Apply THMC to simulate the porosity reduction in a permeable reactive barrieraquifer system

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OUTLINE



INTRODUCTION

Permeable reactive barrier (PRB)



Permeable reactive barrier (PRB)

A method of treating groundwater contaminants in situ.

Using **reactive materials**. Contaminants passes PRB and their concentration will decreases.

PRBs are **sustainable** when used for **30 years or more**.

PRB is commonly used to treat groundwater contamination.

Motivation

Why does porosity reduce and how does it affect PRB?



Permeable reactive barrier (PRB)

How is the long-term effectiveness of PRBs?

Motivation



Li et al. (2005) preview that Porosity reduction from 0.0007 to 0.03 per year

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Literature Reviews

Many models have been used to evaluate the performance of PRB, but there are some limitations.



Measured and simulated concentrations for PRB at U.S. Coast Guard Support Center (MODFLOW and RT3D model) (Li et al., 2005)

Literature Reviews

The position of the highest porosity reduction in PRB is not clear



THMC MODEL

(Thermal-Hydrology-Mechanic-Chemical Processes)

STRENGTH

INTERNAL

EXTERNAL

The computer program is a numerical model of couple THMC through multiple phase.

It is available in 2D and 3D formats.

Incorporate the effect of precipitation/dissolution on the change of pore sizes, hydraulic conductivity, and diffusion/dispersion.

Deal with equilibrium and kinetic reactions.

OPPORTUNITY

The model can be applied to many different situations.



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Objective

Apply THMC to simulate the porosity reduction in a permeable reactive barrier aquifer system

- To identify the most significant variables to consider when evaluating porosity reductions and their impact on performance of PRB.
- Analyzing porosity reduction for a long time.

FUTURE

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METHODOLOGY

FUTURE WORKS

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Flow and transport model

	Aquifer	PRB
	(Homogeneous)	(Homogeneous)
Domain	71m×60m	1m×25m
K	3.9 (m/day)	216 (m/day)
Porosity	0.3	0.6
	No flow: top, bottom	
Boundary conditions	Constant-head (Dirichlet)	Upgradient: background ground
	Upstream and Downstream	water concentrations



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1. Ground water flow model

The steady-state flow through the aquifer and PRB. The governing equation :

$$\nabla \cdot \left[K \cdot (\nabla h + \frac{p}{p_0} \nabla z) \right] + \frac{p^*}{p_0} q = 0$$

K: the hydraulic conductivity (L/T) h: the pressure head (L); z: the potential head (L) p^* : the fluid density of either injection (= p^*) or withdraw (= p) (M/L³) p: the fluid density with dissolved biogeochemical concentrations (M/L³) p_0 : the referenced fluid density at zero biogeochemical concentration (M/L³) q: the source or sink representing the artificial injection or withdrawal of fluid [(L³/L³)/T]

2. Reactive transport model

The governing equation :



 C_i : Concentration of the i-th species (M/L³) V_f : The fluid velocity (L/T) M_i: Source/sink term (M/L³)/T)

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3. Geochemical algorithm

Table 1: Geochemical reactions (Li et al., 2006)

Reaction type	Reaction	Mineral formed	Solubility constant $log(K_{eq})^{a}$
Aerobic iron corrosion	$Fe^0 + H_2O + 0.5O_2(aq) \!\rightarrow\! Fe^{2+} + 2OH^-$	_	-
Anaerobic iron corrosion	$Fe^0 + 2H_2O {\rightarrow} Fe^{2+} + H_2(aq) + 2OH^-$	_	-
Nitrate iron corrosion	$4Fe^{0} + 7H_{2}O + NO_{3}^{-} \rightarrow 4Fe^{2+} + 10OH^{-} + NH_{4}^{+}$	_	-
Microbial sulfate reduction	$SO_4^{2-} + 4H_2(aq) \rightarrow HS^- + OH^- + 3H_2O$	-	-
Equilibrium reaction between bicarbonate and	$\mathrm{HCO}_{3}^{-} \leftrightarrow \mathrm{H}^{+} + \mathrm{CO}_{3}^{2-}$	_	- 10.07
Dissociation of water	$H_2O \leftrightarrow H^+ + OH^-$	-	-14.0
Secondary mineral precipitation/dissolution	$CaCO_3(s) \leftrightarrow Ca^{2+} + CO_3^{2-}$	Calcite/Aragonite	- 8.1
	$CaMg(CO_3)_2(s) \mathop{\leftrightarrow} Ca^{2+} + Mg^{2+} + 2CO_3^{2-}$	Ca-Mg-carbonate	- 17.7
	$MgCO_3(s) \mathop{\leftrightarrow} Mg^{2+} + CO_3^{2-}$	Magnesite	-7.2
	$Mg(OH)_2(s) \mathop{\leftrightarrow} Mg^{2+} + 2OH^-$	Brucite	-11.2
	$MnCO_3(s) \mathop{\leftrightarrow} Mn^{2+} + CO_3^{2-}$	Rhodochrosite	-9.3
	$Mn(OH)_2(am) \leftrightarrow Mn^{2+} + 2OH^-$	Pyrochroite	- 12.9
	$FeCO_3(s) \leftrightarrow Fe^{2+} + CO_3^{2-}$	Siderite	- 10.5
	$Fe(OH)_2(am) \leftrightarrow Fe^{2+} + 2OH^-$	Ferrous Hydroxide	-15.2
	$FeS(am)+H_2O{\leftrightarrow}Fe^{2+}+HS^-+OH^-$	Ferrous Sulfide	-18.4

 $^{\rm a}$ From Krauskopf and Bird (1995) at 15 $^{\circ}{\rm C}$ and 101 kPa.

k: the rate coefficient, S: the iron surface area $[E_A]$: the concentration of DO or nitrate

The reaction rate

Iron corrosion by DO and nitrate

$$r = -kS[E_A]$$

Monod equation

$$r = -k \left(\frac{\left[SO_4^{2^-} \right]}{K_{SO_4} + \left[SO_4^{2^-} \right]} \right) \left(\frac{\left[H_2(aq) \right]}{K_{H_2} + \left[H_2(aq) \right]} \right)$$

Mineral precipitation (r>0) or dissolution (r <0)

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

 K_{eff} : an effective rate coefficient IAP: the ion activity product

The reactive surface area of the ZVI

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):

Reduction of the surface area due to **mineral precipitation** was computed using the method described in Morrison et al.(2003):

$$S_{t(ZVI)} = S_0 \left(\frac{\varphi}{\varphi_0}\right)^{\frac{2}{3}}$$

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Combined to obtain: Li et al.(2006)

 S_0 : the initial reactive surface area φ_0 : initial volume fraction of the ZVI φ : volume fraction of ZVI at time t **\Deltan: the porosity reduction due to mineral precipitation** Tc: the ratio of change in porosity per change in reactive surface area

•••• •••• •••• RESULTS AND •••• DISCUSSION

Parameter

Rate coefficients used in simulation

Reactions	terms	Units	Base case

Aqueous species in influent ground water	Aqueous species concentrations (M)	DO
	Base Case	Water ^e Nitrate ^e
Fe^{2+}	1.0×10^{-10} 1.0×10^{-3}	Microb
Mg^{2+}	1.0×10^{-3}	CaCO ₃
Mn ²⁺ OH ⁻	1.0×10^{-7} 1.0×10^{-7}	FeCO ₃
Alkalinity (HCO ₃ ⁻)	1.0×10^{-3}	Fe(OH)
O_2 (aq)	1.0×10^{-10} 1.0×10^{-5}	res (al
SO ₄ ²⁻	1.0×10^{-3}	MgCO
		MnCO

(Li et al., 2005)

DO ^c	m ³ /m ² -day	2.8×10^{-2}
Water ^c	mole/m ² -day	2.0×10^{-7}
Nitrate ^c	m ³ /m ² -day	1.0×10^{-4}
Microbial sulfate reduction ^d	M/day	1.0×10^{-5}
CaCO ₃	M/day	1.0×10^{-4}
FeCO ₃	M/day	1.0×10^{-4}
Fe(OH) ₂ (am)	M/day	1.0×10^{-4}
FeS (am)	M/day	1.0×10^{-4}
CaMg(CO ₃) ₂	M/day	1.0×10^{-9}
MgCO ₃	M/day	1.0×10^{-4}
MnCO ₃	M/day	1.0×10^{-6}
Mn(OH)2(am)	M/day	1.0×10^{-4}
Mg(OH) ₂	M/day	1.0×10^{-4}

(Li et al., 2005)

^c Reactive surface area of ZVI set at $3.9 \times 10^6 \text{ m}^2/\text{m}^3$.

^d Half-saturation constants for SO₄²⁻ and H₂ (aq) were $K_{SO_4} = 1.0 \times 10^{-4}$ M, and $K_{H_2} = 1.0 \times 10^{-7}$ M, respectively.

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1. Groundwater flow



PRB is more permeable than the surrounding aquifer materials



Water can readily flow through PRB maintaining groundwater hydrogeology while contaminants are treated.

2. Reactive transport Mineral type



Porosity reduction is mainly caused by three mineral aragonite (**CaCO3**), siderite (**FeCO3**), and ferrous hydroxide **Fe(OH**)₂

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Porosity reduction profiles for different combinations of minerals

2. Reactive transport

Influent concentration



Concentration bicarbonate (HCO₃⁻) has the largest effect on porosity reduction

Porosity reduction for high and low concentrations of $HCO_3^- SO_4^{-2-}$

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CONCLUSIONS

Conclusions

- The porosity reduction reaches a **peak the entrance face** (0.0138).

- Aragonite (CaCO₃), siderite (FeCO₃), and ferrous hydroxide Fe(OH)₂ are the most important minerals to include in the geochemical model.

- **Porosity reduction** is most affected by **HCO**₃⁻ concentrations.

FUTURE WORK

INTRODUCTION METHODOLOGY

Workflow

& DISCUSSION

PRELIMINARY RESULTS

Continue running the reactive transport model Comparison of results with field data and previous models Evaluating porosity reduction and long-term results Extending the model (Boundary condition, chemical reaction, etc.) FUTURE

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CONCLUSIONS

Thank you for your attention