MOBILITY AND BIOAVAILABILITY OF ARSENIC, LEAD, COPPER, AND ZINC AT THE AVOCA MINE SITE, COUNTY WICKLOW, IRELAND[1]

Kent S. Whiting [2], Roger L. Olsen, Eibhlin Doyle, and Gerry Stanley

Abstract: The Avoca Mine in County Wicklow, Ireland is a volcanogenic massive sulfide deposit which has been mined for copper intermittently over the past 300 years using both underground and open pit methods. As a result of the mining activities, large areas of the site are covered with mine spoils, and the Avoca River has been impacted by ARD containing metals concentrations which have made the stream habitat unsuitable for native trout and salmon.

An evaluation of the bioavailability of lead and arsenic within the spoils material was performed using a bioassay technique developed by the University of Colorado, ICP, and electron microprobe (EMP) analyses, while the leach ability of zinc and copper within the spoils was evaluated using ICP, and EMP techniques. While the spoils contained on average 900 mg/kg arsenic and 15,000 mg/kg lead, only 0-28% of the lead (average of 6%) and 0-8% of the arsenic (average of 0.5%) was bioavailable. EMP results showed the lead and arsenic to be present mainly within plumbojarosite and other hydroxysulfate phases, which are stable under the low pH conditions within the spoils pore water. The copper and zinc concentrations within the spoils averaged 1750 mg/kg and 420 mg/kg, respectively. EMP results showed that copper and zinc was present in the spoils mainly as primary sulfide minerals. Copper and zinc concentrations were low within the secondary minerals such as plumbojarosite and other hydroxysulfate, reflecting their higher mobility in the system and explaining why copper and zinc are present in much higher concentrations in the ARD and the Avoca River than arsenic and lead.

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[2] Kent S. Whiting LG, Environmental Scientist, CDM, Helena, MT, 59601 Roger L. Olsen Ph.D, Environmental Scientist, CDM, Denver, CO, 80202, Eibhlin Doyle Ph.D, Geologist, Geological Survey of Ireland, Dublin Ireland, Gerry Stanley Ph.D, Geologist, Geological Survey of Ireland, Dublin Ireland

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Introduction

The Avoca mine site is located approximately 50 km south of Dublin in County Wicklow Ireland. The mine site is located on both the east and west sides of the Vale of Avoca, a major river that is formed by the confluence of the Avonmore and Avonbeg tributaries at the "meeting of the waters" made famous by the poet Thomas Moore. The river flows southwest and eventually empties into the sea at the port town of Arklow (see Fig. 1).

Geology and Ore Deposit

The Avoca ore deposit is hosted by the Avoca Formation of Ordovician age, which consists of sericitic tuffs, chlorite tuffs, silicified sericitic lithic and crystal tuffs, and felsites. Pale colored rhyolites, rhyolitic tuffs and breccias are evident in some exposures within the open pits. The volcanic host rocks are also interbedded with sediments of marine origin, and include mudstones, shales and metamorphic phyllites (Gallagher and O'Connor, 1997).

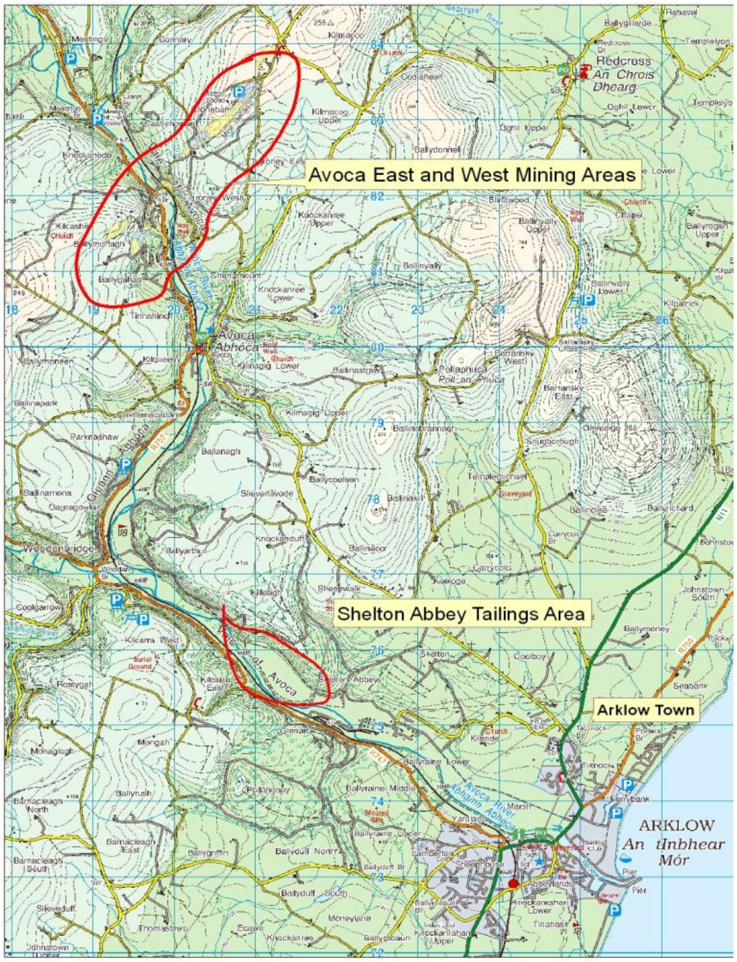


Figure 1 – Avoca Mine Site.

The Avoca Formation and its enclosing sediments dip steeply (50 degrees +) to the southeast. The Formation varies in total thickness from 1,500 – 2,500 meters, depending on location. In Wicklow, the Avoca Formation takes on a lenticular shape which trends NE-SE and varies in width between 2-4 kms. The sequence is at its thickest within the Avoca River valley.

There are numerous basic igneous intrusions in the vicinity of the mines, including the Carrigmore Diorite to the northeast of East Avoca. The Cronebane pit shows marked heterogeneities, with exposed surfaces of porphyry, schist, rhyolite, shales and tuffs.

The Avoca ore bodies occur primarily as banded, massive sulphides. The banded, massive sulphides can be several meters thick, and more than 95% of the associated ore is composed of pyrite (FeS_2), the remainder comprising chalcopyrite ($CuFeS_2$), sphalerite (ZnS), and galena (PbS). Magnetite, hematite, arsenopyrite, pyrrhotite, bismuthinite and native bismuth are trace constituents, while gold is rare (Gallagher and O'Connor, 1997).

Mining History

Industrial-scale Cu mining began at Avoca around 1720, although iron had earlier been exploited in small deposits in the district. From 1839 onwards pyrite mineralization provided economic S ore which became the main product at Avoca.

Mining of Cu and S continued until 1888. During the 18th and 19th centuries, it was estimated that 0.22 Mt of Cu ore grading 6.45 % Cu and 2.4 Mt of pyrite ore grading 35 % S were produced.

The mines were re-opened during World War II to provide an emergency supply of S and this was followed by two further periods of continuous mining for Cu. Production was recommenced in West Avoca in 1958 by St. Patrick's Copper Mines Ltd when the mine was deepened to 200 m below sea level but production problems led to a further cessation of mining in 1962. Avoca Mines Ltd subsequently re-opened the mine in 1969, with underground workings eventually extending to depths of 300 m below sea level. During the same phase of mining, open pit exploitation was also implemented, in the Pond Lode open pit (in West Avoca, which commenced production in 1973), the Cronebane open pit (east of the river, excavated 1971-1975) and East Avoca open pit (excavated between 1978 and 1982). Mining finally ceased in the Avoca area in 1982, by which time an estimated 12 Mt of ore had been extracted from the mines over their working life. An attempt at gold extraction in the Cronebane Pit in the late 1980's proved unsuccessful and was not pursued.

Mining Wastes and Adits

As a result of the extensive mining activities in the area, large quantities of mining wastes and several open pits and adit discharges exist at the site (see Table 1).

Sources of low quality water in East and West Avoca consist of leachate from waste rock piles, tailings, open pits, and underground workings. An example of one of the open pits at the site is shown in Fig. 2, while an adit discharge and spoils pile are shown in Fig. 3 and 4, respectively. Only three of the mine adits flow directly into the Avoca River; the Deep Adit, the Road Adit, and the Ballygahan. The remaining adits either discharge into the underground workings or groundwater.

Table 1 – Avoca Mine Site - Summary of Low pH Metal-Bearing Leachate Sources and Drainages

Area	**Pits**	**Waste Rock Volume (m^3)**	**Tailings Volume (m^3)**	**Flowing Adits**
East Avoca	Cronebane (open) East Avoca (open)	1 million	None known	Deep (255 gpm) Intermediate (134 gpm) Cronebane Shallow (3.3 gpm) Kilmacoo (6.0 gpm)
West Avoca	Pond Lode (backfilled) North Lode (backfilled) Weaver’s (partially backfilled)	400,000	350,000	Road (306 gpm) Ballygahan (1.0 gpm) Spa (4.8 gpm)
Shelton Abbey	None	None known	7 million	None

Figure 2. East Avoca Pit, showing the Intermediate Adit discharge flowing into the pit pond (April 2007).

Figure 3. Deep Adit Discharge (April 2007).

Figure 4. Spoil Piles in Tigroney West

Adit Water Quality

A summary of the dissolved metals and As concentrations for the most important adits is presented in Table 2.

Table 2 – Summary of Adit Water Quality (dissolved concentrations)

Adit	**Intermediate**	**Cronebane Shallow**	**Deep**	**Road**	**Ballygahan**
Flow (gpm)	135	3.4	255	307	1.0
Iron[1]	107.7	22.6	72.3	150.7	10.8
Aluminum[1]	71.4	36.7	102.6	20.9	99.1
Arsenic[1]	0.010	0.034	0.001	0.003	0.022
Copper[1]	3.2	8.9	0.8	0.3	5.2
Zinc[1]	33.0	85.9	47.6	11.0	21.7
Lead[1]	1.3	1.3	1.4	0.3	0.2
Sulfate[1]	799	3,215	1,111	1,401	2,072
pH (su)	4.3	3.9	3.1	3.9	3.8

1. Units are mg/L

The adit water quality is very poor, with very high Fe, Al, Cu and Zn concentrations and a low pH. However, the As and Pb concentrations were comparatively low.

Spoils Quality

A total of 98 surface samples were collected at the nodes of a 50 m by 50 m grid pattern established over each spoil pile. An additional 28 samples were collected from 16 test pits and another 27 samples from 14 boreholes in order to characterize the deeper zones of the piles.

A summary of the metals and arsenic concentrations is presented in Table 3.

Table 3 Summary of Median Metals and Arsenic Concentrations in Spoils (mg/kg)[1]

	Connary		**Mt Platt**	**East Avoca**	**Tigroney West**			**West Avoca**		
	SP25	**SP31**	**SP20/20A**	**SP10**	**SP2**	**SP4**	**SP5**	**SP33**	**SP34**	**SP37/ 37A**
As	894	853	511	288	761	350	804	1657	1394	30
Pb	24522	12022	3552	1645	7464	5915	7687	16479	1234	107
Cu	2177	836	559	1238	1966	1517	2361	1949	571	51
Zn	578	214	188	213	399	212	235	437	91	121

1. Measured by ICPMS

The analyses of the spoils material indicated that concentrations of Cu, Pb, and As were high, while Zn concentrations were relatively low in most areas. The high concentrations of As and Pb in the spoils and the relatively low concentrations in the adit discharges suggest that these elements are much less mobile than Cu and Zn, at the site.

Objectives of the Current Investigation

Arsenic, Pb, Zn, and Cu in the form of arsenopyrite, galena, sphalerite, and chalcopyrite, respectively, are predicted to dissolve via the following reactions:

$$FeAsS\ (s) + 7/2\ O_2 + H_2O \rightarrow Fe^{2+} + SO_4^{2-} + AsO_4^{3-} + 2H^+ \quad (1)$$

$$FeAsS\ (s) + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + SO_4^{2-} + AsO_4^{3-} + 16H^+ \quad (2)$$

$$PbS(s) + 2O_2(aq) \rightarrow Pb^{+2}(aq) + SO_4^{-2}(aq) \quad (3)$$

$$ZnS(s) + 2O_2(aq) \rightarrow Zn^{+2}(aq) + SO_4^{-2}(aq) \quad (4)$$

$$CuFeS_2(s) + 4O_2(aq) \rightarrow Fe^{+2}(aq) + Cu^{+2}(aq) + 2SO_4^{-2}(aq) \quad (5)$$

In addition, trace amounts of these elements within pyrite should also be released during the oxidation of pyrite, as follows:

$$FeS_2\ (s) + 7/2O_2\ (aq) + H_2O\ (l) \rightarrow Fe^{2+}\ (aq) + 2SO_4^{2-}\ (aq) + 2H^+\ (aq) \quad (6)$$

$$FeS_2\ (s) + 14Fe^{3+}\ (aq) + 8H_2O\ (l) \rightarrow 15Fe^{2+}\ (aq) + 2SO_4^{2-}\ (aq) + 16H^+\ (aq) \quad (7)$$

All of the metals and As contained within the sulfide minerals should be released upon oxidation of these phases. The fact that Pb and As are present in relatively high concentrations within the wastes and high concentrations of As and Pb are not present in the adit discharges at the Avoca site suggests one or more of the following:

1) Arsenic and Pb are not present to a significant degree in the pyrite.
2) Arsenopyrite and galena are coarsely crystalline (which slows the rates of reaction), are enclosed within other minerals, or are otherwise unavailable for reaction via equations 1, 2 and 3.
3) Dissolved As and Pb are attenuated soon after release from the source materials

In order to determine if As and Pb are released from the wastes (and to be used for the human health risk assessment), bioassays were performed. The forms of As and Pb within the wastes was determined using electron microprobe analyses (CDM, 2007 and CDM, 2008).

Methodology

Lead and Arsenic Bioassay

Lead and As bioavailability testing was performed in order to evaluate the leaching of these elements within the human gut and to make an assessment of the risk to human health due to ingestion of the mine wastes. In the past, relatively expensive *in vivo* tests have been used in which pigs or other animals are fed the material to be tested (mixed within their feed) and later evaluated for Pb or As content within the stomach. Recently, a relatively inexpensive *in vitro* test has been developed which simulates the conditions of the human gastric system (USEPA, 2007). The *in vitro* test involves performing a leaching test under the conditions of the human stomach. In the test, 1 gram of the <250 µm fraction of the mine waste is placed in an HDPE bottle along with 100 mL of the leach solution. The leach solution is prepared by adding glycine to deionized water and adjusting the pH to 1.5 su using hydrochloric acid. The bottles are then placed in a toxicity characteristic leaching procedure (TCLP) agitator and rotated for 1 hour within a water bath maintained at 37°C. The solution is then filtered through a 0.45 µm membrane and analyzed for Pb and As using EPA Method 6020 (USEPA, 2004). The mass of Pb and As within the initial <250 µm fraction is then compared to the mass leached to obtain a percent leachable Pb and As. The percent leachable is then converted to a percent bioavailable using a known correlation with the in vivo testing.

Bioassay testing was performed on 31 samples collected from the 0-6 inch depth interval of the spoils piles.

Electron Microprobe Analyses

Analyses on a single grain of soil or a single crystal of a precipitate were accomplished using an EMP. Not only can analyses be made on particles as small as 1 micron, but the EMP also provides a visual picture of the soil at magnifications ranging from 40 to 90,000 times. The visual mode is referred to as the "backscatter mode." Information about the relative atomic number of the compounds can be obtained in the backscatter mode due to the contrast in brightness between the low atomic number compounds and the compounds with high atomic numbers.

For example, As and Fe compounds, which have high mean atomic numbers, tend to be bright white in backscatter mode, while silica compounds, with lower mean atomic numbers, are gray and organic carbon is nearly black. Direct visual inspection of the soil also provides information on the associations, morphology, and any reaction rims on the particles, all of which provide insight into the geochemical history of the sample. Soil samples were analyzed on a JEOL 8600 Superprobe located in the Department of Geological Sciences, University of Colorado, Boulder, Colorado.

Operating conditions included a 15 KeV accelerating voltage, 17 NanoAmp cup current, and a 1 to 2 micron beam size. Certified pure element standards were used to determine phase compositions. Wavelength spectrometer crystals TAP for As, PET for Fe and S and LDE1 for oxygen were used for the WDS analyses.

Sample pucks were scanned for As-containing minerals using backscattered electron images. The scanning was done manually by systematically traversing from left to right until the edge of the mount was reached. The puck was then moved up one field of view and scanned from right to left. This process was repeated until the whole mount was scanned.

Typically, the magnification used for scanning samples was 40-100X and 300-600X, depending on the individual sample's grain size distribution. The last setting allowed the smallest identifiable (1 to 2 μm) phases to be found. Once a candidate particle was identified, then the backscatter image was optimized to discriminate any different phases within the particle or its association. Identification of the As-bearing phases was done using both energy-dispersive and wavelength-dispersive spectrometers set for analyses of As, S, Fe, and oxygen.

A summary of the samples collected for EMP analyses are summarized in Table 4.

Table 4 – Summary of Samples Analyzed by Electron Microprobe

Sample ID	**Location**	**Depth (m)**	**Type**	**Collection Method**	**Depth Classification**
SA-17S	Mt Platt (SP20)[1]	0.15	Spoils	Grab	Surface
SA-7A	Shelton Abbey	0.15	Tailings	Grab	Surface
SA-9	West Avoca (SP34B)	0.15	Spoils	Grab	Surface
SA-12	Connary (SP22)	0.15	Spoils	Grab	Surface
BH-WA1 2.55	West Avoca (SP34B)	2.55	Spoils	Borehole	Subsurface
BH-MP1 8	Mt Platt (SP20)	8	Spoils	Borehole	Subsurface
BH-SA1 17.5	Shelton Abbey	17.5	Tailings	Borehole	Subsurface
BH-ET1 2	Emergency Tailings	2	Tailings	Borehole	Subsurface
BH-MP2 16	Mt Platt (SP20)	16	Spoils	Borehole	Subsurface
BH-ET1 7.5	Emergency Tailings	7.5	Tailings	Borehole	Subsurface
TP-CO4 0.3-0.4	Connary (SP31)	0.3	Spoils	Test Pit	Subsurface
TP-CO3 0.9-1.35	Connary (SP31)	0.9	Spoils	Test Pit	Subsurface

1. The spoil pile ID as defined by Gallagher et al., 1997 are provided in parentheses.

The "SA" series of samples (surface grab samples) were collected in April 2007, while the "BH" and "TP" series of samples (borehole and test pit subsurface samples, respectively) were collected in August 2007.

Results

Lead and Arsenic Bioassays

The results of the Pb and As bioassay analyses are provided in Table 5.

Table 5 – Summary of Lead and Arsenic Bioassay Results for the 31 Surface Spoils

	Pb in <250 µm Fraction (mg/kg)	**Percent Relative Bioavailable Pb**	**As in <250 µm Fraction (mg/kg)**	**Percent Relative Bioavailable As**
Minimum	58.6	0	14.8	0
Maximum	56,022	28[1]	2,560	8
Median	5,524	3	706	0

1. Two samples had anomalously high bioavailability, at 22% and 28%. If these samples are excluded, the range is 0-13%.

Electron Microprobe Analyses

Primary Phases Primary sulfides (pyrite, sphalerite, galena, etc.) were rare, and when present were remnants of larger grains and showed signs of dissolution (embayments, pitting, etc.) and weathering products (oxides and sulfates). Figure 5 is a photomicrograph showing pitted and embayed pyrite grains, suggesting that partial oxidation of the grains has occurred. An example of a grain of pyrite which has been almost completely oxidized to iron oxyhydroxide is shown in Fig. 6. Figure 7 shows a pyrite grain in which several analyses were performed, indicating that As was present in concentrations from less than about 100 ppm up to 10,000 ppm (1.0%). Other primary phases present included anglesite ($PbSO_4$), galena, chalcopyrite, and sphalerite (Fig. 8). Note that for the purposes of this investigation, minerals from the supergene ore zone, such as

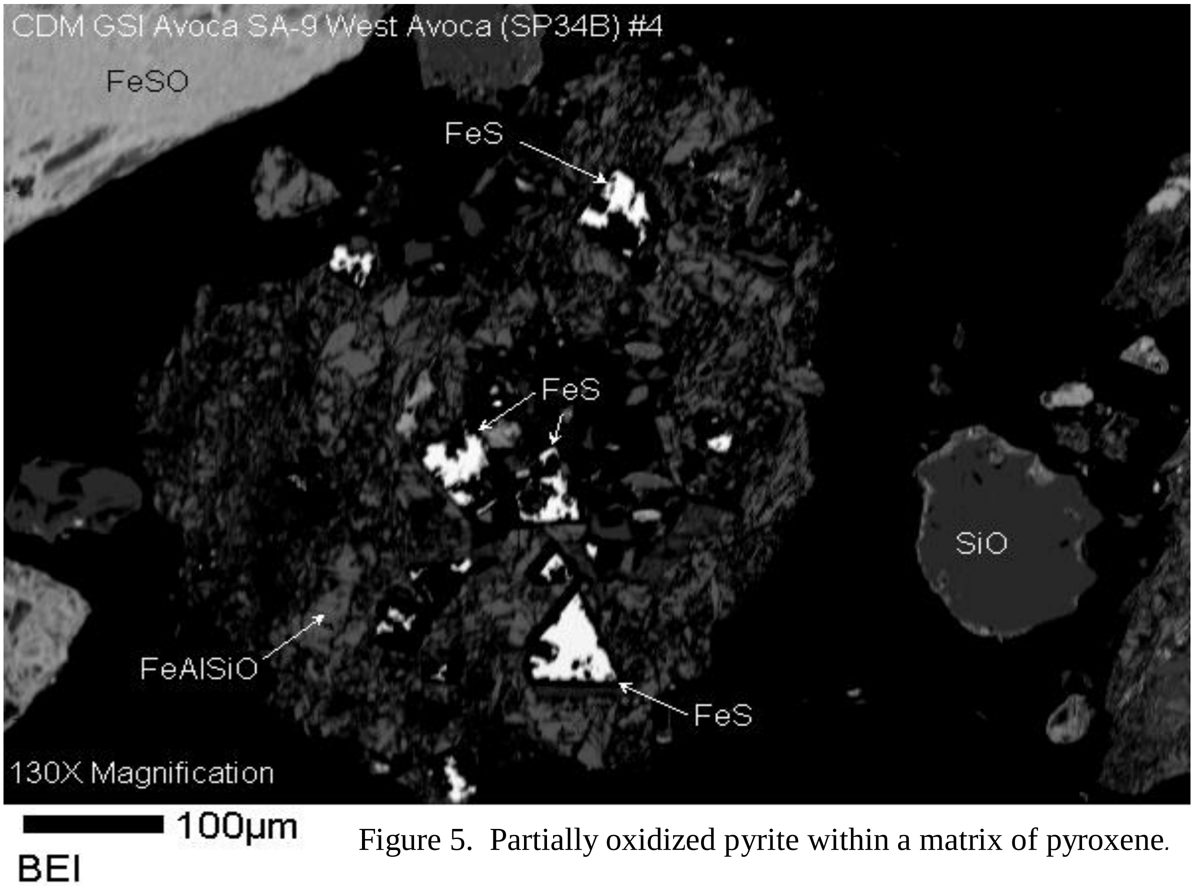


Figure 5. Partially oxidized pyrite within a matrix of pyroxene.

anglesite and copper sulfides are considered “primary”An example of a partially oxidized grain of zinc sulfide consistent with sphalerite.

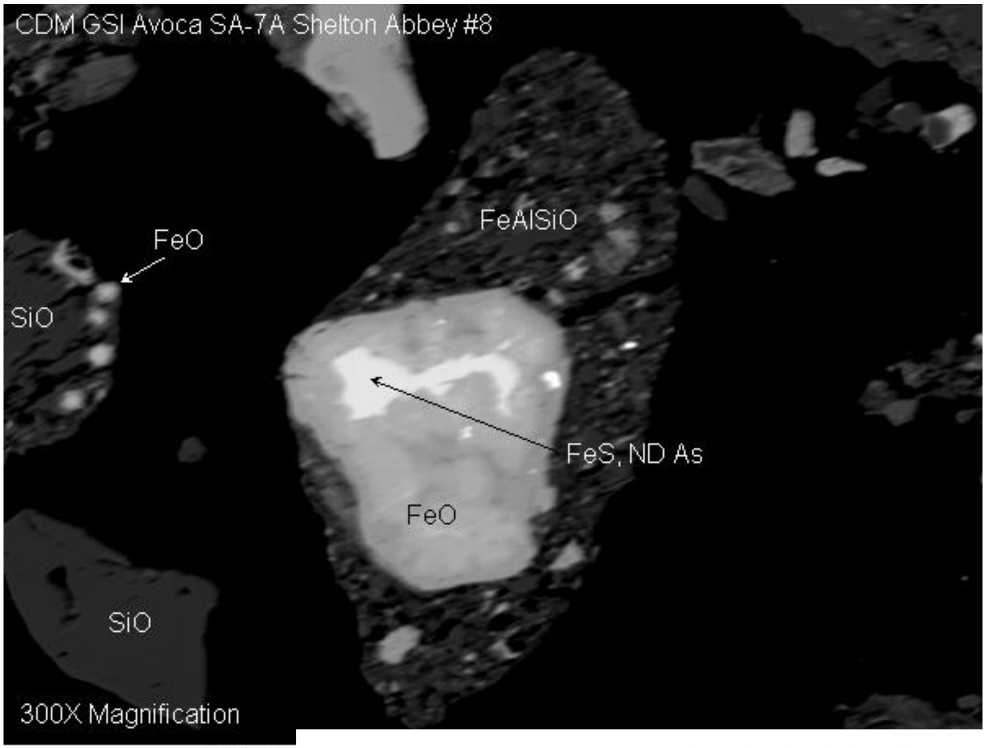


Figure 6. Pyrite grain (FeS) which has been almost completely weathered to iron

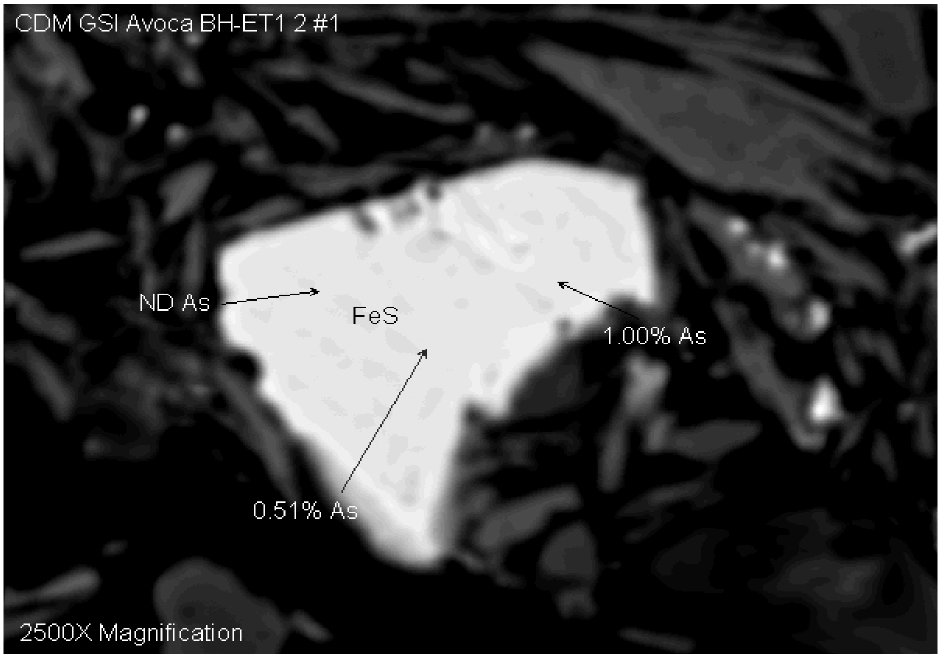


Figure 7. Pyrite grain with varying concentrations of arsenic.

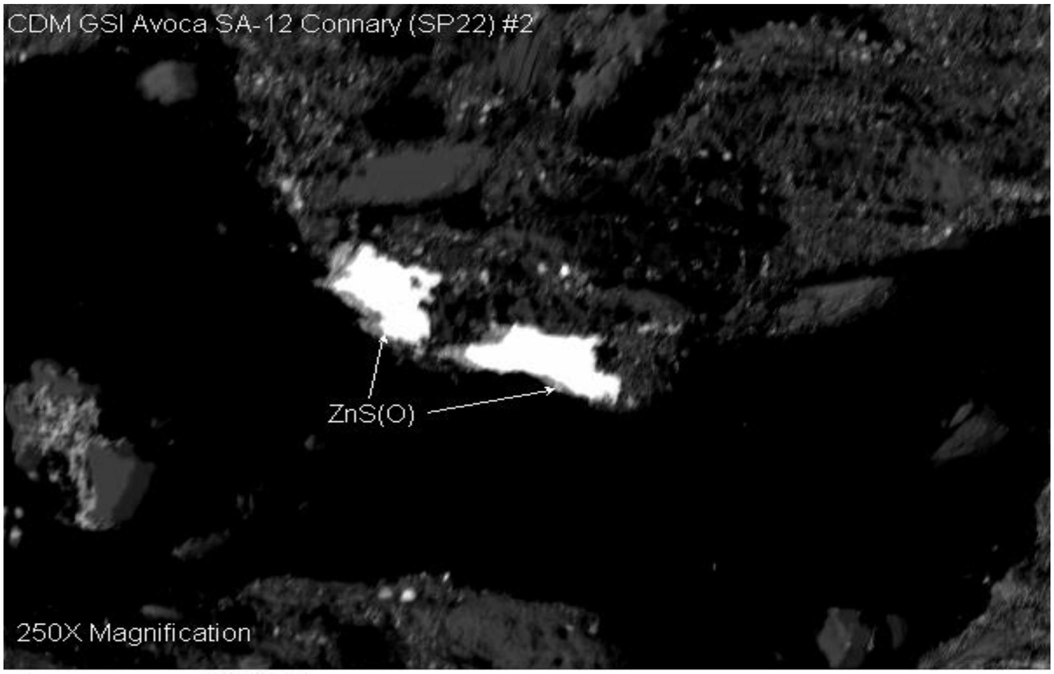


Figure 8. Partially oxidized zinc sulfide.

<u>Secondary Phases</u> The secondary minerals contained high concentrations of Pb and As. Lead was present in high concentrations within plumbojarosite (4.7-21.4%), Pb-schwertmannite (16.5%), and Pb-Al phosphates (17.4-25.9%). The mineral plumbojarosite, which is a lead-bearing Fe hydroxysulfate mineral ($PbFe_6(SO_4)_4(OH)_{12}$), which contains 18% Pb when pure, contained not only high concentrations of Pb, but high As concentrations as well (0.03-6.7%). Figure 9 shows an example of a plumbojarosite grain.

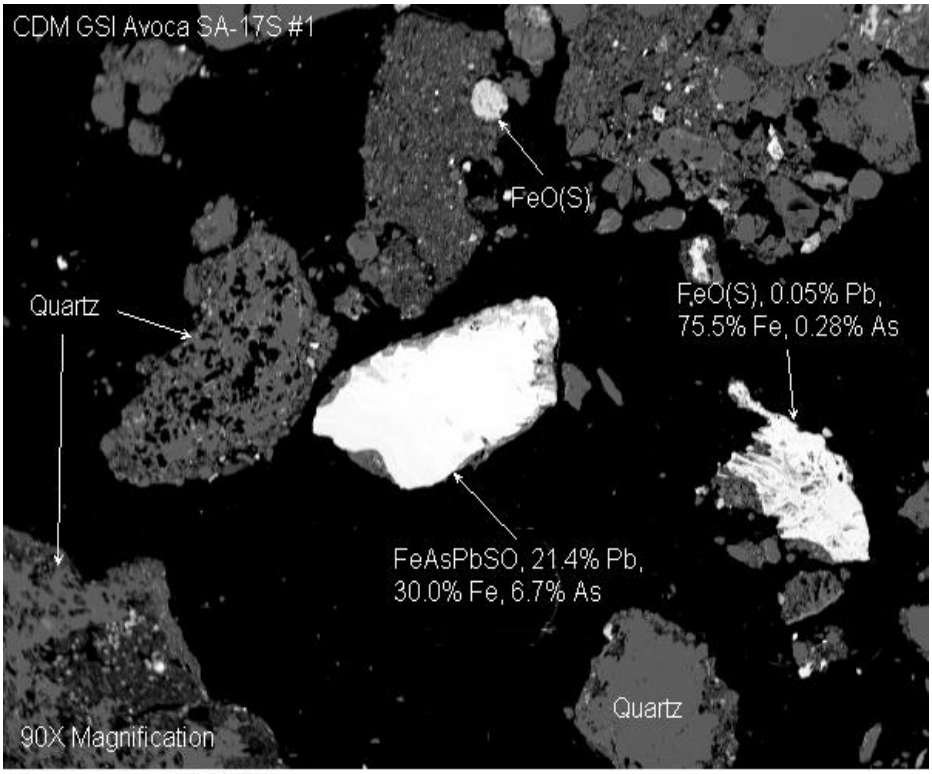


Figure 9. Arsenic-bearing plumbojarosite and schwertmannite (white) along with extensively pitted quartz (gray).

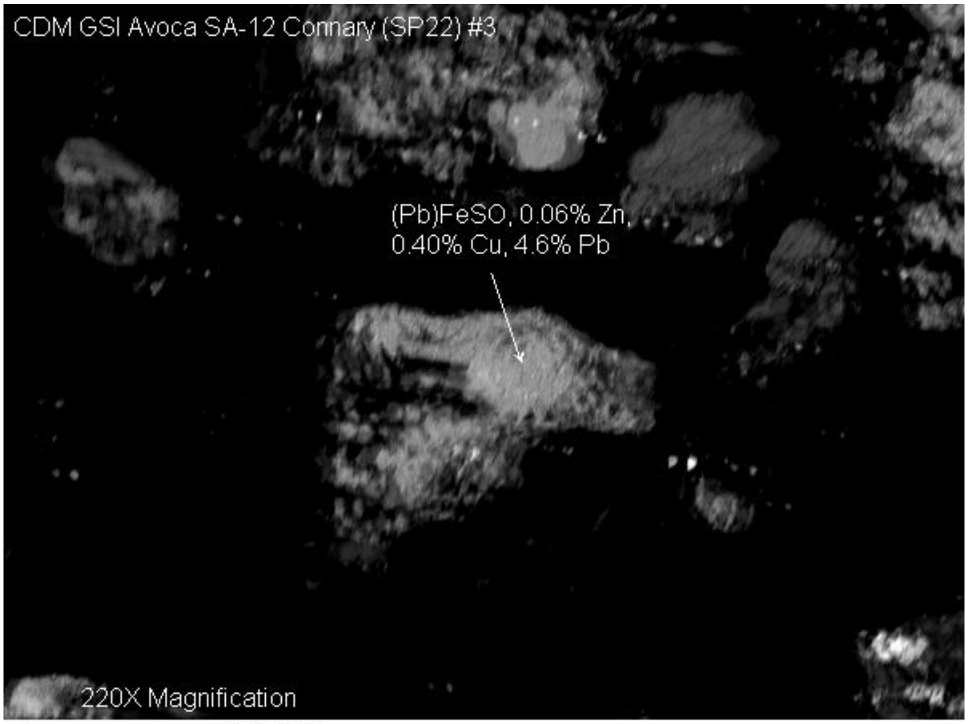
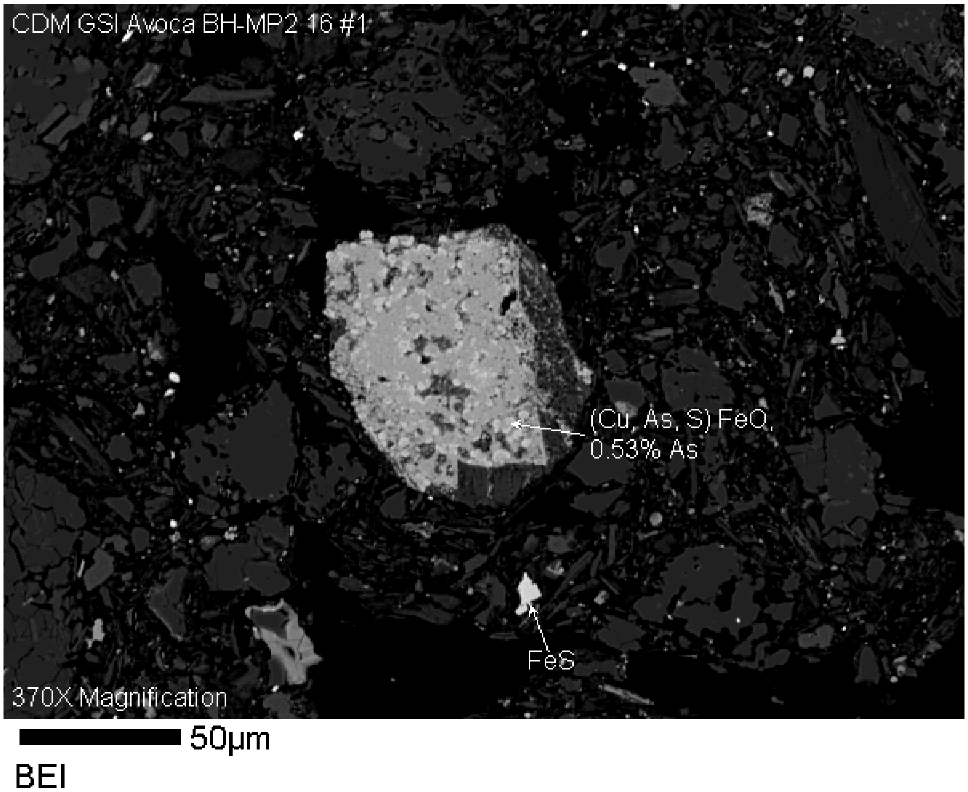


Figure 10. Lead-Bearing Iron Sulfate Phase Consistent with the Mineral Schwertmannite.

Copper (0.4-2.4%) and Zn (0.06-0.16%) were present in relatively low concentrations within plumbojarosite.

Iron oxyhydroxide and schwertmannite were also present (see Fig. 10 and 11), but generally contained three orders of magnitude lower concentrations of Pb (0.016%), an order of magnitude lower concentrations of Zn (0.003%), and an order of magnitude lower As (0.64%) than for the plumbojarosite phase. Copper concentrations (0.19%) were similar.



Summary

Bioassay

The bioassay results indicated that As and Pb within the spoils material have low bioavailability under the conditions present within the human gastric system (i.e. low pH). As similar low pH conditions prevail within the pore water of the spoils piles, the low bioavailability of As and Pb under the conditions of the human gut can be extended to include low mobility of these elements at the site.

Electron Microprobe

Copper and Zn were abundant within the primary minerals (chalcopyrite and sphalerite) but much less abundant in the secondary oxyhydroxides and hydroxysulfates. On the other hand, Pb and As were present in high concentrations in both the primary minerals (arsenopyrite, pyrite, and anglesite) and in the secondary phases (plumbojarosite and phosphates).

Discussion

The mineralogy found in the mine waste samples can be divided into two categories;

- Primary minerals
- Secondary minerals

The primary and secondary mineral forms of As, Pb, Cu, and Zn are summarized in Table 6 below.

Table 6 – Summary of the Forms of Arsenic, Lead, Copper, and Zinc

Parameter	**Primary Phase(s)**	**Secondary Phases**
Arsenic	pyrite (arsenopyrite)[1]	plumbojarosite, schwertmannite, iron oxyhydroxide, (Al-phosphates)
Lead	anglesite[2] (galena)	plumbojarosite, Al-phosphates, (schwertmannite, iron oxyhydroxide)
Copper	chalcopyrite[2], (covellite, chalcocite, etc.)	(plumbojarosite, schwertmannite, iron oxyhydroxide)
Zinc	sphalerite[2]	(plumbojarosite, schwertmannite, iron oxyhydroxide)

1. Phases in parenthesis were a less abundant form of the element than the phases which are not in parenthesis.
2. Most likely phase present based on the mineralogy of the ore body

The conversion of the primary phases to secondary phases is due to oxidation, either within the ore body itself or, more commonly, within the shallower more oxygenated zones on the mine waste. The oxidation of As-bearing pyrite, sphalerite, and chalcopyrite, and the dissolution of anglesite resulted in pore water with high concentrations of As, Pb, Zn, Cu and sulfate. Under the low pH conditions of the pore water, the mineral plumbojarosite is stable. However, based on the EMP results, Pb and As are incorporated into the phase to a much greater extent than Cu and Zn. The result is that As and Pb are removed from the pore water, while Cu and Zn stay in solution, where they are eventually transported to the Avoca River. Jarosite was also found to control As concentrations within arsenopyrite-bearing mine waste at the Nor-Acme Mine, Snow Lake, Manitoba, Canada (Salzsauler et al., 2006).

The formation of As-bearing plumbojarosite explains the low mobility and bioavailability of Pb and As within the mine wastes, despite the high concentrations within the waste materials themselves.

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