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CHAPTER 20. EXTREME ACID MINE DRAINAGE FROM A PYRITIC MASSIVE SULFIDE DEPOSIT: THE IRON MOUNTAIN END-MEMBER

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INTRODUCTION

The mining of pyritic massive sulfide deposits at Iron Mountain has led to the formation of some of the most concentrated acid mine drainage ever recorded. Prior to remediation, the minesite was the source of thousands of kilograms of dissolved Cu, Zn, and Cd, which each year were transported to the Sacramento River, an ecologically sensitive water body that hosts several threatened and endangered species of anadromous fish, including steelhead and winter-run Chinook salmon. Scientific and engineering studies since the early 1980s have provided the basis for on-site remediation activities, which have substantially improved water quality in the receiving waters.

In this chapter, we provide an overview of the mining history and environmental setting at Iron Mountain, describe regulatory and remediation milestones, and provide details of the site characterization. Iron Mountain, before mining, contained about 20.5 Mt (million tonnes) of ‘massive sulfides’, *i.e.*, large masses of pyrite and other sulfide minerals in a host rock composed primarily of rhyolite. Mining opened up these pyritic masses to water and air and created the optimal conditions for pyrite oxidation and production of acid mine drainage: (1) unlimited air permeability, (2) sufficient water permeability, (3) pyrite masses fractured over a wide range of scale, and (4) lack of significant neutralizing capacity by gangue minerals or the host rock.

Although Iron Mountain is in some respects a “worst-case scenario” with regard to the formation of acid mine drainage, the extreme conditions have provided a useful laboratory for improving the understanding of hydrogeochemical, mineralogical, and microbiological processes that affect mine-drainage geochemistry. Some of the hydrogeochemical and mineralogical characteristics observed on a large scale at Iron Mountain can be expected to occur on a more localized scale in other mine-drainage and mine-waste environments.

PHYSICAL SETTING

Geology and mineralization

Iron Mountain is in Shasta County, California, approximately 14 km northwest of the town of Redding (Fig. 1) in the southern part of the Klamath Mountains. The massive sulfide deposits at Iron Mountain comprise the southernmost deposits in the West Shasta mining

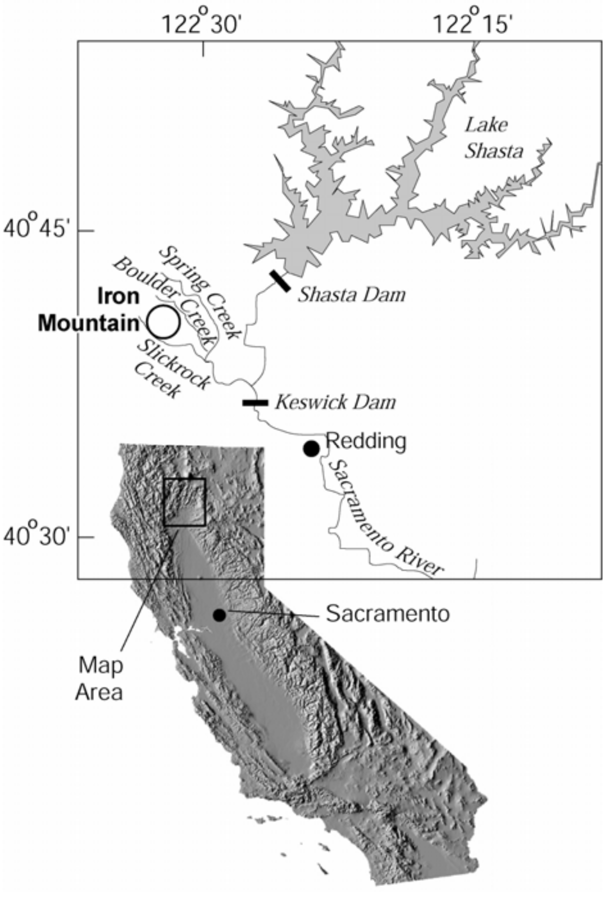

FIG. 1. Map showing the location of Iron Mountain, California (adapted from Nordstrom *et al*. 1999).

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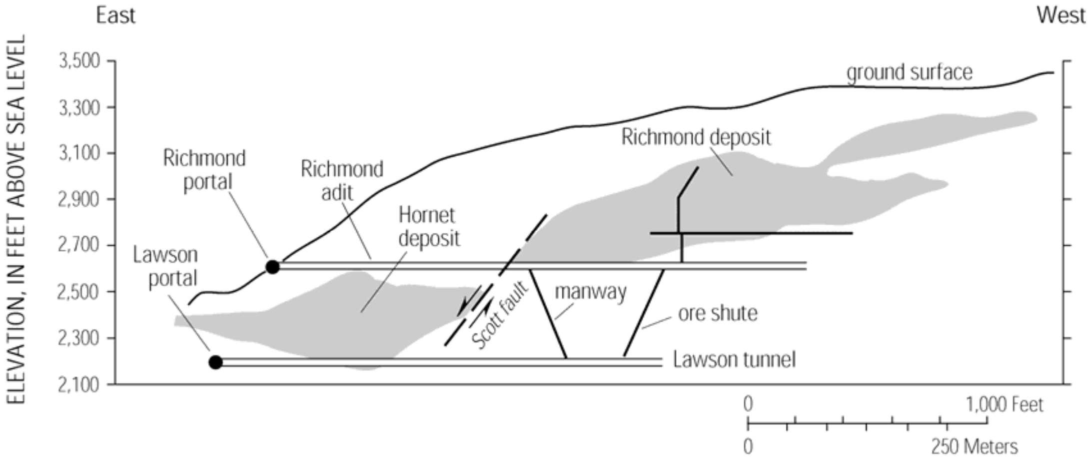

FIG. 2. Cross-section through Iron Mountain, showing massive sulfide deposits and portals draining to Boulder Creek (adapted from Alpers *et al.* 1992).

district (Kinkel *et al.* 1956). The mineral deposits are primarily massive sulfide lenses as much as 60 m thick, containing up to 95% pyrite with variable amounts of chalcopyrite and sphalerite, and averaging about 1% Cu and about 2% Zn. Secondary enrichment in the upper zones of the massive sulfides resulted in high concentrations of Cu (5–10%) and Ag (about 27 g t^{-1}). This enrichment took place at or near the water table during gossan formation. The three largest massive sulfide orebodies, the Brick Flat, Richmond, and Hornet deposits, contain most of the oxidizing sulfides causing the current water-quality problems. These orebodies originally constituted a single massive sulfide body at least 1.4 km long, up to 300 m wide, and more than 60 m thick, that was offset by normal faults (Fig. 2). All three of these orebodies have been mined, causing large changes in the hydrogeology and resulting in highly contaminated waters associated with tunnels, tailings, and waste-rock piles. Some disseminated sulfides occur along the south side of Iron Mountain.

The volcanogenic massive sulfide (VMS) deposits of the West Shasta mining district are Devonian in age and have been classified as Kuroko type, having been formed in an island-arc setting in a marine environment (Albers & Bain 1985). The low Pb content and the lack of clastic sediments in the host-rock section suggest that the deposits of the West Shasta mining district share some important characteristics with the “type 1” VMS deposits of Franklin *et al.* (1998) and the “bimodal-mafic” category of Barrie & Hannington (2000), which are associated with arc-related rifts and bimodal volcanic sequences with a moderate felsic component. Other examples of “type 1” VMS deposits given by Franklin *et al.* (1998) and “bimodal-mafic” deposits given by Barrie & Hannington (2000) are the Noranda (Quebec), and Flin Flon (Manitoba) deposits.

The host rocks at Iron Mountain are the Balaklala Rhyolite and the Copley Greenstone formations. These two units have undergone keratophyric alteration and regional metamorphism during submarine burial and episodic accretion of oceanic crust to the continent. The brittle, fractured nature of the altered volcanic bedrock gives rise to a hydrologic conditions dominated by fracture flow at Iron Mountain. The mineral composition of the altered rhyolite is albite, muscovite–illite (‘sericite’), quartz, kaolinite, epidote, chlorite, and minor calcite; consequently, the assemblage has little acid-buffering capacity. Kinkel *et al.* (1956), Reed (1984), and South & Taylor (1985) have documented the chemical and isotopic compositions of ore, gangue, and host-rock minerals in the West Shasta mining district.

The bedrock in the Iron Mountain area has been subjected to normal faulting, but other deformation has been minimal. The well-preserved structural features of the massive sulfide deposits allow geological reconstruction within uncertainties that prove to be useful in the context of estimating natural pre-mining baseline conditions.

Physiography, climate, and surface hydrology

The summit of Iron Mountain is at an elevation of 1097 m above sea level. The area is drained by Slickrock Creek to the south and Boulder Creek to the north (Fig. 1). Both of these creeks drain into Spring Creek, which flows into Keswick Reservoir, an afterbay to Shasta Lake in the Sacramento River system (Figs. 1, 3). Shasta Dam was constructed during 1938–45, and Keswick Dam in 1941–50. The Central Valley Project, initiated in 1937, included a significant water transfer from the Trinity River watershed to the Sacramento River system in the early 1960s. The transferred water

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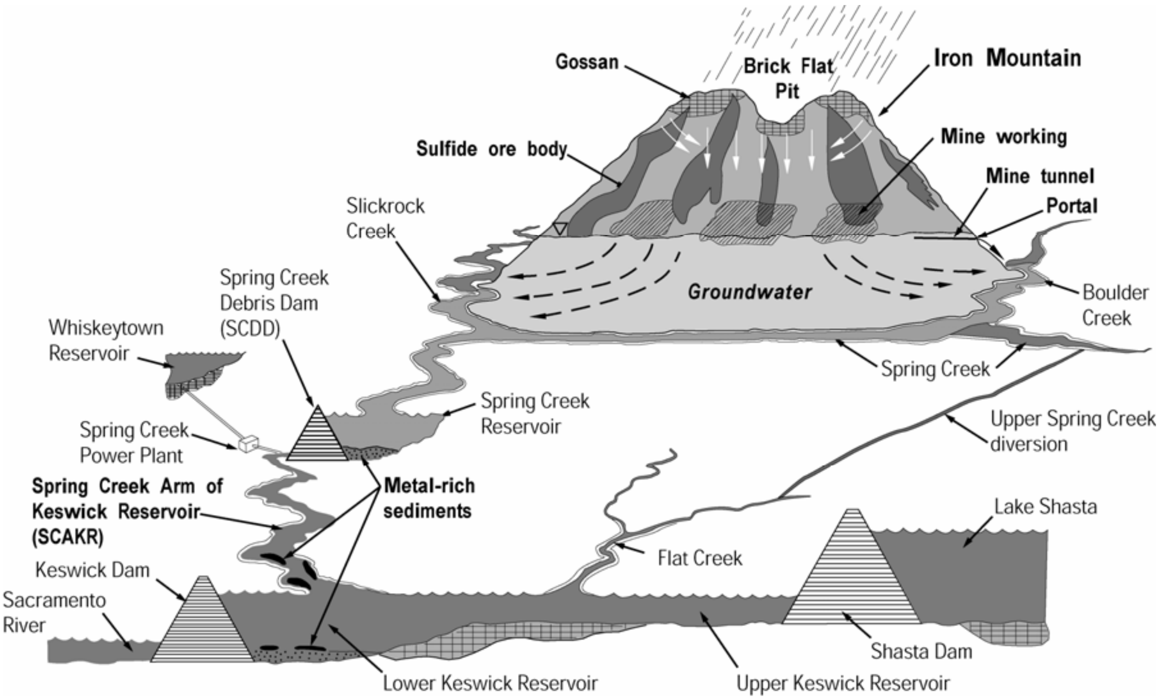

FIG. 3. Schematic diagram showing metal and acid source regions at Iron Mountain and downstream transport pathways to the Sacramento River.

flows into Keswick Reservoir through the Spring Creek Power Plant (SCPP), which receives the water through penstocks originating at the end of a tunnel from Whiskeytown Lake (Figs. 1 and 3).

Rainfall patterns in the Iron Mountain area vary locally because of strong orographic effects. Long-term average rainfall annually ranges from 50 to 60 cm at Redding, 90 to 100 cm at Shasta Dam, and 178 cm at Iron Mountain. A maximum annual rainfall of 338 cm was recorded in 1983. Snow falls every few years at higher elevations on the mountain (typically at elevations >800 m above sea level), but the majority of precipitation is rain. The Mediterranean climate is characterized by a wet season, typically from November through May, and a dry season from May through October. During the period 1893–1996, the monthly average temperature in Redding ranged from 7.5 ºC in January to 27.9 ºC in July, with an annual average mean of 17.8 ºC.

Mining history

'Iron Mountain mine' is really a group of mines within Iron Mountain that includes Old mine, No. 8 mine, Confidence–Complex mine, Mattie mine, Richmond and Richmond Extension mines, Hornet mine, and Brick Flat mine. Brick Flat was mined by open-pit methods whereas the others were primarily underground workings. The commodities Ag, Au, Cu, Fe, Zn, and pyrite (for production of sulfuric acid) were recovered at various times, beginning with the discovery of gossan in the early 1860s and the onset of underground mining in the 1890s, and ending with open-pit mining that ceased in 1962. A brief history of mining, water management, and environmental activities at Iron Mountain is outlined in Table 1.

The mines at Iron Mountain were the largest historical producers of Cu in the state of California. A total of 6.8 Mt of sulfide ore was mined at Iron Mountain, and remaining reserves are estimated at approximately 13.5 Mt (Kaiser Engineering 1981). Weathering of massive sulfide deposits at and near the surface has given rise to large gossan outcrops, enriched in Ag and Au. The 9 Mt of gossan in place prior to mining is the residue from at least 14 Mt of massive sulfide that weathered naturally. Thus, the overall size of the massive sulfide deposit prior to weathering was at least 34 Mt.

During the early stages of mining by the Mountain Copper Company, Ltd. (1897–1907) several smelters were active in the lower part of the Spring Creek drainage, near the town of Keswick and the present site of Keswick Dam (Fig. 1). In 1902, the Mountain Copper Company was sued by the U.S. Forest Reserve because of vegetation damage in the area. After 1907,

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TABLE 1. BRIEF CHRONOLOGY OF MINING AND ENVIRONMENTAL ACTIVITIES AT IRON MOUNTAIN, CALIFORNIA

1860s	Discovery of massive gossan outcropping
1879	Silver discovered in gossan and mining begins
1895	Copper sulfide ore discovered below gossan in Old mine workings
1896	Underground mining begins; ore is shipped to Keswick smelter via an 18 km, narrow-gauge railway
1898–1904	U.S. Forest Reserve sues company for vegetation damage from smelting activities
1907	Local smelting at Kewsick is phased out and ore is henceforth transported to Martinez (California) for processing
1907	No. 8 orebody discovered below Old mine; Hornet mine opened on Boulder Creek
1914	Minnesota flotation mill constructed; first flotation plant in California
1920–43	Crushing and screening plant operated near Hornet mine
1928–42	Gossan mined by open-pit method (Brick Flat pit); ore treated at cyanide plant on Slickrock Creek to extract gold and silver
1931	Minnesota Mill closed
1928	California Fish and Game Commission files complaint regarding tailings dam
1939	State initiates studies of water quality and fish toxicity
1943	Shasta Dam, upstream from Iron Mountain outflows, is completed
1944	Copper cementation plant built on Boulder Creek to remover Cu from water discharging from Richmond and Lawson (Hornet mine) portals
1950	Keswick Dam, downstream from Iron Mountain outflows, is completed
1955	Large landslide from mine waste pile filled Slickrock Creek canyon to depth of 24 m, covering portals to Old mine and No. 8 mine
1955–62	Open-pit mining of pyrite at Brick Flat for sulfuric acid production
1963	Spring Creek Debris Dam is completed, regulating outflow of acid mine waters to the Sacramento River
1967	Stauffer Chemical Company acquires property
1976	Iron Mountain Mines, Inc. acquires property
1976–82	State of California fines owners for unacceptable releases of metals
1977	Copper cementation plant constructed on Slickrock Creek to remover Cu from water discharge and Old/No. 8 mine seep
1983	Iron Mountain listed on National Priorities List (NPL) for EPA Superfund, ranking as the third largest polluter in the State of California
1986–97	Four Records of Decision by EPA have instituted several remedial activities that include partial capping, surface-water diversions, tailings removal, and lime neutralization treatment of the most acidic, metal-rich flows, reducing Cu and Zn loads by 80–90%
2000	Settlement of litigation between EPA and Aventis CropSciences Inc. and Stauffer Management Co. (corporate successors to Mountain Copper Ltd. and Stauffer Chemical Co.)
2002–03	Implementation of additional remedial activities by EPA, including diverting and treating water from Slickrock Creek, bringing overall load reduction of Cu and Zn by 95%

ore was shipped to Martinez, California, for smelting.

Underground mining began in the Slickrock Creek drainage on the south side of Iron Mountain in the area of the Confidence–Complex, Old, and Number 8 mines. Early reports (Kett 1947) of Cu-rich water flowing in the Confidence–Complex mine tunnels indicated that scrap iron may have been used to produce cement copper. By 1915, copper cementation was being used on the Hornet mine water (Kett 1947). The Richmond orebody was discovered about 1915 but it was not mined on a large scale until the late 1920s and the World War II period (1943–47). The Richmond and Hornet underground mines were developed via adits from the north side of Iron Mountain, in the Boulder Creek drainage (Figs. 1, 2). The Richmond Extension mine was developed during the 1940s in a Zn-rich part of the deposit. The Brick Flat open-pit mine near the top of Iron Mountain yielded pyrite for sulfuric acid production between 1955 and 1962.

Once the Richmond haulage tunnel and accompanying drifts were opened, the groundwater table would have dropped in the vicinity of the mine, and air would have easily entered the mine. Mining of the Richmond deposit stopped in 1954. In 1944 a copper cementation plant was built adjacent to Boulder Creek to remove Cu from the combined Richmond and

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Hornet mine effluents. A second copper cementation plant was constructed in 1977 adjacent to Slickrock Creek to remove Cu from the Old/No. 8 mine seeps. A new plant was constructed on Boulder Creek in 1958. The copper-cementation plants were operated through 1994 for economic metal recovery and for reducing environmental impacts resulting from AMD discharges from Iron Mountain. Several proposals for metal recovery from the concentrated mine drainage have been made, but none has been considered technically or economically feasible.

ENVIRONMENTAL HISTORY

Concern with environmental consequences of mining in Shasta County began at the end of the 19th century, soon after mining began. Smith (1902) documented fish kills in the Sacramento River near Redding from the mining activities at Iron Mountain during 1899–1900. During 1902–08, several private lawsuits and an injunction from the U.S. Forest Reserve (precursor to the Forest Service) were served against Mountain Copper Company for severe air pollution from open-air heap roasting (1897–98) and smelters (1898–1907) which denuded the vegetation for 14.4 km south, 5.6 km north, 3.6 km west, and at least 8 km east of the smelters at Spring Creek.

Because of a serious drop in the price of copper and the onset of the Great Depression there was little mining for Cu during the late 1920s and through the 1930s, and little on the environmental aspects seems to have been recorded. Mining for pyrite in the Richmond mine continued during this period. On the Slickrock Creek side of Iron Mountain, approximately 2.3 Mt of gossan were mined from 1929 through 1942 by the open-pit method and were treated at a cyanide plant to extract gold and silver. This mining left several hundred thousand cubic metres of highly erodable As-laden tailings adjacent to Slickrock Creek. Beginning with a 1939 survey by Shaw (1940) of Cu concentrations, pH, and discharges of acid mine waters entering the Sacramento River in Shasta County, the California Department of Fish and Game (CDFG) made several studies of the aquatic toxicity and fish kills. Prior to 1939, the scale of mining and the amount of acid discharge was not as great as it was after WWII because the main excavation of the Richmond mine had not yet been accomplished. In 1942, construction at the spillway site of Shasta Dam was such that it became an impassable barrier to fish migration.

Keswick Dam was completed in 1950 and the reservoir that formed behind it became the site of neutralization for the acid mine waters as well as the large amounts of debris discharging from Iron Mountain through Spring Creek. The debris and the chemical precipitation of metals from the acid waters began depositing rapidly in Keswick Reservoir. Prokopovich (1965) estimated that for the 10-year period 1950–60, a delta formed that was 838 m long, 60–140 m wide, and up to 12 m deep. The total volume of sediment was estimated at 574,000 m^3 or 0.5–1.0 × 10^9 kg, depending on water content. Patrick *et al.* (1956) demonstrated the extreme toxicity of the Spring Creek waters and the sediments deposited in Keswick Reservoir to aquatic biota.

A major flush-out event caused by heavy rains in 1955 led to a massive fish kill, prompting the CDFG and the Regional Water Quality Control Board (Central Valley Region) to study the problem in more depth. A contract was let to the Philadelphia Academy of Natural Sciences, whose report was completed in the summer of 1956 (Patrick *et al.* 1956). Also in 1955, a large waste-rock pile failed on the south side of Iron Mountain, causing a landslide that covered the mine portals of the old workings in that area and filled part of the channel of Slickrock Creek to a depth of about 27 m.

In 1963, Spring Creek Debris Dam (SCDD) was built by the Bureau of Reclamation for the dual purposes of preventing debris from accumulating in area of the tailrace of the SCPP and to regulate the release of acid mine drainage from the SCDD into Keswick Reservoir (Fig. 3). Despite this mitigation, since 1963 more than 20 fish-kill events have occurred in Sacramento River receiving waters below Keswick Dam, with at least 47,000 trout killed during a single week in 1967 (Nordstrom *et al.* 1977). The fish-kill events were apparently related to uncontrolled flow of acid mine drainage over the spillway of the SCDD. The SCDD was built with a design capacity of 7.3×10^6 m^3. The SCDD is designed to release about 19 m^3 sec^{-1} through adjustable gates. During intense rainfall events, the controlled releases are sometimes insufficient to keep the SCDD from filling and spilling.

Detailed studies beginning in the 1970s have demonstrated that Iron Mountain produces some of the most acidic waters in the world (Nordstrom 1977, Nordstrom & Alpers 1999a, Nordstrom *et al.* 2000). Prior to the initiation of the major remediation efforts in the late 1980s, approximately 2300 t of pyrite weathered every year from the Richmond mine alone, and each year about 270 t of dissolved Cd, Cu, and Zn drained from the site into the Sacramento River system (Nordstrom & Alpers 1999a).

Since the completion of Keswick Reservoir in 1950, deposits of metal-rich sediment have accumulated in the Spring Creek Arm of Keswick Reservoir (SCAKR). These sediments consist primarily of hydrous Fe and Al oxides that have formed by the mixing of acidic water from Spring Creek with neutral receiving waters. The sediments and their porewaters have been determined to be toxic to aquatic life, resulting in a paucity of benthic organisms in the

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affected part of Keswick Reservoir.

The city of Redding (with approximately 85,000 residents as of 2001) receives its drinking water from the Sacramento River, downstream from the Iron Mountain site (Fig. 1). An uncontrolled release of Iron Mountain acid mine drainage could potentially threaten the quality of the drinking-water supply. Redding has a contingency plan to use groundwater until metal concentrations in the Sacramento River are suitable.

A memorandum of understanding (MOU) between federal and state agencies in January 1980 established the short- and long-term actions and responsibilities of the regulatory and water-control agencies with regard to minimizing toxicity problems in the vicinity of Spring Creek. The MOU set release schedules and water-quality criteria (to be enforced at a compliance point in the Sacramento River below Keswick Dam), established a monitoring program, and outlined the need for further bioassay tests and modification to the Spring Creek Debris Dam.

Threatened and endangered species of fish, including steelhead trout and winter-run Chinook salmon, have critical habitat and spawning grounds below Keswick Dam. Metal concentrations of SCDD outflow were monitored with the goal of maintaining an appropriate dilution factor with water from Shasta Dam and from Whiskeytown Lake via the SCPP to achieve water-quality criteria at the compliance point. This approach failed occasionally during the 1980s because Spring Creek Reservoir had insufficient capacity to contain the AMD from Iron Mountain, and metal concentrations were too elevated for the available dilution flows.

Copper cementation was utilized from the mid-1940s through the early 1990s to reduce Cu concentrations from the most acidic drainage. When operated effectively, this method removed 80 to 95% of the Cu from the effluent from the Richmond and Hornet mine tunnels, which made up about 80% of the total Cu loading from the minesite. Removal of Cu from the Old/No.8 mine seeps averaged about 50 to 80%. The copper cementation process also increased the Fe concentrations in Boulder, Slickrock, and Spring creeks, contributing to massive growth of bacterial slime and thick deposits of Fe precipitates, including jarosite and hydrous ferric oxides (Nordstrom 1977). Copper cementation had little to no effect on Zn and Cd concentrations.

Superfund investigations and remediation

In 1980, the Comprehensive Environmental Response, Compensation and Liability Act (CERCLA), also known as the Superfund Act, was signed into law. The Superfund Act tasked the U.S. Environmental Protection Agency (EPA) with compiling a prioritized list (the National Priority List, or NPL) of the nation's most polluted sites, and those with the most significant harmful effects on human health and the environment. In the initial ranking of 1983, Iron Mountain was the designated as the third-highest ranked site in California, and one of the highest ranked minesites in the country. Remedial investigations began that same year with an oversight review committee that included state and federal agency representatives.

The EPA issued its first Record of Decision (ROD 1) in 1986, leading to several interim remedial actions (USEPA 1986). A condensed version of the main remedial alternatives that were considered is as follows:

- No action
- Surface-water diversion
- Lime neutralization
- Capping (partial or complete capping of the mountain to prevent infiltration)
- Enlargement of Spring Creek Debris Dam (acid water storage and release structure)
- Groundwater interception
- Air sealing
- Mine plugging
- On-site leaching and solution extraction
- Continued mining under environmentally safe conditions
- Combined alternatives

As a result of ROD 1, Brick Flat Pit and several caved-ground areas on Iron Mountain were capped. Pyritic tailings from the Minnesota Mill site were removed, deposited in the Brick Flat Pit, and capped. The Richmond adit was rehabilitated to allow evaluation of the condition of the underground mine workings.

To increase the efficiency of Spring Creek Reservoir, a major diversion of upper Spring Creek was constructed in 1990. Approximately 40 percent of the Spring Creek watershed was diverted above the confluence with contaminated Boulder Creek; the diversion flows into Flat Creek, which flows into Keswick Reservoir about 1 km upstream of the Spring Creek Arm (Fig. 3). This diversion has resulted in less frequent spills from Spring Creek Reservoir and more efficient operational control of the reservoir. A diversion of Slickrock Creek around the waste-rock landslide area and the buried Old/No. 8 mine portals ("Big Seep") was constructed during 1988–89 in an attempt to reduce metal loads by minimizing leaching of the mine wastes by creek water.

A temporary lime-neutralization water-treatment plant was operated during EPA investigations (winter months of 1989–1994) to treat the effluent from the Richmond and Hornet mines. In 1992, EPA issued its second Record of Decision (ROD 2), which selected construction of a permanent lime-neutralization treatment plant to treat discharges from the Richmond and Lawson portals (USEPA 1992). Several kilometres

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of pipeline were constructed to convey the effluent from these mine portals to the permanent treatment plant, which came online during 1994. The plant was upgraded to utilize a high-density sludge (HDS) process in 1995. The HDS plant greatly increased the efficiency of the water-treatment operation and reduced sludge production by about 60 percent, with a corresponding reduction in sludge haulage costs. An additional benefit of the HDS process at this site is that it will extend the time period for which the Brick Flat pit can be used for sludge disposal to about 100 years and, because of the improved handling characteristics, allows the sludge to be placed in a controlled manner as an engineered fill.

The third Record of Decision (ROD 3) selected treatment of AMD discharges from the buried mine workings in the Slickrock Creek area (USEPA 1993). Wells were installed and water was pumped through a 7.2-km pipeline to the treatment plant. The EPA issued another Record of Decision (ROD 4) which resulted in increasing the capacity of the treatment plant to 24,600 L min^{-1} (USEPA 1997). The year-round treatment of water from both Boulder Creek and Slickrock Creek mine sources has resulted in an 85–90 percent reduction of overall Cu and Zn loads. The combined effects of the Upper Spring Creek and Slickrock Creek diversions and the year-round lime-neutralization plant have greatly improved the compliance with water-quality standards at Keswick Dam.

A settlement of the litigation between EPA and the responsible parties (Aventis CropSciences USA, Inc., formerly known as Rhône Poulenc, Inc., and Stauffer Management Co., the corporate successors to Mountain Copper Company and Stauffer Chemical Co.) resulted in a negotiated settlement in October, 2000, providing EPA with recovery of some of the costs of its remedial investigations and remedial actions (USEPA 2000). The settlement was signed in December 2002 (R. Sugarek written comm. 2003). The cash settlement of $160 M (all figures in U.S. dollars) will fund continuous water treatment until 2030, and an insurance vehicle will pay $514 M to federal and state governments in 2030 to cover future site costs. At that time, the funds will be used to reconstruct the treatment plant, perform additional source reduction, or implement new technology. Additional components of the settlement include a payment to the EPA of approximately $8 M and a payment of $10 M to other state and federal agencies (the natural resource trustees) to fund natural resource restoration projects. The settlement also waives $150 million in past costs, bringing the total amount to close to $1 billion in terms of past and future cleanup costs.

Remedial investigation and feasibility studies of sediments in Keswick Reservoir and Spring Creek Reservoir are ongoing. Some details regarding the characterization of these areas are provided below.

TABLE 2. CHARACTERISTICS OF RICHMOND MINE PORTAL EFFLUENT, 1983–1991

	Mean	Range
Discharge (L s^{-1})	4.4	0.5 – 50
pH	0.8	0.02 – 1.5
Zn (mg L^{-1})	1600	700 – 2600
Cu (mg L^{-1})	250	120 – 650
Zn/Cu (weight ratio)	7.5	2 – 13

After Alpers *et al.* (1992).

SITE CHARACTERIZATION

Underground workings

Water chemistry. A considerable amount of historical data exists for effluent composition and discharge from the Richmond mine because it is the largest single source of dissolved metals, both in terms of concentration and in terms of flux, in the Iron Mountain area. The Richmond orebody was discovered about 1915, but it was not mined on a large scale until the late 1930s and the war years (1940–45). Regular monitoring of the Richmond mine effluent by the California Regional Water Quality Control Board in cooperation with the EPA began in 1983. A summary of the data for discharge, pH, and Cu and Zn concentrations for 1983–91 is shown in Table 2. Further details of Richmond portal effluent composition and discharge can be found in the compilation by Alpers *et al.* (1992).

The chemistry of mine effluent from the Richmond and Lawson portals varies systematically with flow rate. At high discharge, the ratio of Zn to Cu in the effluent from both tunnels is in the range of 2 to 6, whereas at low discharge, this ratio is in the range of 4 to 10 at the Lawson portal and 8 to 13 at the Richmond portal (Fig. 4). Seasonal variability in mine-effluent chemistry can be seen clearly for the 1986–87 monitoring period. Figure 5 covers the period of late November 1986 to April 1987 and records the rainfall (at Shasta Dam), the consequent changes in Richmond mine discharge, Zn and Cu concentrations, and Zn/Cu ratio. One explanation for the large increase in Cu concentrations and the shift in Zn/Cu ratio is the dissolution of underground soluble salts from the flushing effect of meteoric recharge. An observed increase in temperature with increased discharge may be the result of the dilution of concentrated sulfuric acid, the dissolution of soluble salts, and increased pyrite oxidation.

One of the options for remediation of the Richmond mine was to plug it. Many mines have been plugged, but the consequences have not been consistently favorable. The EPA wanted to know what the consequences of plugging the Richmond mine might be; for example, what would be the composition

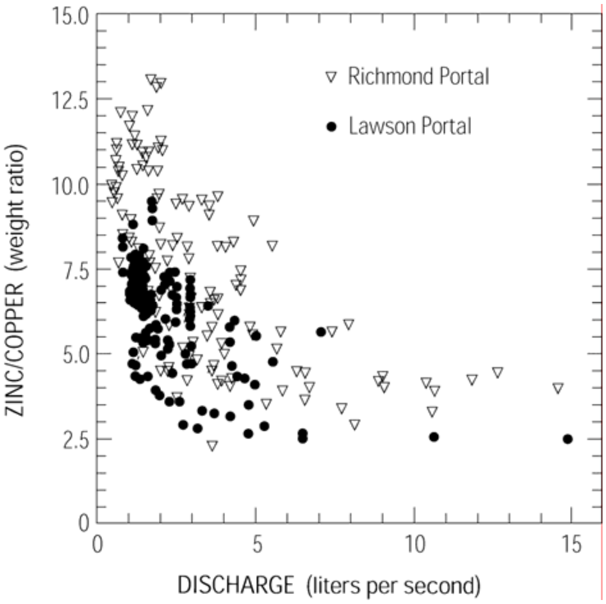

FIG. 4. Variation of Zn/Cu ratio with discharge in mine drainage from Richmond mine and Hornet mine (Lawson tunnel) (adapted from Alpers *et al*. 1992).

of the resultant mine pool? There was, however, no basis on which to speculate without some idea of the underground conditions. Hence, one of the activities under the Superfund Program was an underground survey of the Richmond tunnel and part of the mine workings. Prior to underground renovations in 1989–90, the last underground inspection of the Richmond mine, to the best of our knowledge, was in 1955 (Donald White personal comm. 1989). The last mining of the Richmond mine had occurred in 1955. Other than an occasional inspection by a company employee, there had been no recorded observation of the underground workings for 35–40 years. After underground renovations, entry was safe and on September 10–12, 1990, water and mineral samples were collected; these revealed extremely acidic seeps, with pH values as low as –3.6 (Nordstrom & Alpers 1999b) and total dissolved-solids concentrations of more than 900 g L^{-1} (Nordstrom *et al.* 2000).

The chemical compositions of five of the most acidic waters collected underground in the Richmond mine during 1990–91 are shown in Table 3. These concentrations are the highest ever recorded for As, Cd, Fe, and SO_4, and are nearly the highest for Cu and Zn in groundwater. The high subsurface temperatures (up to nearly 50 ºC), in addition to enhancing pyrite oxidation, have induced the considerable evaporation that has caused the high concentrations of dissolved metals and sulfate.

Negative pH. The reporting of negative pH values has been controversial, and for several good reasons. The conventional definition of pH, based on the former National Bureau of Standards (now National Institute of Standards and Technology) criteria and defined buffer systems, limit the range of definable and measurable pH values to that of 1 to 13. Outside this range, rigorous measurements of pH are challenging. However negative pH values are theoretically possible when the activity of H^+ is greater than one, based on the definition pH = –log $a[H^+]$. For pH values <1.0, a new definition of pH must be used that is consistent with the conventional definition, different buffers must be used, and electrode performance and interferences must be determined. Nordstrom *et al.* (2000) demonstrated an approach, using concentrated sulfuric acid standards and conventional, combination pH electrodes, that has given consistent and reproducible results for determining pH values for the ultra-acidic waters at Iron Mountain.

The currently most acceptable model for activity coefficients for defining pH below 1.0 is the Pitzer ion-interaction approach (Pitzer 1973, 1991; Ptacek & Blowes in Chapter 12, this Volume). Acid mine waters are solutions of sulfuric acid so that the Pitzer model applied to sulfuric acid (Pitzer *et al.* 1977, Clegg *et al.* 1994) serves as a definition for pH. Standardized sulfuric acid solutions would then serve as buffer solutions for calibration, and the remaining question is the performance of standard glass-membrane electrodes under these extreme conditions. Several Orion Ross glass-membrane electrodes and a Sargent–Welch glass-membrane electrode all performed well and could be calibrated up to a sulfuric acid concentration of about 8 molal. (Trade names are for identification purposes only and do not constitute endorsement by the U.S. Geological Survey). Another difficulty facing the definition of pH below 0.0 is the scaling of individual ion-activity coefficients. There is no generally accepted procedure for defining individual ion-activity coefficients without some arbitrary assumptions. Two common methods with the Pitzer approach include 'unscaled' Pitzer equations, and 'MacInnes scaled', using the MacInnes assumption (Plummer *et al.* 1988). The MacInnes assumption is simpler, more flexible for a wide range of complex chemical compositions, and is more consistent with conventional speciation models applied to natural waters (Plummer *et al.* 1988). It could be argued that the MacInnes assumption becomes less defensible at high concentrations, at which the unscaled approach should be more appropriate, but as there is no obvious justification for using one approach over the other, the choice remains arbitrary. In the investigations at Iron Mountain, the MacInnes scaling was used primarily because geochemists who have applied the Pitzer method to the interpretation of brines and saline waters have found the MacInnes assumption

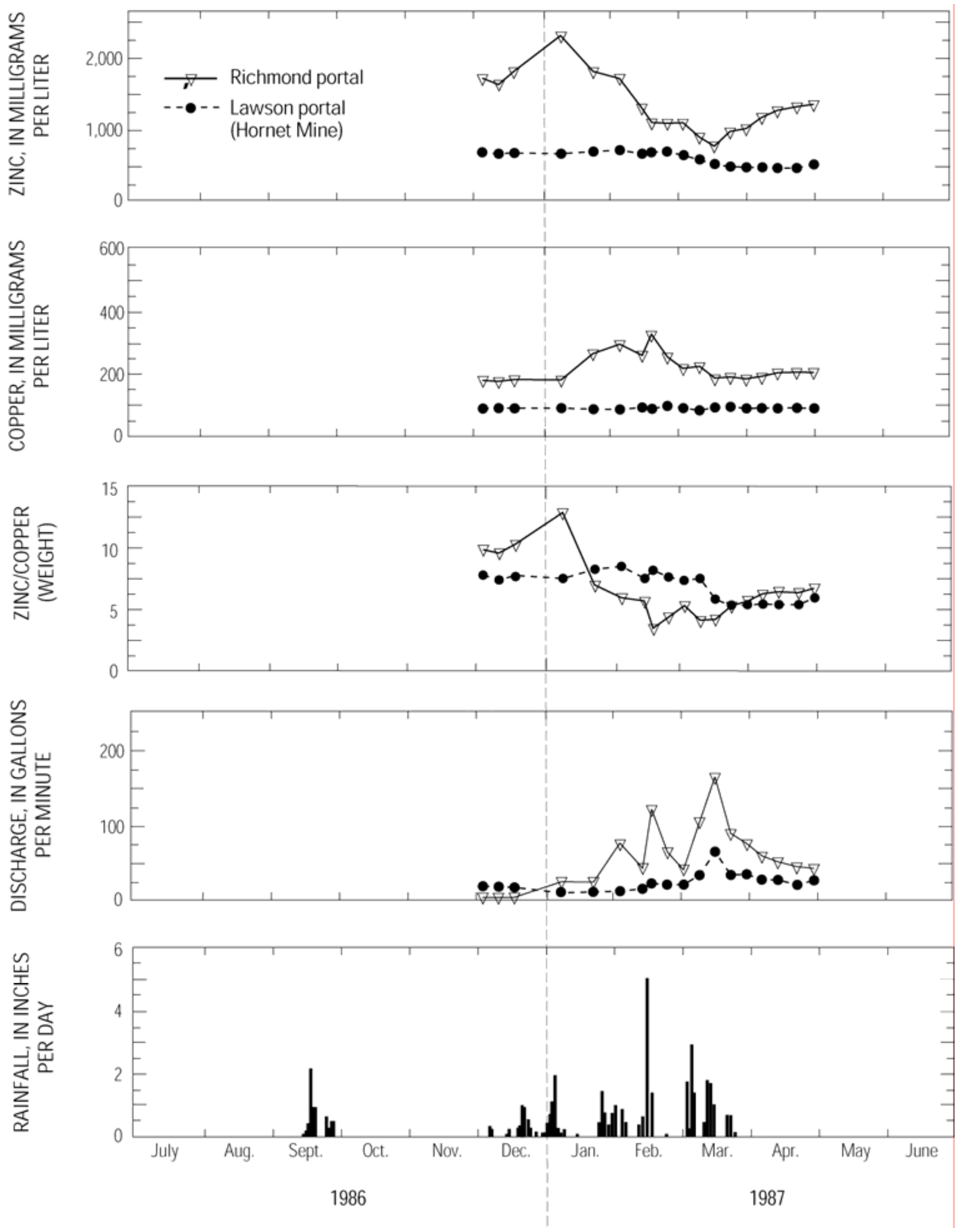

FIG. 5. Variation of Cu and Zn concentrations, Zn/Cu ratio, and discharge from Richmond and Lawson portals, and rainfall with time, 1986–87 (adapted from Alpers *et al.* 1992).

to be more consistent with conventional practice. If the unscaled approach is used, the resultant pH values begin to differ significantly from MacInnes scaling for sulfuric acid solutions with pH values below –0.5. For example, at a sulfuric acid concentration of about 5.0 molal a scaled pH would be –2 whereas the unscaled pH would be notably higher, about –1.2.

Some of the negative-pH mine waters were in apparent equilibrium with prominent soluble salts. For example, water dripping from the tip of a stalactite of zincian-cuprian melanterite had a pH of –0.7 (Table 3). Enormous quantities of highly soluble iron-sulfate salts occur as efflorescences and precipitates within the Richmond mine, coating walls, ceilings, and the floors of the mine, and growing out of muck piles in colorful assemblages. Identification of these soluble salts made it possible to estimate the composition of the mine pool that would form if the mine were to be plugged.

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TABLE 3. CHEMISTRY OF FIVE MOST ACID WATER SAMPLES

Sample	90WA103	90WA109	90WA110A	90WA110C	91WA111
Temp. °C	34.8	38	42	46	28
pH	0.48	–0.7	–2.5	–3.6	−
Element, mg L^{-1}					
Al	2210	6680	1420	–	6470
Sb	4.0	16	29	–	15
As(III)	8.14	38	32	–	74
As(total)	56.4	154	340	–	850
Ba	0.068	0.1	0.2	–	<0.1
Be	0.026	0.1	0.2	–	<0.1
B	1.5	2.5	17	–	–
Cd	15.9	48.3	211	–	370
Ca	183	330	279	–	443
Cr	0.12	0.75	0.6	–	2.6
Co	1.3	15.5	5.3	–	3.6
Cu	290	2340	4760	–	9800
Fe(II)	18,100	79,700	34,500	9790	–
Fe(total)	20,300	86,200	111,000	16,300	68,100
Pb	3.6	3.8	11.9	–	8.3
Mg	821	1450	437	–	2560
Mn	17.1	42	23	–	119
Mo	0.59	1.0	4.2	–	2.3
Ni	0.66	2.9	3.7	–	6.3
K	261	1170	194	–	11.1
Se	0.42	2.1	4.2	–	<2.8
Si (as SiO_2)	170	34	35	–	–
Ag	0.16	0.65	2.4	–	0.70
Na	251	939	416	–	44
Sr	0.25	0.49	0.90	–	–
S (as SO_4)	118,000	360,000	760,000	–	–
Tl	0.44	0.15	0.39	–	1.6
Sn	1.6	15	41	–	–
Ti	5.9	125	1.0	–	–
V	2.9	11	15	–	28
Zn	2010	7650	23,500	–	48,300
Associated Minerals		melanterite	rhomboclase, römerite	rhomboclase	

Adapted from Nordstom & Alpers (1999b).

Mineralogy of soluble salts. Ten soluble Fe-sulfate salts, plus gypsum and chalcanthite, have been identified in the Richmond mine. These minerals and their idealized formulas are listed in Table 4, with the Fe salts in approximate sequence downward from the early formed to the later formed. Rhomboclase occurs as stalactites and stalagmites, and clusters of coquimbite, römerite, copiapite, and voltaite crystals are common throughout the mine. Rhomboclase rarely occurs without voltaite crystals. (For color photographs of several Fe-sulfate salt assemblages, see Nordstrom & Alpers 1999b, the back cover of Alpers *et al.* 2000a, and the URL http://ca.water.usgs.gov/water_quality/acid/pic1.htm).

As long as an acid mine water is in contact with pyrite, the dissolved Fe will remain predominantly in the ferrous state because of the strong reducing capacity of the pyrite. Rapidly flowing mine water will still maintain a high proportion of ferrous iron because the oxidation rate typically is slow enough relative to the flow rate of the water. Consistent with this expectation, the only Fe-sulfate salts containing exclusively ferrous iron (melanterite, rozenite, and szomolnokite), are found close to pyrite sources and associated with the more rapidly flowing waters. Ferric-bearing minerals were observed to form in more stagnant conditions

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TABLE 4. IDEALIZED FORMULAS OF THE SULFATE MINERALS THAT OCCUR IN THE RICHMOND MINE*

Mineral	Idealized Formula
Melanterite	$Fe^{2+}SO_4\cdot7H_2O$
Rozenite	$Fe^{2+}SO_4\cdot4H_2O$
Szomolnokite	$Fe^{2+}SO_4\cdot H_2O$
Copiapite	$Fe^{2+}Fe^{3+}_4(SO_4)_6(OH)_2\cdot20H_2O$
Römerite	$Fe^{2+}Fe^{3+}_2(SO_4)_4\cdot14H_2O$
Coquimbite	$Fe^{3+}_2(SO_4)_3\cdot9H_2O$
Kornelite	$Fe^{3+}_2(SO_4)_3\cdot7H_2O$
Rhomboclase	$(H_3O)Fe^{3+}(SO_4)_2\cdot3H_2O$
Voltaite	$K_2Fe^{2+}_5Fe^{3+}_4(SO_4)_{12}\cdot18H_2O$
Halotrichite–Bilinite	$Fe^{2+}Al_2(SO_4)_4\cdot22H_2O$ – $Fe^{2+}Fe^{3+}_2(SO_4)_4\cdot22H_2O$
Gypsum	$CaSO_4\cdot2H_2O$
Chalcanthite	$CuSO_4\cdot5H_2O$

*Fe salts are listed downward in their general sequence of formation.

which can be considered to be hydrologic ‘dead-ends’, wherein much of the Fe^{2+} has had time to oxidize to Fe^{3+}. Additional evidence for this mineralogical evolution is the observation that melanterite is the first-formed mineral when typical acid mine water is allowed to evaporate under ambient conditions, and rhomboclase and voltaite are the last formed (Buurman 1975).

A Cu–Zn partitioning study of melanterite using water samples from the Richmond mine demonstrated that melanterite prefers Cu to Zn (Alpers *et al.* 1994). The consequences of this partitioning are that portal effluents will have higher ratios of Zn/Cu during the dry season when melanterite is forming underground, and lower Zn/Cu ratios in the wet season when these salts are dissolved and flushed from the mine workings. This trend is seen in the historical data for the effluent from the Richmond mine (Alpers *et al.* 1994).

Data on Zn and Cu contents of melanterite samples from Iron Mountain were presented by Jamieson *et al.* (1999), and were compared by Jambor *et al.* (2000) to literature values from other deposits. Some of the melanterite-group minerals have more Zn than Fe or Cu and therefore are classified as the mineral zinc-melanterite (Jambor *et al.* 2000). Zinc also substitutes for ferrous iron in voltaite. Crystals of voltaite from Iron Mountain that were intergrown with szomolnokite showed systematic variations in Zn–Fe^{2+} substitution (Jamieson & Przybylowicz 1997, Jamieson *et al.* 1999).

Copiapite-group minerals at Iron Mountain include magnesiocopiapite [$MgFe^{3+}_4(SO_4)_6(OH)_2\cdot20H_2O$], aluminocopiapite [$Al_{2/3}Fe^{3+}_4(SO_4)_6(OH)_2\cdot20H_2O$], and copiapite *sensu stricto* [$Fe^{2+}Fe^{3+}_4(SO_4)_6(OH)_2\cdot20H_2O$]. The magnesiocopiapite and aluminocopiapite were found in a moist mass growing directly on pyrite muck-piles (Robinson 2000). Opaque brown porewater with a pH of –1.0 ±0.5 was extracted from the copiapite-group minerals using a centrifuge; this porewater was extremely rich in ferric iron, with Fe(III) = 147 g L^{-1}, Fe_{total} = 160 g L^{-1}, and a density of approximately 1.5 g mL^{-1} (Robinson 2000, Jamieson *et al.* in review). The composition of this fluid is similar to water coexisting with copiapite reported in the experimental study of the Fe_2O_3–SO_3–H_2O system by Posnjak & Merwin (1922). Micro-PIXE (Proton-Induced X-ray Emission) analysis indicates that copiapite-group minerals sequester Zn (average 1420 ppm) and lesser amounts of Cu (average 270 ppm) and As (average 64 ppm) (Jamieson *et al.* in review).

Dissolution of soluble, Fe-sulfate salts (with variable amounts of Cu, Zn, Cd, and Al substituting for the Fe) can generate acidic solutions with high concentrations of dissolved metals. During the rising limb of a stream discharge in central Virginia following the onset of rain, Dagenhart (1980) showed that rapid increases in the concentrations of Cu, Zn, Fe, and Al resulted from the dissolution of efflorescent salts that occurred on upstream tailings and waste-rock piles (Jambor *et al.* 2000). This phenomenon must be common at mine-waste sites and is likely an important cause of fish kills associated with periods of high runoff, especially after prolonged dry periods.

Microbiology. Iron Mountain, especially the Richmond mine, contains rich growths of Fe-oxidizing microbial communities. Recent investigations on the microbiology of the Richmond tunnel drainage have expanded our inventory of microorganisms that live in these harsh environments and increase the rate of production of acid mine drainage. An Fe-oxidizing archaeon, “*Ferroplasma acidarmanus*”, has been discovered that grows optimally at a pH value of 1.2 and a temperature of 45 °C (Edwards *et al.* 2000a; quotation marks indicate that the archaeon does not have a recognized name). It can grow at pH values near 0.0 and was observed to be more abundant in those mine waters of lower pH and warmer temperatures (Bond *et al.* 2000a). *Leptospirillum* spp. (identified as groups I, II, and III) were found in many of the acid slime streamers, and a new uncultured *Leptospirillum* sp. dominated in one subaerial slime community (Bond *et al.* 2000a). Table 5 lists the major microbial groups

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TABLE 5. MICROBES IDENTIFIED IN THE RICHMOND MINE

Microbial Species, Genus, or Affiliation	Reference
Ferroplasma acidarmanus	Edwards *et al*. (1999a, 2000a)
Leptospirillum ferrooxidans	Bond *et al*. (2000a,b); Edwards *et al*. (1999a)
Leptospirillum	Bond *et al*. (2000a,b); Edwards *et al.* (2000a)
Thermoplasmales	Bond *et al.* (2000b)
Acidimicrobium	Bond *et al.* (2000a,b); Edwards *et al.* (1999a)
Sulfobacillus	Bond *et al.* (2000a)
Acidiphilium	Bond *et al.* (2000a); Edwards *et al.* (1999a)
Acidithiobacillus ferrooxidans	Edwards *et al.* (1999a)
Acidithiobacillus caldus	Bond *et al.* (2000a); Edwards *et al.* (1999a)
Leptothrix discophora	Edwards *et al.* (1999a); Robbins *et al.* (2000)

that have been detected within the Richmond mine in biofilms and slime streamers. Other minor species or affiliates are listed in Edwards *et al.* (1999a).

Seasonal variations affected the microbial communities, with the Archaea increasing substantially during the summer dry months and Bacteria increasing during the winter months (Edwards *et al.* 1999b). The occurrence of the well-studied Fe-oxidizer, *Acidithiobacillus ferrooxidans*, was found to be in the outer margins of the weathered mineral deposit, where temperatures were 20–30 °C and pH values 2–3, and not in significant abundance within the mine workings where the temperatures were higher and the pH values were lower. Instead, the Fe-oxidizer, *Leptospirillum*, was more dominant (Schrenk *et al*. 1998). Pyrite crystals were placed in the mine water to study the growth of microbial colonies and to determine how they attached to the pyrite surfaces and how they affected the surfaces, and to determine the rate of dissolution (Edwards *et al*. 1998). McGuire *et al.* (2001) performed additional studies on the kinetics and surface chemistry of pyrite, marcasite, and arsenopyrite dissolution by single cultures and mixed cultures of *Acidithiobacillus caldus*, *Leptospirillum ferrooxidans*, and "*Ferroplasma acidarmanus*" from Iron Mountain. Robbins *et al.* (2000) showed that, in addition to bacteria and archaea, acidophilic or acid-tolerant fungi, ciliates, rotifers, and heliozoans have been found in the pH range 0–2.5 in the Richmond tunnel drainage. Robbins *et al.* (2000) concluded that a significant food chain existed, beginning with the chemolithoautotrophs.

Conditions and duration of sulfide oxidation

Conditions at Iron Mountain are nearly optimal for the production of acid mine waters, and this mine drainage is some of the most acidic and metal-rich reported anywhere in the world (Nordstrom 1977, Alpers *et al.* 1994, Nordstrom & Alpers 1999b). In the Richmond mine, about 7 Mt of massive sulfide remain (Kaiser Engineering 1981). At current weathering rates it would take about 3200 years for the pyrite in the Richmond orebody to oxidize fully. The massive sulfide deposit is about 95% pyrite, and is cut by tunnels, shafts, raises, and stopes, which allow rapid transport of oxygen by air advection. The sulfides are at or above the water table, hence moisture and oxygen have ready access. Airflow is driven by the high heat output from pyrite oxidation. About 1500 kJ of heat are released per mole (120 g) of pyrite. Air enters the main tunnel, heats up in the mine, and then moves upward through raises and shafts to the surface.

The average flux of acid mine drainage from the Richmond portal indicates that about 2400 moles of pyrite are oxidized every hour, producing about 1 kW of power or almost 9000 kW per year. Water temperatures as high as 55 °C have been measured underground. The amorphous silica geothermometer (Fournier & Rowe 1966, Fournier 1985) is consistent with temperatures of more than 50 °C in the subsurface (Nordstrom & Alpers 1999b). In the early days of mining at Iron Mountain, fires were frequent during underground excavation, and temperatures of 221 °C were recorded at the ore surface (Wright 1906).

Predicted consequences of mine plugging

The chemical composition of the mine pool created by plugging the Richmond mine can be estimated by modelling the dissolution of the sulfate salts in a volume of water equivalent to the void space created by the underground workings. The exact proportion of the different type of salts is not known, but the results of the calculations are not particularly sensitive to this factor. The amount of salts stored underground is a more critical factor, and the amount was therefore considered as a variable. Computations were made using measured mineral compositions and the PHREEQE program (Parkhurst *et al.* 1980, now superseded by PHREEQC, version 2, Parkhurst & Appello 1999) for a range of salt volumes. PHREEQE can calculate the speciation and chemical equilibrium

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for mass-transfer processes such as dissolution, precipitation, oxidation–reduction reactions, ion exchange, and gas addition or removal (Alpers & Nordstrom 1999). The results are shown in Figure 6, where the resultant pH in the mine pool is plotted against the volume of added salts under two scenarios: active infiltration, or actively injecting clean water; and passive infiltration, letting the groundwater naturally fill the void spaces. The latter scenario gives a worse picture because passive infiltration would allow more pyrite oxidation and the buildup of more acidic waters. On the basis of visual inspection from the limited subsurface survey, the salts probably occupy about 1% of the volume of the mine workings. As can be seen in Figure 6, however, uncertainty in this value makes little difference. The consequences are that a mine pool of about 600,000 m^3 with a pH at or below 1, with many grams per liter of dissolved metals (much like the current portal effluent), would likely form at or near the top of the groundwater table, in a rock with almost no neutralization capacity and in which the hydrologic flow is governed by fractures, excavations, and drillholes. Thus, plugging the underground mine workings at Iron Mountain presents a remediation scenario that has a high degree of risk, with potentially dangerous results.

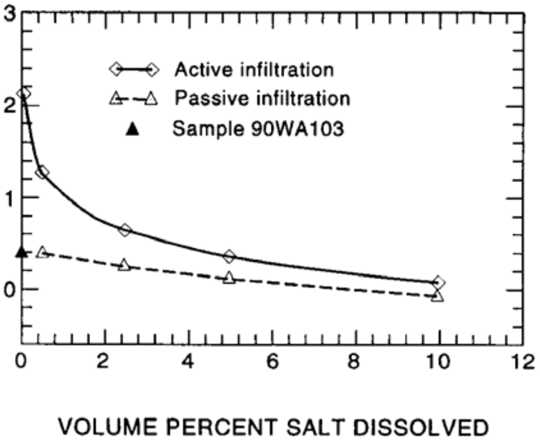

FIG. 6. PHREEQE simulation of water composition for the mine pool after plugging the Richmond mine (adapted from Nordstrom & Alpers 1999b).

The decision to build the larger treatment plant and to treat discharges from the Lawson tunnel (Hornet mine) was influenced by geochemical modelling. Opinion was divided as to whether the flow of acid mine water from the Lawson tunnel originates from the Richmond mine by spillage or leakage or whether the Hornet orebody produces its own contaminant effluent. An ore chute and a raise that connected the two mines were identified from the old mine maps (Fig. 2). Because of its proximity to the surface and the collapsed nature of the mine workings, it was generally agreed that the Hornet mine itself could not be effectively plugged. Consultants had proposed that plugging the Richmond mine would stop or greatly reduce the flow from the Lawson tunnel. However, subsequent investigations have demonstrated that significant portions of the country rock surrounding the Richmond orebody have fractured and would not provide reliable containment of a mine pool. There was also reason to believe that during the intervening years since mining ceased, cave-ins and other ground failures had largely cut off direct connections between the Richmond and Hornet mines. Geochemical modelling by Alpers *et al.* (1992) using the program BALANCE (Parkhurst *et al.* 1982; superceded by PHREEQC, version 2, Parkhurst & Appelo 1999) indicated that no more than 2% of the flow from the Hornet mine (and 6% of the dissolved constituents) could be attributed to water infiltrating from the Richmond mine. The conclusion that the Hornet mine was producing its own AMD made it clear that plugging the Richmond mine, even if successful, would still result in a situation for which a treatment plant would be necessary.

It has been common engineering practice to plug abandoned or inactive mines without monitoring, modelling, or even considering the physical and chemical consequences. Major leaks or failures at plugs, widespread and disseminated seeps of enriched acid mine waters, and increases in subsurface head pressures of more than 100 m have occurred. For some minesites, plugging may ultimately prove to be successful, but more careful planning and technical review are essential to lessen the probability of disastrous results. An important factor in evaluating the potential consequences of mine plugging is the role of soluble salts as a storage and release mechanism for ferric iron, which can act as an oxidant to residual sulfide minerals. Thus, even if plugging results in the desired condition of greatly reducing contact of sulfide minerals with atmospheric oxygen, stored oxidation potential in the form of ferric iron salts can potentially lead to many additional years of sulfide oxidation and formation of acid mine drainage after mine plugging.

Surficial environments and soluble salts

Soluble Fe- and Al-sulfate salts typically are formed by the evaporation of acid-sulfate waters associated with sulfide oxidation. Surficial environments at Iron Mountain where abundant efflorescent sulfate salts have been observed to accumulate in the dry season include seepage areas, streambeds, and areas where surface materials contain significant concentrations of sulfide minerals, such as mine-waste piles and residual sulfide lenses and nodules within gossan outcrops at the top of Iron Mountain. Based on the results of X-ray diffraction and

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chemical analysis, Keith *et al.* (2001) described the occurrence of several evaporative sulfate minerals in the Boulder Creek area, some of which are similar to those described from the Richmond mine (Table 4). The dominant sulfate minerals in the sulfate crusts described by Keith *et al.* (2001) were rhomboclase, ferricopiapite [$Fe^{3+}_{2/3}Fe^{3+}_{4}(SO_4)_6(OH)_2 \cdot 20H_2O$], bilinite [$Fe^{2+}Fe^{3+}_{2}(SO_4)_4 \cdot 22H_2O$], alunogen [$Al_2(SO_4)_3 \cdot 17H_2O$], and kalinite [$KAl(SO_4)_2 \cdot 11H_2O$]. Accessory minerals included gypsum and hexahydrite [$MgSO_4 \cdot 6H_2O$].

The first rainstorm after an extended dry period typically results in a flushing effect that dissolves soluble salts, leading to increased concentrations of metals and sulfate in receiving waters, as discussed above in the context of the underground workings. Detailed monitoring of Boulder Creek during rainstorm events in 1995 and 1996 indicated that the dissolution of soluble salts was a significant source of Fe, Al, Cu, Zn, acidity, and other metals during the first major storm of each wet season (Keith *et al*. 2001).

Estimates of pre-mining baseline conditions

Preliminary paleomagnetic data on Fe-oxide minerals in the gossan show portions with reversed polarity, indicating that the gossan began forming at least 780,000 years ago (Alpers *et al.* 1999, Alpers & Nordstrom 2000). Ore-reserve calculations of original in-place tonnage of gossan (8.5 Mt, Kaiser Engineering 1981), coupled with assumptions regarding the likely range in metal concentrations of the massive sulfide deposits prior to weathering, the mineralogy of the gossan, and the chemical behavior of Fe during weathering, lead to an estimate of 13.5 Mt tons of sulfide ore required to produce the gossan that existed prior to mining. Allowing for physical erosion of gossan and solubilization of some Fe during gossan formation, a conservative addition factor of 100% yields a maximum estimate of about 27 Mt of massive sulfide that were weathered during a period lasting at least 780,000 years.

The geological reconstruction of the massive sulfide deposit combined with the minimum weathering age of 780,000 years leads to a maximum long-term average weathering rate of 17,000 to 34,000 kg of massive sulfide per year. Assuming ranges of Cu and Zn concentrations based on available data, the corresponding average long-term flux of Cu would range from 85 to 1050 kg a^{-1} and that of Zn from 100 to 1230 kg a^{-1}. For comparison, annual post-mining, untreated metal loads based on monitoring data from 1994–97 are estimated at 14,000 to 200,000 kg a^{-1} (R. Sugarek USEPA oral comm. 1997). From these estimates, we infer that the overall impact of mining at Iron Mountain increased metal loads by two to three orders of magnitude above pre-mining baseline conditions.

Receiving waters

Lower Spring Creek and Spring Creek Reservoir. Prior to lime-neutralization treatment of AMD at Iron Mountain, water quality in lower Spring Creek and in Spring Creek Reservoir was very acidic (median pH <3), with elevated concentrations of metals including Al, Cd, Cu, Fe, and Zn. Concentrations of Cu generally exceeded 1 mg L^{-1}. Oxidation of Fe(II) to Fe(III) resulted in widespread precipitation of hydrous ferric oxides. Based on drilling and sampling during 1997, the Fe content of sediments from Spring Creek Reservoir ranged from 6 to 21 wt%, with a mean value of 11%. The mean Cu content in sediments was 510 mg kg^{-1}, with a range of 320 to 960 mg kg^{-1}; Zn concentrations in Spring Creek Reservoir sediment had a mean value of 170 mg kg^{-1}, with a range of 100 to 340 mg kg^{-1} (Nordstrom *et al.* 1999a). The pH values were generally too low for much sorption of Cd, Cu, or Zn to occur in this part of the system.

Since continuous water treatment began at Iron Mountain in 1994, significant improvements in water quality have been observed. Prior to the onset of continuous treatment in 1994, pH values ranged from 2 to 3.7; since January 1995, the median and average pH values have been about 4.0, and the annual range has varied from 3.0 to 5.0 (Fig. 7). A striking feature of the pH time series in lower Spring Creek is the systematic annual cycle, with minimum values in the dry, summer season about 2 pH units lower than the maximum values during the wet, winter season. Processes that likely affect the annual pH cycle are enhanced evaporation and oxidation of aqueous ferrous iron in the summer, and dilution in the winter. At pH values above about 2.2, oxidation of aqueous Fe(II) to Fe(III) is coupled with hydrolysis, which leads to a net decrease in pH (Nordstrom & Alpers 1999a, Nordstrom 2000). Since 1995, Cu concentrations in lower Spring Creek generally have been <1 mg L^{-1}. Nevertheless, an active management program is required to maintain adequate dilution flows from Shasta Dam and the SCPP to result in Cu concentrations <5.6 µg L^{-1} at the compliance point downstream of Keswick Dam.

Keswick Reservoir. Metal-rich sediment deposits that have accumulated in the Spring Creek Arm of Keswick Reservoir (SCAKR) consist primarily of hydrous Fe and Al oxides that have formed by the mixing of acidic water from Spring Creek with neutral receiving waters. The inflow of Spring Creek to the SCAKR is located close to the outflow from the Spring Creek Power Plant (SCPP). The clean, relatively cold water from the SCPP outflow meanders its way around three piles of fine-grained, metal-rich sediments in the SCAKR (Fig. 3). In the thickest pile of sediments, the

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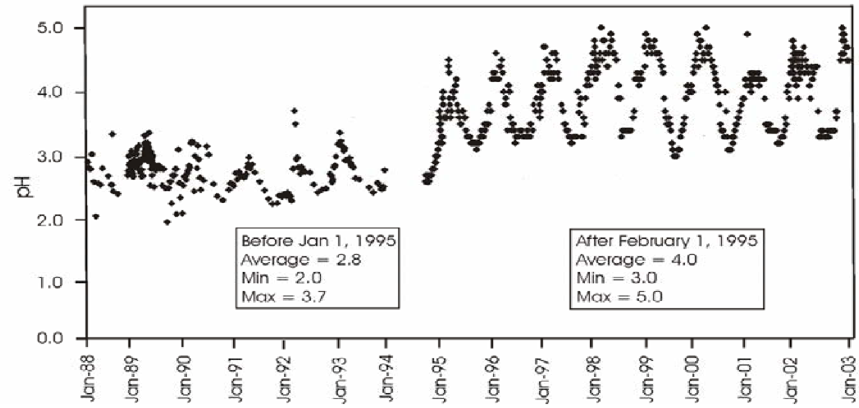

FIG. 7. Variation of pH in Spring Creek Debris Dam discharge, January 1988 – January 2003 (data from the Bureau of Reclamation and the California Regional Water Quality Control Board – Central Valley Region).

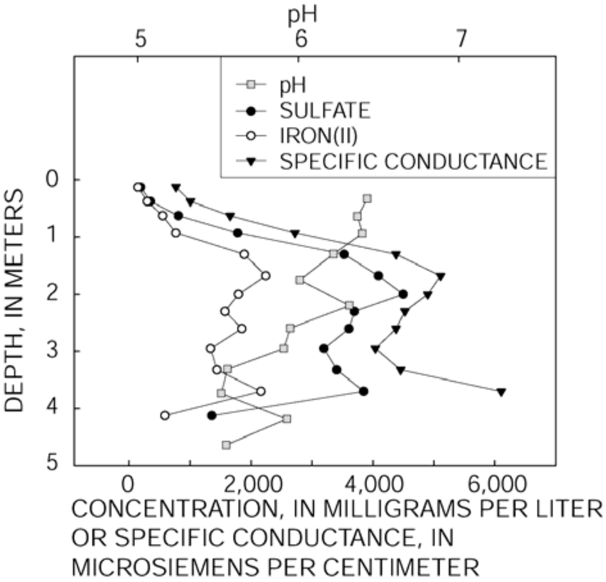

FIG. 8. Concentrations of dissolved Fe(II) and sulfate and values of specific conductance and pH in porewaters from sediments in the Spring Creek Arm of Keswick Reservoir as a function of depth (adapted from Nordstrom *et al.* 1999).

concentration of Cu ranges from 200 to 4800 mg kg^{-1}, with a mean of 1600 mg kg^{-1}; concentrations of Zn range from 85 to 6600 mg kg^{-1}, with a mean of 1200 mg kg^{-1}, and Fe concentrations range from 4 to 47 wt%, with a mean of 17% (Nordstrom *et al.* 1999).

Porewaters extracted in 1997 by centrifugation of the fine-grained sediments in the SCAKR were exceptionally high in dissolved Fe(II); concentrations up to 2000 mg L^{-1} were observed in porewaters from depths of 1.5 to 4 m (Fig. 8). The porewaters had pH values ranging from 5.5 to 6.5, alkalinity values of 0 to 300 mg L^{-1} (as $CaCO_3$), and sulfate concentrations up to 4000 mg L^{-1}. Trace metals in the porewaters were characterized by elevated concentrations of Zn (up to 9 mg L^{-1}) and Mn (up to 43 mg L^{-1}), and by very low concentrations of Cu and Cd (Fig. 9). The porewater data indicate considerable reductive dissolution of Fe with some alkalinity production and little to no sulfate reduction. The presence of Fe-reducing bacteria is strongly suspected.

Metal adsorption and desorption studies were conducted on Kewsick Reservoir sediments to quantify metal partitioning between sediments and water because it is important to estimate the amounts of metals that might be released by dredging the contaminated piles. A composite sediment sample from the SCAKR had a surface area of 47.4 m^2 g^{-1} by the Brunnauer–Emmett–Teller (BET) method (Nordstrom *et al.* 1999). (For reference, hypothetical spherical particles of hydrous Fe oxide, 100 nm in diameter, would have a surface area of about 50 m^2 g^{-1}). The mineralogy of the Fe-rich sediment is, according to Mössbauer spectroscopy, dominated by schwertmannite (J. Friedl written comm. 1998), which is consistent with its elevated sulfate content. Adsorption curves for Zn and Cd were similar to those for Cu, but were shifted to about one pH unit higher (Fig. 10). The adsorption curves are at lower values of pH compared with similar curves for pure hydrous ferric oxide (Dzombak & Morel 1990), which is consistent with a schwertmannite substrate (Webster *et al.* 1998).

Desorption of Cu reached a minimum (with decreasing pH) at pH 5. These results indicate the importance of keeping pH values above 5 to minimize release of aqueous Cu in a resuspension scenario caused by dredging. Release of porewaters rich in dissolved ferrous iron would likely results in rapid Fe oxidation

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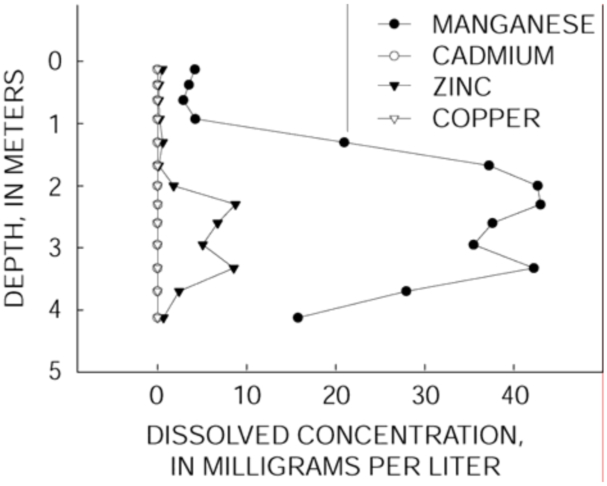

FIG. 9. Concentrations of dissolved Cd, Cu, Mn, and Zn in porewaters from sediments in the Spring Creek Arm of Keswick Reservoir as a function of depth (adapted from Nordstrom *et al.* 1999).

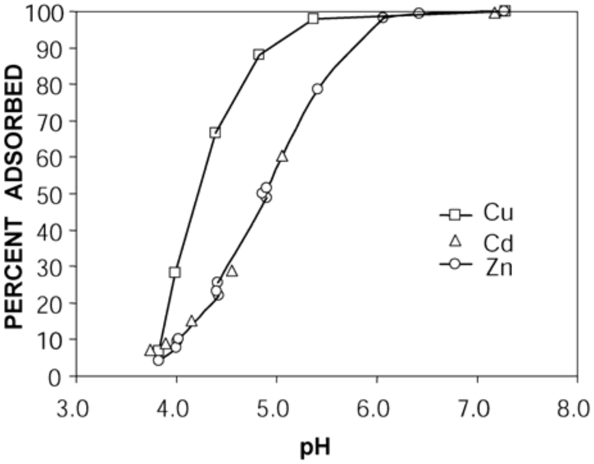

FIG. 10. Adsorption of Cd, Cu, and Zn onto a composite of sediment from the Spring Creek Arm of Keswick Reservoir. For a solid-to-liquid ratio of 11 g L^{-1}, 50 percent of the Cu is adsorbed onto the sediment at pH 4.1, whereas 50 percent of the Cd or Zn are adsorbed between pH 4.8–4.9 (adapted from Nordstrom *et al.* 1999).

and hydrolysis, which would lower the pH. It is unknown whether dredging of the contaminated sediments in the SCAKR area could be accomplished without significant desorption of Cu because of this effect.

Aquatic toxicity tests were conducted on pore-waters and uncentrifuged sediment from the SCAKR to determine the potential effects of sediment resuspension on aquatic life. The crustacean *Ceriodaphnia dubia* was used as a test animal. In 48-h and 96-h tests using porewaters, the dilution factor accounting for 50% mortality of the test organisms (the LC_{50}) ranged from 0.6 to 7.1%, with an average of about 1% (Nordstrom *et al.* 1999). The diluted concentrations of Cu, Zn, and Cd were lower than harmful levels based on published values of LC_{50} from other studies (Finlayson *et al.* 2000). These results indicated that Cu, Zn, and Cd were not the primary cause of toxicity. Further experiments (toxicity identification and evaluation, or TIE) were designed to pinpoint the cause of the toxicity. The chemical activity of Cu, Zn, and Fe were nullified in some of the TIE tests by adding reagents that selectively removed or complexed the individual metals. The TIE tests indicated that dissolved Fe was the primary cause of the toxicity, and that Zn may have been a secondary cause. A set of experiments using only dissolved Fe(II) in three different dilution waters (Shasta Dam, Whiskeytown Lake, and reagent water adjusted for hardness) gave results similar to the porewater tests, demonstrating that a few milligrams of Fe per liter are sufficient to cause acute and chronic toxicity of *Ceriodaphnia dubia* (Nordstrom *et al.* 1999).

The identification of Fe from the porewaters of the Keswick Reservoir sediments as the primary toxicant affecting aquatic life was unexpected and has some serious implications. First, no regulatory aquatic life standard for Fe has been set by the EPA or the State of California, yet Fe seems to be the most serious threat to aquatic life in the contaminated area. Second, dissolved Fe is the most abundant cation in most, if not all, acid mine waters, yet many investigations do not document Fe(II) and Fe(III) concentrations in waters affected by acid mine drainage, and there are no well-known water-quality standards for these constituents. Third, other studies of the aquatic toxicity of dissolved Fe have come to the similar conclusion: that a few milligrams of Fe per liter are unsafe or toxic for aquatic life in freshwaters. Fish kills are the most common environmental problem from mining activities, and the causative agent of acute toxicity may be Fe or Al instead of Cd, Cu, or Zn as more commonly thought.

Sacramento River. The construction of Shasta and Keswick dams resulted in insurmountable barriers to the migration of anadromous fish, including threatened and endangered species of salmon and steelhead. These protected fish species now spawn exclusively below Keswick Dam, which makes this reach of the Sacramento River particularly sensitive with regard to water-quality issues, especially the metal contamination from Iron Mountain.

Metal transport in the Sacramento River system, including the Iron Mountain / Spring Creek source area, was studied in detail by the U.S. Geological Survey

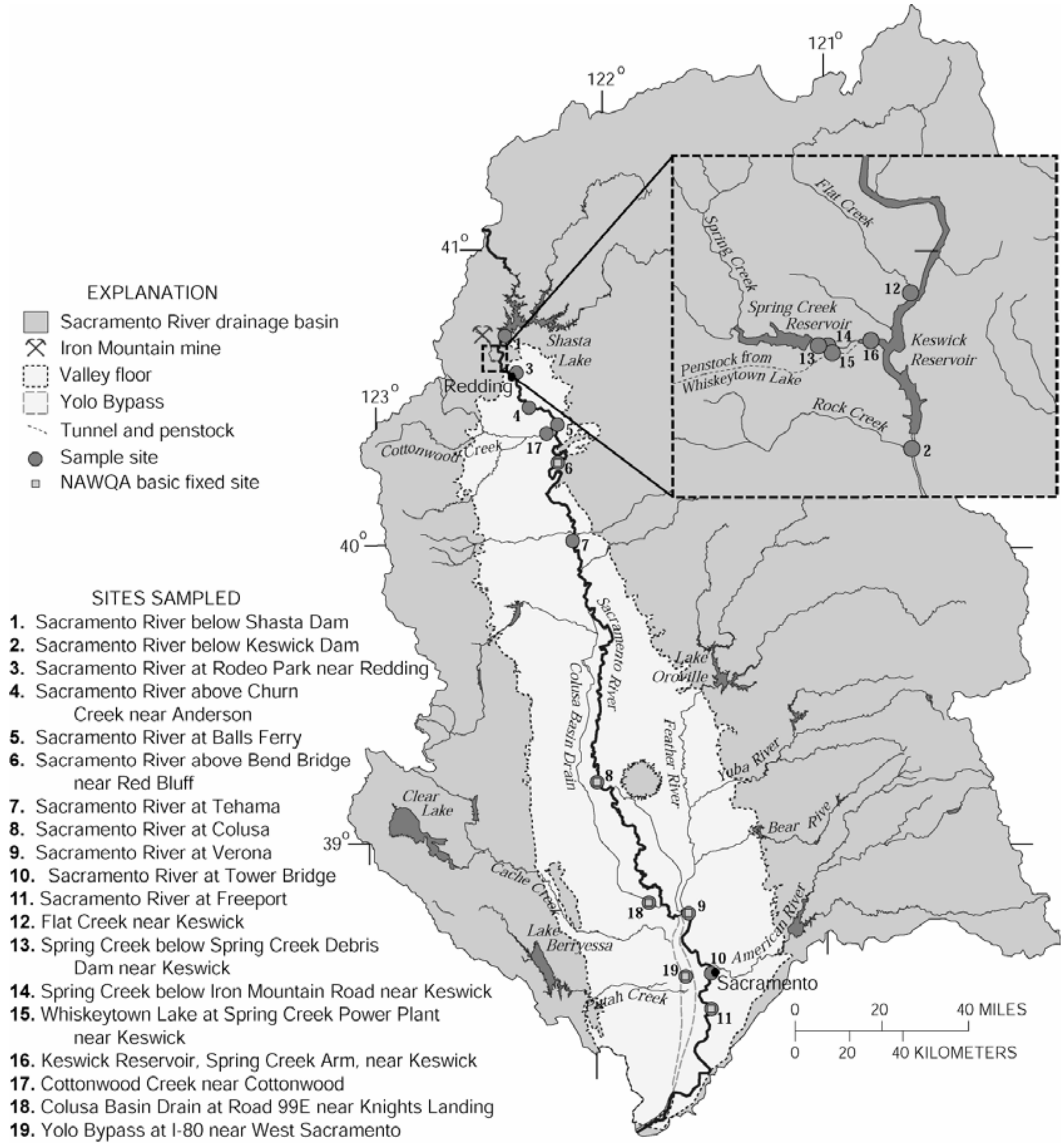

FIG. 11. Map showing location of water and sediment samples for the USGS metals-transport study, 1996–97 (adapted from Alpers *et al*. 2000a).

during the period July 1996 to June 1997 (Alpers *et al.* 2000a,b, Roth *et al*. 2001). Water-quality and streambed-sediment sampling for the metal-transport study was conducted at 19 sites in the Sacramento River watershed (Fig. 11). Ultrafiltration methods using membranes of 10,000 Daltons (equivalent to about 0.005 µm in pore diameter) were used to separate dissolved constituents from colloids, and both fractions were analyzed by ICP–MS methods.

The concentrations of Cd, Cu, Pb, and Zn in Spring Creek below the SCDD were several orders of magnitude higher than the receiving waters from Shasta Dam and Whiskeytown Lake (Fig. 12). Ultrafiltered water samples from the Sacramento River below Keswick Dam were somewhat elevated with regard to concentrations of Cd, Cu, and Zn in comparison with upstream (Shasta Dam) and downstream sampling locations. At the Bend Bridge location, 71 km downstream of Keswick Dam, dissolved Cu concentrations were attenuated to levels comparable to upstream and downstream locations on the main stem of the Sacramento River. Dissolved concentrations of Cd and Zn were somewhat elevated at Bend Bridge compared with values at locations farther downstream

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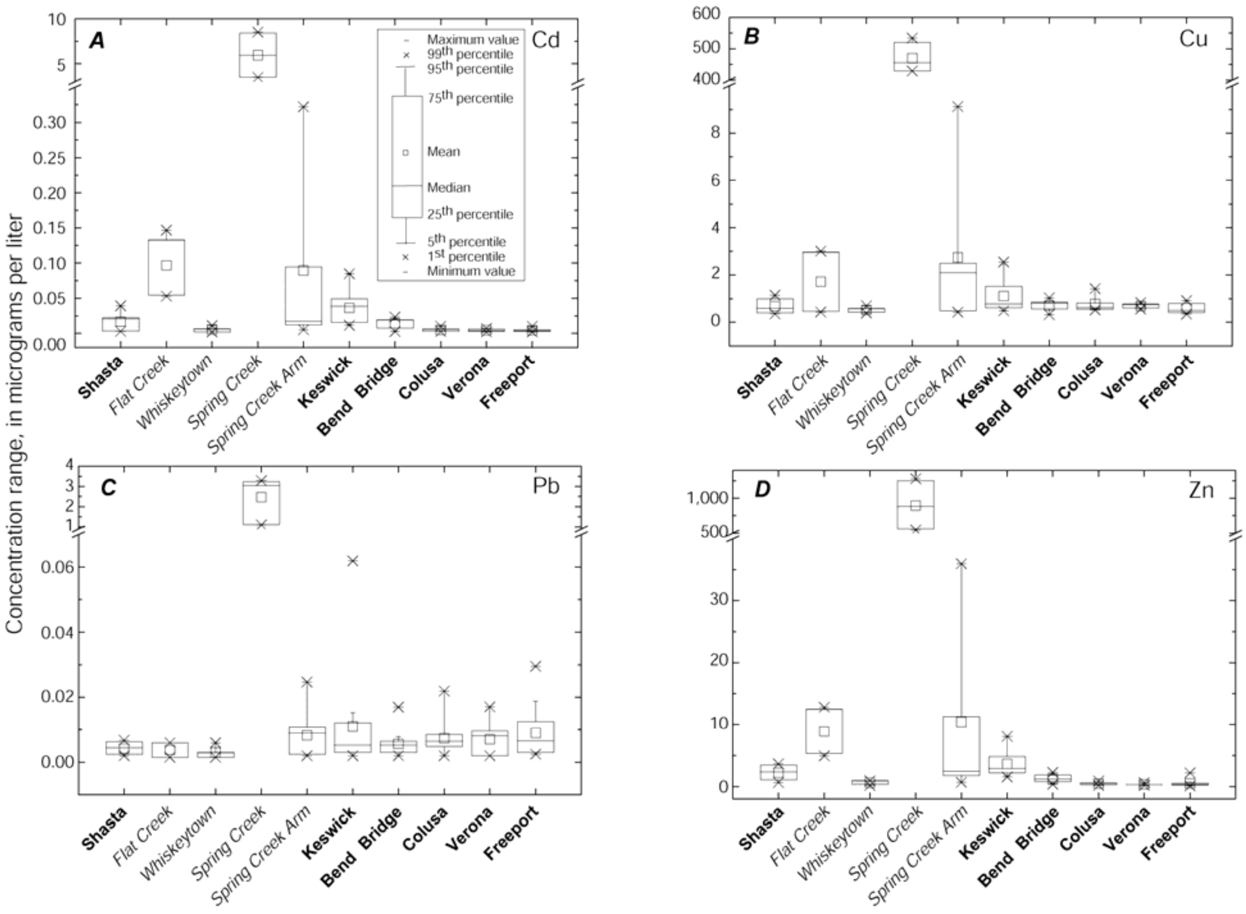

FIG. 12. Concentrations of Cd, Cu, Pb, and Zn in ultrafiltered water samples from tributary (italics) and mainstream (bolded) sites on the Sacramento River, 1996–97 (adapted from Alpers *et al.* 2000a).

(Fig. 12).

Concentrations of trace metals in streambed sediments and colloidal suspended sediment (approximately 0.005 to 1.0 µm size range) from 1996–97 showed a pattern similar to that of the dissolved metals. Iron Mountain (via Spring Creek) is clearly the major source of metals to the Spring Creek Arm of Keswick Reservoir, as illustrated by Cu and Pb concentrations in both colloids and streambed sediments (Figs. 13 and 14). Metal concentrations in streambed sediments were somewhat elevated in samples from Sacramento River sites downstream to Balls Ferry (44 km downstream of Keswick Dam). However, at Bend Bridge (71 km) and other sites farther downstream, the Cu and Pb concentration data were consistently lower than upstream values (Alpers *et al.* 2000a).

Lead-isotope data (Fig. 15) are consistent with the finding that Iron Mountain mine (data from Doe *et al.* 1985) continues to have a major influence on metal loading in the vicinity of Redding, despite the ongoing water treatment. Lead partitions strongly to the particulate phase. The interpretation of Pb isotopes is complicated by the ubiquitous presence in soils of Pb from gasoline additives used from the 1920s to the 1980s in the U.S. It appears that Pb from gasoline additives may represent about half of the lead in colloids and bed sediments in the lower part of the watershed (Dunlap *et al.* 1999).

A study of metal bioaccumulation in the larvae of caddisflies (*Hydropsyche californica*) was conducted by Cain *et al.* (2000) concurrently with the USGS water-quality study. Samples were taken in October 1996 from five Sacramento River locations from Keswick Dam to Tehama (site 7 in Fig. 11), a distance of 118 km downstream. Samples were also taken from Cottonwood Creek (site 17 in Fig. 11), a tributary that served as a regional reference site. The cytosol component of the caddisfly larvae was separated by centrifugation to provide information about the bioavailable, intracellular metal fraction. Metal concentrations in the cytosol indicated exposure to

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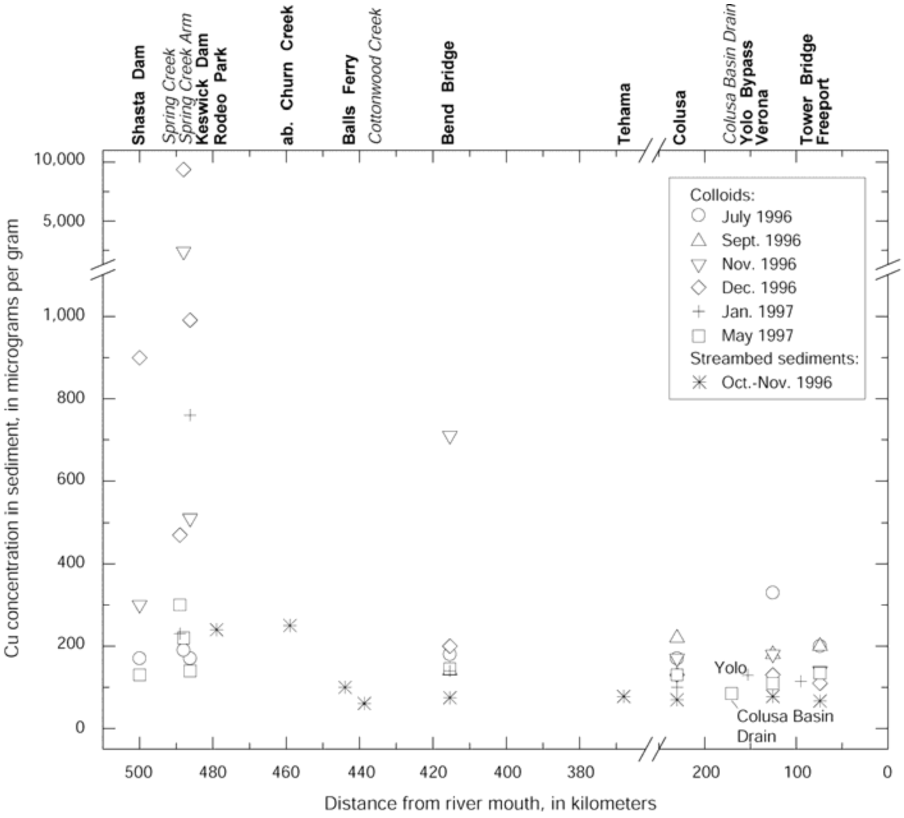

FIG. 13. Plot of the Cu concentrations in suspended colloids and streambed sediments in relation to distance (broken scale) from Sacramento River mouth (adapted from Alpers *et al.* 2000a).

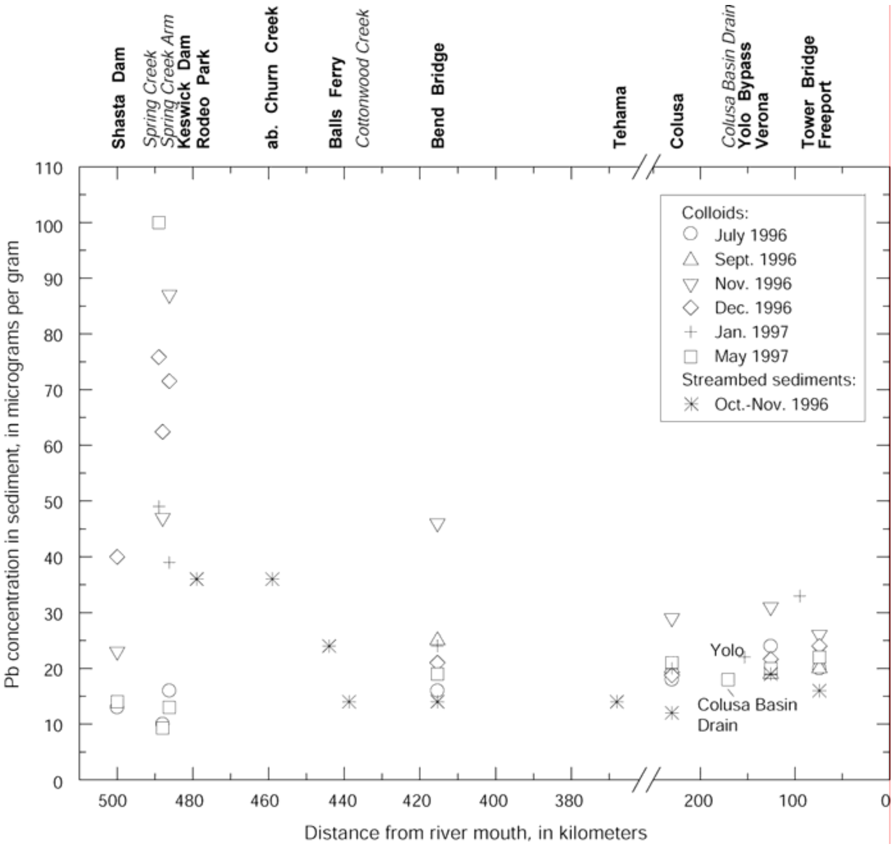

FIG. 14. Plot of the Pb concentrations in suspended colloids and streambed sediments in relation to distance (broken scale) from Sacramento River mouth (adapted from Alpers *et al.* 2000a).

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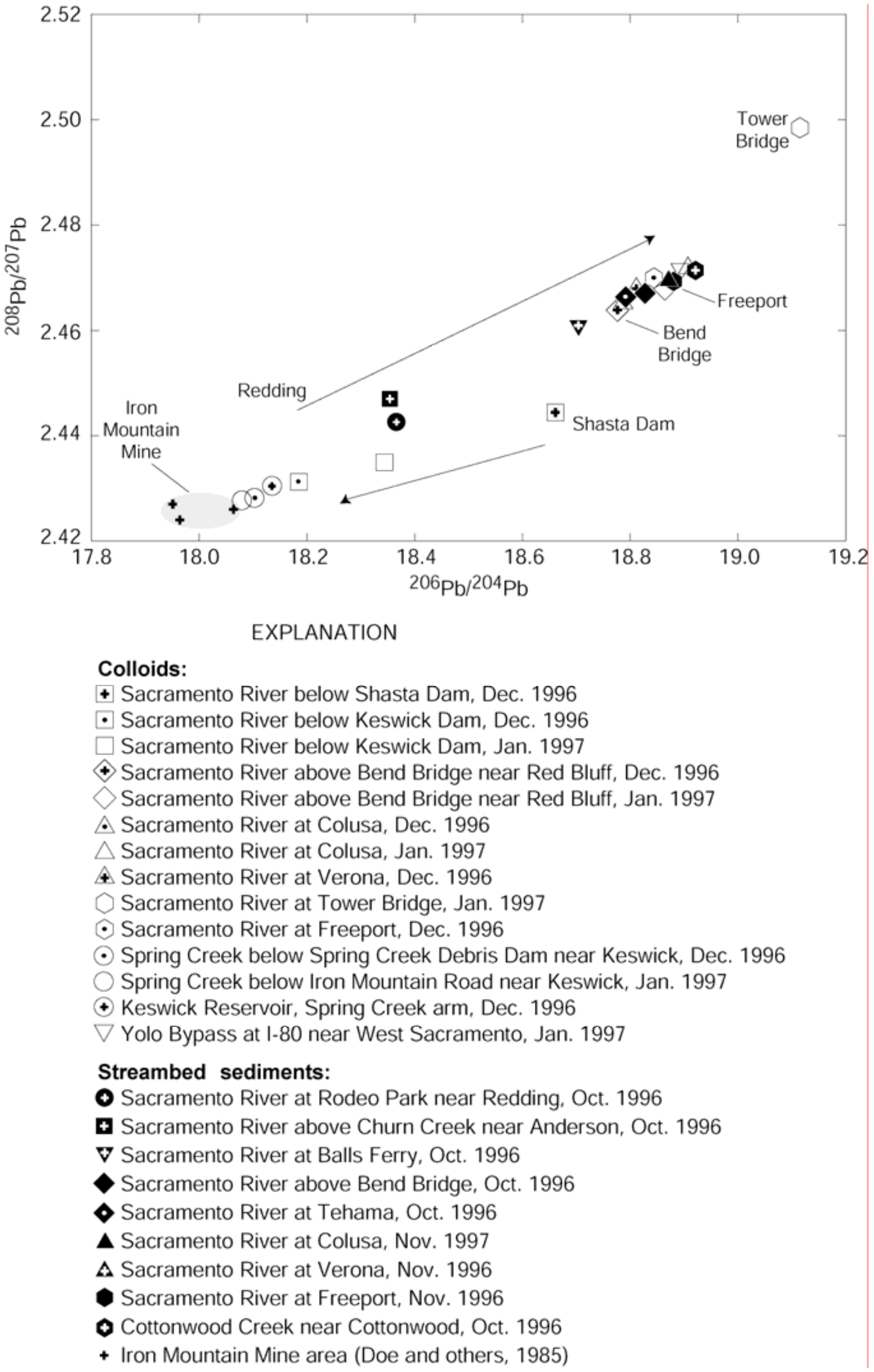

FIG. 15. Plot of $^{206}Pb/^{204}Pb$ versus $^{208}Pb/^{207}Pb$ for suspended colloids and streambed sediments in the Sacramento River watershed (adapted from Alpers *et al*. 2000a).

elevated concentrations of bioavailable Cd, Cu, Pb, and Zn at most locations. Exposures, compared with the regional reference sample, were greatest for Cd. The downstream concentration pattern indicated a primary upstream source of Cd, Cu, and Pb near or upstream from Redding, consistent with concentration gradients in streambed sediments and documented inputs from Iron Mountain and Lake Shasta, which receives drainage from other abandoned mines in the West Shasta mining district. The study did not delineate the

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downstream extent of bioavailable Cd and Zn from Iron Mountain; bioavailable forms of these metals were present 120 km downstream of Keswick Dam.

BENEFITS AND CONSEQUENCES OF WATER TREATMENT

The EPA has collected and treated AMD discharges from Iron Mountain from December 1989 through the present (May 2003), initially by a temporary simple-mix treatment plant, and subsequently by full-scale treatment operations. The Minnesota Flats HDS treatment plant began operation in September 1994 and has continued around-the-clock operations. The treatment process is 99.9% effective in removing dissolved metals from the contaminant stream. From 1989 through 2002, EPA treated more than 4×10^9 L of AMD, removing more than 7×10^5 kg of Cu and 2.6×10^6 kg of Zn from the contaminated discharge.

Discharges from Boulder and Slickrock creeks discharge through SCDD into Keswick Reservoir. Average daily Cu and Zn discharge loads from SCDD were calculated using measured concentrations and the average daily discharges for the period from October 1, 1969 through September 2002. The data demonstrate that the Cu and Zn loading from the Iron Mountain site has been reduced by approximately 85% and 92%, respectively.

The SCDD continues to discharge significant quantities of metals originating from area sources at the Iron Mountain minesite. From 1995 through 2002, an average of 13,600 kg of Cu and 21,000 kg of Zn discharged from the site each year. Monitoring has demonstrated that about two-thirds of this discharge originates from an area of about 65 ha in the Slickrock Creek basin that contains a massive slide, thousands of cubic metres of waste rock, and many collapsed and buried portals. EPA's ROD 4 (1997) selected the capture and treatment of contaminant discharges from this area of Slickrock Creek, to be done through construction of clean-water diversions, roads, AMD pipelines, and a retention reservoir with a capacity of 271,000 m^3. This will lead to improvements in downstream water quality, but may result in accumulation of Cu-contaminated sediments in Spring Creek Reservoir.

The Slickrock Creek impoundment is scheduled for completion in December 2003. Once in place, the contaminant loads from the site will have been reduced by more than 95%. A likely consequence of future increases in pH in lower Spring Creek in association with additional lime neutralization of Iron Mountain mine waters is that some Cu is likely to adsorb or coprecipitate with hydrous ferric oxides forming in Spring Creek Reservoir.

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