REACTIVE SOLUTE TRANSPORT IN ACIDIC STREAMS

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Abstract. Spatial and temporal profiles of pH and concentrations of toxic metals in streams affected by acid mine drainage are the result of the interplay of physical and biogeochemical processes. This paper describes a reactive solute transport model that provides a physically and thermodynamically quantitative interpretation of these profiles. The model combines a transport module that includes advection-dispersion and transient storage with a geochemical speciation module based on MINTEQA2. Input to the model includes stream hydrologic properties derived from tracer-dilution experiments, headwater and lateral inflow concentrations analyzed in field samples, and a thermodynamic database. Simulations reproduced the general features of steady-state patterns of observed pH and concentrations of aluminum and sulfate in St. Kevin Gulch, an acid mine drainage stream near Leadville, Colorado. These patterns were altered temporarily by injection of sodium carbonate into the stream. A transient simulation reproduced the observed effects of the base injection.

Key words: Reactive solute transport modeling, acid mine drainage, geochemical modeling

1. Introduction

Acid mine drainage degrades water quality in many of our nation's streams. Effective remediation at these sites requires an understanding of the diverse physical and biogeochemical processes that control spatial and temporal profiles of concentrations of metals and other acid constituents. This paper presents an approach to site characterization that includes tracer-dilution experiments, synoptic sampling, and reactive transport modeling. Tracer experiments quantify physical transport, and synoptic sampling defines the spatial distribution of constituent concentration in inflow and instream waters. The primary interpretive tool is a reactive solute transport model that characterizes the interplay of transport and chemical reactions producing the observed spatial profiles of concentration. These spatial patterns were altered by an injection of sodium carbonate into the stream. Transient simulations were conducted to interpret the dynamic response of pH and other stream constituents during the base injection.

2. Site and Methods

We applied our site characterization methods to a 1804-meter reach of St. Kevin Gulch, a mountain stream receiving acid mine drainage near Leadville, Colorado (Figure 1). The stream receives metal-rich, acidic water in a series of springs that discharge at the base of a mine dump. Pools, riffles, and cascades in this small ($Q < 20$ L/s) shallow stream cause a rapid mixing of inflows. The 1804-meter reach was divided into 13 subreaches. Water samples were collected at many stream sites, both upstream and downstream from eleven sampled inflows. Upstream from the acid inflows (0-363 m), streamwater was affected by mine drainage, but loads of metals were relatively small. Between 363 and 484 m, the stream became much more acidic, and pH decreased. Downstream from the acidic inflows, Shingle Mill Gulch entered St. Kevin Gulch (at 501 m). This confluence doubled the discharge and increased the pH. Additional loading of some acidic constituents from ground-water seepage occurred in the next downstream reach (526-781 m). In the remaining subreaches, loading was minimal.

Water, Air and Soil Pollution **90**: 195-204, 1996.

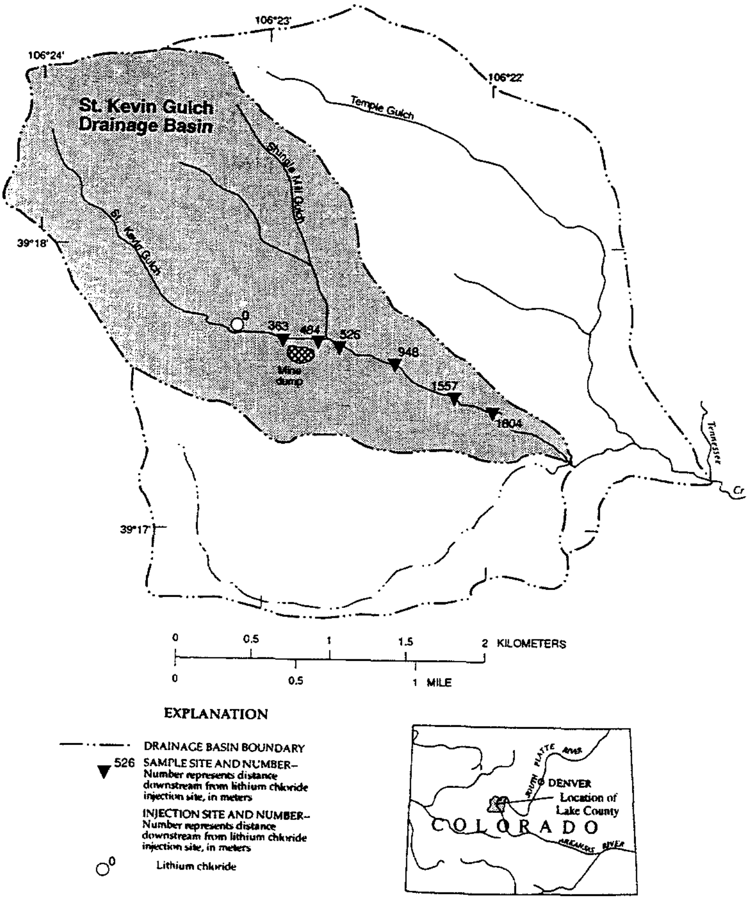

Fig. 1. Location of St. Kevin Gulch drainage basin, indication injection point and sampling sites

2.1 1986 Tracer Injection and Synoptic Sampling.

In August 1986, a tracer solution of 4.7 M LiCl was injected into St. Kevin Gulch at a rate of 27 mL/min for 52 hours. Sampling sites and inflow locations are referenced by their distance downstream from the injection. The arrival of the LiCl pulse and the development of a plateau concentration were observed at six sites, ranging from 26 to 1804 m downstream from the injection (Figure 1). During the plateau period, additional samples were collected from these six sites, from ten surface inflows, from St. Kevin Gulch upstream and downstream from each inflow, and from a pit dug in an area of ground-water seepage. Pressure filtration, using 0.1 µm nitrocellulose membrane filters, operationally defined a dissolved sample. Analysis of acidified samples for metals was by ICP-AES. Ferrous iron was measured in filtered, unacidified samples using the 2,2'-bipyridine colorimetric method. Filtered, unacidified samples were analyzed for chloride and sulfate by ion chromatography. Specific methods were reported by Kimball *et al.* (1994b).

2.2 1988 Transient Modification of Instream pH

On August 25, 1988, instream pH in St. Kevin Gulch was increased in step-wise fashion from 3.5 to 5.8 by injecting a concentrated solution of sodium carbonate. The sodium carbonate injection site was 1306 meters downstream from the LiCl injection site for the 1986 experiment. Sodium chloride was injected simultaneously to enhance the sodium pulse, which was used as a conservative tracer for definition of subreach travel times and transient storage parameters. The injection began at 9.3 hours and continued at a constant rate until 11.9 hours. An increasing rate of injection was sustained until 14.9 hours, when the injection was stopped. As the pulse of increased pH moved downstream, the response of major ions and trace metals was documented by analyzing water samples collected at sites located 24, 70, 251, and 498 meters from the sodium carbonate injection site. This paper will focus on the response at site 24 only.

2.3 Reactive Solute Transport

Physical transport and mixing were simulated by a module that includes advection-dispersion and transient storage (Bencala and Walters, 1983; Runkel and Broshears, 1991). These processes are described by the following equations.

$$\frac{\partial C}{\partial t} = -\frac{Q\partial C}{A\partial x} + \frac{\partial}{\partial x}\left(DA\frac{\partial C}{\partial x}\right) + \frac{q_L}{A}(C_L - C) + \alpha(C_S - C)$$

$$\frac{\partial C_S}{\partial t} = -\alpha\frac{A}{A_S}(C_S - C)$$

where C = solute concentration in the stream $\{ML^{-3}\}$
t = time $\{T\}$
Q = volumetric flow rate $\{L^3T^{-1}\}$
A = cross-sectional area of the stream $\{L^2\}$
x = distance $\{L\}$
D = dispersion coefficient $\{L^2T^{-1}\}$
q_L = inflow rate per unit stream length $\{L^3T^{-1}L^{-1}\}$
C_L = solute concentration in lateral inflow $\{ML^{-3}\}$
α = stream-storage exchange coefficient $\{T^{-1}\}$
C_S = solute concentration in the storage zone $\{ML^{-3}\}$
A_S = cross-sectional area of the storage zone $\{L^2\}$

Kimball *et al.* (1994b) described the removal of metals and other acid constituents from the dissolved phase in terms of first-order rate constants. Figure 2 shows observed and simulated steady-state profiles of aluminum in St. Kevin Gulch both with and without simulation of a first-order removal process. This approach to site characterization is relatively easy to apply and provides engineering parameters that are valuable in site remediation. Instream travel times and stream lengths necessary for various levels of metal removal can be estimated and compared among different stream systems. However, this approach does not describe in rigorous fashion the actual reactions that are causing metal removal.

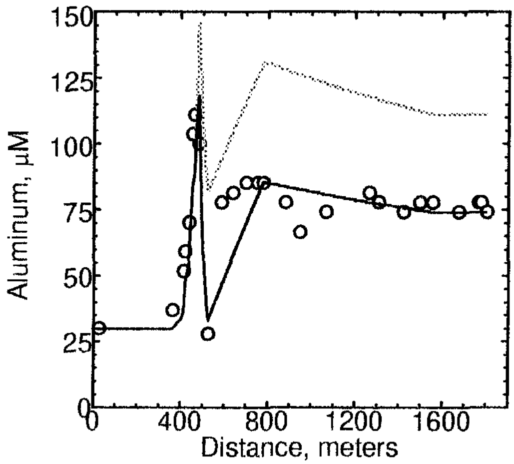

Figure 2. Observed (open circles) and simulated steady-state profiles of aluminum at St. Kevin Gulch in August 1986, assuming conservative (dotted line) and reactive (solid line) behavior. The removal rate coefficient was varied from 1.0×10^{-3} to 1.5×10^{-3} sec^{-1}.

In this paper we explore the use of equilibrium thermodynamic concepts in site characterization. Chemical reactions were simulated by a module based on the geochemical speciation model MINTEQA2 (Allison *et al.*, 1991). This module was coupled with the physical transport module by a sequential iteration method (Runkel, 1993). The geochemical module applies equilibrium thermodynamic concepts in calculations of chemical speciation, including sorption reactions and the formation of aqueous complexes and solid species. This more rigorous geochemical approach has utility in site remediation efforts as it can quantify the behavior of metals under the chemically altered conditions of various remediation scenarios.

3. Results

3.1 1986 Tracer Experiment and Synoptic Sampling

The spatial profile of lithium concentration during the 1986 study is shown in Figure 3. Discharge at each site was calculated by the dilution required to match the measured plateau concentration of the lithium tracer. The downstream increase in discharge was from 6.9 to 19.7 L/s. Discharge declined to 14.7 L/s after a losing subreach near the downstream part of the study area. Travel time for the conservative tracer through the 1804-meter reach was about 5.6 hours. Stream cross-sectional areas were adjusted to reproduce tracer behavior consistent with observed arrival and departure times. The cross-sectional areas of the storage zones and stream-storage exchange coefficients were adjusted to accommodate deviations from traditional advective-dispersive behavior in the observed concentration profiles. A summary of fitted parameters is presented in Table 1. The chemical character of inflows is shown in Table 2.

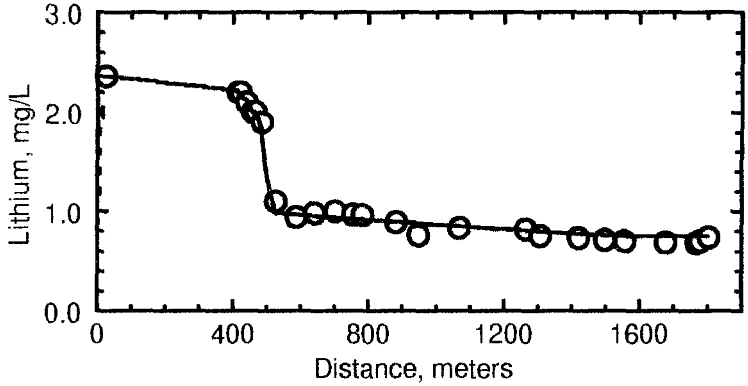

Figure 3. Steady-state profile of lithium from tracer dilution at St. Kevin Gulch, August 1986.

3.2 Steady-State Reactive Transport Simulations

Steady-state reactive transport simulations were conducted to interpret the observed profiles of pH, aluminum, and sulfate (Figure 4). In the first simulation, no solids were specified. In the latter two simulations, aluminum hydroxide or hydroxysulfate solids were permitted to precipitate. When no solid-phase controls were defined, simulated concentration profiles reflected loading near the mine dump and dilution by Shingle Mill Gulch, but remained higher than observed profiles at downstream sites. This discrepancy is a clear indication of chemical reactions that remove these constituents from the dissolved phase. Common controls on metal solubility include the formation of insoluble metal hydroxides. Aluminum, for example, undergoes the following hydrolysis reaction:

$$Al^{3+} + 3H_2O \rightarrow Al(OH)_3 + 3H^+$$

The formation constant for amorphous $Al(OH)_3$, $K_f = \{H^+\}^3\{Al^{3+}\}^{-1}$, has been reported at $10^{-10.8}$; formation constants of more crystalline forms of $Al(OH)_3$ (gibbsite) range from $10^{-9.35}$ to $10^{-8.11}$ (Nordstrom *et al.*, 1990). In the downstream subreaches simulated aluminum concentration was higher than observed concentration even when the least soluble solid phase of gibbsite ($K_f = 10^{-8.11}$) was specified (Figure 4b). This result may reflect use of an unrepresentatively large value for aluminum concentration in inflow seepage in the subreach between 526 and 781 m, or a different solid phase may control aluminum concentration. Sulfate concentration decreased with downstream distance (Figure 4c). This decrease may be explained by the formation of aluminum hydroxysulfate solids. Sulfur is a component of stream-bed sediment in St. Kevin Gulch, where it has been measured as high as 3% by weight (Smith, 1991). Nordstrom (1982) described solid phase controls on aluminum concentration in waters of high sulfate concentration and low pH. A variety of aluminum hydroxysulfate minerals may control aluminum concentration, including jurbanite

Table 1: Parameters for simulation of conservative transport at St. Kevin Gulch, August 1986

Reach boundaries (m)	Maximum discharge (m^3s^{-1})	Stream cross-sectional area (m^2)	Storage zone cross-sectional area (m^2)	Stream-storage exchange coefficient (s^{-1})	Dispersion coefficient (m^2s^{-1})
0-26	6.19×10^{-3}	0.120	0.05	3.0×10^{-5}	0.02
26-484	7.92×10^{-3}	0.097	0.05	2.0×10^{-5}	0.02
484-526	1.51×10^{-2}	0.137	0.25	2.0×10^{-5}	0.02
526-948	1.68×10^{-2}	0.199	0.10	1.5×10^{-5}	0.02
948-1557	1.97×10^{-2}	0.152	0.20	5.0×10^{-5}	0.02
1557-1804	1.47×10^{-2}	0.153	0.10	1.5×10^{-5}	0.02

Table 2: Concentration of sulfate and aluminum and pH at the upstream boundary and at lateral inflows, St. Kevin Gulch, August 1986

Location (m)	Sulfate concentration (mg/L)	Aluminum concentration (mg/L)	pH
0	55	0.81	4.94
372	860	17	2.69
417	980	14	2.66
424	1075	14	2.69
449	1110	16	2.60
459	926	16	2.66
469	794	25	2.72
501	31	0.08	6.51
570	330	22.7	--
851	40	0.37	5.98
1281	72	1.2	3.87
1391	22	0.19	6.19

[$Al(SO_4)OH$], alunite [$KAl_3(SO_4)_2(OH)_6$], and basaluminite [$Al_4(SO_4)(OH)_{10}$]. Based on solubility diagrams presented by Nordstrom (1982), we selected jurbanite as a possible solid phase control within the ambient range of pH and aluminum and sulfate concentration in St. Kevin Gulch. Nordstrom (1982) cited a solubility product, K_{sp} = $\{Al^{3+}\}\{SO_4{}^{2+}\}\{OH^-\} = 10^{-17.8}$ for jurbanite, which at the 15° C average temperature of St. Kevin Gulch is equivalent to a formation constant of $10^{3.45}$. Figure 4 also presents the results of simulations conducted with jurbanite specified as the solid phase control for aluminum. The aluminum (Figure 4b) profile was not reproduced unless the formation constant for jurbanite was increased to $10^{4.25}$, which is somewhat higher than the reported value. Even with this less soluble value for jurbanite, the simulated sulfate concentration remained higher than the observed profile (Figure 4c).

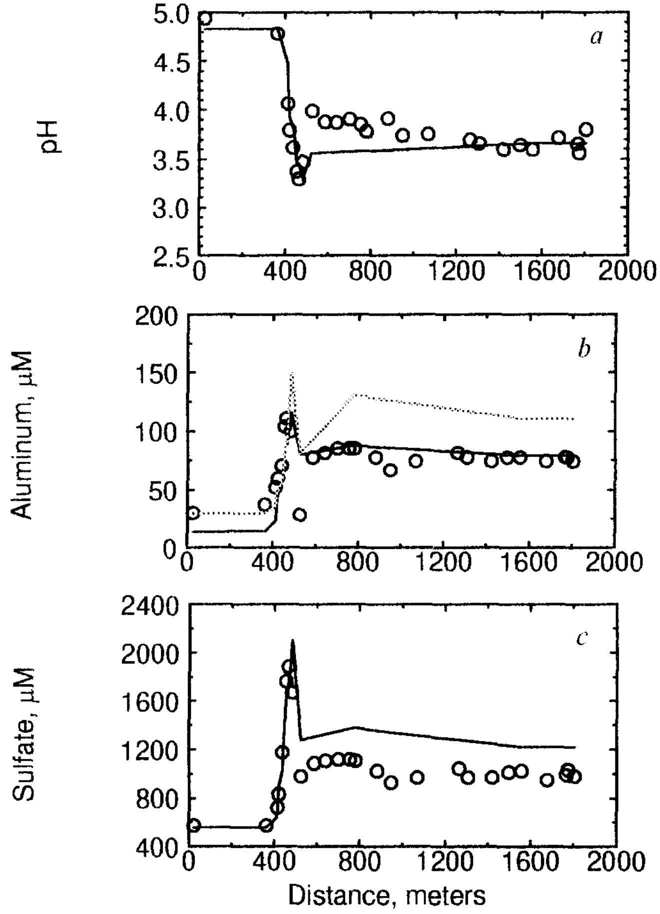

Figure 4. Observed (open circles) and simulated (lines) values of (a) pH and concentrations of (b) aluminum with the controlling solid specified as $Al(OH)_3$, $K_F = 10^{-8.11}$ (dotted line) or jurbanite [$Al(SO_4)OH$, $K_F = 10^{-4.25}$ (solid line)] and (c) sulfate with the controlling solid phase specified as jurbanite, St. Kevin Gulch, August 1986.

3.3 Profiles of pH, aluminum, and sulfate during the 1988 base injection

pH. Prior to the sodium carbonate injection, background pH values were about 3.5. The profile of pH at site 24 during the experiment is shown in Figure 5a. The injection quickly resulted in a pH of 4.2 at site 24. An increased injection rate begun at 11.9 hours eventually resulted in a pH of 5.8 at this site.

Aluminum. Background concentration of aluminum was spatially uniform at about 115 µM before the injection began. When pH increased from 3.5 to 4.2 at site 24, the aluminum concentration at this site did not change (Figure 5b). As pH increased above 5.0, the concentration of dissolved aluminum declined substantially, to less than 1.0 µM at pH 5.8. This decrease in dissolved aluminum was accompanied by an increase in particulate aluminum to more than 100 µM. Thus, the concentration of aluminum in the whole water sample declined only slightly. These observations were consistent with the formation of a slowly settling precipitate. After the injection stopped, dissolved aluminum concentration eventually returned to pre-injection values (Figure 5b). However, for approximately thirty minutes after the injection ended, dissolved aluminum concentration was higher than the background level. This post-injection spike in aluminum concentration indicated the recruitment of aluminum from a finite source. A flow weighted integration of total aluminum concentration versus time at site 24 showed that 27 grams of aluminum were removed from the water column along the first subreach during the injection interval (Kimball *et al.*, 1994a). A similar integration during the post-injection aluminum spike showed that 28 grams of aluminum were recruited back into the water column. This mass balance indicated that the finite source of aluminum during the post-injection spike was dissolution of freshly settled aluminum from the injection period.

Sulfate. Before the pH modification, sulfate concentration in the experimental reach was about 1330 µM (Figure 5c). This concentration remained unchanged until pH exceeded 4.7 and dissolved aluminum concentration began to decline. Sulfate concentration then also declined, to about 1230 µM at pH 5.2; when pH reached 5.6, sulfate concentration increased slightly (to 1270 µM). After the pulse of increased pH was transported downstream, sulfate concentration returned to its ambient level.

3.4 Transient Simulations of pH, Aluminum, and Sulfate

Figure 5 displays simulated pH and dissolved concentrations of aluminum and sulfate. These simulations included carbonate chemistry, precipitation of jurbanite and amorphous basaluminite, and sorptive interactions with the stream bed. The formation constant for amorphous basaluminite ($K_F = \{H^+\}^{10}\,\{Al^{3+}\}^{-4}\{SO_4^{2-}\}^{-1}$) was specified as $10^{-27.46}$ (Nordstrom, 1982). The stream bed was conceptualized as a surface of hydrous iron oxides undergoing double-layer complexation reactions. Kinetic restraints were applied to all interactions between the water column and the stream bed, including sorption-desorption and the dissolution of mass settled to the stream bed during the interval of higher pH.

The simulations reproduced the general features of the pulse of modified pH as it was transported downstream and the accompanying changes in aluminum and sulfate concentrations. Both in the simulations and in the field observations, aluminum was removed from the dissolved phase during the interval of higher pH. Particulate aluminum was removed from the water column by settling and was available for dissolution after the pulse of higher pH had passed. Two stages of sulfate removal were simulated, including an initial stage representing jurbanite precipitation (at about pH 4.3) and a second stage when amorphous basaluminite acted as the solid phase control (at about pH 4.6).

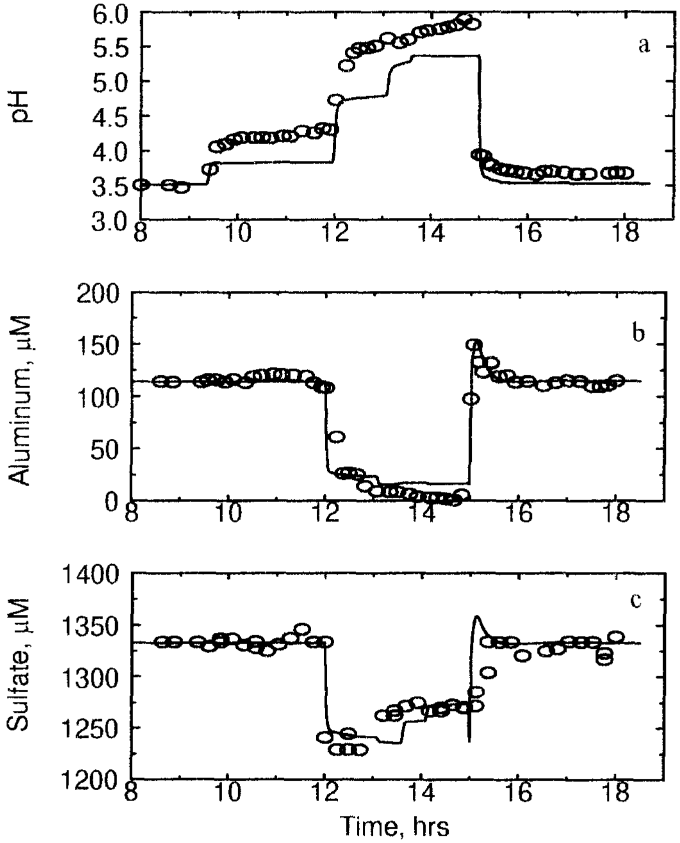

Figure 5. Observed and simulated transient profiles of pH, aluminum, and sulfate 24 meters downstream from a base-injection at St. Kevin Gulch, August 1988, with jurbanite and amorphous basaluminite specified as solid phase controls.

4.0 Conclusions

We have presented an approach to site characterization in streams affected by acid mine drainage. Because interactive processes control the behavior of acid constituents at these sites, a rigorous definition of site hydrology and spatial patterns of contaminant loading is necessary. A reactive solute transport model is offered as an internally consistent means of integrating our knowledge about a site and for testing hypotheses about physical and chemical processes that determine contaminant profiles.

An application at St. Kevin Gulch, a mountain stream receiving acid mine drainage near Leadville, Colorado, has demonstrated the reactive nature of aluminum and sulfate in the stream. Observed profiles of these constituents were reproduced by specifying hydroxysulfate controls on metal solubility. The aluminum profile could not be produced by simulations using the reported range in solubility for $Al(OH)_3$. The aluminum profile could be reproduced only when the formation constant for jurbanite [$Al(SO_4)OH$] was somewhat higher than a reported value. Lack of fit between observed and simulated concentrations of aluminum and sulfate also may be attributable to an unrepresentative value for inflow concentrations in a subreach of major ground-water seepage.

The robustness of the reactive solute transport model was tested further by simulations of a pH modification experiment. Simulations with jurbanite and amorphous basaluminite as solid-phase controls reproduced the observed behavior of pH, aluminum, and sulfate during a step-wise injection of sodium carbonate.

Acknowledgments

This study was supported by the Toxic Substances Hydrology Program of the U.S. Geological Survey. The author gratefully acknowledges the contributions of Briant A. Kimball, Robert L. Runkel, Diane M. McKnight, Kenneth E. Bencala, Katie Walton-Day, and Tracy B. Yager.

References

Allison, J.D., D.S. Brown, and K.J. Novo-Gradac, 1991, *MINTEQA2/PRODEFA2, A geochemical assessment model for environmental systems: Version 3.0 User's Manual,* Rep. EPA/600/3-91/021, U.S. Environmental Protection Agency, Washington, D.C.

Bencala, K.E. and R.A. Walters, 1983, Water Resour. Res. **19**, 718-724.

Kimball,B.A., R.E. Broshears, D.M. McKnight, and K.E. Bencala, 1994a, Effects of instream pH modification on transport of sulfide-oxidation products, in *Environmental Geochemistry of Sulfide Oxidation,* C.N. Alpers and D.W. Blowes, eds., ACS Symposium Series 550, American Chemical Society, Washington D.C., p. 224-243.

Kimball, B.A., R.E. Broshears, K.E. Bencala, and D.M. McKnight, 1994b, Environ. Sci. Technol. **28**, 2065-2073.

Nordstrom, D.K., 1982, Geochim. Cosmochim. Acta **46**, 681-692.

Nordstrom, D.K., L.N. Plummer, D. Langmuir, E. Busenberg, H.M. May, B.F. Jones, and D.L. Parkhurst, 1990, Revised chemical equilibrium data for major water-mineral reactions and their limitations, in *Chemical Modeling of Aqueous Systems II*, D.C. Melchior and R.L. Bassett, eds., American Chemical Society, Washington D.C., p. 398-413.

Runkel, R.L., 1993, *Development and application of an equilibrium-based simulation model for reactive transport in small streams*, Ph.D. dissertation, Dept. of Civil, Environmental, and Architectural Engineering, University of Colorado, Boulder, 202 p.

Runkel, R.L. and R.E. Broshears, 1991, *One dimensional transport with inflow and storage (OTIS): A solute transport model for small streams*, Technical Report 91-01, Center for Advanced Decision Support for Water and Environmental Systems, University of Colorado, Boulder, 85 p.

Smith, K.S., 1991, *Factors influencing metal sorption onto iron-rich sediment in acid-mine drainage, Ph.D. dissertation*, Department of Chemistry and Geochemistry, Colorado School of Mines, Golden, 239 p.