

Evolution of reaction zones in reactive barriers consisting of calcite and glass beads

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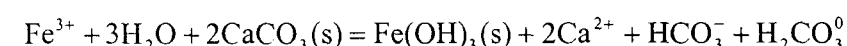
<요약문>

Two-dimensional modeling studies using TOUGHREACT were conducted to investigate the coupling between flow and transport developed as a consequence of differences in density, dissolution/precipitation, and medium heterogeneity. The model includes equilibrium reactions for aqueous species, kinetic reactions between the solid phases and aqueous constituents, and full coupling of porosity and permeability changes resulting from precipitation and dissolution reactions in porous media. Generally, the evolutions in the concentrations of the aqueous phase are intimately related to the reaction-front dynamics. Plugging of the medium contributed to significant transients in patterns of flow and mass transport.

Key word: reactive barrier, calcite, porous medium, geochemical modeling

1. 서론

Often, waters from landfills or mining operations contain elevated concentrations of iron and other metals at low pH. A promising approach to minimize groundwater contamination by acidic metallic compounds is the use of calcareous reactive barriers. For example, in a ferric-calcareous barrier, hydrolysis of Fe³⁺ generates H⁺, which is neutralized by reaction with calcite, causing the formation of ferric oxyhydroxide. Because iron oxyhydroxides form hydrous aggregates capable of reducing porosity and permeability, their precipitation along the front of a contaminant plume is potentially useful in slowing the spread of the contaminant. According to Fryar and Schwartz (1998), the following equation describes the reaction between the acidic, Fe³⁺-bearing solution and calcite:



The main objective of this study is to evaluate the impact of dissolution/precipitation and heterogeneity on mass transport and reaction zone development in a two-dimensional reactive barrier system.

2. 본 론

In this study, chemical evolution within a ferric-calcareous barrier was examined using a two-dimensional model. Specifically, we demonstrated the coupled effects of variable density fluid flow and heterogeneous reactive mass transport and their influence on the reaction front development. The aqueous species involved in the reaction are H^+ , OH^- , Cl^- , Na^+ , Fe^{3+} , ClO_4^- , Ca^{2+} , $H_2CO_3^0$, HCO_3^- and CO_3^{2-} , and the mineral phases are calcite and $Fe(OH)_3(s)$.

The numerical simulations in this study take place in both homogeneous and heterogeneous, saturated porous media. The simulation domain measures 1.82m long and 0.62m high, and 0.10m deep, providing a total volume and inflow area of $0.1133 m^3$ and $0.062 m^2$, respectively. The simulation domain is evenly filled with coarse-grained glass beads (0.75 mm) mixed with 0.3 wt% calcite. Assuming that the effects of calcite on the porosity and hydraulic conductivity are negligible, the hydraulic conductivity values for the 0.75 mm glass beads are estimated to be $4.20 \times 10^{-2} cm/sec$. The inflow rate was fixed at 26.4 ml/min, providing linear velocities of 2.56 cm/hr. An acidic (pH ~ 2.5) contaminant solution consisting of 2000 mg/l NaCl (conservative tracer) and 300 mg/l $Fe(ClO_4)_3$ (reactive tracer) is injected at 6.50 ml/min at $x = 0.2m$ and $z = -0.2 m$.

The simulations were carried out using the non-isothermal reactive geochemical transport code TOUGHREACT (Xu and Pruess, 1998). A computational mesh was created for the model domain using 3,552 elements (74 columns x 48 rows). Modeling parameters are summarized in Table 1. Total concentrations for the resident, inlet, and injection fluids are listed in Table 2. The boundaries at the top and bottom of the tank are impermeable. The elements of the right boundary for flow are assigned constant pressures estimated at hydrostatic condition, while the elements on the left boundary for flow are assigned either a constant flux or constant pressures depending on specific problems. Boundary conditions for concentrations are assigned as a Dirichlet boundary at the left side of the tank, and a free-exit boundary at the right. All other concentration boundaries are assigned as no-flux. Dissolved concentrations are assigned initial values that are in equilibrium with calcite throughout the domain. The initial pH of the system is 8.2 and the density is $998.2 kg/m^3$, whereas the injection source concentration has a pH of 2.3 and a density of $999.7 kg/m^3$.

Chemical heterogeneity of a porous medium influences the pattern of reactions in a highly complex and nonlinear manner. Heterogeneity in permeability is another factor that influences the pathway of reactive plumes. For instance, local heterogeneity can perturb the interface and promote the formation of fingering. Three different cases were examined: homogeneous case, chemically heterogeneous case, and physically heterogeneous case. For the homogeneous case, the porous medium was assumed both chemically (calcite content) and physically (permeability) homogeneous. For the heterogeneous cases, spatially variable random fields for calcite content and for permeability were generated using the Fourier spectral technique of Robin et al. (1993).

Figures 1- 3 show the profiles for permeability, $Fe(OH)_3(s)$, Fe^{3+} , pH, and Cl^- for the homogeneous case, chemically heterogeneous case, and the physically heterogeneous case, respectively. The coupling between geochemical reactions caused by the injection of $Fe(OH)_3$ solution and the density-dependent flow influence the reactions and dissolved plume migration in a complicated manner. Although the main migration direction of the dissolved plume is controlled by the ambient flow of water,

density-driven flow related to the large concentration of dissolved ions in the injected source water caused significant vertical movement to develop in both the dissolved plume and the reaction zone. The reaction zones defined as active precipitation and dissolution propagated much more slowly than the dissolved plume. While the non reactive species (Cl^- , Na^+ , ClO_4^- , Ca^{2+}) spread beyond the reactions zone, the reactive species (Fe^{3+}) is effectively retained in the reaction zone and moves much slowly. The final shape of the reaction zone was significantly influence by the geochemical reactions.

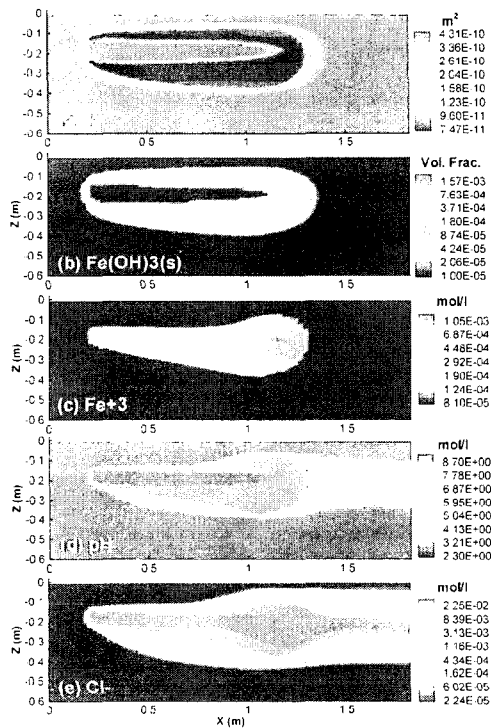


Figure 1. Profiles for the homogeneous case at 38 days: (a) permeability, (b) $\text{Fe}(\text{OH})_3(\text{s})$, (c) Fe^{3+} , (d) pH, and (e) Cl^- .

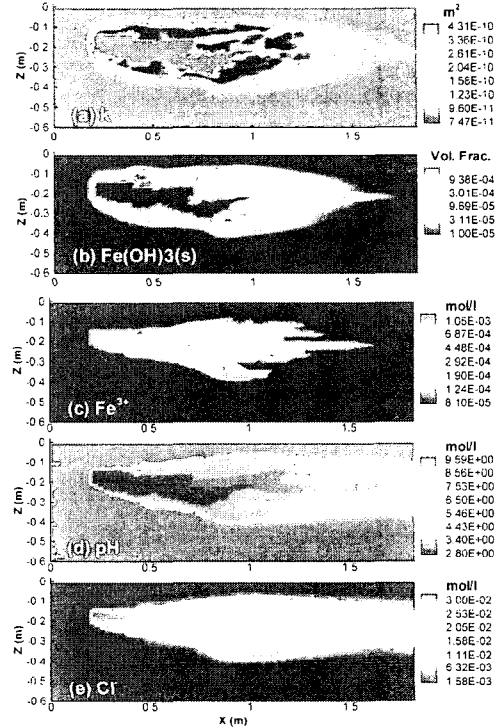


Figure 2. Profiles for the chemically heterogeneous case at 38 days: (a) permeability, (b) $\text{Fe}(\text{OH})_3(\text{s})$, (c) Fe^{3+} , (d) pH, and (e) Cl^- .

It is clear that both chemical and physical heterogeneities significantly impact the progress of heterogeneous reactions and dissolved plumes in the calcite reactive barrier. As shown in Figures 2 and 3, both physical and chemical heterogeneities affected permeability changes in response to precipitation along the fast flowing paths. The two heterogeneous fields generated with different conditions have differing distributions of permeability or calcite content although the mean values are very close. Therefore, a direct comparison of the results obtained from the two cases as to which effect is more significant in controlling the reaction front dynamics is quite difficult. However, one could tell that fingering is more pronounced in the chemically heterogeneous porous medium (Figure 2) than in the physically heterogeneous porous medium (Figure 3).

In two or more dimensions, fully coupled systems can produce fingering patterns. Scalloping or fingering happens when a reactive solute species invades some medium, and the reacted media formed

has a lower permeability than the unreacted media. The formation of fingers at the $\text{Fe}(\text{OH})_3(\text{s})$ redissolution front is due to flow self-focusing that occurs when the altered zone of a reaction front has higher porosity and permeability than that in the unaltered zone.

3. 결론

We demonstrated the coupled effects of variable density fluid flow and heterogeneous reactive mass transport and their influence on developing reaction front. Generally, the evolutions in the concentrations of the aqueous phase are clearly related to the reaction-front dynamics. Plugging of the porous medium contributed to significant transients in patterns of flow and mass transport.

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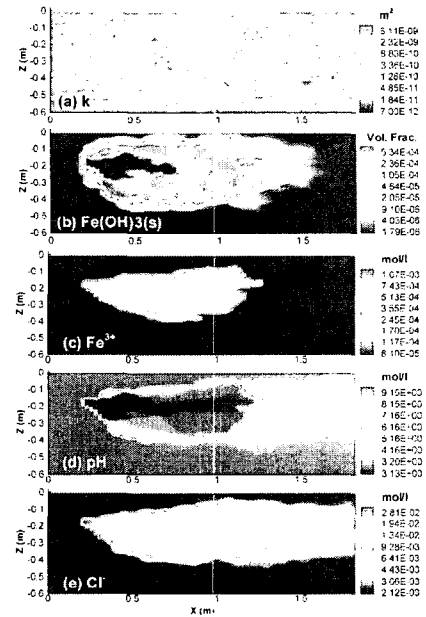


Figure 3. Profiles for the physically heterogeneous case at 38 days: (a) permeability, (b) $\text{Fe}(\text{OH})_3(\text{s})$, (c) Fe^{3+} , (d) pH, and (e) Cl^- .