Calibration of Reactive Transport Models for Remediation of Mine Drainage in Solid-Substrate Biocolumns

Paulo S. Hemi, Ph.D.1; Charles D. Shackelford, Ph.D., M.ASCE2; and Linda A. Figueroa, Ph.D., M.ASCE3

Abstract: Experimental data pertaining to two pairs of solid-substrate sulfate-reducing biocolumns for remediation of mine drainage were used for calibrating and testing new reactive transport models based on sulfate reduction and sulfide precipitation linked to rate-limiting solid-substrate hydrolysis. First-order (F) and Contois (C) kinetics for decomposition as well as different numbers of pools of decomposable materials were proposed in different models (F1–F3 and C1–C3). Effluent sulfate concentrations for one of the columns were used as the basis for calibrating the different models and, due to limitations in the calibration data set, the number of adjustable model parameters was limited using parameter tying. Calibrated models were ranked using Akaike information criterion, and Model C2, followed by Model C1, based on Contois kinetics, emerged as the models that were supported to a greater extent by the data. For an independent experimental data set, model testing was performed using Models C2 and C1 with parameters from the previous calibration resulting in good approximations of effluent sulfate. For the calibration data set, longer-term model predictions for effluent sulfate, decomposable substrates, and microbial populations also were performed. The reactive transport models represent a potentially valuable tool for the design of solid-substrate bioreactors used for the treatment of mining influenced water, although future model validation using longer-term field data sets will be necessary to confirm the model predictions.

DOI: 10.1061/(ASCE)EE.1943-7870.0000234

CE Database subject headings: Calibration; Mining; Models; Organic matter; Sulfate; Wastewater management.

Author keywords: Mining influenced water; Modeling; Solid organic substrates; Sulfate reduction.

Introduction

Abandoned mine land (AML) sites are frequently remote and characterized by problems associated with mining influenced water, such as acid mine drainage (AMD), i.e., low pH water laden with metals from mine tunnels, mill tailings, and waste rock. Such AMD represents a significant environmental problem in terms of impacting streams and groundwater aquifers. For example, approximately 51,700 AML sites are located within only six states of U.S. EPA Region 8 (WGA 1998). Remediation of such mining influenced water can be accomplished via the use of passive treatment systems such as passive bioreactors and permeable reactive barriers. Such elements can be installed to intercept and passively treat contaminated groundwater down gradient from a contaminant source (Benner et al. 1999; Groudev et al. 2003; Whitehead et al. 2005).

In particular, the use of decomposable organic solids to provide slow release of organic substrates in support of biogenic sulfide production and metal-sulfide precipitation in engineered biogeochemical systems allows for low-cost, low-maintenance remediation of mining influenced water at AML sites. For example, the results of several laboratory studies involving sulfate-reducing (SR) flow-through experiments for metal precipitation have demonstrated the potential use of sulfate reduction and metal-sulfide precipitation coupled to the decomposition of organic solids for the remediation of mining influenced water (e.g., Gibert et al. 2004). Examples of solid, decomposable organic materials that have been evaluated for this purpose include sawdust (Tuttle et al. 1969; Wakao et al. 1979), spent mushroom compost (Dvorak et al. 1992; Hammack and Edenborn 1992), fresh alfalfa (Bechard et al. 1994), leaf mulch and wood chips (Waybrant et al. 1998; Chang et al. 2000), and corn stover (Figueroa et al. 2007). Also, some field applications of SR systems in permeable reactive barriers, wetlands, and large-scale bioreactors have been reported (Benner et al. 1999; Groudev et al. 2003; Whitehead et al. 2005).

The design of SR field applications historically has been based on short-term laboratory experiments focusing primarily on changes in inorganic chemistry. Advances in design and predictability are expected to result from enhancing the characterization of suitable organic material, monitoring changes in organic chemistry (e.g., organic substrates) and biological components (e.g., microbial ecology) (Hallberg and Johnson 2005; Place et al. 2006; Pruden et al. 2006), and developing and calibrating biogeochemical simulation tools that include major aspects of the system. Conceptual models for the microbial ecology in SR systems range from complex with multiple linked microbial processes to simpler single process models.

The flowchart shown in Fig. 1, which was used as the basis for the mathematical models presented in this study, includes the hydrolysis of polysaccharides, sulfate reduction based on lactate, and precipitation of metal sulfides. The multiple possible path-
ways for the degradation of complex organic matter were simplified to a model biopolymer (polysaccharide) and a model intermediate compound (lactate), which is analogous to the approach used for the development of activated sludge models (Henze et al. 2000).

More broadly, decomposer groups catalyze the hydrolysis of complex organic materials (e.g., cellulose, protein, lipids) and the fermentation of the hydrolysis products (e.g., glucose) to simpler compounds (e.g., acetate or lactate) (Colberg 1988). The simpler compounds serve as the carbon and energy source for SR bacteria. Fermentation and sulfate reduction require reduced conditions as indicated by the negative redox potential (pe < −3) required for both reactions (Zehnder and Stumm 1988). The pH preference of sulfate reducers has been reported as 6 ≤pH≤ 9 (Widdel 1988). The pH optimum for the anaerobic digestion of solid organic materials is in a similar range of 6.5 ≤pH≤ 8.2 (Speece 1996). The maximum reported rates of sulfate reduction and fermentation are at temperatures above 30°C. Thus, at environmentally relevant temperatures (≥2°C), measurable but slower rates of sulfate reduction are observed (Widdel 1988).

In terms of modeling the rate of sulfate (SO$_4^{2−}$) reduction, Monod kinetics (Monod 1949) has been used to take into account the growth of SR bacteria in some models (Schafer et al. 1998; Prommer et al. 2001; Mayer et al. 2002). However, these models only considered scenarios where soluble organic substrates (e.g., ethanol, lactate) were injected directly or amended to the media. Sustainable systems will be based on the decomposition of solid organic materials as a prerequisite to releasing dissolved bacterial substrates and rate limiting to bioremediation (Tuttle et al. 1969). Although other models have accounted for the linkage between SO$_4^{2−}$ reduction and the rate of organic material decomposition (e.g., Westrich and Berner 1984; Drury 2000), these models have been based only on first-order kinetics and have neglected bacterial fate and surface-limiting considerations.

Recent data from SR biocolumns based primarily on corn stover presented herein are used for calibrating and testing the modeling approaches described subsequently, which are based on modeling sulfate reduction and metal precipitation coupled to solid-phase decomposition (hydrolysis). This study represents an extension of a previous study that evaluated the use of the models to simulate the results of batch equilibrium (no-flow) SR systems (Hemsi et al. 2005). The issue of long-term biocolumn longevity also is addressed with the models, which include the fates of solid decomposable materials and the decomposer bacterial population.

**Development of Models**

As illustrated in Fig. 1, the chemical and biological processes in the models proposed in this study include the following: (1) anaerobic hydrolysis (decomposition) of polysaccharides in solid organic materials due to the activity of a consortium of generally designated decomposer bacteria ($X_{Di}$); (2) SO$_4^{2−}$ reduction based on incomplete oxidation of lactate; and (3) precipitation of metal sulfides due to the release of H$_2$S (hydrogen sulfide). In the models, the rate of sulfate reduction and, consequently, that of metal precipitation is linked to the rate-limiting step of polysaccharide (cellulose and hemicellulose) decomposition (Tuttle et al. 1969; Westrich and Berner 1984; Bechard et al. 1994; Chynoweth and Pullammanappallil 1996; Drury 2000). In turn, polysaccharide decomposition and release of soluble substrates are limited by the extent of solid-phase hydrolysis (Vasiliev et al. 1993; Vavilin et al. 2004; Batstone et al. 2002), which becomes the most significant component in mathematical models representing such biochemical systems.

**Solid-Phase Hydrolysis**

In contrast with the more complex, mechanistic solid-hydrolysis kinetics (e.g., Humphrey 1979), relatively simple first-order and Contois kinetics (Contois 1959) are commonly applied to simulate the anaerobic digestion of organic matter (e.g., Vasiliev et al. 1993; Rittmann and McCarty 2001; Vavilin et al. 2004). Based on first-order kinetics, the rate of hydrolysis, which is the slowest step in polysaccharide decomposition, can be expressed as follows:

$$\frac{d[X_i]}{dt} = -k_{f,i} [X_i]$$  \hspace{1cm} (1)

where $[X_i]$=remaining concentration of decomposable polysaccharide $i$ in terms of dry mass per volume of solution (g/L), $k_{f,i}$=hydrolysis rate coefficient (d$^{-1}$), and $t$=time.

In a surface-limiting process, such as Contois kinetics, the time rate of solid-substrate hydrolysis may decrease as the biomass concentration of decomposer bacteria increases above a limiting value, reflecting surface area and mass transfer limitations. Based on Contois kinetics, the rate of hydrolysis is regulated by the ratio between the concentrations of the remaining decomposable polysaccharide and decomposer bacteria, as follows:

$$\frac{d[X_i]}{dt} = -k_{f,i}[X_i] - \frac{Y_{XdeCE}d[C]}{K_{A,i} + [C]} \frac{d[C]}{dt}$$  \hspace{1cm} (2)

where $[X_i]$=biomass concentration of the decomposer bacteria associated with material $i$ (cell g total mass/L), $k_{f,i}$=Contois specific rate coefficient (d$^{-1}$), $K_{A,i}$=Contois affinity coefficient (g/g), $Y_{XdeCE}$=stoichiometric mass-yield coefficient [see Eq. (4)], $d_{i}=first-order decay coefficient for decomposer bacteria. In Eq. (2), the rate of polysaccharide decom-
position transitions between the two limiting cases of first-order kinetics with respect to \([CE]_j\) at low \([CE]/[X_{d_j}]\) ratios, and first-order kinetics with respect to \([X_{d_j}]\) at high \([CE]/[X_{d_j}]\) ratios (i.e., exponential \(X_{d_j}\) growth). Rate coefficients such as \(k_f\) and \(k_e\) lump the effects of intrinsic material degradability properties, particle characteristics (gradation, surface area), and testing conditions, which are more explicit in more mechanistic models (Humphrey 1979).

### Subsequent Steps

#### Dissolved Organic Substrate

The rate of release of a soluble organic substrate, such as lactate utilized by SR bacteria, can be taken to be directly proportional to the rate of solid decomposition, as well as the growth rate of decomposer bacterial biomass \((X_d)\) [Eq. (3)]. The yield coefficients for proportionality were obtained from the following reaction derived using the half-reaction approach (Rittmann and McCarty 2001):

\[
2C_3H_6O_4 + 0.427H_2O + 0.524NH_4^+ \rightarrow 3.126C_6H_12O_7 + 3.652H^+ + 0.524C_2H_5O_2N^-
\]

where \(C_3H_6O_4\) represents an empirical formula for cells (Rittmann and McCarty 2001), and the stoichiometric mass-yield coefficients for lactate and biomass are \(Y_{LACE} = 0.859 \text{g/g} \) and \(Y_{XACE} = 0.183 \text{g/g} \), respectively.

#### Sulfate Reduction and Metal Precipitation

The rate of sulfate reduction is assumed to be directly proportional to the rate of release of lactate in solution, i.e., as long as \(SO_4^{2-}\) is present. Since the rate-limiting step is solid-substrate hydrolysis, sulfate reduction is assumed in the models to be sufficiently fast.

Stoichiometric mass-yield coefficients for \(Y_{SO4}^{2-}\) and \(Y_{HS}^{2-}\) of 0.507 g/g and 0.180 g/g, respectively, were obtained based on the reaction for sulfate reduction on lactate obtained using the half-reaction approach (Rittmann and McCarty 2001):

\[
2.128C_3H_6O_4 + SO_4^{2-} + 0.077NH_4^+ + 0.051H^+ \rightarrow 2HCO_3^-
\]

An instantaneous-reaction approach is used, with the inherent assumption that any time an amount of the organic substrate (lactate) is produced at a given location within the biocolumn, this amount is transported and consumed in sulfate reduction, i.e., as long as \(SO_4^{2-}\) concentration at the location is greater than \(Y_{SO4}^{2-}[LA]\), where \([LA]\) denotes the lactate concentration. In this case, the stoichiometric amounts of \(SO_4^{2-}\) and \(H_2S\) will be consumed and produced, respectively, at the cell in the model domain, in accordance with the following expressions:

\[
[SO] = [SO] - Y_{SO4}[LA], \quad [HS] = [HS] + Y_{HS}[LA] \quad (6)
\]

where \([SO]\) and \([HS]\) represent sulfate and hydrogen sulfide concentrations, respectively, and the \(Y\) symbols represent the corresponding mass-yield coefficients. Since sulfate is present in the influent solution and, as previously described, is consumed only to the extent of lactate availability (i.e., the limiting reactant), \(SO_4^{2-}\) generally remains in excess along the column.

Similarly, the rate of metal-sulfide precipitation in the biocolumn is assumed to be directly proportional to the rate of release of \(H_2S\), i.e., to be sufficiently fast, as long as metals are present. Any time an amount of \(H_2S\) is released at a given location within the biocolumn, this amount is transported and consumed in metal-sulfide precipitation, i.e., as long as metal concentrations at the location are greater than \(Y_{MEHS}[HS]\), where \([HS]\) denotes the hydrogen sulfide concentration and \(Y_{MEHS}\)=a mass-yield coefficient for metal sulfide precipitation (e.g., ZnS, \(Y_{Zn/HS}\) = 1.919 g/g). The stoichiometric amount of metal will be removed in accordance with the following relation:

\[
[ME] = [ME] - Y_{MEHS}[HS] \quad (7)
\]

#### Model Solution

The experiments are modeled as bioreactors, where the temporal rate of mass accumulation/removal for any species is equal to a combination of the mass production/consumption (reactions) within the reactor and the mass input/output (transport). For each species in the reactor, mass balance can be written generically as an advection-dispersion-reaction equation as follows:

\[
\frac{\partial [c]}{\partial t} = \left( D_{xx} \frac{\partial^2 [c]}{\partial x^2} + D_{yy} \frac{\partial^2 [c]}{\partial y^2} + D_{zz} \frac{\partial^2 [c]}{\partial z^2} \right) - \frac{\partial}{\partial x}(v[c]) + \frac{\partial [c]}{\partial t} \text{reactions} \quad (8)
\]

where \(t=\text{time}, x, y, z=\text{Cartesian coordinate axes, with } x \text{ parallel to the longitudinal direction of flow, } [c] = \text{concentration of a generic species, } D_{xx}, D_{yy}, \text{and } D_{zz}=\text{principal components of the hydrodynamic dispersion tensor in the respective } x, y, \text{and } z \text{directions, } v = q/n, \text{where } q = \text{liquid flux or Darcy velocity, and } n = \text{total porosity is the seepage velocity parallel to the } x \text{ direction, and } \frac{\partial [c]}{\partial t} \text{reactions} = \text{temporal net rate of mass utilization given by biochemical processes as previously discussed. As explained later, the value of } n \text{ was assumed to be 0.73. The values of } v \text{ used for simulation were adjusted based on the experimental value by adjusting the values of hydraulic conductivity } K \text{ and hydraulic gradient } i \text{ (i.e., } q = Ki). \text{Hydrodynamic dispersion was introduced only in terms of a longitudinal dispersivity coefficient } (a_x) \text{ of 0.015 m, with transverse dispersion assumed negligible (i.e., } D_{yy} = D_{zz} = 0). \text{Permeant flow in the bioreactors was simulated with MODFLOW-2000 Version 1.7 (U.S. Geological Survey) as described in Harbaugh et al. (2000). Multispecies reactive transport was simulated with RT3D Version 2.5 (U.S. Department of Energy) as described in Clement (1997). RT3D transport was coupled to a user-defined subroutine containing the biochemical reaction kinetics in this research. In addition, the instantaneous-reaction algorithms [Eqs. (6) and (7)] were encoded into RT3D.}

The model solution requires the simultaneous integration of all interdependent mass-balance equations of the system with respect to time. These equations include a nonlinear partial differential equation for each mobile species and a nonlinear ordinary differential equation for each immobile species. Numerical solution was obtained using reaction operator splitting, where the nonlinear ordinary differential equations (reactions) were solved by Runge-Kutta-Fehlberg integration. Transport time steps, which were on the order of 0.01 d, were selected on the basis of the requirements for advection, dispersion, and sink/source mixing automatically set in RT3D. Multiple time steps for Runge-Kutta
integration were required within each transport time step up to a total of 3,000 integration time steps, after which integration was stopped by the program.

The reactor was modeled as a prismatic, three-dimensional domain, containing nine rows, 61 columns (along the direction of flow), and one layer. The space discretization was 0.5 cm along rows and columns and 4.363 cm of layer height. Flow and transport boundary conditions were defined for one-dimensional flow and transport. Flow boundary conditions consisted of upper and lower specified hydraulic-head boundaries (Dirichlet) at column ends, with no-flow boundaries through each column side. Transport boundary conditions consisted of a specified concentration at ends, with no-flow boundaries through each column side. Transverse estimated as occurring in the measurement of observation variance. Based on the assumption of measured concentrations dependent and focus at placing more weight on data with less variance. The reactor was modeled as a prismatic, three-dimensional domain, containing nine rows, 61 columns (along the direction of flow), and one layer. The space discretization was 0.5 cm along rows and columns and 4.363 cm of layer height. Flow and transport boundary conditions were defined for one-dimensional flow and transport. Flow boundary conditions consisted of upper and lower specified hydraulic-head boundaries (Dirichlet) at column ends, with no-flow boundaries through each column side. Transport boundary conditions consisted of a specified concentration at ends, with no-flow boundaries through each column side. Transverse estimated as occurring in the measurement of observation variance. Based on the assumption of measured concentrations dependent and focus at placing more weight on data with less variance.

**Evaluation of Model Calibration**

The quantitative evaluation of model calibration results involved assessing the magnitude of the sum of weighted squared errors (SWSE) resulting from the comparison between model-predicted concentrations (effluent) and measured values (experimental data) for effluent sulfate over observation times, as follows:

\[
SWSE = \frac{1}{(n-k)} \sum_{i=1}^{n} w_i \left( \frac{[c_{obs,i}] - [c_{sim,i}]}{[c_{obs,i}]} \right)^2
\]  

(9)

where \(n\) = number of observations, \(k = NP + 1\) (where \(NP =\) number of model parameters), \(w_i = \) weight of observation \(i\), and \([c_{obs,i}]\) and \([c_{sim,i}]\) = respective observed and simulated effluent concentrations at the \(i\)th calibration time. By definition, observation weights \(w_i\) are calculated as equal to the inverse of the variance estimated as occurring in the measurement of observation \(i\). For this study, the SWSE was programmed in MATLAB (MathWorks, Natick, Mass.).

**Model Selection**

As described in Poeter and Anderson (2005), the Akaike information criterion \( (AIC_C) \) was used for estimating Kullback-Leibler information, as follows:

\[
AIC_C = n \ln(\sigma^2) + 2k + \frac{2(k+1)}{n-k-1}
\]  

(10)

where \(\sigma^2\) = estimated residual variance, including a sum of weighted squared residuals, calculated on the basis of experimental data (observations) and modeled results, as follows:

\[
\sigma^2 = \frac{1}{n-k} \sum_{i=1}^{n} w_i (c_{obs,i} - c_{sim,i})^2
\]  

(11)

The second and third terms of Eq. (10) are first- and second-order bias terms resulting from a small number of observations \(n\) \(< k < 40\). The weights \(w_i\) apply when the observation errors are independent and focus at placing more weight on data with less variance. Based on the assumption of measured concentrations with apparently an equal error, a single observation variance can be used for the entire experimental data set (i.e., \(w_i = \) const.). For each model, a delta \(AIC_C\) value \( (\Delta)\) and an Akaike weight of evidence \( (w_{A,i})\) can be calculated, as follows:

\[
\Delta_i = AIC_{C,i} - AIC_{C,min}
\]  

(12)

\[
w_{A,i} = \frac{e^{-0.5\Delta_i}}{R \sum_{j=1}^{R} e^{-0.5\Delta_j}}
\]  

(13)

where \(R = \) total number of models being evaluated to select the one that minimizes information loss. Evidence ratios can be obtained as ratios of \(w_{A,k}/w_{A,i}\), where \(k = \) best model in the sense described above, and \(i\) represents any other model in the model set.

**Biocolumn Experiments**

Two pairs of duplicate treatment experiments were performed. The feed influent solutions used in the experiments were collected from two sites located in Colorado, viz. the National Tunnel Adit (NTA) and the Silver Cycle Mine Adit (SCA). The experiments were two-stage systems, with limestone pretreatment reactors for control of \(pH\) and \(Fe^{2+}\) and \(Al^{3+}\) removal followed by anaerobic SR biocolumns (see details in Figueroa et al. 2007). Water qualities for the samples collected at these sites (i.e., influent solutions for the two-stage treatments) and for the effluents from the limestone pretreatment (i.e., influent solutions for the SR biocolumns) are summarized in Table 1. As indicated in Table 1, the limestone pretreatment was aimed at removing excess \(Fe^{2+}\) and \(Al^{3+}\) to avoid the SR biocolumns from clogging, which can cause column failure before depletion of organic substrates.

The experimental data used for this study pertained specifically to \(SO_4^{2-}\) and \(Zn^{2+}\) effluent concentrations from the SR biocolumns. The anaerobic SR biocolumns consisted of 30-cm-long, 5.0-cm-diameter, acrylic tubes adapted with flanges with threaded influent and effluent fittings. Each biocolumn was packed with 17.0 g of corn stover and 194 g of fragmented walnut shells, both passing the 6.35-mm sieve, at equal volumes (i.e., 50% corn stover and 50% walnut shells mixture, by volume). No external inoculum for SR bacteria (e.g., manure) was employed.

**Table 1.** Water Quality for Samples Collected at NTA and SCA Sites and for Influent Solutions Fed to SR Biocolumns, i.e., after Limestone Pretreatments (Figueroa et al. 2007)

<table>
<thead>
<tr>
<th>Chemical constituent</th>
<th>NTA collected water</th>
<th>NTA collected solution to biocolumns</th>
<th>SCA collected water</th>
<th>SCA collected solution to biocolumns</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulfate, (SO_4^{2-}) (mg/L)</td>
<td>900</td>
<td>900</td>
<td>2,100</td>
<td>2,100</td>
</tr>
<tr>
<td>Zinc, (Zn^{2+}) (mg/L)</td>
<td>5–7</td>
<td>1–2</td>
<td>65–75</td>
<td>45–55</td>
</tr>
<tr>
<td>Ferrous iron, (Fe^{2+}) (mg/L)</td>
<td>40</td>
<td>&lt;1</td>
<td>40</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Aluminum, (Al^{3+}) (mg/L)</td>
<td>&lt;1</td>
<td>~0</td>
<td>&lt;1</td>
<td>~0</td>
</tr>
<tr>
<td>pH</td>
<td>6.0–6.5</td>
<td>6.5</td>
<td>5.0–5.5</td>
<td>5.8</td>
</tr>
</tbody>
</table>
Peristaltic pumps were used to generate flow rates from the bottom to the top of each biocolumn at either 60 mL/d of influent solution for the NTA biocolumns or 30 mL/d for the SCA biocolumns. After packing the biocolumns with the solid materials, an average of 433 mL was required to saturate each biocolumn with deionized water, resulting in a total porosity, \( n \), of 0.73. Thus, the nominal solution residence times were 7.2 d in the NTA biocolumns and 14.4 d in the SCA biocolumns. Periodic sampling was performed to measure the outflow rate, pH, alkalinity, sulfate, and dissolved and total metals.

As shown in Table 1, a major difference between NTA and SCA biocolumns was the influent concentrations for Zn\(^{2+}\). This difference is significant, since zinc has been reported to have inhibitory effects on the growth of sulfate reducers above 25–50 mg/L \(\text{H_2O}^{849}/\text{Utgikar et al. 2003}/\text{H_2O}^{850} \), and cellulolytic fermenters above 1 mg/L free zinc concentration \(\text{Ruhs et al. 2006}/\text{H_2O}^{849}\). Sulfate concentrations were calculated directly from the total measured sulfur in aqueous solution. Total sulfur and metals were analyzed by inductively coupled plasma-absorbance emission spectroscopy (ICP-AES) Perkin Elmer Optima 3000. Samples were filtered through 0.45-\(\mu\)m syringe-tip filters, diluted with Milli-Q water, and acidified to pH 2 with trace metals-grade nitric acid Mallinckrodt. The detection limits were 0.05 mg/L and 0.002 mg/L for sulfur and zinc, respectively. Values of pH were measured using an Orion 910500 probe and Series 200 meter (Denver Instruments, Arvada, Colo.). Organic compositions of the corn stover and walnut shells were determined by Venot (2008) using hot water (TAPPI 1999) and acid extractions (Templeton and Ehrman 1995) coupled with total dry weight (sample dried at 103°C) and organic content measurement, by the difference between total dry weight and fixed solids dried at 550°C.

**NTA Biocolumns**

As shown in Fig. 2a, the measured effluent solution pH for the NTA duplicate biocolumns (NTA-1 and NTA-2) indicated similar trends, with pH values being lower than 5 at the onset of the experiments and lower than 6 for pore volumes of flow, PVF \(=\text{V}_{\text{infl}}/L\), where \(v=\text{constant seepage velocity}, t=\text{time}, \text{and } L=\text{column length}\), <5.5, and subsequently increasing to 6.5 and 7.5 at \(\sim10\) and \(\sim16\) PVF, respectively. The early-time pH that generally was lower than that of the influent solution coming from the limestone pretreatment (6.0–6.5) may be indicative of material leaching. Subsequently, the increasing effluent pH occurring in both columns may be attributed to alkalinity production by sulfate reduction.

As shown in Fig. 2b, effluent sulfate concentrations were approximately stabilized between \(\sim500\) and 600 mg/L at \(\sim15\) PVF, which is below the concentration level of the influent solution supplied to the columns (900 mg/L). Sulfate removal after 30 d (4.3 PVF) stabilized at an average rate of sulfate reduction of \(\sim0.28\) mmol S/L d\(^{-1}\). As shown in Fig. 2c, removal of zinc to <0.1 mg/L occurred for both NTA biocolumns within approximately 21 d (3 PVF).

**SCA Biocolumns**

Compared to the NTA duplicate columns, the pair of SCA biocolumns (SCA-1 and SCA-2) was tested under double the solution residence time, albeit with significantly higher [Zn\(^{2+}\)] in the influent solution. The experimental results from the pair of SCA biocolumns were distinct. As shown in Fig. 3(a), measured effluent pH for SCA-1 increased from 5 to 5.5 (PVF < 2) to 7.0
\[ \leq \text{pH} \leq 7.5 \text{ for PVF} > 7 \text{ to 8. In contrast, effluent pH for SCA-2} \]

\[ \text{remained at significantly lower levels, both near the onset of the} \]

\[ \text{experiment (4.5} \leq \text{pH} \leq 5, \text{ for PVF} = 2 \text{ to 3) and in the longer term} \]

\[ (\text{pH} = 6 \text{ for } 5 \leq \text{PVF} \leq \text{end of test}). \text{ Therefore, the SCA-2 failed} \]

\[ \text{during the test.} \]

Possible explanations for the distinct results include the fact that the SCA biocolumns were under more stress due to higher [Zn\textsuperscript{2+}] than were the NTA biocolumns, as well as the possibility of experimental error in the case of the failure of SCA-2. For example, there was a 30-d lag in the startup of the SCA-2, with differences in temperature and flow conditions during the initial period of the test. In addition, a 10-d loss of flow occurred at early times for the SCA-2, which may have resulted in depletion of sulfate and a synergistic community of fermenters, acidogens, and methanogens developing, thereby hindering the development of full sulfate reduction in this column. The results shown in Figs. 3(b and c) corroborate the poorer performance of SCA-2.

As shown in Fig. 3(b), effluent sulfate concentrations varied more widely than those for the NTA experiments, but approximately stabilized at \(~1,750 \text{ mg/L at } \sim 12 \text{ PVF for SCA-1. Sulfate removal after 50 d (3.6 PVF) stabilized at an average rate of sulfate reduction of} \sim 0.29 \text{ mmol S/L d}^{-1}, \text{ similar to that of the NTA biocolumns. As shown in Fig. 3(c), the removal of zinc to} \lesssim 0.1 \text{ mg/L occurred for both SCA biocolumns within approximately 2 PVF for SCA-1. Based on the pH and} \text{SO}_4^{2-} \text{ trends described above, SCA-2 was considered to have failed and the data were disregarded.} \]

**Solid Substrates**

The initial amounts of solid decomposable material (polysaccharide, g/L) in a given biocolumn were not explicitly known, but were not simply equal to the total dry mass of packed organic materials. Fractions such as lignin (\(~25–35\%\), by dry mass, in woods, \(15–20\%\) in leaves and grass), protected/recalcitrant polysaccharide tissues (\(~15–20\%)\), and water soluble organics and inorganics (\(~5\%\) in woods, \(15–25\%\) in leaves and grass) were discounted due to significantly lower rates of degradation of these solids and washout of the water soluble components (e.g., Sylvia et al. 1998). For the corn-stover material utilized in this research, the fractions of lignin and water soluble organics were determined to be 15 and 16\%, respectively (Venot 2008).

Combining representative percentages, a 50\% degradable polysaccharide fraction (dry-mass basis) was considered for the corn stover. Estimates of lignocellulosic material biodegradability by the methods of Chandler et al. (1980) and Van Soest (1994) using the corn-stover composition reported by Venot (2008) were 40 and 60\%, respectively. Thus, the 17 g of packed corn stover were simulated as 20 g/L of initial decomposable polysaccharides. Walnut shells, which are far less degradable than corn stover, represented the structural granular medium in the biocolumns. The decomposable polysaccharides were assumed as \(~10\%\) on a dry-mass basis, which is consistent with the degradable fraction estimated using the method by Van Soest (1994) for a holocellulose to lignin ratio of 1.5. Thus, the 194 g of packed material were simulated as 40 g/L of initial decomposable polysaccharides.

**Previous Parameter Values**

The previous study by Hemsi et al. (2005) focused on approximating experimental rates of sulfate reduction at 25°C in batch
Table 2. Decomposition Rate Equations, Adjustable and Tied Parameters, and Initial Concentration Values Employed in Models F1–F3 and C1–C3

<table>
<thead>
<tr>
<th>Model</th>
<th>s</th>
<th>Decomposition rate equations (i = 1…s)</th>
<th>Adjustable</th>
<th>Tied</th>
<th>Initial concentration (g/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>F1</td>
<td>1</td>
<td>( \frac{d[CE_i]}{dt} = -k_i[CE_i] )</td>
<td>( k_{f,1} )</td>
<td>—</td>
<td>[CE(_i)] = 20</td>
</tr>
<tr>
<td>F2</td>
<td>2</td>
<td>( \frac{d[CE_i]}{dt} = -k_i[CE_i] )</td>
<td>( k_{f,1} )  ( k_{f,2} = 0.1 ) ( k_{a,1} )</td>
<td>( [CE(_i)] = 20 )  ( [CE(_2)] = 40 )  ( [LA] = 0 )</td>
<td></td>
</tr>
<tr>
<td>F3</td>
<td>3</td>
<td>( \frac{d[LA]}{dt} = Y_{LA/CE} \sum_i \left( \frac{d[CE_i]}{dt} \right) )</td>
<td>( k_{f,1} )  ( k_{f,2} = 0.1 ) ( k_{a,1} ) ( k_{a,2} = 10 ) ( k_{a,1} )</td>
<td>( [CE(_i)] = 20 )  ( [CE(_2)] = 40 )  ( [CE(_1)] = 4 )  ( [LA] = 0 )</td>
<td></td>
</tr>
<tr>
<td>C1</td>
<td>1</td>
<td>( k_{c,1} ) ( K_{a,1} )  ( d_1 = 0.1 ) ( k_{c,1} )</td>
<td>—</td>
<td>( [CE(_1)] = 20 )  ( [CE(_2)] = 0.1 )  ( [LA] = 0 )</td>
<td></td>
</tr>
<tr>
<td>C2</td>
<td>2</td>
<td>( \frac{d[CE_i]}{dt} = -k_i[CE_i] \left( \frac{[CE_i][X_{d,i}]}{K_{a,i} + [CE_i][X_{d,i}]} \right) )</td>
<td>( k_{c,1} )  ( K_{a,1} )  ( k_{a,2} = 0.1 ) ( k_{a,1} ) ( d_1 = 0.1 ) ( k_{c,1} ) ( d_2 = 0.1 ) ( k_{c,2} )</td>
<td>( [CE(_i)] = 20 )  ( [CE(_2)] = 40 )  ( [CE(_1)] = 4 )  ( [LA] = 0 )</td>
<td></td>
</tr>
<tr>
<td>C3</td>
<td>3</td>
<td>( \frac{d[LA]}{dt} = Y_{LA/CE} \sum_i \left( \frac{d[CE_i]}{dt} \right) )</td>
<td>( k_{c,1} )  ( K_{a,1} ) ( k_{a,2} = 0.1 ) ( k_{a,1} ) ( k_{a,3} = 10 ) ( k_{a,1} ) ( K_{a,2} = 40 )  ( K_{a,3} = 40 ) ( K_{a,1} ) ( d_1 = 0.1 ) ( k_{c,1} ) ( d_2 = 0.1 ) ( k_{c,2} ) ( d_3 = 0.1 ) ( k_{c,3} )</td>
<td>( [CE(_i)] = 20 )  ( [CE(_2)] = 40 )  ( [CE(_1)] = 4 )  ( [LA] = 0 )</td>
<td></td>
</tr>
</tbody>
</table>

Note: s = number of substrates; \( Y_{LA/CE} = 0.859 \) g/g; \( Y_{X_d/CE} = 0.181 \) g/g; and initial ratio \([X_{d,i}]/[CE_i] = 0.005\).

Results

Experimental results in terms of sulfate removal rates ranged between 0.1 and 0.3 mmol S/L d\(^{-1}\), which were within the range from 0.1 to 2 mmol S/L d\(^{-1}\) observed in laboratory and field studies (Wildeman et al. 1997; Waybrant et al. 1998; Neculita et al. 2007). Tuttle et al. (1969) reported rates from −0.1 to 0.2 mmol S/L d\(^{-1}\) for wood-dust SR biocolumns for AMD remediation tested at 22°C.

Model Calibration

The different models proposed are shown in Table 2. The definition of Models F1–F3 and C1–C3 is aimed at investigating the effects of the type of kinetics used for solid-substrate hydrolysis (F = first-order versus C = Contois) and the number of pools of decomposable materials considered. Each model was calibrated by minimizing the calibration error (SWSE) between simulated and experimental NTA-1 effluent concentrations for SO\(_4^{2-}\) versus time (Tables 3 and 4). Rates of sulfate reduction, effluent concentrations for Zn\(^{2+}\), and the final dry mass of solid organic material were compared in the figures.

Inverse modeling (e.g., Poeter and Hill 1997) was not employed in this study. The optimization routine for searching

Table 3. SWSE Values Obtained during Calibration of First-Order Models F1–F3 as a Function of Tested \( k_{f,1} \) Values

<table>
<thead>
<tr>
<th>First-order models</th>
<th>( k_{f,1} ) (d(^{-1}))</th>
<th>SWSE (10(^{-5}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>F1</td>
<td>( 3 \times 10^{-3} )</td>
<td>5.56</td>
</tr>
<tr>
<td></td>
<td>( 4 \times 10^{-3} )</td>
<td>4.41</td>
</tr>
<tr>
<td></td>
<td>( 4.5 \times 10^{-3} )</td>
<td>4.09</td>
</tr>
<tr>
<td></td>
<td>( 5 \times 10^{-3} )</td>
<td>3.92</td>
</tr>
<tr>
<td></td>
<td>( 6 \times 10^{-3} )</td>
<td>3.94</td>
</tr>
<tr>
<td></td>
<td>( 7 \times 10^{-3} )</td>
<td>4.36</td>
</tr>
<tr>
<td>F2 ( (k_{f,2} = 0.1 ) ( k_{f,1} ))</td>
<td>( 3 \times 10^{-3} )</td>
<td>4.13</td>
</tr>
<tr>
<td></td>
<td>( 4 \times 10^{-3} )</td>
<td>3.14</td>
</tr>
<tr>
<td></td>
<td>( 4.5 \times 10^{-3} )</td>
<td>2.99</td>
</tr>
<tr>
<td></td>
<td>( 5 \times 10^{-3} )</td>
<td>3.03</td>
</tr>
<tr>
<td></td>
<td>( 6 \times 10^{-3} )</td>
<td>3.63</td>
</tr>
<tr>
<td></td>
<td>( 7 \times 10^{-3} )</td>
<td>4.78</td>
</tr>
<tr>
<td>F3 ( (k_{f,2} = 0.1 ) ( k_{f,1} )) ( (k_{f,3} = 10 ) ( k_{f,1} ))</td>
<td>( 1 \times 10^{-3} )</td>
<td>6.51</td>
</tr>
<tr>
<td></td>
<td>( 2 \times 10^{-3} )</td>
<td>4.90</td>
</tr>
<tr>
<td></td>
<td>( 2.5 \times 10^{-3} )</td>
<td>4.96</td>
</tr>
<tr>
<td></td>
<td>( 3 \times 10^{-3} )</td>
<td>5.32</td>
</tr>
<tr>
<td></td>
<td>( 4 \times 10^{-3} )</td>
<td>6.61</td>
</tr>
<tr>
<td></td>
<td>( 5 \times 10^{-3} )</td>
<td>8.33</td>
</tr>
</tbody>
</table>

Note: \( k_{f,i} \) = first-order decomposition rate coefficient for substrate i and \( w_i = 0.0016 \) (mg/L)\(^{-2}\) [Eq. (9)].
The different models proposed for this study include first-order (F1–F3) and Contois (C1–C3) models (Table 2). For each model, a minimum value of SWSE was obtained after testing the model against the experimental data for different values of model parameters, i.e., $k_f$ for first-order models and $k_c$ and $K_A$ for Contois models. The results for SWSE are shown in Tables 3 and 4 for first-order and Contois models, respectively, with calibrated models having SWSE values ranging from ~3 to $5 \times 10^{-5}$ for first-order models and from ~1 to $5 \times 10^{-5}$ for Contois models.

Contois models were observed, in general, to adhere more closely to the experimental data points than first-order models as denoted by the resulting lower SWSE values. Eq. (9) includes $(n-k)$ in the denominator accounting for the difference in number of model parameters between the models. As shown in Table 5, AIC$_C$, AIC$_C$ = Akaike information criterion value; $\Delta_i$ = delta AIC$_C$ value for model $i$; $w_{AIC}$ = Akaike weight of evidence for model $i$; $w_{AIC,C}/w_{AIC}$ = weight of evidence ratios relative to Model C2; number of observations in NTA-1 data set, $n=13$.

Effect of Type of Kinetic Model

The different models proposed for this study include first-order (F1–F3) and Contois (C1–C3) models (Table 2). For each model, a minimum value of SWSE was obtained after testing the model against the experimental data for different values of model parameters, i.e., $k_f$ for first-order models and $k_c$ and $K_A$ for Contois models. The results for SWSE are shown in Tables 3 and 4 for first-order and Contois models, respectively, with calibrated models having SWSE values ranging from ~3 to $5 \times 10^{-5}$ for first-order models and from ~1 to $5 \times 10^{-5}$ for Contois models.

Contois models were observed, in general, to adhere more closely to the experimental data points than first-order models as denoted by the resulting lower SWSE values. Eq. (9) includes $(n-k)$ in the denominator accounting for the difference in number of model parameters between the models. As shown in Table 5, AIC$_C$, $\Delta_i$ = Akaike weight of evidence [Eqs. (10), (12), and (13)], and evidence ratios were calculated for each of the calibrated proposed models. The results indicated that the proposed C2 and C1 model hypotheses were supported to a greater extent by the data, since for these models the lowest AIC$_C$ values of 25.3 and 26.5 were obtained. For first-order models F1–F3, the AIC$_C$ values ranged from ~35 to 40.

Effect of Number of Pools of Decomposable Materials

As previously described, models with a single pool of decomposable materials were designed to contain the equivalent of a 20-g/L initial concentration of decomposable polysaccharides in only corn stover. Dual-substrate models included an initial 20 and 40 g/L of decomposable polysaccharides in the corn stover and fragmented walnut shells. The triple-pool models included a third pool of a more easily degradable, nearly soluble saccharide at an initial concentration of 4 g/L (Table 2). During model calibration, within each group of proposed models (first-order versus Contois), the lowest values of SWSE were obtained when calibrating the dual-substrate Models F2 and C2, with calibrated dual-substrate models having SWSE values of $2.99 \times 10^{-5}$ for Model F2 and $1.15 \times 10^{-5}$ for Model C2. In addition, the value of SWSE for the single-substrate Model C1 was $1.29 \times 10^{-5}$.

Also, within each group of models (first-order versus Contois), the lowest values of AIC$_C$ were obtained for dual-substrate models (F2 and C2). Although Model F2 was the best of the first-order models considered in this study, Models C2 and C1 were superior to Model F2 by a considerable amount, as denoted by Model F2 having a $\Delta_i$ value of 9.5 (with respect to the best model in the set, i.e., Model C2) compared to the value of 1.2 for Model C1. As discussed in Poeter and Anderson (2005), relative to the best model in the set, models with $\Delta_i<2$ are very good models, whereas models with $4<\Delta_i<7$ have less empirical support. In most cases, models with $\Delta_i>\sim 10$ can be dismissed from further consideration.
Effect of Initial Biomass of Decomposer Bacteria

Additional simulations performed using the C2 Contois model as shown in Table 2, but with different values for the initial biomass population of decomposer bacteria assumed for simulation, were performed and SWSE values were obtained. As shown in Table 2, the initial value for \([X_d]/[CE]\) of 0.005 was considered in this study, as previously tested by Hemsi et al. (2005). The effect of the initial biomass of decomposer bacteria was evaluated by performing simulations with values for \([X_d]/[CE]\) that differed from the previous value by a factor of 10 i.e., 0.0005 and 0.05. For the assumptions considered in the Contois models shown in Table 2, the lowest values of SWSE were obtained for the initial value for \([X_d]/[CE]\) of 0.005.

Simulated trends for effluent concentrations of \(\text{SO}_4^{2-}\) and rates of sulfate uptake, and total remaining equivalent concentration of solid substrates, versus time are compared to the measured experimental data in Figs. 4(a–c). Three models are shown in these figures, i.e., Models F2, C1, and C2, whereas Models C1 and C2 were the best of the proposed models, as shown in Table 5.

In Fig. 4(a), the simulated results for Model F2 differ from the results obtained with Contois Models C1 and C2 in that Model F2 displays the lowest early-time effluent \(\text{SO}_4^{2-}\) concentrations. As shown in Fig. 4(b), the time rate of sulfate reduction with Model F2 is a maximum at the beginning of the simulation and declines monotonically with time as the solid substrate is consumed, as previously observed for simulation of sulfate reduction in solid-substrate batch tests (Hemsi et al. 2005). Comparing effluent \(\text{SO}_4^{2-}\) modeled by C1 and C2, Model C2 presents higher rates of sulfate reduction than Model C1 due possibly to some combination of the effects of having higher \(k_c\) for the corn stover i.e., 0.4 d\(^{-1}\) versus 0.3 d\(^{-1}\) in Model C1 and containing the walnut substrate. The ability to explain the results in terms of \(k_c\) values is somewhat complicated by the differences in \(K_A\) in these models (15 g/g versus 7.5 g/g). However, for times >105 d, the rate of sulfate reduction predicted by Model C1 surpasses that of Model C2, despite the effect of the presence of walnut shells. This observation suggests that, for the parameter tying assumptions considered, the most impacting substrate was corn stover. Simulated effluent concentrations for \(\text{Zn}^{2+}\) for the test duration of 130 d remained approximately zero for Models F2, C1, and C2, in agreement with the data shown in Fig. 2(c).

The experimental data provided for the comparison shown in Fig. 4(c) are based on the measured variation in the total dry mass of solid substrate per bioreactor (average) after 130 d of 5.0 g. As shown in Fig. 4(c), Models C1 and C2 resulted in good simulations of the measured mass variation in solid organic substrate, assuming that walnut shell mass variation was negligible. Decom-
Poser bacteria biomass versus time is shown in Fig. 4(d) for Model C2, i.e., for decomposers associated with corn-stover and walnut-shell substrates.

Model Testing

Models C2 and C1, which resulted in the lowest AIC<sub>c</sub> values in model ranking based on experimental data from NTA-1, were subsequently used in attempts to model the experimental results of an independent test, SCA biocolumn 1 (i.e., SCA-1). As shown in Fig. 5, model simulations of effluent SO<sub>4</sub><sup>2−</sup> concentrations versus time compare well to experimental data (i.e., measured effluent SO<sub>4</sub><sup>2−</sup> in SCA-1 versus time), for calibrated Models C2 and C1. The computed values of SWSE for these simulations with respect to the SCA-1 data (Fig. 5) are 2.1 x 10<sup>−5</sup> for Model C2 and 4.0 x 10<sup>−5</sup> for Model C1, assuming w<sub>j</sub> = 0.0016 (mg/L)<sup>−2</sup>, as assumed for the previous calibrations. Therefore, Model C2, which was the best model among the proposed models in this study for simulating NTA-1 data, also was the best model for simulating experimental data from the independent SCA-1 experiment. One factor to bear in mind in terms of the SCA-1 data is that the possible biological inhibition due to Zn<sup>2+</sup> was not considered in the models, but may have occurred in SCA-1 due to the reasons previously explained.

Model Prediction: Longevity of NTA-1

Assessments of longevity for biological passive treatment systems are widely recognized as a major issue related to design and operation. Modeling was applied in attempting to predict longer-term behavior (i.e., beyond the testing time of 130 d) for the NTA-1 biocolumn, considering the best calibrated models in this study, Models C2 and C1. The longer-term behavior of NTA-1 was modeled considering a total time of 730 d (2 yr).

As shown in Fig. 6(a), effluent SO<sub>4</sub><sup>2−</sup> concentrations were predicted to increase and approach influent concentrations after ~300 d of biocolumn operation for Model C1 and to remain slightly less than influent concentration (~850 mg/L) for Model C2. This time is interpreted, for both models, as being associated with the end of decomposition of degradable polysaccharides in corn stover as shown in Fig. 6(b). The models also predicted the remaining mass of degradable polysaccharides in corn stover to be depleted and the associated bacterial population (equivalent biomass concentration) to decline reaching zero at ~400 d. This predicted biocolumn longevity is a function of the small particle size of the corn stover and the limited amount of bioavailable substrate. Increased operational life in a field implementation will require the modification of the substrate mixture to include a larger fraction of bioavailable substrate and also should include larger particles to decrease the overall rate of organic substrate decomposition.

Conclusions

New reactive transport models for the bioremediation of mining influenced waters in solid-phase bioreactors were calibrated against experimental data, tested for an independent data set, and employed for predictions of biocolumn longevity beyond testing time. First-order (F) and Contois (C) kinetics for decomposition as well as different numbers of pools of decomposable materials were proposed in different models (F1–F3 and C1–C3). Calibrations were quantified by assessing calibration error SWSE on the basis of model predictions of biocolumn effluent concentrations for SO<sub>4</sub><sup>2−</sup> against data from Column NTA-1. Due to limitations in the calibration data set, the number of adjustable model parameters was limited using parameter tying. Calibrated models were ranked using the Akaike information criterion (AIC<sub>c</sub>). Models based on Contois kinetics with initial population of decomposer bacteria corresponding to [X<sub>v</sub>]/[CE]=0.005 and kinetic parameters for decomposition of corn stover k<sub>c</sub>=0.4 d<sup>−1</sup> and K<sub>A</sub>=15 g/g (Model C2, with tied parameters for walnut shells)
and $k_s = 0.3$ d$^{-1}$ and $K_s = 7.5$ g/g (Model C1) attained the lowest values of AIC$C_p$. Thus, Models C2 and C1 (i.e., based on Contois kinetics) emerged as the models that were supported to a greater extent by the data. As a result, model testing was performed for the independent SCA-1 biocolumn data considering only Models C2 and C1 and parameter values from calibration (NTA columns). Comparisons of the modeling and experimental results indicated good approximations of effluent sulfate, with overall discrepancy (SWSE) within the range of calibration errors obtained for the calibration data sets.

Finally, model prediction of biocolumn longevity was performed on the calibration data set (NTA-1). The predicted performance indicated that the experiment would have remained operative, i.e., before depleting the SR capacity, for an additional $\sim 200$ d after termination of the biocolumns in the laboratory. Future model validation using longer-term field data sets will be necessary to confirm model predictions.

Acknowledgments

This research was funded by the U.S. EPA Science to Achieve Results (STAR) Program under Grant No. R-82951501-0 as part of the U.S. EPA’s Rocky Mountain Regional Hazardous Substance Research Center. The writers are grateful to Dr. E. Poeter for assistance on the application of multimodel ranking.

References


