

# Challenges in modeling evolving reactivity: Examples from groundwater contamination and remediation studies

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## 1 INTRODUCTION

Significant advances have been made in recent years with respect to the modeling of complex reactive transport systems. Increased computer resources now allow the simulation of two- and three-dimensional problems involving a large number of unknowns and various geochemical processes. The parameter demand for these simulations is significant, but numerical models have nevertheless proven useful to test and investigate conceptual models in a quantitative manner, provided adequate aqueous, gaseous and mineralogical data is available. One of the remaining challenges focuses on the issue of evolving reactivity, which can manifest itself in changing (bio)-geochemical reaction rates or changes in the mixing characteristics of pore water and/or NAPL's within an aquifer. If part of the objective of a modeling study is to investigate the evolution of a system, evolving reactivity often needs to be taken into account. Here, we utilize two examples involving the remediation of contaminated groundwater to highlight the importance of the consideration of evolving reactivity, when modeling long-term system evolution. All simulations presented were conducted using the multicomponent reactive transport model MIN3P (Mayer et al., 2002).

## 2 PERMEABLE REACTIVE BARRIERS

### 2.1 *Elizabeth City Site – North Carolina*

Multicomponent reactive transport modeling was conducted for the permeable reactive barrier at the Coast Guard Support Center near Elizabeth City, N.C (Mayer et al., 2001). The zero-valent iron barrier was installed to treat groundwater contaminated by hexavalent chromium and chlorinated solvents (Blowes et al., 1999). Among the simulated processes were contaminant destruction and the reduction of other electron acceptors causing the consumption of the treatment material, and the precipitation of secondary minerals.

### 2.2 *Simulation Results*

The model results were able to illustrate the removal of Cr(VI) and the chlorinated solvents by the reactive barrier and demonstrate that reactions other than the remediation reactions most significantly affect the water chemistry in the barrier. In particular sulfate reduction and iron corrosion appear to control the evolution of the pore water while passing through the treatment system. The associated pH increase causes the precipitation of significant amounts

of carbonate, hydroxide and sulfide mineral phases (Figure 1). The original simulation results indicate that secondary mineral formation has the potential to decrease the porosity in the barrier over the long term and suggest that the precipitation of minerals is concentrated in the up-gradient portion of the barrier (Figure 1). Decreasing iron reactivity due to passivation was not accounted for in this study. However, it was hypothesized that passivation causes less depletion of the treatment material and precipitation of secondary minerals in the inflow area than simulated (Mayer et al., 2001).

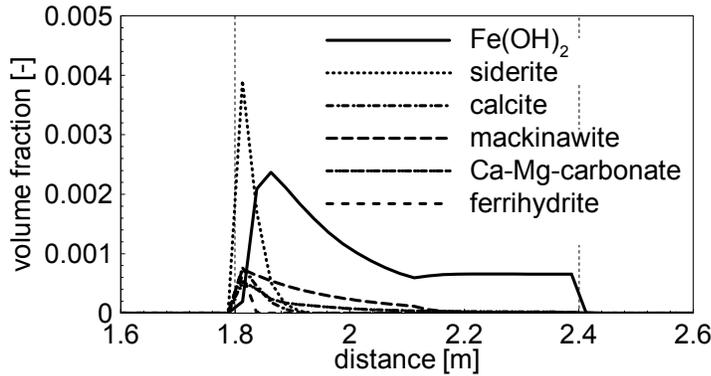


Figure 1: Simulated volume fractions of secondary minerals in reactive barrier after 240 days

### 2.3 Comparison to Field Observations

The simulations presented above have been continued to 4 years of barrier operation and the accumulated inorganic carbon (Figure 2) and sulfur (not shown) has been compared to measured accumulations extracted from cores (Wilkin et al., 2002). Although observed and simulated results compare well in general, the observed data shows a near continuous mass distribution of precipitate within the first 5-6 cm of the barrier, while the simulated results show a continuous decrease in precipitate accumulation along the flowpath. The observed data indicate that some passivation may have taken place, which was not accounted for by the model.

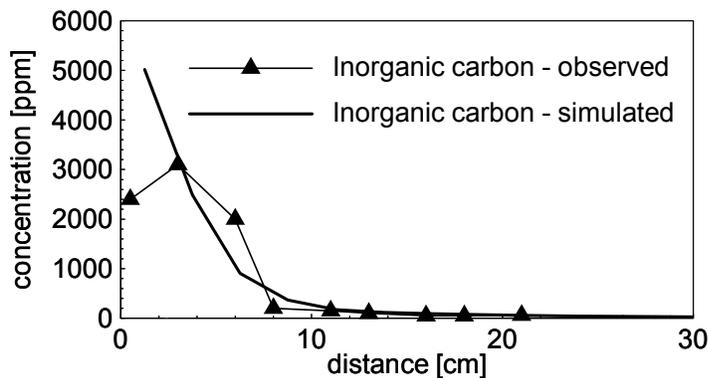


Figure 2: Simulated and observed inorganic carbon contents after 4 years (Data from Wilkin et al., 2002)

### 2.4 Long term column studies

Currently, column studies are conducted at the University of Waterloo (Jeen, Blowes and Gillham, work in progress), which confirm the hypothesis that passivation due to carbonate

mineral precipitation is occurring. These observations highlight the need to account for evolving reactivity in reactive transport models. Other processes that may affect system reactivity in permeable reactive barriers include the formation of hydrogen gas bubbles, or the depletion of the more reactive portion of treatment materials (e.g.: Herbert et al., 2000).

### 3 IN SITU CHEMICAL OXIDATION USING PERMANGANATE

#### 3.1 *Connecticut Site*

Three-dimensional simulations of permanganate oxidation of chlorinated solvents are being conducted for a site located near Hartford, Connecticut. At this site, in-situ chemical oxidation of the DNAPL using potassium permanganate was tested over a seven month period in 2000 and 2001 (Stewart, 2002). The oxidant delivery methodology was based on the inject-and-leave method (Nelson et al., 2000) and relied on two sequential injections of potassium permanganate solutions with concentrations approaching aqueous solubility. The simulations account for the movement of variable density fluids, water table mounding, and evolving aqueous permeability due to the dissolution of non-wetting fluids and the dissolution/precipitation of mineral phases. The geochemical reaction network includes kinetic expressions describing dissolution and precipitation of mineral phases, DNAPL dissolution, and the intra-aqueous oxidation reaction between permanganate and dissolved TCE. Mineral phases in the simulations include calcite and manganese oxides, and organic carbon is used to simulate the oxidant demand of the aquifer. The spread of the oxidant, and the reaction between the oxidant and TCE was monitored over time using an array of multilevel monitoring points (Stewart 2002), which is available for comparison with the simulated results.

#### 3.2 *Simulation Results*

To illustrate the problem, simulated data for aqueous permanganate, and TCE are shown in Figure 3. An initial evaluation of model performance is being performed by comparing observed and simulated data for aqueous permanganate, chloride, and dissolved TCE. The data indicate the model accurately depicts the lateral extent of the spread of permanganate, and generally predicted aqueous chloride concentrations within a factor of 2 of the field data. However, the permanganate data indicated that the model generally under-predicting the persistence of the permanganate in the immediate vicinity of the aquitard contact, where NAPL is present.

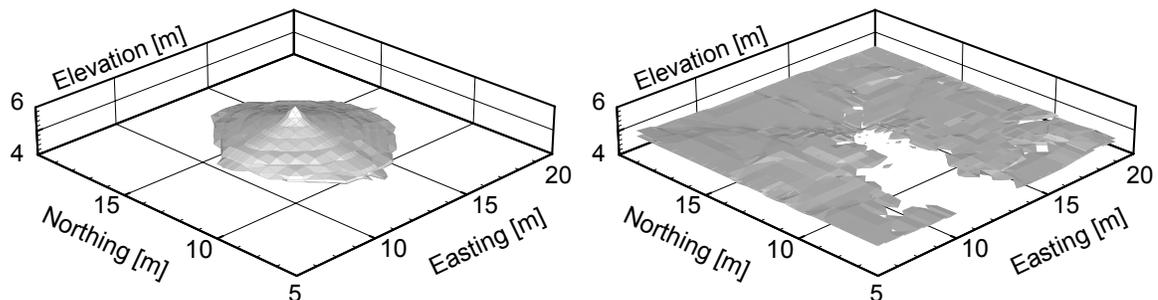


Figure 3: 1 g/L permanganate iso-contour surface (left) and 1 percent DNAPL volume fraction iso-contour surface (right) at 14 days following initial permanganate injection. Injection point location was 12.5 m northing, 12.5 m easting, and elevation 5.6 meters

There are several factors that may affect persistence of permanganate, or in other words system reactivity, most of which are related to the precipitation of manganese oxides.  $MnO_2$ -precipitation may result in a permeability decrease, which may be counteracted by carbonate mineral dissolution. The precipitation of manganese oxides may also affect system reactivity (limiting the dissolution of both NAPL and carbonate minerals). These results suggest that at least some of these processes need to be included in the model formulation to allow a more realistic simulation of in-situ chemical oxidation.

#### 4 CONCLUSIONS

Examples from groundwater remediation are particularly useful to illustrate the effects of evolving reactivity due to rapid reaction rates, a high degree of disequilibrium, steep geochemical gradients, and pronounced geochemical changes. However, many of these conclusions are also valid for large scale reactive transport studies, even in pristine aquifers. Processes of importance include decreases in reactivity due to the formation of surface coatings and passivation (Wunderly et al., 1996, Mayer et al., 2002), increase in reactivity due to generation of surface sites (e.g.: Postma and Appelo, 1998), but also permeability changes due to changes in aqueous phase saturation as a result of NAPL dissolution or gas formation, which may result in hydraulic exclusion. Some of these processes have been considered previously in reactive transport models, but to date have not been included in a comprehensive manner. This limits the applicability of reactive transport models to study system evolution and to use these models in a predictive sense. Reasons for the lack of implementing evolving reactivity include the inherent complexity of the interacting processes, the difficulty of quantifying the processes that control reactivity, and their often site-specific nature.

#### REFERENCES

- Blowes, D. W., Gillham, R. W., Ptacek, C. J., Puls, R. W., Bennett, T. A., Bain, J. G., Hanton-Fong, C. J., and Paul, C. J., 1999. An in-situ permeable reactive barrier for the treatment of hexavalent chromium and trichloroethylene in groundwater: Vol. 2: Performance monitoring, U. S. Environmental Protection Agency, EPA/600/R-99/095b.
- Herbert, R.B., Benner, S.G. and Blowes, D.W. 2000, Solid phase iron - sulfur geochemistry of a reactive barrier for treatment of mine drainage, *Appl. Geochem.*, 15, 1331 - 1343.
- Mayer, K. U., D. W. Blowes, and E. O. Frind, 2001. Reactive transport modelling of groundwater remediation by an in-situ reactive barrier for the treatment of hexavalent chromium and trichloroethylene, *Water Resour. Res.*, 37:3091-3103.
- Mayer, K. U., E. O. Frind, and D. W. Blowes, 2002. Multicomponent Reactive Transport Modeling in Variably Saturated Porous Media Using a Generalized Formulation for Kinetically Controlled Reactions, *Water Resour. Res.*, 38, doi: 10:1029/2001WR000862.
- Nelson, M.D., Parker, B.L., Al, T.A., Cherry, J.A. and Loomer, D. 2001. Geochemical reactions resulting from *in situ* oxidation of PCE DNAPL by  $KMnO_4$  in a sandy aquifer. *Env. Sci. Technol.*, 35:1266-1275.
- Postma, D, and Appelo, C. A. J., 2000. Reduction of Mn-oxides by ferrous iron in a flow system: column experiment and reactive transport modeling, *Geochim. Cosmochim. Acta*, 64:1237-1247.
- Stewart, C., 2002. Density-driven permanganate solution delivery and chemical oxidation of a thin trichloroethylene DNAPL pool in a sandy aquifer, M.Sc Thesis, University of Waterloo, Ontario, Canada.
- Wilkin, R. T., Puls, R. W., and Sewell, G. W., 2002. Long term performance of permeable reactive barriers using zero-valent iron: An evaluation at two sites. U.S. Environmental Protection Agency Research Brief. EPA/600/S-02/001.
- Wunderly, M. D., Blowes, D. W. and Frind, E. O. and Ptacek, C. J., 1996. Sulfide mineral oxidation and subsequent reactive transport of oxidation products in mine tailings impoundments: A numerical model, *Water Resour. Res.*, 32:3173-3187