

Using Imaging Spectroscopy to Cost-Effectively Locate Acid-Generating Minerals at Mine Sites: An Example from the California Gulch Superfund Site in Leadville, Colorado

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1. Introduction

The Leadville mining district, located at an elevation of 3000 m in the Central Colorado Rockies, has been mined for gold, silver, lead and zinc for more than 100 years. This activity has resulted in the dispersal of waste rock and tailings, rich in pyrite and other sulfides, over a 30 km² area including the city of Leadville. Oxidation of these sulfides releases lead, arsenic, cadmium, silver, and zinc into snowmelt and thunderstorm runoff, which drains into the Arkansas River, a main source of water for Front Range urban centers and agricultural communities. The U.S. Environmental Protection Agency (EPA), U.S. Bureau of Reclamation (USBR), contractors, and responsible parties are remediating the mined areas to curtail further releases of heavy metals into various drainage tributaries of the Arkansas River. Mineral maps made by the U.S. Geological Survey (USGS) from AVIRIS data collected over this mining district were used to focus remediation efforts by locating the point sources of acid drainage.

2. Method

The sulfide oxidation process is biologically driven along complex chemical pathways with feedback reactions that enhance the speed and magnitude of oxidation (Nordstrom, 1982). Release of heavy metals is facilitated by sulfide oxidation, since many of the sulfides contain the heavy metals (e.g. Pb, As, Cd, Ag, and Zn). The oxidation-weathering process of many sulfide minerals produces low pH water in which the heavy metals dissolve as aqueous phases that are then transported as runoff into nearby streams creating acid mine drainage. Secondary minerals such as copiapite, jarosite, schwertmannite, goethite, ferrihydrite, and hematite are formed by sulfide oxidation and subsequent precipitation from metal-rich water. These secondary minerals are Fe-rich and usually hydroxyl-bearing, making it possible to identify them on the basis of their characteristic spectral signatures. As the pH of a mining impacted stream increases by mixing with higher pH water from tributaries, these secondary minerals precipitate out as stream bed coatings or suspended sediments. Because some of the heavy metals can substitute for Fe, they may also precipitate from solution as constituents of secondary minerals or as contaminants sorbed onto the surfaces of the secondary minerals (Smith and Macalady, 1991; Alpers et al., 1994). Subsequent pulse of low pH water may dissolve the secondary minerals or desorb metals thus remobilizing the heavy metals and transferring them downstream.

The sulfide mineral pyrite is the primary source of acid drainage. Because direct spectral detection of pyrite is hampered by its low reflectance level, its broad Fe-absorption, and rapidly formed coating of secondary minerals, pyrite can only be detected when it is coarse grained or compositionally impure (G. Plumlee, pers. comm., 1996). However, our observations indicate that pyrite weathers first to jarosite, and then to goethite (Table 1), forming a sequence where the degree of oxidation is indicated by the type of secondary mineral exposed at the surface. Therefore, an indirect way to find oxidizing pyrite is to look for areas where the secondary minerals grade through the established oxidation sequence (e.g. those areas with jarosite surrounded by goethite). Quite fortuitously, the presence of heavy metals and low pH often associated with the mine waste prevent the growth of vegetation over most waste piles leaving them exposed and suitable for detection with

remote sensing.

Table 1. Pyrite and Secondary Minerals

Pyrite	FeS_2 *
Jarosite	$(\text{H}_3\text{O}, 0.5\text{Pb}, \text{Na}, \text{K})\text{Fe}^{3+}_3(\text{SO}_4)_2(\text{OH})_6$
Goethite	$\alpha\text{-FeO}(\text{OH})$
Hematite	$\alpha\text{-Fe}_2\text{O}_3$

* Formulas from Fleisher (1980)

The large size of the Leadville mining district and presence of spectrally detectable secondary minerals associated with pyrite oxidation makes imaging spectroscopy effective for locating those minerals related to the acid mine drainage sources. AVIRIS data was collected over Leadville on July 27, 1995 (see Swayze et al., 1996). Data were calibrated from radiance to reflectance using ATREM (Gao et al, 1992) and a ground calibration site as described in Clark et al. (1995).

Calibrated AVIRIS reflectance data were spectroscopically mapped using the Tricorder algorithm (Clark et al., 1995 and references therein; Clark et al., in prep.). Tricorder, an expert system, is capable of simultaneously analyzing spectra of solids, liquids, and gases. Tricorder's primary subroutine is a modified least-square shape-matching algorithm which compares spectra of unknown materials to hundreds of reference library spectra and identifies the best match. This subroutine uses thresholds on band depth, fit, and continuum slope to help constrain the spectral matching. The spectral library used to map AVIRIS Leadville data contains 160 reference spectra of individual secondary minerals and mineral mixtures. Because the 0.4 - 1.35 μm spectral region is dominated by electronic absorptions due to transition metals (such as Fe) and the 2.0 to 2.5- μm region is dominated by molecular vibrational absorptions, maps of the spectrally dominant materials in each wavelength region were produced for the Leadville AVIRIS scene.

3.0 Mapping Results

Mineral maps created by Tricorder reveal characteristic mineral assemblages centered over the mine dumps and tailings which are rich in pyrite. Field checks demonstrate that highly acidic water formed in the pyrite-rich piles is gradually neutralized as it spreads away from the dumps. This process deposits progressively less acidic secondary minerals in rough concentric zones centered on the dumps, creating diagnostic patterns easily recognized on the electronic absorption mineral map. The centers of the zones are jarosite-rich and have a high acid-generating capacity that produces acidic water containing heavy metals. This zone is surrounded by a jarosite + goethite zone which is itself surrounded by an outer most goethite zone. To facilitate comparison with features on the ground, the mineral map was geometrically registered and overlaid on orthophoto information for the Leadville area. It shows concentric secondary mineral zones around many of the waste piles helping to pinpoint the sources of acid drainage. Such an engineering product allows rapid prioritization of remediation sites.

3.1 Ground Truth

To test the hypothesis that the secondary mineral zones can be used to indirectly measure pH and metal mobility, a ground verification leach study was conducted at the pile with the clearest pattern of concentric mineral zones. Rock samples were collected and spectral reflectance measurements were made every 10 m along a 250 m traverse across the mineral zones at the Venir waste rock pile located 4 km southeast of Leadville at an elevation of 3600 m. Distances along the traverse were measured using a tape starting from the western end of the traverse line. The traverse starts in the forest west and down slope from the Venir pile and proceeding up the steep west side onto the flat top of the pile. The traverse then continues past abandoned buildings on the eastern margin of the pile and extends into forest east and slightly up slope of the pile.

The locations of rock samples relative to the mineral zones were determined by two methods. The first

method involved registering the mineral maps made from AVIRIS data to a registered aerial photo of the Venir pile then plotting the sample points on the composite image. This presentation gives the correlation of each sample to mineralogy determined spectrally from AVIRIS. The second method used mineralogy determined from the field spectra. A minimum of 10 spectra were measured at each sample collection station with an ASD FR spectrometer. Spectra were averaged, corrected to true reflectance with a NIST spectralon correction, and then mapped for mineralogy with the Tricorder algorithm. This gives the correlation of each sample to mineralogy determined on the ground.

The AVIRIS mineral maps show the pile as a jarosite zone surrounded by a broad skirt of goethite slightly wider on the down slope side of the pile. A thin jarosite + goethite zone maps along the steep west-facing slope of the pile forming a transition zone between the jarosite zone and outer goethite skirt. This jarosite + goethite zone continues around the southern and eastern margin of the pile pinching out along the north margin where the jarosite zone is in direct contact with the goethite skirt. Correlation between AVIRIS and ground spectra is nearly one-to-one except near buildings with rusted metal roofs. In these areas the roofs contribute a goethite spectral component in addition to that from jarosite on the ground resulting in a combined jarosite + goethite spectral signature at the 17 x 17 meter spatial scale of AVIRIS pixels at this elevation. The ground spectra indicate that the actual jarosite + goethite zone is much narrower along the eastern margin of the pile. Because of this spectral interference the geochemical measurements described below were keyed to mineral zones derived from the ground traverse.

3.2 pH and Metal Mobility Tests

The rock samples were analyzed for leachate pH and metal mobility using wet chemistry. Samples were sieved and the < 4 mm fraction was split for grinding and bulk chemical analysis for elements with inductively coupled plasma - atomic emission spectroscopy (ICP-AES). The remaining unground sample split was subjected to the EPA 1312 Synthetic Precipitation Leach Procedure (SPLP) which involved adding 2 liters of slightly acidified deionized water to 100 g of sample and agitating the mixture for 18 hours. Leachate pH was measured before filtering and trace metals were measured with inductively coupled plasma - mass spectroscopy (ICP-MS) on the filtered leachate.

Results of the chemical analyses show that the mineral zones can be used to map pH and metal mobility. For instance, pH of the leachate is 4.5 - 6 in the goethite zones, 2.5 - 3.5 in the jarosite + goethite zone, and 2.3 - 2.5 in the jarosite zone (Figure 1). Bulk trace metal concentrations show only a weak correlation to mineral zones with the ranges of metal concentrations in each zone overlapping the others (Figure 2). However, leachable trace metal concentrations show a good correlation to the mineral zones with metals 20 - 100 times more mobile in the jarosite and jarosite + goethite zone compared to the goethite zone. Leachable metal concentrations vary over nearly three orders of magnitude compared to only one order of magnitude for the bulk metal concentrations. This relationship indicates that bulk metal concentration, usually measured with field x-ray fluorescence (XRF), does not accurately predict the leachability of trace metals. The jarosite and jarosite + goethite zones pose a serious contamination threat if they boarder streams capable of transporting metal-rich water and suspended sediment. Because jarosite quickly decomposes outside of its pH range, it is rapidly coated with goethite. Areas where the goethite zone intersects streams may mark the deposits of storm events during which acid drainage traveled beyond the jarosite and jarosite + goethite zones.

4. Conclusions

Spectral mineral maps made with AVIRIS data using the USGS Tricorder algorithm have assisted remediation efforts at the California Gulch Superfund Site at Leadville, Colorado. The maps identified concentric zones of secondary minerals in bull's-eye patterns that pinpoint the sources of acid drainage. Field tests verify that spectral mineral maps can be used to indirectly measure pH and metal mobility of surface runoff emanating from these waste rock and tailings piles. Use of XRF bulk metal concentrations to screen wastes may overestimate the amount of material that needs to be remediated. A GIS system that integrates mineral maps with topography and drainage information could be used to screen drainage basins for those areas contributing the most acid and metals to nearby streams.

Mineral maps made from AVIRIS data provided a rapid method to screen entire mining districts for

sources of acid and metals. What it took 52 days to do on the ground and in the lab for the Venir pile (i.e. sample collection, preparation, and leaching) was done using AVIRIS and Tricorder in a little over two days. Use of mineral maps created from AVIRIS data has saved taxpayers \$2 million and accelerated remediation by 2.5 years at the California Gulch Superfund Site (S. Vance, EPA, pers. comm, 1997). This technology can be used to save time and money at other mine sites where carbonate in the waste rock is unable to neutralize the acidity created by pyrite oxidation. Additional studies are underway at the Ray Mine in Arizona, and in the Mother Load Gold Belt in California. Widespread use of this screening technique depends on the willingness of the EPA to approve its use for cleanup on a production basis.

5. References

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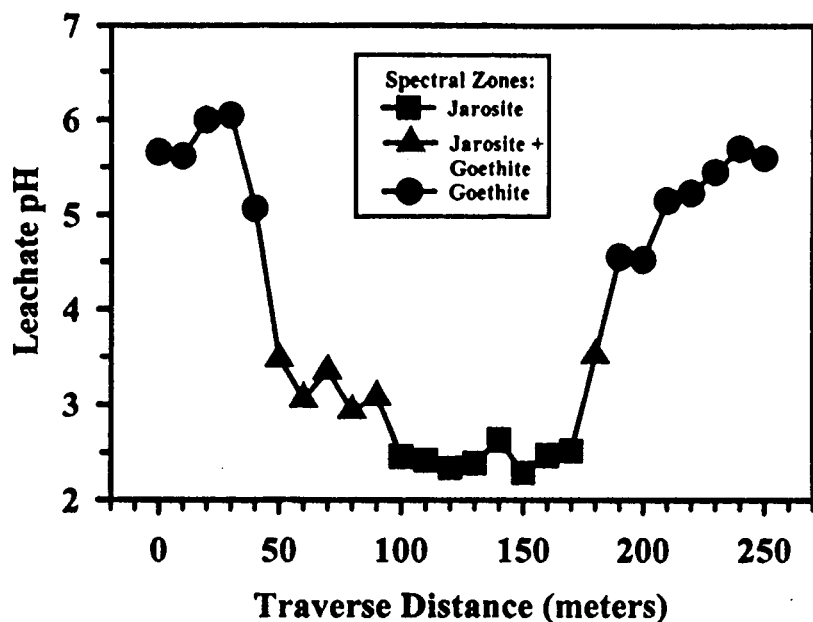


Figure 1. Leachate pH as a function of distance along the traverse across the Venir waste rock pile.

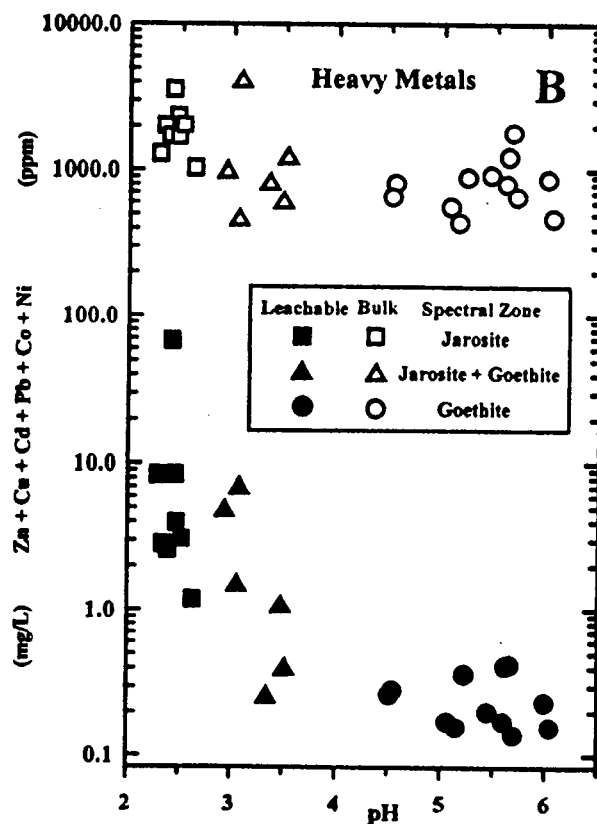
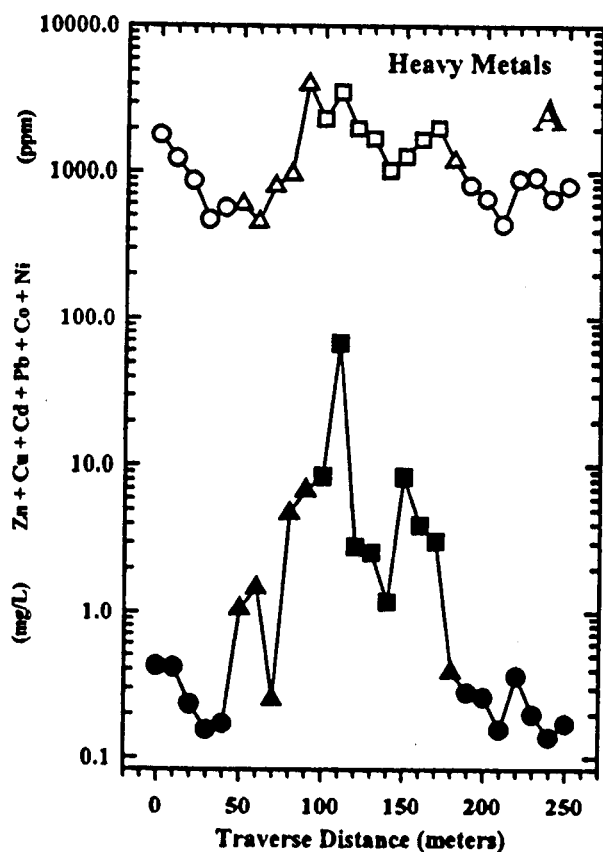


Figure 2. A) Concentration of bulk and leachable heavy metals across the Venir waste rock pile. B) Ficklin diagram of heavy metals versus leachate pH. Leachable heavy metals vary over nearly three orders of magnitude with metals in the jarosite and jarosite + goethite zones 20-100 times as mobile as in the goethite zone.