Impact of Mineral Fouling on Hydraulic Behavior of Permeable Reactive Barriers

by Lin Li1, Craig H. Benson2, and Elizabeth M. Lawson3

Abstract

This paper describes reactive transport simulations conducted to assess the impact of mineral fouling on the hydraulic behavior of continuous-wall permeable reactive barriers (PRBs) employing granular zero-valent iron (ZVI) in carbonate-rich alluvial aquifers. The reactive transport model included a geochemical algorithm for simulating corrosion and mineral precipitation reactions that have been observed in ZVI PRBs. Results of simulations show that porosity and hydraulic conductivity of the ZVI decrease over time and that flows are redistributed throughout the PRB in response to fouling of the pore space. Under typical conditions, only subtle changes occur within the first 10 years (i.e., duration of the current field experience record with PRBs), and the most significant changes do not occur until the PRB has operated for at least 30 years. However, changes can occur sooner (or later) if the rate at which mineral-forming ions are delivered to the PRB is higher (or lower) than that expected under typical conditions (i.e., due to higher/lower flow rate or inflowing ground water that has higher/lower ionic strength). When the PRB is more permeable than the aquifer, the median Darcy flux in the PRB does not change appreciably over time because the aquifer controls the rate of flow through the PRB. However, seepage velocities in the PRB increase, and residence times decrease, due to porosity reductions caused by accumulation of minerals in the pore space. When fouling becomes extensive, bypassing and reductions in flow rate in the PRB occur.

Introduction

The permeable reactive barrier (PRB) is a passive treatment technology used to remove contaminants from ground water. As contaminated ground water flows through a PRB, contaminants are degraded, transformed, or immobilized as they interact with the reactive medium. PRBs generally are used for long-term treatment and are expected to be in service for decades. Most PRBs are continuous-wall or funnel-and-gate designs. In the United States, the continuous-wall design is most common (EPA 2002).

Particles of zero-valent iron (ZVI) are used as the reactive medium in most PRBs because of the broad range of contaminants that can be treated through the redox conditions imposed by corrosion of iron. Contaminants treated with ZVI PRBs include chlorinated solvents, radionuclides, pesticides, and heavy metals. The corrosion reactions also result in pH conditions that induce precipitation of secondary minerals (Phillips et al. 2000; Rob et al. 2000; Furukawa et al. 2002; Gu et al. 2002; Phillips et al. 2003; Wilkin et al. 2003). These minerals may precipitate in the pores of the PRB, a process referred to as mineral fouling, which results in changes in the porosity and hydraulic conductivity of the reactive medium along with changes in iron reactivity (Mackenzie et al. 1999; Farrell et al. 2000; Sarr 2001; Wilkin et al. 2003). These alterations may cause redirection of flowpaths, changes in residence time, and reductions in effectiveness (Blowes et al. 2000; Sarr 2001; Kamolpornwijit et al. 2003; Vikesland et al. 2003). Changes in residence time are particularly important because contaminants must remain within the reactive medium long enough to ensure that the treatment goals are met.

Field data from ZVI PRBs indicate that mineral fouling generally has not been problematic (Wilkin and Puls 2003). However, even the earliest PRBs have been in service for less than a decade, and some laboratory and field
investigations have suggested that mineral fouling in PRBs may result in preferential flow and/or blockage of flow (e.g., Sarr 2001; Kamolpornwijit et al. 2003; Vikeseland et al. 2003). Consequently, the impact that mineral fouling will have on the long-term (decades) hydraulic behavior of PRBs remains unclear. In this study, a model simulating ground water flow and reactive transport was used to evaluate how mineral fouling may affect the hydraulic behavior of PRBs over decades of continuous flow in carbonate-rich alluvial aquifers. An assessment was made of changes in the porosity and hydraulic conductivity of the reactive medium and how these changes alter flow and the residence time in the PRB. Changes in the distribution of hydraulic head within and around the PRB along with the pathways of flow in and around the PRB were also evaluated.

**Background**

A summary of field observations regarding geochemical conditions and the effects of mineral fouling of PRBs is presented in Table 1. Iron corrosion generally results in pH between 10 and 11 for 100% ZVI PRBs. Minerals precipitating in response to these pH conditions include iron oxides (magnetite, hematite), iron (oxy)hydroxides (ferrous hydroxide, ferric hydroxide, green rust, goethite, lepidocrocite), and carbonates (calcite, aragonite, siderite) (Odziemkowski et al. 1998; Mackenzie et al. 1999; Phillips et al. 2000; Roh et al. 2000; Beck et al. 2001; Furukawa et al. 2002; Phillips et al. 2003; Satapanajaru et al. 2003). Appreciable reductions in concentrations of major ions, such as Ca$^{2+}$ and Mg$^{2+}$, occur in response to mineral precipitation.

Field studies have shown that accumulation of minerals in ZVI reduces the porosity and hydraulic conductivity, affects the surface area for reactivity, and alters flowpaths (Blowes et al. 2000; Sarr 2001). Porosity reductions ranging from 0.0007 to 0.03 per year have been reported (Table 1), with the largest porosity reductions occurring near the entrance face. The rate of porosity reduction is a function of the ground water chemistry and flow rate, with greater amounts of minerals accumulating when the inflowing ground water has higher concentrations of dissolved mineral-forming ions (Blowes et al. 2000; Phillips et al. 2003). For example, the flow velocity and influent concentration for the PRB at the Denver Federal Center are up to triple those for the PRB at the U.S. Coast Guard Support Center. Solid-phase inorganic carbonates accumulate 4 to 20 times faster in the PRB at the Denver Federal Center site than in the PRB at U.S. Coast Guard Support Center site (Wilkin et al. 2003). Similar observations have been made in laboratory column studies (Kamolpornwijit et al. 2003; Vikeseland et al. 2003).

Decreases in hydraulic conductivity of ZVI have been measured using slug tests and estimated based on porosity reductions. Annual reductions in hydraulic conductivity range between a factor of 1.5 and 7.0 (Table 1). The rate at which the hydraulic conductivity decreases generally corresponds to the rate of porosity reduction (Morrison 2003), although in some cases the reduction in hydraulic conductivity is greater than can be attributed to porosity reduction alone (Sarr 2001). For example, the hydraulic conductivity of a PRB in Copenhagen, Denmark, decreased from 5.7 to 0.8 m/d in 18 months (a factor of 7.0), while the expected reduction of hydraulic conductivity was only a factor of 1.1 based on the molar volumes of mineral precipitates (Killerich et al. 2000).

Spatial variability in aquifer hydraulic properties can also affect the rate at which minerals precipitate in the pore space and their distribution (Mergener 2002; Li et al. 2004). For example, analyses were conducted on 279 samples from 70 cores collected from a PRB at Monticello, Utah, to evaluate the spatial distribution of minerals (Morrison 2003). Mineral precipitation was largest near the middle and edges of the PRB and penetrated deeper into the PRB in these regions.

**Methods**

The purpose of this study was to assess how mineral fouling may affect the hydraulic behavior of PRBs over their service life. The conceptual model is a continuous-wall PRB and a portion of the surrounding aquifer (Figure 1), with the PRB oriented perpendicular to the primary direction of ground water flow. The PRB is composed of ZVI particles. Hydraulic conductivity of the aquifer is spatially variable so as to represent the heterogeneity inherent in natural systems. As ground water flows through the PRB, the iron is corroded by dissolved oxygen (D.O.) and water, which elevates the pH and causes secondary mineral precipitation. This model is intended to represent a common continuous-wall PRB and does not necessarily reflect the design of any particular PRB, including those cited in Table 1.

Ground water flowing into the PRB is assumed to be in chemical equilibrium. The major constituents in the inflowing ground water are assumed to be Fe$^{2+}$, Ca$^{2+}$, CO$_3$$^{2-}$, OH$^{-}$, HCO$_3$$, D.O.$ These ions are assumed to form three minerals: aragonite or calcite (CaCO$_3$), siderite (FeCO$_3$), and ferrous hydroxide (Fe(OH)$_2$) (am)). Contaminant transformations were ignored because the amount of iron corrosion and mineral precipitation caused by reduction of chlorinated compounds or toxic heavy metals generally is negligible relative to that due to other processes, even though the transformations are intrinsic to the remediation process (Gillham 1999; Mayer et al. 2001; Morrison 2003; Wilkin et al. 2003).

The ions and minerals included in the model were selected based on results of a sensitivity analysis conducted by Li (2004), which showed that calcite, siderite, and ferrous hydroxide generally comprise most of the secondary mineral mass that precipitates in the pore space of PRBs. The sensitivity analysis also showed that addition of other minerals (e.g., MgCO$_3$, Mg(OH)$_2$, Mn(OH)$_2$ (am), CaMg(CO$_3$)$_2$, MnO$_2$, and FeS (am)) resulted in negligible changes in porosity reduction. Moreover, the three minerals included in the model represent the most common minerals observed in column and field studies (Schuhmacher et al. 1997; Blowes et al. 1999; Gu et al. 1999; Mackenzie et al. 1999; Liang et al. 2000; Phillips et al. 2000; Roh et al. 2000; Beck et al. 2001; Phillips et al. 2003; Satapanajaru et al. 2003; Wilkin et al. 2003).
<table>
<thead>
<tr>
<th>Site Location and References</th>
<th>PRB Characteristics</th>
<th>HCO₃⁻ or CO₂⁻ (mM)</th>
<th>Ca (mM)</th>
<th>Mg (mM)</th>
<th>SO₄²⁻ (mM)</th>
<th>Secondary Minerals in PRB (observed in cores)²</th>
<th>Impact on PRB³</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Canadian Forces Base,</strong></td>
<td>Continuous trench</td>
<td>GW¹ 8.1</td>
<td>2.8</td>
<td>7.0</td>
<td>0.1 to 2.0</td>
<td>Trace amount of iron oxides, CaCO₃, and FeCO₃ within first few millimeters from entrance face after 4 years</td>
<td>No biofouling, no cementation, no decline in performance over 5 years, no measurable decrease in iron reactivity</td>
</tr>
<tr>
<td><strong>Borden, Ontario,</strong></td>
<td>installed in 1991 to</td>
<td>ZVI 8.7</td>
<td>1.6</td>
<td>2.6</td>
<td>0.1 to 2.0</td>
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<tr>
<td><strong>Canada (O’Hannesin and Gillham 1998)</strong></td>
<td>remove TCE and PCE in ground water; 5.5 m wide, 10 m deep, 1.6 m thick, 22% ZVI (0.15- to 0.35-mm particle size), and 78% coarse sand. Ground water velocity = 0.1 m/d</td>
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<tr>
<td><strong>Lowry Air Forces Base,</strong></td>
<td>Funnel and gate</td>
<td>GW 6.5</td>
<td>5.5</td>
<td>ND⁶</td>
<td>ND⁶</td>
<td>Carbonates, silica, ferrous compounds at entrance face</td>
<td>Porosity reduction = 0.024/year (initial porosity = 0.60). After 4 years, ground water near eastern funnel moves toward nearby creek rather than gate</td>
</tr>
<tr>
<td><strong>Colorado (Sarr 2001)</strong></td>
<td>installed in 1995 to</td>
<td>ZVI 10.0</td>
<td>0.5</td>
<td>ND⁶</td>
<td>ND⁶</td>
<td></td>
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</tr>
<tr>
<td><strong>Moffett Federal Airfield,</strong></td>
<td>remove TCE, PCE, DCE, and VC; 3-m-wide, 6-m-deep, 1.5-m-thick gate containing 100% ZVI</td>
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<tr>
<td><strong>Mountain View, California</strong></td>
<td>(Yabusaki et al. 2001)</td>
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<tr>
<td><strong>Industrial Site,</strong></td>
<td>Continuous trench</td>
<td>GW 7.1</td>
<td>4.7</td>
<td>3.9</td>
<td>2.7</td>
<td>Measured: magnetite, hematite, aragonite, marcasite (FeS₂); estimated: Fe(OH)₃, Fe₂(OH)₃, siderite, FeS, Mg(OH)₂, green rust.</td>
<td>Porosity reduction = 0.015 to 0.030/year (initial porosity = 0.66); no biofouling</td>
</tr>
<tr>
<td><strong>New York</strong></td>
<td>installed in 1996 to</td>
<td>ZVI 10.5</td>
<td>0.2</td>
<td>0.1</td>
<td>0.2</td>
<td></td>
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<tr>
<td><strong>Vogans et al. 1999;</strong></td>
<td>remove TCE and DCE; 3-m-wide, 5.5-m-deep, 1.8-m-thick gate with 6-m-wide funnel, 100% ZVI (1.5 m²/g specific surface area) in gate with pea gravel on both sides; ground water velocity = 0.01 to 0.13 m/d</td>
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<tr>
<td><strong>Sarr 2001)</strong></td>
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<tr>
<td><strong>Denver Federal Center,</strong></td>
<td>Continuous trench</td>
<td>GW 7.4</td>
<td>4.8</td>
<td>2.3</td>
<td>0.5</td>
<td>Calcite, aragonite, siderite, green rust</td>
<td>Porosity reduction = 0.03/year (assumed initial porosity = 0.6)</td>
</tr>
<tr>
<td><strong>Denver, Colorado</strong></td>
<td>installed in 1996 to</td>
<td>ZVI 9.0 to 10.0</td>
<td>0.8</td>
<td>0.2</td>
<td>0.3</td>
<td></td>
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</tr>
<tr>
<td><strong>McMahon et al. 1999;</strong></td>
<td>remove TCE, DCE, and TCA; four gates 12 m wide and up to 9.5 m deep; 0.6 m thick (gates 3 and 4), 1.2 m thick (gate 2), and 1.8 m thick (gate 1), 100% ZVI (0.25- to 2.0-mm particle size, 0.7 m²/g specific surface area) in gates with pea gravel on both sides; ground water velocities in gate 1 and 2 = 0.11 to 0.38 m/d</td>
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<td><strong>Furukawa et al. 2002;</strong></td>
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<tr>
<td><strong>U.S. Coast Guard Support</strong></td>
<td>Funnel and gate</td>
<td>GW 7.5</td>
<td>7.3</td>
<td>2.5</td>
<td>2.0</td>
<td>Lepidocrocite, magnetite, aragonite, siderite, green rust, and FeS at entrance of gates; gate 2 has the most mineral precipitates, which form near the entrance face</td>
<td>Porosity reduction = 0.006 in gate 1, and 0.062 in gate 2 in the first 25 mm into the ZVI after 3.8 years. Precipitation exacerbated in gate 1 due to high flow rate</td>
</tr>
<tr>
<td><strong>Center, Elizabeth City,</strong></td>
<td>installed in 1996 to</td>
<td>ZVI 10.0</td>
<td>1.7</td>
<td>0.0</td>
<td>0.0 to 3.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>North Carolina (Blowes et al. 1999; Furukawa et al. 2002; Wilkin et al. 2002, 2003)</strong></td>
<td>remove TCE, Cr(VI); 46 m wide, 7.3 m deep, 0.6 m thick; 100% ZVI (0.4-mm median particle size, 0.8 m²/g specific surface area); ground water velocity ranged from 0.13 to 0.18 m/d</td>
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</tr>
</tbody>
</table>

¹ GW = influent ground water
² ZVI = zero-valent iron
³ Impact on PRB
<table>
<thead>
<tr>
<th>Site Location and References¹</th>
<th>PRB Characteristics</th>
<th>pH</th>
<th>HCO₃⁻ or CO₃²⁻ (mM)</th>
<th>Ca (mM)</th>
<th>Mg (mM)</th>
<th>SO₄²⁻ (mM)</th>
<th>Secondary Minerals in PRB (observed in cores)²</th>
<th>Impact on PRB³</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y-12 Site, Oak Ridge, Tennessee (Phillips et al. 2000; Gu et al. 2002; Phillips et al. 2003)</td>
<td>Continuous trench installed in 1996 to remove U, Tc, nitric acid, and PCE; 68.5 m wide, 6.7 to 9.1 M deep, 0.6 M thick; 100% ZVI with gravel on both sides; ground water velocity = 2.2 m/d</td>
<td>GW</td>
<td>6.7</td>
<td>5.4 to 10.7</td>
<td>5.0</td>
<td>0.8</td>
<td>0.8</td>
<td>Goethite, lepidocrocite, mackinawite, maghemite, magnetite, calcite, siderite, aragonite, FeS throughout cores collected after 30 months of operation</td>
</tr>
<tr>
<td>Freight Yard, Copenhagen, Denmark (Killerich et al. 2000; Sarr 2001)</td>
<td>Continuous trench installed in 1998 to remove DCE; 15.2 M wide, 6.0 M deep, 1.0 M thick; 100% ZVI; ground water velocity = 0.1 m/d</td>
<td>GW</td>
<td>7.7</td>
<td>10.0</td>
<td>3.3</td>
<td>ND</td>
<td>1.0</td>
<td>Estimated 18 kg/m³ pore space Fe(OH)₂, 3.7 kg/m³ CaCO₃, 3.7 kg/m³ FeCO₃, and 1.1 kg/m³ FeS precipitate in the PRB per year</td>
</tr>
<tr>
<td>Former mill site, Monticello, Utah (Morrison 2003)</td>
<td>Funnel and gate installed in 1999 to remove U and V; 30-m wide, 4.5- to 6.0-m deep, 1.2-m thick gate with surry cutoff walls on either side; 100% ZVI (0.9- to 2.4-mm particle size) in gate with pea gravel on both sides; upgradient pea gravel contains 13% ZVI</td>
<td>GW</td>
<td>6.7</td>
<td>2.5</td>
<td>8.5</td>
<td>ND</td>
<td>ND</td>
<td>Magnetite, CaCO₃; spatially variable distribution of mineral precipitates; northern edge of gravel/ZVI zone has a higher solid-phase Ca concentration than southern edge and penetration of solid-phase Ca concentration along with the ground water flow into the ZVI zone</td>
</tr>
</tbody>
</table>

²Core samples of ZVI analyzed to identify secondary minerals.
³Porosity reductions estimated based on stoichiometry and changes in concentration.
⁴GW: mean value for influent ground water.
⁵Mean value in ZVI.
⁶ND: no data available.
TCE = trichloroethylene; PCE = perchloroethylene; DCE = dichloroethylene; VC = vinyl chloride; TCA = trichloroethane; CR(VI) = chromium (VI); U = uranium; Tc = technetium; V = vanadium.
Ground Water Flow and Reactive Transport Models

Flow and transport in the PRB and the surrounding region of the aquifer were simulated using the ground water flow model MODFLOW (McDonald and Harbaugh 1988) and the reactive transport model RT3D (Clement 1997). A geochemical algorithm developed by Li (2004) was added to RT3D for simulating the reaction kinetics associated with the redox and mineral precipitation-dissolution reactions that occur in PRBs. Li (2004) describes in detail how the combination of MODFLOW and RT3D is used to simulate flow, transport, and geochemical reactions in PRBs and show that predictions made with the MODFLOW-RT3D model are in general agreement with field data from PRBs. A summary is presented in this section of key aspects of the models.

A three-dimensional domain was used to simulate flow in the PRB and the surrounding aquifer. Heterogeneity in the aquifer hydraulic conductivity was simulated using the turning bands random field generator described in Elder et al. (2002), which is based on the algorithm described in Tompson et al. (1989). The intent was to generate a reasonably realistic three-dimensional distribution of aquifer hydraulic conductivity (i.e., a single realization) simulating the heterogeneity inherent in natural aquifers (e.g., along the lines described in Tompson et al. 1989). The generator was not used to create multiple stochastic realizations for a probabilistic analysis.

Hydraulic conductivity of the aquifer was assumed to be lognormally distributed and was characterized by the geometric mean hydraulic conductivity ($K_g$), the standard deviation of the logarithm of hydraulic conductivity ($\sigma_{\log K}$), and the correlation lengths ($\lambda$) along the principal axes (Elder et al. 2002; Li et al. 2004). Many of the simulations described herein were conducted for “typical” hydraulic properties associated with a sandy aquifer as described in Elder et al. (2002) (i.e., $K_g = 3.9 \text{ m/d, } \sigma_{\log K} = 1.0, \lambda_1 = 3 \text{ m, } \lambda_2 = 1 \text{ m, } \lambda_3 = 0.5 \text{ m}$). This aquifer is referred to as the “base case” herein.

A continuous-wall PRB is located in the middle of the domain. The PRB is oriented perpendicular to the average direction of ground water flow and is 10 m deep, 25 m wide, and 1 m thick. The PRB is assumed to have uniform hydraulic conductivity ($K_p$) at the time of installation (216 m/d for the base case). Spatial variability in the initial hydraulic conductivity of the PRB was not incorporated based on the analysis by Elder et al. (2002), which shows that the effects of heterogeneity in hydraulic conductivity of the reactive medium are small relative to the effects due to aquifer heterogeneity. The initial porosity of the ZVI was set at 0.60, which falls within the typical range (0.55 to 0.65) reported for the porosity of ZVI (Sarr 2001). The porosity of ZVI is large, relative to granular media having similar particle size, because of the angularity and oblong shape of ZVI particles. The total and effective porosities of the ZVI were assumed to be

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Table 2
Reactions Included in Geochemical Algorithm with Kinetic Rate Expressions, Solubility Constants, and Rate Coefficients

<table>
<thead>
<tr>
<th>Reactions</th>
<th>Mineral Formed</th>
<th>Kinetic Rate Expression</th>
<th>Solubility Constant Log ($K_{eq}$)</th>
<th>Rate Coefficients ($k_i$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iron corrosion</td>
<td>Aragonite/calcite</td>
<td>$-k_{CaS}(1-a_{Ca^{2+}} a_{CO_3^{2-}}/K_{eq})$</td>
<td>-8.1</td>
<td>2.6 \times 10^{-8} \text{ mol/m}^2 \text{ d}</td>
</tr>
<tr>
<td>FeCO$_3$(s) $\rightarrow$ Fe$^{2+}$ + CO$_3^{2-}$</td>
<td>Siderite</td>
<td>$-k_{FeS}(1-a_{Fe^{2+}} a_{CO_3^{2-}}/K_{eq})$</td>
<td>-10.5</td>
<td>2.6 \times 10^{-8} \text{ mol/m}^2 \text{ d}</td>
</tr>
<tr>
<td>Fe(OH)$_2$(am) $\rightarrow$ Fe$^{2+}$ + 2OH$^{-}$</td>
<td>Ferrous hydroxide</td>
<td>$-k_{FeS}(1-a_{Fe^{2+}} a_{OH^{-}}/K_{eq})$</td>
<td>-15.2</td>
<td>2.6 \times 10^{-8} \text{ mol/m}^2 \text{ d}</td>
</tr>
</tbody>
</table>

1. $k$ = rate coefficient; $S$ = reactive surface area of ZVI; $a$ = activity of aqueous species. Activity coefficients were calculated using the extended Debye-Huckel equation.
3. Initial reactive surface area of ZVI was set at 3.9 \times 10^6 \text{ m}^2/\text{m}^3.
4. aer = aerobic; an = anaerobic.

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Figure 1. Conceptual model of a PRB surrounded by a portion of a heterogeneous aquifer ($K_g = 3.9 \text{ m/d, } \sigma_{\log K} = 1.0, \lambda_1 = 3.0 \text{ m, } \lambda_2 = 1.0 \text{ m, } \lambda_3 = 0.5 \text{ m, and } K_p = 216 \text{ m/d}$).
equal, based on tracer tests reported by Kamolpornwijit et al. (2003) and Vikesland et al. (2003).

Steady-state flow was simulated in the heterogeneous aquifer and PRB using MODFLOW. The model domain consisted of 250 columns, 120 rows, and 20 layers, which represents a flow domain of $71 \times 60 \times 10$ m. The grid spacing was 0.5 m in the vertical and lateral directions. In the longitudinal (flow) direction, the grid size varied from 0.3 to 0.1 m, with the smaller spacing (0.1 m) being used within the PRB. The size of the domain and the level of discretization were determined based on a parametric analysis, which is described in Li (2004). This analysis identified the domain size needed so that flow and transport in the vicinity of the PRB were not affected by the boundaries and the grid spacing needed to accurately represent the flowpaths and residence times in the PRB. Unconfined flow was assumed with specified-head boundaries set along the east and west ends of the aquifer (Figure 1). An average hydraulic gradient of 0.01 was imposed to yield seepage velocities ranging from 0.05 to 0.20 m/d, which are typical of conditions observed in the field during PRB studies (Table 1). No-flow boundaries were used for the lateral, top, and bottom boundaries.

Reactive transport was simulated with RT3D, which uses the head solution from MODFLOW as input. The transport-modeling domain was a subdomain of that used for flow modeling and consisted of the PRB and a small region of the surrounding aquifer. A parametric analysis was conducted by Li et al. (2004) to determine the minimum size of the transport domain where the boundaries would not influence transport within the PRB. Based on this analysis, the upstream boundary was located 0.1 m upgradient of the entrance face, the downstream boundary was located 0.2 m downgradient from the exit face, and the side boundaries were located 0.5 m from the sides of the PRB.

The transport time step was automatically adjusted by RT3D to ensure that the cell-based Courant number was <1.0 (Zheng and Bennett 2002). Li (2004) found that reducing the maximum Courant number to <1 had no effect on the transport solution but increased the computational time. Heterogeneity in the hydraulic conductivity of the aquifer was assumed to be the source of macroscopic dispersion (Anderson 1997). Microscopic dispersion caused by pore-scale mixing was simulated using a small dispersivity (0.0007 m, Li 2004). The molecular diffusion coefficient was assumed to be $3 \times 10^{-5}$ m$^2$/d (Anderson 1984). However, the magnitude of the diffusion coefficient and pore-scale dispersivity had negligible effect on the transport results because of the dominant effect of macroscopic hydrodynamic dispersion (Li 2004).

The initial concentration of each species in the PRB was assumed to be zero. Li (2004) found that the transport simulation was sensitive to the initial concentrations only within the first 15 d of operation. The upstream boundary was assigned the concentration of ions in ground water and was assumed to be spatially uniform and time invariant. The bottom boundary was assigned as no flux. All other boundaries were assigned a Cauchy boundary condition with no dispersive flux (Zheng and Bennett 2002; Li 2004).

**Geochemical Algorithm**

The geochemical algorithm is described in detail by Li (2004). A synopsis is provided here. A summary of the geochemical reactions and their reaction rates is presented in Table 2. A pseudo–first order reaction rate ($r$) proportional to the reactive surface area ($S$) of ZVI and the D.O. concentration was assumed for iron corrosion by oxygen (Blowes et al. 1999; Mayer et al. 2001):

$$r = -kS[D.O.]$$

where $k$ is the rate coefficient. For iron corrosion by water, the reaction rate was assumed to be proportional only to the reactive surface area of ZVI (Reardon 1995; Blowes et al. 2000; Chen et al. 2001; Mayer et al. 2001; Yabusaki et al. 2001; Yabusaki et al. 2001; Alowitz and Scherer 2002; Gandhi et al. 2002; Westerhoff 2003).

The kinetics of mineral precipitation-dissolution were assumed to follow transition state theory (Lichtner et al. 1996; Ayora et al. 1998; Hunter et al. 1998; Lasaga 1998; Mayer et al. 2001; Saaltink et al. 2001; Yabusaki et al. 2001). Comparisons between field data and model predictions by Mayer et al. (2001), Yabusaki et al. (2001), and Li (2004) indicate that this approach reasonably replicates conditions existing in PRBs. The reaction rate is expressed as (Mayer et al. 2001):

$$r = -k_{eff} \left(1 - \frac{\text{IAP}}{K_{eq}}\right)$$

where $r$ is the rate of mineral precipitation, $k_{eff}$ is an effective rate coefficient, IAP is the ion activity product, and $K_{eq}$ is the solubility constant for the reaction. The mineral reactions and their solubility constants are summarized in Table 2. For simplicity and computational efficiency, mineral dissolution was excluded. In a comparison of simulations with both precipitation and dissolution and precipitation only, Li (2004) found that the mineral mass differed by only 0.01% when both precipitation and dissolution were included in the model.

Mineral precipitates formed in the iron medium were assumed to be immobile, and the pore space occupied by the minerals was estimated from the molar volume of each mineral. The pore volume reduction at a given location was computed as the total pore volume occupied by the mineral precipitates at the location less the pore volume gained by dissolution of iron. The porosity reduction was calculated as the pore volume reduction in a finite-difference grid cell divided by the cell volume.

The reactive surface area of the ZVI was reduced over time to account for dissolution of iron and deposition of minerals on the surface of the ZVI. The effect of iron dissolution was simulated using the method employed by Mayer et al. (2001):

$$S_T = S_0 \left(\frac{\phi}{\phi_0}\right)^{2/3}$$

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where \( S_t \) is the reactive surface area of the ZVI at time \( t \), \( S_0 \) is the initial reactive surface area, \( q_0 \) is initial volume fraction of the ZVI, and \( \varphi \) is volume fraction of ZVI at time \( t \). Reduction of the surface area due to mineral precipitation was computed using the method described in Morrison (2003):

\[
S_t = S_0 - \Delta n \frac{T_c}{T_c} 
\]

(4)

where \( \Delta n \) is the porosity reduction due to mineral precipitation and \( T_c \) is a proportionality constant equivalent to the thickness of an evenly distributed coating of precipitate on the iron surface.

Hydraulic Conductivity Reduction

Reductions in the hydraulic conductivity of the ZVI were estimated using the Kozeny-Carmen equation (Bear 1972):

\[
K_p = \frac{1}{5M^2} \left( \frac{\rho_w g}{\mu} \right) \left( \frac{n^3}{(1-n)^2} \right)
\]

(5)

where \( n \) is the porosity of the reactive medium at some location in the PRB, \( M \) is the specific surface of the iron particles (ratio of surface area and bulk volume), \( \rho_w \) is the density of water, \( g \) is the gravitational constant, and \( \mu \) is the absolute viscosity of water. Mineral precipitation and iron dissolution during mineral fouling may change \( M \). However, the relationship is a complex function of the geometry of iron particles, the shape of the secondary minerals, and the location of the mineral precipitates. Thus, \( M \) was assumed to be constant, which results in a conservative error.

The hydraulic conductivity after a porosity reduction \( \Delta n \) can be expressed as:

\[
K_p = K_{po} \left[ \frac{n_0 - \Delta n}{n_0} \right]^3 \left/ \left[ \frac{1-n_0 + \Delta n}{1-n_0} \right]^2 \right.
\]

(6)

where \( K_{po} \) and \( n_0 \) are the initial hydraulic conductivity and porosity of the ZVI in the PRB, respectively. The reduction in hydraulic conductivity predicted by Equation 6 is nonlinearly related to the porosity reduction (i.e., the rate of decrease in hydraulic conductivity increases as the porosity reduction becomes larger). Only mineral precipitates were assumed to contribute to \( \Delta n \). The effects of accumulation of gas and biological matter were ignored due to difficulties in modeling these effects. Gas and biological matter may exacerbate the effects of the porosity reductions reported herein, although field data to date do not indicate that either has an appreciable effect on PRBs.

Other hydraulic conductivity models could have been used to develop an expression like Equation 6 (e.g., Lichtner et al. 1996; Ayora et al. 1998; Bolton et al. 1999; Morrison 2003). However, none of the models has been shown to be superior for predicting changes in the hydraulic conductivity of ZVI. Moreover, the model used to predict the hydraulic conductivity is not particularly important because the hydraulic conductivities predicted by most hydraulic conductivity models differ by not more than 10% (Li 2004).

A parametric study was conducted to determine how often the hydraulic conductivity and porosity in the PRB need to be updated (Li 2004). Base case properties were used for the hydraulic conductivity of the aquifer and the PRB along with the rate coefficients in Table 2 and the base case ground water concentrations in Table 3. Ten-year simulations were conducted with updating conducted monthly, bimonthly, semiannually, annually, biannually, and one time (at the end of 10 years). Comparison of the results showed that annual updating was adequate (Li 2004). For example, porosity reductions after 10 years of operation differed by <1% when the updating period was 1 year or less, whereas differences as large as 5% were observed for updating at intervals >1 year. Annual updating was used in all simulations.

Residence Times

Residence times within the PRB were defined using the particle-tracking code Path3D (Zheng 1991), which uses the head solution from MODFLOW as input. One thousand particles were released from a source 25 m wide by 10 m deep that was located 20 m upgradient from the PRB. Path3D calculates the position and travel time of each particle by moving particles through a series of time steps.

### Table 3

<table>
<thead>
<tr>
<th>Aqueous Species in Influent Ground Water</th>
<th>Aqueous Species Concentrations (M)</th>
<th>Typical Range for Natural Ground Water(^1)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Base Case</td>
<td>High-Concentration Case</td>
</tr>
<tr>
<td>Fe(^{2+})</td>
<td>(1.0 \times 10^{-10})</td>
<td>(1.0 \times 10^{-10})</td>
</tr>
<tr>
<td>Ca(^{2+})</td>
<td>(1.0 \times 10^{-3})</td>
<td>(2.2 \times 10^{-3})</td>
</tr>
<tr>
<td>OH(^{-})</td>
<td>(1.0 \times 10^{-7})</td>
<td>(1.0 \times 10^{-7})</td>
</tr>
<tr>
<td>HCO(_3^-)</td>
<td>(1.0 \times 10^{-3})</td>
<td>(3.0 \times 10^{-3})</td>
</tr>
<tr>
<td>CO(_2^{2-})</td>
<td>(1.0 \times 10^{-7})</td>
<td>(4.0 \times 10^{-7})</td>
</tr>
<tr>
<td>O(_2) (aq)</td>
<td>(1.0 \times 10^{-10})</td>
<td>(1.0 \times 10^{-10})</td>
</tr>
</tbody>
</table>

\(^1\)From Freeze and Cherry (1979), Hem (1985), and Langmuir (1997).

\(^2\)ND = no data.
steps. The residence time of each particle in the PRB was calculated as the difference between travel times corresponding to entry and exit of the PRB.

**Results of Simulations**

A series of simulations were conducted to evaluate the general effects that mineral fouling may have on the hydraulic properties and behavior of PRBs, i.e., porosity, hydraulic conductivity, seepage velocities, residence times, heads, flowpaths, and flow rates. Hydraulic and geochemical properties for the base case were used as input unless noted otherwise.

**Porosity and Hydraulic Conductivity Reduction**

Average and maximum porosity reductions in the PRB are shown in Figure 2a as a function of distance from the entrance face of the PRB for 10, 30, and 50 years after installation. The apparent linear variation in porosity reduction, particularly near the entrance face, is an artifact of the discretization used in the model. Thin lines correspond to the average porosity reduction (arithmetic mean of the porosity reduction in all cells comprising the PRB at a given distance from the entrance face), whereas thick lines correspond to the maximum porosity reduction (greatest porosity reduction in all cells comprising the PRB at a given distance from the entrance face). These porosity reductions are net reductions caused by the combined precipitation of all minerals less the volume of iron dissolved. The maximum possible porosity reduction is 0.60, which is the initial porosity of the PRB. The predicted porosity reductions range between 0.007 and 0.013 per year, which is within the range reported in field studies (Table 1).

For all times, the average and maximum porosity reductions reach a peak near the entrance face, which is followed by a decrease and then leveling off (~0.75 m from the entrance face). For example, after 30 years of operation, the maximum porosity reduction peaks at 0.38 and then levels off at 0.20. Both the average and maximum porosity reductions increase over time as minerals accumulate. After 50 years, the maximum porosity reduction reaches 0.60 (i.e., complete blockage in some pores) near the entrance face and the peak average porosity reduction is ~80% of the pore space. Thus, at 50 years, substantial blockage of the PRB has occurred. Even at 30 years, approximately one-half of the pore space has been blocked in some portions of the PRB.

The difference between the average and maximum porosity reductions reflects the impact that flow heterogeneity has on the rate of mineral precipitation. These differences are greatest near the entrance face because mineral precipitates in this region largely consist of carbonate minerals, and the rate at which these minerals accumulate is controlled by the spatially varying rate at which mineral-forming ions (i.e., primarily \( \text{Ca}^{2+}, \text{CO}_3^{2-}, \text{OH}^-, \text{HCO}_3^- \)) enter the PRB via advection. The difference between the maximum and average porosity reductions in the region between the entrance face and midplane increases over time, which reflects the higher rate at which minerals accumulate in pores associated with preferential flowpaths. In contrast, the maximum and average porosity reductions are indistinguishable near the exit face of the PRB. Porosity reductions near the rear of the PRB are caused almost exclusively by ferrous hydroxides, which are formed primarily by ions generated by corrosion processes (\( \text{Fe}^{2+} \) and \( \text{OH}^- \)) within the PRB rather than ions entering the PRB via inflowing ground water.

The effect that mineral accumulation has on hydraulic conductivity within the PRB is shown in Figure 2b, which shows the hydraulic conductivity ratio (\( K_p/K_{po} \)) computed with Equation 6 as a function of distance into the PRB from the entrance face. Thick lines correspond to the minimum \( K_p/K_{po} \) (i.e., largest porosity reductions), and thin lines correspond to the average \( K_p/K_{po} \). A decrease in hydraulic conductivity is reflected as \( K_p/K_{po} < 1 \) (upper horizontal line in Figure 2b). When \( K_p/K_{po} \) falls below 0.018 (lower horizontal line in Figure 2b), portions of the PRB are less permeable than the geometric mean hydraulic conductivity of the aquifer, a condition that may cause bypassing.

Both the minimum and average \( K_p/K_{po} \) decrease over time in response to the accumulation of minerals. Over the first 10 years, the reductions in hydraulic conductivity are modest and all portions of the PRB remain much more permeable than the aquifer as has generally been observed in the field (Wilkin and Puls 2003). After 30 years, some regions of the PRB are less permeable than the aquifer, but the average hydraulic conductivity of the PRB remains above the hydraulic conductivity of the aquifer regardless of distance from the entrance face. Thus, for this example, the PRB should still convey flow

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**Figure 2.** Porosity reduction (a) and hydraulic conductivity reduction and (b) after 10, 30, and 50 years of operation as a function of distance from the entrance face of the PRB. Base case hydraulic properties were used as input.
efficiently even after 30 years of operation, which is greater than the service life generally expected for PRBs (15 to 20 years, Blowes et al. 2000). However, after 50 years of operation, large reductions in hydraulic conductivity have occurred up to the midplane of the PRB. These reductions in hydraulic conductivity may cause flow alterations and partial bypassing of the PRB.

Redistribution of Flows in the PRB

Darcy fluxes at the entrance face of the PRB are shown in Figure 3 at the onset of operation and after 10, 30, and 50 years of operation. Dark shading corresponds to high Darcy fluxes, and light shading corresponds to low Darcy fluxes. The Darcy fluxes are spatially variable at all times (0, 10, 30, and 50 years), which reflects flow heterogeneities in the aquifer caused by spatial variability in the aquifer hydraulic conductivity.

Only a few differences exist between the distribution of Darcy fluxes at 0 and 10 years, which reflects the modest reductions in hydraulic conductivity occurring during this period (Figure 2b). Regions with the highest Darcy fluxes (~0.5 m/d, shaded black) become slightly smaller between 0 and 10 years, and those with moderate Darcy flux (~0.03 to 0.06 m/d, shaded gray) have become slightly larger. These effects are more pronounced at 30 (Figure 3c) and 50 years (Figure 3d). At 50 years, regions that initially had the highest Darcy fluxes (and the most rapid mineral accumulation) have transitioned to regions having the lowest velocities (Figure 3d). In effect, mineral precipitation in the pore space is redistributing flows from the most permeable to the pathways that are moderately permeable.

Box plots are shown in Figure 4a of the distribution of Darcy fluxes in the entire PRB. The centerline in the box corresponds to the median (50th percentile), the outer edges of the box correspond to the 25th and 75th

Figure 3. Darcy fluxes at the entrance face of the PRB (i.e., looking into the entrance face of the PRB): (a) initial; (b) 10 years of operation; (c) 30 years of operation; and (d) 50 years of operation. Base case hydraulic properties were used as input. PV = cumulative pore volumes of flow through the PRB.

Figure 4. Box plots of (a) Darcy flux; (b) seepage velocity; and (c) residence time in the PRB initially, after 10, 30, and 50 years of operation. Base case hydraulic properties were used as input.
percentiles, and the whiskers (outermost lines) correspond to the 10th and 90th percentiles of the Darcy flux. The median Darcy flux in the PRB remains relatively constant (~0.054 m/d) over time even though the hydraulic conductivity of the ZVI is decreasing because overall control on flow is imposed by the aquifer (i.e., the aquifer controls the flow rate because the aquifer materials are less permeable, on average, than the PRB medium) (Elder et al. 2002). However, the highest Darcy fluxes decrease as preferential flowpaths in the PRB, which connect permeable facies in the adjacent aquifer, become fouled by minerals. After 50 years, the 90th percentile Darcy flux has decreased from 0.11 to 0.077 m/d (Figure 4a) in response to those regions of the PRB that are completely fouled (Figure 3d).

Seepage Velocity and Residence Time

Box plots of seepage velocities (i.e., the local linear pore water velocity, defined as the local Darcy flux/local porosity) and residence times in the PRB are shown in Figures 4b and 4c, initially and after 10, 30, and 50 years. In contrast to the Darcy flux (Figure 4a), the distribution of seepage velocity gradually increases over time (Figure 4b). Concurrently, the residence time decreases gradually, with the largest reductions in residence time occurring after 10 years of operation (Figure 4c), i.e., outside the existing range of field experience for PRBs. The seepage velocity increases, and the residence time decreases, because the porosity is decreasing due to mineral fouling (the mean porosity decreases from initial 0.60 to 0.25 over 50 years), while the Darcy flux remains relatively constant due to the overall control by the aquifer.

Hydraulic Head Distribution and Flow Bypassing

Distributions of hydraulic head along a transect passing orthogonally through the centerline of the PRB are shown in Figure 5, at the onset and after 50 years. These distributions are comparable to those existing along other orthogonal transects through the PRB (Li 2004). The average hydraulic gradient across the PRB more than doubles during the 50-year period in response to the reductions in hydraulic conductivity caused by fouling. However, the changes in hydraulic head generally are subtle and probably could not be resolved from natural temporal variations.

The effects of fouling are not sufficient to cause an appreciable amount of bypassing or reductions in the flow rate (Figures 6a and 6b), even though by 50 years

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Figure 5. Distribution of hydraulic head along a transect passing orthogonal through the centerline of the PRB: (a) initial and (b) after 50 years of operation. Base case hydraulic properties were used as input.
some portions of the PRB are extensively fouled (Figures 2 and 3). After 50 years, only 16% of the flowpaths originally passing through the PRB bypass the PRB, and the flow rate has only decreased by a factor of 1.2. However, a much different condition may be realized for conditions that result in a greater rate of mineral accumulation, such as higher flow rates due to a more permeable aquifer or ground water with higher ionic strength. Flowpaths are shown in Figures 6c and 6d for the same aquifer conditions, except $K_g = 10.6$ m/d (i.e., 2.7 $\times$ $K_g$ for the base case). After 50 years of operation in the more permeable aquifer, many flowpaths diverge as they approach the PRB (72% of the flowpaths originally passing through the PRB bypass the PRB completely at 50 years), and the flow rate is reduced by a factor of 3.7.

**Effect of Inflowing Ground Water Concentrations**

The effect of ionic strength of the inflowing ground water is shown in Figure 7 in terms of porosity reductions, flow rate, and residence time for ground water with higher, lower, and base case concentrations. These simulations were conducted to evaluate how mineral fouling might differ in aquifers having higher or lower ionic strength than considered in the base case. Concentrations used as input are summarized in Table 3. The high and low influent concentrations fall within the range of typical ground water geochemistry reported in the literature (Freeze and Cherry 1979; Hem 1985; Langmuir 1997).

Maximum porosity reductions after 10 years of operation as a function of distance from the entrance face of the PRB are shown in Figure 7a. When the concentration is higher, porosity reductions are larger and minerals penetrate deeper into the PRB because more mineral-forming ions are available in the inflowing ground water. The effect of concentration on flow rate through the PRB is shown in Figure 7b. Little change in hydraulic conductivity occurs during the first 20 years regardless of concentration. After 30 years, however, the flow rate diminishes more rapidly, with a greater rate of reduction when the influent concentration is higher. The effect of higher concentration at 50 years is particularly dramatic. For this case, the flow rate through the PRB is only 28% of the initial flow rate.

The effect of concentration on residence time is shown in Figure 7c with box plots at 0, 10, 30, and 50 years. Over time, the median residence time decreases and becomes less variable for nearly all cases, especially...
when the concentration is higher. At 50 years, however, the higher influent concentration causes a large decrease in the median residence time as well as an increase in the variability in residence time (e.g., the 90th percentile residence time increases to 13.5 d for the high-concentration case). This unusual distribution of residence times reflects the extensive clogging that has occurred at 50 years caused by the higher influent concentration and the corresponding effect on flowpaths and travel time.

**Effect of Aquifer Properties**

Additional simulations were conducted to evaluate how the findings presented might differ if the aquifer had hydraulic properties different from those of the base case. Simulations were conducted with $K_g = 1.4, 3.9,$ and $10.6 \text{ m/d}$ to address different hydraulic conductivities and $\sigma_{\ln K} = 0.5, 1.0, 1.5, \text{ or } 3.0$ to simulate different levels of heterogeneity (Gelhar 1993; Anderson 1997; Elder et al. 2002). The correlation length of the aquifer hydraulic conductivity was not varied because a sensitivity analysis by Li (2004) showed that correlation length has less effect on fouling than $K_g$ and $\sigma_{\ln K}$. In all cases, the initial hydraulic conductivity of the PRB is greater than the geometric mean hydraulic conductivity of the aquifer.

Results of the simulations are shown as box plots in Figure 8 in terms of residence time in the PRB. Conditions that correspond to higher velocities in the aquifer and PRB (i.e., higher $K_g$ or $\sigma_{\ln K}$) result in more rapid mineral precipitation, faster reductions in hydraulic conductivity within the PRB, and greater reductions in residence time because mineral-forming ions are being delivered to the PRB at a higher rate. For example, the median residence time decreased 60% over 50 years for $K_g = 10.6 \text{ m/d}$ compared to 44% for $K_g = 3.9 \text{ m/d}$. Similarly, the 25th percentile residence time decreased 83% over 50 years for $\sigma_{\ln K} = 3.0$ compared to 41% for $\sigma_{\ln K} = 0.5$. Thus, mineral fouling will occur more quickly in aquifers where the hydraulic conductivity is higher or more variable.

**Summary and Conclusions**

A series of simulations were conducted with the ground water flow model MODFLOW and the reactive transport model RT3D to evaluate how mineral fouling affects the hydraulic behavior of PRBs in carbonate-rich alluvial aquifers. Porosity and hydraulic conductivity reductions in the PRB were determined as a function of time, and their impact on the distribution of Darcy fluxes, seepage velocities, residence times, heads, flowpaths, and flow rates was investigated. Sensitivity to influent concentration and aquifer properties was also evaluated.

Results of the simulations show that little change in hydraulic behavior occurs within 10 years from the time of installation, which is consistent with field experience to date. Significant changes in hydraulic behavior should be expected after ~30 years due to larger reductions in porosity and hydraulic conductivity. After 50 years, large regions of PRBs may become clogged and the PRB is likely to become less permeable than the aquifer, resulting in appreciable bypassing of ground water. The magnitude of these effects is influenced greatly by the rate at which major ions enter the PRB via advection. Thus, fouling should occur more quickly in aquifers that are more permeable, exhibit greater spatial variability in hydraulic properties, or have higher ionic strength. Field data from PRBs at the Denver Federal Center and the U.S. Coast Guard Support Center, although collected over a short time relative to the anticipated life span of the PRBs, are consistent with these observations.

Because the reactive medium in PRBs generally is more permeable than the surrounding aquifer materials, the Darcy flux in a typical PRB is expected to remain fairly constant over time because the flow is controlled by the aquifer materials. Flow control by the PRB only occurs after mineral fouling has become extensive. However, redistribution of flows will occur throughout the operation life of the PRB. Flows through more permeable pathways tend to diminish over time because these
pathways accumulate minerals at a greater rate, resulting in reduced variability in the Darcy flux. Moreover, the seepage velocity will gradually increase, and the residence time will decrease, because porosity reductions occur while the Darcy flux remains essentially constant.

Each of these findings is predicated on the realism of predictions made with numerical model developed for this study. The model was developed using accepted and well-documented methods from the literature and has been found to reliably predict conditions currently being observed in the field. However, limited field and laboratory data exist to confirm that the methods that were used can simulate long-term field conditions. Accordingly, additional research and monitoring are necessary to confirm that the performance anticipated from this study is borne out in the field.

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