



A case against K_d -based transport models: natural attenuation at a mill tailings site

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Abstract

This study compares numerical modeling results of contaminant transport using a multi-component coupled reactive mass transport model and a distribution coefficient (K_d)-based transport model. The study site is a contaminated groundwater aquifer underneath a uranium mill tailings pond in the western USA. Advective–dispersive–reactive transport is simulated for a 5-year period of intrusion of tailings fluid into the shallow aquifer, followed by flushing with uncontaminated upgradient groundwater for 1600 years. The coupled model shows that groundwater–sediment interactions result in multiple concentration waves, strong interactions among solutes, and chemical heterogeneity in both space and time. As a result, calculated K_d values vary spatially and temporarily. None of these characteristics can be simulated with a K_d -based model. These results illustrate the shortcomings of the K_d approach, the usage of which is prevalent in the regulatory environment.

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1. Introduction

Accurate prediction of the fate and transport of regulated metals and radionuclides in the subsurface of abandoned mining sites is critical to the assessment of environmental impact and to the development of effective remediation technologies. In prevailing practice, this task has been largely addressed by the use of K_d -based “reactive” transport models. The partitioning of a solute between the aquifer solid matrix and groundwater is described by the linear isotherm or distribution coefficient, K_d ,

$$K_{d,i} = \frac{S_i}{C_i}, \quad (1)$$

where S_i and C_i represent the concentrations of component i bound to the solid matrix (mg/kg) and in

groundwater (mg/l), respectively, and K_d usually has units of ml/g.

Other commonly used isotherms for predicting partitioning of solute between aqueous solution and solid matrix include the Langmuir isotherms and Freundlich isotherms. The Langmuir isotherm states that

$$S_i = \frac{K_L b C_i}{1 + C_i K_L}, \quad (2)$$

where K_L is the Langmuir isotherm constant, and b is related to the maximum site concentration on the solid surface.

The Freundlich isotherm states that

$$S_i = K_F C_i^n, \quad (3)$$

where K_F and n are constant. If $n = 1$, the above formula reduces to the linear adsorption isotherms; n is typically less than 1. Most often, linear, Langmuir, and Freundlich isotherms are used as a lumped parameter that describes the removal of contaminants from

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groundwater, regardless of the chemical reaction mechanisms, e.g., adsorption, ion exchange, and the precipitation of pure solids and solid solutions (Langmuir, 1997, p. 356).

Substitution of Eq. (1) into the advective–dispersive–reactive (ADR) transport equation results in a mathematical expression that can be solved analytically and numerically (see Zheng, 1990 for mathematical development). Because of this mathematical simplicity, the likely assurance of an answer in a short period of time at low cost, and easy measurements of K_d values from batch and column tests, use of K_d -based models is widespread in the regulatory environment. A similar situation exists for the Langmuir and Freundlich isotherms, but they are less used. The discussion that follows is therefore centered on the K_d -based transport models.

However, K_d , Langmuir, and Freundlich isotherms are phenomenological and empirical parameters. It is well known that they are insufficient to describe the complex geochemical reactions that control the distribution of solutes between groundwater and aquifer matrix in subsurface environments (Reardon, 1981; Cederberg et al., 1985; Yeh and Tripathi, 1991; Stumm and Morgan, 1996; Langmuir, 1997; Bethke and Brady, 2000; Zhu et al., 2001; Zhu and Burden, 2001; Zhu et al., 2002; Zhu and Anderson, 2002). Bethke and Brady (2000) recently summarized the poor fit of K_d -based models to laboratory and field data. In particular, K_d -based models have failed to predict the long contamination tail observed at many sites that have gone through extensive pump-and-treat remediation.

In the situation of active or abandoned mining sites with acid mine drainage problems, the shortcomings of the K_d approach become more severe because mining impacted groundwater systems are reactive, involving multiple components that interact with each other, and are chemically heterogeneous. Multiple, sharp reaction fronts are involved, and these fronts evolve through space and time (Zhu et al., 2001). Despite the well-known pitfalls of the K_d approach, it has been continuously used in environmental assessments of acid mine drainage (see Superfund Public Information System, distributed by the US EPA, September, 2000).

A more theoretically sound approach to the simulation of reactions and flow in chemically complex and heterogeneous environments is the use of *coupled reactive transport models* in which the advective–dispersive transport equations are solved together (Schwartz and Domenico, 1973; Walsh, 1983; Cederberg et al., 1985; Lichtner, 1985; Yeh and Tripathi, 1991; Steefel and Lasaga, 1994; Raffensperger and Garven, 1995; Zhu et al., 1996). For example, in the code of PHREEQC Version 2.0 (Parkhurst and Appelo, 1999), the reaction term in the ADR equation is solved separately for each finite difference cell by using a chemical module

in which chemical speciation and partitioning between the solid matrix (including mineral surfaces) and aqueous solutions are calculated based on thermodynamic equilibrium and associated mass-balance equations (see Parkhurst, 1995).

In this study, we used both PHREEQC version 2.0 and a K_d -based transport model to simulate the reactive transport and natural attenuation of a contaminated aquifer in an abandoned uranium mill tailings site in Wyoming, USA. Results from these two models are compared to illustrate the deficiencies of the K_d -based models. This comparison shows that coupled models allow for better representation of multiple component transport in a chemically heterogeneous environment.

2. Site contamination and hydrogeological setting

The Bear Creek Uranium site is located in the southern part of the Powder River Basin in Wyoming (Fig. 1), where a uranium mill operated from the 1970s to the mid-1980s. Sulfuric acid and sodium chlorate were used to dissolve and oxidize the uranium. Spent acids and tailings slurries were piped to unlined tailings ponds. An estimated 3.3 million tons of tailings and 880 million gallons of liquid effluent have been disposed into the tailings pond. The tailings fluid has a pH between 1.5 and 3.5, a total dissolved solid (TDS) content close to 20,000 mg/l, and high concentrations of arsenic (As), beryllium (Be), cadmium (Cd), chromium (Cr), lead (Pb), molybdenum (Mo), nickel (Ni), selenium (Se), radium (^{226}Ra , ^{228}Ra), thorium (^{230}Th), and uranium (U) (Zhu et al., 2002).

Seepage from the disposal ponds into the underlying N sand of the Eocene Upper Wasatch Formation and alluvium aquifer has formed an acid plume (Fig. 2). The N sand and alluvium at the site is comprised primarily of quartz, microcline, a small amount of plagioclase, and about 2 wt% calcite (Sharp and Gibbons, 1964; Zhu et al., 2002). The measured total iron concentration in the Wasatch Formation is about 0.4 wt % as Fe (Sharp and Gibbons, 1964). Groundwater occurs 3–8 m below land surface. Numerous aquifer tests have been performed to evaluate transmissivities and storage coefficients. The hydraulic conductivity for the alluvium at Lang Draw is estimated at 3 m/d and, for N sand beneath the tailings impoundments is 0.9 m/d (GeoTrans, 1987, 1995, unpublished reports). A groundwater flow model was developed, and modeling results show that groundwater flows preferentially in the alluvium along Lang Draw, where the permeability is high, and to the northeast from the bend of the Impoundment Dam (GeoTrans, 1987, 1995, unpublished reports). These flow paths are supported by groundwater pH data, which outline the plume of lower pH groundwater

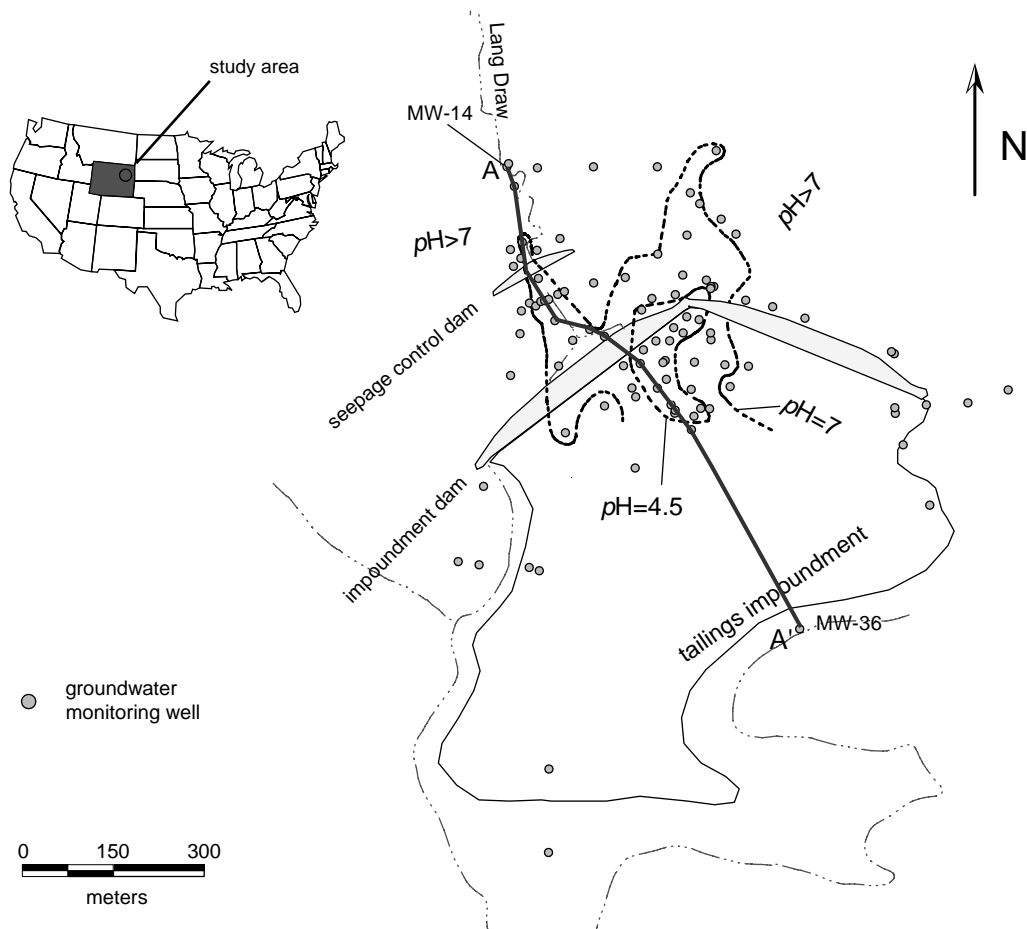


Fig. 1. Plan view of mine site and tailings impoundment. Dashed lines are pH contours, which delineate flow paths at site. Arrows indicate direction of groundwater flow.

(Fig. 1). Regional groundwater flows from the south of the site beneath the tailings basin and to the north.

To contain the migration of the plume downgradient, low-pH water was pumped from wells installed along the Lang Draw downgradient from the impoundment dam and piped into constructed evaporation basins within the tailings impoundment. Over time, the pumping efficiency of these wells decreased significantly. The current reclamation plan is to install a low-permeability cover on the tailings ponds to prevent further infiltration from precipitation. Results from hydrological modeling show that tailings pore water will cease to drain into the underlying N sand 5 years after the cover installation. After that time, the plume will be flushed by uncontaminated upgradient groundwater. The distance of the migration of the acid plume and regulated contaminants will depend on “natural attenuation,” the reactions of aquifer minerals with contaminated groundwater. The transport models are designed for this “cover and attenuate” reclamation plan.

3. Transport models

3.1. Coupled multi-component reactive transport model

An 800 m strip along cross-section A–A' (Fig. 2) was discretized into 200 cells for PHREEQC simulations. A uniform and constant Darcy velocity of 15 m/year calculated from the flow model (GeoTrans, 1987, unpublished data) and an effective porosity of 0.3 from measurements of core samples were used along the entire cross-section. A dispersivity of 10 m was calibrated from Cl^- distribution (Zhu et al., 2001). A total of 11 aqueous components—H, Ca, Mg, Cl, CO_3^{2-} , Al, SO_4^{2-} , Fe^{3+} , Na, K, and Si—and six minerals— $\text{Al}(\text{OH})_3(\text{a})$, $\text{Fe}(\text{OH})_3(\text{a})$, calcite, gypsum, $\text{SiO}_2(\text{a})$, and illite—were included in the simulations. The generalized double diffuse layer model of Dzombak and Morel (1990) was used to model adsorption of SO_4^{2-} , H^+ , Mg^{2+} , and Ca^{2+} onto $\text{Fe}(\text{OH})_3(\text{a})$ surfaces, and of SO_4^{2-} , H^+ onto $\text{Al}(\text{OH})_3(\text{a})$ surfaces. The surface acidity constants and

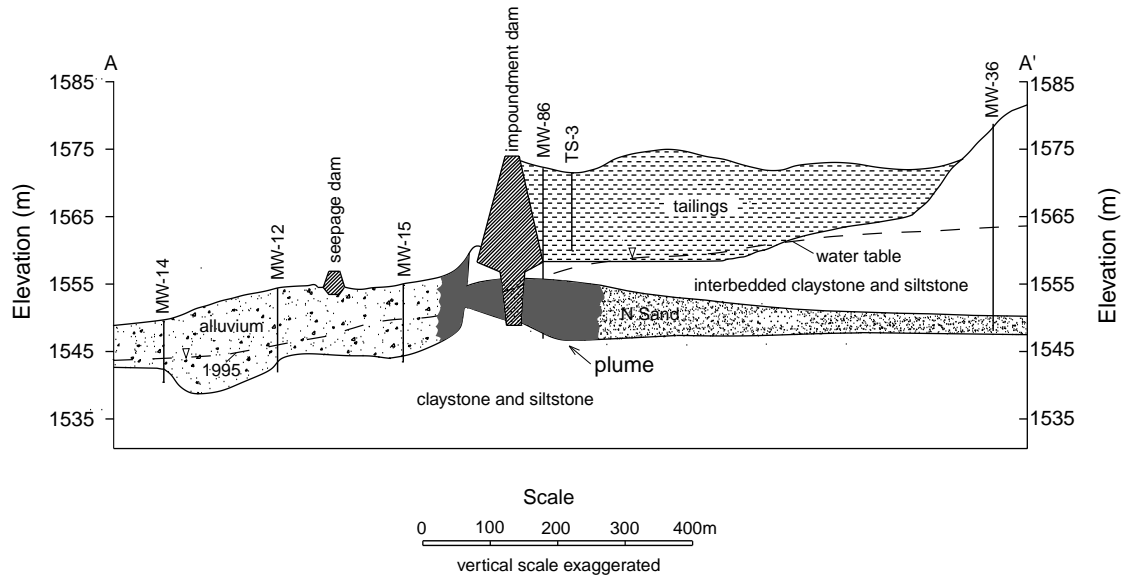


Fig. 2. Cross-section A–A' from Fig. 1. Groundwater flows from right to left. One-dimensional finite difference model starts approximately at tailings dam and continues along flow path.

intrinsic complexation constants for adsorption of SO_4^{2-} onto $\text{Al}(\text{OH})_3(\text{a})$ are from Stumm (1992). The site densities and surface areas for $\text{Al}(\text{OH})_3(\text{a})$ are from Meng and Letterman (1993). All parameters and surface complexation constants for adsorption of ions onto $\text{Fe}(\text{OH})_3(\text{a})$ are from Dzombak and Morel (1990). No data for Mg^{2+} and Ca^{2+} adsorption onto $\text{Al}(\text{OH})_3(\text{a})$ surfaces are available. However, modeling results show that Mg^{2+} and Ca^{2+} adsorption onto $\text{Fe}(\text{OH})_3(\text{a})$ is weak and negligible (hence, not discussed further below). The adsorption of Mg^{2+} and Ca^{2+} adsorption onto $\text{Al}(\text{OH})_3(\text{a})$ surfaces is likely also weak and would not influence the modeling results.

Initial conditions were specified to reflect site conditions in 1994 (Table 1), when a large number of groundwater samples were analyzed before the remedial action (Zhu et al., 2002). While the pore fluid chemistry has been analyzed, mineral compositions of the aquifer matrix were not determined, and that represents a common but serious shortcoming in site investigations (see Zhu and Burden, 2001). Alluvium deposits in the area unaffected by acid seepage have a neutralization capacity of up to 0.92 mol/l calcite equivalent. To be conservative, a 0.2 mol/l of calcite was used in the model. A value of 0.2 mol/l $\text{Fe}(\text{OH})_3(\text{a})$ was assigned to the first 100 m. Background $\text{Fe}(\text{OH})_3(\text{a})$ in the aquifer (101–800 m in the one-dimensional domain) were assumed to be 0.4 mol/l, approximately 20% of the measured total iron (0.4 wt%) in the Wasatch sandstones. Cauchy flux boundary conditions were used for both ends of the 1D strip. To represent the reclamation

Table 1
Initial conditions for the reactive transport model^a

Zone	I	II	III	IV
Length	100 m	140 m	300 m	260 m
Cells	1–25	26–60	61–135	136–200
Pore water	TS-3	MW-86	MW-15	MW-12
Temp (°C)	25	25	25	25
pH	3.8	4.5	6.5	6.7
Ca^{2+}	310	420	650	550
Mg^{2+}	1000	700	250	150
HCO_3^-	6.3	6.3	1450	878
Al^{3+}	1020	230	1.33	1.15
SO_4^{2-}	16,500	8100	1650	1500
Fe^{3+}	1950	926	2.18	0.69
SiO_2	40.5	10	9.7	8.4
K^+	60	42	18	14
Cl^-	550	400	375	275
Na^+	360	278	212	265
<i>Minerals (mol/l)</i>				
$\text{Al}(\text{OH})_3(\text{a})$	0, u	0.01	0.01	0.01
Gypsum	0.2	0.2	0	0
$\text{SiO}_2(\text{a})$	0, u	0, u	0, u	0, u
Illite	0, u	0, u	0	0
$\text{Fe}(\text{OH})_3(\text{a})$	0.2	0.4	0.4	0.4
Calcite	0, u	0, u	0.2	0.2

^a Concentrations for pore fluids are in mg/l, except for pH and temperatures and mol/l for solids; u: unsaturated; s: saturated. Fluids flow from cell 1–200.

Table 2
Boundary fluxes (third-type) used in simulations^a

Concentrations	First 5 years TS-3	After 5 years MW-36
pH	3.8	7.4
Ca ²⁺	310	158
Mg ²⁺	1000	21
HCO ₃ ⁻	6.3	153
Al ³⁺	1020	0.01
SO ₄ ²⁻	16,500	425
Fe ³⁺	1950	0.1
SiO ₂	40.5	5.6
K ⁺	60	7
Cl ⁻	550	25
Na ⁺	360	61

^aConcentration units for pore fluids are mg/l, except for pH and temperatures.

conditions, the incoming fluid had the chemistry of tailings pore fluid for the first 5 years and that of uncontaminated upgradient groundwater thereafter (Table 2).

3.2. K_d -based models

The one-dimensional finite-difference code Bio1D (Srinivasan and Mercer, 1987) was used for transport simulation. The code can simulate ADR transport and biodegradation. In this study, all transport parameters and initial and boundary conditions were set to resemble the coupled transport model as closely as possible. However, Bio1D can only simulate the transport of one solute at a time and cannot simulate the interactions of multiple solutes. Therefore, only the transport of sulfate is simulated for the comparison. Three K_d values were used: K_d of 0 (no retardation), 1, and 5 ml/g.

4. Results and model comparison

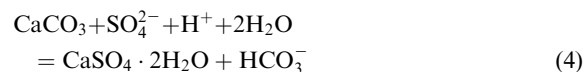
The two different approaches are illustrated by the reactive transport of SO₄²⁻ below. Sulfate, although not regulated by Nuclear Regulatory Commission for uranium mill tailings sites, is regulated by the State of Wyoming and the US Environmental Protection Agency (EPA). The EPA secondary drinking water standard is 250 mg/l. Sulfate discharge at the site has greatly exceeded the regulatory threshold.

4.1. Coupled model results

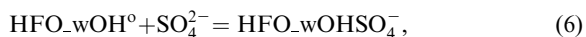
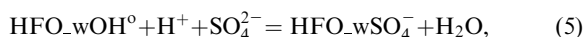
In this section, the results from the coupled model simulations are analyzed in terms of the values of effective K_d and the geochemical factors that determine

them. The spatial and temporal variations of the K_d values are highlighted. This variability is then underscored to point out the oversimplification of chemistry in K_d -based transport models.

When intruding acidic tailings fluid reacts with aquifer matrix, SO₄²⁻ concentration is reduced by the precipitation of gypsum



and also by surface adsorption



where the symbol HFO-w stands for the “weak” site of hydrous ferrous oxide (HFO) surface (Dzombak and Morel, 1990). Sulfate adsorption reactions onto Al(OH)₃(a) surfaces are similar to (5) and (6) (Stumm, 1992). In the Dzombak and Morel (1990) surface complexation model of HFO, the “strong” sites on HFO are 40 times less than the “weak” sites. Hence, adsorption of major ions like SO₄²⁻ is not influenced by the strong sites, which is therefore neglected in our simulation and discussion.

The gypsum precipitated in the aquifer and SO₄²⁻ adsorbed on mineral surfaces created a secondary source of sulfate contamination. That is, SO₄²⁻ contamination is apparently abated due to retardation. However, SO₄²⁻ removed from groundwater is stored in the solid matrix, and later is released when groundwater chemistry changes. During the flushing of the plume by uncontaminated upgradient groundwater, a part of the natural attenuation scheme, gypsum dissolution and SO₄²⁻ desorption are the dominant reactions affecting SO₄²⁻ transport.

Fig. 3a, on the left axis, shows the breakthrough curves (BTC) for sulfate in the last cell of the 1D domain. A concentration peak associated with the advective–dispersive front is followed by a concentration plateau reflecting equilibrium with gypsum. When all gypsum was expended, SO₄²⁻ concentrations dropped sharply and were controlled by desorption reactions.

Effective K_d values for sulfate can be calculated from simulation results based on the following equation:

$$K_{d,\text{eff}} = \frac{(C_{\text{gypsum}} + C_{\text{s,HFO}} + C_{\text{s,HAO}}) \theta}{C_{t,\text{aq}} \rho_b}, \quad (7)$$

where C are concentrations in mol/l, subscript s stands for surface species, and $C_{t,\text{aq}}$ denotes total dissolved sulfate concentrations. HFO and HAO stand for hydrous ferric oxides and hydrous aluminum oxides, respectively. $C_{\text{s,HFO}}$, $C_{\text{s,HAO}}$, and $C_{\text{s,gyp}}$ stand for concentrations of sulfate bound to HFO, HAO surfaces, and in gypsum, respectively.

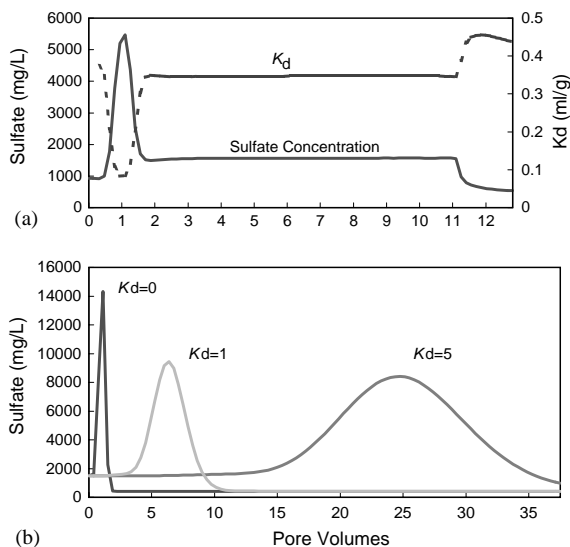


Fig. 3. Breakthrough curves (BTCs) for sulfate at 200th cell from: (a) coupled reactive transport model. Left axis shows total aqueous sulfate concentrations and right axis shows effective K_d calculated from Eq. (7); (b) BTC from K_d -based model.

Fig. 4 shows the $K_{d,eff}$ (ml/g) distribution at the end of 5 years of tailings water intrusion and at 100 and 200 years of flushing with uncontaminated groundwater. $K_{d,eff}$ varies spatially from 0.08 to 4.88 ml/g, a 60-fold change. More significantly, $K_{d,eff}$ values change with time.

The changes of calculated effective K_d are related to the types of chemical reactions that determine the partitioning of SO_4^{2-} between solid matrix and groundwater. This is illustrated in Fig. 5, in which the portions of K_d attributed to adsorption onto HFO, HAO, and gypsum are calculated separately according to Eq. (7). We can see in different time and space domains, different K_d values are determined by different mineral or mineral surface–water interactions.

At the end of 5 years of acidic tailings fluid intrusion (0 years flushing), a near constant K_d value is maintained at the first 250 m segment of the simulated flow path. This constant K_d value results from a constant gypsum concentration of 0.2 mol/l in the aquifer (Zhu et al., 2001, 2002) and a constant SO_4^{2-} source term. Sulfate adsorbed on the mineral surfaces are insignificant to the K_d values in this area. A peak K_d value occurs at the calcite dissolution-gypsum precipitation front because precipitation of $Al(OH)_3$ make available more reactive surface sites for SO_4^{2-} adsorption and, hence, solid-bound SO_4^{2-} increases. At the meantime, the aqueous SO_4^{2-} drops significantly because of gypsum precipitation, leading to higher K_d values. K_d values drop sharply downstream from the gypsum precipitation zone because of less SO_4^{2-} in the solid matrix (no gypsum), but

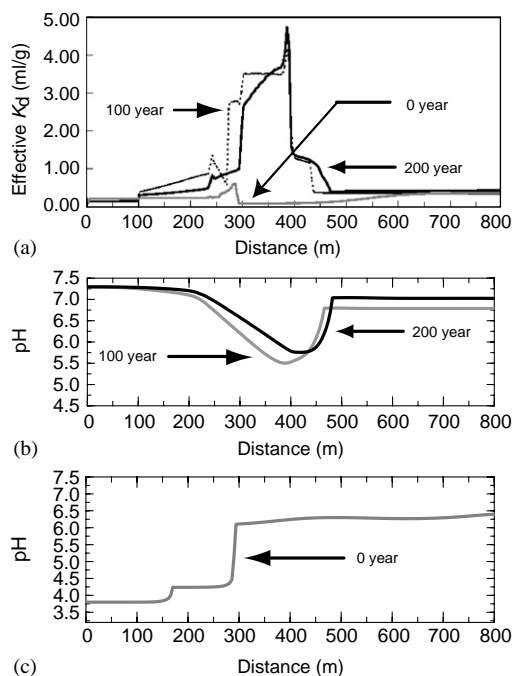


Fig. 4. (a) Effective K_d values calculated from results of coupled reactive transport simulation and (b) groundwater pH at 100, 200 flushing; and (c) groundwater pH at 0 year flushing.

the advective–dispersive SO_4^{2-} front nevertheless brings a high aqueous SO_4^{2-} concentration to this location. Further downstream, the partitioning of sulfate is controlled by surface adsorption reactions. Because available surface sites are constant in this segment of the model, K_d values increase gradually as the advective–dispersive SO_4^{2-} front spreads downstream.

Much larger K_d values are calculated during the flushing period than during the intrusion period. This occurs in the time-space domains where gypsum is present in the aquifer. During flushing, aqueous SO_4^{2-} concentrations are low in uncontaminated upgradient groundwater. A plateau of large K_d values coincides with the presence of gypsum in the aquifer, e.g., from ~270 to 450 m at 100 years flushing (Fig. 5). Where there are both gypsum and more surface sites present in the aquifer, K_d values are even larger, e.g., at ca. 400 m from the inlet. This is because the aqueous SO_4^{2-} concentration is now determined by the equilibrium with gypsum and is constant downstream from the gypsum dissolution front. Hence, K_d variations are largely determined by the concentrations of solid-bound SO_4^{2-} .

After all gypsum is dissolved, at approximately 176 years, K_d values are determined by surface desorption reactions and the aqueous SO_4^{2-} concentration becomes three times lower than the concentration controlled by

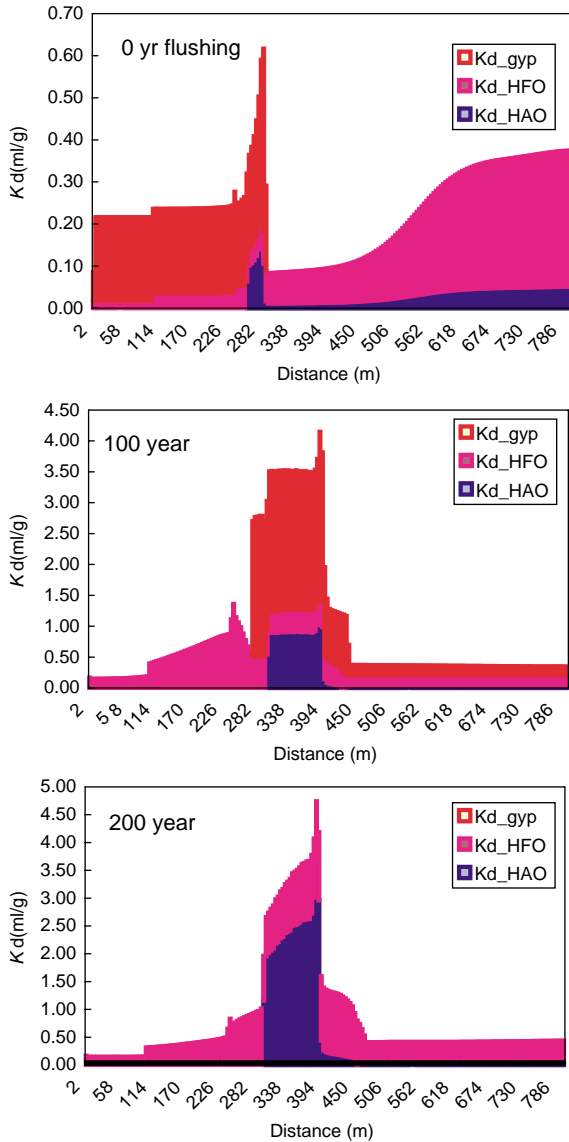


Fig. 5. Contributions of K_d values from mineral-bounded sulfate in gypsum (K_{d_gyp}), on hydrous ferric oxide (K_{d_HFO}), and on hydrous aluminum oxides (K_{d_HAO}). This is a stacked-area diagram. Total K_d values are same as in Fig. 4.

equilibrium with gypsum. The amount of SO_4^{2-} adsorbed onto mineral surfaces is determined by solution pH and by the availability of surface sites (amount of $Fe(OH)_3(a)$ and $Al(OH)_3(a)$ in the aquifer). Therefore, the plateau of large K_d values coincides with, mainly, the presence of $Al(OH)_3(a)$ at 300–400 m at 200 years (Fig. 5). Lower pH favors SO_4^{2-} adsorption onto oxide surfaces. The K_d values near the plateau are coincident with the pH plume (Fig. 4). Near the inlet, high pH leads to less adsorption of SO_4^{2-} onto the mineral surface and to small K_d values.

4.2. K_d model results

Fig. 3b shows the BTC predicted using the K_d approach. Sulfate transport using $K_d = 0, 1,$ and 5 were simulated. With a K_d of 5 ml/g, the retardation factor is 29. As shown in Fig. 3b, the K_d approach can only predict one concentration wave, not multiple waves as predicted by the coupled model (Zhu et al., 2001). This outcome will not be changed by using different values of K_d , because the wave speed of the reaction front is determined by

$$\frac{v}{1 + \partial S / \partial C'} \tag{8}$$

whereas the K_d approach predicts the wave speed as

$$\frac{v}{1 + K_d} \tag{9}$$

where v stands for linear velocity of groundwater (Lichtner, 1996). With complex geochemistry, as shown in the coupled model, $\partial S / \partial C'$ is not constant. In fact, multiple concentration fronts are produced. By definition, the K_d approach only simulates one reaction front.

4.3. Model comparison

The multiple reaction fronts predicted from the coupled model are a more plausible geochemical scenario, given the solution chemistry and minerals in the aquifer. However, the K_d -based approach can only simulate, conceptually, a steady progression of a single front that gradually depletes the source term through time, but does not provide for the possibility of a secondary release and contamination pulse as water chemistry changes.

These conceptual differences cannot be changed with proper K_d values. A smaller K_d value would predict a higher SO_4^{2-} concentration peak with a shorter contamination period, and a larger K_d value would predict a lower peak sulfate concentration but more persistent contamination through time (Fig. 6). This can be shown with bounding calculations. A K_d value of 5 would produce a peak concentration of 8500 mg/l, a peak close to that predicted from the coupled reactive transport simulation. However, the arrival time is after 25 pore volumes, or 400 years, and sulfate concentrations are still above background after 600 years. To predict a return to near background concentrations after 11 pore volumes or 176 years—the same as that predicted by the coupled reactive transport model (Fig. 3)—a K_d value of 1 needs to be used. Although the predicted natural attenuation is now comparable, the peak concentration is 9500 mg/l, higher than that predicted by the coupled reactive transport approach.

This observation can be explained by the nature of K_d and coupled approaches. A larger K_d implies a higher concentration of sulfate bound to the solid matrix with

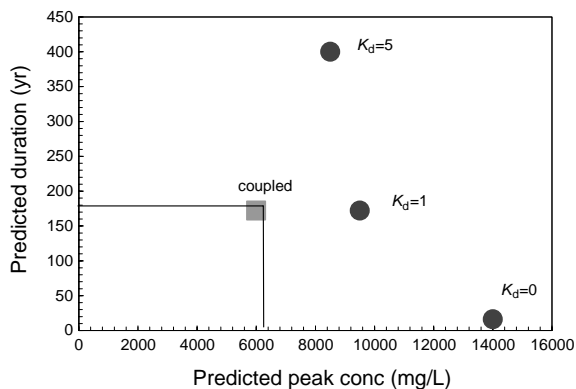


Fig. 6. Comparison of peak concentrations and duration of sulfate concentration above near-background level predicted from coupled and K_d -based transport models.

respect to groundwater. Although it will predict a shorter distance and lower concentrations at a given time during the uploading stage, it results in a larger source of contaminants during the flushing stage. The sulfate concentrations in the solid matrix are not a part of the mass balance.

The coupled approach, on the other hand, includes solid-bound sulfate in the overall mass balance. Hence, it has a limited source during flushing. Unlike the K_d approach, the sulfate concentrations in the aqueous phase are not proportional to the amount of gypsum in the solid matrix; they are controlled by the solubility of gypsum.

Although coupled models are capable to simulate more complex reactive transport patterns, and reproduce more plausible geochemical effects in the contamination problem, both models should be tested against well-controlled experimental and field data sets. The coupled models also have serious shortcomings:

- (1) the tailings fluids have high ionic strength, but an extended Debye–Hückel equation, which is only applicable to low ionic strength and particularly NaCl dominated electrolyte solutions (see PHREEQC manual, Parkhurst and Appelo, 1999), is used in PHREEQC;
- (2) uncertainties in thermodynamic properties for aqueous species and solid phases can result in order of magnitude errors in equilibrium constants used in the models;
- (3) although the surface complexation theory has a firm thermodynamics footing, whether the theory and, particularly, databases derived for laboratory formed solids can be applied to field problems with composite geological materials is untested;
- (4) chemical kinetics plays a significant role in the near surface environment. However, we know little rates and rate laws; and

- (5) lastly, chemical heterogeneities, in term of mineral species, abundances, and spatial variations, are seldom measured, but critical to coupled models (Zhu and Burden, 2001).

Stumm and Morgan (1996) pointed out that the K_d -based models work well in describing the partitioning of hydrophobic organic contaminants. Lastly, although the results from the coupled model highlight the effects of chemical heterogeneities on contaminant transport, the high computational cost of couple models would prohibits a probabilistic approach. In this regard, K_d -based models still have their time-honored place.

5. Concluding remarks

Although the pitfalls of the K_d -based approach have long been recognized, it remains the prevailing industrial and regulatory practice (Brady and Bethke, 2000). A large number of regulatory decisions are still based on K_d -based models, as evidenced in the published Records of Decisions (RODs, Superfund Public Information System, distributed by the US EPA, September, 2000). This study has compared modeling results from a K_d -based model with results from a coupled, multi-component reactive transport model at an abandoned uranium mill tailings site. The results presented here have applications to a variety of contaminated sites where complex chemistry dominates contaminant transport. However, a critical step toward better applications of coupled models is to compare modeling results to historic data, although in reality, such data sets are hard to come by.

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