



A process model of natural attenuation in drainage from a historic mining district

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Abstract

A process model was used to better understand the controls on the chemical evolution of drainage in a historic mining district. At the Pecos Mine Operable Unit, New Mexico, drainage near the waste rock pile is acidic (pH varies from 3.0–5.0) and carries high concentrations of Zn, Al, Cu and Pb. As drainage flows toward the Pecos River, pH increases to greater than 7 and heavy metal content decreases. A process model of natural attenuation in this drainage shows the main controls on pH are reaction with a local bedrock that contains limestone, and concurrent mixing with tributary streams. Models that account for both calcite dissolution and mixing reproduce the observed decrease in aqueous metal concentrations with increasing pH. Contaminant concentrations attenuate primarily via two distinct pathways: Al, Cu, Fe and Pb precipitate directly from solution, whereas Zn, Mg, Mn and SO₄ concentrations decrease primarily through dilution. Additionally, Pb adsorbs to precipitating hydroxide surfaces. © 2000 Published by Elsevier Science Ltd. All rights reserved.

1. Introduction

Acid drainage from metal mining districts is a well-recognized source of environmental contamination (Förstner and Wittman, 1981; Kelly, 1988). Oxidation of metal sulfides in mines, mine dumps, and tailings impoundments produces acidic, metal-rich waters that can contaminate local surface water and groundwater. Acidic waters are toxic to fish, flora and aquatic insects. Heavy metals carried by mine drainage into the surrounding environment interfere with aquatic

ecosystems. In addition, acid drainage can threaten drinking water supplies and irrigation systems downstream from mining sites.

Many factors affect the chemistry of mine drainage. The initial chemistry depends on a variety of geological and geochemical controls, including the type and abundance of metal-bearing sulfides in ore and wall rock, kinetic rates of ore and wall rock dissolution, permeability of the ore deposit or mine tailings, and the ability of the host rock to buffer acidity (Plumlee et al., 1992; Strömberg and Banwart, 1994).

In some cases, particularly where host rock is capable of buffering drainage, metal content attenuates to background concentrations before drainage leaves the mine site. A primary control on the process of metal attenuation is acid neutralization. Neutralization can occur where the drainage encounters rock of high

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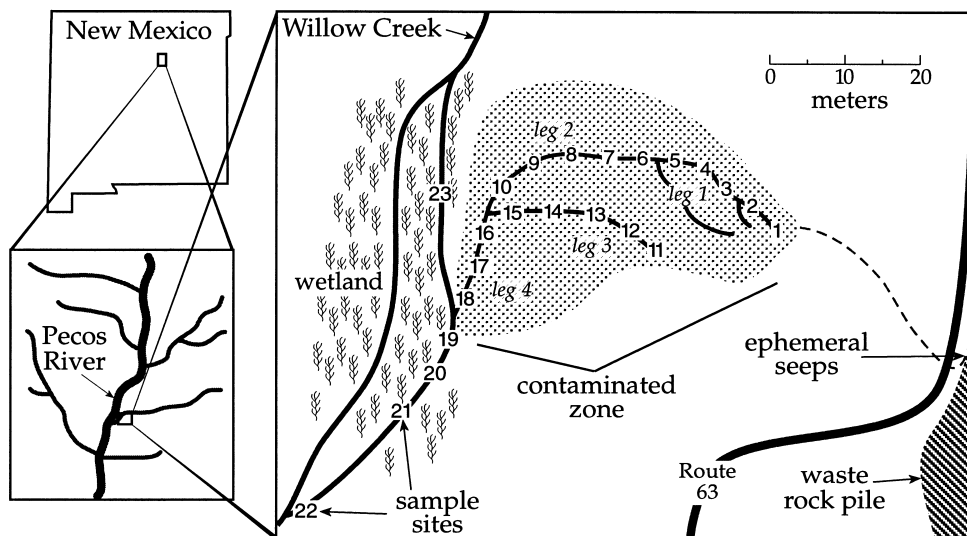


Fig. 1. Contaminated drainage at the Pecos Mine Operable Unit. Numbers indicate sample sites along the drainage pathway: sites 1–5 = leg 1, sites 6–10 = leg 2, sites 11–15 = leg 3, sites 16–22 = leg 4.

buffering capacity, when CO_2 degasses, and where drainage mixes with ambient waters (Chapman et al., 1983). As pH increases, aqueous metal species tend to precipitate as hydroxide, oxyhydroxide, or hydroxysulfate phases (Kimball et al., 1994). Metals may also adsorb onto surfaces of these newly formed precipitates, removing the metals from solution (Nordstrom, 1982; Chapman et al., 1983). As well, simple dilution can attenuate metal concentration, independent of chemical reaction.

To develop an effective remediation strategy, it is important to understand how these factors affect drainage chemistry. In this study, the authors present a quantitative model of the processes responsible for

acid neutralization and metal attenuation in mine drainage. The Pecos Mine Operable Unit provides a natural laboratory for studying drainage chemistry: the drainage is initially acidic and rich in metals, but over a short distance the drainage pH increases and metal concentrations approach levels observed in pristine areas.

2. Description of study area

The Pecos Mine Operable Unit, located in the southern Sangre de Cristo mountains in New Mexico (Fig. 1), produced Cu–Pb–Zn ore intermittently from

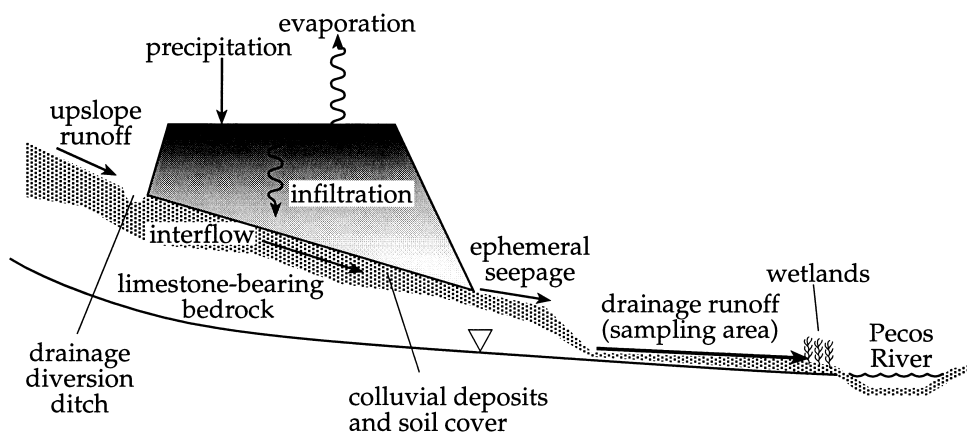


Fig. 2. Conceptual model of drainage through the waste rock pile and to the Pecos River (modified from Stoller, 1994). Triangle marks position of the water table. Figure not to scale.

1881 to 1939. Waste rock from mining operations was deposited in a pile on top of a preexisting drainage channel, and covers about 0.077 km². An aerial tramway carried ore to a nearby processing mill. Mill tailings were deposited at the processing site, which has undergone remediation by containment and burial (Stoller, 1994).

The waste rock pile was deposited on top of a section of a Pennsylvanian age sedimentary conglomeratic unit consisting of siliciclastic and limestone material (Stoller, 1993). Lithologically, the waste rock is dominated by quartz-chlorite and biotite schists (Stoller, 1993) typical of the subsurface metamorphosed shear zone that hosts the ore bodies (Krieger, 1932; Riesmeyer and Robertson, 1979). The waste rock pile contains about 2550 m³ of heterogeneous material (Stoller, 1994), with clasts ranging in size from fine sand to boulders.

Observation wells installed within the pile indicate it is largely unsaturated and that the water table lies below the base of the pile (Fig. 2). Flow through the dump is primarily vertical (Stoller, 1993). Within the

dump, atmospheric O₂ reacts in the presence of rain-water to dissolve metal sulfides, producing acid and adding heavy metals to solution. Ephemeral seeps drain the resulting acidic, metal-rich water from the base of the dump at several points. Continual contaminated flow emerges from seeps downslope from the dump, amid limestone cobbles and boulders from the underlying conglomerate.

Drainage from the seeps has killed about 500 m² of wetland flora. It flows toward the Pecos River in shallow channels (about 3–5 cm in depth) that overflow during rain events. A branch of Willow Creek, which drains regions north of the contaminated zone, joins the drainage after site 18 (Fig. 1). The mixed drainage then flows into the Pecos River about 80 km south of the river's headwaters. The river is a significant water source for eastern New Mexico, a predominantly agricultural area. As part of the Pecos State Forest, portions of the river downstream of the mine are used for recreational fishing, and a fish hatchery is located 23 km south of the Pecos Mine Operable Unit.

Contaminated drainage comes into direct contact

Table 1

Aqueous concentrations (mg/l) of filtered samples from the Pecos Mine Operable Unit drainage. Distance is measured upstream from site 22. Figure 1 shows sample locations

	Sample number	Distance (m)	pH	O ₂ (aq)	Zn	SO ₄	Mg	Ca	Al	Cl	Cu	Mn	Total Fe	Fe ⁺⁺	Fe ⁺⁺⁺	Pb
Leg 1	1	77.7	4.1	10	2211	8120	538	441	105.80	68.4	22.41	14.79	0.82	0.00	0.82	0.41
	2	74.7	4.7		1048	4250	281	356	20.45	58.8	10.65	10.40	0.87	0.61	0.26	0.21
	3	71.6	4.8		897	4240	296	267	16.56	52.5	10.88	3.86	2.00	1.14	0.86	0.24
	4	68.6	5.3		568	2110	138	151	4.59	33.6	5.28	6.87	1.46	1.28	0.18	0.06
	5	65.5	5.5	5	681	2480	185	270	1.02	37.3	1.44	6.90	1.17	0.84	0.33	0.01
Leg 2	6	62.5	4.7		568	5110	138	151	4.59	53.7	5.28	6.87	1.46	0.43	1.03	0.06
	7	59.4	4.7		1435	5210	363	382	48.55	54.1	13.75	11.54	1.05	0.39	0.66	0.34
	8	56.4	4.7		1210	4550	322	354	36.73	49.8	11.13	11.19	0.93	0.47	0.46	0.40
	9	53.3	4.7		1239	4540	318	355	33.78	49.7	10.66	11.39	0.91	0.41	0.50	0.38
	10	50.3	4.7		1269	4750	318	355	33.78	50.7	10.66	11.39	0.91	0.42	0.49	0.38
Leg 3	11	70.1	4.2	10	1752	6260	448	509	93.79	53.70	18.83	16.17	1.35	0.02	1.34	0.20
	12	65.5	4.5		1232	4320	308	388	44.64	42.00	13.01	12.58	1.94	0.87	1.07	0.10
	13	61.0	5.8		476	2120	117	298	0.1	21.70	0.23	7.43	0.23	0.13	0.10	0.00
	14	57.9	5.6		411	1990	169	296	1.54	21.10	1.73	7.37	2.63	2.47	0.16	0.05
	15	53.3	5.3		581		195	313	4.85		4.45	7.89	2.30	2.37	0.00	0.18
Leg 4	16	47.2	4.5	6	1138	4280	283	363	33.35	42.70	10.67	10.75	2.24	1.32	0.92	0.49
	17	44.2	4.8		929	3510	254	322	18.00	36.40	9.52	9.36	3.13	2.27	0.86	0.44
	18	41.1	4.9		893	3380	252	314	16.00	35.80	9.98	9.32	3.05	2.33	0.72	0.46
	19	37.5	5.8	6	448	2140	141	224	1.49	23.80	3.06	4.99	3.68	3.66	0.02	0.03
	20	35.1	5.9		516	2020	141	238	1.48	23.70	2.94	5.22	2.85	2.75	0.10	0.05
	21	30.5	6.0		447	1710	129	221	0.74	20.90	1.98	4.79	1.95	1.60	0.35	0.02
	22	0.0	7.2		135	603	59	127	0.13	9.20	0.39	1.74	0.04	0.00	0.04	0.01
Willow Creek	23	55.5	7.2	3	3	119	26	41	0.00	9.30	0.01	4.00	7.68	6.82	1.86	0.00

with limestone in the underlying formation in the vicinity of the seeps. The limestone shows evidence of dissolution: it is cracked and discolored compared to limestone unaffected by the drainage. A soil layer increasingly covers the limestone with increasing distance from the seeps.

Water from unmined areas flows down gradient (south) over and through saturated soils, mixing with drainage water at sites 3–10 and 13–18 (Fig. 1). Near the seeps, a red precipitate coats the drainage channels. A white to blue gelatinous precipitate forms as the drainage flows away from the seeps, immediately downstream from the red precipitate. This white precipitate is particularly abundant at sites where the drainage appears to either mix with background water or react with limestone. Limestone is well exposed near the seeps. In these areas, drainage appears to mix concurrently with background waters and react with the underlying bedrock.

3. Methodology

Surface drainage was sampled from the seeps to beyond the confluence of the mine drainage with Willow Creek in August, 1996 (Fig. 1). Groups of samples were taken from sites spaced 3–4 m apart. At each site, temperature and pH were recorded and samples were stored in acid washed 60 ml HDPE bottles. The first 3 samples were filtered using a pre-rinsed Nalgene filter holder with a receiver connected to a hand vacuum pump, mounted with a 0.1 μm Gelman filter. One sample, intended for major cation analysis, was acidified with HNO_3 to a pH of <1.5. The second sample was acidified with HCl to allow the distribution of Fe between Fe(II) and Fe(III) species to be determined. The third filtered sample was left unacidified for anion analysis. Filters from these 3 samples were saved for X-ray diffraction analysis of the solid material. Samples were placed on ice for transport to the laboratory and refrigerated until analyzed. In addition, dissolved O_2 content was measured at several sites using a CHEMmets[®] kit.

Concentrations of major cations, anions, and Fe redox distribution were determined in the lab 3 weeks after sampling. Cation concentrations were determined by inductively coupled plasma spectrometry. Anion contents were analyzed by ion chromatography. Iron(II) concentrations were determined colorimetrically by UV-spectrophotometry using ferrozine as the coloring agent, and Fe(III) concentrations were calculated by difference. Table 1 shows the results. Several samples from the filters were ground using agate pellets for bulk analyses by X-ray diffraction.

4. Analytical results

Results of the analyses (Table 1) show that pH increases along the various legs of the drainage. The metal content of the drainage decreases as the pH increases. At the seep sources, concentrations greatly exceed suggested maximum contamination levels (MCL values; Table 2). Within 80 m of the seep source concentrations have attenuated to levels approaching those found in Willow Creek upstream of the drainage.

To determine the significance of mixing with background water, species concentrations are plotted in Fig. 3 against SO_4 , which is taken as a conservative tracer. Mixing lines in this figure represent concentration trends expected through simple dilution of the most SO_4 -rich water (site 1) by Willow Creek water (site 23). The SO_4 concentration of sample 22, the most dilute sample, suggests that mixing ratios reach 15 kg background water to 1 kg drainage water. Values that fall above a mixing line reflect addition to solution via mineral dissolution or desorption from mineral surfaces. When values fall below the mixing line, aqueous species have been removed from solution via mineral precipitation or adsorption.

Although SO_4 in mine drainage is not necessarily a conservative tracer, SO_4 concentrations in this study are sufficiently high compared to Fe and Al concentrations that it exhibits conservative behavior. Nordstrom (1982); Chapman et al. (1983) suggest that SO_4 is removed from solution via the precipitation of Al hydroxysulfate phases such as alunite, basaluminite, and possibly also jurbanite. Pecos Mine drainage has a pH too high for jurbanite stability. Precipitating all of the aluminum in solution as alunite and/or basaluminite results in removal of less than 5% of the original SO_4 concentration; this result is considered to be within experimental and analytical error of SO_4 concentration measurements. Species concentrations could

Table 2
National suggested maximum contaminant levels (MCLs) for various elements found in the Pecos Mine contaminated drainage

Contaminant	MCLs (ppm)
Al	0.050–0.20
Pb	0.015
Fe	0.3
Mn	0.05
Zn	5.0
Cu	1.3
SO_4	250

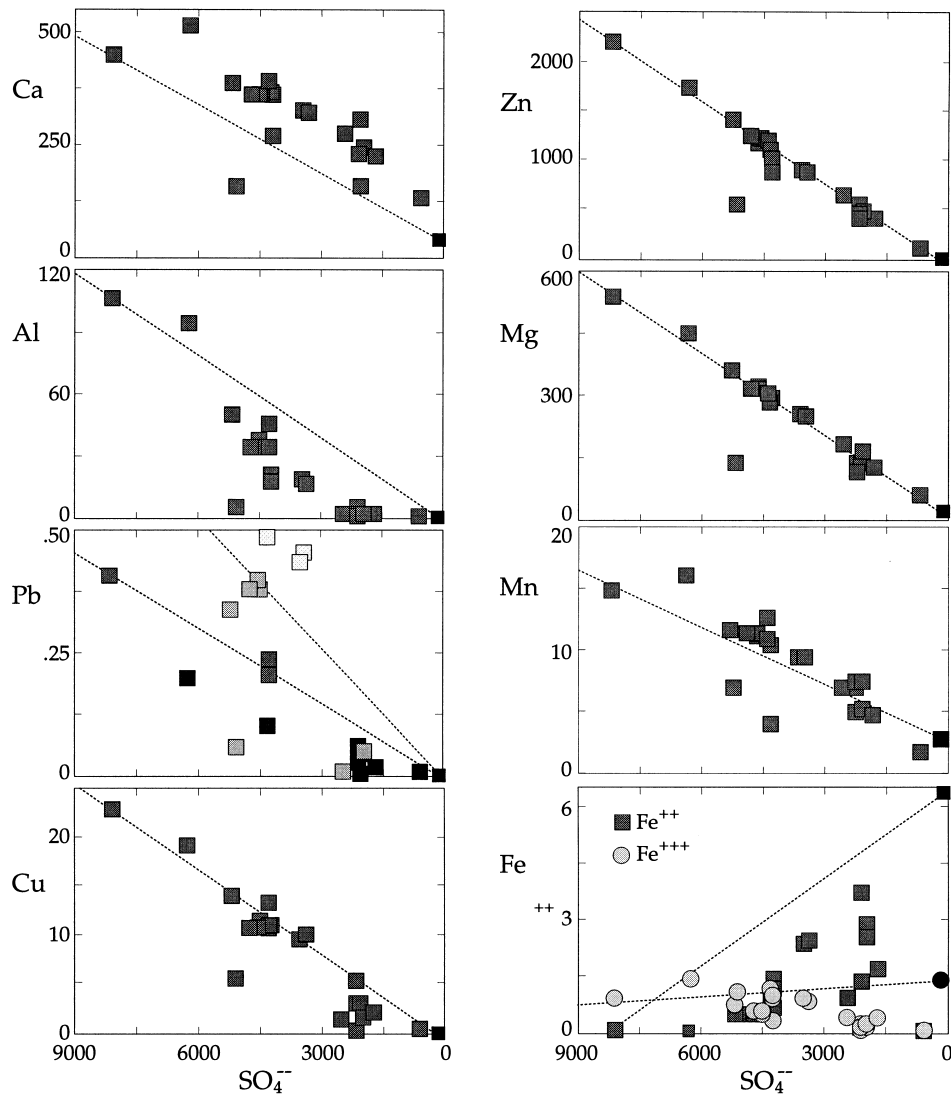


Fig. 3. The dashed line represents concentrations that would result solely from mixing of mine water with background water. Concentrations below this line indicate removal of the aqueous species from solution (e.g. via precipitation), whereas concentrations falling above the line represent an addition to solution, such as mineral dissolution. Black squares are measured concentrations at site 23.

also be plotted against Cl^- with qualitatively the same results. However, since Cl^- concentrations are two orders of magnitude smaller than SO_4 concentrations, they are subject to higher analytical error.

Measured Ca concentrations are as much as 125 mg/kg higher than would be expected in the mixed fluid (Fig. 3). Therefore, Ca must have been added to solution, probably by dissolving calcite from the underlying formation. Conversely, Al, Cu, and Pb concentrations fall below the mixing line. These metals likely were removed from solution through precipitation of OH, SO_4 , or sulfate phases. Alternatively,

they may have sorbed on surfaces of precipitating phases. Iron concentrations also fall below the mixing line; however, the mixing line for Fe has positive slope as Willow Creek water has higher concentrations of Fe than the drainage water. Willow Creek flows through an iron-rich swamp north of the drainage. This Fe is primarily in the reduced state. Zinc, Mg and Mn concentrations fall along mixing lines. Neither precipitation nor dissolution reactions affect the concentrations of these metals.

Solids filtered from solution were analyzed by X-ray diffraction. Fig. 4 shows some XRD patterns. These

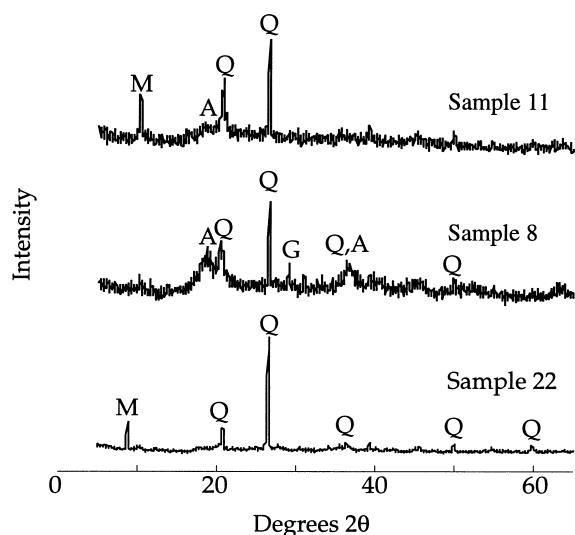


Fig. 4. X-ray diffraction patterns from micronized dehydrated field samples. See Fig. 1 for site locations. Q = quartz, A = aluminum hydroxide, M = mica, G = gypsum.

samples show few well defined peaks; reflections from quartz dominate the pattern. Samples 8 and 11 exhibit peaks consistent with Al hydroxide. The broad, low intensity peaks centered around $20^\circ 2\theta$ in samples 8 and 11 are indicative of amorphous or poorly crystalline material, which is typical with acid drainage precipitates (e.g. Nordstrom, 1982; Chapman et al., 1983; Brady et al., 1986). The XRD results indicate the particulate material is a mixture of precipitates from solution such as Al oxide, and residual phases from dissolving limestone from the underlying formation.

5. Process modeling

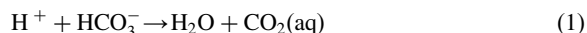
To describe the geochemical process or processes responsible for the observed trends in pH and metal content, the authors developed a reaction model using the React program (Bethke, 1998) to predict changes in the chemistry of the evolving drainage. React, a part of The Geochemist's Workbench[®], a commercially available software package, is designed to simulate reaction processes such as mass transfer, redox reactions, and mixing in geochemical systems. The Lawrence Livermore National Laboratories (Delany and Lundeen, 1989) database of mineral and species equilibrium constants was used. Bethke (1996) describes the basis of the simulations and the numerical solution methods employed.

The authors considered several hypotheses to explain the observed changes in drainage chemistry: that (1)

mixing background water into drainage water affected its chemistry, (2) the solution was neutralized as a result of dissolving limestone, and (3) these two processes occurred concurrently. Each of the processes works to raise drainage pH.

For the model, an initial system is taken that consists of 1 kg of mine drainage water, the chemical composition of which is constrained by analyses of samples from site 1. The fluid is assumed to maintain equilibrium with O_2 and CO_2 in the atmosphere. Mixing is simulated with background fluids, reaction with limestone, or both processes concurrently, by incrementally changing the system as aliquots of minerals or fluid, or both, are added. The calculation reflects how the system evolves chemically over the course of the reaction process.

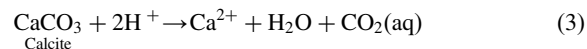
In the simulation, adding a neutral water with low metal concentrations to the contaminated drainage increases pH because the total number of H^+ ions per kilogram of solution is diluted. In addition, background water contains HCO_3^- ions that react with acid to form aqueous CO_2



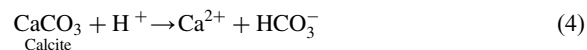
some of which may be subsequently lost to the gas phase



To simulate the dissolution of limestone, calcite is added to the initial drainage water. As calcite dissolves, pH increases due to

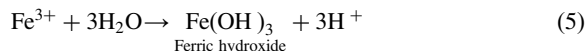


producing additional aqueous CO_2 that may degas via reaction (2). Later in the reaction, where pH has increased to above about 6.7, the reaction

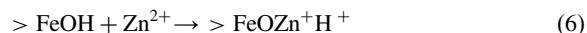


consumes acid.

As acid in the drainage is neutralized, metal concentrations can attenuate in several ways. As pH increases, metals may precipitate directly, e.g.



In addition, precipitates such as ferric hydroxide may scavenge metals from solution through sorption reactions; e.g.



where $> FeOH$ represents a reactive site on the surface

of the adsorbing mineral ferric hydroxide, and $>FeOZn^+$ represents the same site complexed with a Zn ion. Metal concentrations decrease via these precipitation and adsorption reactions, and, in the case of mixing, by simple dilution.

In the simulations, incremental addition of either Willow Creek water, calcite, or both, proceeds until the system attains a pH equal to that measured in the field downstream from the drainage (site 22). Over the course of the reaction, stable minerals in the LLNL database that are unlikely to precipitate within a short period of time (e.g. hematite) are suppressed from the calculations. This choice favors the precipitation of less stable phases [e.g. ferric hydroxide: $Fe(OH)_3(s)$]. Minerals not considered in the calculations are listed in Table 3. Adsorption of metals to hydrous ferric oxides is modeled using the model developed by Dzombak and Morel (1990). Adsorption to Al hydroxides is also modeled using a similar model (Berger, 1999).

5.1. Mixing

The chemistry of Willow Creek water from site 23 is used to model mixing observed at the site. The water in Willow Creek upstream of the mine drainage has a pH of 7.2 and low metal concentrations. Willow Creek has a pH very similar to that measured downstream from the drainage; to increase drainage pH to approximately the downstream pH solely via mixing requires a mixing ratio of at least 200 parts background water to one part drainage water (Fig. 5). Very little mineral mass precipitates over the course of the simulation; as a result, metal concentrations decrease during mixing along simple dilution curves, as shown in Fig. 6. These predicted concentrations fall below the observed concentrations.

Table 3
Minerals in the LLNL database (Delany and Lundeen, 1989) that are not considered in the calculations

Al-bearing minerals:	diaspore (AlOOH)
Fe-bearing minerals:	ferrite [(Zn,Cu)Fe ₂ O ₄] goethite (FeOOH) hematite (Fe ₂ O ₃)
Mn-bearing minerals:	birnessite (Mn ₈ O ₁₉ H ₁₀) bixbyite (Mn ₂ O ₃) hausmannite (Mn ₃ O ₄) manganite (MnOOH) pyrolusite (MnO ₂) todorokite (Mn ₇ O ₁₂ ·3H ₂ O)
Zn-bearing minerals:	smithsonite (ZnCO ₃)

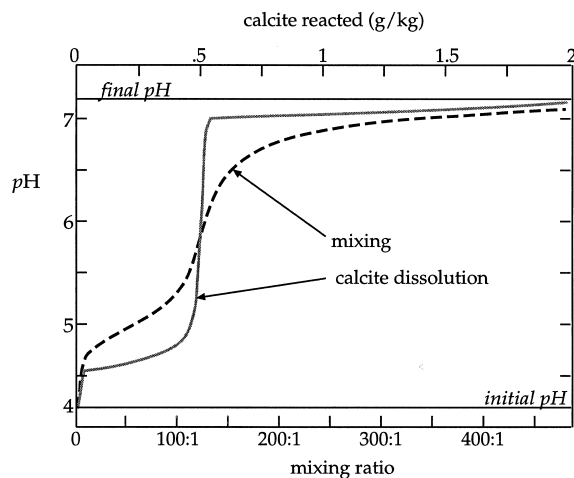
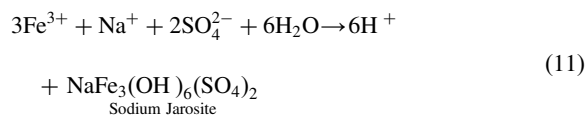
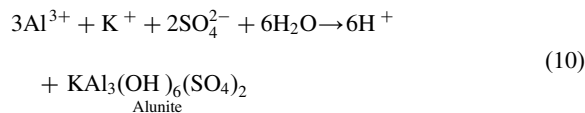
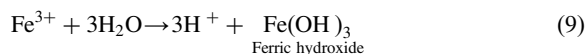


Fig. 5. Modeled change in pH for 1 kg of drainage water as a result of dissolution of calcite from limestone in the underlying bedrock (solid line), and mixing with Willow Creek water (dashed line).

5.2. Reaction with carbonate rocks

To evaluate the consequences of reaction with limestone that underlies the waste rock pile, calcite was reacted into the original drainage. The model predicts that pH increased due to reactions 3 and 4, as shown in Fig. 5. In the process of increasing pH to the measured downstream pH, almost 3 g of calcite dissolved into 1 kg of drainage water. The decreasing H^+ ion concentration causes a number of mineral phases to precipitate (Fig. 7), via the following:



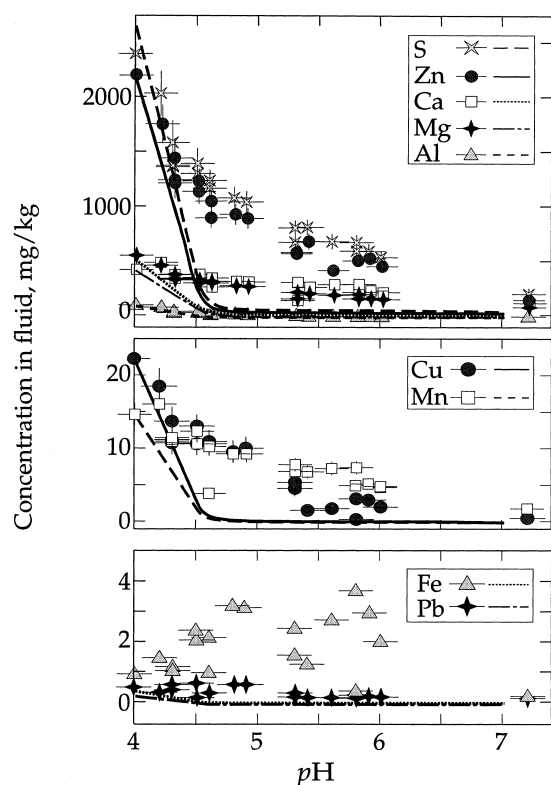


Fig. 6. Predicted concentrations (lines) of major aqueous species as pH increases due to mixing with Willow Creek water. Measured concentrations are plotted as points versus pH measured in the field.



In addition, gypsum precipitates



due to a common ion effect driven by the addition of Ca to solution through the dissolution of calcite.

These reactions remove metal species from solution. Fig. 8 shows how dissolved concentrations attenuate in the simulation. Zinc, S, Al, Cu, Fe and Pb attenuate abruptly at the onset of precipitation. Magnesium and Mn concentrations remain high over the course of the reaction. Calcium concentrations increase as calcite dissolves into solution (Fig. 8).

5.3. Combined pathway

As discussed previously, observations at the site

suggest that over the initial stretches of the drainage, rock dissolution and fluid mixing between drainage and background water occur concurrently. In Fig. 3, Ca concentrations deviate above the pure mixing line by 80–125 mg/kg. It is assumed that calcite dissolution accounts for the addition of Ca. To reproduce the extent of dilution suggested by the observed decrease in SO_4 concentration, we mix 15 kg of background water into one kilogram of drainage fluid. The fluid's Ca content in excess of that expected during conservative mixing depends on the amount of calcite that dissolves, as shown in Fig. 9. The general trend of calcium concentration can be explained well by a reaction process in which about 250 mg of Ca (per kg of drainage fluid) dissolve over the initial portion of the mixing process, or concurrent with mixing ratios of up to about 3 kg background water to 1 kg drainage water. The 250 mg of Ca is equivalent to 624 mg of calcite. The calcite dissolves completely and no further calcite is added during subsequent mixing. Fig. 9 shows the pathway taken in such a process.

Dissolution of calcite and mixing with background water drives an increase in the pH via reactions 1, 3 and 4. Most of the CO_2 produced is subsequently lost to the gas phase. The increase in pH drives precipitation of Al hydroxide, tenorite, Fe(III) hydroxide, jarosite, and alunite, via reactions 7–11, as shown in Fig. 10. Fig. 11 shows the predicted behavior of aqueous species concentrations compared to measured drainage concentrations. In this simulation, predicted concentrations match the observed values better than in the previous two simulations.

6. Discussion

Results of this study show the chemical evolution of drainage from the Pecos Mine can be explained by the combined effects of calcite dissolution and mixing with background water. Neither dissolution nor mixing alone, however, can explain trends in chemical composition as the drainage flows from the seeps toward the Pecos River. Using the constraints on Ca provided by field data, a model that combines dissolution and mixing predicts an attenuation of aqueous species concentrations that more closely matches concentrations observed in the field (Fig. 11) than either mixing or calcite dissolution alone (Figs. 6 and 8).

In the combined model, calcite dissolution and mixing together increase pH to a value of 6. Continued mixing alone increases pH to a value of 7.2. Aluminum, Cu and Fe precipitate directly from solution. This prediction agrees with observations made above, that concentrations of these elements fall below conservative mixing lines (Fig. 3). Moreover, most of the Cu

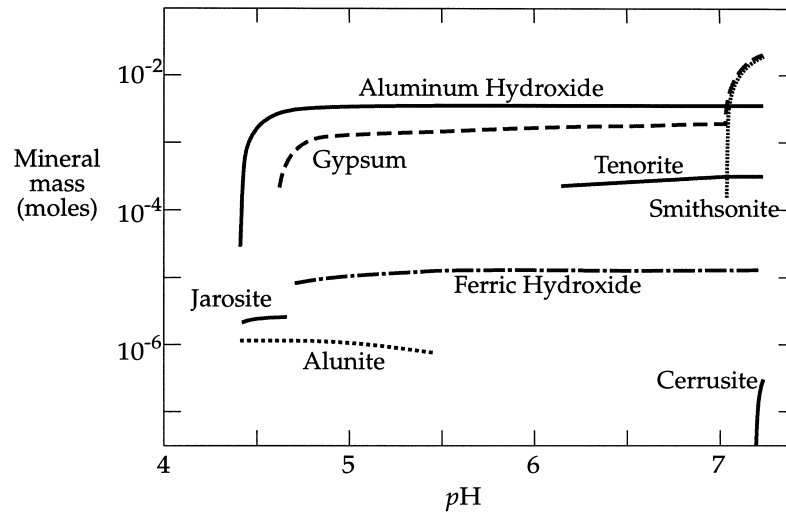


Fig. 7. Predicted cumulative mineral assemblage precipitated as pH increases as a result of calcite dissolving into one kg of drainage water.

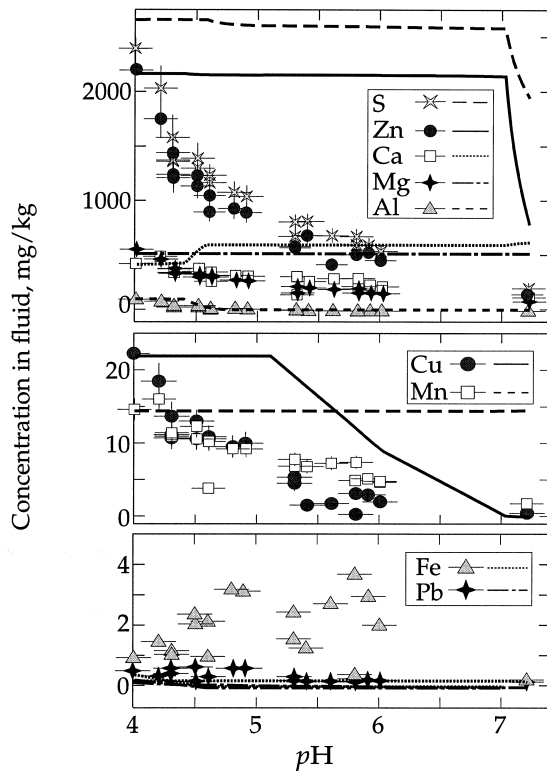


Fig. 8. Predicted concentrations (lines) of major aqueous species as pH increases due to dissolution of calcite. Measured concentrations are plotted as points versus pH measured in the field.

concentrations that depart from the mixing line do so at later stages of the mixing process, which is consistent with the model prediction of tenorite precipitation. In the calculation, Zn and Mg attenuate through simple mixing, also consistent with data in Fig. 3. The model predicts Mn attenuation through simple mixing when precipitation of oxidized Mn minerals are excluded (Table 2). Manganese oxidation is pH dependent, and kinetically inhibited at pHs observed in the field (Stumm, 1981).

Adsorption as a potential metal scavenger does not play a significant role in metal attenuation. Ferric hydroxides have a high affinity for aqueous metal species; however this phase does not precipitate in sufficient quantities to affect the aqueous concentrations of scavengeable metals. Aluminum hydroxide precipitates in greater quantities; however, it has a much lower site density than hydrous Fe(III) oxide (Anderson and Benjamin, 1990). Aluminum hydroxide preferentially scavenges Pb from solution such that up to 10% of aqueous Pb is adsorbed on hydroxide surfaces. Aqueous metal concentrations attenuate primarily by direct precipitation of mineral phases, or via simple dilution. Although these mineral phases are likely colloidal upon precipitation, wetland vegetation downstream from the site trap such particles (Stoller, 1996), and any metal transport downstream is likely to be primarily due to bedload transport (McLemore et al., 1993).

Predicted Fe concentrations (Fig. 11) do not show particularly good agreement between the predicted and observed values. Iron concentrations in the Pecos Mine Operable Unit drainage are fairly low compared to typical acid drainages (Smith et al., 1994). Because the

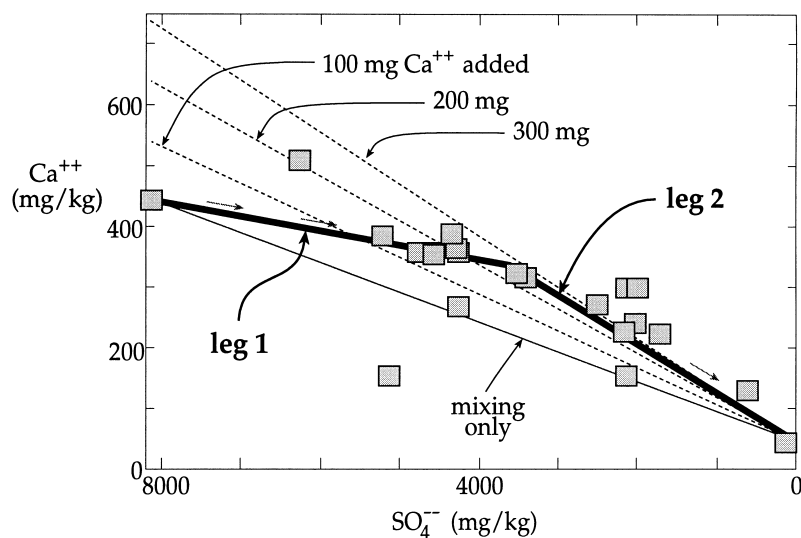


Fig. 9. Trend in Ca concentration predicted by combined reaction pathway. Dashed lines show mixing lines for an initial fluid containing progressively more Ca. Symbols show measured Ca concentrations from Fig. 3. In leg 1 of the simulation (heavy line), 2.5 kg of background water and 250 mg of Ca are added to solution. In leg 2, the remaining 12.5 kg of background water is added.

background water from Willow Creek has higher Fe concentrations (of primarily reduced Fe) than any of the drainage samples, mixing represents an addition of Fe to the drainage. Water flowing downstream into the mine drainage may add Fe to drainage water more rapidly than Fe oxidizes and precipitates from solution.

If mixing alone is considered in the calculation, attenuation along simple mixing curves occurs earlier than is observed in the field (Fig. 6). The largest discrepan-

cies in this case are between measured and calculated concentrations of Zn, Cu and Ca. In a model that accounts for calcite dissolution alone, metal concentrations attenuate rapidly with the onset of solid precipitation. Metal attenuation observed in the field is continuous rather than abrupt; therefore, with the exception of Fe and Ca, this model overestimates metal concentration over most of the reaction path (Fig. 8). The model's prediction of Ca concentration is most striking, as predicted Ca contents increase along

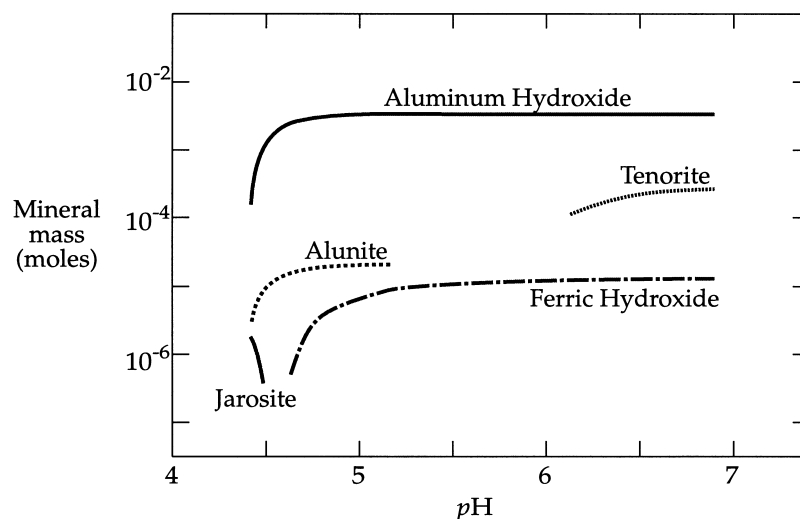


Fig. 10. Predicted mineral assemblage as pH increases due to concurrent mixing with Willow Creek water and calcite dissolution.

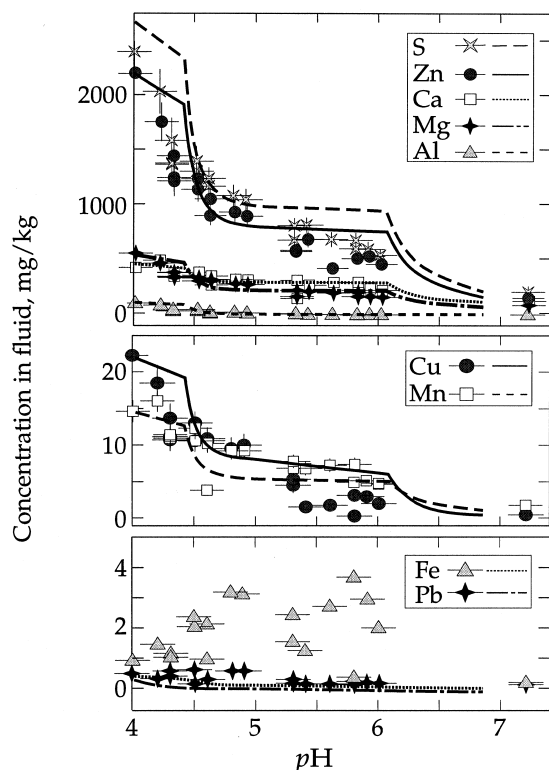


Fig. 11. Predicted concentrations (lines) of major aqueous species as drainage pH increases due to concurrent mixing with Willow Creek water and calcite dissolution. Measured concentrations are plotted as points versus pH measured in the field.

the drainage path whereas measured Ca concentrations decrease. The dissolution model adds Ca to the system through calcite dissolution but provides no pathway for lowering Ca concentration.

7. Conclusions

This study shows that the primary geochemical control governing the acid drainage chemistry at the Pecos Mine Operable Unit cannot be the result of one but must be at least two processes including mineral buffering and dilution by mixing with ambient waters. Geochemical modeling is used to demonstrate the relative importance of CaCO_3 dissolution and mixing with more dilute waters on the attenuation of both acidity and metal contamination. Drainage chemistry is best modeled by mixing 15 kg ambient water into 1 kg mine water over the course of the flow path, with concurrent dissolution of about 0.6 g of calcite over the initial portion of the reaction. Calcite dissolution is

most important near the seeps; downstream, mixing seems to operate alone.

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