

IRONITE: A POTENTIALLY FERTILE SOURCE OF SOIL CONTAMINATION

Ironite fertilizer is a common source of iron and nitrogen for lawns, gardens, and agricultural crops. The fertilizer is made from processed mine tailings left over from an inactive silver mine in Humboldt, Arizona. While the beneficial reuse of mine tailings are—by U.S. law under the Bevill Exemption—not defined as hazardous waste, there are concerns that this fertilizer could leave dangerous amounts of arsenic and lead in the ground. Previous studies by the manufacturer found that better than 95% of the arsenic was bound with iron and sulfide into the mineral arsenopyrite (FeAsS), and that this is further insulated when surrounded by pyrite (FeS). The manufacturer's study also found that most of the lead is safely bound in the mineral galena (PbS). However, researchers from the U.S. Environmental Protection Agency (EPA), utilizing the MR-CAT 10-ID and XOR/PNC 20-BM beamlines at the APS, found that by the time the fertilizer gets from the factory to the store, the arsenopyrite and the galena have decomposed, leaving arsenic bound to ferric oxides, and lead bound into anglesite. Both of these states could result in arsenic and lead leaching into the soil and being bioavailable to living creatures, human and otherwise.

To study the composition of Ironite, the EPA researchers bought bags of the fertilizer from commercial retail stores—two in Ohio and one in Florida—in order to test the composition of the fertilizers as sold to a user, not simply after recovery from the mine wastes. The researchers used x-ray absorption spectroscopy (XAS) at 20-BM and 10-ID to study the granular fertilizer both as bought and after having been crushed to less than $44\ \mu\text{m}$. Mössbauer spectra of the samples were also collected in order to study the iron chemical content. Lastly, the EPA researchers put the Ironite through aging studies to see how it degraded.

The dominant peak provided by x-ray absorption spectroscopy showed the arsenic in Ironite to be $1.57\ \text{\AA}$ from its nearest neighbor. This is indicative of the arsenic-oxygen bond distance in scorodite ($\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$), as opposed to the $\sim 2.35\text{-}\text{\AA}$ bond arsenic has to sulfur in arsenopyrite. A secondary, less intense peak, however, was consistent with this arsenic-sulfur bond, suggesting the Ironite has a mix of both types of bonds. The researchers' analysis shows that 60% to 70% of the arsenic is bound by oxygen in either scorodite or with iron oxides and the rest is bound in arsenopyrite (Fig. 1). Because the studies done by the manufacturers found much more arsenopyrite, the EPA researchers offer the explanation that scorodite is more stable in oxygenated environments than arsenopyrite. The original arsenopyrite likely decomposed over time once packaged for retail.

The studies performed on behalf of the manufacturer also showed that lead is found in Ironite, reporting that 82% to 91% of the lead exists in the form of galena (PbS) and 6% to 17% exists as anglesite (PbSO_4). However, x-ray absorption near edge structure analysis done by the EPA researchers indicates

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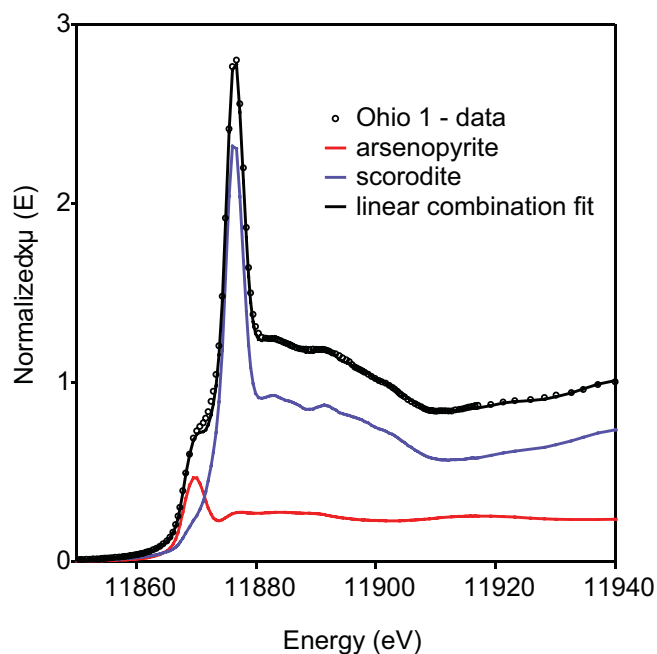


Fig. 1. Linear combination fit of an Ironite 1-0-0 sample purchased in Ohio, demonstrating an Fe-O-As-type structure similar to scorodite as the dominant As environment (60%-70%) in Ironite. Arsenopyrite, an Fe-S-As-type structure, accounts for the balance of As in Ironite.



The Ironite facility at Humboldt, AZ. The orange mountain in the background is the pile of mine waste from which Ironite is derived.

that anglesite is the dominant phase. The EPA group offers a similar explanation as for the arsenic: During storage for commercial sale, the parent material containing lead undergoes further oxidation and transformation to mineral phases that are more stable under atmospheric conditions.

Mössbauer spectroscopy was used to examine the iron chemistry that might be controlling the arsenic availability to the environment. At room temperature, there was a clear identification of pyrite, but other phases were hard to identify. Once the samples were cooled to 4.2K, however, a peak for ferrihydrite could be seen. There was not substantial evidence for scorodite, so on the basis of the high proportion of arsenic associated with iron oxides as identified with the XAS, the most probable explanation is that arsenic reacts with ferrihydrite by sorption, coprecipitation, or both.

The EPA scientists also wanted to study how arsenopyrite ages in the environments where Ironite is used. While the manufacturer's studies show that 95% of the arsenic is in arsenopyrite, the mineral can degrade further when placed in oxygenated environments, such as on a lawn. These researchers studied Ironite after it sat in buffered water for one day and for a month. After the one-day period, both arsenopyrite and arsenic associated with ferric oxides were present. After a month, no arsenopyrite was present. Sitting in buffered water is not the equivalent of being used as a fertilizer—but this nonetheless shows that arsenopyrite is susceptible to chemical transformation in regularly watered lawns.

Having shown that the arsenic and lead in Ironite sold in stores does not remain in the same mineral state as at the factory, and that it can degrade even further once placed on a lawn,

the EPA team emphasized that while the idea of using waste products from mines for beneficial products is a good one, careful consideration and scrutiny must be applied to determine if the benefits outweigh the environmental cost and risks posed by accidental ingestion and contamination of water resources. Specifically, because a January 2006 EPA regulation limits the amount of arsenic in drinking water to 10 $\mu\text{g}/\text{liter}$, the benefits of applying a potential source of arsenic need to be carefully evaluated. — *Karen Fox*

See: Aaron G.B. Williams, Kirk G. Scheckel*, Thabet Tolaymat, and Christopher A. Impellitteri, "Mineralogy and Characterization of Arsenic, Iron, and Lead in a Mine Waste-Derived Fertilizer," *Environ. Sci. Technol.* **40**, 4874 (2006). DOI: 10.1021/es060853c

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The U.S. Environmental Protection Agency, through its Office of Research and Development, funded and managed the research described here. It has not been subject to Agency review and, therefore, does not necessarily reflect the views of the Agency. No official endorsement should be inferred. PNC-CAT facilities at the Advanced Photon Source and research at these facilities are supported by the U.S. DOE Office of Science Grant No. DEFG03-97ER45628, the University of Washington, a major facilities access grant from NSERC, Simon Fraser University, and the Advanced Photon Source. MR-CAT operations are supported by the Department of Energy and the MR-CAT member institutions. Use of the Advanced Photon Source was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. W-31-109-ENG-38.