

MINERAL REACTIONS IN A COLORADO MINE DUMP: IMPLICATIONS FOR REMEDIATION IN ARID AND SEMI-ARID ENVIRONMENTS¹

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Abstract: Preliminary examination of a combined mine/mill waste dump from the Topeka Mine, near Central City, Colorado, reveals four alteration zones distributed vertically within the waste pile. The surface of the waste pile contains unaltered waste rock with fresh metal-sulfide minerals. The interior of the waste pile (exposed by excavation) contains a leached zone, below which is a cemented zone in which pore spaces are filled with the minerals copiapite ($\text{Fe}^{2+} \text{Fe}^{3+}_4(\text{SO}_4)_6(\text{OH})_2 \cdot 20 \text{H}_2\text{O}$), and coquimbite ($\text{Fe}^{3+}_2(\text{SO}_4)_3 \cdot 9 \text{H}_2\text{O}$). Copiapite and coquimbite are highly soluble and normally precipitate from fluids with pH = 0.8 to 1.5 (Nordstrom and others, 1979). They are ordinarily associated with altered ore minerals that are protected from direct precipitation. Adjacent to the cemented zone, jarosite and gypsum have precipitated on and among grains of primary waste rock, indicating less extensive alteration and higher pH than in the cemented zone. Below the cemented zone, the dump exhibits only slight chemical alteration: even minerals highly susceptible to chemical alteration (pyrite, hornblende, biotite) are largely unreacted in this interior unaltered zone.

The alteration patterns within the mine dump suggest that the dump is not flushed by fluids. The Topeka Mine dump is located at an elevation of 2840 m (9320 feet). The average annual precipitation at the site is 51 cm (20 inches) per year and occurs as winter snow or as intermittent intense summer thunderstorms. Precipitation probably penetrates a few centimeters or meters immediately after a rain storm or snow melt period, allowing bacterial oxidation of sulfides within the temporarily saturated zone. After a fluid infiltration event, however, the surface of the dump dries rapidly while reacted fluids gradually precipitate dissolved components as copiapite and coquimbite within the waste. Remediation of a dump of this type under arid or semi-arid conditions must account for the fact that surface materials are only slightly reacted, but the interior may contain highly reactive, possibly metal-rich, soluble sulfate minerals.

Additional Key Words: abandoned mine waste, metal contamination, soluble minerals, stream contamination, arid climate, sulfide oxidation, copiapite, coquimbite, melanterite.

Introduction

The upper Clear Creek drainage near Central City, Colorado contains mine waste and mill tailings from over 2000 gold/silver mines and prospects dating back to the discovery of gold in Clear Creek in 1859 (Sims and others, 1963). Although some of the mine waste and mill tailings piles have been disturbed, many of the dumps in the Central City - Blackhawk area have been in place for 75-130 years. Careful study of these dumps may reveal important information about the nature and rates of alteration processes, may help to assess potential threat of mine waste and mill tailings to surface and groundwaters, and may provide information critical to remediation decisions. Because the primary ore in the region includes a variety of sulfide minerals, the threat of acid mine drainage and release of metals is significant. The purpose of the present study is to describe the distribution of secondary alteration minerals within an excavated mine dump and, by interpreting the relative importance of alteration and hydrologic processes, assess the potential threat of old mine dumps in the region.

Geographic and Physiographic Setting

The Topeka Mine dump is located approximately 3 miles southwest of Central City, Colorado (105° 32' W, 39° 46' 56" N). The site is in upper Russell Gulch, a tributary of North Clear Creek, which ultimately enters the South Platte River near Denver (Figure 1). The Topeka Mine effectively ended production of gold ore in 1913, thus the minimum age of the tailings is 81 years. The mine waste lies on a south-facing slope at an elevation of 2840 meters (9320 feet). The tailings pile is approximately 200 meters (656 feet) long and 70 meters (230 feet) wide, and has a maximum depth of about 20 meters (66 feet). The dump was partially excavated in 1992 as part of a secondary gold recovery and waste remediation project, and most of the

¹ Paper presented at the 1995 National Meeting of the American Society for Surface Mining and Reclamation, Gillette, Wyoming, June 5-8, 1995.

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samples described in the present study were taken from the exposed interior of the dump during the spring and summer of 1994. Annual precipitation at the study site is about 50 cm (20 inches) per year and occurs mostly as winter snow or as intermittent heavy summer thunderstorms.

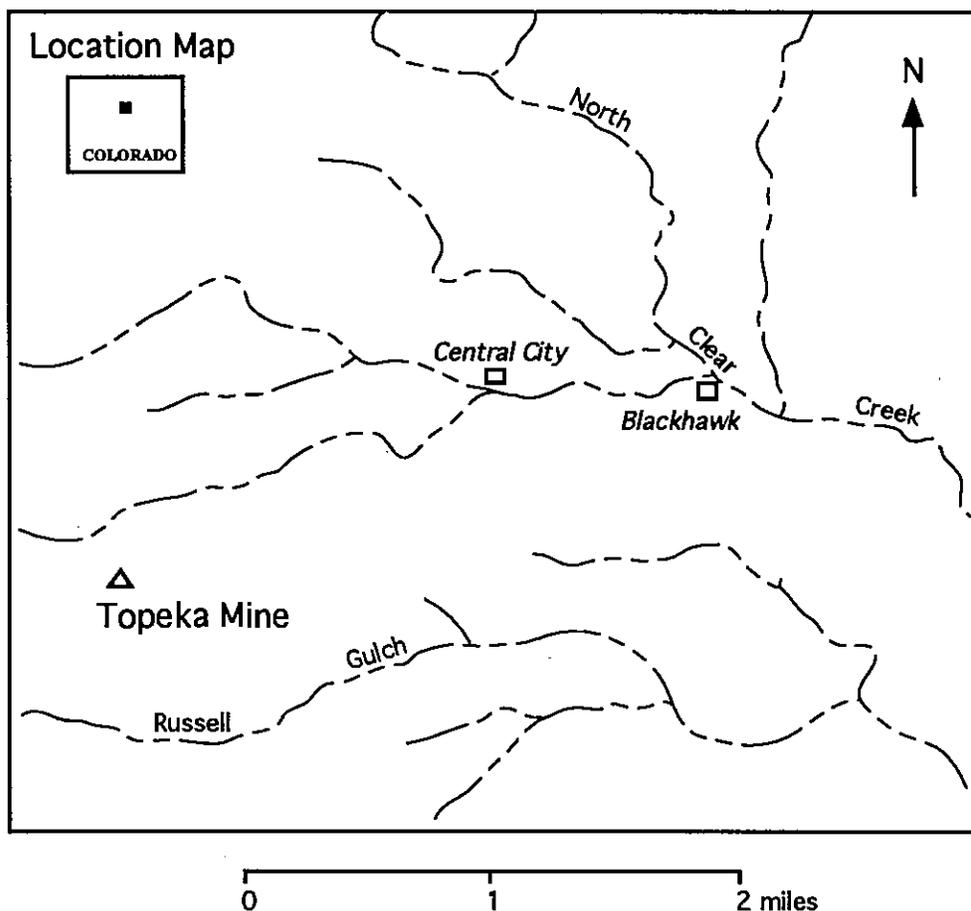


Figure 1. Map showing location of Topeka Mine, near Central City, Colorado (after Sims and others, 1963)

Primary Ore Mineralogy and Mine Waste Composition

The gold and silver ore mined in the Clear Creek drainage around Central City occurs in veins along fractures and faults in metamorphic host rock. The host rock in the study area is dominantly gneiss and schist, and host rock minerals consist mostly of quartz, plagioclase, hornblende, and biotite with lesser amounts of several other metamorphic minerals. No carbonate host rocks exist in this area and, thus, the neutralization potential of the host rock is small; carbonate minerals (calcite, siderite, rhodochrosite) occur as gangue minerals in some ores, but only in relatively small amounts.

The sulfide minerals from the ore zones that are primarily responsible for the acid generation in the mine waste are spatially zoned within the mining district. Sims and Barton (1962) describe four zones at Central City, each containing a different suite of sulfide minerals. The variation in sulfide mineralogy within these four zones has been shown to determine the composition of waters issuing from mines in the Central City district (Wildeman and others, 1974). Therefore, understanding and predicting the chemical reactions within mine waste from different zones within this mining district must also consider the differences in primary sulfide mineralogy. The Topeka Mine lies within the "intermediate" zone of Sims and Barton (1962). Ore within this zone contains pyrite, sphalerite, galena, and copper minerals (chalcopyrite, bornite). Sphalerite, galena, and chalcopyrite not only react in different ways and at different rates than pyrite, but their reactions would release Zn, Pb, and Cu into reacting fluids and generate different amounts of acid (Rimstidt and others, 1994). It is the fate of these metals that we must understand in order to assess the potential threat of these old mine dumps.

The Topeka Mine dump contains both mine and mill waste and is very heterogeneous. Not only does the size of primary particles range from submicrometer to tens of centimeters, but different zones within the dump contain different particle size distributions. Thus, zones containing primarily waste rock from the mine have both high porosity and high permeability owing to the extreme variability of particle sizes, whereas other zones contain primarily fine-grained mill waste and are only slightly permeable. This textural variability within the mine dump may have profound effects on the hydrology of the dump and the rate at which the sulfide minerals react. Thus the heterogeneity of the tailings is likely to produce gross variations in alteration mineral zonation.

Sample Collection and Analytical Methods

Remediation and gold recovery operations in 1992 exposed an interior section of the Topeka Mine waste pile, which contains both mine waste and mill tailings. The excavation permitted sampling from the upper surface of the dump down to approximately 7 meters (23 feet) into the center of the waste pile. A total of 28 samples were taken from the upper surface, flanks, and interior of the mine waste. Samples were taken from the immediate surface in order to assess the effects of surface weathering, and also from trenches dug into the surface and flanks of the dump to examine the variability of reactivity with depth. The surface of the exposed face of the dump interior was sampled, and the surface of the exposed face was also penetrated to sample deeper within the interior because water-soluble salts had coated the surface in the two years since excavation. Samples of about 1 kilogram each were collected in plastic zip-loc bags to preserve the hydration state existing in the field.

Although several of the samples were slightly moist when collected (January and July, 1994), there was insufficient fluid in the waste to collect for analysis. Several of the samples were leached by placing 5 grams of solid into 100 ml of distilled water. The mixture was allowed to equilibrate for one hour and then centrifuged to separate the fluid from the solids. Leach solutions were analyzed using a Corning Model 135 pH/ion meter with an Orion combination Ross electrode for pH measurements, and flame atomic absorption spectrophotometry for elemental analysis.

The bulk mineralogy of each sample was determined using conventional X-ray powder diffraction techniques (Klug and Alexander, 1974). Each sample was X-rayed as soon as possible after removal from the sealed plastic bags because of the ephemeral nature of some of the water-soluble minerals. In some cases, samples were analyzed several times over a period of days while left to dry in air, and changes in mineral characteristics were observed (primarily degree of crystallization).

Because most samples of mine waste collected contained a substantial proportion of very fine-grained material, several samples were examined using the scanning electron microscope (SEM). A small (1-2 cm) fragment of coherent material was glued to an aluminum SEM stub and coated with a conductive layer of either gold or graphite. Samples were viewed on a Cambridge Stereoscan SEM. Qualitative and semiquantitative elemental analysis of minerals were obtained in the SEM using an energy dispersive X-ray spectrometer attachment.

Alteration Zones in the Waste Pile

After examining the waste pile in the field and analyzing the mineral composition from samples taken from the surface and interior of the dump, four mineralogical zones have been identified (Figure 2):

1. Surficial unaltered zone
2. Leached zone
3. Cemented zone
4. Interior unaltered zone

Neither the surficial unaltered zone or the interior unaltered zone is pristine. Both zones exhibit some signs of alteration. However, they are the least altered or oxidized zones within the dump. The surficial unaltered zone blankets the exterior of the dump. It is highly variable in thickness but is generally a maximum of a few centimeters thick and consists mostly of materials that have lain on or near the surface of the dump since disposal. The materials on the surface include coarse-grained, shiny, untarnished pyrite and other sulfide minerals plus unaltered feldspars, biotite, and amphibole. These materials show little or no signs of oxidation or weathering. Included in the surficial unaltered zone, however, are boulders and large rock fragments coated with Fe-oxides. These coatings indicate that some surface oxidation has occurred during their 81 years of exposure, but it has not been severe enough to corrode all of the coarsely crystalline pyrite.

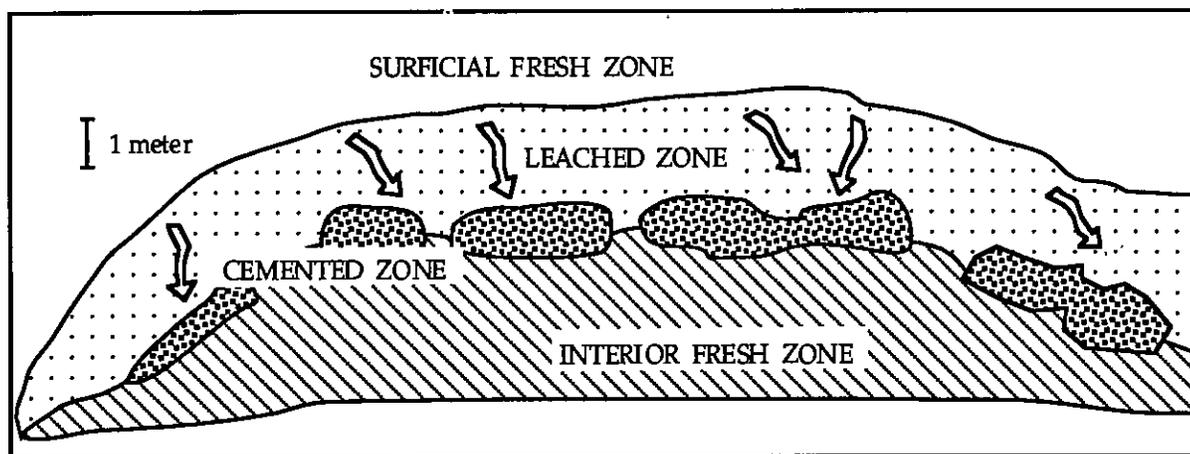


Figure 2. Schematic drawing of alteration zones within the Topeka Mine dump. The total depth of the dump is about 20 meters. The excavated section of the dump (shown here) is approximately 8-10 meters. Only a small portion of the dump is depicted.

Beginning a few centimeters below the surface, and extending to a depth of approximately 1-3 meters (3-10 feet) is a leached zone consisting of altered silicate minerals (feldspar, biotite, hornblende, quartz) and oxidized sulfide minerals, with secondary gypsum and jarosite. This zone is also highly variable in thickness and depends partly upon the small-scale hydrologic characteristics of the dump. Although we have not yet conducted detailed chemical analyses on these materials, the waste in this zone commonly appears bleached and altered, suggesting depletion of soluble elements.

The leached zone is underlain by a compact, K-depleted zone of pore-filling secondary minerals, some of which are soluble in water. This cemented zone is dominated by the minerals copiapite ($\text{Fe}^{2+}\text{Fe}^{3+}_4(\text{SO}_4)_6(\text{OH})_2 \cdot 20 \text{H}_2\text{O}$) and coquimbite ($\text{Fe}^{3+}_2(\text{SO}_4)_3 \cdot 9 \text{H}_2\text{O}$). X-ray diffraction data for the cemented zone minerals is shown in Figure 3. Both copiapite and coquimbite are found in low pH (0.8-1.5) environments and both reflect mildly oxidizing conditions (Nordstrom and others, 1979). Copiapite contains both ferric and ferrous iron, coquimbite contains only ferric iron and may form in a slightly more oxidized microenvironment or may form as an oxidation product of copiapite. Both minerals are highly hydrated and are highly soluble in water. The precipitation of these minerals has produced a cemented zone approximately 1-2 meters (3-6 feet) thick. The zone varies in thickness and in some places appears to occur in discontinuous pods or lenses. Copiapite and coquimbite occur in massive zones with gypsum and jarosite, grading outward into zones that contain only gypsum and jarosite as secondary alteration products.

Examination of the cemented zone with SEM reveals the textural relationships among the secondary alteration minerals. Samples from the cemented zone contain a framework of precipitated laths or fibers of gypsum within the pore spaces of the waste. The needles and laths of gypsum are, in turn, coated with later secondary Fe alteration minerals, including copiapite, coquimbite, and possibly melanterite ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) (Figure 4), though melanterite was not identified by X-ray diffraction. In addition, copiapite occurs as masses of tapered lath-like crystals coating the surface of the waste pile (Figure 5). The physical relationships among the crystals of the various minerals indicates a system out of equilibrium or reflects microenvironmental equilibrium (Nordstrom and others, 1979). The physical arrangement of the minerals demonstrates the order in which they have precipitated and shows that the Fe-sulfates precipitated after the gypsum. Because the secondary Fe-sulfate minerals are so similar chemically, it becomes extremely difficult to distinguish among them using the elemental analyzer in the SEM, though they can be easily distinguished from gypsum, jarosite, and primary silicate minerals. Thus, even though we can say that gypsum is coated by Fe-sulfate minerals exhibiting a variety of crystal forms and morphologies, it is not possible at this time to determine which specific Fe-sulfate minerals assume the various forms.

Beneath the cemented zone, the tailings are generally only slightly altered and contain only minor amounts of gypsum and jarosite as alteration minerals. In this lower zone, called here the interior unaltered zone, the primary minerals are either fresh or only slightly altered. The extent of this zone is impossible to discern at this time because only a few feet of waste is exposed below the cemented zone.

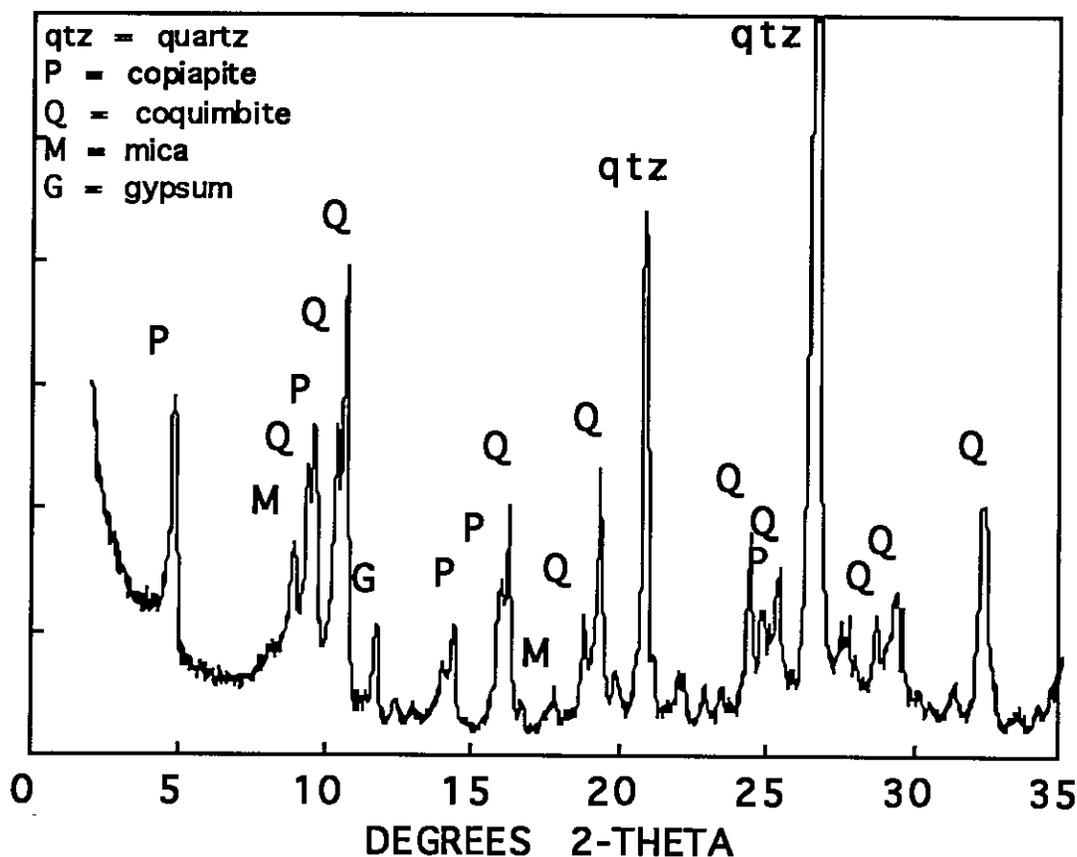


Figure 3. X-ray powder diffraction data for copiapite, coquimbite, and other waste minerals from the cemented zone of the Topeka Mine dump. $\text{CuK}\alpha$ radiation was used.

Leaching Experiments

Because the secondary Fe-sulfate minerals (copiapite and coquimbite) are quite soluble in water (Nordstrom and others, 1979), and because several metals may substitute isomorphously within the structures of these minerals, it is possible that these secondary minerals contain potentially toxic metals that are subject to regulation. Because we are interested in knowing whether such minerals may release metals if dissolved, a series of dissolution experiments were undertaken to examine the behavior of these cementing minerals when flushed with water. Ten grams of each of five samples from within and adjacent to the cemented zone were placed in 200 ml of distilled water and the pH of the resulting solutions was determined after 2 hours equilibration time at 22°C, and the solutions were centrifuged until clear and then analyzed for several metals (Table 1). Sample KS-1, taken from the center of the cemented zone, demonstrated the nature of the anticipated release of acid and metals. This sample produced a solution pH of 2.1 and the solution was enriched in Fe, Al, Cu, Zn, and Mn. Moving vertically away from the center of the cemented zone at the excavated face of the dump, the solution pH increased and concentration of dissolved Fe and Al decreased. In fact, the relationship between the pH of the solution and the concentrations of Fe and Al is striking when plotted on a log-log plot (Figure 6a, 6b). This strong correlation is not surprising, considering that both Fe and Al are highly soluble at low pH and form hydroxyl complexes and precipitates as pH increases.

The relationship between pH and K concentration is equally striking, but is an inverse correlation (Figure 6c). The minerals that precipitate from low pH fluids are not expected to contain large amounts of competing cations, such as K. Thus, when these minerals are dissolved in water, little K is released. As pH increases (concentration of H^+ decreases), more cations may be incorporated into the precipitate and are released when the solids are placed in water.

Copper shows a mild inverse correlation between concentration and pH (Figure 6d), but the correlation appears less striking than for Fe and Al. The range of Cu values is much smaller than for Fe and

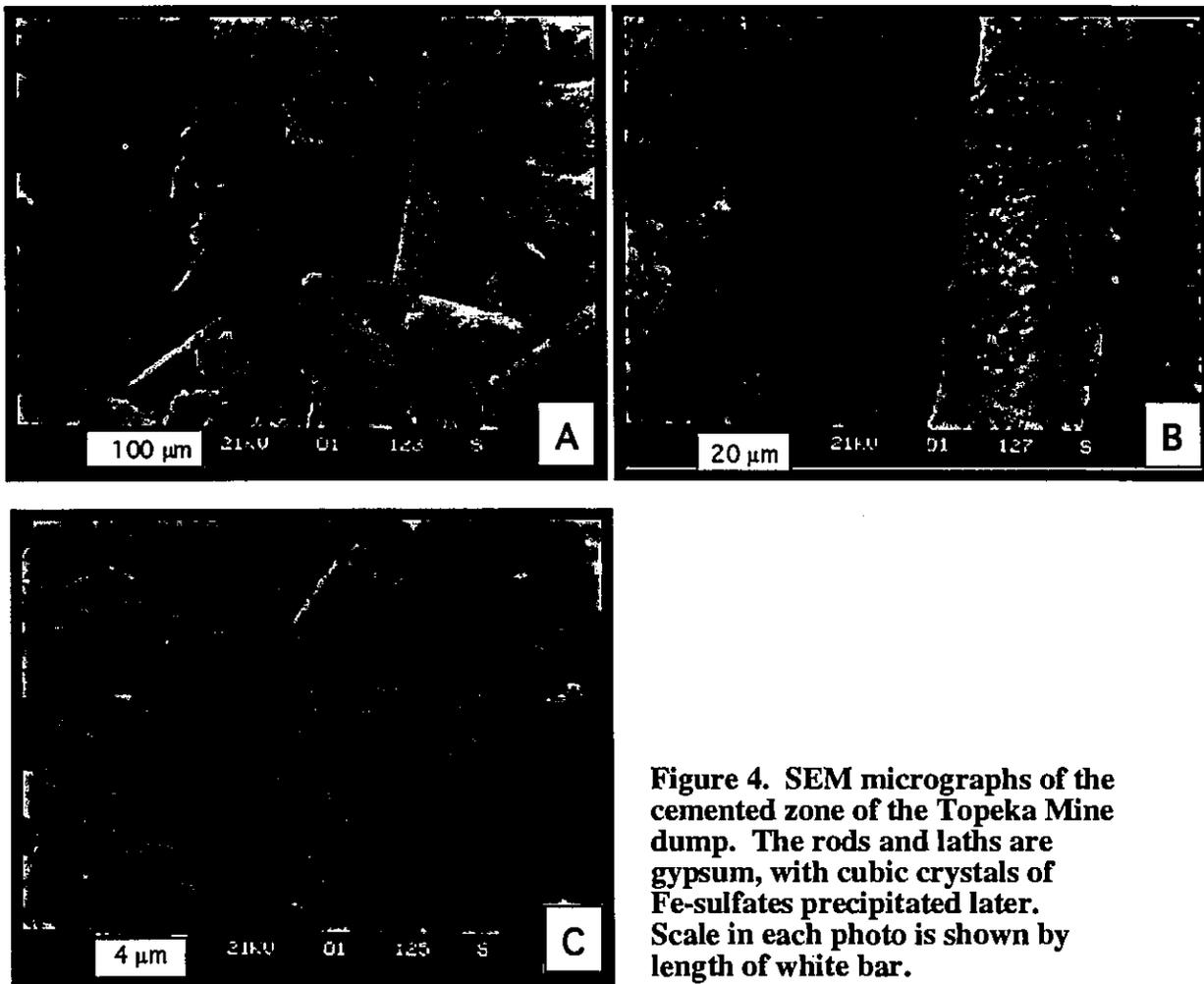


Figure 4. SEM micrographs of the cemented zone of the Topeka Mine dump. The rods and laths are gypsum, with cubic crystals of Fe-sulfates precipitated later. Scale in each photo is shown by length of white bar.

Al, and Cu is less likely to be affected by pH than Fe and Al. Zn and Mn exhibit no relationship to pH at all, though both are released in significant concentrations (Figures 6e, 6f). Therefore, the cemented zone clearly contains significant amounts of metals that are potentially toxic when released in the event of contact with water, but the release of Fe, Al, Cu, and acid is far less from the bulk of the tailings pile surrounding the cemented zone.

Each of the solutions produced by mixing the minerals from the cemented zone with water was allowed to evaporate to dryness at 60°C and the resulting solid precipitate analyzed by X-ray diffraction. Though the amount of precipitate produced by each sample was inversely proportional to the pH of the solution, each produced the mineral rhomboclase ($\text{Fe}^{3+} \cdot \text{H}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$) when dried. Because the Fe-sulfate species precipitated from such solutions is temperature sensitive (Reardon and Beckie, 1987), rhomboclase is not necessarily the mineral that would precipitate from these solutions under natural conditions.

Discussion

Layered alteration patterns within sulfide mine waste have been described previously. Boorman and Watson (1976) discovered a "hard pan" layer composed predominantly of Fe-oxides and hydroxides in sulfide-rich mine waste from Cu-Zn-Pb mining in New Brunswick. The hard pan layer is situated at the base of an oxygenated saturated zone near the surface of the waste pile in which bacteria catalyze the oxidation of sulfides. The soluble oxidation products are leached from the oxidation zone and transported downward by infiltration. When the solutions reach saturation with respect to various Fe-minerals within the vertically changing chemical conditions, they precipitate a variety of Fe-rich phases and form the hard pan layer. A similar scenario was described by McSweeney and Madison (1988) in mine waste from Pb-Zn mining in southwest Wisconsin. Although the geometric relationships among the alteration zones were similar to those of Boorman and Watson (1976), the cemented zone contained Fe-sulfate minerals, including copiapite.

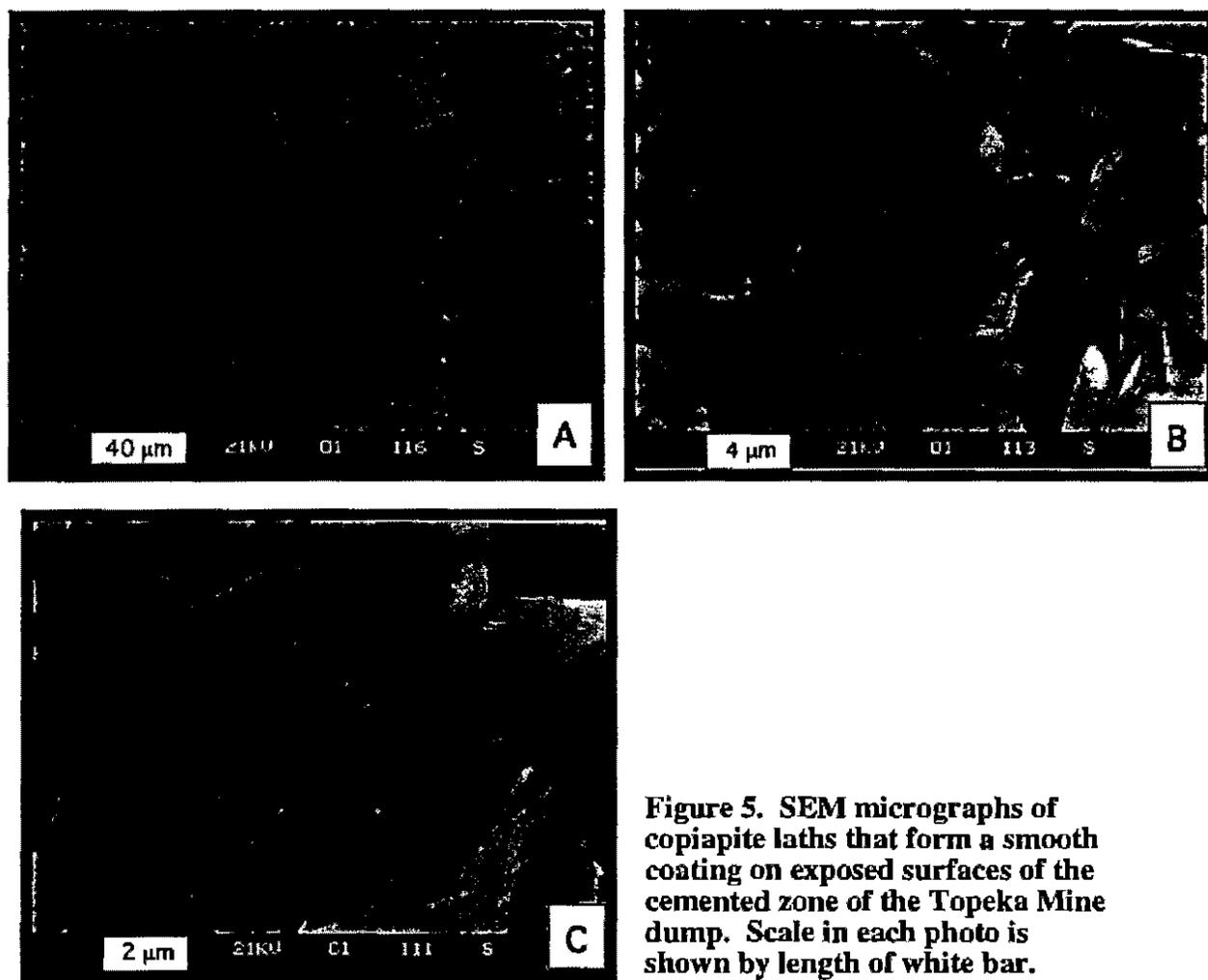


Figure 5. SEM micrographs of copiapite laths that form a smooth coating on exposed surfaces of the cemented zone of the Topeka Mine dump. Scale in each photo is shown by length of white bar.

Table 1. Chemical composition of solutions of samples mixed with water (10 grams solid in 200 ml water). All metal concentrations are reported in $\mu\text{g/ml}$.

<u>SAMPLE</u>	<u>pH</u>	<u>Fe</u>	<u>Al</u>	<u>K</u>	<u>Cu</u>	<u>Zn</u>
KS-1	2.1	7200	520	0.1	35.0	520
KS-2	2.6	540	120	0.2	8.0	160
KS-3	3.7	23	88	0.7	12.5	600
KS-4	4.4	0.19	1.8	3.6	1.6	260
KS-5	4.5	0.08	2.2	4.2	1.0	620

<u>SAMPLE</u>	<u>Mn</u>	<u>Co</u>	<u>Ni</u>	<u>As</u>	<u>Pb</u>	<u>Cd</u>
KS-1	110	2	2	12	<1	2
KS-2	35	<1	<1	<1	<1	<1
KS-3	29	<1	<1	<1	<1	2
KS-4	27	<1	<1	<1	<1	<1
KS-5	116	<1	<1	<1	<1	4

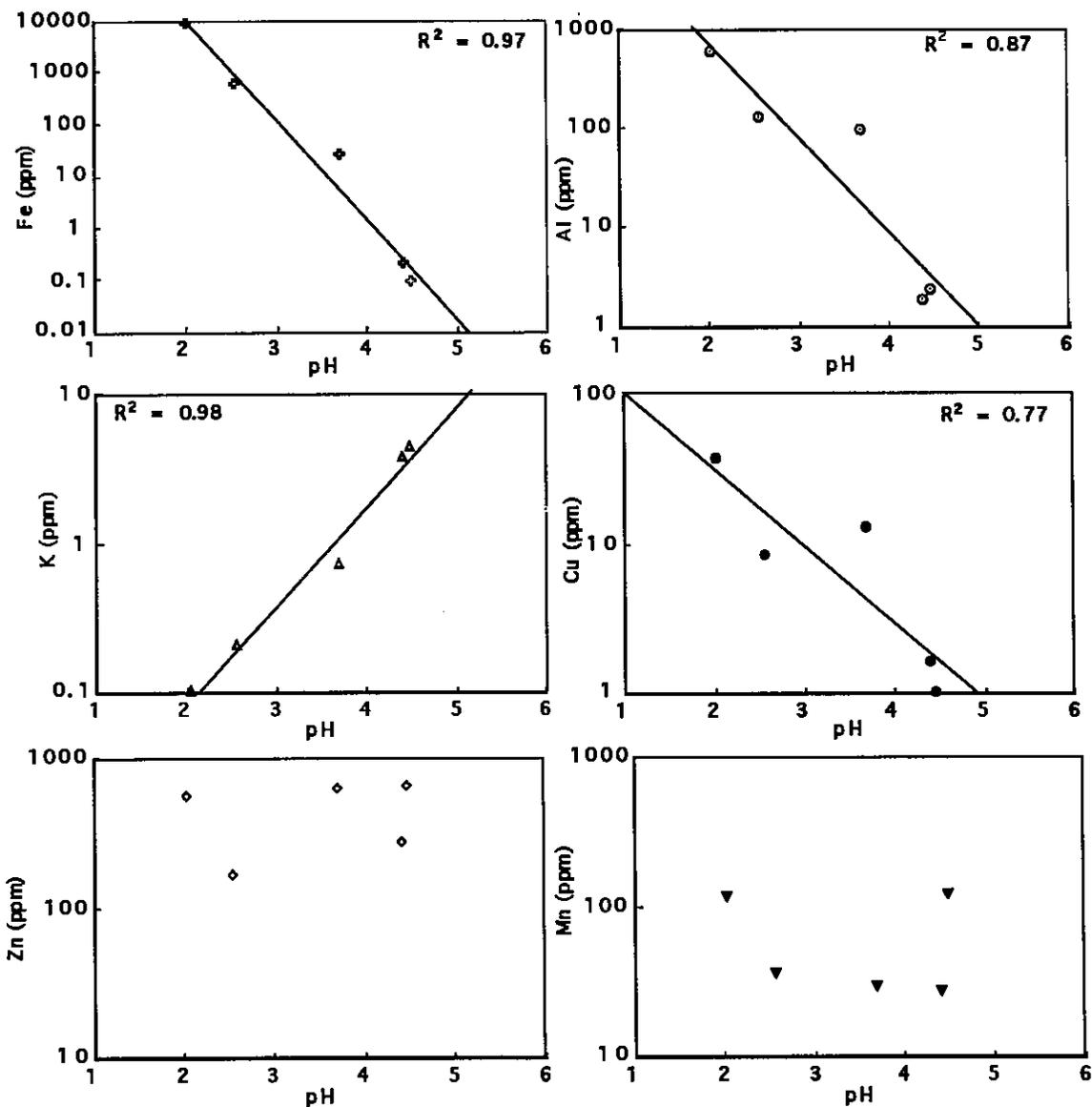


Figure 6. pH vs. dissolved metals in leachate from samples taken from the cemented zone of the Topeka Mine dump. The sample producing the lowest pH was from the center of the cemented zone, and incrementally higher pH represents samples taken from further from the center of the cemented zone. (a) pH vs. dissolved Fe, (b) pH vs. dissolved Al, (c) pH vs. dissolved K, (d) pH vs. dissolved Cu, (e) pH vs. dissolved Zn, and (f) pH vs. dissolved Mn.

Blowes and others (1991) re-examined the tailings that Boorman and Watson (1976) had studied and also investigated a similar set of tailings from Cu-Zn mining in Quebec. Again, they identified an oxidized and leached zone at the top of the dump, an underlying cemented zone which is composed of Fe-oxides or sulfates (including melanterite), and an underlying zone of relatively unaltered mine waste. In all three of these mine waste alteration scenarios the cemented zone is enriched in Cu, Zn, and Pb, as well as Fe and other metals.

Although no detailed studies have been performed on the hydrology of the Topeka Mine waste pile, circumstantial evidence suggests that the dump is rarely saturated with water and that fluids do not routinely penetrate the pile. The total amount of precipitation in the area is low (51 cm (20 inches) per year), despite the high elevation, and much of that precipitation occurs as intense thunderstorms during the summer. The physical setting of the dump confirms that the waste pile remains unsaturated or dry most of the time. For example, the waste dump sits directly upon a dark, organic-rich soil which has been exposed by the recent excavation. The soil shows little evidence of contact with fluids descending from the overlying waste except for the presence of minor amounts of gypsum. There is no evidence for fluids issuing from the toe of the

dump, and the physiography of the site indicates that the water table must be a substantial distance beneath the ground surface. There are no surface streams or permanent stream channels within several hundred meters of the site. Conversely, there is strong evidence for surface wash from the intermittent summer thunderstorms. The surface of the waste pile is cut by rills and gullies, and substantial amounts of tailings have been washed downslope. Therefore, even though the surface of the dump has been washed by severe thunderstorms, there exists little or no evidence for flushing of the interior of the tailings pile by fluids.

With this in mind, the scenario for formation of the cemented layer, composed of highly soluble Fe-sulfate minerals, within the tailings pile may be formulated. 1) Small amounts of water enter the upper surface of the waste dump by melting of snow or during a thunderstorm. The volume of water is insufficient to saturate the entire thickness of the dump, and the upper zone alone is moistened. At the surface, drying is rapid and iron and sulfur oxidizing bacteria cannot metabolize sulfide minerals effectively in dry material. Thus, a thin layer of sulfidic material remains unaltered at the surface of the dump. 2) Immediately below the surface of the dump there is a zone of waste that periodically becomes saturated by oxygenated fluids, allowing the metabolic activity of iron- and sulfur-oxidizing bacteria to catalyze the oxidation of sulfide minerals (Singer and Stumm, 1970). 3) The descending fluids transport the soluble products of oxidation into the waste pile, but there is insufficient fluid to flush the entire thickness of the dump and oxygen becomes depleted by chemical and biological reactions. 4) Thus at a certain depth within the dump, determined by fluid volume, oxygen content, and rates of evaporative concentration, the fluids become supersaturated with respect to secondary minerals and those minerals precipitate at that depth. 5) This layer of pore-filling minerals then becomes a retardant to subsequent fluid flow and the layer grows in thickness and continuity, cutting off the fluids from the deeper levels of the dump. This results in a mine dump consisting of stratified zones of alteration as shown in Figure 2.

Implications for Remediation Strategies

During the approximately 81 year lifetime of the Topeka Mine tailings pile, a zone of water-soluble metal-bearing Fe-sulfate minerals has formed in the interior of the dump. These soluble minerals have not been flushed to release the metals that are concentrated there. Even after 81 years of exposure to winter snows and summer thunderstorms, the metals released by oxidation of the upper zone of the dump have been transported to a depth of a few feet within the dump. However, once this dump was excavated, the cemented layer containing the soluble materials was exposed to snow and summer thunderstorms. Surface textures of the cemented zone indicate that some of the copiapite and coquimbite has been dissolved and reprecipitated as smooth coatings on the surface of the dump, demonstrating the ease with which the material is remobilized when exposed to water.

If the entire dump is excavated and moved to a different site, the soluble metal-bearing minerals will potentially be exposed to direct contact with precipitation. If that occurs, the soluble sulfate minerals will dissolve and release the metals and acid into the reacting fluids, producing a serious chemical hazard to streams and groundwater. Thus the material would need to be completely remediated or isolated from moisture immediately. Alternatively, if there is no compelling reason to move the tailings, these preliminary data suggest that mine dumps with characteristics of the Topeka Mine dump, located in similar areas of low precipitation, may pose little threat to surface or groundwaters, except for stormwater runoff, and may be strong candidates for in-place closure techniques (Lewis-Russ and duPont, 1994).

It is important to note that precipitation patterns vary dramatically in mountainous areas, and that some areas relatively nearby receive much greater amounts of precipitation than the Central City area. Increased precipitation may seriously change the dynamics of oxidation and transport within the mine tailings and each situation must be evaluated individually based on local waste characteristics, physiography, and weather patterns.

Summary and Conclusions

These preliminary analyses suggest that the formation of alteration zones within the Topeka Mine dump have produced a steady state environment within the tailings that has allowed little or no metal-bearing fluid to emerge from the mine waste even after more than 81 years. Such long-term stability in mine waste may be important when decisions are made about remediation requirements and techniques for sulfide-rich mine waste in low-precipitation areas.

Acknowledgments

We thank Maxine Stewart and Solution Gold, Inc., for access to the excavated Topeka Mine dump; Kathy Smith and Geoff Plumlee for helping coordinate the field work and analytical work; John B. McHugh for atomic absorption analysis of the leachates. We also thank Kathy Smith, Helen Folger, and two anonymous reviewers for helping to improve the manuscript.

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