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Mineralogical compositions of aquifer matrix as necessary initial conditions in reactive contaminant transport models

Chen Zhu^{a,*}, David S. Burden^b

^a *Department of Geology and Planetary Science, University of Pittsburgh, 321 Old Engineering Hall, Pittsburgh, PA 15260, USA*

^b *Robert S. Kerr Environmental Research Laboratory, US Environmental Protection Agency, Ada, OK 74820, USA*

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Abstract

Mineralogical compositions and their spatial distributions are important initial conditions for reactive transport modeling. However, popular K_d -based “reactive” transport models only require contaminant concentrations in the pore fluids as initial conditions, and minerals implicitly represent infinite sources and sinks in these models. That situation results in a general neglect of mineralogical characterization in site investigations. This study uses a coupled multi-component reactive mass transport model to predict the natural attenuation of a ground water plume at a uranium mill tailings site in western USA. Numerous ground water geochemistry data are available at this site, but mineralogical data are sketchy. Even given the well-defined pore fluid chemistry, variations of secondary mineral species and mineral abundances in the aquifer resulted in significantly different modeling outcomes. Results show that the amount of calcite in the aquifer determines the distances of plume migration. The possible presence of jurbanite, an aluminum sulfate phase, can store acidity temporarily but cause more severe contamination on a later date. The surfaces of iron oxyhydroxides can store significant amounts of sulfate and protons and serve as a second source for prolonged contamination. These simulations under field conditions illustrate that mineralogical compositions are an essential requirement for accurate prediction of contaminant fate and transport. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Mineralogy; Contaminant transport; Uranium; Acid mine drainage; Modeling

* Corresponding author. Tel.: +1-412-624-8766; fax: +1-412-624-3914.
E-mail address: czhu@pitt.edu (C. Zhu).

1. Introduction

Detailed mineralogical analyses are seldom performed in routine site investigations. By mineralogical analyses, we refer to laboratory procedures that are designed to answer the questions: (1) What mineral species are present in the aquifer? (2) What are their chemical compositions? (3) What are their crystallinities and reactivities under surficial conditions? (4) What are their abundances? (5) What are their spatial distributions? (6) What are their surface areas? These questions can be answered by using techniques such as X-ray diffraction (Cullity, 1978), petrographic microscopy (Kerr, 1977; Ineson, 1989), scanning electron microscopy (SEM) (Goldstein et al., 1992; Reed, 1996), electron microprobe (Goldstein et al., 1992; Reed, 1996), and for fine-grained materials, transmission electron microscopy (TEM) or high resolution TEM (HRTEM) (Spence, 1988; Williams and Carter, 1996). Methods or procedures that measure the bulk properties of the solid matrix, such as acid digestion, sequential extraction (Chao, 1972; Chao and Zhou, 1983; Loeppert and Inskeep, 1996), and ion-exchange capacity (Jackson, 1985), give indirect but valuable evidence of mineral species and abundance.

The Committee on Ground Water Cleanup Alternatives at the National Research Council (National Research Council, 1994) partially attributed the failure of traditional pump-and-treat remediation systems to the lack of understanding of site geochemistry. One may argue that a large part of the geochemistry that is not well understood is mineralogy, in the form of the questions posed above. Understanding these properties is important for accurate predictions of the fate and transport of contaminants by using numerical models. Modeling results have been used routinely in risk assessment, remedial designs, and regulatory decisions related to ground water contamination (National Research Council, 1990).

The lack of mineralogical studies, despite the millions of dollars spent on site investigation, is analogous to a better-known situation where site investigations and site monitoring have typically included analyses of only the contaminants of concern in ground water samples. The major ions that indicate ground water geochemistry are not included (Davis, 1988). This costly negligence results from a lack of appreciation of the interactions among aqueous species in ground water that may affect contaminant transport.

A similar lack of appreciation of the *complexity* of the interactions between contaminants and minerals and mineral surfaces has led to the neglect of mineralogy during site characterization and the popularity of K_d -based models. K_d -based “reactive” transport models use one parameter to describe the partitioning of a contaminant between solid matrix and ground water (see below for details) and, thus, they mask the complexity of solid-water interactions. In the K_d approach, only the initial concentrations of contaminants in the pore fluids are explicitly required for input, but not the mineral compositions. Hence, studies of the solid phases have been geared toward K_d measurements, by using site sediments and ground water. Typically, these K_d values vary by orders of magnitude (Thomas, 1987; National Research Council, 1994). This variability, to a large extent, reflects the variations of mineralogical compositions and mineral surface properties, which again are usually not characterized in laboratory experiments. These in-situ K_d numbers are of little value because of their large variability and also because K_d

values change as mineralogical compositions of the aquifer matrix change with time (Reardon, 1981; Zhu et al., 2001a,b). In short, most aquifers are chemically heterogeneous in both space and time, and this heterogeneity is reflected in the mineralogy.

Characterization of mineralogical compositions in contaminated aquifers is often difficult because many of the matrix minerals are formed under Earth surficial conditions and are thus fine-grained and poorly crystalline. Mineral assemblages and mineral compositions may also be heterogeneous at a scale that is difficult or impossible to model using today's technology. Amid these concerns, it is difficult to persuade a funding agency of the need for an extensive study of site mineralogy. However, neglect of mineralogical heterogeneity has contributed to the costly failure of remediation techniques (Wood, 2000). To illustrate the importance of mineralogy in contaminant transport models, this study examined the sensitivity of the predicted migration of an

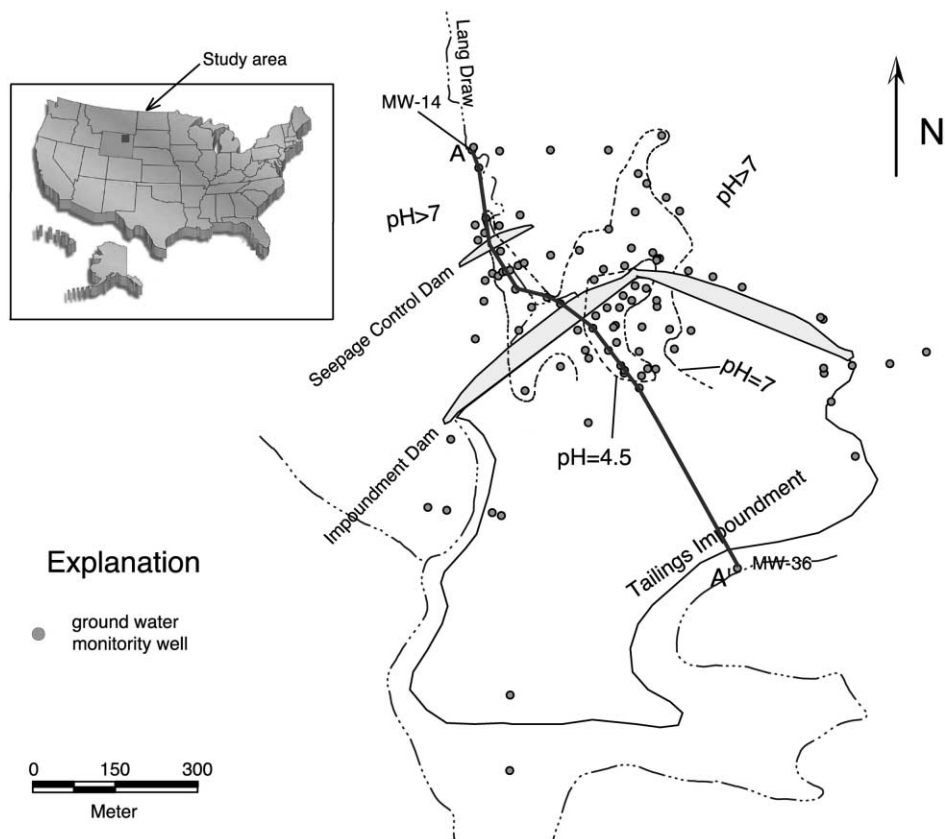


Fig. 1. Plane view of the mine site and tailings impoundment. The dashed lines are ground water pH contours, which delineate the flow paths at the site. The model domain is along the cross-section A–A'.

acid plume at an abandoned uranium mill tailings site in western USA (Bear Creek Uranium) to mineralogical compositions of the aquifer.

Bear Creek Uranium is a mill tailings impoundment site located in Wyoming, USA (Fig. 1). At the site, a large database of ground water geochemistry (Zhu et al., 2001a) was generated from numerous ground water samples that have been collected from over 100 pumping and monitoring wells in the last three decades. However, the mineralogy of the aquifer was inferred indirectly from chemical extraction procedures on sediment cores and speciation-solubility modeling of ground water geochemistry. In this study, a coupled reactive transport code (PHREEQC, Parkhurst and Appello, 1999) was used to simulate the migration of the acid plume under different scenarios of product minerals and mineral abundance. The results show that, even when the pore fluid chemistry and the contaminant source-term are well-defined, modeling predictions very much depend on the knowledge of product minerals and mineral compositions of the aquifer.

2. K_d -based versus thermodynamically based reactive transport models

In the K_d -approach, the partitioning of a solute between aquifer solid matrix and ground water is described by the partitioning 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 ground water (mg/l), respectively; and K_d commonly has units of ml/g. The effect of chemical reactions in the aquifer on the transport of component i is taken into account of by substituting Eq. (1) into the advective–dispersive–reactive (ADR) transport equation. The one-dimensional transport in a saturated porous media (Bear, 1972) is,

$$\frac{\partial C}{\partial t} = D_L \frac{\partial^2 C}{\partial x^2} - \bar{v} \frac{\partial C}{\partial x} - \frac{\rho_b}{\theta} \frac{\partial S}{\partial t} \quad (2)$$

Substitution of Eq. (1) into Eq. (2) obtains,

$$R \frac{\partial C}{\partial t} = D_L \frac{\partial^2 C}{\partial x^2} - \bar{v} \frac{\partial C}{\partial x} \quad (3)$$

where t denotes time (T), x is distance (L), ρ_b is the bulk density of the aquifer (M/L³), R is the retardation factor, and θ is the porosity (dimensionless). \bar{v} stands for the average linear velocity of ground water (M/L) and D_L is the longitudinal hydrodynamic dispersion coefficient (L²/T) (Bear, 1972).

The derived retardation factor, R ,

$$R = 1 + \frac{K_{d,i} \rho_b}{\theta}, \quad (4)$$

represents the impediment of the concentration front with respect to the bulk mass of water,

$$R = \frac{\bar{v}}{\bar{v}_c}, \quad (5)$$

where \bar{v}_c is the velocity of $C/C_o = 0.5$ point on the concentration profile of the retarded constituent (Domenico and Schwartz, 1998). Similar expressions of Eq. (4) can be found for Langmuir and Freundlich isotherms, which can be substituted into Eq. (3).

It is not apparent from Eq. (3) that mineralogical compositions of the aquifer are needed to solve Eq. (3); only contaminant concentrations in the pore fluids are needed as initial conditions. However, one must bear in mind that mineralogy is implicitly embedded in the K_d values or retardation factors used in the model, and the constants are only applicable when the mineralogy is the same as or similar to that in experimental measurements. As chemical heterogeneities of the aquifer solid matrix vary spatially, the retardation factors should also vary in spatial domains with different mineral assemblages. Some transport codes allow assignments of different K_d or retardation factors to different spatial domains (e.g., MT3D, Zheng and Wang, 1999). However, K_d values and retardation factors can also change with time as mineralogical transformations take place with time (Reardon, 1981; Bethke and Brady, 2000; Zhu et al., 2001a,b).

In thermodynamically based *coupled reactive transport models*, the advective–dispersive transport equations are solved together, either simultaneously or sequentially, with the mass action and mass balance equations for chemical reactions (Walsh, 1983; Cederberg et al., 1985; Lichtner, 1985; Yeh and Tripathi, 1991; Steefel and Lasaga, 1994; Raffensperger and Garven, 1995). These models are referred to as coupled models because two sets of equations are solved together. In this case, these are the partial differential equations for advective–dispersive transport and non-linear algebraic equations for chemical reactions. For example, the reactive transport option in the US Geological Survey code PHREEQC is a one-dimensional finite-difference model (Parkhurst and Appello, 1999) and uses a split-operator scheme. The term $(\rho_b/\theta)(\partial S/\partial t)$ in Eq. (2) is solved separately for each cell by using a chemical module, PHREEQC, in which chemical speciation and partitioning between the solid matrix (including mineral surfaces) and aqueous solutions are calculated based on the mass balance and mass action equations (see Parkhurst, 1995). Within each time step, the advective transport is calculated by using an upwind finite difference scheme, which is followed immediately by a calculation of chemical reactions. Then, dispersive transport is calculated using a central difference scheme (see Appello and Postma, 1994). This is again followed by a calculation of chemical reactions.

While the isotherm-retardation approach (Eq. 3) relies on empirical relationships to describe chemical reactions, the coupled models treat the chemical reactions based on thermodynamic laws. In the latter formulation of the transport problem, minerals are required explicitly as initial conditions. Both the mineral species and their mole concentrations are assigned to each cell, and this information is used in the mass balance equations to be solved. This requirement necessitates information on the spatial distribution of minerals or chemical heterogeneities. For simulating surface adsorption reactions, the surface areas and densities of the surface sites of minerals are also needed in the

input. Thus, minerals and mineral surfaces become *finite* sources and sinks for contaminants.

3. The example of the Bear Creek Uranium site

The differences between empirically based reactive transport models and thermodynamically based coupled reactive transport models can be illustrated well by contaminant transport problems in acid mine drainage-impacted aquifers. In this paper, we examine the contaminant transport problems at the Bear Creek Uranium site. Past mining, milling, and processing of uranium has resulted in hundreds of millions tons of mill tailings in the United States, Canada, Australia, Germany, South Africa, and many other countries (Abdelouas et al., 2000). Tremendous amounts of resources are currently being devoted to reclaiming ground water aquifers contaminated by tailings fluids. Most clean-up activities are planned, at least partially, based on the results of reactive transport models. Accurate prediction of the fate and transport of hazardous constituents is critical to the assessment of environmental impact and the development of effective remediation technologies.

3.1. Site contamination

Bear Creek Uranium is located in the southern part of the Powder River Basin in Wyoming, USA (Fig. 1). A uranium mill operated here from the 1970s to the mid-1980s. Sulfuric acid and sodium chlorate were used to dissolve and oxidize uranium. Spent acids and tailings were piped in slurry to unlined tailings ponds. The tailings fluid has a pH between 1.5 and 3.5, a total dissolved solids (TDS) 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). Seepage from the disposal ponds into the underlying N sand and alluvium aquifer of the Upper Wasatch Formation has formed an acid plume. Detailed descriptions of the site hydrogeology, geochemistry, and field data are given in Zhu et al. (2001a).

The reclamation plan for the site 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 aquifer 5 years after the cover installation. After that time, the plume will be flushed by uncontaminated upgradient ground water. The distance of the migration of the acid plume and regulated metals and radionuclides will depend on the “natural attenuation” or the reactions of aquifer minerals with contaminated ground water and hydrodynamic dispersion. The transport model is designed to predict the acid plume migration under this “cover and attenuate” reclamation plan.

3.2. Model description

An 800 m strip along the transect A–A' (see Fig. 1) was discretized into 200 cells. Transport parameters are listed in Table 1. The successive pH buffer reaction model

Table 1
Transport parameters in the model

Parameters	Symbols	Values	Units
pore velocity	\bar{v}	50	m/year
longitudinal dispersivity	α_L	10	m
effective porosity	θ	30	%
time step	Δt	0.08	year
molecular diffusion coefficient	D^0	0	
grid size	Δx	4	m

(Zhu et al., 2001a) is used as the conceptual geochemical model for the reactive transport simulations. A total of 11 aqueous components, H, Ca, Mg, Cl, C, Al, S, Fe, 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, are considered in the model. Thermodynamic properties for aqueous species and solids are discussed in Zhu et al. (2001b). For simplicity, chemical reactions were calculated at 25°C and 1 bar, although measured ground water temperatures range from 12°C to 16°C. The local equilibrium assumption was used.

The diffuse double layer model (Dzombak and Morel, 1990) is used for modeling surface adsorption onto hydrous ferric oxide (HFO) and amorphous aluminum hydroxide (AAH) surfaces. Because transport simulation is limited to the major ions in the present study, only adsorption onto the “weak site” is included. The concentrations of “strong” site sorbants are too low to affect the major ion transport (Zhu et al., 2001a,b).

Initial conditions are specified to reflect site conditions in 1994. The domain was divided into four zones, for which pore water chemistry and aquifer mineral compositions are tabulated in Table 2. While pore fluid chemistry was analyzed in September 1994, mineral compositions of the aquifer matrix were only derived indirectly (Zhu et

Table 2
Initial conditions of pore fluid chemistry^a
Ground water flows from cell 1 to 200.

Zone	I	I	II	III
Length	100 m	140 m	300 m	260 m
cells	1–25	26–60	61–135	136–200
Temperature (°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

^aConcentrations are in mg/l, except for pH and temperatures. Mineral abundances varied for different simulations and are indicated in the text.

Table 3
Boundary fluxes (third-type) used in the simulations^a

Concentrations	First 5 years	After 5 years
Temperature (°C)	25	25
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.

al., 2001a). This uncertainty is addressed in this study by varying the mineral species and the amount of minerals as initial conditions.

Third-type or Cauchy flux boundary conditions were used for both ends of the 1D strip. To emulate the reclamation conditions, the incoming fluid has the chemistry of tailings pore fluid for the first 5 years and of uncontaminated upgradient ground water thereafter (Table 3).

3.3. Numerical modeling results

Numerical simulations of reactive transport were performed for a period of 5 years of seepage by tailings fluid into the aquifer and 200 years of flushing of the contaminated aquifer by uncontaminated upgradient ground water. The results are discussed as sensitivity of the modeling results to mineralogical compositions as initial conditions, in terms of the advancement of the acidic plume migration and breakthrough of pH and SO₄²⁻ near the property boundary.

3.3.1. Calcite and gypsum in the aquifer

To evaluate the sensitivity of modeling outcome to the amounts of calcite and gypsum in the aquifer, three different abundances of calcite were used in the simulations: 0.04, 0.4 and 1.7 wt.%. Results show that calcite abundances in the alluvium determine the distances of migration of the low-pH plume (Fig. 2). In these simulations, surface adsorption reactions were not included. Fig. 3 shows the pH and SO₄²⁻ breakthrough curves (BTC) at the right margin of the simulated domain. When calcite in the aquifer is at 0.04 wt.%, all calcite in the aquifer is expended and the low-pH plume has migrated outside of the simulated domain. By trial and error, the threshold calcite abundance needed to buffer all the acid in the aquifer was found to be approximately 0.16 wt.%. When calcite concentration is above the threshold of 0.16 wt.%, pH and SO₄²⁻ breakthrough curves are independent of the amount of calcite in the aquifer

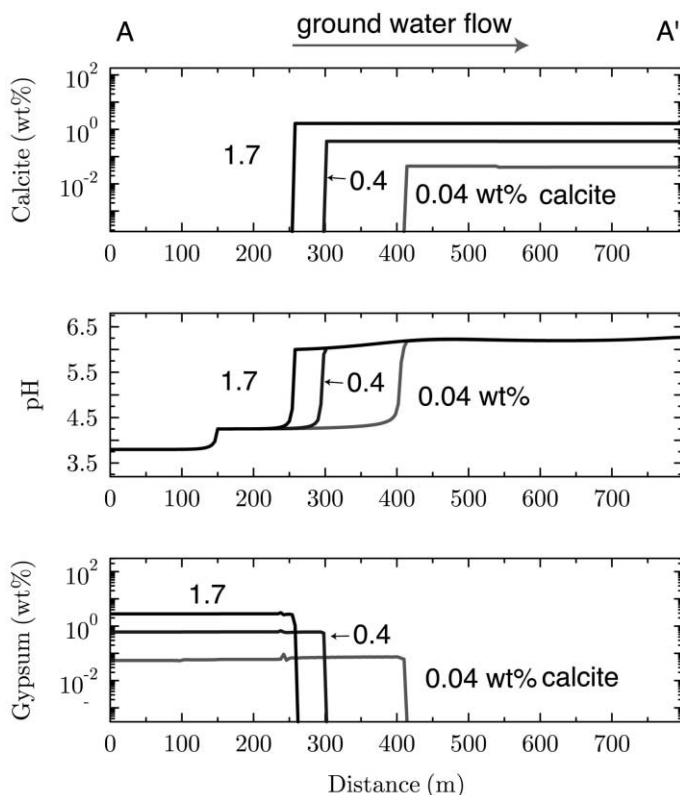
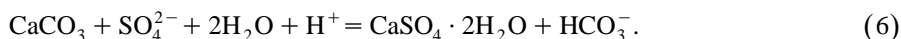


Fig. 2. Simulated distributions of calcite, pH, and gypsum in the aquifer after 5 years tailings fluid intrusion, with calcite abundance of 0.04, 0.4 and 1.7 wt.%, respectively. Surface adsorption was not included in the simulations.

downgradient of the plume, conforming to the “downstream equilibrium condition” (Walsh et al., 1984).

The presence of calcite in the underlying aquifer at the site was confirmed by acid fizzle test, and the amounts of calcite were estimated from acid neutralization tests. Calcite ranges from 0.6 to 2 wt.% in 26 samples from eight boreholes (Zhu et al., 2001a).

Gypsum is a product of acidic water reaction with calcite in the aquifer through the reaction,



According to Eq. (6), the moles per liter of gypsum produced in the plume are equal to the moles per liter of calcite consumed. Modeling results show that precipitation of gypsum causes a sharp drop in SO_4^{2-} concentration and a retarded SO_4^{2-} front. The pH of pore fluids are determined by the ratio of activities of HCO_3^- and SO_4^{2-} , where a pH drop coincides with a SO_4^{2-} peak (Zhu et al., 2001b). However, both SO_4^{2-} and HCO_3^-

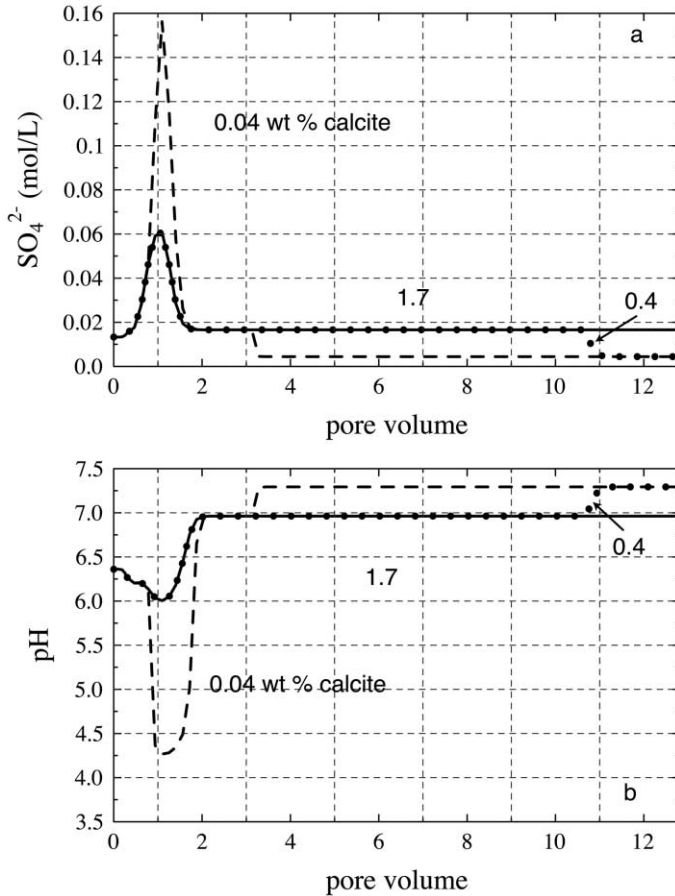


Fig. 3. Breakthrough curves for SO_4^{2-} and pH at the 200th cell, with calcite abundances of 0.04 (dashed line), 0.4 (dotted line) and 1.7 wt.% (solid line), respectively. The 0.4 and 1.7 lines overlap in most parts.

concentrations are controlled by equilibrium reactions so that the presence of calcite and gypsum, not their amounts, determines the pH drop. Hence, the same pH drops are produced for simulations with different amounts of calcite when calcite abundance is above the threshold of 0.16 wt.% (Fig. 3).

In simulations with 0.04 wt.% calcite, all calcite was expended, producing a low pH front breakthrough (Fig. 3b). A SO_4^{2-} peak at the concentration of influent passes through the column. This concentration is higher than the US EPA secondary drinking water standards (sMCL) of 250 mg/l for SO_4^{2-} . Modeling results show that the lowest pH point of 4.3 is buffered by $\text{Al}(\text{OH})_3$ (a). Ground water pH is a sensitive parameter for metal and radionuclide adsorption and mobility. Hence, whether or not a low pH breakthrough occurs has significant impact on the viability of remediation alternatives.

The duration of SO_4^{2-} concentrations above natural background (745 mg/l or 0.008 mol/l, Sharp and Gibbons, 1964), which is a regulatory criterion for the state of

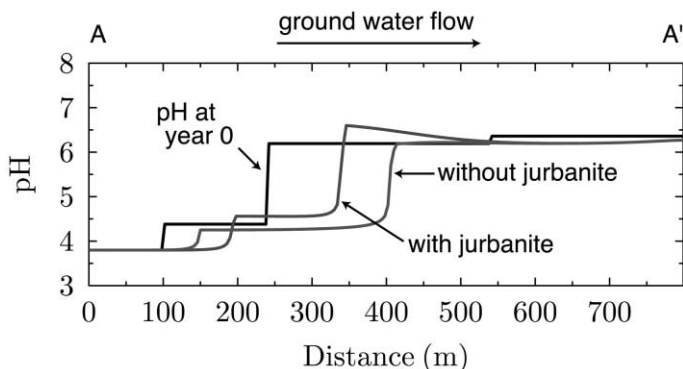
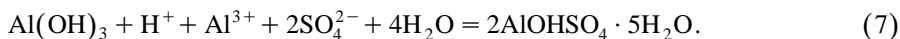


Fig. 4. Simulated distributions of pH at the fifth year of tailings fluid intrusion, for simulations with jurbanite and without jurbanite, respectively. The pH distribution at year 0 (initial condition) is shown for reference. Calcite abundance is 0.04 wt.%. Surface adsorption was not included in the simulations.

Wyoming, is a function of the amount of gypsum produced. In other words, gypsum is the source of SO_4^{2-} contamination. Modeling results show that the amount of gypsum produced is proportional to the amount of calcite present in the aquifer if reaction (6) is the dominant natural attenuation reaction for SO_4^{2-} . Although a large amount of calcite in the aquifer is beneficial to limit the migration of acidic plume, it also means a longer period of SO_4^{2-} contamination. Calculations show that, with 1.7 wt.% calcite, SO_4^{2-} contamination will persist after 200 years of flushing, compared with 167.5 and 47.5 years for 0.4 and 0.04 wt.% calcite, respectively.

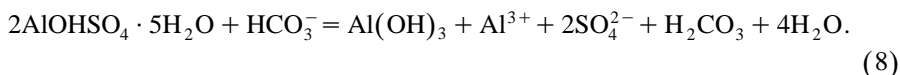
3.3.2. Different secondary aluminum and sulfate phases

Numerical simulation shows that the migration of the low-pH plume and the time needed to return to background concentrations are different when jurbanite ($\text{Al}(\text{OH})\text{SO}_4 \cdot 5\text{H}_2\text{O}$) is added to the possible mineral phases and the tailings fluid is saturated with respect to jurbanite. When jurbanite is in the mineral phases, amorphous $\text{Al}(\text{OH})_3$ is altered to jurbanite through the reaction,



Reaction (7) buffers the pH to about 4.7. Because reaction (7) consumes less H^+ than the $\text{Al}(\text{OH})_3$ dissolution reaction, the reaction front buffered by the aluminum phase now advances further. On the other hand, because the precipitation of jurbanite “stored” some Al^{3+} (part of the acidity of the tailings fluid), the calcite-buffered pH front migrates more slowly than when jurbanite is not included (Fig. 4).

When the source of acidic water is terminated and the aquifer is flushed by uncontaminated upgradient ground water, entrained acidic water continually migrates downstream. Modeling results indicate that at the upgradient side, flushing causes the dissolution of jurbanite,



Reaction (8) buffers ground water to a pH slightly lower than reaction (7). Only when jurbanite is expended does the pH of ground water return to the background value (Fig. 5). Because the flushing front is retarded by the dissolution of jurbanite, a long low-pH period is seen near the property boundary.

With jurbanite, the sulfate peak is reduced because precipitation of jurbanite preceded gypsum precipitation. During flushing, SO_4^{2-} concentration is controlled first by the gypsum dissolution reaction and then by reaction (8). Only after jurbanite is expended does sulfate concentration return to the background value.

The simulation results show that the presence of jurbanite in the plume would worsen the overall contamination problem. The period of SO_4^{2-} concentrations above background and a low pH would be longer. Jurbanite acts as a “time bomb”—it delays the low-pH breakthrough, only to later release acid and SO_4^{2-} . Hence, these simulation

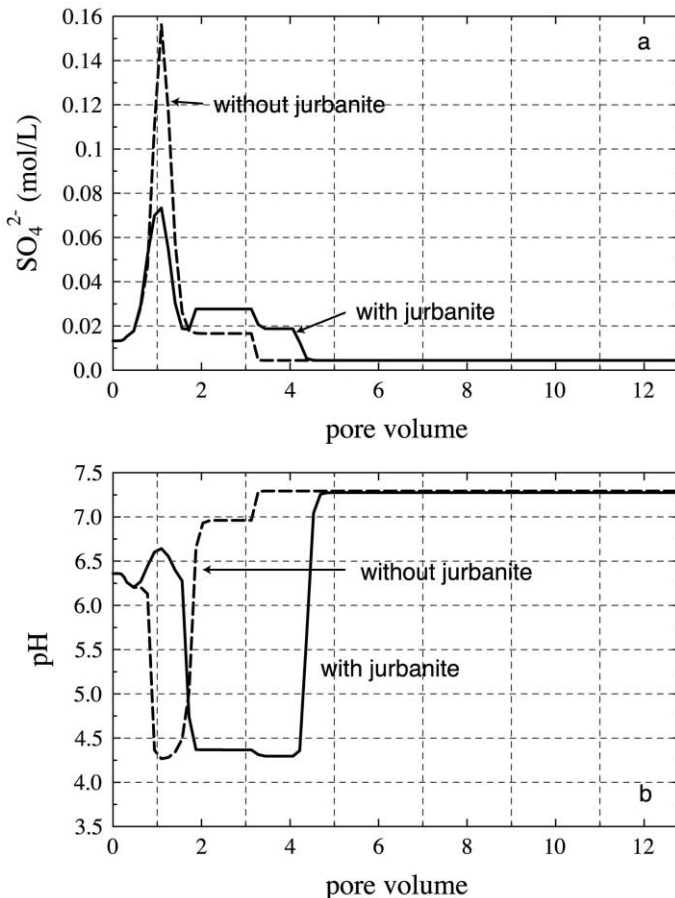


Fig. 5. Breakthrough curves for SO_4^{2-} and pH at the 200th cell, with jurbanite and without jurbanite, respectively. Calcite abundance is 0.04 wt.%.

results show that different secondary minerals can affect the plume migration significantly.

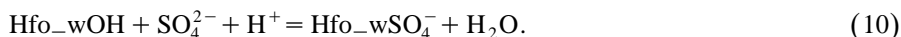
Nordstrom (1982) postulated that jurbanite might be the aluminum sulfate phase that controls Al^{3+} solubility at a $\text{pH} < 3\text{--}5$ in acidic solutions with high SO_4^{2-} . Stollenwerk (1994) showed that the use of a modified solubility product for jurbanite explained Al^{3+} solubility at $\text{pH} < 4.7$. However, direct analyses of aluminum sulfate phases at acid mine drainage sites are lacking, and the potential for an aluminum sulfate phase to control Al^{3+} and SO_4^{2-} solubilities at low pH is unknown.

3.3.3. Abundance and reactivity of iron oxyhydroxide

To illustrate the need to characterize mineral species and mineral surface properties, simulations were performed using various amounts of HFO (0.0, 0.08 and 0.64 wt.%). Simulations show that reactions between acidic tailings fluids and iron oxyhydroxide surfaces consumed H^+ through the reaction



where the symbol Hfo_w denotes the surface species on the weak site, following Parkhurst and Appello (1999). The formation of surface species Hfo_wSO_4^- at low pH also removed H^+ from the solution,



Therefore, surface adsorption slightly slows the low-pH plume migration, and less calcite in the aquifer is dissolved as a result (Fig. 6).

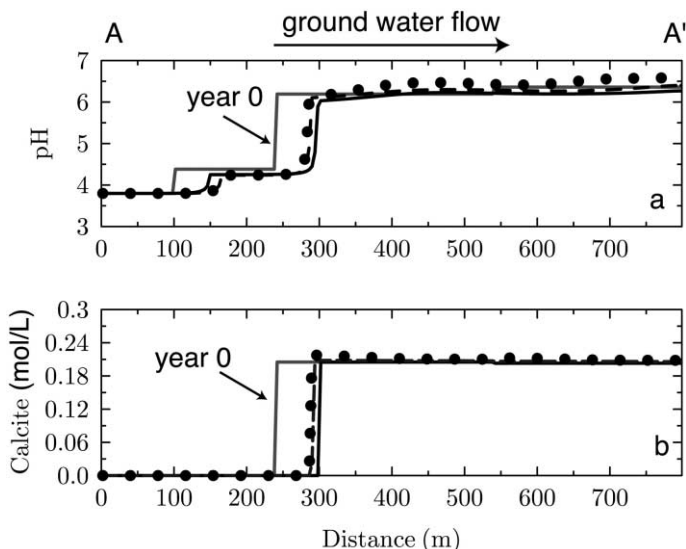


Fig. 6. Simulated distributions of pH and calcite in the aquifer after 5 years tailings water intrusion, with HFO abundances of 0 (solid line), 0.08 (dashed line) and 0.64 wt.% (dotted line), respectively. The pH distribution at year 0 (initial condition) is shown for reference. Calcite abundance is 0.4 wt.% or 0.2 mol/l.

HFO surfaces exert much more significant control on ground water pH during flushing. Including surface adsorption, the low pH front migrates at a slower rate and the pH value during the pH drop is buffered to a higher value. The more HFO in the aquifer, the slower the rate of pH migration and the higher the pH of ground water (Fig. 7b). During flushing, H^+ is released from HFO surfaces. The slow release rate causes a diffusive pH front in contrast to a sharp front, as is the case when surface adsorption is not included (Fig. 7b). The pH of ground water during an extended period of flushing is controlled by the surface reactions.

Although the concentration of sulfate was mainly controlled by the precipitation/dissolution of gypsum (Fig. 7a), SO_4^{2-} stored on mineral surfaces constitutes a second source of contamination. After all gypsum is expended, the concentration of sulfate in the ground water is controlled by the surface reactions, and the concentration is slightly above the background value even after many pore volumes (Fig. 7a).

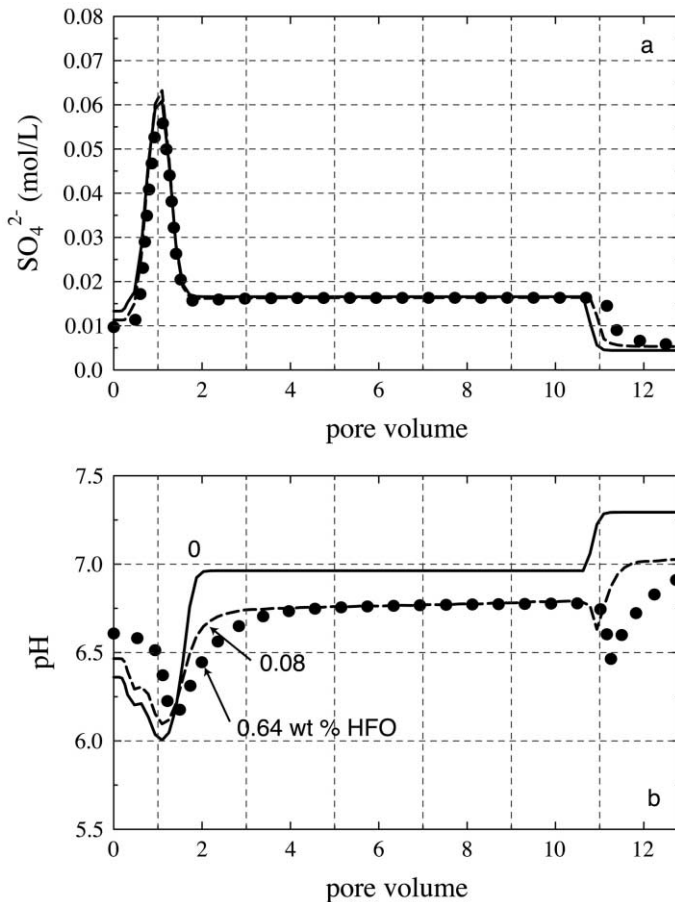


Fig. 7. Breakthrough curves for SO_4^{2-} and pH at the 200th cell, with HFO abundances of 0 (solid line), 0.08 (dashed line) and 0.64 wt.% (dotted line), respectively. Calcite abundance is 0.4 wt.%.

The upper Wasatch Formation in the region contains up to 0.4 wt.% of Fe (Sharp and Gibbons, 1964). The iron mineral species was not identified but presumably is hematite. The reactivity and surface areas of this iron species are unknown and can be difficult to measure. In addition to the primary iron minerals in the aquifer, iron oxyhydroxide was also “freshly” precipitated as a secondary mineral, a product of interactions between aquifer mineral matrix and acid tailings water. Modeling work in the past has found that the use of total measured amounts of Fe in the model causes overestimation of adsorption. Parkhurst (1995) found that the use of the measured amount of iron from the Central Oklahoma Aquifer for surface adsorption simulation produces unreasonable results and hence used only 10% of the measured amount. Sanders and Toran (1995) found similar problems and used 10% of the measured amount of amorphous iron in a shallow aquifer at the Oak Ridge site. Stollenwerk (1994) and Brown et al. (1998) used about 5% of the measured iron content to calculate active adsorption sites for the Pinal Creek acid mine drainage site.

Such order of magnitude “parameter adjustment” reflects our poor understanding of subsurface mineralogy and surface reactivity (e.g., site densities of different iron mineral species). In the Upper Wasatch sandstones in the Powder River basin, some of the iron is in clay minerals, not in iron oxides (Sharp and Gibbons, 1964), and hence some adjustments of the total Fe in the sandstone are justifiable. The modeling results make it apparent that the lack of this mineralogical characterization hinders our ability to predict contaminant fate and transport, especially for toxic metals and radionuclides.

4. Concluding remarks

As attention has turned to chemical heterogeneity of the subsurface in hydrogeology (Wood, 2000), the problem of poor mineralogical information is becoming prominent. In prevailing practices, extended ground water monitoring wells are installed and samples are analyzed frequently, thereby delineating “ground water plumes” and establishing background concentrations. However, a “contamination plume” should include both contaminated pore water and contaminated sediments, and background conditions should include mineralogical compositions of the aquifer and its spatial variations.

In this study, the need for identifying mineral species, characterizing spatial distribution of minerals, and determining mineral surface properties in contaminant transport modeling is demonstrated through a case study of a uranium mill tailings seepage contamination problem. Numerical simulations using a coupled reactive mass transport code show that the migration of H^+ , SO_4^{2-} , and other major ground water constituents depend on specified mineral compositions as initial conditions. Ideally, a more convincing case can be made if sediment cores are available for mineralogical analyses and the results are incorporated in the model. Unfortunately, as pointed out in Section 1, mineralogical analyses are not seen as essential to regulators and responsible parties. Therefore, it is important to document the significance of mineralogical knowledge in terms of predicting contaminant transport related to practical concerns, such as acid plume migration and pH and SO_4^{2-} breakthrough. It is reasonable to postulate that the fate and transport of toxic metals and radionuclides of low concentrations will have an

even greater sensitivity to mineralogical compositions. Such links will help to highlight the need for good groundwork in mineralogical studies amid the use of ever more complex transport models.

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