certain ions will not necessarily be consistent with other measured properties of the reactive cell (e.g., pH, alkalinity). Furthermore, the reaction rates are operating within the context of flowing groundwater. The character of spatial variations in species concentrations in the reactive cell are the direct result of the interplay between rates of transport and rates of reaction.

Engineered in situ reactive cells are highly amenable to reactive transport modeling. The system being modeled is better controlled and characterized than most environmental situations. In this case, the chemical components and their concentrations entering the reactive cell were comprehensively studied and Fe<sup>0</sup> was initially the only mineral in the cell.