

EFFLORESCENT SALTS AND THEIR EFFECTS ON WATER QUALITY AND MINE PLUGGING

D. Kirk Nordstrom

U.S. Geological Survey
3215 Marine St.,
Boulder, CO 80303, U.S.A.
e-mail: dkn@usgs.gov

ABSTRACT

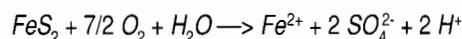
Efflorescent salts are a familiar site in association with pyrite oxidation and mine waste materials. These salts should not be overlooked during remedial investigations of mine sites because they contribute to the solute load of surface waters during rainstorm-runoff events. Mine plugging can cause detrimental results from the formation of a very acidic mine pool when underground efflorescent minerals are dissolved. In some environments, mine plugging should be avoided because of both physical and chemical consequences that can cause more damage than not plugging.

INTRODUCTION

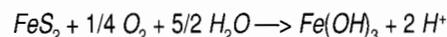
Mining of metal sulfide mineral deposits for Cu, Zn, Au, Ag, Sn, and Pb is the backbone of our modern industrial society. Unfortunately, the wastes from extraction, milling, and mineral processing can have devastating effects on the ecosystem. Numerous streams, rivers, lakes, reservoirs, estuaries, and coastal environments worldwide have been used as dumping grounds for mining and processing wastes. Mortality of invertebrates, fish, rodents, livestock, and crops have been noted since the days of the Greek and Roman civilizations. In the order of billions of fish in the U.S. have been killed from mining activities in the U.S. (Nordstrom and Alpers, 1999a). Exposure of workers and nearby residents to the toxic emissions of smelters and flue dusts has caused human injuries and death in addition to the risks associated with underground and above-ground extraction of ores.

In the U.S. alone, many tens of billions of tons of mining and mineral processing wastes have been generated, according to the U.S. Environmental Protection Agency (EPA). Descriptions of 66 "damage cases" can be accessed at the EPA web site (www.epa.gov, search for Mining and Mineral Processing Wastes). The Aznalcóllar mine flood disaster in the Guadiamar River, southern Spain, has been a unfortunate reminder that greater effort is needed to prevent environmental destruction from the effects of mining.

Acid mine drainage is produced primarily by the oxidation of pyrite in the presence of air and water:



The dissolved ferrous iron continues to oxidize and hydrolyze as long as the water is out of contact with the pyrite surface:



producing additional acidity. These reactions are catalyzed by iron- and sulfur-oxidizing bacteria, especially *Thiobacillus* and *Leptospirillum* species. Biocatalysis can increase rates by up to 6 orders of magnitude (Nordstrom and Southam, 1997; Nordstrom and Alpers, 1999). These processes are natural and naturally acidic drainage is well-known from many locations (Runnells and others, 1992). Mining dramatically increases the oxidation rates by enhancing the availability of air and water to pyrite surfaces. Blasting, drilling, rock removal, construction of tunnels, manways, shafts, adits, and other openings, ore grinding, crushing, and tailings and waste rock dumps create large volumes of high surface area sulfides.

Another process often overlooked is the formation, oxidation, and dissolution of efflorescent salts. Acid mine waters are fairly concentrated solutions that easily form efflorescent salts upon evaporation. These salts appear in a range of colors from white to yellow to red to blue and to green on any surfaces where evaporation is possible. Acidity and metals formerly contained in the mine water are now stored in the salts which can be dissolved quickly when exposed to rain, to flowing surface waters, or to a rising ground-water table. This paper focuses on the consequences of efflorescent salt formation and dissolution on metal transport and remediation activities such as mine plugging.

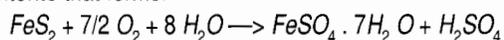
FORMATION OF SOLUBLE, EFFLORESCENT SALTS

A large number of efflorescent minerals are known to form in acid mine waste environments (Nordstrom and Alpers, 1999a,b). Although a complete list can be quite long, a few salts occur more frequently than others. These minerals and their chemical formula are given below in Table 1 based on data from Nordstrom (1982), Nordstrom and Alpers (1999a,b) and Dagenhart (1980). Included in this list are the main iron and aluminum salts found in mine waste environments. Other metal sulfate salts are often found and a more complete list of these can be found in Nordstrom and Alpers (1999a).

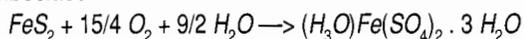
Mineral	Idealized formula
Melanterite	$\text{Fe}^{\text{II}}\text{SO}_4 \cdot 7\text{H}_2\text{O}$
Rozenite	$\text{Fe}^{\text{II}}\text{SO}_4 \cdot 4\text{H}_2\text{O}$
Szomolnokite	$\text{Fe}^{\text{II}}\text{SO}_4 \cdot \text{H}_2\text{O}$
Copiapite	$\text{Fe}^{\text{II}}\text{Fe}_4^{\text{III}}(\text{SO}_4)_6(\text{OH})_2 \cdot 20\text{H}_2\text{O}$
Römerite	$\text{Fe}^{\text{II}}\text{Fe}_2^{\text{III}}(\text{SO}_4)_4 \cdot 14\text{H}_2\text{O}$
Coquimbite	$\text{Fe}_2^{\text{III}}(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$
Kornelite	$\text{Fe}_2^{\text{III}}(\text{SO}_4)_3 \cdot 7\text{H}_2\text{O}$
Rhombochase	$(\text{H}_3\text{O})\text{Fe}^{\text{III}}(\text{SO}_4)_2 \cdot 3\text{H}_2\text{O}$
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-pickeringite-bilnite	$\text{Fe}^{\text{II}}(\text{Al},\text{Mg},\text{Fe}^{\text{III}})_2(\text{SO}_4)_4 \cdot 22\text{H}_2\text{O}$
Alunogen	$\text{Al}_2(\text{SO}_4)_3 \cdot 17\text{H}_2\text{O}$

Table 1. Idealized formulae of common sulfate minerals found as efflorescent salts.

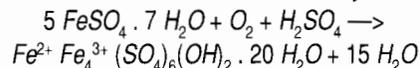
It is important to make note of several aspects of this list in Table 1. First, the iron sulfate salts are tabulated in more or less the sequence from first-formed to last-formed, based on field observations and lab studies (Buurman, 1975; Nordstrom and Alpers, 1999a). Second, the three primary variables controlling the appearance of a salt are temperature, humidity, and degree of oxidation. Phase equilibrium and solubility studies in the chemical literature provide helpful information on these relationships. Third, when melanterite is formed from pyrite oxidation the reaction stoichiometry dictates that 1 mole of sulfuric acid forms for every mole of melanterite that forms:



whereas when the oxidized iron sulfate mineral rhombochase is formed, all of the reaction product is contained in the rhombochase:



Fourth, when copiapite is formed from melanterite (documented in Nordstrom, 1982), there must be some sulfuric acid present to make the reaction stoichiometry balance:



And, fifth, these minerals have a large capacity to allow substitution of numerous other metals for the iron and aluminum. Solid substitutions can occur over the entire compositional range depending on the composition of the water from which the mineral is forming. Hence, the chemical composition of an efflorescent mineral assemblage can be as variable as the evaporating waters from which they form.

The distribution of trace metals between the salt and the water can play a major role in determining the variations in mine water compositions during seasonal changes. A partitioning study of Cu and Zn in cuprian zincian melanterite demonstrated that melanterite prefers copper over zinc (Alpers and others, 1994). If this partitioning controls Zn/Cu ratios in the effluent water then higher ratios would be expected during the dry season when melanterite is forming and lower ratios in the wet season when melanterite is dissolving. This trend is, indeed, seen in the seasonal data of effluent from the main mine portal.

CONSEQUENCES OF EFFLORESCENT MINERAL DISSOLUTION

Efflorescent salts will accumulate during dry periods as long as some small amount of water or humidity is available. During rainstorm events, the rain and/or runoff and/or rising ground water and/or interflow will dissolve these soluble salts and may increase the solute concentrations of the waste stream. When this occurs, the loading of metals in a stream or river can increase sharply from increases in both the discharge and the concentration. This phenomenon might well contribute to the correlation of major fish kills with rainstorm-flush out events occurring early in the wet season or after significant periods of dry weather. Dagenhart (1980) identified the mineralogy of efflorescent sulfates in the Contrary Creek drainage basin, central Virginia which contained three major mine tailings piles. He then monitored the runoff water and found that short spikes in increased metal concentrations, especially for Fe, Al, Cu, and Zn, occurred during the rising limb of the discharge near the mouth. The concentration of Mn did not change during the rising discharge event, consistent with the lack of Mn in the soluble efflorescences.

Another example comes from Iron Mountain, California where the most acid effluent on the site discharges from the Richmond Mine (Alpers and others, 1992). Variations in composition of this effluent occur with seasonal changes and with storm events related to the formation and dissolution of soluble efflorescent salts (Alpers and others, 1994). During the early storms of fall, 1984, large increases in metal concentrations,

sulfate concentrations, and decreases in pH could be observed (Alpers and others, 1992; 1994; Nordstrom and others, 1990).

The last example of the consequences of efflorescent mineral formation addresses mine plugging as a remediation alternative. Mine plugging is often used to retain or prevent the release of acid mine water from a mine portal. As either a temporary or permanent solution to the problem there can be seriously detrimental consequences to mine plugging. These consequences can be identified when the following questions are considered: How long does a plug last? Where is the weakest part of a mine plug installation? What happens to the ground water flow conditions? Where does the water flow? What is the composition of the mine pool created by the plug? Given 5-20 years will the loading of metals in the receiving drainage decrease or increase? Will most all the reacting sulfides be underwater all the year, even in periods of drought? The answers to these questions should be considered, at least qualitatively, before approving of plugging as a remediation technique for a site.

For the Richmond Mine at the Iron Mountain Superfund site, California, mine plugging was given serious consideration as a remedial measure. One of the questions, however, was what would be the chemical composition of the mine pool created by the installation of plugs. To answer this question, a survey was undertaken in September of 1990 to document the chemical conditions that existed underground. No one had been underground for about 35-40 years and during this time period, enormous growths of efflorescent salts had occurred. Stalactites and stalagmites of rhomboclase, voltaite and coquimbite that reached more than 10 meters high and a meter across were found. The underground survey revealed pools and drip water having negative pH and, forming from them, most of the minerals found in Table 1 (Nordstrom and Alpers, 1999b). Some of the highest concentrations of metals and sulfate ever reported can be found in these waters. The high subsurface temperatures (30-50 or more °C) have induced considerable evaporation, which, in addition to the oxidation of pyrite, has caused these very high concentrations.

Estimation of the mine pool composition after plugging of the Richmond Mine was accomplished by computing the chemistry after dissolution of these salts in a volume of water equivalent to the void space created by the underground workings. The exact amount and proportion of all the minerals is not well-known, but the proportion is not a sensitive factor and the amount was considered as a variable. Computations were made with the PHREEQE program (Parkhurst and others, 1980; now superseded by Parkhurst, 1995). The results indicated that nearly 1 million m³ of water with pH less than 1 and many grams per liter of dissolved metals located at or near the top of the ground-water table would be formed, in a rock type that has almost no neutralization capacity and in which the flowpaths are governed by fracture flow. Thus, plugging would suggest a remediation scenario that has a high degree of potential risk

associated with it. Other metal sulfide mines that have been plugged and monitored tend to show an increase in the dissolved solids concentrations, most likely for the same reasons.

Mine plugs have occasionally failed, sometimes with disastrous results. Often the rock is not competent next to the seal to provide sufficient resistance for 100 m or so of acid water that backs up behind it. In some instances, the acid water comes gushing out another opening like an artesian spring. In other instances, the metal loading in the downstream drainage is not different (or worse) than before plugging. And, in some instances, the water is contained and does not appear to be a problem. However, no work has been done on the hydrogeology at these sites to determine where the water is going. Some of them may be time bombs that have yet to be discovered. Mine plugging may be successful at some sites, but careful planning and hydrogeochemical peer review is necessary to prevent disastrous consequences.

CONCLUSION

Prevention and control of acid mine drainage at large, complex mine sites can be a very challenging and expensive task. The nature of the site makes it difficult to assess the effectiveness of the remediation and the relative risks and costs of alternatives and their contingencies. It should be mandatory to consider the following guidelines for remediation efforts:

- Form a multi-disciplinary technical advisory team to advise the regulatory agencies, review data and interpretations, and to make recommendations. Mine sites are complex functions of geology, hydrology, geochemistry, pedology, meteorology, microbiology, and mining and mineral processing history. Their remediation is subject to considerations of economics, available technology, and potential land use. I have never met an engineer who is proficient in all of these areas. Furthermore, assessing risks involves toxicology, epidemiology, wildlife biology, and public perception. Professionals in these areas can contribute substantially to the wisest choice of remediation strategies and to public awareness and education.
- The effectiveness of a remedial alternative cannot be easily quantified or predicted. We must admit that remediation has an experimental quality to it and, therefore, some research is required to affect the best and most appropriate remediation available. Both long-term and short-term research are needed. In the short term, focused, site-specific research can help with a particular site remediation. In the long term, we need to continue to develop better remediation techniques that might utilize mine wastes and mineral deposits of lower grade.
- Apply a phased, iterative approach to mine remediation. Our natural inclination is to identify the worst part of a hazardous waste site and attempt to clean that up.

However, there is often no single remedial solution that would clean up >80% of the problem on a permanent and maintenance-free basis. Options do exist that are low-risk and low-cost and that should help reduce the problem while research on the remainder can be continued.

- Find methods to promote extraction or recycling of low-grade resources. Many mine sites have already undergone further metals extraction and recycling. Additional research into metals recovery from both mine waters and waste piles should be pursued in an effort to gain some economic advantage from the cleanup process.

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