Geochemistry and Reactive Transport of Metal Contaminants in Ground Water, Pinal Creek Basin, Arizona

James G. Brown, Pierre D. Glynn, and R.L. Bassett

ABSTRACT

Activities related to more than a century of large-scale copper mining in the Pinal Creek Basin in central Arizona have contaminated the regional alluvial aquifer and perennial streamflow with acidity and metals. Water-chemistry and solid-phase analyses and computer-aided geochemical modeling were used to understand the evolution of the ground-water plume between 1984 and 1998. The ground-water plume consists of three hydrochemical zones: (1) an acidic zone, which contains large concentrations of metals and has a pH that ranges from 3.6 to about 5; (2) a transition zone where carbonate-mineral dissolution causes pH to increase to above 5, which results in the precipitation of iron hydroxide and the adsorption of trace metals such as nickel and zinc; and (3) a neutralized zone, which contains large concentrations of manganese, calcium, and sulfate, and has a pH of about 6 to 7. Inverse geochemical modeling using NET-PATH revealed that, in addition to calcite dissolution, silicate dissolution was required to account for the mass transfers of calcium and magnesium across the transition zone. Analysis of the measured changes in plume geochemistry was aided by PHREEQC reactive-transport modeling, which helped determine that oxidation-reduction reactions were significant in the acidic zone of the plume through the late 1980's. The local equilibrium assumption required by reactive-transport modeling probably was invalid for oxidation-reduction reactions that involved manganese and, to a lesser extent, neutralization reactions that involved calcite. Sensitivity analyses indicated that the rate of advance of the pH front was highly sensitive to the initial calcite concentration, and that ground water along a flow path near the base of the alluvium was in partial or indirect contact with the atmosphere, possibly through mixing with shallower water.

INTRODUCTION

Activities related to more than a century of large-scale copper mining in the Pinal Creek Basin in central Arizona (fig. 1) have contaminated the regional aquifer and perennial streamflow. Potential contaminant sources include mine tailings, unlined surface-water impoundments of mine-process water, heap-leach areas, and occasional spills of contaminated water into streambeds. Acidic ground-water contamination has a pH of about 3.6 to 5, and neutralized-contaminated water has a pH that ranges from about 6 in the aquifer to 8 in perennial streamflow. Contaminants that occur in large concentrations are iron (Fe), sulfate (SO_4), manganese (Mn), copper (Cu), cobalt (Co), nickel (Ni), zinc (Zn), and other metals. Investigations by the U.S. Geological Survey (USGS) at the site have been ongoing since 1984 and are a collabora-tive effort among USGS scientists and investigators at several universities.

The purpose of this paper is to give an overview of recent and ongoing ground-water investigations at the site with a focus on the results of inverse modeling and reactive-transport geochemical modeling that were used to help understand the important processes that control the movement and distribution of contaminants in ground water. Information gained from these investigations should provide insight into processes that occur at other sites similarly contaminated.

The regional aquifer includes two distinct lithologic units. The older of the two is semiconsolidated to consolidated basin fill that is Tertiary in age. The unit has a maximum thickness of more than 1,000 meters (m) and consists of conglomerates, sand, silt, and fine-grained lakebed sediments. Incised into the basin fill in the major drainages is an unconsolidated alluvium that is less
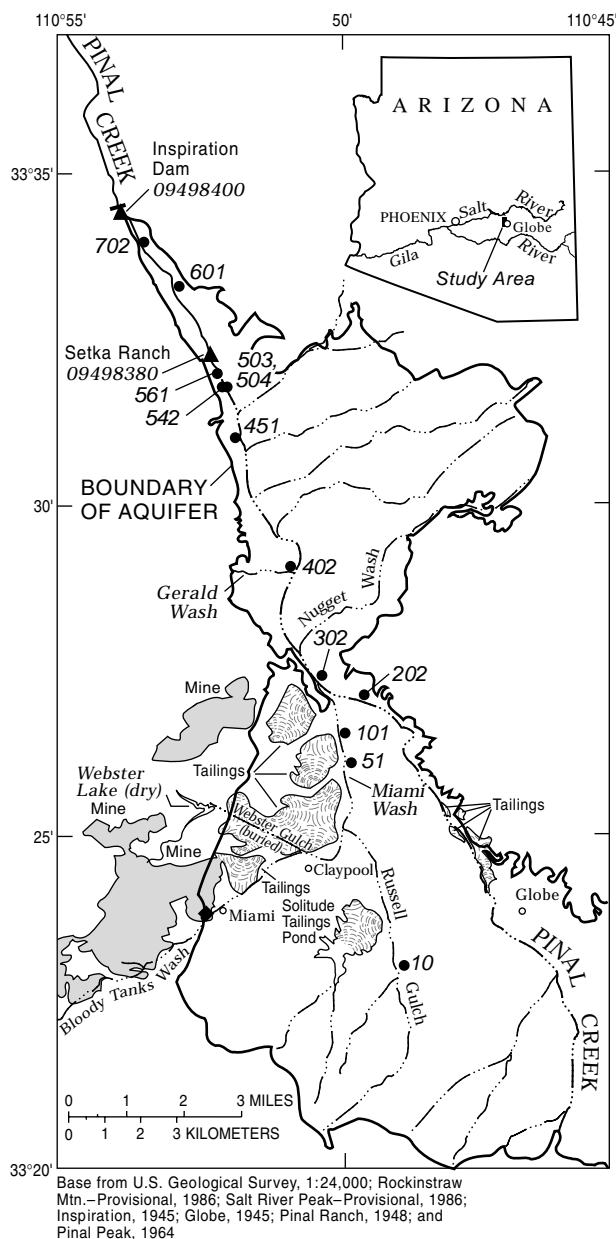
EXPLANATION

——·—·— INTERMITTENT STREAM

DATA SITES—Number
is site identifier

101 ●   Monitor well

09498380 ▲ Streamflow-gaging
station

Figure 1. Pinal Creek Basin, Arizona

than 50 m thick and contains more than 90 percent
sand and gravel. Detailed discussions of the geol-
ogy and hydrogeology of the basin have been pub-
lished in Peterson (1962), Brown and Eychaner
(1996), and Neaville and Brown (1994).

METHODS

From 1984 to 1996, 37 monitor wells and 6
test holes were drilled into the alluvium and shal-
low basin fill at 12 locations in or near contami-
nated areas. Aquifer materials collected at the time
of drilling were analyzed by particle-size analysis,
macroscopic- and microscopic-mineralogical iden-
tification (Eychaner and others, 1989), x-ray dif-
fraction (Lind and Stollenwerk, 1996), sequential
extractions (Ficklin and others, 1991a, b), column
and batch experiments (Stollenwerk, 1994, 1996),
and other methods. Water samples were collected
from most monitor wells one or two times a year
and analyzed for major ions and trace elements to
characterize the distribution and movement of con-
taminants. Less frequently, ground water from
selected wells was analyzed for stable isotopes, tri-
tium, chlorofluorocarbons, and dissolved gases.
Ongoing investigations include the examination of
changes in aquifer materials that have been
exposed to contaminated water in wells for periods
ranging from 6 to18 months. The purpose of these
investigations is to examine changes in mineralogy
and the rates of selected geochemical reactions in
acidic and neutralized ground water.

Several computer geochemical models have
been used in the analysis of contaminant move-
ment at the site. Stollenwerk (1994) used PHRE-
EQE (Parkhurst and others, 1980) and MINTQA2
(Allison and others, 1980) to analyze the important
reactions that controlled the evolution of the plume
through the mid-1980's using laboratory batch and
column experiments, and geochemical modeling.
Glynn and Brown (1996) used NETPATH (Plum-
mer and others, 1991) and PHREEQC (Parkhurst,
1995) to refine Stollenwerk's findings and examine
the possible effects of reactions not considered by
Stollenwerk. Brown and others (1998) used PHRE-
EQC's transport capabilities to help examine the
changes observed in the ground-water plume from
1984–94. This paper provides an overview of the
analysis of Glynn and Brown (1996), extends the
model of Brown and others (1998) through 1998,
and summarizes the major findings.

DISTRIBUTION OF HYDROCHEMICAL
ZONES IN THE AQUIFER

The ground-water plume in the Pinal Creek
Basin can be separated into three major zones

(fig. 2) on the basis of aqueous and solid-phase geochemistry. An acidic zone in which the pH of the ground water was between 4 and 5 in 1998 extends from Miami Wash to well 561.

The acidic zone contains large concentrations of dissolved metals and other contaminants. In 1984, concentrations of dissolved Fe, Mn, and aluminum (Al) at well 51 were 57, 1.3, and 11.1 mmol/L, respectively (table 1). Metals, such as Cu, Co, Ni, and Zn, occurred in the acidic zone at concentrations that ranged from 0.02 to more than 2 mmol/L.

Downgradient from the acidic zone is a transition zone characterized by steep pH and redox gradients and the precipitation and adsorption of metals. In 1984, this zone was about 1.5 km south of the future location of well 451. In this zone, calcite ($CaCO_3$) and, to a lesser extent, dolomite ($CaMg(CO_3)_2$), react with and partially neutralize acidic ground water according to the reactions:

$$CaCO_3 + H^+ = Ca^{2+} + HCO_3^-,$$
and
$$CaMg(CO_3)_2 + 2H^+ = Ca^{2+} + Mg^{2+} + 2HCO_3^-.$$
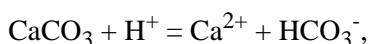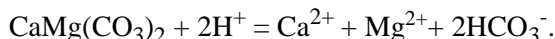
Oxidation and reduction reactions are important as well. The reductive dissolution of Mn oxide is coupled to the oxidation and precipitation of Fe hydroxide (Stollenwerk, 1994). The overall reaction can be written as:

$$MnO_{2(s)} + 2Fe^{2+} + 4H_2O \rightarrow 2Fe(OH)_{3(a)} + 2H^+ + Mn^{2+}.$$
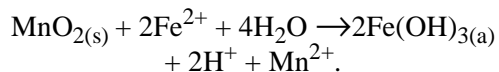
Although this last reaction produces protons, the net result of reactions in the transition zone was to raise the pH from about 5 to about 6.

Metals, such as Cu, Co, Ni, and Zn, are adsorbed to Fe hydroxide and possibly other surfaces in the transition zone because of the increase in pH (Stollenwerk, 1994).

Advective flow moves through the alluvium at an average velocity of 5 meters per day (m/d), which is about 7 times the rate of movement of the acidic front (Eychaner, 1991). As a result, contaminants that remain in solution as the pH increases move beyond the transition zone into the neutralized zone (fig. 2), and eventually surface in the perennial reach of Pinal Creek. Neutralized water generally contains large concentrations of calcium (Ca), Mn, and SO_4; other contaminants, including Fe, Cu, Co, Ni, and Zn, occur at concentrations less than 1 mmol/L (table 1).

Mineral species and other solid phases in the regional aquifer were characterized by the examination and analysis of drill cores and cuttings. Calcite and Mn oxide are present in uncontaminated alluvium, the basin fill, and the neutralized zone of the plume. Sequential extractions of aquifer material and the measured water chemistry indicate that in the acidic zone of the plume most if not all the Mn oxide and carbonate minerals have been dissolved by reaction with the acidic ground-water plume. Minerals present throughout the aquifer include Fe hydroxide and the silicate minerals orthoclase and plagioclase feldspar, muscovite, biotite, and tremolite. The degree to which each reacts with contaminated ground water varies.
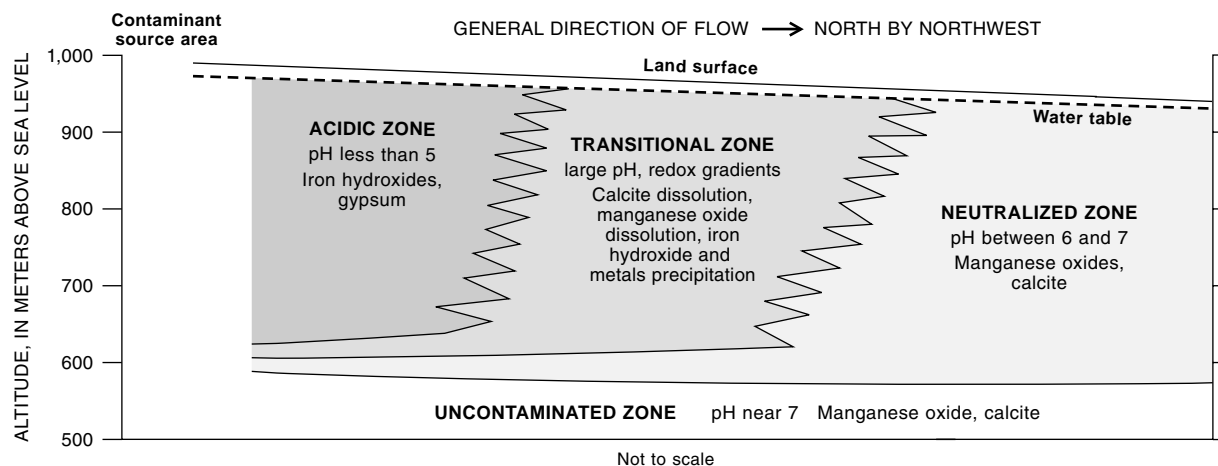

Figure 2. Generalized longitudinal section indicating hydrochemical zones in aquifer.

Table 1. Measured water chemistry and related data for water in selected wells and in streamflow, Pinal Creek Basin, 1984–97

[Values are in millimoles per liter (mmol/L) except for pH. At most locations, earliest available analysis is shown. Dashes indicate no data; km, kilometer; m, meter; <, less than; PCID, Pinal Creek at Inspiration Dam; Depth, depth of well below land surface]

Well number	Distance along flow path (km)	Date of sample	Well depth (m)	pH	Dissolved oxygen (DO as O)	Calcium (Ca)	Magnesium (Mg)	Sodium (Na)	Potassium (K)	Alkalinity	Total inorganic carbon (TIC)	Sulfate (SO_4)
51	0	11–84	33.4	3.6	<0.02	12	16	10	0.24	---	---	100
101	.7	11–84	36.1	3.6	<.02	12	12	8.3	.25	---	---	74
202[1]	---	03–85	12.3	7.2	.46	1.2	.37	.96	.036	2.3	---	.7
302	2.1	11–84	35.8	3.5	---	17	12	7.0	.21	---	---	72
402	5.8	11–84	20.9	4.2	<.02	13	5.8	3.5	.19	---	---	27
451	10.1	03–89	24.4	4.9	<.006	15	5.5	3.6	.28	---	4.7	25
503	11.4	07–86	25.3	6.2	.01	15	5.8	3.4	.11	2.0	---	21
542	11.4	05–97	19.8	4.3	.01	7.7	3.3	2.4	.16	---	1.3	14
561	11.8	05–97	15.3	5.0	.01	7.6	3.1	2.5	.17	---	1.7	13
601	14.2	11–92	8.6	6.4	.04	13	4.5	3.3	.11	2.9	---	18
702	16.3	05–90	7.3	7.0	.006	14	5.1	3.0	.16	3.5	---	18
PCID[1]	---	01–93	---	7.7	.64	1.4	.31	.33	.087	.93	---	1.5

Well number	Distance along flow path (km)	Chloride (Cl)	Fluoride (F)	Silica (Si)	Iron (Fe)	Manganese (Mn)	Aluminum (Al)	Copper (Cu)	Cobalt (Co)	Nickel (Ni)	Strontium (Sr)	Zinc (Zn)
51	0	11	---	1.7	57	1.3	11.1	2.4	0.18	0.065	0.017	0.29
101	.7	10	---	1.6	39	1.0	8.54	1.7	.14	.054	.018	.18
202[1]	---	.48	---	.36	.00072	<.0006	<.003	.00016	<.00034	<.0085	.0023	<.00023
302	2.1	8.7	---	1.8	32	1.1	6.69	1.5	.12	.051	.034	.14
402	5.8	4.0	---	1.4	6.3	.91	.409	.30	.030	.019	.020	.046
451	10.1	5.1	.53	1.1	2.5	1.9	1.53	.18	.031	.020	.018	.53
503	11.4	3.7	.021	1.0	.0032	.82	.0007	.0005	<.0007	.007	.240	.0029
542	11.4	1.3	.19	1.1	1.1	.81	.213	.075	---	.005	.013	.037
561	11.8	1.3	.25	1.1	.00016	1.0	.13	.076	.020	.012	.013	.039
601	14.2	2.4	.01	.72	.00072	.031	<.0004	<.0005	<.0002	<.0005	.024	.00038
702	16.3	2.3	.013	.46	.019	.052	.186	<.002	<.003	<.008	.027	.00026
PCID[1]	---	.11	.02	---	.0001	.00098	---	.00047	---	---	---	<.00005

[1]Not on simulated flow path.

INVERSE GEOCHEMICAL MODELING

Inverse geochemical modeling has been used at Pinal Creek to help identify and understand the important chemical reactions and physical processes that controlled the evolution of the contaminant plume. Glynn and Brown (1996) used the geochemical codes NETPATH and PHREEQC to examine some plausible reaction models that might have been responsible for the changes in ground-water chemistry that have been measured across the transition zone.

Inverse modeling uses a mass-balance approach to determine the reactions responsible for observed changes in water chemistry between two wells along a flow path. Inverse modeling requires that the system be in a chemically steady-state condition if the wells are sampled at the same time. Because contaminated ground water at the study site was not at steady state, Glynn and Brown (1998) considered the chemical changes between wells that occurred over a period of time equal to the estimated ground-water travel time between the two wells. The inverse-modeling approach also assumes that all potentially important reactions were considered and that the important existing and potential solid phases in the aquifer were known. The assumption of a steady-state flow field also is required. The computer codes do not require that the postulated reactions be thermodynamically feasible, although the thermodynamics of any postulated reaction should be considered when evaluating potential models.

Required input for inverse modeling includes chemical analyses for the selected wells, the chemical composition of solid phases (minerals or amorphous solids) and dissolved gases in the aquifer, and some knowledge about which minerals and gases have the potential to react with the ground water. NETPATH and PHREEQC allow for the initial water to be mixed with one or more waters along the flow path to produce the final water.

Glynn and Brown (1996) examined dozens of models using different combinations of plausible and not so plausible solid- and gas-phase reactants and different assumptions concerning the degree to which the flow path was in contact with gases in the unsaturated zone. Space limitations here preclude a detailed discussion of particular models. Instead, this paper focuses on the common characteristics shared by the more plausible models and will summarize major conclusions.

The analysis of Glynn and Brown (1996) considered a flow path across the transition zone from well 402 (sampled on January 12, 1989) to well 503 (sampled on November 22, 1991). Mixing with uncontaminated water along the flow path was represented by water from well 504 (sampled on November 22, 1991), which is perforated in uncontaminated basin fill. The chemical composition of water from these wells during 1989–91 was similar to that during 1984–89 (table 1); although contaminant concentrations generally decreased from 1984–89. Three minerals were required to be included in all models: calcite, geothite (FeOOH), and gypsum ($CaSO_4$).

For most models, the system was considered closed to atmospheric oxygen because the flow path across the transition zone was more than 7 m below the water table during 1989–91. Dissolved-oxygen concentrations of water from shallow wells at both sites indicated that essentially all the oxygen moving downward from the unsaturated zone into the plume was consumed near the water table. Although the well openings were not in contact with the unsaturated zone, the degassing of carbon dioxide (CO_2) was allowed in some models because CO_2 had the potential of leaving the flow path through diffusion or mixing processes.

The NETPATH models considered to be most plausible shared several characteristics—the dissolution of calcite and dolomite ($CaMg(CO_3)_2$), and the precipitation of rhodochrosite ($MnCO_3$) and gypsum. The results of the PHREEQC simulations were similar, except that accounting for analytical uncertainty (a feature unavailable in NETPATH) resulted in some significantly different results. When a 5-percent relative uncertainty was assumed for SO_4, the precipitation of gypsum was not necessary. This was because SO_4 occurred at concentrations more than 5 times that of Ca, and the uncertainties in the SO_4 concentrations were large in relation to the measured mass transfer of Ca between wells 402 and 503.

A significant conclusion from the NETPATH and PHREEQC inverse modeling was that in order to satisfy the mass-balance constraints on Ca and Mg, the dissolution of Ca-Mg silicates was required. The measured increase in dissolved strontium (Sr) along the flow path was additional

evidence of silicate dissolution along the flow path (Glynn, 1991). Solid-phase mass transfers of rhodochrosite and Al were significant particularly in models that allowed no CO_2 exsolution.

GROUND-WATER REACTIVE TRANSPORT, 1984–98

From 1984 to 1998, the concentrations of most contaminants in the acidic zone decreased primarily because of the drainage of an unlined surface-water impoundment that contained acidic mine-process water, other source control measures, remedial pumping that began in the mid-1980's, and recharge of uncontaminated ground water from record high streamflow in 1993. This paper focuses on the most contaminated well at each monitor well group. At each site, this generally was the well perforated closest to the contact with the alluvium and the underlying basin fill. The wells were located along, or reasonably close to, an assumed flow path near the base of the alluvium. Lithologic evidence of a boulder zone near the base of the alluvium was additional evidence that the zone near the base of the alluvium was a preferred pathway for contaminants.

A one-dimensional reactive-transport model was developed using PHREEQC (Parkhurst, 1995) to help characterize the reactions and processes that were responsible for the measured changes in plume geochemistry from 1984 to 1994 (Brown and others, 1998). Equilibrium reactive-transport modeling requires some of the same assumptions as inverse modeling. One such assumption was that the wells in the model were located along a flow path; another was that all important reactions were accounted for. Unlike inverse modeling, equilibrium reactive-transport modeling assumes that water along the flow path reacts to a local equilibrium with selected solid phases in the aquifer. As a result, some of the reactions considered for inverse modeling (silicate dissolution, for example) were not included in the reactive-transport model because these reactions were known to be slow in relation to the travel time of water through contaminated alluvium.

PHREEQC uses a mixing-cell approach (Appelo and Postma, 1993) to simulate contaminant transport. In this approach, a series of mixing cells is set up in which geochemical reactions are calculated. In this simulation, these reactions involve water, minerals, and surfaces to which selected constituents may adsorb or desorb. Before each transport step, the aqueous and solid-phase equilibrium condition is calculated. Water is then shifted to the next adjacent cell where equilibrium is then re-established through the precipitation or dissolution (if the solid phase is present) of the required solid phases. For this analysis, dispersion was simulated using the mixing option. A dispersivity of 30 m was used for this analysis on the basis of a review of field estimates of dispersivities made by Gelhar and others (1992). Glynn and Brown (1996) found that varying the dispersivity from 0 to 10 percent of the length of the flow path had little effect on movement of the acidic front except where the initial calcite concentration was <0.03 mol/kg H_2O. This concentration was less than half the initial calcite concentration used in the neutralized zone of the present model.

For this report, the reactive-transport model of Brown and others (1998) was extended to June 1998. Water from well 51, the monitor well closest to upgradient contaminant sources, was used as inflow to the model. The flow path from well 51 to well 702 (fig. 1) was divided into 82 cells, which were each 200 m long. The earliest available water-chemistry analysis for each well (table 1) along the flow path was used to define the initial conditions for the model. Simulated input for missing constituents were estimated from the earliest available analysis. For example, total inorganic carbon (TIC) was first measured in 1987 and was used to represent 1984 conditions in the model. Between wells, initial water chemistry in each cell consisted of water from a nearby well, or a mixture of water from the nearest upgradient and downgradient wells, as appropriate. The minerals included in the model (table 2) in each cell were determined on the basis of solid-phase analyses. Gypsum and Fe hydroxide were assumed to be initially present along the entire flow path. Adsorption along the flow path was assumed to occur on the Fe hydroxide that is present throughout the aquifer (Stollenwerk, 1994). Calcite was assumed to be initially present in the neutralized zone and absent in the acidic zone where calcite would have been substantially depleted or completely consumed by acidic ground water. Sequential extractions by Ficklin and others (1991a, b) indicated that extractable Mn was present at much lower concentrations

Table 2. Mineral reactions and solubility-product constants used in simulation of reactive transport

[*logKsp*, log of the solubility- product constant]

Mineral	Reaction	LogKsp
Calcite	$CaCO_{3(c)} = Ca^{2+} + CO_3{}^{2-}$	-8.48
Gypsum	$CaSO_{4(c)}*2H_2O = Ca^{2+} + SO_4{}^{2-} + 2H_2O$	-4.58
Iron hydroxide	$Fe(OH)_{3(a)} + 3H^+ = Fe^{3+} + 3H_2O$	4.89
Manganese oxide	$MnO_{2(c)} + 4H^+ + e^- = Mn^{2+} + 2H_2O$	41.38
Aluminum-mineral equilibria: $Al(OH)_{3(a)}$	$Al(OH)_{3(a)} + 3H^+ = Al^{3+} + 3H_2O$	10.8
$AlOHSO_4$	$AlOHSO_{4(s)} + H^+ = Al^{3+} + SO_4{}^{2-} + H_2O$	-3.23
Rhodochrosite	$MnCO_{3(c)} = Mn^{2+} + CO_3{}^{2-}$	-11.13

in the acidic zone than in the neutralized zone. Because of this, most if not all of the reactive Mn oxide in aquifer material was assumed to be reductively dissolved with the passage of the transition zone, and the simulated concentration of Mn oxide in the acidic zone was set to 0 in the model. Under these conditions, simulated Fe behaved as a conservative constituent in the acidic zone and reacted with Mn only in cells where Mn oxide was present.

Conservative Transport

Chloride (Cl) is a conservative constituent at Pinal Creek (Stollenwerk, 1994) and was used to measure the degree to which contaminated water was diluted by uncontaminated water along the flow path. Uncontaminated ground water from the underlying basin fill and tributary alluvium was represented in the model by water from well 202, which is in Pinal Creek alluvium about 1 km upstream from the mouth of Miami Wash. Dilution from flood-related recharge was represented in the model by a sample of water from Pinal Creek at Inspiration Dam obtained during a flood in January 1993. Both sources of uncontaminated inflow were mixed with contaminated ground water in each cell in amounts necessary to match measured Cl concentrations in wells along the flow path.

In 1984, the Cl concentration of water decreased from 11.0 mmol/L at km 0 to 3.95 mmol/L at km 5.8 (fig. 3). From km 5.8 to the end of the flow path (km 16.3), Cl decreased only slightly to 2.34 mmol/L in 1990. Because of contaminant-source removal, remedial pumping, and significant ground-water recharge in the early 1990's, Cl concentrations decreased along the entire flow path from 1984 to 1998. By 1998, the trend observed in 1984 had disappeared, and Cl concentrations were about equal along the flow path. Distribution of Cl simulated with PHREEQC matched measured concentrations reasonably well using mixing fractions that ranged from 0.06 at the upstream end of the model to 0.01 at the downstream end. (Water resulting from a mixing fraction of 0.06 consisted of 94-percent contaminated water and 6-percent uncontaminated water.) For 1993, the fraction of water mixed with contaminated water in each cell was increased slightly from km 3 to 11.4 to account for recharge of uncontaminated water from the 1993 flood.

Acidity and Related Equilibria

Unlike Cl, pH and other species, including Al, Ca, inorganic carbon, SO_4, Mn, and Fe, were affected by chemical reactions with solids in the aquifer or gases in the unsaturated zone. The pH along the flow path defined the acidic, transition, and neutralized zones in the aquifer. In 1984, the pH in the acidic zone was about 3.8, and by 1998, the pH had risen slightly to about 4 (fig. 4). Stollenwerk (1994) attributed the persistence of low pH in the aquifer to the gradual desorption of protons from Fe hydroxide surfaces in the aquifer. Several reactions acting in combination controlled the pH in the plume. The dissolution of calcite and mixing of contaminated ground water with uncontaminated ground water increased the pH. The
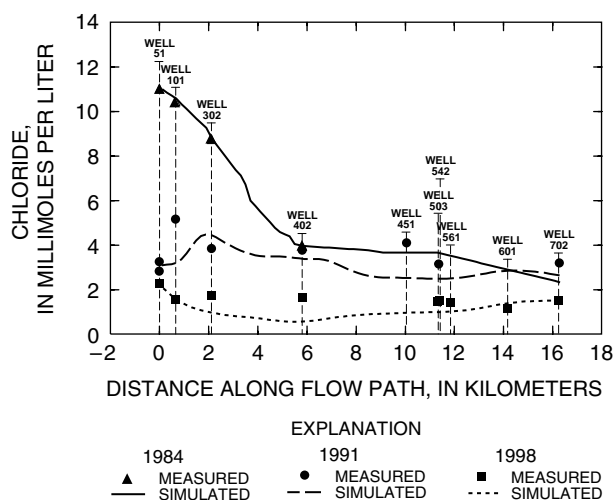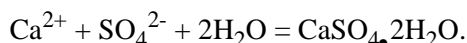
Figure 3. Measured and simulated concentrations of chloride along the flow path in the aquifer, 1984, 1991, and 1998, and locations of wells.

Figure 4. Measured and simulated ph along the flow path in the aquifer, 1984, 1991, and 1998.

reductive dissolution of Mn oxide and the consequent oxidation and precipitation of Fe hydroxide decreased the pH, as did the gradual desorption of protons from Fe hydroxide surfaces.

Concentrations of Ca in the aquifer were controlled by equilibrium with calcite and gypsum, and by mixing of contaminated ground water with uncontaminated ground water. Calculations using PHREEQC indicated that water in the acidic part of the flow path was slightly supersaturated or in equilibrium with gypsum from 1984 until 1991 and was increasingly undersaturated from 1992 to 1998 (fig. 5). Gypsum equilibria can be expressed by the following reaction:

$$Ca^{2+} + SO_4^{2-} + 2H_2O = CaSO_4 \cdot 2H_2O.$$

Although this reaction does not directly affect the pH, the increase in dissolved Ca that results from the redissolution of precipitated gypsum increases the calcite saturation index and indirectly plays a role in acidity equilibria.

Concentrations of Ca in water at km 0 decreased slightly from 12 mmol/L in 1984 to 11 mmol/L in 1992 and then decreased abruptly to 3.9 mmol/L in 1994 after the aquifer received recharge from flooding in 1993. Ca increased to 7.8 mmol/L by 1998 (fig. 6). During the same period, Cl decreased by a factor of 3.6, which indicates that dissolution of gypsum was responsible for the small decreases in measured Ca concentrations relative to Cl concentrations.

As previously mentioned, carbonate mineral dissolution in the transition zone increased the pH
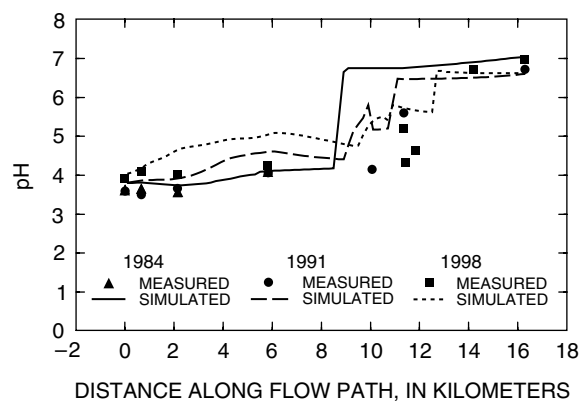
from about 4 to greater than 6. Calcite saturation indices were between –0.2 and –1.0 at km 14.2 in the neutralized zone (fig. 7), which indicated that calcite dissolution in the transition zone was not sufficient to bring partially neutralized water into equilibrium with calcite. Ground water was undersaturated with calcite at km 14.2, and equilibrium with calcite was established by km 16.3. The saturation indices indicate that calcite dissolution in the neutralized zone was responsible for the measured increase in Ca along the flow path from km 10 to km 16 through 1998.

From 1984 to 1998, simulated concentrations of Ca generally were larger than measured concentrations (fig. 6). The measured decreases in Ca from 1991 to 1998 were not reflected in the model, probably because simulated gypsum dissolution was greater than that in the aquifer. Beginning in 1991 (figs. 5 and 6), acidic water became undersaturated with respect to gypsum; however, the model maintained equilibrium through dissolu-
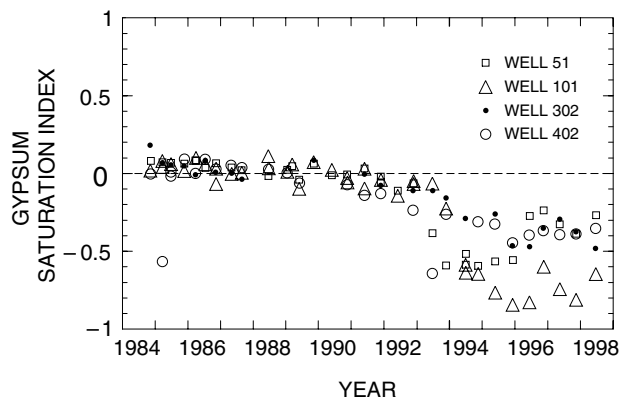

Figure 5. Saturation indices for gypsum in water from wells in the acidic part of the flow path, 1984–1998.

tion with gypsum. The simulated concentration of gypsum initially in the acidic part of the aquifer estimated from sequential extractions done by Ficklin (1991a, b) probably was unreasonably large.

Iron, Manganese, and Oxidation-Reduction Reactions

As previously mentioned, concentrations of Fe and Mn were controlled in part by oxidation-reduction reactions in the transition zone and mixing of contaminated ground water with uncontaminated ground water along the flow path. Mn also may sorb to Fe hydroxide surfaces under certain conditions. In 1984, concentrations of dissolved Fe decreased from 57 mmol/L at km 0 to less than 10 mmol/L at km 5.8 (fig. 8), which is a factor of about 6. Over the same interval, Cl decreased by a factor of 3 (fig. 3) and Mn decreased by less than half, from 1.3 mmol/L to 0.9 mmol/L (fig. 9). These differences suggest that oxidation-reduction reactions in part controlled the concentrations of Fe and Mn more than 2 km upgradient from the transition zone. In addition, the simulated and measured concentrations of dissolved Fe and Mn at km 6 differed significantly in the late 1980's. In 1987 at km 5.8, the simulated concentration of Fe was greater than the measured concentration, and the simulated concentration of Mn was less than the measured concentration. Because the initial modeled concentration of Mn oxide was 0 in the acidic zone, simulated Fe moved conservatively through the acidic zone to the transition zone where reaction with Mn oxides occurred. The differences between measured and simulated concentrations of Mn and Fe at km 5.8 provided additional evidence for the continued reductive dissolution of Mn oxides and oxidation and precipitation of Fe in the acidic zone.

In the transition zone, simulated Mn concentrations were unreasonably large (fig. 9) probably because the reductive dissolution of Mn is kinetically controlled. The simulated attainment of equilibrium with each transport step caused excessive Mn dissolution in the transition zone. Although Stollenwerk (1994) observed a peak of similar magnitude in a column experiment using acidic ground water and alluvium from the site, such a peak has not been observed in the field. The slight decrease in concentrations of dissolved Mn
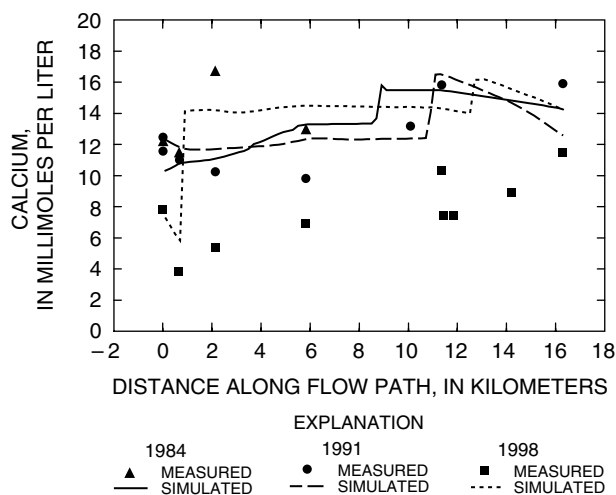

Figure 6. Measured and simulated concentrations of dissolved calcium along the flow path in the aquifer, 1984, 1991, and 1998.
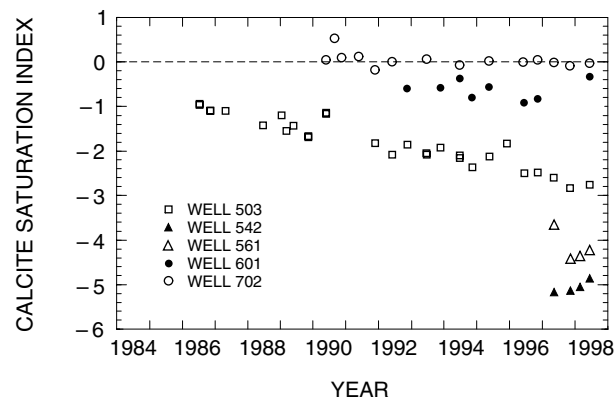

Figure 7. Saturation indices for calcite in the transition and neutralized zones of the plume, 1984–98.

between km 12.1 and km 16.2 was attributed to rhodochrosite precipitation on the basis of measured saturation indices near 0 at km 16.2 (Brown and others, 1998).

Aluminum Equilibria

Inverse modeling indicated that the measured attenuation of Al across the transition zone was in part controlled by mineral reactions. The determination of the solubility controls on dissolved Al over the range in pH measured in the plume, however, remains problematic. Stollenwerk (1994) used amorphous aluminum hydroxide ($Al(OH)_{3(a)}$; table 2) as the solubility control above a pH of 4.5, and a mineral with the formula
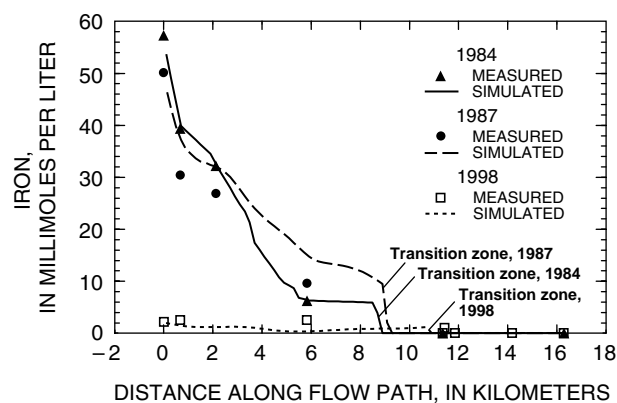
Figure 8. Measured and simulated concentrations of dissolved iron along the flow path in the aquifer, 1984, 1987, and 1998.

Figure 9. Measured and simulated concentrations of dissolved manganese along the flow path in the aquifer, 1984, 1991, and 1998.

AlQHSO$_4$ below a pH of 4.5, but changed the equilibrium constant by more than an order of magnitude to obtain a reasonable fit between his simulation and measured concentrations of dissolved Al.

Because the precipitation of each mineral releases protons to solution, Al mineral reactions could have a significant effect on pH in the plume. Because of the uncertainties related to the control on dissolved Al concentrations below a pH of 4.5, however, no controls were placed on Al solubility in the present simulation.

SENSITIVITY ANALYSES

As is the case with many field studies, the physical and chemical characteristics of the ground-water flow system in the Pinal Creek Basin were determined on the basis of sparse or incomplete data. Similarly, the reactions that control the movement and transformation of the plume have not been determined with absolute certainty. Sensitivity analyses are useful, therefore, to examine the effects of uncertainty on reactive transport in the plume. Uncertainties considered below are the calcite content, the nature of reactions with gases in the unsaturated zone, and Al-mineral equilibria. Not discussed here because of space limitations are the uncertainties in initial solid-phase concentrations, other than calcite, and slow reactions that may nonetheless be significant.
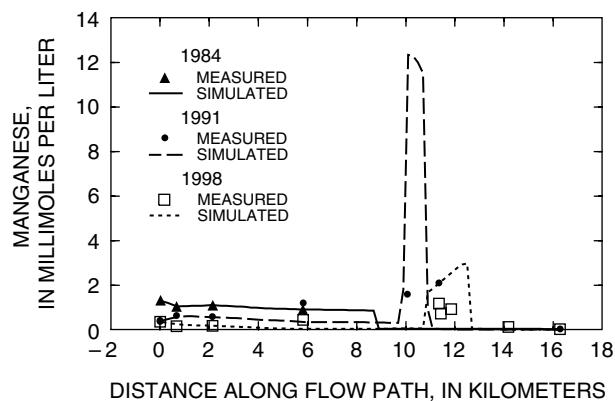
Calcite Content

The calcite content of 0.075 mol/kg H$_2$O used to simulate transport from 1984 to 1998 was estimated on the basis of a mass balance of Ca done on Stollenwerk's (1994) column experiment. At this concentration, the movement of the simulated pH front had a retardation factor of 7. A calcite concentration of 0.038 mmol/kg H$_2$O was used as the lower limit in this sensitivity analysis. Other measurements have yielded larger concentrations. Stollenwerk (1994) measured 0.17 mol/kg H$_2$O of calcite in the uncontaminated alluvium used in his experiment. Buffer-capacity measurements done by Hydro Geo Chem, Inc. (1989) yielded carbonate content estimates that ranged from 0.125 mol/kg H$_2$O in sand and gravel to 0.76 mol/kg H$_2$O in calcareous clay. Adjusting these values for the average particle size of sediments at monitor well group 500 yielded a value of 0.29 mol/kg H$_2$O, which was used as the upper limit in this sensitivity analysis.

Increasing the calcite content in the neutralized zone from 0.075 to 0.29 mol/kg H$_2$O reduced the rate of movement of the acidic front from by a factor of 9 (fig. 10). Decreasing the calcite content to 0.038 mol/kg H$_2$O increased the rate of movement by a factor of 1.7 and created a zone from km 11 to km 12 where Mn oxide dissolution occurred in the absence of calcite dissolution. Such a zone (and pH's associated with those conditions) has not been observed in the field. Glynn and Brown (1996) noted a similar zone when the initial

carbonate-mineral to Mn oxide ratio was greater than 3:2.

Carbon Dioxide Exchange

The simulation of the plume at Pinal Creek was made with the assumption that the plume was closed to the in-gassing of oxygen from the unsaturated zone and the out-gassing of CO_2 to the unsaturated zone. Field values of dissolved oxygen suggest that the system is closed, but the extent to which CO_2 does or does not decrease along the flow path through mixing or diffusion cannot be known with complete certainty. Opening the system to CO_2 at a constant pCO_2 of $10^{-1.33}$ atmospheres (calculated from measured concentrations of total inorganic carbon, TIC) decreased by less than 0.25 km the distance traveled by the pH front from 1984 to 1998. For both simulations, the 1993 decrease in simulated TIC marked the point at which carbonate dissolution was complete upgradient from km 11.4). The simulations indicate that when carbonate dissolution is ongoing, keeping the system closed allowed for unreasonable buildup of TIC in the neutralized zone (fig. 11). After all the simulated calcite had dissolved, the closed system simulated that the TIC concentrations were in good agreement. These results indicate that the water along the flow path was in partial or indirect contact with the atmosphere possibly through mixing with shallower water that is in direct contact with the unsaturated zone. More realistic simulation of this (and other gas-exchange processes) will require the use of a two-dimensional model.
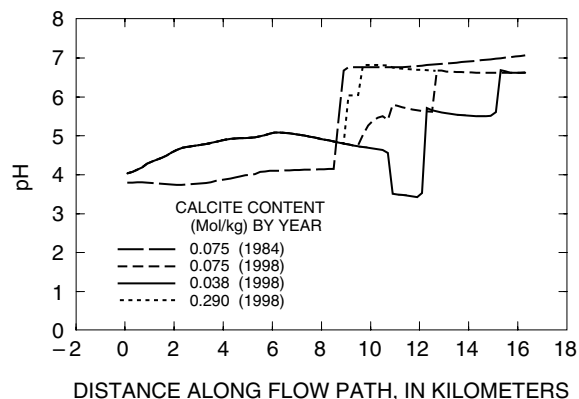
Aluminum Equilibria

Because of the uncertainty regarding the solid-phase controls on Al solubility, no controls were placed on dissolved Al in the model. The effects of Al solid phases on the movement of the pH front were explored by a sensitivity analysis that allowed for the control of dissolved Al concentrations by $Al(OH)_{3(a)}$ and $AlOHSO_4$. Initial concentrations of these minerals were set to 0. By allowing for the precipitation and redissolution of these minerals, the simulated pH from km 0 to km 10 was as much as one unit less in 1998. Between km 9 and km 10, the pH decreased by as much as one unit. These changes had little effect on the rate of movement of the simulated acidic front of the plume. Glynn and Brown (1996) simulated flow between wells 402 and 503 and found that allowing $AlOHSO_4$ to precipitate rather than $Al(OH)_{3(a)}$ increased the retardation factors of the rhodochrosite and Al solid-phase dissolution fronts, which are associated with the breakthrough of the low pH front.

CONCLUSIONS

From 1984 to 1998, concentrations of contaminants in the alluvial aquifer in Pinal Creek Basin, Arizona, decreased as a result of mixing, recharge, source removal, remedial pumping, and chemical reactions. Inverse and reactive-transport geochemical modeling were used to help understand the important reactions and processes that controlled the measured changes in chemistry. The major conclusions of this analysis are as follows.
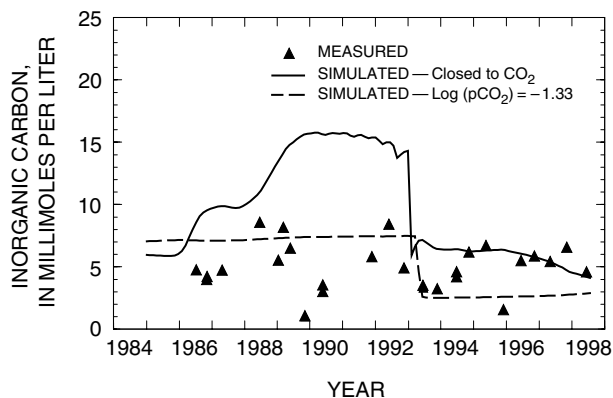

Figure 10. Simulated pH for selected concentrations of calcite in aquifer material, 1984 and 1998.

Figure 11. Measured and simulated concentrations of total inorganic carbon in water at km 11.4, 1984–98.

NETPATH and PHREEQC inverse modeling indicated that in order to satisfy the mass-balance constraints on Ca and Mg, the dissolution of Ca-Mg silicates were required. Rhodochrosite and Al solid-phase mass transfers were significant, particularly in models that allowed no CO_2 exsolution.

Simulated and measured concentrations of Fe, Mn, and Ca differed mainly because water along the flow path appeared not to be in a state of local equilibrium. The lack of equilibrium is related at least in part to slow reaction kinetics, but an apparent lack of equilibrium also could result from diffusion processes that limit the interaction of solid-phase surfaces with solutes in the aquifer. Distinguishing reaction kinetics from diffusion limitations in the subsurface is difficult if not impossible at the present time.

Because of the apparent lack of equilibrium, the primary usefulness of the model was as a means of comparing the system at Pinal Creek with a system in local equilibrium. Although the equilibrium approach provided insight as to which processes at the site were kinetically controlled and which were not, future work will require a kinetic modeling approach to more thoroughly characterize selected reactions between the plume and aquifer materials and will require the use of a two- or three-dimensional reactive-transport model.

From 1984 to 1990, water along the flow path was supersaturated or in equilibrium with gypsum, and gypsum equilibria controlled dissolved concentrations of Ca and SO_4. Beginning in 1991, water in the acidic part of the plume became increasingly undersaturated with gypsum indicating that the gypsum available for dissolution in the aquifer became limited beginning in about 1991.

Rhodochrosite precipitation probably was responsible for the measured attenuation in dissolved Mn in the neutralized zone. For reactions involving gypsum and rhodochrosite, the assumption of a local geochemical equilibrium generally was valid.

For oxidation-reduction reactions, the local equilibrium assumption generally was not valid. Reaction kinetics appear to control the measured concentrations of dissolved Fe and Mn in the acidic and transition zones.

For reactions involving calcite, the local equilibrium assumption did not appear valid. Although dissolution of calcite in the transition zone was not sufficient to establish equilibrium, calcite undersaturation decreased along the flow path in the neutralized zone, and equilibrium was reached by the end of the flow path.

Sensitivity analysis indicated that the rate of advance of the pH front was highly sensitive to the initial calcite concentration. Increasing the calcite content from 0.075 to 0.29 mol/kg H_2O reduced the calculated rate of advance of the pH front by a factor of 9. Decreasing the calcite content to 0.038 mol/kg H_2O increased the rate of the pH front advance by a factor of 1.7.

Opening the system to CO_2 at a constant pCO_2 of $10^{-1.33}$ atmospheres produced a better agreement between measured and simulated concentrations of dissolved TIC when calcite dissolution was occurring. After simulated calcite was completely consumed, better agreement between measured and simulated concentrations of dissolved TIC was achieved when the exsolution of CO_2 was not allowed. The simulations indicate that when calcite dissolution is ongoing, keeping the system closed allowed for unreasonable buildup of dissolved carbon in the neutralized zone. After all the simulated calcite had dissolved, the simulated carbon concentrations in the closed system were in good agreement. Water along the flow path was in partial or indirect contact with the atmosphere possibly through mixing with shallower water that is in direct contact with the unsaturated zone. More realistic simulation of this (and other gas-exchange processes) will require the use of a two-dimensional model.

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