Appendix J
Permeable Reactive Barrier Modeling Report

March 2023
Former Reynolds Metals Reduction Plant – Longview

Permeable Reactive Barrier Modeling Report

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ABBREVIATIONS

1Q	first quarter
2Q	second quarter
3Q	third quarter
4Q	fourth quarter
Axens AA	ActiGuard F 14×28 activated alumina obtained from Axens Canada Specialty Aluminas Inc.
bgs	below ground surface
BMP	Black Mud Pond
$CaCO_3$	calcium carbonate
CDID	Consolidated Diking Improvement District
cm	centimeter
cm/sec	centimeters per second
cm^2/sec	square centimeters per second
CPT	cone penetration test
DAF	dilution-attenuation factor
Final EDR	*Final Engineering Design Report, Version 2*
HPT	hydraulic profiling tool
mg/L	milligrams per liter
mL	milliliter
NAVD88	North American Vertical Datum of 1988
PDI	pre-design investigation
PRB	permeable reactive barrier
SCM	surface complexation model
wt %	weight percent

1 Introduction

This *Permeable Reactive Barrier Modeling Report* describes modeling work completed to support the design of permeable reactive barriers (PRBs) for groundwater remediation at the former Reynolds Metals Reduction Plant in Longview, Washington. This report is an appendix of the *Final Engineering Design Report, Version 2* (Final EDR), prepared in accordance with the cleanup action as specified in the *Cleanup Action Plan* (Ecology 2018a) pursuant to Consent Decree No. 18-2-01312-08 (Ecology 2018b).

1.1 Site Description

The site is located at 4029 Industrial Way near Longview, Washington, in unincorporated Cowlitz County. The property includes approximately 460 acres and is relatively flat and is approximately 10 feet above mean sea level and bounded by the Columbia River to the south; Consolidated Diking Improvement District (CDID) drainage ditches to the north, west, and east; Industrial Way along the northern boundary; and private property to the east.

1.2 Purpose

The purpose of this appendix is to present the geochemical modeling work that supports the design of the PRBs to remove fluoride from groundwater that will be installed along the northwestern perimeter of the Closed Black Mud Pond (BMP) Facility and specifically supports the Final EDR by providing the reactive media mixture, minimum PRB width, and expected PRB lifetime.

1.3 Report Organization

The remainder of this report is organized as follows:

- **Section 2 – Permeable Reactive Barrier Technology** includes a general description of the PRB technology for fluoride removal from groundwater.
- **Section 3 – Modeling Approach** describes the geochemical reactive transport modeling approach.
- **Section 4 – Permeable Reactive Barrier Model Development and Calibration** describes the development of a geochemical reactive transport model and its calibration to laboratory treatability data.
- **Section 5 – Simulation of Field-Scale Permeable Reactive Barrier Scenarios** compares the predictive simulation results for alternative PRB configurations.
- **Section 6 – Summary and Recommendations** presents the recommended PRB width and reactive media mix.
- **Section 7 – References** includes a list of references cited throughout the report.

2 Permeable Reactive Barrier Technology

A PRB is a passive groundwater treatment technology. A PRB is a permeable wall installed in the subsurface that is packed with a mixture of reactive media in a supporting aggregate matrix. As contaminated groundwater flows through the permeable wall, the reactive media remove target contaminants to reduce concentrations in groundwater exiting the PRB. The key properties determining the effectiveness of a PRB are as follows: 1) permeability; and 2) reactivity. A PRB needs to be permeable so that contaminated groundwater can flow through it instead of being diverted elsewhere or mounding on the upgradient side of the PRB. A PRB also needs to have sufficient reactivity to ensure contaminants are removed from groundwater that passes through the PRB down to target concentrations. Fluoride is the target contaminant for the PRBs to be installed at the site.

2.1 Reactive Media

Several reactive media were evaluated for fluoride removal in the *Treatability Study Report* (Appendix I of the Final EDR) to select suitable reactive media for the PRBs. Laboratory batch tests were performed to evaluate a number of candidate reactive media, including activated alumina, calcium phosphates (bone meal, bone char, and rock phosphate), carbonates (calcite and siderite), hydrotalcite, and magnesium oxide. The testing included fluoride removal rates, removal efficiency, uptake capacity, stability of the sequestered fluoride, and potential secondary water quality effects from the reactive media. In addition to treatment performance, the hydraulic performance of the reactive media was also considered in selecting suitable reactive media for the PRBs. Based on these evaluations, activated alumina was selected. The specific product that will be used for PRB construction is ActiGuard F 14×28 activated alumina obtained from Axens Canada Specialty Aluminas Inc. (Axens AA).

2.2 Permeable Reactive Barrier Design

The PRB consists of a mixture of reactive media (activated alumina) and aggregate. The key design parameters include reactive media mass loading, thickness of the PRB parallel to groundwater flow, and hydraulic conductivity of the PRB matrix. The PRB needs to meet the following performance criteria:

- The PRB will remove fluoride from groundwater discharging to CDID Ditch No. 14.
- The dose of reactive media in the PRB will be sufficient to treat the discharging groundwater for as long as the fluoride concentrations could result in exceedance in CDID Ditch No. 14.
- The PRB will not result in unacceptable secondary water quality issues as a result of reaction of groundwater with the reactive media.
- The PRB will be designed to minimize potential for clogging and/or development of preferential pathways.

3 Modeling Approach

A geochemical reactive transport model was developed for the PRB using PHREEQC (Parkhurst and Appelo 2013). PHREEQC simulates 1D advective-dispersive flow and geochemical reactions between groundwater and the PRB media. The geochemical model incorporates a high-quality thermodynamic database (minteq.v4.dat), which includes data for aqueous species, redox reactions, minerals, gases, adsorbing surfaces, and ion exchange. The thermodynamic database was augmented with equilibrium constants for fluoride adsorption on aluminum hydroxide surfaces (Karamalidis and Dzombak 2010).

Fluoride has a strong affinity for adsorption on aluminum oxide surfaces, and activated alumina removes fluoride from solution by adsorption (Fletcher et al. 2006; Hao and Huang 1986; Tang et al. 2009). Adsorption of fluoride and other ions on activated alumina is represented by a surface complexation model (SCM) in PHREEQC. Fluoride surface complexation reactions are rapid and modeled as instantaneous equilibrium reactions. Equilibrium constants for surface complexation reactions of fluoride and other ions on activated alumina (γ-Al_2O_3) are not available in the literature. However, a comprehensive database of surface complexation reactions of fluoride and other ions on the gibbsite (γ-$Al[OH]_3$) surface—one of the mineral forms of aluminum hydroxide—has been compiled by Karamalidis and Dzombak (2010). In contact with water, the surface of activated alumina becomes hydrated, and surface binding sites are represented by aluminol (≡AlOH) groups. Aluminol groups are also the binding sites for adsorption onto gibbsite. Conceptually, the surface binding sites on gibbsite and hydrated activated alumina are similar and are expected to have similar affinities for binding different ions. Therefore, the gibbsite SCM was used as a surrogate for activated alumina surface complexation in the model. The main difference between the two sorbents is the binding site density (i.e., the concentration of binding sites per unit mass or surface area of sorbent phase). This was accounted for by calibrating the model to the activated alumina column test data (Appendix I).

Fluoride concentrations in water can also be regulated by equilibrium precipitation and dissolution of fluoride-containing minerals with dissolved calcium such as fluorite (CaF_2). Other potential solid phases—such as calcite, ferrihydrite, siderite, pyrolusite, and rhodochrosite—were also included in the model to assess potential for clogging of the PRB medium due to secondary precipitates. These solid phases are allowed to precipitate within a model cell if their solubility is exceeded and also redissolve according to the saturation state of the groundwater.

4 Permeable Reactive Barrier Model Development and Calibration

A 1D reactive transport model was constructed in PHREEQC to test the reaction network and calibrate model parameters to the results of column tests for Axens AA. The details of the laboratory column tests are described in the *Treatability Study Report* (Appendix I of the Final EDR). Briefly, the laboratory flow-through column tests were performed to measure the fluoride breakthrough curves for mixtures of Axens AA with sand using groundwater from monitoring well RL-2S. The tests were carried out using 4.2-centimeter (cm)-diameter, 25-cm-long polycarbonate columns. Axens AA was mixed with sand in two different mass ratios (15:85 and 30:70) and packed into the columns to achieve a total depth of 22 cm. Groundwater was pumped in an up-flow direction through the columns at a constant flow rate of 0.3 milliliters per minute for a total of 4 weeks. In the 15% Axens AA column, effluent fluoride concentrations began to increase after approximately 18 pore volumes, whereas in the 30% Axens AA column, fluoride breakthrough occurred after approximately 40 pore volumes. The alkaline pH of the influent groundwater was neutralized by the column media for approximately 15 to 25 pore volumes. The Axens AA columns also removed phosphate from influent groundwater to very low levels for the duration of the tests. The 1D reactive transport model was calibrated to the measured fluoride breakthrough curves by adjusting the sorption site density of activated alumina and dispersivity of the column porous medium.

The column model configuration is shown in Figure J1. The column test operating conditions and model input parameters are given in Table J1. The inflow boundary condition in the model is a fixed concentration boundary represented by RL-2S groundwater and summarized in Table J2. Influent fluoride concentrations and pH are the averages of values measured for the influent solution reservoir over the duration of the column tests. The outflow boundary condition is a time-varying concentration boundary. Aqueous chemical speciation and mass transfer associated with mineral dissolution-precipitation and surface complexation reactions within the column are computed by the model.

Figure J1
Column Test Model Configuration

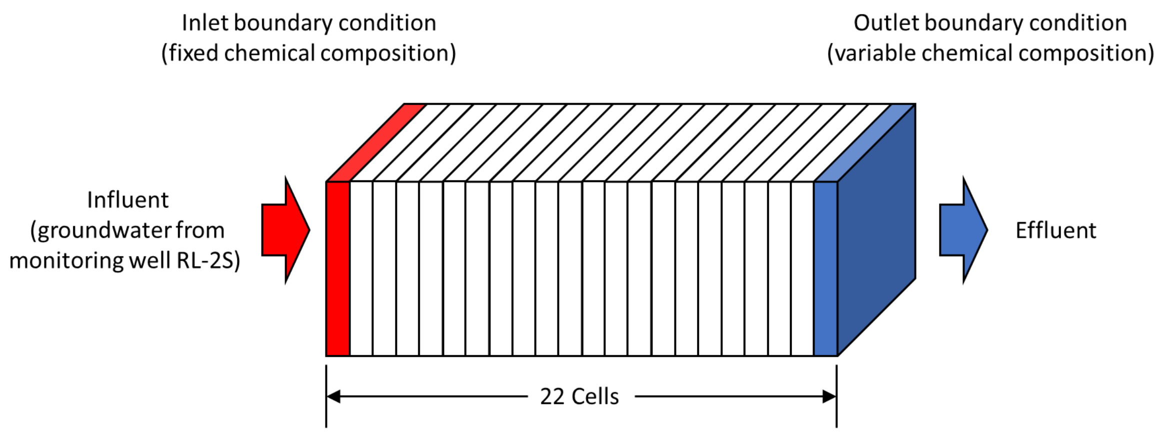


Table J1
Column Test Operating Conditions and Column Model Input Parameters

Parameter	Value	Units
Column Test Operating Conditions		
Column Length	22	cm
Flow Rate	0.30	mL per minute
Porosity	0.30	--
Linear Velocity	31	cm per day
Activated Alumina/Sand Mass Ratio	15/85 30/70	wt % (dry basis)
Model Input Parameters		
Number of Cells	22	--
Cell Length	1	cm
Time Step	982	seconds
Total Simulation Time	30	days
Dispersivity	5.0*	cm
Diffusion Coefficient	6×10^{-6}	cm^2/sec

Notes:
--: not applicable
*: calibrated to fluoride breakthrough curve

Table J2
Column Influent Water Chemistry

Parameter	Value	Units
pH	9.5	--
pe[1]	2.0	--
Fluoride	75	mg/L
Phosphate-P	20	mg/L
Alkalinity	4,000	mg/L as $CaCO_3$
Sodium	2,300	mg/L
Potassium	3.0	mg/L
Magnesium	4.0	mg/L
Calcium	40	mg/L
Iron	10	mg/L
Manganese	0.05	mg/L
Aluminum	0.5	mg/L
Ammonia	280	mg/L as N
Chloride	40	mg/L
Sulfate	200	mg/L as S

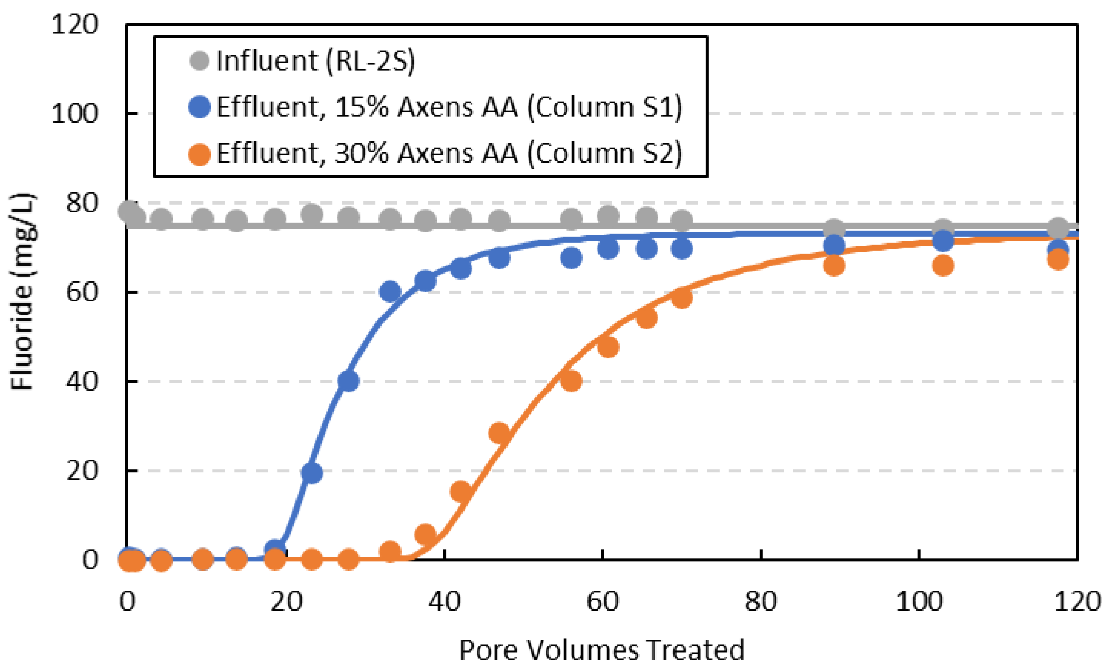
Notes:
--: not applicable
1. Negative logarithm of electron activity ($-\log\{e^-\}$)

The surface complexation reactions and associated equilibrium constants for sorption of fluoride and phosphate on activated alumina summarized in Table J3 are based on the gibbsite SCM (Karamalidis and Dzombak 2010). The aluminol surface site density of gibbsite is 0.29 moles per mole gibbsite. To calibrate the model to the site-specific column data, this value was adjusted to 0.14 moles per mole of aluminum in activated alumina. As shown in Figure J2, the model-simulated fluoride breakthrough curves are an excellent match to the laboratory column breakthrough curves.

Table J3
Surface Complexation Reactions on Activated Alumina

Surface Complexation Reaction	Log K	Reference
$\equiv AlOH + H^+ = \equiv AlOH_2^+$	7.17	Karamalidis and Dzombak (2010)
$\equiv AlOH = \equiv AlO^- + H^+$	-11.18	
$\equiv AlOH + F^- + H^+ = \equiv AlF + H_2O$	8.78	
$\equiv AlOH + F^- = \equiv AlOHF^-$	2.88	
$\equiv AlOH + 2F^- + H^+ = \equiv AlF_2^- + H_2O$	11.94	
$\equiv AlOH + PO_4^{3-} + 3H^+ = \equiv AlH_2PO_4 + H_2O$	26.89	
$\equiv AlOH + PO_4^{3-} + 2H^+ = \equiv AlHPO_4^- + H_2O$	19.37	
$\equiv AlOH + PO_4^{3-} + H^+ = \equiv AlPO_4^{2-} + H_2O$	13.57	

Figure J2
Simulated and Measured Fluoride Breakthrough Curves for Activated Alumina Column Tests



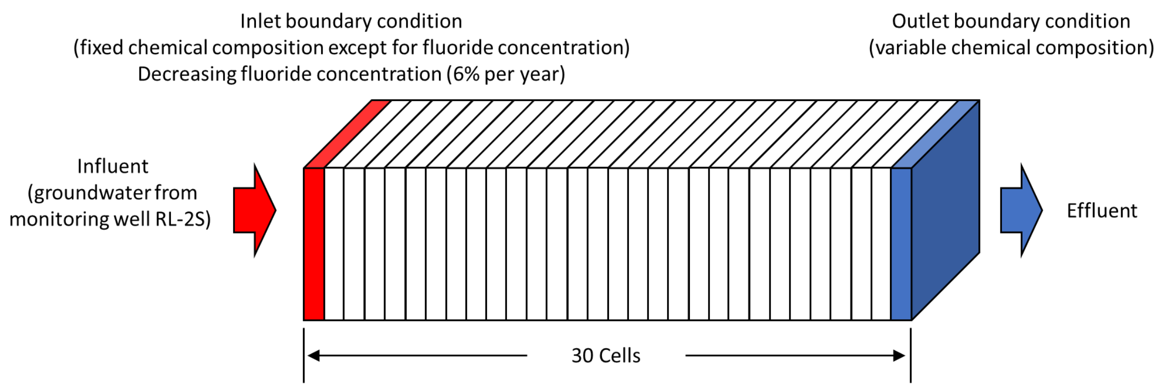
Notes:
Symbols are measured data.
Lines are model simulations.

5 Simulation of Field-Scale Permeable Reactive Barrier Scenarios

The calibrated reactive transport model presented in Section 4 was adapted to simulate a field-scale PRB in order to determine the dose of activated alumina needed to remove fluoride from groundwater for the duration of elevated groundwater fluoride discharge to CDID Ditch No. 14.

The model configuration is shown in Figure J3. The inflow boundary condition in the model is a time-varying concentration boundary. As discussed in Section 5.3, fluoride concentrations in monitoring wells located along the PRB alignment have been decreasing over time at an average rate of 6% per year. A PRB width of 3 feet along the principal groundwater flow direction was selected based on constructability considerations. The 1D model domain is divided into 30 equally sized grid cells containing a mixture of activated alumina and sand with an effective porosity of 0.3. The outflow boundary condition is a time-varying concentration boundary.

Figure J3
Field-Scale PRB Model Configuration



The model was used to simulate the fluoride breakthrough curves for a series of PRB scenarios in which the activated alumina dose was varied. For the present purposes, breakthrough is defined as a fluoride concentration exceeding 18 milligrams per liter (mg/L) in groundwater exiting the PRB. This PRB performance threshold is based on the 1.8-mg/L surface water screening level for CDID Ditch No. 14 and includes a default dilution-attenuation factor (DAF) of 10 to account for mixing of groundwater with surface water within the ditch. Incorporation of a DAF is appropriate because the CDID ditch receives groundwater discharge from both sides (including areas where fluoride contamination is not present), and the DAF is applied to the surface water screening level, which is less than the cleanup level.

The PRB design life is determined by the duration of groundwater with fluoride concentrations greater than the breakthrough criteria entering the PRB. In turn, the fluoride mass flux to the PRB over its design life determines the dose of activated alumina in the PRB. Mass flux is the product of groundwater velocity and fluoride concentration. Evaluations of groundwater velocities and fluoride concentrations along the PRB alignment and the PRB design life are presented in the following section.

5.1 Groundwater Fluoride Concentrations

5.1.1 Current Conditions

Fluoride concentrations in groundwater have been measured in several monitoring wells and depth-discrete direct push samples collected during the pre-design investigation (PDI) along the PRB alignment (Figure 6-2 of the Final EDR). A total of 58 sample results, including all the depth-discrete data, and the most recent sample results for monitoring wells provide a comprehensive picture of the distribution of fluoride in groundwater both laterally and with depth along the PRB alignment. Summary statistics for fluoride concentrations are provided in Table J4. For modeling purposes, the average value of 53.5 mg/L was used as the initial concentration for the groundwater entering the PRB.

Table J4
Summary Statistics for Fluoride in Groundwater Along the PRB Alignment

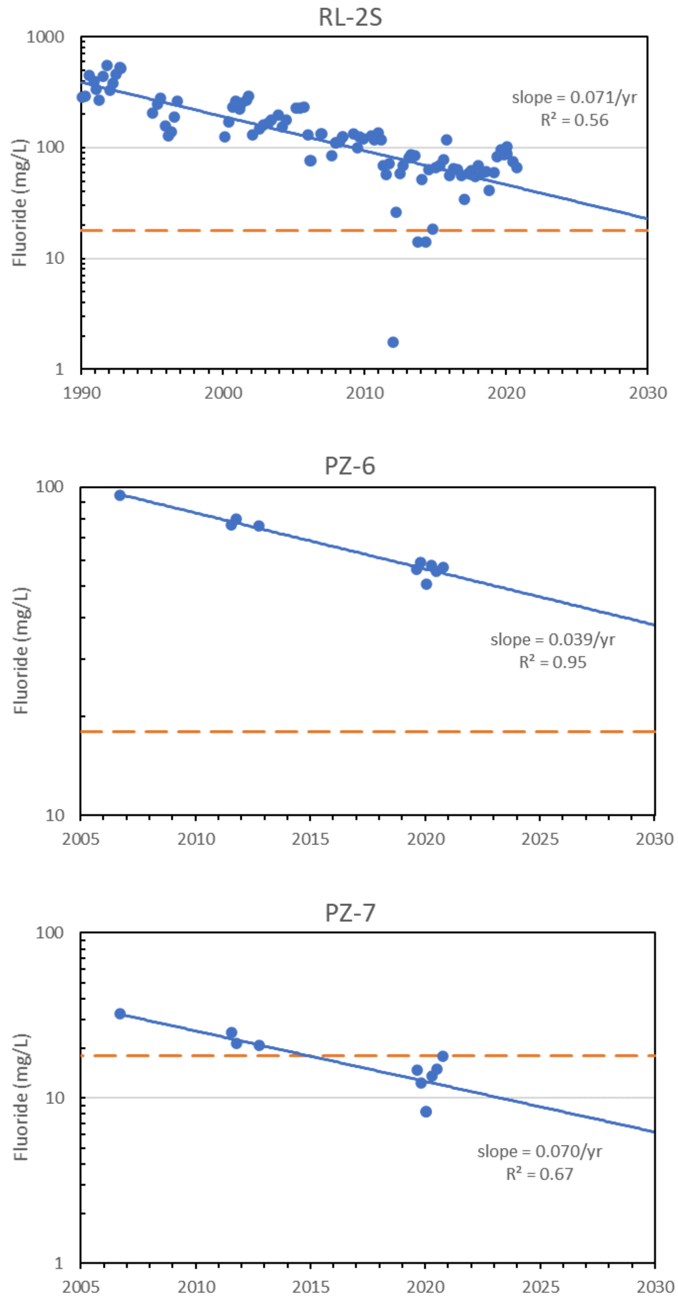
Value	Concentration (mg/L)
Minimum	0.2
Maximum	583
Mean	53.5
Standard Deviation	118.9
Median	4.0
66th Percentile	18
75th Percentile	39.8
90th Percentile	140

5.1.2 Temporal Trends and Future Concentrations

Fluoride concentrations in monitoring wells located along the PRB alignment have been decreasing over time. This is due to the slow post-closure flushing of residual fluoride in groundwater beneath the Closed BMP Facility. Fluoride time series data from three monitoring wells (PZ-7, PZ-6, and RL-2S, from south to north along the PRB alignment) were used to determine the rate of decrease of fluoride concentration due to ongoing natural attenuation, which was used in conjunction with recent fluoride concentrations to develop the PRB design life.

Fluoride concentrations in the three monitoring wells are described by an exponential decreasing trend with time (Figure J4) with rates of 0.071, 0.039, and 0.070 per year for RL-2S, PZ-6, and PZ-7, respectively. The average decay rate for the three datasets is 0.060 (i.e., 6%) per year.

Figure J4
Fluoride Concentration Time Trends in Monitoring Wells Located Along the PRB Alignment



Notes:
The solid line is an exponential fit to the data.
The dashed line is the 18 mg/L fluoride threshold.

5.2 Groundwater Flow Velocity

This section describes the development of groundwater flow velocities for the PRB model. The PRB backfill will be more permeable than the surrounding aquifer soils; therefore, the expected groundwater flow velocity through the PRB can be calculated from the ambient groundwater flow rate based on Darcy's Law using Equation J1:

Equation J1

$$v = \frac{K_h \times i}{n_e}$$

where:

v	=	linear groundwater velocity through the PRB
K_h	=	horizontal hydraulic conductivity of native material
i	=	horizontal hydraulic gradient
n_e	=	effective porosity of PRB backfill

5.2.1 Horizontal Hydraulic Conductivity of Native Material

The PRBs will be constructed in the Upper Alluvium, which consists of interbedded silt and fine-grained sand layers with minor fractions of silty sand, sandy silt, and clay interbeds. Therefore, the hydraulic conductivity of the Upper Alluvium is expected to vary over several orders of magnitude.

Horizontal hydraulic conductivity is estimated from empirical measurements, including pumping test, slug test, and low-flow sampling records. In addition, a cone penetration test (CPT) also provides hydraulic conductivity estimates, although these estimates are better indicators of changes in the relative magnitude of hydraulic conductivity over depth rather than absolute values. Sections 5.2.1.1 through 5.2.1.4 describe each type of hydraulic conductivity estimate.

5.2.1.1 Pumping Tests and Slug Tests

Hydraulic conductivity was estimated from aquifer tests and slug tests performed at several Upper Alluvium monitoring wells (Reynolds and CH2M Hill 1991). The estimates range from 0.1 foot per day (3.8×10^{-5} centimeters per second [cm/sec]) to 1.5 feet per day (5.4×10^{-4} cm/sec). The two monitoring wells along the PRB alignment, RL-2S and RL-2D, have hydraulic conductivity estimates of 0.13 and 1.5 feet per day, respectively.

Slug tests were performed in 2006 at 10 Upper Alluvium monitoring wells: G1-D, G2-D, G3-D, G4-D, G5-D, G6-D, G7-D, R1-D, RL-3D, and RL-4D (Anchor QEA 2015, Appendix D-2). Estimated hydraulic conductivity values vary between 0.0025 foot per day (8.8×10^{-7} cm/sec) to 16 feet per day (5.6×10^{-3} cm/sec), with a geometric mean of 0.22 foot per day (7.9×10^{-5} cm/sec). Among these 10 monitoring wells, well G7-D is located along the PRB alignment, with an estimated hydraulic conductivity of 0.0053 foot per day. The soil type in the screen interval is silt.

5.2.1.2 Low-Flow Sampling Records

During the 2019 PDI, groundwater samples were collected at direct push locations for field screening of fluoride concentrations. The steady-state drawdown and corresponding pumping rate were used to estimate hydraulic conductivity using the Thiem equation (Kruseman and de Ridder 1990). Drawdown data were only available from specific depth intervals in PDI-PRB-DP-04, PDI-PRB-DP-05, and PDI-PRB-DP-08. The values range from 0.14 to 4.3 feet per day (5.0×10^{-5} to 1.5×10^{-3} cm/sec).

Drawdown data were also collected during routine sampling of the monitoring wells and piezometers (RL-2S, RL-2D, PZ-6, and PZ-7). Hydraulic conductivity was estimated from transient drawdown data using the AQTESOLV Pro (HydroSOLVE, version 4.50) based on the Cooper-Jacob equation. When steady-state drawdown was reached during sampling, the Thiem equation was also used to estimate hydraulic conductivity. For the wells or piezometers where both the Cooper-Jacob and Thiem analyses were performed, the arithmetic average of the two estimates was calculated. The average values for each well range from 0.10 to 0.92 foot per day (3.6×10^{-5} to $.02\times10^{-4}$ cm/sec).

5.2.1.3 Cone Penetration Test Data

Hydraulic conductivity estimates were also made from the CPT log information. CPT location PDI-PRB-PC-01 is on the PRB alignment. The hydraulic conductivity estimates at this location range from 0.0024 foot per day (8.5×10^{-7} cm/sec) to 0.15 foot per day (5.5×10^{-5} cm/sec).

5.2.1.4 Hydraulic Profiling Tool Data

Hydraulic profiling tool (HPT) profile data provide information on variations in relative hydraulic conductivity with depth. Although absolute values of hydraulic conductivity can be estimated using an empirical relationship between HPT response and measured hydraulic conductivity, these estimates are considered semiquantitative at best, and the empirical relationship has poor predictive power for lower conductivity materials (e.g., less than 1 foot per day). As such, HPT-derived estimates are not as reliable quantitatively as values determined by the other methods. HPT profiling was performed at locations PDI-PRB-DP-09 and PDI-PRB-DP-10. The hydraulic conductivity estimates range from 0.32 (1.1×10^{-4} cm/sec) to 40 feet per day (1.4×10^{-2} cm/sec). Overall, this range of values is significantly higher than the values estimated by other methods, indicating a high bias.

5.2.1.5 Results

As shown in Table J5, hydraulic conductivity estimates from all available data along the PRB alignment range between 0.0024 and 19.2 feet per day. As discussed in Section 5.2.1.4, the

HPT-based values are not quantitative and are therefore less reliable; nevertheless, the values were included in calculating a geometric mean of 0.28 foot per day. The hydraulic conductivity values follow a lognormal distribution; therefore, the geometric mean is a representative measure. This value was used to estimate the groundwater flow into the PRB according to Equation J1. The PRB media-sand mix gradation will be designed to have an effective hydraulic conductivity nominally greater than this value (e.g., 1 to 5 feet per day) to minimize the likelihood of flow bypassing. This will also ensure a more even distribution of flow within the PRB.

Table J5
Summary of Hydraulic Conductivity Data

Location ID	Depth Interval (feet bgs)	Hydraulic Conductivity[1] (cm/s)	Hydraulic Conductivity[1] (feet per day)	Data Source[2]
PDI-PRB-DP-04	5 to 10	**1.5E-03**	**4.3**	2020 PDI low-flow, Thiem
	10 to 15	**2.2E-04**	**0.62**	2020 PDI low-flow, Thiem
	15 to 20	**5.5E-04**	**1.6**	2020 PDI low-flow, Thiem
PDI-PRB-DP-05	10 to 15	**5.0E-05**	**0.14**	2020 PDI low-flow, Thiem
	15 to 20	**1.0E-03**	**2.8**	2020 PDI low-flow, Thiem
	20 to 25	**1.0E-03**	**2.8**	2020 PDI low-flow, Thiem
PDI-PRB-PC-01	1.2 to 8.5	**2.7E-05**	**0.075**	CPT
	8.5 to 13.3	**8.5E-07**	**0.0024**	CPT
	13.3 to 18.9	**5.5E-05**	**0.15**	CPT
	18.9 to 24.0	**8.6E-07**	**0.0024**	CPT
	24.0 to 39.7	**2.0E-06**	**0.0056**	CPT
PDI-PRB-DP-08	25 to 30	**3.0E-04**	**0.85**	2020 PDI low-flow, Thiem
PDI-PRB-DP-09	7 to 30	6.8E-03	**19.2** (12.8)	HPT
PDI-PRB-DP-10	13 to 30	3.8E-03	**10.9** (7.3)	HPT
RL-2S	7.5 to 17.5	4.0E-05	0.11	2Q 2019, low-flow, Thiem
		2.1E-05	0.061	1Q 2019, low-flow, Cooper-Jacob
		4.7E-05	0.13	Short-term pumping test (1984)
	Average	**3.6E-05**	**0.10**	--
RL-2D	25 to 35	8.0E-05	0.23	1Q 2018 low-flow, Thiem
		3.9E-05	0.11	1Q 2018, low-flow, Cooper-Jacob
		1.0E-04	0.28	1Q 2019, low-flow, Thiem
		1.3E-05	0.036	1Q 2019, low-flow, Cooper-Jacob
		5.4E-04	1.5	Short-term pumping test (1984)
	Average	**1.5E-04**	**0.44**	--

Location ID	Depth Interval (feet bgs)	Hydraulic Conductivity[1] (cm/s)	Hydraulic Conductivity[1] (feet per day)	Data Source[2]
PZ-6	7.5 to 11.9	3.5E-04	0.99	3Q 2019, low-flow, Thiem
		9.5E-05	0.27	3Q 2019, low-flow, Cooper-Jacob
		5.3E-04	1.5	4Q 2019, low-flow, Thiem
		3.2E-04	0.92	4Q 2019, low-flow, Cooper-Jacob
	Average	**3.2E-04**	**0.92**	--
PZ-7	8.4 to 17.8	1.8E-04	0.51	3Q 2019, low-flow, Thiem
		6.8E-05	0.19	3Q 2019, low-flow, Cooper-Jacob
		1.7E-04	0.48	4Q 2019, low-flow, Thiem
		6.6E-05	0.19	4Q 2019, low-flow, Cooper-Jacob
	Average	**1.2E-04**	**0.34**	--
Minimum		8.5E-07	0.0024	--
Maximum		1.5E-03	19.2	
Geometric mean[3]		6.1E-05	0.28	

Notes:
--: not applicable

1. Values used to calculate hydraulic conductivity summary statistics are in bold type.
2. Hydraulic conductivities were estimated from low-flow sampling records using the Thiem method (steady-state drawdown) and Cooper-Jacob method (transient drawdown). For locations where both the Thiem method and Cooper-Jacob method were used, arithmetic mean was calculated for both methods. Low-flow sampling records include the 2020 PDI work and routine groundwater sampling in 2018 and 2019. Data from falling head slug tests conducted in October 2006 were analyzed using the Bouwer and Rice method. CPT and HPT were performed during the 2020 PDI.
3. The geometric mean for hydraulic conductivity was calculated excluding the two HPT-derived estimates because these are not quantitative.

5.2.2 Hydraulic Gradient

The horizontal hydraulic gradient is estimated using water levels in the well pair RL-2S/2D and the CDID ditch in 2018 and 2019, as shown in Table J6. The hydraulic gradient ranges from 0.004 to 0.026 foot per foot, with an average of 0.013 foot per foot.

Table J6
Summary of Hydraulic Gradients

Well ID	Distance to CDID Ditch No. 14 (feet)	Period	Groundwater Elevation[1] (feet NAVD88)	Surface Water Elevation[1,2] (feet NAVD88)	Hydraulic Gradient (feet per foot)
RL-2S	100	1Q 2019	2.12	0.48	0.016
		2Q 2019	1.70	0.20	0.015
		3Q 2019	1.99	1.52	0.005
		4Q 2019	2.16	1.36	0.008
		1Q 2018	3.10	0.51	0.026
		2Q 2018	1.78	0.15	0.016
		3Q 2018	1.52	1.13	0.004
		4Q 2018	1.47	0.62	0.009
PZ-6	50	3Q 2019	1.80	1.52	0.006
		4Q 2019	2.20	1.36	0.017
PZ-7	60	3Q 2019	2.32	1.52	0.013
		4Q 2019	2.69	1.36	0.022
				Minimum	0.004
				Maximum	0.026
				Average	0.013

Notes:

1. Groundwater and surface water elevations were measured during routine site monitoring.
2. Surface water elevations were collected at the CDID Up monitoring station.

5.2.3 *Effective Porosity*

An effective porosity of 0.3 is used for the reactive medium. Because the reactive medium is expected to be similar to well-graded sand, a lower range value for the range of sand porosity from the literature, which is between 25% and 50%, is used (Fetter 2001; Freeze and Cherry 1979).

5.2.4 *Range of Groundwater Velocities*

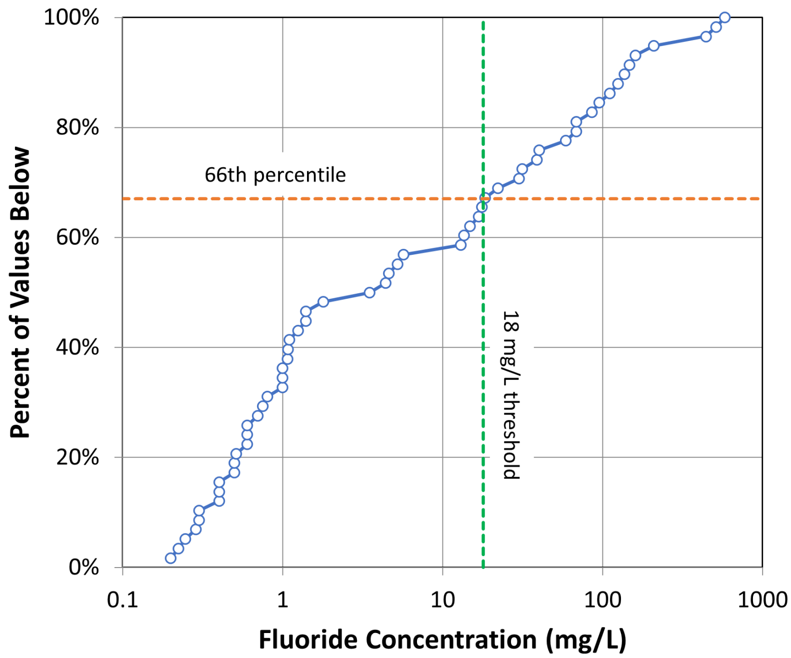
The expected range of groundwater velocities through the PRB were calculated using Equation J1 and the parameters summarized in Sections 5.2.1 through 5.2.3. The geometric mean of hydraulic conductivity (0.28 foot per day) and the range of hydraulic gradients from Table J6 were used to calculate the range of groundwater velocities for the PRBs as a whole. Calculated groundwater velocities within the PRB ranged from 1.3 to 8.7 feet per year, with an average of 4.4 feet per year. As discussed earlier, the hydraulic conductivity of the PRB media will be in the upper range of aquifer hydraulic conductivity (1 to 5 feet per day) to prevent flow bypassing and provide for equalization of spatial variations in flow.

In addition, a higher groundwater velocity value was developed for sensitivity analyses evaluating potential early breakthrough in areas of higher hydraulic conductivity in order to inform the development of the performance monitoring plan for the PRBs. A linear velocity value of 26 feet per year was derived from the 90th percentile hydraulic conductivity value (5.6 feet per day) and the minimum gradient (0.004). The use of the minimum gradient is justified in this case because there is no evidence for a localized source of enhanced recharge along the PRB alignment. In absence of such and in accordance with Darcy's Law, higher conductivity zones will develop lower hydraulic gradients than less conductive zones.

5.3 PRB Design Life

The PRB design life is based on the duration of time during which groundwater with concentrations exceeding the threshold of 18 mg/L (defined at the beginning of Section 5) will continue to flow toward CDID Ditch No. 14. The average PRB design life is estimated to be 18 years, based on the average current fluoride concentration along the PRB alignment (53.5 mg/L; Table J4) and an average decrease of fluoride concentrations in inflowing groundwater of 6% per year. However, local estimates of the design life of the PRB will vary due to spatial variability in fluoride concentrations and mass flux along the alignment. The design life for sections with higher-than-average fluoride concentrations will be longer than 18 years, and conversely, the design life for sections where fluoride concentrations are currently below average will be less than 18 years. For example, a PRB design life of 35 years is estimated using the 90th percentile fluoride concentration (Table J4). The threshold value of 18 mg/L corresponds to the 66th percentile of fluoride concentrations measured in groundwater along the western edge of the Closed BMP Facility that would discharge to the CDID ditch (Figure J5). In other words, groundwater is estimated to already be below the 18 mg/L threshold over a significant portion of the cross-sectional area that will be intercepted by the PRBs. Fluoride removal from these portions of the PRBs and discharge of fluoride-free groundwater, as well as discharge of lower fluoride groundwater from areas along the alignment that are outside of the PRBs, will contribute significantly to reduced fluoride concentrations in CDID Ditch No. 14.

Figure J5
Cumulative Distribution of Fluoride Concentrations in Groundwater Discharged to the CDID Ditch



Note:
The threshold value of 18 mg/L corresponds to the 66th percentile of fluoride concentrations measured in groundwater along the western edge of the Closed BMP Facility that would discharge to the CDID ditch.

5.4 Model Simulations and Results

The model was used to simulate fluoride breakthrough for a series of PRB scenarios in which the activated alumina dose was varied. The scenarios were run for the 3-foot-wide PRB with the calculated average linear groundwater velocity of 4.4 feet per year and an influent groundwater chemistry identical to RL-2S (Table J2) except for fluoride concentration. The initial fluoride concentration was set at the calculated average within the PRB alignment (53.5 mg/L; Table J4)) and decreases at a rate of 6% per year, as discussed in Section 5.1.2.

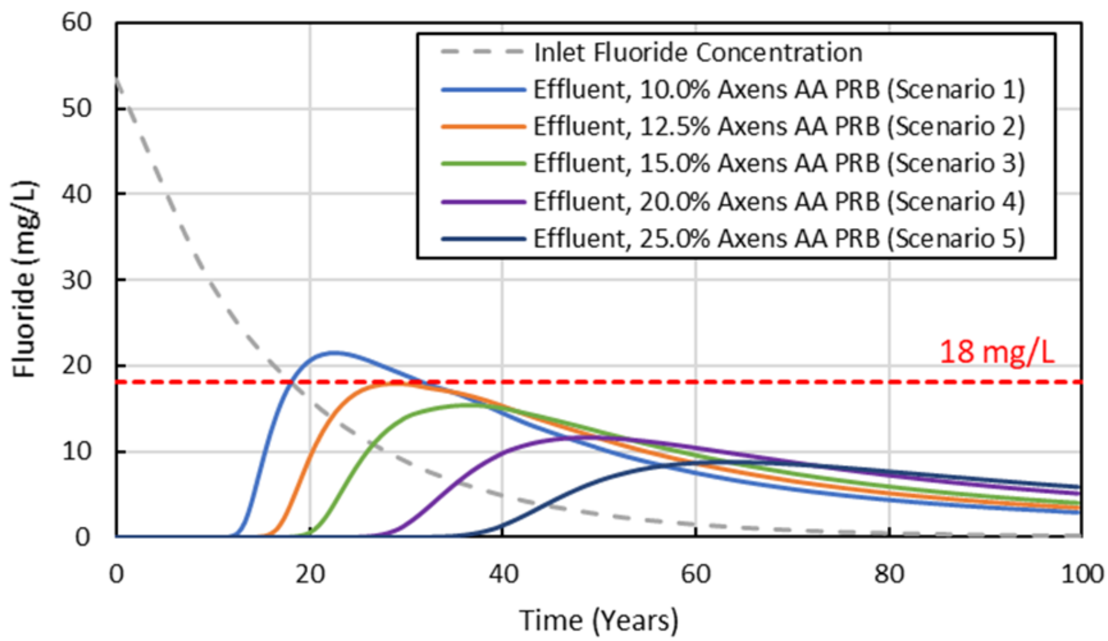
The model results are shown in Figure J6. Predicted fluoride breakthrough times are summarized in Table J7. The average PRB design life of 18 years (based on time for PRB influent fluoride concentrations to decrease below the 18 mg/L threshold) is achieved with a 10% activated alumina dose (Scenario 1 in Table J7). However, PRB effluent concentrations are predicted to increase, peaking at 22 mg/L after approximately 24 years, before declining again (Figure J6). The transient delayed fluoride peak is due to partial fluoride desorption from the PRB as the media re-equilibrates with the lower influent groundwater concentrations. Increasing the activated alumina dose

(Scenarios 2 to 5 in Table J7) progressively delays the transient peak arrival time and reduces the peak fluoride concentration. An activated alumina dose of 12.5% provides sufficient additional absorption capacity to suppress the desorption that would occur after concentrations entering the PRB drop below the 18 mg/L fluoride threshold, ultimately preventing threshold exceedances in the groundwater exiting the PRB. The PRB media dose is therefore designed to be robust enough that future media replacement is not anticipated to be necessary.

Table J7
Summary of Fluoride Breakthrough Times for PRB Scenarios

Scenario	PRB Media Composition (wt %)		Time to Breakthrough of Fluoride Greater than 18 mg/L (years)
	Activated Alumina	Sand/Pea Gravel	
1	10	90	18
2	12.5	87.5	∞
3	15	85	∞
4	20	80	∞
5	25	75	∞

Figure J6
Simulated Fluoride Breakthrough Curves for PRBs as a Function of Activated Alumina Dose



5.4.1 Sensitivity Analysis

Additional simulations were performed to assess the potential impact of variations of fluoride mass flux along the PRB alignments on fluoride breakthrough times and to assess the effectiveness of a higher activated alumina dose on fluoride breakthrough time in higher mass flux zones in order to inform the development of the long-term monitoring program for the PRBs.

As discussed in Section 5.2.4, the average groundwater velocity entering the PRBs, based on the geometric mean hydraulic conductivity of upgradient soils, is 4.4 feet per year, with a range from 1.3 to 8.7 feet per year due to the range of hydraulic gradient. An upper value for the groundwater velocity, based on the 90th percentile hydraulic conductivity estimate, was also calculated and found to be 26 feet per year. For sensitivity analysis, 4.4 and 26 feet per year were selected to bracket the range of groundwater velocities.

The average fluoride concentration in groundwater collected from multiple depth intervals along the PRB alignment is 53.5 mg/L, and the 90th percentile value is 140 mg/L (Table J4). These values were used to bracket the range of influent fluoride concentrations for sensitivity analysis.

Sensitivity model runs were performed using combinations of the mean and upper values of groundwater velocity and influent fluoride concentration. These included two high mass flux zone scenarios (mean velocity/high fluoride and high velocity/mean fluoride) and one extreme mass flux zone scenario (high velocity/high fluoride). The high mass flux zone scenarios were simulated for a range of activated alumina doses from 12.5% to 25% by weight of the PRB media. The results of the sensitivity model runs are presented in Table J8 and compared to the baseline scenario (mean velocity/mean fluoride) in terms of PRB breakthrough times for fluoride concentrations exceeding 18 mg/L.

Table J8
PRB Breakthrough Time Sensitivity Analysis

Scenario	Groundwater Velocity (feet per year)	Initial Fluoride Concentration (mg/L)	Activated Alumina Dose in PRB (wt %)			
			12.5%	15%	20%	25%
			Time to Breakthrough of Fluoride Greater Than 18 mg/L (years)			
Baseline	4.4	53.5	∞	∞	∞	∞
High Flux Zone	4.4	140	10	12	18	23
	26	53.5	3	4	5	6
Extreme Flux Zone	26	140	2	2	3	3

The sensitivity model run results indicate that fluoride breakthrough could occur in sections of the PRB with high fluoride mass flux within 2 to 10 years. These zones, however, represent a small portion of the total width of PRBs. Based on the distribution of groundwater velocities and fluoride concentrations, the high flux zones, based on 90th-percentile values, may represent less than 10% of the PRBs. The extreme flux scenario, which is based on the 90th-percentile velocity and 90th-percentile fluoride concentration, likely represents a mass flux that occurs along only 1% of the PRBs. Fluoride concentrations associated with the majority of the groundwater flow exiting the PRBs will be treated to very low levels and will provide for ongoing dilution of fluoride discharged from high mass flux zones to the CDID ditch.

Increasing the activated alumina dose delayed the time to breakthrough of concentrations above the 18 mg/L threshold in higher mass flux zones but is not predicted to completely suppress breakthrough or the desorption peak. For example, doubling the dose approximately doubled the time to breakthrough for the high flux zone scenarios but had a smaller effect on the extreme flux zone scenario. Therefore, increasing the activated alumina dose does not present a clear benefit with regard to high mass flux zones because the activated alumina dose for the baseline scenario (12.5%) was developed to provide sufficient treatment to be protective of surface water quality along the overall PRB alignment.

However, understanding the potential time frames for PRB media exhaustion along zones of higher fluoride mass flux is useful for informing and designing the performance monitoring plan for the PRBs. For example, long term monitoring will initially occur at a quarterly frequency during the first 2 years to detect and address areas of early breakthrough but could be reduced to annual thereafter.

5.4.2 Clogging Potential

Biogeochemical reactions and mineral transformations within the PRB media can result in changes in porosity over time. The elevated pH of groundwater is not conducive to, and likely inhibits, biological activity, and the biological fouling potential is considered low. Porosity reduction due to mineral precipitation may also lead to clogging of the PRB and result in preferential pathways and flow bypassing. The PRB model accounts for potential mineral precipitates (Section 3). No significant mineral precipitates were formed in the activated alumina PRB model simulations. The PRB media also includes pea gravel to minimize clogging potential. Therefore, the potential for clogging of the PRB will be very low.

6 Summary and Recommendations

A reactive transport model was developed, calibrated, and used to determine the optimal dose of activated alumina for the PRBs that will be installed at the site. The model simulates the key geochemical and hydrological processes, including advection, dispersion, and adsorption, that control the fate and transport of fluoride and other major ions within the PRB and predicts the fluoride concentration in groundwater exiting the PRB over time. The model was calibrated using data obtained from laboratory column tests, in which the columns were packed with a mixture of activated alumina (Axens AA) and quarry sand; both materials were obtained from the specific sources that will be used for PRB construction. The calibrated model was used to predict fluoride breakthrough for site groundwater entering the PRB. A 3-foot-wide PRB containing 12.5% by weight (dry basis) activated alumina was determined to be protective of surface water quality in CDID Ditch No. 14. Hydraulic clogging potential of the PRB media was evaluated and considered not to be significant.

Sensitivity analyses were also performed to assess the impact of zones of high fluoride mass flux on fluoride breakthrough in the PRBs. The sensitivity analyses indicate that fluoride breakthrough in zones of high to extremely high fluoride mass flux, representing 10 and 1% of the total width of PRBs, respectively, could occur within 10 to 2 years. Increasing the dose of activated alumina in the PRBs will delay the breakthrough from high mass flux zones but will not suppress it. However, as these high flux zones represent a very minor portion of the total width of the PRBs, their potential impact on surface water quality in CDID Ditch No. 14 will also be commensurately small. Finally, the predicted breakthrough times for high mass flux zones provide a technical basis the long-term monitoring framework. Therefore, the proposed design for a 3-foot-wide PRB containing 12.5% by weight activated alumina is determined to provide long-term groundwater treatment that will be protective of surface water quality in CDID Ditch No. 14.

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