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Adding Sodium Hydroxide To Study Metal Removal in a Stream Affected by Acid Mine Drainage

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RESEARCH SUMMARY

Fisher Creek, a stream affected by acid mine drainage in the Beartooth Mountains of Montana, was studied to determine the extent to which copper (Cu) and zinc (Zn) would be removed from stream water when pH was increased by a pulse of sodium hydroxide (NaOH). The creek, near Cooke City in southwestern Montana, has a pH of 3.4. Water temperature, pH, and concentrations of dissolved and particulate elements were measured below the point where NaOH was injected. MINTEQA2, a chemical equilibrium speciation program, was used to calculate the amount of each element in dissolved, adsorbed, and precipitated phases during the NaOH pulse. Ferrihydrite ($\text{Fe}(\text{OH})_3(\text{am})$) controlled Fe^{3+} concentrations throughout the study period. A hydrous oxide of aluminum (Al) precipitated at the beginning of the NaOH pulse, dissolved during the middle of the pulse when the pH exceeded 10, precipitated at the end of the pulse, and dissolved after the pulse as the stream reacidified. The form of the Al hydrous oxide could not be identified. Precipitation of pyrochroite ($\text{Mn}(\text{OH})_2$) and brucite ($\text{Mg}(\text{OH})_2$) controlled dissolved manganese (Mn) and magnesium (Mg) levels during the NaOH pulse. Dissolved Cu and Zn concentrations were reduced to <0.01 mg/L during the NaOH pulse. MINTEQA2 predicted that Cu and Zn would be adsorbed by hydrous Fe oxide at the beginning and end of the NaOH pulse. At the high pH levels during the middle of the pulse they should have been desorbed. MINTEQA2 also predicted that the stream was undersaturated with respect to $\text{Cu}(\text{OH})_2$ and $\text{Zn}(\text{OH})_2$ throughout the pulse. Because Cu and Zn were completely removed from the stream water during the entire pulse, not just the beginning and end, the mechanism responsible for removing them was postulated to be coprecipitation with $\text{Fe}(\text{OH})_3(\text{am})$. Although the pH adjustment study indicated that precipitated $\text{Fe}(\text{OH})_3(\text{am})$ could rapidly remove Cu and Zn from a stream affected by acid mine drainage, the pH should be maintained in an optimal range (7 to 8.5) to maximize removal by adsorption.

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INTRODUCTION

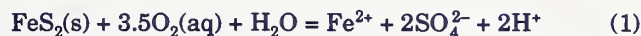
Acid mine drainage (AMD) and acidic streams with high concentrations of metals from metal sulfide deposits oxidized after being exposed by mining are common throughout the Western United States (Amacher and others, in press; Fillipek and others 1987; Theobald and others 1964). Many of these metal sulfide deposits are located in mountainous regions where normally pristine watersheds have been severely impacted by AMD containing high concentrations of metals such as manganese (Mn), iron (Fe), copper (Cu), zinc (Zn), and aluminum (Al) from mine sites abandoned long ago (Amacher and others, in press). Of these metals, Cu is the most toxic to aquatic life (Förstner and Wittman 1983). Restoring watersheds impacted by AMD to anything approaching a pristine state is unlikely, given the difficulty in controlling AMD and the remote, rugged locations of many high-elevation sites.

Methods to control AMD can generally be classified into two types: (1) prevention at the source and (2) treatment to remove acidity, metals, and sulfur. Prevention generally seeks to keep metal sulfide deposits from oxidizing; drainage waters then will not have the acidity and metals concentrations typical of AMD. Treatment may include raising the pH to precipitate hydrous metal oxides of Fe, Al, and Mn, and to adsorb other metals (Cu and Zn) on the metal oxides. Wetland systems remove metals and sulfur from AMD by uptake by plants, adsorption by organic matter, and reducing sulfates to sulfides that precipitate (U.S. Bureau of Mines 1988). These control strategies have met with varying degrees of success. Before we discuss them in more detail, we need to examine the chemistry of metal sulfide oxidation.

Metal Sulfide Oxidation Mechanisms

The mechanisms and factors influencing the rates of metal sulfide oxidation are known primarily from studies of pyrite oxidation (Brown and Jurinak 1989a,b;

Moses and others 1987; Nordstrom 1982). Ferric iron and oxygen are the principal oxidants:



Fe^{3+} oxidizes pyrite much faster than O_2 does, but the process is thought to begin with oxidation by dissolved oxygen.

Ferrous iron (Fe^{2+}) produced during pyrite oxidation can itself be oxidized by O_2 to Fe^{3+} . That Fe^{3+} can then oxidize pyrite according to reaction (2). The ensuing autoxidation cycle generates considerable amounts of acidity. The rate of oxidation of Fe^{2+} by O_2 is very slow and is independent of pH below a pH of about 3. Above pH 3, however, the oxidation rate increases with increasing pH.

Certain microorganisms such as *Thiobacillus ferrooxidans* catalyze the oxidation of Fe^{2+} by O_2 , greatly increasing the oxidation rate. Under acidic conditions, microbially catalyzed oxidation of Fe^{2+} is more important than oxidation that is not microbially catalyzed. Under neutral or alkaline conditions, oxidation that is not microbially catalyzed becomes significant. Temperature and pH also influence the growth of microorganisms that catalyze oxidation of Fe^{2+} . Besides catalyzing reactions in water, *Thiobacillus ferrooxidans* may also help oxidize pyrite on the surface of exposed minerals.

Prevention of Metal Sulfide Oxidation

Prevention generally involves keeping metal sulfides from coming in contact with the O_2 that begins the autoxidation cycle. Measures include sealing adits to keep air from coming in contact with metal sulfides, burying mining wastes that contain metal sulfides, and adding chemicals to inhibit the growth and activity of microorganisms that catalyze the oxidation of pyrite (U.S. Bureau of Mines 1988).

Sealing underground mine workings to lessen sulfides' exposure to air seems to be a good control

strategy. Unfortunately, once sulfides have been exposed to air, the autoxidation cycle is difficult to arrest. The Fe^{3+} produced by oxidation of Fe^{2+} continues to oxidize pyrite (Stumm and Morgan 1981). In addition, it is rarely possible to completely seal off all exposed sulfides from air. To completely control AMD production, all exposed sulfides must be returned to a reducing environment. Deep burial of sulfide-containing wastes, especially when they are flooded, attempts to restore a reducing environment where sulfides will remain stable.

Treatment of AMD

Using lime to treat AMD does not control the problem at its source; it requires continual addition of lime to raise pH and precipitate or adsorb metals from AMD. The hydrous metal oxides of Fe, Al, and Mn will precipitate as pH increases; they adsorb other metals such as Cu and Zn (Dzombak and Morel 1990; Kinniburgh and Jackson 1981).

Recently, wetlands have been evaluated for their ability to treat water affected by AMD (U.S. Bureau of Mines 1988). In aerobic-anaerobic wetlands, metals are removed from AMD by four processes: (1) accumulation in plant communities growing in the aerobic surface layer, (2) adsorption on organic matter in the aerobic surface layer, (3) precipitation and adsorption on metal oxides in the aerobic layer, and (4) precipitation as relatively insoluble metal sulfides in the reducing environment of the anaerobic lower layer. However, metals are introduced into the food chain when they are taken up by plants, and loading rates must be kept low to avoid overwhelming the wetlands' ability to absorb metals.

In anaerobic wetlands no plant communities are needed to treat AMD. Sulfur-reducing microorganisms reduce sulfate to sulfide and precipitate metals. Because metal sulfides are so insoluble, all but very low levels of metals can be removed from the water. The major disadvantage of using anaerobic wetlands is that AMD loading rates must be relatively low to avoid exceeding the rate at which the microorganisms can reduce sulfate. Furthermore, anaerobic wetlands are sensitive to temperature because they depend on growth of microorganism populations. Anaerobic wetlands must be insulated to operate during winter in cold climates, and AMD loading rates must be reduced during winter to avoid exceeding the system's capacity to reduce sulfate.

Acid mine drainage from the McLaren and Glengarry Mines, two old abandoned Cu mines on opposite sides of Fisher Mountain in the Beartooth Mountains of Montana, contaminate the headwaters of Daisy and Fisher Creeks. Daisy Creek, affected by the McLaren Mine, is a headwater stream of the Stillwater River; Fisher Creek, affected by the Glengarry Mine, is a

headwater stream of the Clark's Fork of the Yellowstone River. Noranda Minerals Exploration and Crown Butte Mines, Inc., are exploring the area around Fisher and Henderson Mountains for possible operation of a gold mine. Their mine permit application is being processed. Reclamation plans for the area have been developed; the AMD control measures proposed for the old McLaren and Glengarry Mines as well as the new mine include closing portals, back-filling pits, and saturating a proposed tailings impoundment with water to keep metal sulfides in their reduced state.

Previous Studies

The Intermountain Research Station has been conducting long-term research in the Beartooth Mountains to identify the factors limiting reclamation and to develop methods that will repair impacts from past and present mining. Over the long term, we hope to restore, at least partially, an intact, functioning ecosystem.

Research begun recently attempts to assess the impact of AMD on watersheds in the area, identify how metals are removed from streams receiving AMD, develop models to accurately predict AMD impacts on streams, and evaluate methods of preventing or mitigating AMD. Research using hydrologic mass balance calculations, geochemical modeling, and sediment analysis has identified the processes controlling metals concentrations in these streams (Amacher and others 1991a,b, in press). Iron concentrations are controlled by precipitation of hydrous Fe^{3+} oxide (ferrihydrite), photoreduction of hydrous Fe^{3+} oxide coatings on stream sediments, and microbially mediated oxidation of Fe^{2+} . Aluminum concentrations appear to be controlled by dilution from uncontaminated inflows or precipitation of hydrous Al oxides. Copper concentrations are controlled by dilution or by adsorption on hydrous Fe^{3+} oxides. Manganese and SO_4 concentrations are controlled by dilution from inflows. Much of this research is ongoing.

One of the potentially most significant findings is that the hydrous Fe^{3+} oxide coatings on stream sediments adsorbed Cu from stream waters when the pH was greater than 5.5 (Amacher and others 1991a, in press). As inflows added alkalinity to the streams, Cu concentrations associated with the hydrous Fe^{3+} oxides in stream sediments increased. Maximum concentrations of Cu in sediments were found several thousand meters downstream from the AMD sources. This suggests a possible AMD mitigation strategy to augment other methods proposed for the area. Even if prevention methods such as closing portals, back-filling pits, burying wastes, and saturating tailings impoundments are effective, some AMD may still flow into Daisy and Fisher Creeks. Wetlands may play some role in treating AMD in these watersheds.

However, their effectiveness will be limited by the toxicity of Al and Cu to wetland plants, the need to insulate the wetlands for most of the year, and the need for relatively low AMD loading rates. If the pH of the streams affected by AMD could be raised by increasing the alkalinity of their inflows, then hydrous Fe³⁺ oxide coatings on stream sediments would scavenge Cu from stream water. The metal precipitation and adsorption zone can be confined to a relatively short reach of stream near the AMD source, extending the buffer zone between stream reaches affected by AMD and downstream reaches containing aquatic life.

The best way to raise the pH of streams affected by AMD is to increase the alkalinity of uncontaminated tributaries. Putting limestone rock in the lower reaches of these tributaries would be the cheapest and easiest way to increase their alkalinity. Both Daisy and Fisher Creeks have numerous tributaries that substantially increase their flow. Most tributaries in upstream reaches near the AMD sources have low alkalinity because they do not flow through calcareous rock. Tributaries farther downstream contribute most of the incoming alkalinity; this is where most of the Cu is adsorbed (Amacher 1991a, in press). If the channels of the upstream tributaries were lined with crushed limestone rock, the increased alkalinity could neutralize the AMD in the main streams. The lower ends of these tributaries are accessible by roads, so the limestone rock could be readily placed there. Adding limestone rock to the main stream channels affected by AMD would not work as well, because precipitating hydrous Fe³⁺ oxides would coat the rock, sealing it from the water.

Present Study

Before trying this approach, we wanted to assess whether precipitating hydrous Fe³⁺ oxides would scavenge Cu from stream water as pH increased. In general, such adsorption reactions are quite fast (Sparks and Zhang 1991), so Cu should be removed rapidly. We conducted a pH adjustment study at Fisher Creek to test this hypothesis. A pulse of NaOH was applied to the stream to rapidly increase pH and precipitate hydrous Fe³⁺ oxide, which would adsorb Cu. We measured the amounts of various elements in the dissolved and particulate phases during the NaOH pulse. We used MINTEQA2, a chemical equilibrium speciation program, to determine the possible solid phases formed during the pulse. If the precipitation and adsorption reactions occurred sufficiently fast relative to the mixing and transport rates within the stream, near equilibrium conditions could be maintained. Then, chemical equilibrium speciation models could be used to evaluate possible controls on the concentrations of metals in the dissolved and particulate phases. A pH range

of 7 to 8.5 was targeted. MINTEQA2 calculations and sediment analysis (Amacher and others 1991a, in press) indicated this is the pH range for maximum Cu adsorption by hydrous Fe³⁺. Even though NaOH would not be used as a final treatment to adjust the pH of these streams, it can be used to test the ability of hydrous Fe³⁺ oxide to scavenge Cu under field conditions.

MATERIALS AND METHODS

Fisher Creek is located about 5 km north of Cooke City, MT, in the Gallatin National Forest. Fisher Creek is one of the headwater streams that form the Clark's Fork of the Yellowstone River. It begins in a glacial cirque just below Lulu Pass (2,963 m) between Fisher and Scotch Bonnet Mountains. Acid mine drainage from the adit of the Glengarry Mine, an abandoned copper mine, flows into Fisher Creek a few hundred meters below the glacial cirque. The AMD has severely impacted the stream with concentrations of Mn, Fe, Cu, Al, and sulfur (S) that are substantially higher than those in the area's relatively pristine natural waters (Amacher and others, in press).

pH Adjustment

Twenty liters of 10 M NaOH were added to Fisher Creek about 350 m below the Glengarry Mine adit at a rate of 1 L/min beginning at 10:33 a.m. on August 30, 1992. Water samples were collected at a point about 280 m below the injection point at 2-min intervals for the next 80 min. Additional samples were collected 90, 105, 120, 150, and 180 min after injection. The last sample was collected at 1:35 p.m.

Each 40-mL sample of stream water was collected with a 50-mL plastic syringe. The sample was immediately filtered through a 47-mm polycarbonate membrane filter holder containing a 0.2- μ m polycarbonate membrane filter. Three aliquots of filtered sample were pipetted into 16- by 125-mm plastic snap-cap test tubes for Fe²⁺ (10 mL), reactive Fe (Fe²⁺ + Fe³⁺) (5 mL), and total elemental analysis (10 mL). The membrane filter holder was disassembled, and the membrane filter was placed into a 22-mL plastic scintillation vial.

The pH and temperature of the stream water were monitored continuously with a Ross combination pH electrode (Orion No. 811500) and automatic temperature compensator (Orion No. 917001) connected to an Orion Model SA250 portable pH meter. The meter and electrodes were calibrated using pH 4.00 and 7.00 buffers immediately before the start of the NaOH injection. The calibration was rechecked after the experiment. The measured pH had changed only 0.01 pH unit from the buffer values.

The stream discharge was determined at the sample collection point before NaOH injection by measuring

Fisher Creek's cross-sectional area and flow velocity using a Marsh-McBirney Model 201D portable water current meter.

Sample Analysis

Fe²⁺ and reactive Fe were measured in the filtered water samples using the 2,2'-bipyridine method (Skougstad and others 1978). Color development reagents were added in the field after all the samples were collected. Sample absorbencies were measured at 520 nm in the laboratory. To determine Fe²⁺, 0.5 mL of 0.2 percent 2,2'-bipyridine solution was added to one of the 10-mL aliquots of each sample. One mL of deionized water was added to each of the aliquots, followed by 1 mL of 4.3 M sodium acetate buffer solution (290 g of sodium acetate trihydrate dissolved in deionized water and diluted to 500 mL).

To determine reactive Fe, 5 mL of deionized water was pipetted into each of the 5-mL aliquots of sample. After adding 0.5 mL of 0.2 percent 2,2'-bipyridine solution and 1 mL of 10 percent hydroxylamine hydrochloride solution (10 g of NH₂OH·HCl dissolved in deionized water plus 4 mL of concentrated HCl diluted to 100 mL with deionized water), the aliquots were allowed to stand for at least 30 min. Then 1 mL of 4.3 M sodium acetate buffer solution was added. Ferric iron was determined as the difference between reactive Fe and Fe²⁺.

The concentrations of total dissolved Al, calcium (Ca), Cu, Fe, potassium (K), magnesium (Mg), Mn, sodium (Na), S, and Zn were determined in the remaining 10-mL aliquot of each sample using inductively coupled plasma atomic emission spectrophotometry (ICPAES) after acidification with 100 µL of concentrated HNO₃. A complete listing of the dissolved element concentrations is given in appendix A.

To determine the amount of particulate Fe oxide and associated elements, 20 mL of 0.25 M NH₂OH·HCl — 0.25 M HCl solution (Chao and Zhou 1983) was added to each scintillation vial containing a membrane filter, and the vials were allowed to stand overnight while the particulate Fe oxides dissolved. The resulting solutions were analyzed by ICPAES. A complete listing of the particulate element concentrations is given in appendix B.

Data Analysis

Temperature, pH, and element concentrations in each of the water samples were input into MINTEQA2 version 3.0 (Allison and others 1990), a chemical equilibrium speciation program, to calculate ionic species activities, ion activity products (IAP's), and saturation indexes for various solid phases.

In addition, simulations were run using the pH sweep feature of MINTEQA2 to calculate amounts of elements

in dissolved, adsorbed, and precipitated phases as the pH was systematically varied. Dissolved element concentrations just before arrival of the NaOH pulse (14 min after NaOH began to be added) were used as initial input values for the pH sweep simulations. Amounts of elements in dissolved, adsorbed, and precipitated phases were calculated at pH levels corresponding to different times (min) after the injection of NaOH:

Minutes	pH	Minutes	pH
14	3.41	50	9.78
20	3.88	52	8.14
22	4.61	54	6.25
24	6.32	56	5.39
26	10.34	58	4.90
28	11.22	62	4.54
34	11.73	74	4.25
40	12.15	105	4.05
46	11.60	180	3.66
48	11.00		

The measurements covered the full range of pH levels observed during the NaOH pulse. Solids allowed to precipitate during the pH sweep were wustite (Fe(OH)₂), ferrihydrite (Fe(OH)₃(am)), aluminum hydroxide (Al(OH)₃(am)), gibbsite (Al(OH)₃), jurbanite (AlOHSO₄), pyrochroite (Mn(OH)₂), copper hydroxide (Cu(OH)₂), brucite (Mg(OH)₂), and portlandite (Ca(OH)₂). These were the solid phases most likely to form during the brief passage of the NaOH pulse. Supersaturation with respect to other solid phases may have been attained, but kinetic constraints make it unlikely that these phases would have formed during the brief NaOH pulse (Stumm and Morgan 1981).

Adsorption of Cu, Zn, and Ca on hydrous Fe³⁺ oxide during the pH sweep simulations was modeled using the diffuse-layer model (DLM) of Dzombak and Morel (1990). The hydrous Fe³⁺ oxide parameters needed to model adsorption as a function of pH are listed in table 1. Two adsorption cases were considered. In the first case, the total dissolved Fe present in the stream just before the NaOH pulse arrived was assumed to precipitate as ferrihydrite during the pulse. This was equivalent to 12.3 mg/L of particulate Fe as Fe₂O₃. In the second case, adsorption by the hydrous Fe³⁺ oxide coatings on streambed sediments was also considered. Adsorption by such coatings seems likely given the stream's shallow depth; much of the water column is in contact with the streambed as numerous riffles indicate. It is necessary to estimate some concentration of hydrous Fe³⁺ oxide that will account for adsorption by both suspended and streambed hydrous Fe³⁺ oxide. Because we had no way to measure the contribution of streambed hydrous Fe³⁺ oxide, we selected an arbitrary value of 10 times the suspended particulate Fe (123 mg/L as Fe₂O₃). This gives a relative comparison of the change in adsorption expected

Table 1—Hydrous ferric oxide (HFO) parameters needed to model surface complexation using the diffuse-layer model (Dzombak and Morel 1990). In Case 1, the total dissolved Fe was assumed to precipitate as ferrihydrite ($\text{Fe}(\text{OH})_3(\text{am})$) during the NaOH pulse. Case 2 arbitrarily uses a value 10 times larger to represent the hydrous Ferric oxide on streambed sediments where copper, zinc, and calcium might be adsorbed

	Case 1	Case 2
HFO concentration as Fe_2O_3 , mg/L	12.3	123
Concentration of type 1 sites, M	6.90×10^{-7}	6.90×10^{-6}
Concentration of type 2 sites, M	2.76×10^{-5}	2.76×10^{-4}
Surface area of HFO, m^2/g	600	600

when the equivalent concentration of hydrous Fe^{3+} oxide is increased by a factor of 10. A two-site adsorption model was assumed in the adsorption calculations. Concentrations of type 1 and type 2 sites were calculated using the data given by Dzombak and Morel (1990) for synthetic hydrous Fe^{3+} oxide. A surface area of $600 \text{ m}^2/\text{g}$ was assumed (Dzombak and Morel 1990).

RESULTS AND DISCUSSION

When this study was conducted (August 30, 1992), discharge in Fisher Creek was quite low ($0.00268 \text{ m}^3/\text{s}$). Because of the low flow and the small size of the stream (180 cm wide by 2.7 cm average depth at the sampling point), solar radiation increased water temperature 6°C from the time NaOH was injected (10:33 a.m.) until the study concluded (1:35 p.m.) (fig. 1). Because the initial water temperature of 7°C differed significantly from the reference temperature of 25°C used for the thermodynamic database in MINTEQA2, all MINTEQA2 calculations used temperature-corrected equilibrium constants according to the van't Hoff equation:

$$\log K_T = \log K_{T_r} - \frac{\Delta H_r^\circ}{2.303 R} \left[\frac{1}{T} - \frac{1}{T_r} \right] \quad (3)$$

where K is the equilibrium constant, T is the temperature of the system to be modeled ($^\circ\text{K}$), T_r is the reference temperature (298.15°K), ΔH_r° is the standard enthalpy change of the chemical reaction (cal/mol), and R is the molar gas constant ($1.987 \text{ cal}/\text{mol}/^\circ\text{K}$). Equilibrium constants of hydrous oxides of Al (gibbsite and related minerals) are particularly sensitive to temperature (Hem and Roberson 1990).

pH

The NaOH added to the stream caused a large increase in stream pH (3.4 to 12.1) while the pulse passed the sampling point (fig. 1). The increase was well above the target range of 7 to 8.5. The solute arrival

time (at one-half the peak height of the ascending portion of the peak) was estimated to be about 25 min. The solute travel distance was estimated to be about 280 m based on stream distance measurements using a hip chain type of distance meter. Thus, the average solute travel velocity was about 0.19 m/s .

During the approximately 30 min when the NaOH pulse was passing the sampling point, a maximum pH of 12.15 was observed. The pH was above 10 most of this time. At these high pH levels, metals would be expected to precipitate as hydroxides (Stumm and Morgan 1981).

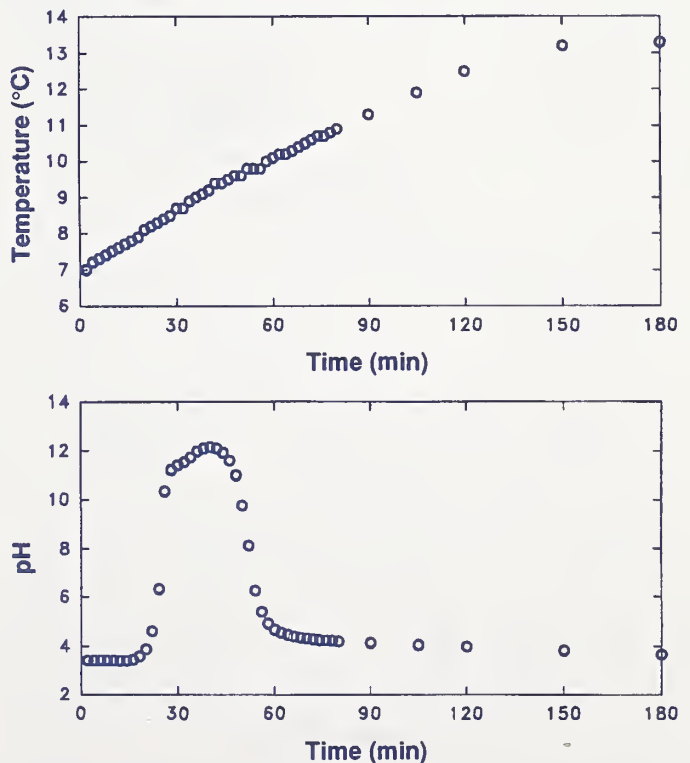


Figure 1—Temperature (top) and pH (bottom) of Fisher Creek during the pH adjustment study.

The steep slope of the leading edge of the pH response peak indicates that solute dispersed very little during the 25 min solute travel time. The pH response peak is slightly asymmetric, exhibiting some tailing. At the end of the 3-h sampling period the pH had not yet returned to the original value of 3.4. The tailing of the pH response peak may indicate the slow dissolution of hydrous metal oxides precipitated by the NaOH pulse.

Changes of Element Concentrations as pH Changes

The increase in stream water pH from the NaOH pulse produced order of magnitude changes in the concentrations of dissolved and particulate forms of Na, Mg, Ca, Mn, Fe, Cu, Zn, Al, and S. With increasing pH all the dissolved forms of Fe (Fe^{2+} , Fe^{3+} , reactive Fe, and total dissolved Fe) decreased to detection limit levels (<0.02 mg/L). They increased as pH decreased following the NaOH pulse (fig. 2). The ICPAES and 2,2'-bipyridine analytical methods gave essentially identical results for total dissolved Fe. Ferrous iron (Fe^{2+}) comprised the major portion of dissolved Fe throughout the entire pH range in which measurable Fe was found. Ferric iron (Fe^{3+}) was significant only

at highly acidic pH levels ($<\text{pH } 4$). The decrease in dissolved Fe was accompanied by a corresponding increase in particulate Fe (fig. 2), which was presumed to be freshly precipitated $\text{Fe}(\text{OH})_3(\text{am})$, also known as ferrihydrite.

Dissolved Fe^{2+} decreased as pH increased because of two possible reactions: (1) precipitation of $\text{Fe}(\text{OH})_2$ or (2) oxidation of Fe^{2+} to Fe^{3+} , which then precipitated as $\text{Fe}(\text{OH})_3(\text{am})$. The oxidation rate of Fe^{2+} by O_2 is very slow at acidic pH levels, but increases rapidly as pH increases (Eary and Schramke 1990). Above pH 7 the half-life of Fe^{2+} decreases to seconds. MINTEQA2 simulations using the pH sweep feature indicated that $\text{Fe}(\text{OH})_2$ could have precipitated at the highest pH levels observed during passage of the NaOH pulse.

A net loss of Fe from the stream water was observed on the tailing end of the NaOH pulse (fig. 2). At 180 min total (dissolved + particulate) Fe in the stream water decreased by about 25 percent compared to total Fe before the NaOH pulse arrived. This net loss of Fe from the stream water probably represents sedimentation of coagulated $\text{Fe}(\text{OH})_3(\text{am})$ particulates and the adsorption of $\text{Fe}(\text{OH})_3(\text{am})$ coatings on streambed sediments. As pH slowly approached the original level at the end of the sampling period, total Fe in the stream water (now comprised mostly of dissolved Fe) slowly increased, reflecting the slow dissolution of precipitated $\text{Fe}(\text{OH})_3(\text{am})$.

The NaOH pulse was accompanied by a decrease in the dissolved forms of Cu and Zn and an increase in their particulate forms (fig. 3). The two metals were probably adsorbed by $\text{Fe}(\text{OH})_3(\text{am})$ as it precipitated, or they precipitated as $\text{Cu}(\text{OH})_2$ or $\text{Zn}(\text{OH})_2$. Total (dissolved + particulate) Cu and Zn decreased during the NaOH pulse, slowly increasing as the stream reacidified afterward. Thus, some adsorbed or precipitated Cu and Zn settled in the streambed sediments during the NaOH pulse. These compounds dissolved after the pulse, releasing the Cu and Zn from the sediment. The Zn data have less precision than those for Fe or Cu because Zn concentrations were much lower.

The behavior of Mn was similar to Fe, Cu, and Zn (fig. 4). Dissolved Mn decreased when the NaOH pulse arrived and particulate Mn increased, indicating that Mn either coprecipitated with $\text{Fe}(\text{OH})_3(\text{am})$ or precipitated as $\text{Mn}(\text{OH})_2$, also known as pyrochroite. As with Fe, Cu, and Zn, total Mn in the stream water decreased during the pulse, indicating that some settled in the sediments.

Aluminum exhibited somewhat different behavior than Fe, Cu, Zn, or Mn. Dissolved Al decreased rapidly when the NaOH pulse arrived, increased during the middle of the pulse, decreased at the end of the pulse, and slowly increased as the stream reacidified afterward (fig. 4). Increases and decreases in particulate Al mirrored those of dissolved Al. The increases and decreases coincided with the rapid pH

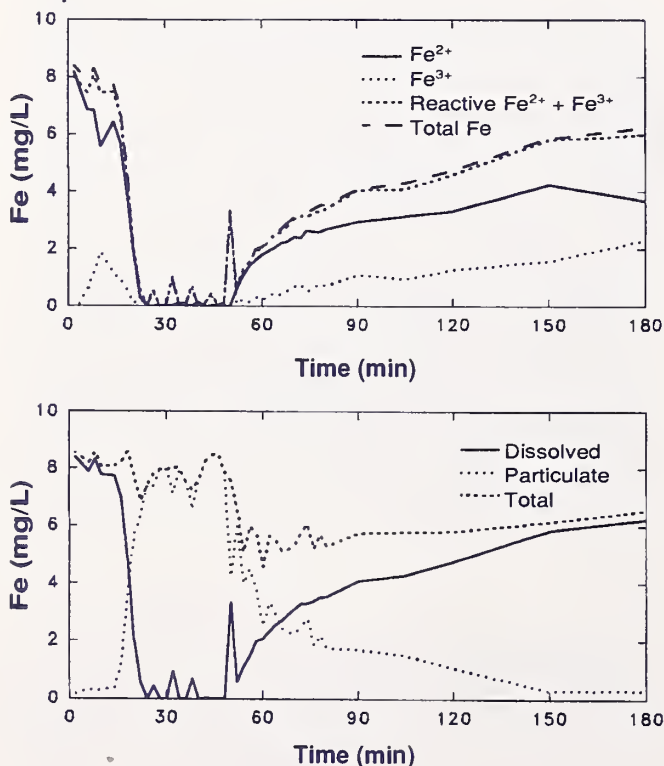


Figure 2—Concentrations of dissolved Fe species (top) and dissolved, particulate, and total Fe (bottom) in Fisher Creek during the pH adjustment study.

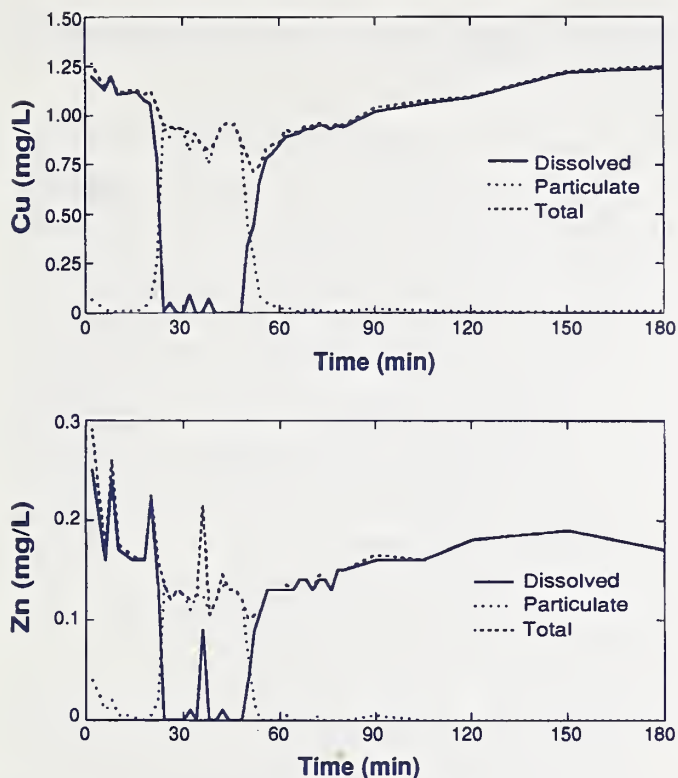


Figure 3—Concentrations of dissolved, particulate, and total Cu (top) and Zn (bottom) in Fisher Creek during the pH adjustment study.

changes at the beginning and end of the pulse. Total Al decreased at the beginning and end of the pulse. These observations are consistent with precipitation of Al in some phase as the NaOH arrived, dissolution of that phase as the pH increased to above 10, precipitation of the solid phase as the pH rapidly dropped once the NaOH pulse had passed, and dissolution as the stream slowly reacidified.

Sulfur's behavior was different. Dissolved S increased during the NaOH pulse, decreasing as the stream reacidified afterward (fig. 4). Particulate S was negligible throughout the experiment, even during the NaOH pulse. The major form of dissolved S was assumed to be SO_4 . Previous measurements on Fisher Creek water samples using the BaCl_2 turbidimetric method (American Public Health Association and others 1985) have shown that SO_4 comprised essentially all the ICPAES-measured total S (Amacher and others 1993).

The source of the S appearing in the stream water during the NaOH pulse likely was SO_4 adsorbed to hydrous Fe^{3+} oxide coatings on streambed sediments that desorbed as pH increased. Sulfate ions adsorb to hydrous Fe^{3+} oxide at low pH, but desorb at neutral to alkaline pH levels (Dzombak and Morel 1990). Selective extraction of Fisher Creek sediments has

shown large concentrations of exchangeable SO_4 and SO_4 associated with hydrous Fe^{3+} oxides in sediments at low pH (Amacher and others 1993). Other possible sources of the increase in dissolved S during the pulse include oxidation of metal sulfides in stream sediments and dissolution of jurbanite (AlOHSO_4), or jarosite ($\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$), or both.

Selective extraction methods have shown that metal sulfides comprise only a very small fraction of streambed sediments in Fisher Creek (Amacher and others, in press). Furthermore, the hydrous Fe^{3+} oxides that uniformly coat the streambed sediments would effectively seal the metal sulfides from contact with the NaOH. In addition, kinetic constraints would likely rule out metal sulfide oxidation because the concentration of dissolved S increased and decreased in about 30 min with passage of the NaOH pulse. Thus, metal sulfide oxidation was probably not a source of the dissolved S during the pulse.

Jarosite ($\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$) dissolution was unlikely to be a source of the dissolved S. Iron appears to precipitate as ferrihydrite ($\text{Fe}(\text{OH})_3(\text{am})$) in Fisher Creek, based on thermodynamic calculations and sediment analysis (Amacher and others 1991a, in press). Although MINTEQA2 calculations indicated that Fisher

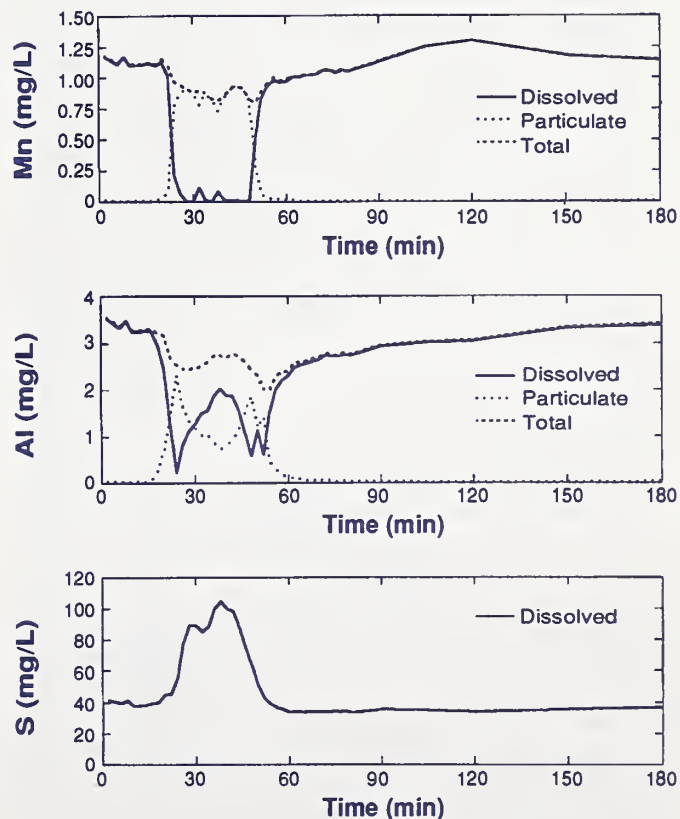


Figure 4—Concentrations of dissolved, particulate, and total Mn (top), Al (middle), and S (bottom) in Fisher Creek during the pH adjustment study.

Creek waters are supersaturated with respect to jarosite, no evidence of jarosite formation has been observed in Fisher Creek. The characteristic yellow color of precipitated jarosite has not been observed on streambed sediments, nor has X-ray diffraction analysis detected jarosite in the sediments. Jarosite apparently forms in streams with lower pH levels and higher SO_4 levels than those found in Fisher Creek (Nordstrom 1982).

Dissolved Na concentrations tracked the increase in pH associated with the NaOH pulse (fig. 5). Particulate Na was negligible; Na is not adsorbed by metal oxides (Sposito 1984).

The behavior of dissolved and particulate Mg was similar to that of Fe, Cu, Zn, and Mn (fig. 5). The precipitation of $\text{Mg}(\text{OH})_2$ (brucite) is expected to control the concentration of dissolved Mg at the pH levels observed during the NaOH pulse. Adsorption of Mg on ferrihydrite is not expected (Dzombak and Morel 1990).

Unlike the other cations, little particulate Ca was observed during the NaOH pulse (fig. 5). Also, total Ca showed the largest net loss from the stream water during the NaOH pulse. Adsorption of Ca by hydrous Fe and Al coatings on streambed sediments is the

most likely explanation for these results (Kinniburgh and Jackson 1981).

Precipitation of Hydrous Metal Oxides

Precipitation of hydrous metal oxides has been suggested as the most likely explanation for the decrease in dissolved metal concentrations and the increase in particulate metal concentrations associated with the NaOH pulse. Because these hydrous metal oxides are amorphous or have little structure, X-ray diffraction evidence of their existence during passage of the NaOH pulse is impossible to obtain. Instead, we compared ion activity products (IAP's) calculated from the experimental data by MINTEQA2 with equilibrium constants (solubility products, K_{sp}) for the various hydrous metal oxides under consideration.

Using the precipitation of ferrihydrite as an example, IAP's will be expressed in the following manner. The precipitation reaction for ferrihydrite is



The IAP for this reaction is

$$\text{IAP} = (\text{Fe}^{3+})(\text{OH}^-)^3 \quad (5)$$

and is thus defined as the product of the activities of the Fe^{3+} and OH^- ions. Equation (5) can also be expressed in terms of negative logarithms of the ionic activities:

$$p\text{IAP} = p\text{Fe}^{3+} + 3p\text{OH} \quad (6)$$

The $p\text{Fe}^{3+}$ and $p\text{OH}$ in equation (6) are analogous to pH. Because $p\text{Fe}^{3+}$ and $p\text{OH}$ are negative logarithms, as $p\text{Fe}^{3+} + 3p\text{OH}$ increases, the magnitude of the IAP actually decreases.

Close correspondence of IAP and K_{sp} for a given mineral indicates that the solid and solution phases are likely to be in equilibrium. When IAP is greater than K_{sp} , the solution is supersaturated for a given mineral; when the IAP is less than K_{sp} , the solution is undersaturated. These relationships are for pure mineral phases with standard state activities of 1. Comparison of IAP data with K_{sp} 's cannot prove if precipitation has occurred; it merely indicates the possibility a given phase will precipitate. Coprecipitation will produce solid phases with activities greater than or less than 1. Thus, a coprecipitated phase may form even when the IAP is less than the K_{sp} for the pure phase (Sposito 1984).

Enthalpy and equilibrium constant data for the most likely solids to precipitate during the NaOH pulse are listed in table 2. Because the water temperature differed from the reference temperature of 25 °C, the enthalpy data was used to correct equilibrium constants based on the van't Hoff equation.

One of the major problems of using equilibrium IAP calculations to determine possible solid phases is the accuracy of the thermodynamic databases. Equilibrium

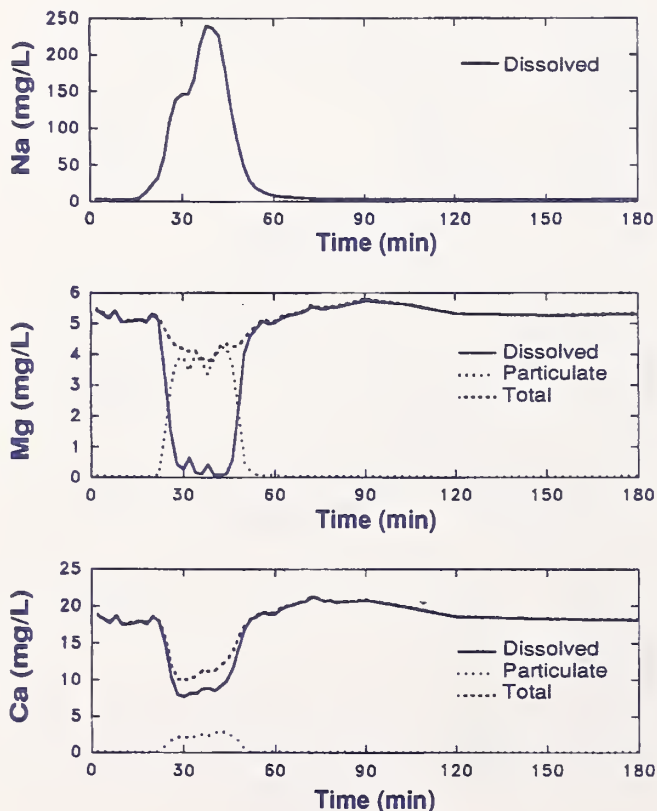


Figure 5—Concentrations of dissolved, particulate, and total Na (top), Mg (middle), and Ca (bottom) in Fisher Creek during the pH adjustment study.

Table 2—Thermodynamic data for possible solids precipitated from Fisher Creek during the pH adjustment study. The log *K* values are for a reference temperature of 25 °C (298 °K) and zero ionic strength

Mineral	Reaction	Nordstrom and others (1990)		MINTEQA2	
		ΔH_f° kcal/M	log <i>K</i>	ΔH_f° kcal/M	log <i>K</i>
Ferrihydrite	$\text{Fe}^{3+} + 3\text{H}_2\text{O} = \text{Fe}(\text{OH})_3(\text{am}) + 3\text{H}^+$	—	-3.0 to -5.0	—	-4.891
Al(OH) ₃ (am)	$\text{Al}^{3+} + 3\text{H}_2\text{O} = \text{Al}(\text{OH})_3(\text{am}) + 3\text{H}^+$	26.5	-10.8	27.045	-10.38
Gibbsite (microcrystalline)	$\text{Al}^{3+} + 3\text{H}_2\text{O} = \text{Al}(\text{OH})_3(\text{mcr}) + 3\text{H}^+$	24.5	-9.35	—	—
Gibbsite (crystalline)	$\text{Al}^{3+} + 3\text{H}_2\text{O} = \text{Al}(\text{OH})_3(\text{cr}) + 3\text{H}^+$	22.8	-8.11	22.8	-8.77
Jurbanite	$\text{Al}^{3+} + \text{H}_2\text{O} + \text{SO}_4^{2-} = \text{AlOHSO}_4 + \text{H}^+$	—	—	—	3.23
Pyrochroite	$\text{Mn}^{2+} + 2\text{H}_2\text{O} = \text{Mn}(\text{OH})_2 + 2\text{H}^+$	—	-15.2	22.59	-15.088
Cu(OH) ₂	$\text{Cu}^{2+} + 2\text{H}_2\text{O} = \text{Cu}(\text{OH})_2 + 2\text{H}^+$	—	—	15.25	-8.64
Tenorite	$\text{Cu}^{2+} + \text{H}_2\text{O} = \text{CuO} + 2\text{H}^+$	—	—	15.24	-7.62
Brucite	$\text{Mg}^{2+} + 2\text{H}_2\text{O} = \text{Mg}(\text{OH})_2 + 2\text{H}^+$	27.1	-16.84	25.84	-16.792
Portlandite	$\text{Ca}^{2+} + 2\text{H}_2\text{O} = \text{Ca}(\text{OH})_2 + 2\text{H}^+$	31.0	-22.8	30.69	-22.675

constants for the formation of a given solid phase may differ by orders of magnitude in various databases. When equilibrium constants may be inaccurate by several orders of magnitude, deducing the correct solid phases with them is extremely difficult, if not impossible.

Two sources were used for the thermodynamic data listed in table 2. Nordstrom and others (1990) compiled a consistent set of enthalpy and equilibrium constant data that appear to represent the best available constants to date. The applicable data are given in table 2. The corresponding constants used by MINTEQA2 are listed for comparison. In general, the Nordstrom and others (1990) and MINTEQA2 constants correspond within half an order of magnitude (within 0.5 log units). However, an equilibrium constant for the formation of a particular amorphous hydrous metal oxide may vary by several orders of magnitude because of: (1) the ill-defined nature of the solid phase, (2) the lack of a distinct boundary between particulate and dissolved phases because of the presence of colloidal particles, and (3) changes in the IAP as coagulation and crystallinity change with the age of the precipitate (Macalady and others 1990). Although the amorphous hydrous metal oxides tend to form first with rapid increases in pH, they are not the most thermodynamically stable phases. As the precipitates age, new crystalline solid phases are formed (goethite (FeOOH) forms from (Fe(OH)₃(am)), gibbsite (Al(OH)₃) forms from Al(OH)₃(am), tenorite (CuO) forms from Cu(OH)₂, etc.) (Stumm and Morgan 1981).

Hydrous Fe³⁺ oxides show the greatest variation in IAP. Freshly precipitated, amorphous, colloidal Fe(OH)₃ has IAP values (pFe³⁺+3pOH) ranging from 37 to 39, while more crystalline Fe oxides such as goethite have values of 43 to 44 (Macalady and others 1990). Recently, Macalady and others (1990) used

model-generated Fe³⁺ activity values to compute IAP values for Fe(OH)₃(am) (12 to 200 h after precipitation) and obtained a pFe³⁺+3pOH value of 38.3 ± 0.4 (mean ±1 standard deviation for all their experimental IAP values).

When the experimental IAP values from the Fisher Creek adjustment study are plotted with IAP values marking the upper and lower limits for Fe(OH)₃(am) given by Macalady and others (1990), it is apparent that Fe(OH)₃(am) controlled Fe³⁺ solubility during our pH adjustment study (fig. 6). Before the NaOH pulse arrived, pFe³⁺+3pOH values in Fisher Creek ranged from 39.5 to 40.1, indicating equilibrium with a mixture of Fe(OH)₃(am) and more crystalline Fe oxides (probably goethite). As the pulse arrived, Fe concentrations decreased to levels at or below the detection limits of the 2,2'-bipyridine and ICPAES methods, so reliable IAP's could not be calculated. At the end of the pulse, as the stream reacidified, reliable IAP values could again be calculated. Except for one value, they were within the range for Fe(OH)₃(am) indicated by Macalady and others (1990)—37.9 to 38.7. The IAP values increased with time as would be expected as the freshly precipitated Fe(OH)₃ aged. Even though the pH decreased fairly rapidly after the NaOH pulse had passed, Fe(OH)₃(am) apparently dissolved rapidly enough to remain near or at equilibrium with stream water. McKnight and Bencala (1989) also observed rapid changes in precipitation and dissolution of hydrous Fe oxide streambed sediment coatings after a pH adjustment study.

Figure 6 shows the observed pAl+3pOH values, together with the temperature-corrected pAl+3pOH values for amorphous Al(OH)₃, microcrystalline Al(OH)₃ (gibbsite), and crystalline Al(OH)₃ (calculated from the Nordstrom and others [1990] enthalpy and equilibrium constant data given in table 2). At the beginning

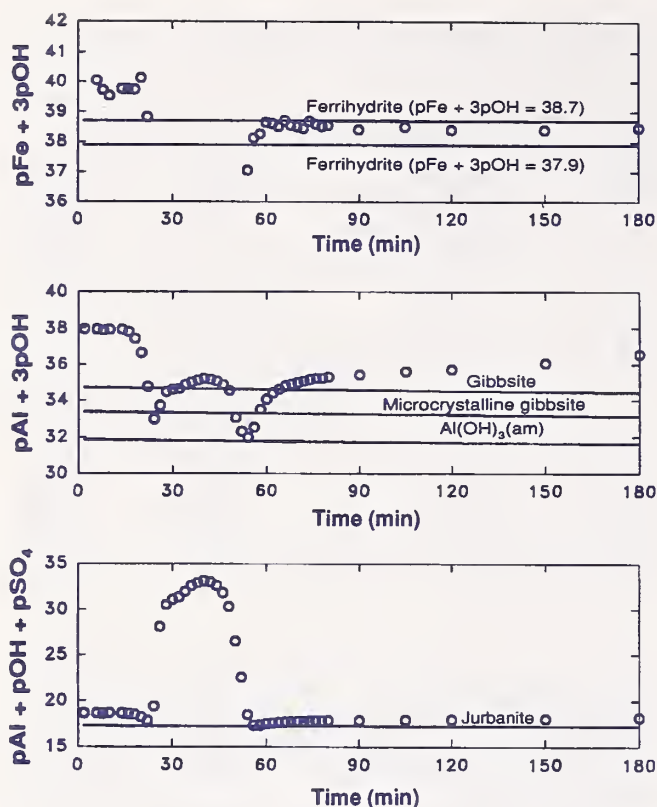


Figure 6—Ion activity products (IAP's) for possible Fe (top) and Al (middle and bottom) solid phases in Fisher Creek during the pH adjustment study. The open circles are IAP's calculated from the concentration data by MINTEQA2. The lines are equilibrium solubility limits of the indicated solids calculated from the thermodynamic data of table 2, except for ferrihydrite where the solubility limits were taken from Macalady and others (1990). Data points above a line indicate undersaturation with respect to that solid; data points below a line indicate supersaturation.

of the NaOH pulse, Al in the stream water became supersaturated with respect to gibbsite (both crystalline and microcrystalline). Gibbsite may have formed because dissolved Al decreased and particulate Al increased during this period. As the pH increased above 11, the Al solid phase began to redissolve, and the stream water became undersaturated with respect to gibbsite. After NaOH peaked, pH rapidly decreased and the stream water again was supersaturated with respect to gibbsite. Dissolved Al decreased and particulate Al increased during this period. Eventually, the pH decreased so far that the stream was undersaturated with respect to gibbsite again. Aluminum in the stream water increased as particulate Al dissolved. Our data track the gibbsite precipitation/dissolution scenario just presented, but it is unlikely that equilibrium with gibbsite was attained during the brief NaOH

pulse. Although formation of $\text{Al}(\text{OH})_3(\text{am})$ is kinetically more likely than gibbsite, the $\text{pAl}+3\text{pOH}$ values we observed were always greater than $\text{pAl}+3\text{pOH}$ for $\text{Al}(\text{OH})_3(\text{am})$, indicating undersaturation. However, the equilibrium constant for $\text{Al}(\text{OH})_3(\text{am})$ may not be very accurate. Also, bayerite (another form of $\text{Al}(\text{OH})_3$) reportedly forms at alkaline pH levels rather than gibbsite (Hem and Roberson 1990). Bayerite is only slightly more soluble than gibbsite (Apps and Neil 1990). Another possibility is precipitation of a mixed amorphous Fe-Al hydroxide with a different IAP than $\text{Al}(\text{OH})_3(\text{am})$. Mixed Fe-Al hydroxide gels are readily formed (Kinniburgh and Jackson 1981). Given the low likelihood a crystalline precipitate formed during the brief NaOH pulse, the formation of a mixed Fe-Al hydroxide gel seems the most likely explanation for the observed changes in concentrations of dissolved and particulate Al.

At the beginning and end of the NaOH pulse, the concentration of dissolved Al might have been controlled by precipitation and dissolution of jurbanite (AlOHSO_4). The experimental $\text{pAl}+\text{pOH}+\text{pSO}_4$ values were very near the IAP value for jurbanite (from the data of van Breemen [1973]) (fig. 6). However, while the pH was increasing or decreasing, Fisher Creek was undersaturated with respect to jurbanite. Furthermore, the lack of S in the particulate phase samples collected at the beginning and end of the NaOH pulse (fig. 4) argues against the precipitation of jurbanite. No direct evidence for formation of this phase was obtained.

Pyrochroite (MnOH_2) was the solid phase most likely to form at the highest pH levels during the NaOH pulse (fig. 7). The $\text{pMn}+2\text{pOH}$ values could not be obtained at the peak of the NaOH pulse because Mn concentrations were at or below the ICPAES detection limit (<0.01 mg/L). The temperature-corrected $\text{pMn}+2\text{pOH}$ line for pyrochroite was obtained using the enthalpy data from MINTEQA2 and the equilibrium constant from Nordstrom and others (1990) (table 2). MINTEQA2 calculations using the pH sweep feature revealed that the initial Mn concentration in the stream would be supersaturated with respect to pyrochroite at the highest pH levels obtained during the NaOH pulse. Oxidation of Mn^{2+} to Mn^{3+} or Mn^{4+} and formation of manganese oxides were not likely during the brief NaOH pulse. However, Fe oxides increase the oxidation rate of Mn^{2+} (Eary and Schramke 1990). Manganese may have coprecipitated with Fe.

The observed increase in dissolved Cu and the increase in particulate Cu might be explained by precipitation of $\text{Cu}(\text{OH})_2$. However, Fisher Creek was undersaturated with respect to $\text{Cu}(\text{OH})_2$ throughout the NaOH pulse, according to MINTEQA2 calculations (fig. 7). The MINTEQA2 calculations did indicate supersaturation with respect to tenorite (CuO)

Fisher Creek remained undersaturated with respect to $\text{Ca}(\text{OH})_2$ throughout the NaOH pulse (fig. 8).

MINTEQA2 Predictions of Dissolved Element Concentrations

The pH sweep feature of MINTEQA2 was used to calculate the amount of each element in dissolved, adsorbed, and precipitated phases as pH was systematically varied. The observed concentrations of dissolved Fe^{3+} and those predicted by MINTEQA2 are shown in figure 9. The concentrations of Fe^{3+} predicted by MINTEQA2 assumed ferrihydrite precipitated during the NaOH pulse. The equilibrium constant for ferrihydrite used by MINTEQA2 (table 2) predicts the observed Fe^{3+} concentrations fairly closely, especially at the end of the NaOH pulse. MINTEQA2 predicted that ferrihydrite would redissolve at the highest pH levels observed. Experimental data did

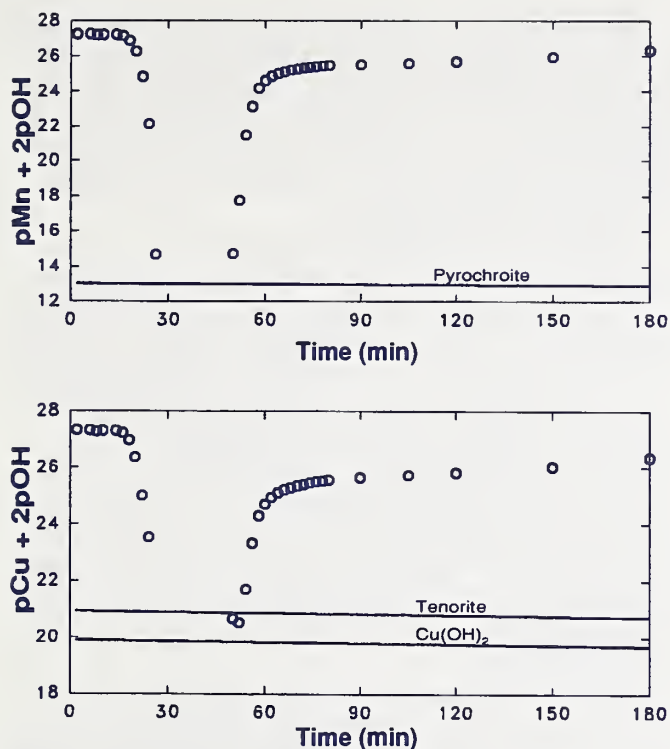


Figure 7—Ion activity products (IAP's) for possible Mn (top) and Cu (bottom) solid phases in Fisher Creek during the pH adjustment study. The open circles are IAP's calculated from the concentration data by MINTEQA2. The lines are equilibrium solubility limits of the indicated solids calculated from the thermodynamic data in table 2. Data points above a line indicate undersaturation with respect to that solid; data points below a line indicate supersaturation.

at the highest pH levels observed (fig. 7). Direct formation of this phase without $\text{Cu}(\text{OH})_2$ having formed first seems unlikely given the short duration of the NaOH pulse. Adsorption or coprecipitation of Cu by the $\text{Fe}(\text{OH})_3(\text{am})$ is a more likely possibility.

Brucite ($\text{Mg}(\text{OH})_2$) precipitation is most likely responsible for the observed decrease in dissolved Mg and increase in particulate Mg (fig. 8). The experimental $\text{pMg}+2\text{pOH}$ values agree with the temperature-corrected $\text{pMg}+2\text{pOH}$ line for brucite using the Nordstrom and others (1990) data from table 1. Kinetic considerations also argue for brucite precipitation (Stumm and Morgan 1981). No other solid phase would be likely to form during the short duration of the NaOH pulse. Evidently, this phase precipitates rapidly and dissolves rapidly, given the symmetry of the experimental $\text{pMg}+2\text{pOH}$ data (fig. 8).

Calcium was lost from solution during the pulse, but portlandite ($\text{Ca}(\text{OH})_2$) precipitation was not responsible.

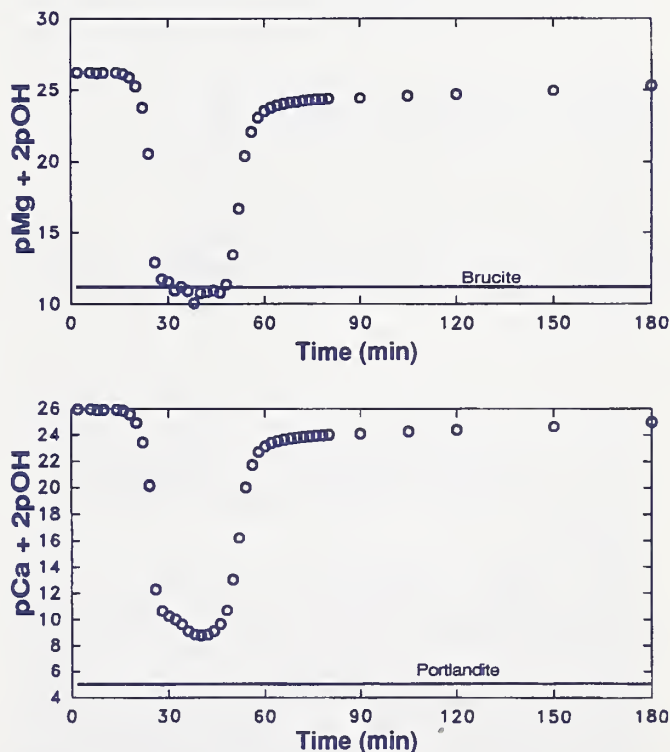


Figure 8—Ion activity products (IAP's) for possible Mg (top) and Ca (bottom) solid phases in Fisher Creek during the pH adjustment study. The open circles are IAP's calculated from the concentration data by MINTEQA2. The lines are equilibrium solubility limits of the indicated solids calculated from the thermodynamic data in table 2. Data points above a line indicate undersaturation with respect to that solid; data points below a line indicate supersaturation.

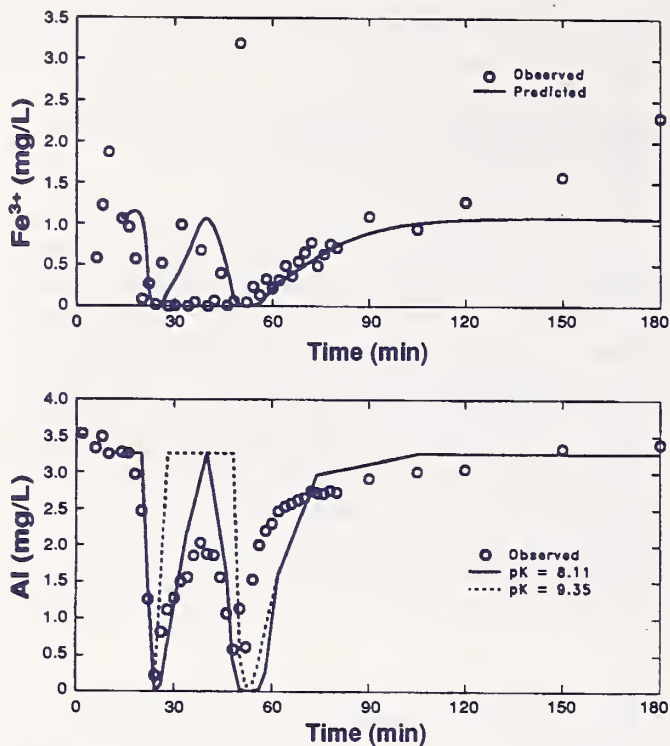


Figure 9—Observed and predicted (MINTEQA2) dissolved Fe^{3+} (top) and Al (bottom) concentrations in Fisher Creek during the pH adjustment study, assuming precipitation of ferrihydrite and gibbsite, respectively. The predictions of dissolved Al concentrations consider the possibility that two types of gibbsite might precipitate, crystalline ($\text{pK} = 8.11$) and microcrystalline ($\text{pK} = 9.35$).

not confirm this prediction (fig. 9). Kinetic constraints may have prevented ferrihydrite from dissolving during the brief period when the highest pH levels were observed.

MINTEQA2 correctly predicted the precipitation, dissolution, reprecipitation, and redissolution of Al during the NaOH pulse (fig. 9), but we do not know exactly which solid phases formed and how kinetic constraints affected precipitation and dissolution. It is unlikely that equilibrium between the Al solid phase and solution Al was maintained throughout the NaOH pulse. The lines predicted by MINTEQA2 are for two types of gibbsite, crystalline ($\text{pK} = 8.11$) and microcrystalline ($\text{pK} = 9.35$). The crystalline gibbsite line came closest to the data, but this phase was least likely to form during the brief NaOH pulse. Formation of amorphous $\text{Al}(\text{OH})_3$ or microcrystalline gibbsite was more likely, but these phases are too soluble to account for the observed Al concentrations. Thus, formation of a mixed Fe-Al hydroxide gel was the most likely possibility.

The concentrations of dissolved Mn and Mg predicted by MINTEQA2 agree well with the data (fig. 10). The predicted solubilities assumed precipitation of pyrochroite and brucite, respectively. Apparently these phases precipitated and dissolved sufficiently fast to be near or at equilibrium with the solution phase during the NaOH pulse.

Although MINTEQA2 predicted little Ca would be adsorbed by hydrous Fe^{3+} oxide, a substantial amount of Ca was associated with the particulate phase (fig. 11). MINTEQA2 predicted negligible adsorption of Ca, assuming all dissolved Fe at the beginning of the NaOH pulse precipitated as ferrihydrite and remained suspended in the stream water (12.3 mg/L as Fe_2O_3). Actual Ca concentrations associated with the particulate phase (fig. 5) were much higher than the line predicted by MINTEQA2 (fig. 11), indicating some other sorption mechanism besides adsorption by particulate hydrous Fe^{3+} oxide. Kinniburgh and Jackson (1981) reported that Ca is readily adsorbed by hydrous Al oxides at high pH.

More Ca was lost from the stream water than any other element, indicating sorption by streambed sediments. An additional MINTEQA2 simulation increased the concentration of particulate Fe by a factor of 10

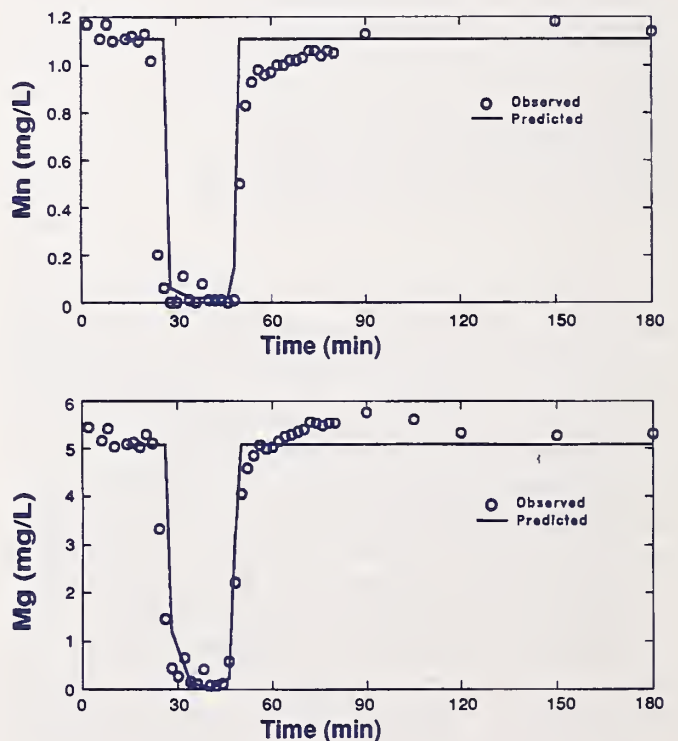


Figure 10—Observed and predicted (MINTEQA2) dissolved Mn (top) and Mg (bottom) concentrations in Fisher Creek during the pH adjustment study, assuming precipitation of pyrochroite and brucite, respectively.

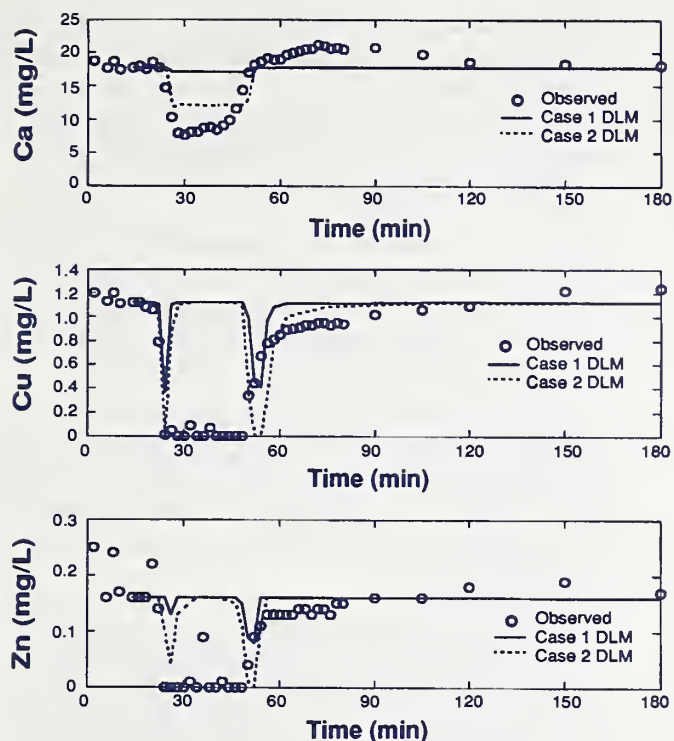


Figure 11—Observed and predicted (MINTEQA2) dissolved Ca (top), Cu (middle), and Zn (bottom) concentrations in Fisher Creek during the pH adjustment study, assuming adsorption by hydrous Fe^{3+} oxide. The diffuse-layer model (DLM) predictions are based on the assumption that total dissolved Fe in the stream precipitated as ferrihydrite (case 1 in table 1) or that adsorption also occurred on Fe^{3+} oxide coatings on streambed sediments (case 2 in table 1).

(123 mg/L as Fe_2O_3). This increased the predicted adsorption (fig. 11). There is no reliable way to determine the concentration of particulate Fe actually contributed by streambed sediments. It must be quite large, given the large amount of Ca removed from solution that cannot be accounted for in the suspended particulate phase (fig. 5). Thus, MINTEQA2 could give only a qualitative prediction of Ca adsorption by streambed sediments.

Adsorption predicted by MINTEQA2 failed to account for the decrease in dissolved Cu except at the beginning and end of the NaOH pulse (fig. 11). At the pH levels observed during the middle of the NaOH pulse, Cu was expected to desorb and appear in solution again. Because Cu concentrations remained at or below the ICPAES detection limit (<0.01 mg/L) throughout the NaOH pulse, some mechanism besides adsorption must have been operating. Since $\text{Cu}(\text{OH})_2$ precipitation could not account for the observed decrease in dissolved Cu, coprecipitation appears to be the only other plausible mechanism. As $\text{Fe}(\text{OH})_3(\text{am})$ began

to precipitate at the start of the NaOH pulse, Cu may have been adsorbed by the precipitating $\text{Fe}(\text{OH})_3(\text{am})$. As the pH increased further, Cu may have become trapped within the precipitating $\text{Fe}(\text{OH})_3(\text{am})$ amorphous gel and coprecipitated along with it. The diffuse-layer model predictions of Cu adsorption were more reliable at the beginning and end of the NaOH pulse, assuming all dissolved Fe precipitated (particulate $\text{Fe} = 12.3$ mg/L as Fe_2O_3), rather than during the pulse, when pH values were higher. Most of the Cu removed from solution could be accounted for in the suspended particulate Fe (fig. 3). Thus, if the pH of the stream could be adjusted and held in a range where Cu adsorption is maximized, virtually all the dissolved Cu should be removed by the freshly precipitated $\text{Fe}(\text{OH})_3(\text{am})$.

Adsorption predicted by MINTEQA2 also failed to account for the observed concentrations of dissolved Zn, except at the beginning and end of the NaOH pulse (fig. 11). As with Cu, Zn adsorbed by hydrous Fe^{3+} oxide was predicted to desorb at the highest pH levels during the middle of the NaOH pulse. Therefore, coprecipitation of Zn with $\text{Fe}(\text{OH})_3(\text{am})$ is the most plausible mechanism to account for the experimental results. MINTEQA2 calculations indicated that the stream water remained undersaturated with respect to $\text{Zn}(\text{OH})_2$.

Implications for Removing Metals From Streams Affected by Acid Mine Drainage

The pH levels reached during the NaOH pulse were substantially higher than the target pH range of 7 to 8.5. We added the NaOH solution too quickly. Further pH adjustment studies are planned on Fisher Creek. By adding NaOH more slowly, we can decrease the maximum pH attained during the NaOH pulse, providing a better test of the hypothesis that Cu can be rapidly removed by raising the pH to increase adsorption on $\text{Fe}(\text{OH})_3(\text{am})$. According to MINTEQA2 simulations, dissolved Al and Cu concentrations will be near zero in the target pH range of 7 to 8.5 because Al precipitates as $\text{Al}(\text{OH})_3$ and Cu adsorbs on $\text{Fe}(\text{OH})_3(\text{am})$. Aluminum and copper are the metals of most concern in Fisher Creek because they are potentially toxic to aquatic life. Dissolved Fe, Mn, and Zn concentrations will also be near zero. Dissolved Mg and Ca concentrations probably will not change much. Dissolved S will increase because S will desorb from the hydrous Fe oxides on streambed sediments. The increased S will have little impact on downstream waters because it will be diluted by flows from incoming tributaries that have low levels of S.

In practice, NaOH would not be used to neutralize AMD. The most feasible method would be to add alkalinity to the stream. Adding limestone rock to a stream affected by AMD would add alkalinity and

increase pH, but hydrous Fe oxides would eventually coat the limestone rock, effectively sealing it off from the stream waters. A better approach would be to add limestone rock to the channels of uncontaminated tributaries. These tributaries would increase the alkalinity of the stream affected by AMD, raising pH, precipitating hydrous Al and Fe oxides, and increasing the adsorption of Cu and Zn. Fisher Creek has numerous tributaries that add considerable quantities of water to the stream. In the upper stream reach affected by AMD, tributaries do not add significant alkalinity because they do not flow over calcareous rock strata. If the alkalinity of this upstream reach is increased, Cu will adsorb to the hydrous Fe³⁺ oxides coating the streambed sediments several hundred meters upstream from where Cu is now being adsorbed (Amacher and others 1992). This will confine the zone affected by AMD to the upstream portion of Fisher Creek, better protecting downstream waters by lengthening the buffer zone between areas affected by AMD and pristine stream reaches.

SUMMARY AND CONCLUSIONS

A pH adjustment study was conducted at Fisher Creek in southwestern Montana to determine the amounts of elements in dissolved and particulate phases during an NaOH pulse. Twenty liters of 10 M NaOH were added to Fisher Creek at the rate of 1 L/min. Water samples were collected periodically 280 m below the NaOH injection point and filtered through 0.2- μ m membrane filters. The filtrates and collected particulates were analyzed for Na, K, Mg, Ca, Mn, Fe, Cu, Zn, Al, and S by ICPAES. Water samples were also analyzed for Fe²⁺ and reactive Fe by the 2,2'-bipyridine colorimetric method. Temperature and pH were monitored continuously. MINTQA2, a chemical equilibrium speciation program, was used to determine the likelihood that various solid phases would form during the NaOH pulse. The results of this study lead to the following conclusions:

- Dissolved Fe³⁺ concentrations during the NaOH pulse were controlled by precipitation or dissolution of ferrihydrite (Fe(OH)₃(am)). Equilibrium between dissolved Fe³⁺ and ferrihydrite was maintained for most of the pulse.
- Precipitation or dissolution of some form of Al(OH)₃ or a mixed Fe-Al hydroxide gel appeared to be responsible for observed increases and decreases in dissolved and particulate Al during the NaOH pulse, but the nature of this phase could not be identified. Equilibrium between dissolved Al and Al(OH)₃ did not appear to be maintained.
- Dissolved Mn concentrations were controlled by precipitation or dissolution of pyrochroite (Mn(OH)₂) during the NaOH pulse.

- Dissolved Mg concentrations were controlled by precipitation or dissolution of brucite during the NaOH pulse.
- Dissolved Cu and Zn concentrations were controlled by coprecipitation with Fe(OH)₃(am) during the NaOH pulse.
- Changes in dissolved Ca concentrations could not be adequately accounted for by precipitation of Ca(OH)₂ or by adsorption by suspended particulate Fe. Adsorption by streambed sediments seems to be the likely alternative.
- Precipitation of hydrous oxides of Al and Fe and their adsorption of Cu and Zn occur rapidly enough to remove these metals from streams affected by AMD, but the pH must be maintained at optimum levels for maximum precipitation and adsorption.
- In practice, the best way to increase the pH of streams affected by AMD would be to increase the alkalinity of stream tributaries by adding limestone rock to tributary channels. The increased alkalinity would increase the pH in the affected stream, precipitate hydrous oxides of Al and Fe, and increase removal of Cu and Zn by adsorption. Limestone rock in stream channels affected by AMD would be ineffective because precipitating Fe oxides would coat the rock, sealing it from the stream water.

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APPENDIX A: WATER ANALYSIS DATA FOR pH ADJUSTMENT STUDY AT FISHER CREEK, MT, ON AUGUST 30, 1992

Time	Temp.	pH	Al	Ca	Cu	Fe ²⁺	Fe ³⁺	Reactive Fe ²⁺ + Fe ³⁺	Total Fe	Mg	Mn	Na	S	Zn
Min	°C		-----mg/L-----											
2	7.0	3.42	3.52	18.70	1.20	8.16	—	7.97	8.37	5.44	1.17	2.93	41.3	0.25
4	7.2	3.42												
6	7.3	3.42	3.33	17.66	1.13	6.86	.59	7.45	7.88	5.17	1.11	2.55	39.3	.16
8	7.4	3.42	3.48	18.66	1.20	6.82	1.22	8.04	8.29	5.42	1.17	2.70	41.2	.24
10	7.5	3.42	3.25	17.43	1.11	5.58	1.87	7.45	7.75	5.04	1.10	2.39	37.6	.17
12	7.6	3.41												
14	7.7	3.41	3.27	17.69	1.12	6.41	1.06	7.47	7.71	5.09	1.11	2.77	38.3	.16
16	7.8	3.45	3.26	17.93	1.12	5.73	.96	6.69	6.99	5.12	1.12	4.96	39.6	.16
18	7.9	3.58	2.97	17.54	1.08	4.06	.57	4.63	4.85	5.03	1.10	11.56	40.2	.16
20	8.1	3.88	2.47	18.58	1.06	1.91	.09	2.00	1.99	5.29	1.13	22.05	44.6	.22
22	8.2	4.61	1.26	17.73	.79	.32	.27	.59	.52	5.11	1.02	32.37	45.4	.14
24	8.3	6.32	.22	14.73	.01	.02	.02	.04	0	3.34	.20	59.94	55.2	0
26	8.4	10.34	.81	10.30	.05	.02	.52	.54	.42	1.46	.06	109.21	77.9	0
28	8.5	11.22	1.11	7.95	0	.04	0	.04	0	.43	0	138.66	89.3	0
30	8.7	11.42	1.27	7.64	0	.03	.01	.04	0	.26	0	145.39	88.8	0
32	8.7	11.53	1.50	8.12	.09	.02	.99	1.01	.94	.64	.11	145.45	85.1	.01
34	8.9	11.73	1.56	8.10	0	.11	—	.10	0	.15	.01	165.49	88.2	0
36	9.0	11.98	1.86	8.73	0	.04	.05	.09	0	.10	0	214.17	100.1	.09
38	9.1	12.10	2.03	8.84	.07	.02	.68	.70	.68	.41	.08	239.57	104.4	0
40	9.2	12.15	1.88	8.43	0	.13	—	.06	0	.07	.01	236.49	99.6	0
42	9.4	12.10	1.86	9.09	0	.02	.07	.09	.02	.07	.01	226.02	97.9	.01
44	9.4	11.93	1.56	9.88	0	.02	.40	.42	0	.11	.01	180.56	87.2	0
46	9.5	11.60	1.06	11.60	0	.05	.01	.06	0	.57	0	125.00	74.0	0
48	9.6	11.00	.58	14.44	0	.02	.06	.08	0	2.22	.01	81.84	62.7	0
50	9.6	9.78	1.13	17.00	.34	.03	3.19	3.22	3.32	4.05	.50	48.87	50.2	.04
52	9.8	8.14	.61	18.15	.44	.57	.05	.62	.59	4.58	.83	28.84	42.4	.09
54	9.8	6.25	1.53	18.63	.67	1.04	.24	1.28	1.10	4.84	.93	18.69	38.9	.11
56	9.8	5.39	2.01	19.11	.78	1.39	.14	1.53	1.50	5.07	.98	13.68	36.6	.13
58	10.0	4.90	2.20	18.86	.81	1.60	.33	1.93	1.98	4.99	.96	10.10	35.3	.13
60	10.1	4.67	2.30	18.95	.85	1.78	.22	2.00	2.06	5.02	.97	8.00	33.8	.13
62	10.2	4.54	2.47	19.61	.89	1.93	.32	2.25	2.31	5.15	1.00	6.79	34.2	.13
64	10.2	4.46	2.53	19.96	.90	2.04	.49	2.53	2.55	5.24	1.00	5.91	33.8	.13
66	10.3	4.40	2.57	20.19	.91	2.20	.37	2.57	2.70	5.28	1.02	5.33	34.1	.14
68	10.4	4.35	2.62	20.48	.93	2.26	.54	2.80	2.92	5.34	1.02	4.97	34.0	.14
70	10.5	4.32	2.65	20.60	.93	2.40	.65	3.05	3.11	5.39	1.03	4.55	33.9	.13
72	10.6	4.28	2.74	21.16	.95	2.37	.77	3.14	3.29	5.55	1.06	4.14	34.2	.14
74	10.7	4.25	2.72	21.00	.95	2.64	.49	3.13	3.30	5.53	1.06	3.85	34.3	.14
76	10.7	4.23	2.71	20.63	.93	2.59	.63	3.22	3.38	5.48	1.04	3.66	34.2	.13
78	10.8	4.22	2.75	20.73	.95	2.58	.75	3.33	3.51	5.53	1.06	3.62	34.5	.15
80	10.9	4.19	2.73	20.45	.94	2.68	.71	3.39	3.54	5.53	1.05	3.42	33.6	.15
90	11.3	4.13	2.93	20.74	1.02	2.95	1.09	4.04	4.07	5.76	1.13	3.31	35.6	.16
105	11.9	4.05	3.02	19.72	1.06	3.14	.94	4.08	4.29	5.61	1.25	3.12	34.9	.16
120	12.5	3.98	3.05	18.54	1.09	3.32	1.27	4.59	4.75	5.32	1.30	2.88	34.0	.18
150	13.2	3.82	3.33	18.26	1.22	4.23	1.57	5.80	5.85	5.26	1.18	2.87	35.5	.19
180	13.3	3.66	3.39	18.09	1.24	3.69	2.30	5.99	6.23	5.30	1.14	3.07	36.8	.17

**APPENDIX B: PARTICULATE ANALYSIS DATA FOR pH ADJUSTMENT STUDY
AT FISHER CREEK, MT, ON AUGUST 30, 1992**

Time	Temp.	pH	Al	Ca	Cu	Fe	Mg	Mn	Na	S	Zn
Min	°C		-----mg/L-----								
2	7.0	3.42	0.03	0.15	0.07	0.16	0.05	0.01	0.10	0.30	0.04
4	7.2	3.42									
6	7.3	3.42	.03	.09	.02	.29	.04	.01	.04	.20	.01
8	7.4	3.42	.01	.05	.01	.27	.01	0	.02	.10	.02
10	7.5	3.42	.03	.14	.01	.28	.05	.01	.01	.35	.01
12	7.6	3.41									
14	7.7	3.41	.02	.08	.01	.38	.03	.01	.01	.25	.01
16	7.8	3.45	.06	.07	.01	1.20	.03	.01	.01	.25	0
18	7.9	3.58	.25	.10	.03	3.72	.04	.01	.04	.70	0
20	8.1	3.88	.70	.09	.07	5.72	.04	.03	.08	1.00	.01
22	8.2	4.61	1.46	.15	.26	6.32	.10	.09	.23	1.15	.02
24	8.3	6.32	2.32	.96	.95	7.41	1.48	.77	.37	.50	.14
26	8.4	10.34	1.65	1.68	.89	7.37	3.00	.88	.70	.85	.12
28	8.5	11.22	1.34	2.10	.94	7.97	3.81	.92	.82	1.00	.13
30	8.7	11.42	1.19	2.23	.93	7.94	3.93	.89	1.06	1.10	.13
32	8.7	11.53	1.02	2.03	.82	7.12	3.46	.78	1.49	1.10	.11
34	8.9	11.73	1.04	2.38	.91	7.97	3.96	.87	.89	.95	.13
36	9.0	11.98	.88	2.46	.85	7.52	3.77	.83	.80	.85	.13
38	9.1	12.10	.72	2.29	.75	6.55	3.35	.73	.98	.80	.11
40	9.2	12.15	.81	2.73	.86	7.60	3.83	.84	1.01	.85	.12
42	9.4	12.10	.93	2.87	.95	8.21	4.19	.90	1.06	.80	.14
44	9.4	11.93	1.16	2.76	.97	8.47	4.24	.93	1.39	1.10	.13
46	9.5	11.60	1.55	2.25	.96	8.47	3.67	.92	.48	.70	.13
48	9.6	11.00	1.86	1.64	.88	7.86	2.06	.82	.81	.80	.12
50	9.6	9.78	1.19	.41	.46	4.24	.45	.29	.12	.15	.06
52	9.8	8.14	1.42	.08	.27	5.98	.19	.06	.07	.75	.02
54	9.8	6.25	.45	.06	.08	3.98	.08	.03	.04	.55	0
56	9.8	5.39	.28	.07	.05	4.48	.06	.02	.03	.60	0
58	10.0	4.90	.19	.24	.04	3.72	.09	.02	.11	.85	0
60	10.1	4.67	.09	.12	.01	2.51	.05	.01	.05	.55	0
62	10.2	4.54	.12	.20	.04	3.33	.08	.02	.06	.70	.01
64	10.2	4.46	.08	.07	.01	2.94	.03	.01	.01	.50	0
66	10.3	4.40	.05	.04	.01	2.42	.03	.01	.01	.35	0
68	10.4	4.35	.05	.05	.02	2.26	.03	.01	.01	.25	0
70	10.5	4.32	.04	.09	.02	2.25	.04	.01	.01	.40	0
72	10.6	4.28	.06	.19	.01	2.51	.05	.01	.21	.45	.01
74	10.7	4.25	.04	.05	.01	2.78	.03	.01	0	.35	0
76	10.7	4.23	.03	.06	0	1.82	.03	.01	.01	.40	0
78	10.8	4.22	.04	.07	.01	2.19	.04	.01	.01	.35	0
80	10.9	4.19	.03	.15	.01	1.75	.04	.01	.02	.45	0
90	11.3	4.13	.03	.11	.02	1.68	.04	.01	.01	.35	.01
105	11.9	4.05	.02	.07	.02	1.50	.02	0	.01	.35	0
120	12.5	3.98	.02	.05	.01	1.07	.01	0	0	.25	0
150	13.2	3.82	.02	.05	.01	.29	.02	0	.01	.10	0
180	13.3	3.66	.03	.13	.01	.31	.04	.01	.02	.25	0

Amacher, Michael C.; Brown, Ray W.; Kotuby-Amacher, Janice; Willis, Angelee. 1993. Adding sodium hydroxide to study metal removal in a stream affected by acid mine drainage. Res. Pap. INT-465. Ogden, UT: U.S. Department of Agriculture, Forest Service, Intermountain Research Station. 17 p.

Fisher Creek, a stream affected by acid mine drainage in the Beartooth Mountains of Montana, was studied to determine the extent to which copper and zinc would be removed from stream water when pH was increased by a pulse of sodium hydroxide. As stream pH increased, copper and zinc were rapidly and completely removed from stream water by adsorption or coprecipitation with freshly precipitated hydrous ferric oxide. In practice, the best way of increasing the pH of streams impacted by acid mine drainage would be to increase the alkalinity of tributaries by lining their channels with limestone rock.

KEYWORDS: chemical precipitation, adsorption, pH, copper, zinc



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