Negative pH, Efflorescent Mineralogy, and the Challenge of Environmental Restoration at the Iron Mountain Superfund site or why not to plug a Mine

D. Kirk Nordstrom

US Geological Survey, 3215 Marine St., Suite E-127, Boulder, CO 80303 USA, E-Mail: dkn@usgs.gov

Investigations at the Richmond Mine of the Iron Mountain copper deposit in northern California have documented the most acidic waters, the highest metal concentrations (measured in $g \cdot L^{-1}$), and the highest sulfate concentrations (760 $g \cdot L^{-1}$) anywhere. Underground drip waters have been found with negative pH values, as low as -3.6, and densities similar to those of some minerals, up to 1.45 $g \cdot cm^{-3}$. Copious quantities of soluble metal sulfate salts such as melanterite, chalcanthite, coquimbite, rhomboclase, voltaite, copiapite, and halotrichite have been identified and some of these appear to be in equilibrium with the analyzed waters. Geochemical calculations show that, under a mine-plugging remediation scenario, these salts would dissolve and the resultant 600,000 m^3 mine pool would have a pH of 1 or less and contain several grams per liter of dissolved metals, much like the current portal effluent water, but 100 meters head of this water would be sitting above the ground-water table in a rock that has no neutralization capacity. Plugging would not stop the ground-water flow from underground to the surface. Remedial actions have greatly reduced metal loads into downstream drainages 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.

1   Introduction

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 (NORDSTROM 1982; NORDSTROM & SOUTHAM 1997; NORDSTROM 2000). A simplified representation of this chemical process is given by the reaction of pyrite with air and water,

$$FeS_{2(s)} + \tfrac{7}{2}O_{2(g)} + H_2O_{(l)} \rightarrow Fe^{2+}_{(aq)} + 2SO^{2-}_{4(aq)} + 2H^+_{(aq)} \quad (1)$$
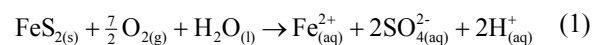
in which the product is a solution of ferrous sulfate and sulfuric acid. The dissolved ferrous iron continues to oxidize and hydrolyze when the mine water is no longer in contact with pyrite surfaces,

$$Fe^{2+}_{(aq)} + 0.25O_{2(g)} + 2.5H_2O_{(l)} \rightarrow Fe(OH)_3(s) + 2H^+_{(aq)} \quad (2)$$
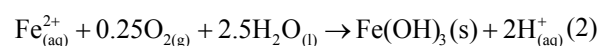
producing additional acidity. Iron- and sulfur-oxidizing bacteria, especially *Acidithiohiobacillus ferrooxidans*, are known to catalyze these reactions at low pH, increasing reaction rates by several orders of magnitude NORDSTROM (2003). These processes occur naturally and, indeed, natural acidic drainage is well known from many locations (RUNNELLS et al. 1992). 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 rates of sulfide oxidation and metal discharge in mined areas are estimated to be orders of magnitude faster than natural rates.

Another process, the formation of soluble, efflorescent salts, plays an important role in the environmental consequences of mining. 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 these salts that can quickly be dissolved by a rising ground-water table or by rain and flowing surface waters. 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.

2 Iron Mountain

Iron Mountain is located in Shasta County, California, approximately 9 miles northwest of the town of Redding (Figure 1), in 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. Gold, silver, copper, iron, zinc, and pyrite (for sulfuric acid production) were recovered at various times beginning in the early 1860's and ending with the termination of open-pit mining in 1962. Iron Mountain was once the largest producer of copper in California, and now it produces some of the most acidic waters in the world. Prior to the late 1980's when major remediation efforts began, approximately 2,500 tons of pyrite weathered every year from the Richmond Mine alone and water containing about 300 tons per year of dissolved cadmium, copper, and zinc drained into the Sacramento River. During periods of high runoff, sudden surges of acid mine waters have caused massive fish kills that state and federal agencies have investigated since 1939 (more than 20 fish kill events up to a maximum of 100,000 fish killed at one time since 1963). Furthermore, Redding (about 100,000 residents, Figure 1) receives its drinking water from the river, downstream from the mine site. Metal-rich sediments containing toxic porewaters deposited in Keswick Reservoir where Spring Creek empties into the Sacramento River.

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 & ALPERS 1999; NORDSTROM et al. 2000). In the Richmond Mine, about 8 millions tons of massive sulfide remain. 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 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 are 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
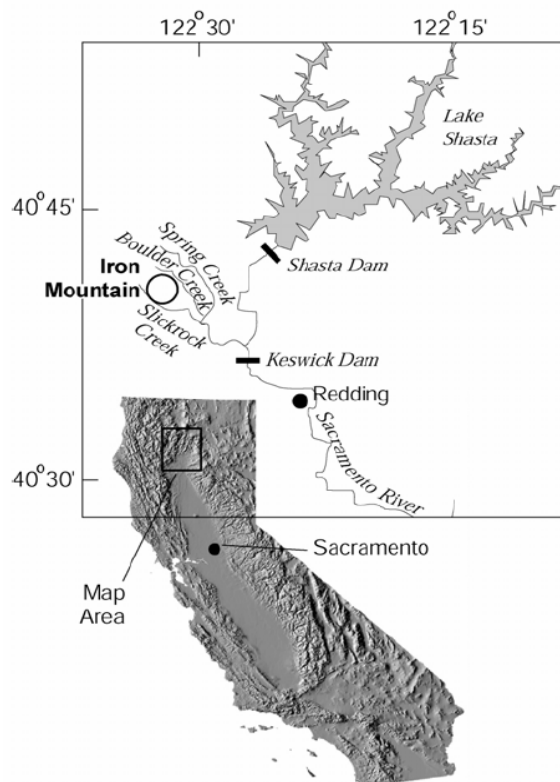

Figure 1: Map showing location of Iron Mountain, California (adapted from NORDSTROM et al. 1999).

2,400 moles of pyrite are 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 (WRIGHT 1906).

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 (1986–92) 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 tour, to the best of our knowledge, was in 1955
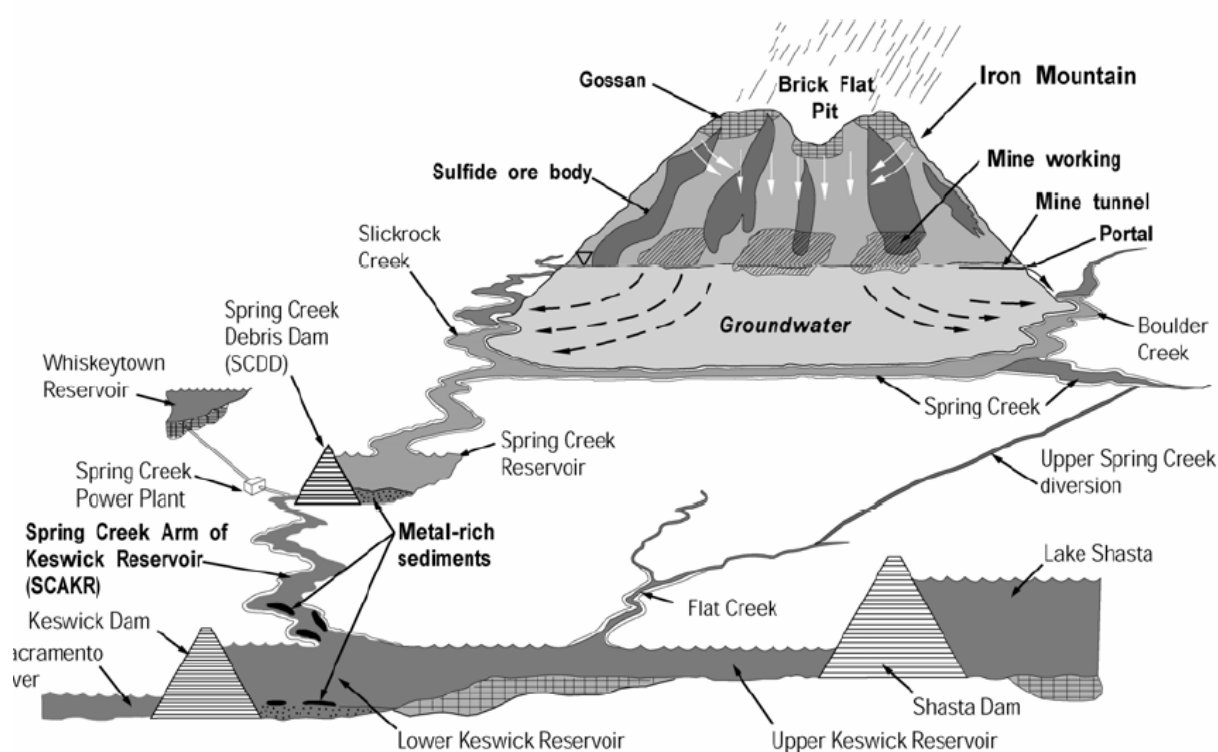
Figure 2: Schematic diagram showing metal sources and transport from Iron Mountain to the Sacramento river.

(DON WHITE, personal communication, 1989). The last mining had occurred in the late 1940's. 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 revealing extremely acidic seeps with pH values as low as -3.6 and total dissolved solids concentration of more than 900 g·L^{-1}.

The chemical compositions of three of the most acidic waters found underground in the Richmond Mine during 1990–91 are shown in table 1. These concentrations are the highest ever recorded for As, Cd, Fe, and 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 limit 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. Acid mine waters are solutions of sulfuric acid so that the Pitzer model applied to sulfuric acid (PITZER et al. 1977) 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 (Any use of trade, product, or firm names is for descriptive purposes only and does not imply endorsement by the U.S. Government) 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. 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 water. 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 stalactite of zincian-cuprian melanterite had water dripping from the tip that had a pH of -0.7 (table 1). 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.

Table 1: Three extreme acid mine water samples from the Richmond Mine. Dashed line indicates no determination was made.

Sample	90WA109	90WA110A	90WA110C
Temperature, ^{o}C	38	42	46
pH	-0.7	-2.5	-3.6
Element, mg·L^{-1}			
Aluminum	6,680	1,420	-
Antimony	16	29	-
Arsenic	154	340	-
Barium	0.1	0.2	-
Beryllium	0.1	0.2	-
Cadmium	48.3	211	-
Calcium	330	279	-
Chromium	0.75	0.6	-
Cobalt	15.5	5.3	-
Copper	2,340	4,760	-
Iron (II)	79,700	34,500	9,790
Iron (total)	86,200	111,000	16,300
Lead	3.8	11.9	-
Magnesium	1,450	437	-
Manganese	42	23	-
Molybdenum	1.0	4.2	-
Nickel	2.9	3.7	-
Potassium	1,170	194	-
Selenium	2.1	4.2	-
Silicon (as SiO_2)	34	35	-
Silver	0.65	2.4	-
Sodium	939	416	-
Strontium	0.49	0.90	-
Sulfur (as SO_4)	360,000	760,000	-
Thallium	0.15	0.39	-
Tin	15	41	-
Titanium	125	1.0	-
Vanadium	11	15	-
Zinc	7,650	23,500	-
Associated Minerals	Melanterite	rhomboclase, römerite	rhomboclase

3 Soluble salts and conse-quences of the mine-plugging scenario

Ten soluble iron-sulfate salts plus gypsum and chalcanthite were identified in the Richmond Mine. Rhomboclase was found as stalactites and stalagmites and clusters of coquimbite, römerite, copiapite, and voltaite crystals were common throughout the mine. Rhomboclase was rarely found without voltaite crystals.

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 (now superseded by PHREEQC; PARKHURST & APPELO 1999) 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. The results are shown in figure 3, 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 ground water 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 figure 3, however, an error 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 ground-water 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.
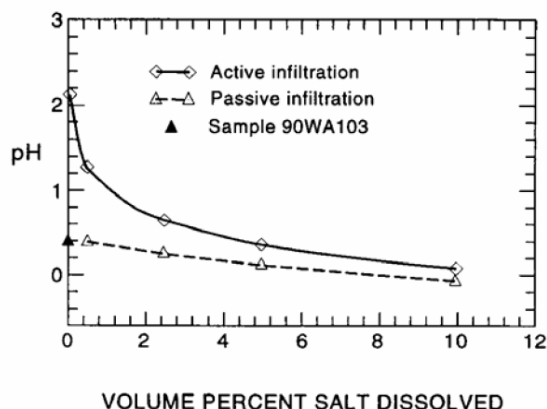

Figure 3: Change in pH with increase in dissolved salts.

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 sub-surface head pressures of more than one hundred meters have occurred. For some 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.

4 Conclusions

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 make 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 based on our experiences at Iron Mountain.

First, there is tremendous value to having a technical advisory team of multi-disciplinary 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. Assesing such risks involves toxicology, epidemiology, wildlife biology and dealing with public perception. To ignore professionals in these areas, who can contribute to both 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 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 made it possible to foresee the potential consequences of a remedial option and to plan a remediation strategy. The results of long-term research at the USGS 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, 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.

5 Acknowledgments

6 References

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