ABSTRACT

Reactive-transport processes in the Wightman Fork/Alamosa River system downstream of the Summitville Mine, south-central Colorado, were simulated under low-flow conditions using the OTIS and OTEQ solute transport modeling programs. Simulation results revealed that Ca, Cu, Mg, Mn, Na, Zn, Cl, F, and SO₄ are conservative in the stream reach, whereas pH, Fe, and Al are non-conservative. Simulations that allow precipitation of Fe(OH)₃ and Al(OH)₃ match observed water quality more closely than conservative simulations. The pH could not be adequately simulated without assuming that tributary inflows had pH values of about 8 or higher and alkalinities of 50-110 milligrams per liter (mg/L). Subsequent sampling confirmed these predictions.

INTRODUCTION

The Summitville Mine is located along the upper Alamosa River in south-central Colorado (fig. 1). Gold was first discovered at Summitville in 1870 (King, 1995). Until about 1985, gold was extracted from the deposit using conventional techniques of underground mining, including the sinking of shafts, removal of the ore, and transporting it to smelters where it was refined. More recently, highly disseminated gold was recovered by the cyanide heap-leach process. The process consists of placing relatively low-grade ore on a large pad and spraying a sodium cyanide solution over its top. The leachate solution is recovered from the bottom of the pad and transported to a central area where the gold is removed from the cyanide solution. An aerial photograph of the mine workings, demonstrating the extent of removal of the mountainside, is shown in figure 2.

Much of the residual rock contains sulfide minerals that oxidize rapidly to form sulfuric acid solution because they have been exposed to the atmosphere during mining. This solution contains elevated concentrations of Fe, Al, Cu, Zn, Cd, Mn, and other metals that can be toxic to plants and animals living downstream.

In December 1992, the Colorado Department of Public Health and Environment (CDPHE) requested assistance from the Environmental Protection Agency (EPA) and Superfund Emergency Response was authorized. The U.S. Geological Survey (USGS) began water-quality investigations at Summitville, Terrace...
Figure 2. Aerial photograph of the Summitville Mine workings, August, 1994 (from King, 1995).

Reservoir, and farther downstream in 1993 (fig. 1; King, 1995; Walton-Day and others, 1995; Balistrieri and others, 1996; Stogner and others, 1996). The USGS began routine water-quality monitoring in the upper Alamosa River (Alamosa River and tributaries above Terrace Reservoir) in 1995. The USGS began a reactive-transport modeling project in 1998 that includes preliminary modeling of 1997 data, tracer-injection studies, calibration of models, and simulations of reactive-transport under different remediation scenarios. The results of this investigation will be used by EPA and CDPHE to designate regulatory requirements and to achieve water-quality goals for the Alamosa River/Terrace Reservoir system. In mid-1998, CDPHE assumed management of the site, and began working with the USGS to characterize the upper Alamosa River system. The ultimate goal is to devise a long-term remediation strategy that will allow restoration of the Alamosa River and Wightman Fork to near pre-mining conditions. The purpose of this paper is to report on the preliminary modeling of the 1997 data.

One aspect of stream characterization is to describe the watershed in as much detail as possible. In the Alamosa River Basin, two synoptic studies, one at high flow and the other at low flow, will help quantify solute sources and sinks.

MODELING APPROACH

Conservative transport processes are modeled using the computer program OTIS (One-dimensional Transport with Inflow and Storage; Runkel, 1998). Reactive transport processes are modeled using program OTEQ (OTis with EQuilibrium calculations; Runkel and others, 1996a). OTIS models the conservative transport of solutes subject to the physical processes of advection, dispersion, transient storage, and lateral inflow. OTEQ combines the physical process description of OTIS with the chemical equilibrium capabilities of MINTEQ (Allison and others, 1991). This combination allows OTEQ to simulate pH-dependent processes such as precipitation and sorption in the context of physical transport.

Analytical results from low-flow synoptic samples collected on August 14, 1997 were selected for this study. For the preliminary modeling study, the study area was divided into 20 model reaches (fig. 3). The first reach begins at USGS sampling station 5.5 on Wightman Fork, just downstream of its confluence with Cropsy Creek (WF5.5). Cropsy Creek historically carried most of the discharge from the mine site and presently carries the effluent from the Summitville Mine treatment plant. The last reach ends about 300 meters above USGS sampling station 34.5 on the Alamosa River (AR34.5). For this simulation, the Alamosa River above its confluence with Wightman Fork (AR45.5) is considered a tributary, that is, its discharge and solute masses are represented as lateral inflow in reach 2. Other tributaries include Jasper Creek, Burnt Creek, Spring Creek, Fern Creek, Castleman Gulch, Silver Creek, Lieutenant Creek, and Ranger Creek (inflow to reaches 5, 7, 9, 11, 13, 15, 17, and 19, respectively).

Modeled Solutes

For the preliminary OTEQ calculations, only a subset of 7 components (SO$_4$-, total excess H (H$^+$), Al, Fe(II), Fe(III), Cu, and CO$_3$) is considered. This approach is consistent with previous OTEQ simulations in other mine drainage streams (Broshears and others, 1996; Runkel and others, 1996b). Future simulations based on the complete component set will be used to evaluate the correctness of this assumption.
Figure 3. Schematic diagram of model reaches for the transport simulations; circled numbers are stream reach numbers; note that the present simulation does not incorporate revised distances. For this simulation, the Alamosa River above its confluence with Wightman Fork (AR45.5) is considered a tributary.

Upstream Boundary Conditions

The effect of the choice of upstream boundary conditions on the model results is significant. Upstream boundary conditions were chosen using the three approaches described below.

The upstream boundary conditions for SO4, Al, and Cu were set to the analytically determined concentrations at WF5.5 (408, 29.8, and 3.7 mg/L, respectively).

Analytical results for the modeled reach did not include Fe redox species, but total dissolved Fe = 11.3 mg/L was determined. For these preliminary simulations, Fe(II) and Fe(III) were estimated by assuming that the concentration of Fe(III) was half the total dissolved Fe concentration. Since Fe oxidation was not modeled, this approach ignores consequent effects such as production of hydronium ions. This approach may require refining for future simulations.

Values for H^+ and total inorganic carbon (TIC) were obtained by separate simulation using the program MINTEQA2 (Allison and others, 1991). The pH was fixed at the value of 3.6 observed at WF5.5, and equilibration with atmospheric CO2 was allowed. The resulting H^+ = 3.68E-4 M and CO3^2- = 3.60E-5 M values computed by MINTEQA2 were used as input to OTEQ.

Streamflow Parameters

The effect of the choice of cross-sectional areas, lateral inflow rates, and lateral inflow concentrations on the model results is frequently significant. Thus, these parameters must be defined as accurately as possible.

Cross-Sectional Areas and Lateral Inflow Rates

Values for these two components were calculated using equations (1) and (2):

\[ v = \frac{d}{t}, \]  
\[ A = \frac{Q}{v}, \]

where

- \( v \) is stream velocity,
- \( d \) is distance,
- \( t \) is travel time,
- \( A \) is stream cross-sectional area, and
- \( Q \) is stream discharge.

Measured cross-sectional areas were not available. The available distances, travel times, and discharges were used to calculate velocities (eq. 1) and cross-sectional areas (eq. 2).

Values for lateral inflow rates were calculated by dividing the difference between discharges at the ends of a reach by the length of
the reach. Thus, the units of this parameter are cubic meters per second per meter.

**Lateral Inflow Concentrations**

Values for lateral inflow concentrations were calculated or estimated using data available at the time of the simulation. Total excess H and TIC were determined for all inflows by running MINTEQA2 simulations with pH fixed at observed values and with dissolved carbonate species at equilibrium with atmospheric CO₂.

Analytical results were available only for AR45.5 and Jasper Creek. For these two reaches (Reaches 2 and 5), Al, SO₄, and Cu concentrations were set to observed values. Iron redox species concentrations were set to observed Fe(II) and Fe(III) values for the upper Alamosa River. For Jasper Creek, all Fe was assumed to be present as Fe(II), since at pH 7.0 the concentration of dissolved Fe(III) would be too low to measure.

For the remaining tributaries, only pH and water temperature were available; thus, Al, SO₄, Fe(II), and Cu were set to the following background concentrations: 0.02, 10, 0.02, and 0.001 mg/L.

Stream discharge more than doubled along the initial reach from station WF5.5 to Wightman Fork above its confluence with the Alamosa River (WF0.0). However, no lateral inflow tributaries were monitored; thus, no flow or concentration parameters were available. Consequently, inflow Al, SO₄, Fe(II), and Cu concentrations were set to background as above. Total excess H and TIC were calculated using MINTEQA2 for Jasper Creek water chemistry and a pH fixed at 8, with inorganic carbonate species at equilibrium with atmospheric CO₂.

Of the 20 stream reaches considered, 10 were “base flow” reaches for which there existed no flow or chemistry information. For these 10 reaches, input parameters were estimated using a process analogous to that described above.

**Geochemical Parameters**

Temperature and ionic strength are spatially invariant within OTEQ. Therefore, since nearly all chemical reactions in the reach are nearly complete by the confluence of Wightman Fork and the Alamosa River, the temperature and ionic strength observed at stations WF0.0 and WF5.5 were used to set these two parameters to 8°C and 0.015 molal.

Defaults were retained for the solubility equilibrium constants for the precipitation reactions for Al(OH)₃ and Fe(OH)₃:

\[
\text{Al}^{3+} + 3\text{H}_2\text{O} = \text{Al(OH)}_3 + 3\text{H}^+, \quad (3)
\]

and

\[
\text{Fe}^{3+} + 3\text{H}_2\text{O} = \text{Fe(OH)}_3 + 3\text{H}^+. \quad (4)
\]

The respective default log \( K \) values of !8.77 and !4.891 for microcrystalline gibbsite and ferrihydrite solubility were used in the simulation. Uncertainties of other variables affecting Fe and Al removal from the water column were sufficiently large that sensitivity testing of variations in the log \( K \) values was not warranted at this time.

**RESULTS**

The OTIS simulations indicated that Fe and Al were reactive in reach 1, and that other solutes, including Ca, Cu, Mg, Mn, Na, Zn, Cl, F, and SO₄, exhibited conservative behavior.

For the reactive (OTEQ) simulations, emphasis was placed on the initial reach from WF5.5 to WF0.0. Conservative and reactive simulation results for pH, Fe, and Al are shown in figures 4-6. Figures 7 and 8 illustrate conservative simulations of SO₄ and Cu. The diamonds on the figures denote the mixture of WF0.0 and AR45.5 water, which was calculated using a discharge mass-balance relation for conservative mixing.

Using tributary inflows with pH values of about 8.2 and alkalinites derived using equilibrium with atmospheric CO₂, the reactive simulation of pH from Wightman Fork below its confluence with Crospy Creek to above its confluence with the Alamosa River predicts the downstream pH in Wightman Fork remarkably well (fig. 4). The conservative simulation predicts the pH at the confluence calculated using the discharge mass-balance relation for conservative mixing remarkably well, as expected. However,
the pH for the Alamosa River 23 km downstream

Figure 4. OTEQ simulation of pH assuming CO₂ at equilibrium with the atmosphere and ferrihydrite and gibbsite allowed to precipitate (low flow, 8/14/97).

Figure 5. OTEQ simulation of dissolved Fe assuming CO₂ at equilibrium with the atmosphere and ferrihydrite and gibbsite allowed to precipitate (low flow, 8/14/97).

Figure 6. OTEQ simulation of dissolved Al assuming CO₂ at equilibrium with the atmosphere and ferrihydrite and gibbsite allowed to precipitate (low flow, 8/14/97).

Figure 7. Conservative simulation of dissolved SO₄ (low flow, 8/14/97).

measure and use actual Fe(II) and Fe(III) concentrations.

For the reactive Fe simulation (fig. 5), the Fe(III) concentration was set to one-half the total Fe concentration, based on the total dissolved Fe concentration measured at WF5.5. The fit of the reactive Fe simulation could be improved by increasing the proportion of Fe(III) slightly; however, a more effective approach might be to

For the reactive Al simulation (fig. 6), the model overpredicts Al precipitation in Wightman Fork. Use of an equilibrium constant for a more soluble phase such as amorphous Al(OH)₃ may allow for a more accurate fit to the observed data.

The model simulates the observed SO₄ concentrations in Wightman Fork well (fig. 7), but underpredicts them in the Alamosa River. This may be caused by use of inflow SO₄ concentration estimates that are smaller than the actual concentrations.
Although the model accurately simulates the Cu concentration calculated using the conservative mixing equation at the confluence of Wightman Fork and the Alamosa River, the model overpredicts the Cu concentration observed at WF0.0 (fig. 8), suggesting that chemistry of this constituent is nonconservative. For Cu, the overprediction is small; thus the loss can be attributed to coprecipitation with or adsorption by Fe and Al oxyhydroxides. A reactive simulation (not shown) that modeled sorption of Cu to freshly precipitated hydrous ferric oxide (HFO) did not predict removal of appreciable quantities of Cu. This is most likely because the observed pH at WF0.0 is 4.8, whereas most Cu sorption occurs at pH values greater than 5 (Dzombak and Morel, 1990).

One possible explanation for the reduced Cu concentration at WF0.0, as compared with the simulated concentration, is precipitation or sorption of Cu in microenvironments where the acidic Wightman Fork water mixes with high-pH, high-alkalinity tributary water. While the pH of Wightman Fork water is not significantly changed by the relatively small-volume inflows, the precipitation or sorption may well be irreversible. Such microenvironment heterogeneity cannot be modeled at the scale of the present simulation.

During simulation runs it was necessary to assume values for pH, alkalinity, and SO$_4$ of many tributaries. Simulation results indicated that higher pH values and higher alkalinity and SO$_4$ concentrations may be present. Many of the refined pH values and alkalinity concentrations were later confirmed in field samples, providing a compelling illustration of the power of the reactive transport modeling approach as a tool to guide field investigations. Tributary inflows to Wightman Fork and parts of the Alamosa River were found to have pH 8 and alkalinity 50-110 mg/L, as predicted.

Plans for future work include completion of preliminary modeling for a high-flow scenario, correcting modeled distances based on revised estimates, and adding data which have recently become available for several tributaries along both Wightman Fork and the Alamosa River. Each of these improvements could significantly enhance the accuracy, and hence usefulness, of data to be gathered from a synoptic study planned for the spring of 1999.

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