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## Negative pH, efflorescent mineralogy, and consequences for environmental restoration at the Iron Mountain Superfund site, California

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**ABSTRACT** The Richmond Mine of the Iron Mountain copper deposit contains some of the most acid mine waters ever reported. Values of pH have been measured as low as –3.6, combined metal concentrations as high as 200 g/liter, and sulfate concentrations as high as 760 g/liter. Copious quantities of soluble metal sulfate salts such as melanterite, chalcantite, coquimbite, rhomboclase, voltaite, copiapite, and halotrichite have been identified, and some of these are forming from negative-pH mine waters. Geochemical calculations show that, under a mine-plugging remediation scenario, these salts would dissolve and the resultant 600,000-m<sup>3</sup> mine pool would have a pH of 1 or less and contain several grams of dissolved metals per liter, much like the current portal effluent water. In the absence of plugging or other at-source control, current weathering rates indicate that the portal effluent will continue for approximately 3,000 years. Other remedial actions have greatly reduced metal loads into downstream drainages and the Sacramento River, primarily by capturing the major acidic discharges and routing them to a lime neutralization plant. Incorporation of geochemical modeling and mineralogical expertise into the decision-making process for remediation can save time, save money, and reduce the likelihood of deleterious consequences.

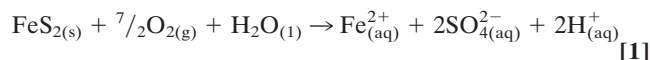
### Mining and Water Quality

Mining of metallic sulfide ore deposits (primarily for Ag, Au, Cu, Pb, and Zn) produces acid mine waters with high concentrations of metals that have harmful consequences for aquatic life and the environment. Deaths of fish, rodents, livestock, and crops have resulted from mining activities and have been noted since the days of the Greek and Roman civilizations. Mining and mineral processing have always created health risks for miners and other workers. In addition, mining wastes have often threatened the health of nearby residents by exposure to emissions of sulfur dioxide and oxides of As, Cd, Pb, and Zn from smelter stacks and flues, metal-contaminated soils, and waters and aquatic life with high concentrations of metals. As with most forms of resource extraction, human health risks accompany mineral exploitation.

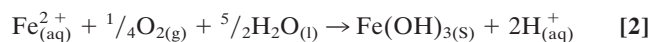
In 1985, the U.S. Environmental Protection Agency (EPA) estimated that 50 billion tons (45 × 10<sup>12</sup> kg; 1 ton = 907 kg) of mining and mineral processing wastes had been generated in the United States and about 1 billion tons would continue to be generated each year (1). More recently, the EPA has described 66 “damage cases” at their web site ([www.epa.gov](http://www.epa.gov), search for *Mining and Mineral Processing Wastes*, accessed Sept. 9, 1998) in which environmental injuries from mining

activities in the U.S. are detailed. Government records indicate that many millions, perhaps billions, of fish have been killed from mining activities in the U.S. during this century (2). Incidents of arsenic poisoning in residents of Thailand result from arsenic contamination of the shallow groundwaters because of weathering of mine wastes (3). A mine flood disaster in Spain occurred in April 1998 in which about 6 million m<sup>3</sup> of acid water and sulfide tailings escaped from a breached impoundment and covered about 6,500 acres of farmland and river banks along a 70-km reach of the Guadiamar River with fine-grained sulfides (details at [www.csic.es](http://www.csic.es)). Numerous rivers, estuaries, and reservoirs throughout the world have been used as dumping grounds for the large volumes of waste produced during mineral extraction and processing. Mineral processing, in addition to fossil fuel and metal utilization, has increased the concentration of selected metals and nonmetals in the atmosphere. The emissions of As, Cd, Cu, Pb, Sb, and Zn from anthropogenic sources are all greater than emissions from natural sources, sometimes several times higher (4, 5).

Acid mine drainage is produced primarily by the oxidation of the common iron disulfide mineral pyrite. Pyrite oxidation is a complex process that proceeds rapidly when this mineral and other sulfides are exposed to air. A simplified representation of this chemical process is given by the reaction of pyrite with air and water,



in which the product is a solution of ferrous sulfate and sulfuric acid. The dissolved ferrous iron continues to oxidize and hydrolyze when the mine water is no longer in contact with pyrite surfaces,



producing additional acidity. Iron- and sulfur-oxidizing bacteria, especially *Thiobacillus ferrooxidans*, are known to catalyze these reactions at low pH, increasing reaction rates by several orders of magnitude (6). These processes occur naturally and, indeed, natural acidic drainage is well known from many locations (7). Mining has the overall effect of dramatically increasing the oxidation rates by providing greater accessibility of air through mine workings, waste rock, and tailings, by creating greater surface area exposure through blasting, grinding, and crushing, and by concentrating sulfides in tailings. The overall rates of sulfide oxidation and metal

Abbreviation: EPA, Environmental Protection Agency.

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release in areas affected by mining are estimated to be orders of magnitude faster than natural rates.

Another process, sometimes overlooked, plays an important role in the environmental consequences of mining: the formation of soluble, efflorescent salts. Acid ferrous sulfate solutions often become so enriched through rapid pyrite oxidation and evaporation that soluble salts form. These often appear as white, blue-green, yellow to orange or red efflorescent coatings on surfaces of waste rock, tailings, and in underground or open-pit mines. Acidity and metals, formerly contained in the acid mine water, are stored in the salts, which can quickly be dissolved by a rising groundwater table or be dissolved when exposed to rain and flowing surface waters, and then infiltrate to groundwaters. The Iron Mountain Mine Superfund site is an extreme example of how the formation of soluble efflorescent minerals can make certain remediation alternatives much more risky and potentially disastrous than might otherwise be imagined.

### Iron Mountain

Iron Mountain is located in Shasta County, California, approximately 14 km northwest of the town of Redding (Fig. 1), in the southern part of the Klamath Mountains. "Iron Mountain Mine" is really a group of mines within Iron Mountain that include Old Mine, No. 8 Mine, Confidence-Complex, Brick Flat Open Pit Mine, Mattie Mine, Richmond and Richmond Extension Mines, and Hornet Mine. Ag, Au, Cu, Fe, Zn, and pyrite (for sulfuric acid production) were recovered at various times beginning in the early 1860s and ended with the termination of open-pit mining in 1962. Iron Mountain was once the largest producer of Cu in the state of California, and now it produces some of the most acidic waters in the world. Prior to the late 1980s when major remediation efforts began, approximately 2,500 tons of pyrite weathered every year from one mine alone (the Richmond Mine) and water containing about 300 tons per year of dissolved Cd, Cu, and Zn drained from the site into the Sacramento River. During periods of high runoff, sudden surges of acid mine waters into the Sacramento River have caused massive fish kills, which state and federal agencies have investigated since 1939. More than 20 fish-kill events have occurred in Sacramento River receiving waters since 1963, with at least 47,000 trout killed during a single week in 1967 (8).

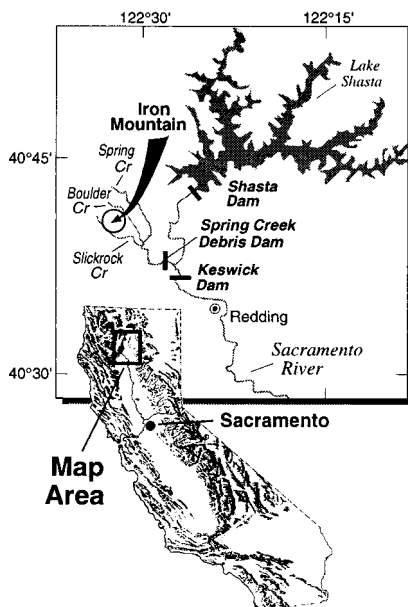


FIG. 1. Location of Iron Mountain Mine, California (adapted from ref. 15).

Furthermore, the town of Redding (with approximately 100,000 residents) receives its drinking water from the Sacramento River, downstream from the Iron Mountain site. Large, metal-rich sediment deposits containing toxic porewaters have built up in Keswick Reservoir, where the Spring Creek drainage from Iron Mountain empties into the Sacramento River. A brief history of mining, water management, and environmental action at Iron Mountain is outlined in Table 1.

The mineral deposits are primarily massive sulfide lenses as much as 60 m thick containing up to 95% pyrite, variable amounts of chalcopyrite and sphalerite, and averaging about 1% Cu and about 2% Zn. Some disseminated sulfides occur along the south side of the mountain. The deposits at Iron Mountain and elsewhere in 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 (9). The country rock is the Balaklala Rhyolite, a keratophytic rhyolite that has undergone regional metamorphism during episodes of 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 rhyolite is albite, sericite, quartz, kaolinite, epidote, chlorite, and minor calcite; consequently it has little buffering capacity. Kinkel and others (10), Reed (11), and South and Taylor (12) have documented the chemical and isotopic compositions of ore, gangue, and country-rock minerals in the West Shasta mining district. Weathering of massive sulfide deposits at and near the surface has given rise to large gossan outcrops, enriched in Ag and Au. The 10 million tons of gossan in place prior to mining is the residue from at least 15 million tons of massive sulfide that weathered naturally. A total of 7.5

Table 1. Brief chronology of Iron Mountain mining and environmental activities

Year	Activity
1860s	Discovery of massive gossan outcropping
1879	Silver discovered in gossan and mining begins
1897	Mountain Copper Co. acquires property and underground mining begins
1902	U.S. Forest Reserve sues company for vegetation damage from smelting activities
1907	Smelting ends and ore is transported to Martinez, CA, for processing
1928	California Fish and Game Commission files complaint regarding tailings dam
1939	State initiates water quality and fish toxicity studies
1943	Shasta Dam, upstream from Iron Mountain outflows, is completed
1950	Keswick Dam, downstream from Iron Mountain outflows, is completed
1955–1962	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 Co. acquires property
1976	Iron Mountain Mines, Inc., acquires property
1976–1982	State of California fines company for unacceptable releases of metals
1983	Iron Mountain listed on National Priorities List (NPL) for EPA Superfund, ranking as the third-largest polluter in the State of California
1986–1998	Four Records of Decision by EPA have instituted several remedial activities that include partial capping, surface-water diversions, tailings removal, and lime neutralization of the most acidic, metal-rich flows, reducing copper and zinc loads by 80–90%

million tons of sulfide ore was mined at Iron Mountain, and remaining reserves are estimated at approximately 15 million tons (13), so the overall size was at least 37.5 million tons prior to weathering. Preliminary paleomagnetic data on iron oxides in the gossan show portions with reversed polarity, indicating the gossan began forming at least 780,000 years ago. Secondary enrichment in the upper zones of the massive sulfides resulted in high concentrations of Cu (5–10%) and Ag (about 1 oz/ton). This enrichment took place at or near the water table during gossan formation.

Three main massive sulfide ore bodies, the Brick Flat, the Richmond, and the Hornet, include most of the oxidizing sulfides causing the current water-quality problems. These ore bodies are thought to be parts of a single massive sulfide body about 0.8 km long, over 60 m wide, and over 60 m thick that was offset by two normal faults (Fig. 2). All three of these bodies have been mined, and the consequences include large changes in the hydrogeology, resulting in highly contaminated waters from tunnels, tailings, and waste rock piles.

### Acid Effluent from the Richmond Mine

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 (14, 15). In the Richmond Mine, about 8 million tons of massive sulfide remain (13). At current weathering rates it would take about 3,200 years for the pyrite in the Richmond ore body to fully oxidize. The massive sulfide deposit is about 95% pyrite and is excavated by tunnels, shafts, raises, and stopes which allow rapid transport of oxygen by air advection. The sulfides are at or above the water table so that moisture and oxygen have ready access. Airflow is driven by the high heat output from pyrite oxidation. About 1,500 kJ of heat is released per mole (120 g) of pyrite. Air enters the main tunnel, heats up in the mine, then travels up through raises and shafts to the surface. The average flux of acid mine drainage from the Richmond portal indicates that about 2,400 mol of pyrite is oxidized every hour, producing about 1 kW of power or almost 9,000 kW per year. Water temperatures as high as 47°C have been measured underground, and the amorphous silica geothermometer (16, 17) would suggest temperatures of at least 50°C in the subsurface. In the early days of mining at Iron Mountain, fires were frequent during underground excavation, and temperatures of 430°F (221°C) were recorded at the ore surface (18).

A considerable amount of historical data exist 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 district. The Richmond ore body was discovered about 1915 but it was not mined on a large scale until the late 1930s and the war years (1940–1945). 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 1983–1991 is shown in Table 2. Further

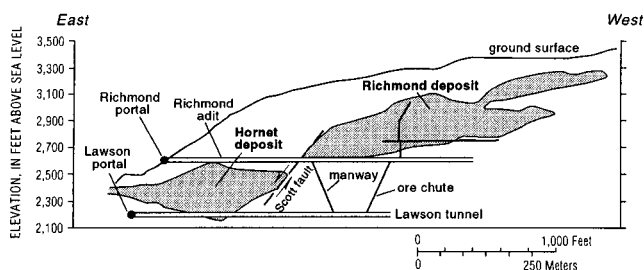


FIG. 2. Cross-section of Iron Mountain (adapted from ref. 15).

Table 2. Richmond Mine portal effluent characteristics, 1983–1991

	Mean	Range
Discharge, liter/s	4.4	0.5–50
pH	0.8	0.02–1.5
Zinc, mg/liter	1,600	700–2,600
Copper, mg/liter	250	120–650

Data are from ref. 19.

compilation and details of Richmond portal effluent composition and discharge can be found in Alpers *et al.* (19).

The variability in the Richmond effluent with time can be seen quite clearly for the 1986–1987 monitoring period. Fig. 3 covers the time period of late November 1986 to April 1987 and shows the rainfall (at Shasta Dam), and the consequent changes in Richmond Mine discharge and copper and zinc concentrations. One explanation for the large increase in copper concentrations is the dissolution of underground soluble salts from the flushing effect of meteoric recharge (see below). 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 obvious 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 the composition of the resultant mine pool be? There was, however, no basis on which to speculate without some idea of the underground conditions. Hence, one of the activities of the Second Remedial Investigation Phase (1986–1992) under the Superfund Program was an underground survey of the Richmond tunnel and part of the mine workings. Prior to underground renovations in 1989–1990, the last underground tour, to the best of our knowledge, was in 1955 (Don White, U.S. Geological Survey, personal communication, 1989). The last mining had occurred in the late 1940s. 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

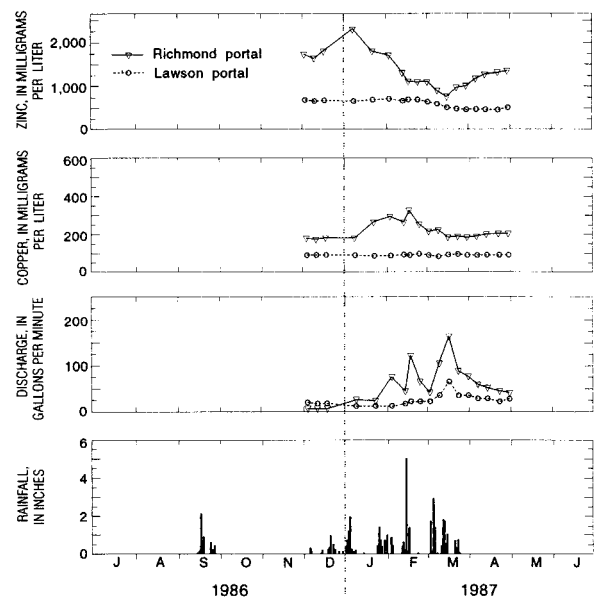


FIG. 3. Variations in rainfall, discharge, and copper and zinc concentrations for the Richmond portal effluent, 1986–1987 (adapted from ref. 19).



collected. They revealed extremely acidic seeps with pH values as low as  $-3.6$  and total dissolved solids concentration of more than 900 g/liter.

The chemical compositions of five of the most acidic waters found underground in the Richmond Mine during 1990–1991 are shown in Table 3. These concentrations are the highest ever recorded for As, Cd, Fe, and  $\text{SO}_4$  and nearly the highest for Cu and Zn in groundwater. The high subsurface temperatures have induced considerable evaporation, which, in addition to pyrite oxidation, has caused the high concentrations of dissolved metals and sulfate.

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 criteria and defined buffer systems limits the range of definable and measurable pH values to that of 1 to 13. Outside this range, the concept and measurement of pH are difficult at best. Furthermore, 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. The most acceptable model for activity coefficients at present for defining pH below 1.0 is the Pitzer ion-interaction approach (20, 21). Acid mine waters are solutions of sulfuric acid, so the Pitzer model applied to sulfuric acid (22, 23) could serve 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. Another difficulty facing the definition of pH below 0.0 is 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 (24). 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 (24). It could be argued that the MacInnes assumption becomes less defensible at high concentrations where the unscaled approach should be more appropriate, but there is no obvious justification for using one approach over the other and the choice remains arbitrary. In the present investigations, the MacInnes scaling was used primarily because geochemists who have applied the Pitzer method to the interpretation of brines and saline waters find the MacInnes assumption 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 these negative-pH mine waters were in apparent equilibrium with prominent soluble salts. For example, a

Table 3. Compositions of five extremely acid mine water samples from the Richmond Mine

Element	Concentration of element in sample, mg/liter				
	90WA103 34.8°C pH 0.48	90WA109 38°C pH $-0.7$	90WA110A 42°C pH $-2.5$	90WA110C 46°C pH $-3.6$	91WA111 28°C —
Aluminum	2,210	6,680	1,420	—	6,470
Antimony	4.0	16	29	—	15
Arsenic(III)	8.14	38	32	—	74
Arsenic (total)	56.4	154	340	—	850
Barium	0.068	0.1	0.2	—	<0.1
Beryllium	0.026	0.1	0.2	—	<0.1
Boron	1.5	2.5	17	—	—
Cadmium	15.9	48.3	211	—	370
Calcium	183	330	279	—	443
Chromium	0.12	0.75	0.6	—	2.6
Cobalt	1.3	15.5	5.3	—	3.6
Copper	290	2,340	4,760	—	9,800
Iron(II)	18,100	79,700	34,500	9,790	—
Iron (total)	20,300	86,200	111,000	16,300	68,100
Lead	3.6	3.8	11.9	—	8.3
Magnesium	821	1,450	437	—	2,560
Manganese	17.1	42	23	—	119
Molybdenum	0.59	1.0	4.2	—	2.3
Nickel	0.66	2.9	3.7	—	6.3
Potassium	261	1,170	194	—	11.1
Selenium	0.42	2.1	4.2	—	<2.8
Silicon (as $\text{SiO}_2$ )	170	34	35	—	—
Silver	0.16	0.65	2.4	—	0.70
Sodium	251	939	416	—	44
Strontium	0.25	0.49	0.90	—	—
Sulfur (as $\text{SO}_4$ )	118,000	360,000	760,000	—	—
Thallium	0.44	0.15	0.39	—	1.6
Tin	1.6	15	41	—	—
Titanium	5.9	125	1.0	—	—
Vanadium	2.9	11	15	—	28
Zinc	2,010	7,650	23,500	—	49,300
Associated mineral(s)		Melanterite	Rhombochase, römerite	Rhombochase	

A dash indicates no determination was made.



FIG. 4. Growth of cuprian melanterite in a manway of the Richmond Mine with stalactite dripping pH =  $-0.7$  water into plastic beaker. (Photo by D.K.N. and C.N.A.)

stalactite of zincian-cuprian melanterite had water dripping from the tip that had a pH of  $-0.7$  (Table 3 and Fig. 4). Enormous quantities of highly soluble iron sulfate salts were found as efflorescences and precipitates, coating walls, ceilings, and floors of the mine and growing out of muck piles in colorful assemblages. Identification of these soluble salts made it possible to estimate what the composition of a mine pool formed by mine plugging might be.

#### Soluble Salts and Consequences of the Mine-Plugging Scenario

Ten soluble iron sulfate salts plus gypsum and chalcantinite were identified in the Richmond Mine. These minerals and their idealized formulae are listed in Table 4, with the iron salts in approximate sequence downward from the early formed to the later formed. Rhomboclase was found as stalactites and stalagmites (Fig. 5), and clusters of coquimbite, römerite, copiapite, and voltaite crystals were common throughout the mine (Fig. 6). Rhomboclase was rarely found without voltaite crystals.

As long as an acid mine water is in contact with pyrite, the dissolved iron will remain 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 is often slow enough relative to the

Table 4. Idealized formulae of sulfate minerals found in the Richmond Mine

Mineral	Idealized formula
Melanterite	$\text{Fe}^{\text{II}}\text{SO}_4 \cdot 7\text{H}_2\text{O}$
Rozenite	$\text{Fe}^{\text{II}}\text{SO}_4 \cdot 4\text{H}_2\text{O}$
Szomolnokite	$\text{Fe}^{\text{II}}\text{SO}_4 \cdot \text{H}_2\text{O}$
Copiapite	$\text{Fe}^{\text{II}}\text{Fe}_4^{\text{III}}(\text{SO}_4)_6(\text{OH})_2 \cdot 20\text{H}_2\text{O}$
Römerite	$\text{Fe}^{\text{II}}\text{Fe}_2^{\text{III}}(\text{SO}_4)_4 \cdot 14\text{H}_2\text{O}$
Coquimbite	$\text{Fe}_3^{\text{III}}(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$
Kornelite	$\text{Fe}_2^{\text{III}}(\text{SO}_4)_3 \cdot 7\text{H}_2\text{O}$
Rhomboclase	$(\text{H}_3\text{O})\text{Fe}^{\text{III}}(\text{SO}_4)_2 \cdot 3\text{H}_2\text{O}$
Voltaite	$\text{K}_2\text{Fe}_5^{\text{II}}\text{Fe}_4^{\text{III}}(\text{SO}_4)_{12} \cdot 18\text{H}_2\text{O}$
Halotrichite–bilinite	$\text{Fe}^{\text{II}}(\text{Al}, \text{Fe}^{\text{III}})_2(\text{SO}_4)_4 \cdot 22\text{H}_2\text{O}$
Gypsum	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$
Chalcantinite	$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$

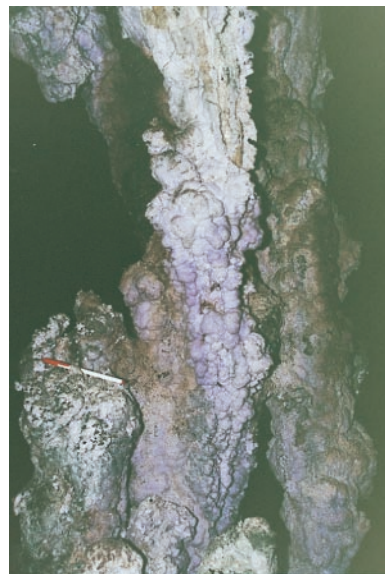


FIG. 5. Stalagmite of rhomboclase (white) and coquimbite (purple) in the Richmond Mine. (Photo by C.N.A. and D.K.N.)

flow rate of the water. Consistent with this expectation, the only iron sulfate salts containing exclusively ferrous iron, melanterite, rozenite, and szomolnokite, are found close to pyrite sources and associated with more rapidly flowing waters. Ferric-bearing minerals are found to form in more stagnant conditions and can be considered to be hydrologic “dead-ends,” where much of the  $\text{Fe}^{\text{II}}$  has had time to oxidize to  $\text{Fe}^{\text{III}}$ . 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 (25).

A copper–zinc partitioning study of melanterite demonstrates that melanterite prefers copper over zinc (15). The consequences of this partitioning are that portal effluents will tend to 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 on the Richmond Mine effluent (15).

Dissolution of these soluble, iron sulfate salts (with variable amounts of copper, zinc, cadmium, and aluminum substituting

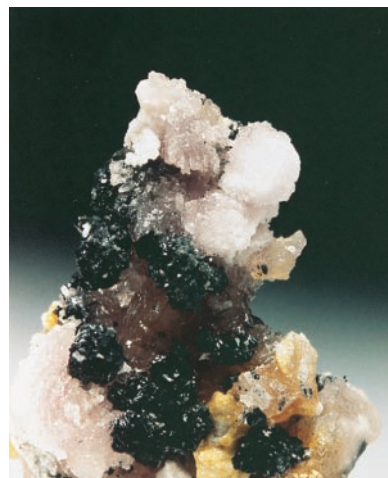


FIG. 6. Cluster of coquimbite, voltaite, and copiapite from the Richmond Mine. (Photo by G. Robinson, Canadian Museum of Nature, Ottawa.)

for the iron) can generate acidic solutions with high concentrations of dissolved metals. During the rising limb of a stream discharge in central Virginia after the onset of rain, Dagenhart (26) showed that rapid increases in the concentrations of Cu, Zn, Fe, and Al resulted from the dissolution of efflorescent salts found on upstream tailings and waste rock piles. This phenomenon must be common at mine waste sites and is likely to be an important cause of fish kills associated with periods of high runoff, especially after prolonged dry periods. Now we consider the consequences of dissolution of the enormous quantity of salts in the Richmond Mine in a mine-plugging scenario.

The chemical composition of the mine pool created by plugging the Richmond Mine can be estimated by allowing these salts to dissolve 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 so that was considered a variable. Computations were made by inputting the mineral compositions to the PHREEQE program (ref. 27, now superseded by PHREEQC, ref. 28) for a range of salt volumes. PHREEQE can calculate the speciation and chemical equilibrium for mass transfer processes such as precipitation, dissolution, oxidation-reduction reactions, ion exchange, and gas addition or removal (29). The results are shown in Fig. 7, where the resultant pH in the mine pool is plotted against the volume of added salts under two scenarios: active infiltration (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 acid waters. The salts probably occupy about 1% of the volume of the mine workings based on visual inspection from the limited subsurface survey. As can be seen in Fig. 7, however, an error in this value makes little difference. The consequences are that a mine pool of about 600,000 m<sup>3</sup> with a pH at or below 1, with many grams of dissolved metals per liter (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 drill-holes. Thus, plugging presents a remediation scenario that has a high degree of risk with potentially dangerous results.

It has been common engineering practice to plug abandoned or inactive mines without monitoring, modeling, 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 mine

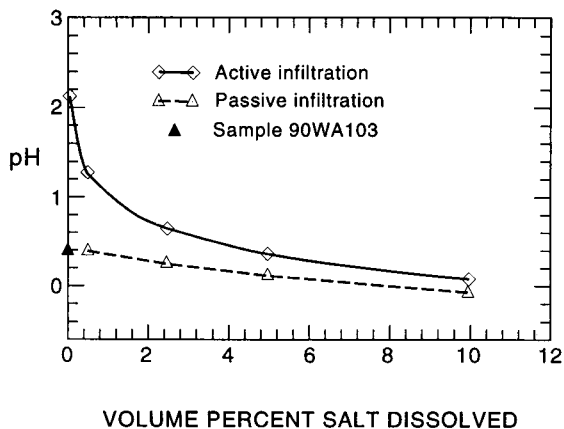


FIG. 7. PHREEQE simulation of water composition for mine pool after plugging the Richmond Mine.

sites, plugging may ultimately prove to be successful, but more careful planning and peer review are essential to lessen the probability of disastrous results.

### Regulatory Investigations and Remediation

Several investigations and regulatory actions at Iron Mountain have been initiated by California State agencies over the last few decades. These are too lengthy to summarize here. Since the original listing of Iron Mountain on the National Priorities List in 1983, the EPA has authorized four Records of Decision (RODs) and has considered numerous options for remediation. A condensed version of the main remedial alternatives 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)
- Ground-water interception
- Air sealing
- Mine plugging
- On-site leaching and solution extraction
- Continued mining under environmentally safe conditions
- Combined alternatives

Surface-water diversions have been installed to divert clean headwater streams around contaminated areas. The waters that are the largest sources of metal loadings have been captured and diverted to a lime neutralization plant. In the late 1980s, an emergency lime neutralization plant with a capacity of about 60 gallons per minute (gpm; 1 gallon =  $3.8 \times 10^{-3}$  m<sup>3</sup>) was installed to handle the worst flows from the Richmond and Hornet portals. By December of 1992, this plant had been expanded to handle 140 gpm, but was operated only 4 months per year during highest flows. In July of 1994 a new plant with a capacity of about 1,400 gpm began operation at the Minnesota Flats tailings site. In 1996 it was upgraded to 2,000 gpm, and high-density sludge treatment was added. Now it accepts drainage from Slickrock Creek (pumped from Old Mine and No. 8 Mine workings) as well as the Richmond and Hornet Mine portal effluents.

The decision to build the larger treatment plant and to treat discharges from the Lawson tunnel (Hornet Mine) was also influenced by geochemical modeling. 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 ore body 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. However, consultants proposed that plugging the Richmond Mine would stop or greatly reduce the flow from the Lawson tunnel. 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 from the Richmond to the Hornet.

Alpers and others (19) studied the historical data on rain-fall-discharge relationships between the two mines, Zn/Cu ratios as a signature of reactions within each mine site, and mass balance calculations for the two portal effluents. The most definitive method of determining the possible influence of the Richmond Mine water on the Lawson tunnel effluent was a mass balance approach. Using the known water compositions discharging from each mine and knowing the composition of the minerals that are reacting to form the effluent



waters, it is possible to calculate the mass amounts of minerals dissolved or precipitated to produce these waters by using the BALANCE program (30). Mineral reaction signatures were developed for each mine effluent separately, and then Richmond effluent was mixed with clean ground water and allowed to precipitate and dissolve additional minerals to determine if it was possible to derive the Lawson effluent from the Richmond. No version of this mass balance model produced a water that matched the Lawson effluent. Next, Richmond effluent was also mixed with Lawson effluent, and geochemical reaction was allowed, to see how much effluent each mine could be contributing to the Lawson. The model results indicated that not more than about 2% of the Richmond effluent could be present in the Lawson effluent. Therefore, the Hornet Mine is producing its own effluent independently of the Richmond Mine. Even if the Richmond Mine were successfully plugged, water from the Hornet would continue to be a significant problem and it would have to be treated.

The fourth Record of Decision, issued in September of 1997, selected the construction of a dam on Slickrock Creek. This structure will capture the largest remaining loads of Cu and Zn and divert them to the neutralization plant for treatment. The remaining remediation is now focused on Boulder Creek, lower Spring Creek, Spring Creek Reservoir, and the metal-enriched sediments that formed in Keswick Reservoir from the neutralization of acid mine waters for nearly 50 years.

The EPA and the potentially responsible parties remain in legal contention over the appropriate final remediation approaches to be used at Iron Mountain and the costs. Both the U.S. Government and the potentially responsible parties have funded a considerable number of investigations, remediation efforts, legal fees, and oversight management. The loads of copper, zinc, and cadmium into the Sacramento River have been reduced by 80–90%, and further remediation is in progress or being planned. The main challenge that remains is how to find a permanent (and passive) treatment solution in light of the fact that the mine drainage will continue for approximately 3,000 years unless the sulfide ore is mined out.

## Conclusion

Prevention and control of contamination at mine sites is a challenging task, and remediation of large inactive mine sites such as Iron Mountain has proven to be extraordinarily difficult, complex, and expensive, not to mention litigious. The physical and chemical nature of the site makes it difficult to assess the effectiveness of remediation and the relative risks and costs of various alternatives and their contingencies. There are no easy solutions to these types of environmental problems, but several important points can be made about cleanup of mine waste sites on the basis of our experiences at Iron Mountain.

First, there is tremendous value to having a technical advisory team of multidisciplinary professionals, without an obvious conflict of interest, to advise the regulatory agencies, to review data, and to make recommendations. Mine sites and their contaminants are complex functions of the geology, hydrology, geochemistry, pedology, meteorology, microbiology, and mining and mineral processing history, and their remediation is subject to considerations of economic limitations, available technology, and potential land use. Furthermore, the risks of failed remediation or no action are often poorly known. Assessing such risks involves toxicology, epidemiology, wildlife biology, and dealing with public perception. To ignore professionals in these areas, who can contribute both to the wisest choice of remediation strategies and to public awareness and education is to invite mistakes.

Second, the effectiveness of a remedial alternative usually cannot be easily quantified or predicted. Hence, we must admit that remediation is experimental. Research is required to

effect the best and most appropriate remediation available at a given time for a given site. Both long-term and short-term remediations are needed. For the short term, we need to fill in the knowledge gaps, especially as they pertain to a particular site. For the long term, we need to continue to develop better remediation techniques and mining and processing techniques that can utilize mine wastes and mineral deposits of lower grade. Mineralogical and geochemical knowledge make it possible to foresee the potential consequences of a remedial option and to plan a remediation strategy. The results of long-term research by the U.S. Geological Survey provided technical tools (computer programs for geochemical modeling and procedures for measuring pH) that could be used to answer important questions regarding remediation scenarios.

Third, it would seem prudent to proceed on mine waste cleanup in a phased, iterative approach. Our natural inclination is to identify the worst part of a hazardous waste site and attempt to clean it up. For Iron Mountain, there is no single remedial solution that would clean up 90% of the problem on a permanent and maintenance-free basis (with the exception of completely mining the mountain). There are, however, several options (most of which have been exercised) that are low risk and low cost and should reduce the discharge of acid mine waters. These options can be instituted while deliberations and research continue to find the long-term solution.

Fourth, mine waste sites commonly contain low-grade resources that are potentially mineable—it requires the right technology to make resource recovery economic. In an age of increasing recycling, recycling strategies should be applied to mine sites. Many mine wastes have already undergone further metals extraction and others could be stockpiled or tested for new uses. Additional research into metal recovery from acidic solutions could also provide economic incentive to recycling metals from mine drainage waste streams.

Finally, Iron Mountain has been an extraordinary and extreme environment in which to study and document the processes of acid mine water production and efflorescent mineral formation, the value of which goes far beyond just the immediate remediation needs. The processes and properties found at Iron Mountain are probably commonplace at metal sulfide mine and mineral processing sites, but usually on a smaller scale. We now have some direct observations of the composition of water that produces efflorescent minerals. We have some idea of the consequences of efflorescent mineral dissolution when a mine is plugged. We can estimate the geochemical consequences of various remediation scenarios for mine sites with better confidence. Unraveling the dynamic processes that affect water–mineral interactions is often critical to solving hazardous waste problems in the hydrogeologic environment.

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1. USEPA (U.S. Environmental Protection Agency) (1985) *Wastes from Extraction and Beneficiation of Metallic Ores, Phosphate Rock, Asbestos, Overburden from Uranium Mining, and Oil Shale: Report to Congress* EPA/530-SW-85-033.
2. Nordstrom, D. K. & Alpers, C. N. (1999) in *Environmental Geochemistry of Mineral Deposits*, eds. Plumlee, G. S. & Logsdon, M. J., Reviews in Economic Geology (Soc. Econ. Geol., Littleton, CO), in press.



3. Choprapawon, C. (1998) Abstracts of International Conference on Arsenic Pollution of Ground Water in Bangladesh: Causes, Effects, and Remedies; Dhaka, Feb. 8–12, 1998, pp. 77–78.
4. Church, T., Arimoto, R., Barrie, L. A., Dehairs, F., Dulac, F., Jickells, T. D., Mart, L., Sturges, W. T. & Zollar, W. H. (1990) in *The Long-Range Atmospheric Transport of Natural and Contaminant Substances*, ed. Knap, A. H. (Kluwer, Dordrecht, the Netherlands), pp. 37–58.
5. Buat-Ménard, P. (1993) in *Global Atmospheric Chemical Change*, eds. Hewitt, C. N. & Sturges, W. T. (Elsevier Science, Amsterdam), pp. 271–311.
6. Nordstrom, D. K. & Southam, G. (1997) in *Geomicrobiology: Interactions between Microbes and Minerals*, eds. Banfield, J. F. & Nealson, K. H., Reviews in Mineralogy (Mineral Soc. Am., Washington, DC), Vol. 35, pp. 361–390.
7. Runnells, D. D., Shepard, T. A. & Angino, E. E. (1992) *Environ. Sci. Technol.* **26**, 2316–2322.
8. Nordstrom, D. K., Jenne, E. A. & Averett, R. C. (1977) *Heavy metal discharges into Shasta Lake and Keswick Reservoir on the Sacramento River, California—A Reconnaissance During Low Flow*, U.S. Geological Survey Open-File Report 76-49.
9. Albers, J. P. & Bain, J. H. C. (1985) *Econ. Geol.* **80**, 2072–2091.
10. Kinkel, A. R., Hall, W. E. & Albers, J. P. (1956) *Geology and base-metal deposits of the West Shasta copper-zinc district, Shasta County, California*, U.S. Geological Survey Professional Paper 285.
11. Reed, M. H. (1984) *Econ. Geol.* **79**, 1299–1318.
12. South, B. C. & Taylor, B. E. (1985) *Econ. Geol.* **80**, 2177–2195.
13. Kaiser Engineering (1990) *Iron Mountain Mine Property, West Shasta District, California—Technical Review. Prepared for Iron Mountain Mines, November 1981*.
14. Nordstrom, D. K. (1977) Ph.D. Dissertation (Stanford Univ., Stanford, CA).
15. Alpers, C. N., Nordstrom, D. K. & Thompson, J. M. (1994) in *Environmental Geochemistry of Sulfide Oxidation*, eds. Alpers, C. N. & Blowes, D. W., American Chemical Society Symposium Series (Am. Chem. Soc., Washington, DC), Vol. 550, pp. 324–344.
16. Fournier, R. O. & Rowe, J. J. (1966) *Am. J. Sci.* **264**, 685–697.
17. Fournier, R. O. (1985) in *Geology and Geochemistry of Epithermal Systems*, eds. Berger, B. R. & Bethke, P. M., Reviews in Economic Geology (Soc. Econ. Geol., Littleton, CO), Vol. 2, pp. 45–61.
18. Wright, L. T. (1906) *Eng. Min. J.* **81**, 171–172.
19. Alpers, C. N., Nordstrom, D. K. & Burchard, J. M. (1992) *Compilation and interpretation of water-quality and discharge data for acidic mine waters at Iron Mountain, Shasta County, California 1940–91*, U.S. Geological Survey Water-Resources Investigations Report 91-4160.
20. Pitzer, K. S. (1973) *J. Phys. Chem.* **77**, 268–277.
21. Pitzer, K. S. (1991) in *Activity Coefficients in Electrolyte Solutions*, ed. Pitzer, K. S. (CRC Press, Boca Raton, FL), 2nd Ed., pp. 75–153.
22. Pitzer, K. S., Roy, R. N. & Silvester, L. F. (1977) *J. Am. Chem. Soc.* **99**, 4930–4936.
23. Clegg, S. L., Rard, J. A. & Pitzer, K. S. (1994) *J. Chem. Soc. Faraday Trans.* **90**, 1875–1894.
24. Plummer, L. N., Parkhurst, D. L., Fleming, G. W. & Dunkle, S. A. (1988) *A computer program incorporating Pitzer's equations for calculation of geochemical reactions in brines*, U.S. Geological Survey Water-Resources Investigations Report 88-4153.
25. Buurman, P. (1975) *Geologie en Mijnbouw* **54**, 101–105.
26. Dagenhart, T. V., Jr. (1980) M.S. thesis (Univ. of Virginia, Charlottesville).
27. Parkhurst, D. L., Thorstenson, D. C. & Plummer, L. N. (1980) *PHREEQE—A computer program for geochemical calculations*, U.S. Geological Survey Water-Resources Investigations Report 80-96.
28. Parkhurst, D. L. (1995) *User's guide to PHREEQC—A computer program for speciation, reaction-path, advective-transport, and inverse geochemical calculations*, U.S. Geological Survey Water-Resources Investigations Report 95-4227.
29. Alpers, C. N. & Nordstrom, D. K. (1999) in *Environmental Geochemistry of Mineral Deposits*, eds. Plumlee, G. S. & Logsdon, M. J., Reviews in Economic Geology (Soc. Econ. Geol., Littleton, CO), in press.
30. Parkhurst, D. L., Plummer, L. N. & Thorstenson, D. C. (1982) *BALANCE—A computer program for calculating mass transfer for geochemical reactions in ground water*, U.S. Geological Survey Water-Resources Investigations Report 82-14.