LABORATORY STUDIES OF SPHALERITE DECOMPOSITION: APPLICATIONS TO THE WEATHERING OF MINE WASTES AND POTENTIAL EFFECTS ON WATER QUALITY[1]

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Abstract. Sphalerite [(Zn,Fe)S] from Mississippi Valley type (MVT), volcanogenic massive sulfide (VMS), and polymetallic vein (PMV) ore deposits show variable rates of dissolution and resulting aqueous metals concentrations under acid conditions. An important control on dissolution rates is solubilized iron that eventually produces Fe(III), a strong oxidant of sphalerite. VMS (high Fe and Cd) and PMV (high Fe and metals) sphalerite samples showed faster rates of sphalerite dissolution (10^{-9} to 10^{-10} mol/L/s Zn^{+2}) and Fe solubilization (10^{-9} to 10^{-10} mol/L/s total Fe), and higher aqueous trace metals compared to MVT sphalerite that has low Fe and trace metals; these characteristics are manifested by slower rates of sphalerite dissolution (10^{-10} to 10^{-11} mol/L/s Zn^{+2}) and Fe solubilization (10^{-12} mol/L/s total Fe), and low aqueous metals compared to VMS and PMV samples.

Aqueous concentrations of major (Fe, Zn) and trace (Cu, Cd, Pb, Mn) elements depended on the original composition and rate of dissolution of sphalerite. Fine-grained, high-Fe VMS sphalerite (6.7 wt.%) leached at pH 2-3 (25° C) produced dissolved Fe and Zn approaching 50 and 180 mg/L, respectively, within 1 week; Cu and Pb were 3 and 250 µg/L, respectively. The same sphalerite leached at pH 4.0 or higher took two months to yield comparable concentrations. Coarse-grained VMS sphalerite leached for several months at a pH of 4.0 yielded only 100 µg/L Fe and 9.2 mg/L Zn. PMV sphalerite (4.2 wt.%) had a Zn solubilization rate and trace metal concentrations similar to the VMS sample, but a faster Fe solubilization rate (10^{-8} mol/L/s Fe_{tot}).

Low-iron sphalerite (0.2-0.3 wt.%) from MVT deposits produced Zn concentrations similar to the VMS sphalerite at pH 2.0 but lower concentrations at pH 4.0. At both pH values, aqueous Fe from the high-Fe VMS sample was 100 times that from the MVT sample. Trace metals showed a range of concentrations that generally depended on their original abundance in the solid and their solubilities in the acid solution. Because sphalerite from different ore deposits can be major sources of aqueous metals that may affect the composition of nearby surface and ground water, the potential metal contribution of non-pyritic minerals such as sphalerite should be a major consideration during all stages of economic development of an ore deposit.

Additional Key Words: acid drainage, mine waste, aqueous chemistry

Introduction and Background

In metal-mining wastes undergoing acidic decomposition, pyrite (FeS_2) weathering usually dominates the aqueous chemistry. However, where pyrite is low in abundance or metals content, dissolution of monosulfide ore minerals such as sphalerite [$(Zn,Fe)S$] may contribute significant amounts of dissolved metals to effluent waters (Jambor, 2003). The rates of solubilization of major and trace metals, and their subsequent geochemical pathways after release from sphalerite, have not been as well-characterized as they have been for pyrite. Yet these rates and pathways are key to understanding how metal-mining wastes and acid rock/acid mine drainage (ARD/AMD) evolve, and are critical components in assessing and predicting water quality in the vicinity of a reactive mine waste (Salmon and Malmstrom, 2004). The dissolution of sphalerite under acid conditions was studied using samples from three major ore-deposit types: Volcanogenic massive sulfide (VMS; the term "volcanic-associated" is often used), Mississippi Valley type (MVT), and polymetallic vein deposits (PMV). These deposits may vary widely in major and trace element compositions, but are generally characterized by having elevated Fe, Al, Cu, Pb, and Zn, abundances (Plumlee et al., 1995); in addition, MVT deposits are typically highly enriched in Pb and Zn (Leach et al., 1995).

Sphalerite compositions can vary among different sulfide-mineral deposit types. Iron may be substituted within the ZnS structure (St. Marie and Kesler, 2000), or present in associated trace minerals such as pyrrhotite ($Fe_{1-x}S$) or pyrite. Element substitutions present in sphalerite in one type of deposit may be low or absent in sphalerite from other deposits. In the samples used in this study, Cd is high in sphalerite from the MVT deposits (≤ 5200 ppm) compared with sphalerite from VMS and PMV deposits (≤ 1000 ppm), whereas Pb is low in the MVT sphalerite (≤ 13 ppm) but is high in VMS and PMV sphalerite (up to 8150 ppm). Other trace elements such as Cu and Mn also show a range of concentration in the different sphalerite samples.

VMS deposits are generally high in Fe (>5 wt.%) as a result of their formation in association with Fe-rich mafic rocks such as basalts (Taylor et al., 1995). Iron is a dominant element in these systems and generally is present as either pyrite or pyrrhotite. Depending on whether the adjacent rocks were mafic or silicic, VMS deposits may be enriched in Cu and Zn, or in Zn and Pb, respectively (Taylor et al., 1995).

MVT mineralization may produce sphalerite both high and low in Fe. In the Metaline district of northeastern Washington, USA, two distinct episodes of MVT-like mineralization have been noted, one the result of an Fe-poor fluid and a second the result of an Fe-rich fluid (St. Marie and Kesler, 2000). The two mineralization events with highly contrasting Fe concentrations resulted in ore minerals, including sphalerite, that have correspondingly higher or lower Fe contents. High-Fe deposits commonly have pyrite and pyrrhotite as major Fe-bearing minerals, and Fe-rich sphalerite. Low-Fe deposits may have pyrite and pyrrhotite present, but usually in minor to trace amounts, and sphalerite may be a dominant ore mineral. The dissolution of the sphalerite-rich fraction of ore deposits, in the presence or absence of minor or trace accessory minerals or varying concentrations of substituted elements, has not been thoroughly documented. For example, the environmental effects resulting from mining or disturbance of MVT ore deposits are largely unknown (Leach et al., 1995). It generally has been assumed that because these deposits are typically hosted by carbonate rocks, the aqueous mobility of potentially toxic elements such as Cd, Pb, and Zn will be controlled and limited by carbonate chemistry. However, some situations may provide opportunities for these metals to become more mobile,

such as movement into local aquifers via tailings ponds or dispersion by smelting activities (Leach et al., 1995; Krause and Dwire, 1999).

Polymetallic vein deposits are replacement or vein types associated with sedimentary (usually carbonate) or igneous host rocks. The Leadville district of central Colorado is an example of this type of mineralization where both host-rock types are present. Major- and trace-metal contents vary even within the same ore deposit (Plumlee et al., 1995) but typically are moderate to high in Fe because of the presence of abundant pyrite in the assemblage. Similar to MVT deposits, the carbonate host rocks tend to mitigate or neutralize acid production and drainage, but in deposits hosted by igneous rocks, highly acidic drainage may develop (Scharer et al., 2000).

Objectives

Because the composition of individual sphalerite and trace sulfide minerals associated with the sphalerite can vary widely in different deposit types, it is likely that the sphalerite-rich fraction will undergo acid dissolution (weathering) at differing rates and produce effluents containing variable concentrations of dissolved metals. We have examined sphalerite dissolution from the three different ore deposit types under a variety of controlled geochemical conditions. The objectives of this work are to determine the rates of release of metals via acid dissolution of sphalerite and to characterize the aqueous metal concentrations produced.

Methods

Sample Characterization and Preparation

The sphalerite samples (Table 1) are from the Winston Lake deposit, Ontario, Canada (VMS-WL-01); Gordonsville mine, central Tennessee mining district, USA (MVT-CT-01); Blue Goose mine, Tri-State district, Missouri, USA (MVT-BG-01); and Leadville district, Colorado, USA The VMS and MVT samples were taken from archived ore material collected at the mines. The PMV sample was taken from a mine-waste pile at an elevation of 3400 m and approximately 5 km east of Leadville, Colorado; it is from an igneous-hosted, rather than carbonate-hosted, deposit. Each original sample was about 10 kg, and after removal of major gangue material, 30 g of bulk sphalerite was used to prepare the samples for reaction. It is noted here that high-purity sphalerite was not required, as the dissolution study was concerned not only with the sphalerite, but also any microscale accessory minerals or elements associated with the sphalerite. The interaction of sphalerite with these "impurities" was important to characterize the resulting aqueous compositions from each ore deposit type.

Samples were first disaggregated using a ceramic mortar and pestle, and then the sphalerite fraction was hand-separated from the gangue. The bulk sphalerite separate was ground in a mortar and pestle, sieved to recover grain sizes from <600 to >250 μm, then split into two aliquots. One aliquot was set aside as the coarse-grained sample for reaction, and the other was "micronized" in a ball mill to produce average particle sizes of approximately 10 μm ("fine-grained" sphalerite). The two aliquots were taken as representative of the extremes of particle sizes that might be present in metal-mine wastes.

The surface area of each aliquot was measured by the three-point N_2 BET method (Gregg and Sing, 1995). The <600 to >250 μm samples have a small surface area, <0.7 m^2/g; the micronized aliquot surface areas are higher and range from 2.08 to 3.08 m^2/g. Samples MVT-

CT-01, MVT-BG-01, and PMV-LV-01 were prepared only as micronized aliquots; therefore, the only coarse-grained sample that was reacted was VMS-WL-01.

Table 1. Selected major- and trace-element compositions of Winston Lake (VMS-WL-01), Central Tennessee (MVT-CT-01), Blue Goose (MVT-BG-01), and Leadville (PMV-LV-01) sphalerite samples.

Sample	Ag	As	Cd	Co	Cu	Fe*	Mn	Pb	Sb	Sn	Zn*	S*
VMS-WL-01	10	6.6	1000	170	380	6.7	760	1400	1.7	7.2	61.8	33.8
MVT-CT-01	0.24	6.1	2200	2.6	470	0.3	<2	9.7	0.5	<0.5	68.4	33.5
MVT-BG-01	3.3	6.8	5200	4.9	190	0.2	<2	13	4.8	<0.5	68.9	33.2
PMV-LV-01	27	24	<2	<2	190	4.2	88	8150	NA	<5	66.3	31.5

*Fe, Zn, and S in wt %; all others in ppm. NA = not analyzed

A portion of each fine-grained sample was used for chemical analysis; selected major- and trace-element abundances determined by ICP–MS (inductively coupled plasma – mass spectrometry) are summarized in Table 1. The samples represent a spectrum of compositions with respect to Fe and trace metal contents (Table 1).

Laser ablation analysis of the high-Fe (6.7 wt.%) VMS-WL-01 sample showed chemical differences at the microscale because of alternating bands of trace pyrite and major Fe-rich sphalerite in the sample. Semi-quantitative X-ray diffraction (XRD) of the sample detected sphalerite, quartz, and accessory pyrrhotite. Pyrite was not detected by XRD, indicating that its content is <5 volume percent of the sample. Petrographic analysis confirmed the presence of trace amounts of pyrrhotite and pyrite intergrown with major sphalerite. The overall lack of pyrite suggests that most of the Fe is substituted in sphalerite or is present in pyrrhotite rather than in pyrite. The wurtzite polymorph was not detected by XRD in any sample.

In MVT-CT-01 and MVT-BG-01, total Fe content does not exceed 0.3 wt.%, and neither pyrite nor pyrrhotite was detected by XRD, suggesting that Fe is substituted in sphalerite. Mineralogy of the original sample PMV-LV-01 indicated pyrite was the dominant sulfide mineral with approximately equal abundances (5-10 wt.%) of sphalerite and galena as minor ore minerals. Chemical analysis of the bulk (separated and prepared) sphalerite sample used in the dissolution experiments showed an intermediate Fe content (4.2 wt.%).

<u>Dissolution Conditions</u>

Both pH-stat and free-drift (non-statted) experiments were run from pH 2.0 to 7.0 at 25° C. Reaction times ranged from a few days to several months, depending on the particle size and pH. The focus in this report is on the pH-statted experiments at pH 4.0 or less, which produced high aqueous metal concentrations over shorter time periods (100 to 600 h). The reaction was terminated when soluble Fe:Zn remained almost constant for two or three consecutive samples. The maximum variation in the free-drift runs below pH 4 was ≤1 pH unit, and ±0.1 units for the pH-stat runs.

A 2-piece cylindrical glass reaction vessel with a top fitted with ports for the pH electrode, titrant addition (0.1 N HCl or H_2SO_4), sampling, and temperature monitoring was used in all experiments. The vessel was cleaned three times with aqua regia (3 conc. HNO_3:1 conc. HCl) then rinsed 3 times with deionized water prior to usage in an experiment. The sphalerite samples

were rinsed in reagent-grade acetone to remove oxidation products such as elemental sulfur (S°) that might have been present, then dried before being used in an experiment.

An initial ratio of 400 g (mL) solution to 1 g solid was used in all experiments but one. (A smaller ratio of 200:1 was used in one experiment to examine the effect of having a greater amount of solid initially present under otherwise similar conditions). The solid was added to the pH-adjusted solution (time=0), and rapid magnetic stirring was started immediately. As the vessel was open to the air via the ports, reducing conditions were not established during a run. Aqueous samples filtered through a 0.45 μm filter were taken over the reaction period and analyzed for 44 major and trace elements by ICP-MS (Lamothe et al., 2002). Total elemental S° was determined by cyanolysis in acetone (Bartlett and Skoog, 1954) to form the $(Fe^{+3}SCN)^{+2}$ complex. The concentration of the complex was determined spectrophotometrically (465 nm) using a standard line derived from analysis of solutions containing 1, 5, 10, 20, and 25 ppm complexed reagent-grade S°. Total solution sulfide ($H_2S_{(aq)}$ + HS^-) was quantified using a methylene blue spectrophotometric method (Hach Chemical Co., 1996).

Results and Discussion

Aqueous Metal Concentrations from Dissolution of Fine-Grained VMS Sphalerite

Leaching of the VMS-WL-01 fine-grained sphalerite released several major and trace elements into the aqueous phase. Figure 1 shows that the leach at pH 2-3 (non-statted) produced dissolved Zn and Fe concentrations approaching 180,000 and 50,000 μg/L, respectively, within one week of reaction. The trace metals Cu and Pb measured 3 μg/L and 250 μg/L, respectively, by the end of the week-long run. The ratio of solution to solid in this experiment (Fig. 1) was 200, that is, the mass of sphalerite was twice that in other experiments. The resulting Fe and Zn concentrations are at least 2 times higher than in experiments with lower added sphalerite. In experiments at pH >4 using the fine-grained sample, longer reaction times (up to 2 months) were needed before metal concentrations reached levels similar to those at pH 2-3 after one week.
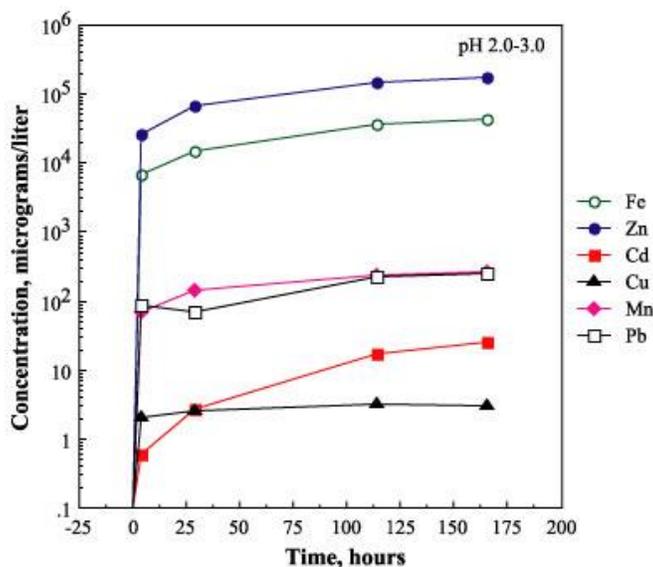

Figure 1. Aqueous metal concentrations resulting from the dissolution of fine-grained, high-Fe VMS-WL-01 sphalerite in a non-pH-stat (free-drift) reaction. The pH varied from 2.0 to 3.0 during the run.

Figures 2a and 2b illustrate metal concentrations obtained from experiments with VMS-WL-01 at fixed pH values of 2.0 and 4.0, respectively. Zinc, Fe, and Mn concentrations generally increase throughout the course of each experiment. At 100 hours, about 3 times more Zn is present at pH 2.0 than at pH 4.0; most other metals are produced in higher concentration at lower pH. Lead is initially several hundred μg/L at pH 2.0, but then declines after the beginning of the run and remains nearly constant. Geochemical modeling indicates that $PbSO_4$ (anglesite) becomes saturated and should precipitate at pH 2.0. At pH 4.0, lead in solution continues to increase over time, indicating Pb and SO_4^{-2} concentrations are insufficient to produce saturation with anglesite.

Initially, more Cu is solubilized at pH 4.0, but then the concentration declines for the remainder of the run. The decline may be the result of increased adsorption of Cu to mineral surfaces at the higher pH. In general, results at pH 2.0 suggest dissolution of sphalerite permits relatively continuous release of metals, but as pH increases to 4.0, pH-dependent differences in mineral solubilities begin to limit or affect some aqueous metal concentrations.

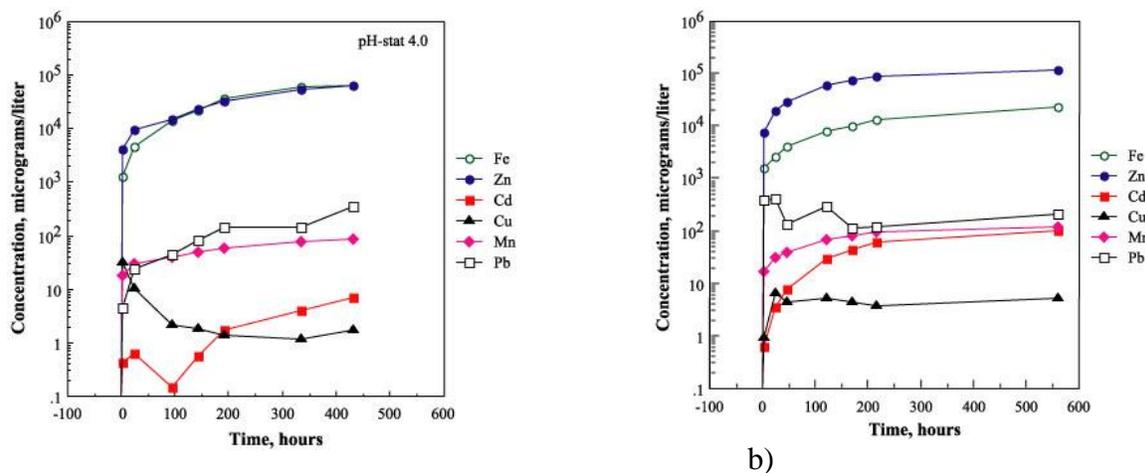a)   b)

Figure 2. Aqueous metal concentrations resulting from the dissolution of fine-grained, high-Fe VMS-WL-01 sphalerite at a) pH 2.0 and b) pH 4.0.

Aqueous Metal Concentrations from Dissolution of Coarse-Grained VMS Sphalerite

Under otherwise similar conditions at pH 4.0, coarse-grained VMS-WL-01 produces much lower metal concentrations compared to the fine-grained sample, even after several months of reaction (Fig. 3). By the end of the experiment, dissolved Fe and Zn remain about 400 and 6 times lower, respectively, compared to the final leachate from the fine-grained sample (Fig. 2b).

Aqueous Metal Concentrations from Dissolution of Fine-Grained MVT Sphalerite

MVT-CT-01 produces zinc concentrations at pH 2.0 (Fig. 4a) similar to VMS-WL-01 (Fig. 2a). However, maximum iron concentrations are 50 times less compared to VMS-WL-01. At pH 4.0 (Fig. 4b), zinc from MVT-CT-01 is about 10 times lower than VMS-WL-01 (Fig. 2b). Zinc concentrations are 10 times lower from the dissolution of MVT-CT-01 at pH 4.0 compared to pH 2.0; data from sample MVT-BG-01 were similar to those of MVT-CT-01.
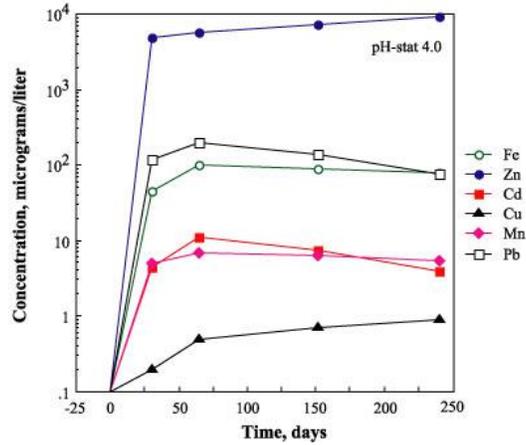
Figure 3.   Aqueous metal concentrations resulting from the dissolution of coarse-grained sphalerite VMS-WL-01 at pH 4.0.
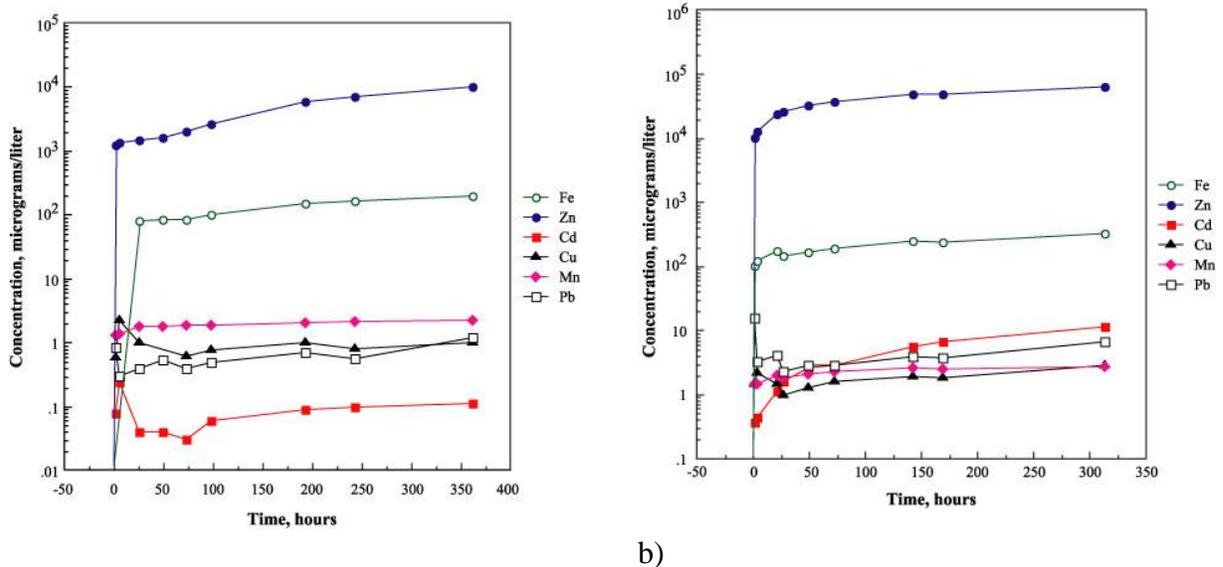

a)

b)

Figure 4.   Aqueous metal concentrations resulting from the dissolution of fine-grained, low-iron sphalerite MVT-CT-01 at a) pH 2.0 and b) pH 4.0.

Aqueous Metal Concentrations from Dissolution of Fine-Grained PMV Sphalerite

As only one PMV sample has been leached to date, dissolution data for this ore deposit type is limited. The aqueous metal concentrations generated during the leach at pH 2.0 are shown in Fig. 5. This sample had the fastest rate of iron solubilization (approximately 10^{-8} mol/L/s Fe_{tot}) of all experiments. The rate of Zn solubilization, however, was comparable to the rates obtained from the other sphalerite samples (~10^{-10} mol/L/s Zn^{+2}).
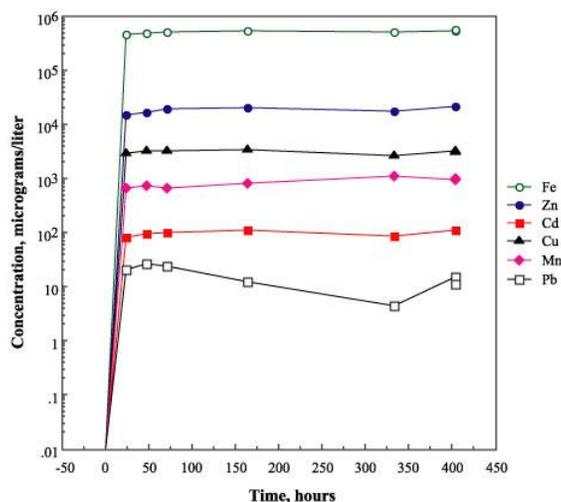
Figure 5. Aqueous metal concentrations resulting from the dissolution of fine-grained sphalerite PMV-LV-01 at pH 2.0.

Formation of Solid Reaction Products

Elemental S was a product of the leaching reaction of all samples at low pH (2.0-4.0). At higher pH (4.0) and longer reaction time, elemental S became a more abundant product. The highest total sulfide concentrations in solution were present in the first 8 hours of reaction, and ranged from 1.35 to 1.96 mg/L at pH 2.0 for MVT-CT-01 and VMS-WL-01, respectively. In most HCl-based experiments, SO_4^{-2} was not detectable until near the end of the run, indicating a slow rate of conversion (oxidation) of sulfide to SO_4^{-2} Isotopic analysis of product sulfate ($\delta^{34}S_{SO4}$ CDT) from all runs showed only a narrow range of minor fractionation (-1.1 to 0.7 per mil) from the original sphalerite.

After adjusting the pH of a filtered aliquot of the VMS-WL-01 leachate from 4.0 to near 7.0 with 1.0 N KOH, and allowing the solution to evaporate, amorphous ferric oxyhydroxide was produced. Ferric oxyhydroxide did not form from (unadjusted) lower pH solutions (≤4.0), rather, metal-rich chloride or sulfate salts were precipitated as the solution evaporated.

Color and Texture of Reacted VMS Sphalerite

After eight months of continuous reaction, the texture and color of the original coarse-grained crystalline VMS-WL-01 sphalerite (Fig. 6a) had been dramatically altered, and abundant coatings of yellow-gray, fine-grained, X-ray amorphous, Fe- and sulfate- rich phases were present on the sphalerite and quartz grains (Figs. 6b).

Estimates of Rates of Dissolution (Aqueous Zinc and Iron Production)

Because the sphalerite samples are impure, a rate specific for dissolution of a pure ZnS solid cannot be derived. However, the rate of production of aqueous Zn can be used as an estimate of sphalerite decomposition. For VMS-WL-01 at pH 2.0, the Zn solubilization rate is about 3 times faster than at pH 4.0 (Table 2). For MVT-CT-01 at pH 2.0, the Zn solubilization rate is about 12 times faster than at pH 4.0. At pH 2.0, the rate of Zn solubilization for VMS-WL-01 is about 1.5 times faster than MVT-CT-01. The Zn solubilization rates (Table 2) are in general agreement

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with the results of Rimstidt et al. (1994), who obtained a rate of 3.9 x 10^{-10} mol m^{-2} sec^{-1} for dissolution of solid sphalerite via oxidation by ferric iron at pH 2.0 and 40° C.
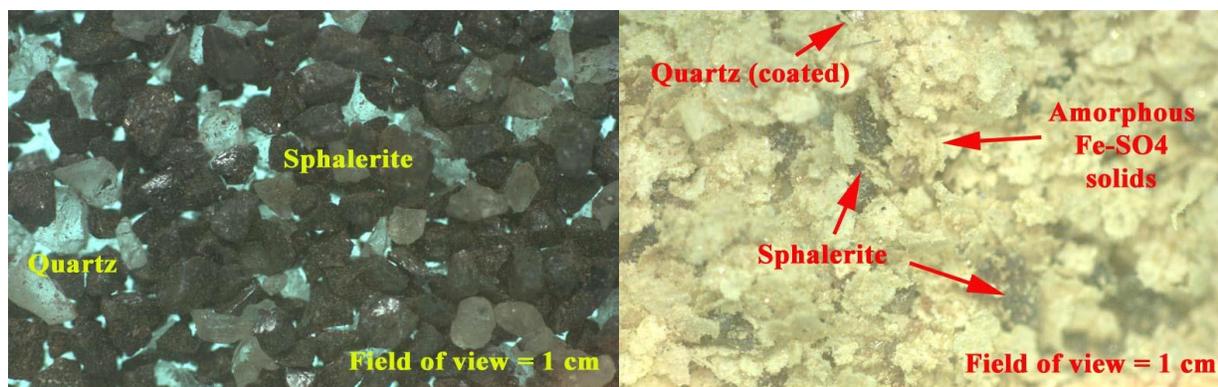
a)   b)

Figure 6.   a)Unreacted coarse-grained VMS-WL-01 sphalerite (dark grains; grain diameters approximately 1 mm), and b)VMS-WL-01 after 8 months of reaction.   Yellow material consists primarily of iron- and sulfate-rich amorphous phases.

At pH 2.0, the iron solubilization rate for VMS-WL-01 is approximately 2 orders of magnitude greater than for MVT-CT-01.   The faster dissolution rate for VMS-WL-01 at pH 2.0 likely results from the oxidative action of ferric iron on the sphalerite (Perez and Dutrizac, 1991).

Figure 7 is a plot of the log of the rate of total iron (Fe$_{tot}$) solubilization versus the weight percent of Fe in the solid sphalerite.   In general, a trend of faster rates of Fe release is seen as the amount of Fe in the sphalerite increases.   The MVT samples comprise the group at the lower left while the VMS samples form the group at the upper right.   The PMV sphalerite falls off of this trend by a large amount, however.
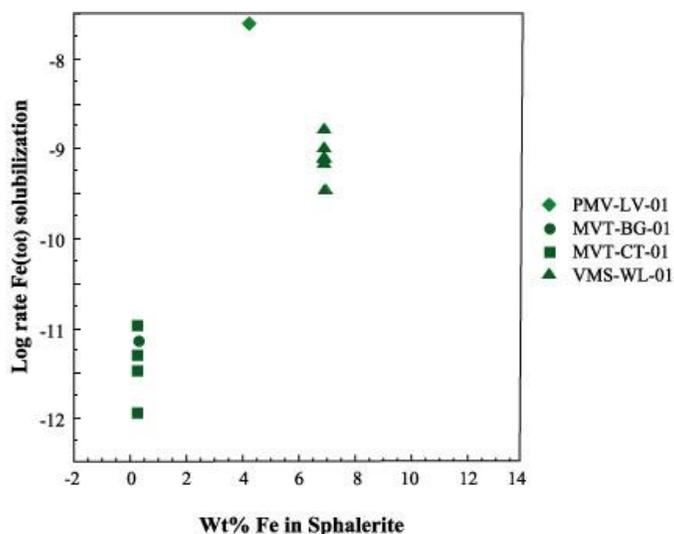

Figure 7.   Plot of the (log) rate of iron solubilization versus weight percent total iron in sphalerite.

The fast rate of Fe solubilization observed for PMV-LV-01 may be partly the result of the original high pyrite content. This particular sample (from a waste pile) may have undergone weathering such that small but undetectable amounts of ferric oxyhydroxide were present. We speculate that the faster rate of Fe solubilization may be an artifact of this weathering that has made (ferric) iron readily-available. However, the Zn solubilization rate is in accord with other rates obtained in the study (Table 2). Additional work is needed before rate information can be reliably determined for the PMV sample.

Table 2. Summary of rates of Zn and Fe solubilization versus sphalerite and acid type, pH, and surface area.

(Zn,Fe)S	Acid	pH	Zn Sol rate	log rate	Fetot Sol rate	log rate	SA,m²/g
VMS-WL-01	HCl	2.0	2.16×10^{-9}	-8.67	3.28×10^{-10}	-9.48	2.08
VMS-WL-01	HCl	2-3	5.70×10^{-9}	-8.24	1.57×10^{-9}	-8.80	2.08
VMS-WL-01	HCl	4.0	6.75×10^{-10}	-9.17	7.49×10^{-10}	-9.12	2.08
MVT-CT-01	HCl	2.0	1.48×10^{-9}	-8.83	7.06×10^{-12}	-11.15	3.08
MVT-CT-01	HCl	3.0	2.31×10^{-10}	-9.63	4.53×10^{-12}	-11.34	3.08
MVT-CT-01	HCl	4.0	1.17×10^{-10}	-9.93	3.94×10^{-12}	-11.40	3.08
VMS-WL-01	HCl	3.0	1.53×10^{-9}	-8.81	1.08×10^{-9}	-8.97	2.08
VMS-WL-01	H_2SO4	2.0	4.20×10^{-9}	-8.38	9.55×10^{-10}	-9.02	2.08
MVT-CT-01	None	6.4-5.1	2.59×10^{-11}	-10.59	1.19×10^{-12}	-11.92	3.08
MVT-BG-01	H_2SO4	3.0	3.91×10^{-10}	-9.41	7.64×10^{-12}	-11.12	2.96
PMV-LV-01	H_2SO4	3.0	8.02×10^{-10}	-9.09	2.48×10^{-8}	-7.60	NA

Sol rate = solubilization rate in mol/L/s of Zn^{2+} or total iron (Fetot); SA = surface area; NA = not analyzed.

Summary and Conclusions

Weathering of Sulfide Mine Wastes

The results show that sphalerite is likely to be a significant source of metals when low-pH weathering of mineralized waste rock occurs. Although the Zn and Fe contents were different in the original VMS-WL-01 and MVT-CT-01 sphalerite samples, at pH 2.0, the rate of Zn solubilization was similar but the rate of Fe solubilization was 2 orders of magnitude faster for the VMS-WL-01 sample. Thus, the rate of Fe release from (high-iron) ZnS in a mine waste will be accelerated with increasingly lower pH values. In turn, the increased size of the Fe pool may lead to faster decomposition of the entire mine waste through the catalytic effect of microbes on the rate of oxidation of Fe^{+2} to Fe^{+3}, wherein Fe^{+3} participates in the oxidation of pyrite (Salmon and Malmstrom, 2004; Weisener et al., 2003; Nordstrom and Southam, 1997). The results indicate that characterization of the composition and mineralogy of a metal-mine waste would be extremely important components of remediation strategies. Remediation of mine-related sites or materials also should take into account the oxidation-reduction and pH conditions, which are key controls on the rate of sphalerite dissolution.

It should be noted the rates observed in this experimental study are likely to be faster than would be observed in a field situation. There are several reasons for this: 1) The sphalerite generally will not be "isolated" from the rest of the waste material, and thus would be subject to additional influences such as increased Fe(III) production from pyrite weathering and(or) Fe-oxidizing microbes. 2) If carbonate is present, it should buffer acid generation and thus resist extreme changes in pH. 3) Water saturation and sample agitation are not likely to be constant in a waste-pile environment. Water flow through a pile (whether from local ground water or

percolating surface water) is likely to be on an intermittent basis. The sphalerite will remain in place, and thus limit the exposure of surface area for reaction with any available water. Formation of metal-sulfate coatings on mineral surfaces can (temporarily) further impede reaction progress (Rimstidt et al., 1994). 4) Variations in dissolved O_2 would be expected in a field situation, particularly if the sphalerite is located in the saturated zone. Lack of O_2 would slow the rates of abiotic oxidation of aqueous Fe(II) and oxidation of solid sphalerite; in the experiments, oxygen was not a limiting factor.

The formation of solid ferric oxyhydroxide upon adjustment of leachate pH to near neutrality has important consequences for the continued dissolution of sphalerite in mine-waste piles. The iron solids could temporarily store metals and acidity, and then supply these to the system upon resolubilization (Desborough et al., 1999). The released ferric iron could then act as an oxidant to promote further dissolution of sphalerite or pyrite.

<u>Potential Effects on Water Quality</u>

Several potentially-toxic elements are released from the different sphalerite samples. Table 3 summarizes the maximum concentration of a particular element that was released during dissolution at the pH values shown. The MVT samples produced the fewest number of elements whose concentrations exceed USEPA primary (enforceable) or secondary (recommended) drinking water standards (USEPA, 2003), whereas the high-iron VMS samples produced the greatest number of elements that exceed the standards.

In sample MVT-BG-01, only sulfate and zinc were present at maximum concentrations that exceeded the standard. Sample MVT-CT-01 exceeded the Cd, Pb, Al, Fe, and Zn limits at pH 2.0, but exceeded only the Al and Zn standards at pH 4.0. Solutions from sample VMS-WL-01 exceeded Cd, Pb, Fe, Mn, and Zn limits at low pH (2.0 - 4.0), but results from a "control" experiment at higher pH (7.2) showed that VMS-WL-01 exceeded only the Pb and Mn standards. The table shows that the two MVT samples, which have high solid-phase Cd (Table 1), actually produce little aqueous Cd except at the lowest pH (2.0).

The results indicate that leaching at low pH produces the highest concentrations of elements of environmental concern. Whether these metals remain soluble and are able to move into nearby surface or ground water will depend on many factors, such as pH, metal solubility, water flow conditions, and redox potential (Krause and Dwire, 1999). Nonetheless, the results show that at low pH, many metals that are potentially toxic are mobilized from solid sphalerite. Although the rate of release depends on grain size, even large sphalerite grains generate detectable concentrations of dissolved metals at low pH with increasing reaction time.

Dissolution of metal-bearing sphalerite and release of metals to solution can be rapid at low pH in both acid chloride and acid sulfate systems. The aqueous metal concentrations produced will depend primarily on the original geochemical composition of the sphalerite, particularly iron content, and the rate at which the mineral dissolves. In general, the highest concentrations of trace metals were produced at the lowest pH values, and increasing pH resulted in lower solution metal concentrations. Low-Fe samples (MVT) dissolved at slower rates than high-Fe samples (VMS, PMV), indicating the importance of Fe^{+3} in the decomposition process. The rates of sphalerite dissolution, the chemical composition of the sphalerite, and the solution pH are three important factors that influence the evolution of sphalerite-bearing metal-mine waste solids and associated waters. Forthcoming work will examine the pathways of the released metals, for example, when ferric oxyhydroxide precipitates form or when the metal interacts with other

species such as carbonate ion. The individual effects of dissolved O_2, Fe^{+3} iron, and pH on the dissolution process will also be studied, as will the determination of specific sources and contributions of solubilized iron from different mineral phases.

Table 3. Comparison of maximum concentrations of major and trace metals obtained from dissolution of (Zn,Fe)S to USEPA primary and secondary drinking water standards. Values in bold italics are those that exceed the EPA standard.

Element/ Compound	MCL (µg/L)	VMS-WL-01			MVT-CT-01			MVT-BG-01	VMS-WL-01 control
	Primary Standard	pH 2.0	pH 3.0	pH 4.0	pH 2.0	pH 3.0	pH 4.0	pH 3.0	pH 7.2
Sb	6	<0.3	1	2.1	<0.3	<0.3	<0.3	<0.3	0.6
As	10	2	2	2	<1	<1	<1	<1	<1
Ba	2000	17.4	103	*2700*	403	84	73	12	36
Be	4	0.07	0.09	0.1	<0.05	<0.05	<0.05	<0.05	<0.05
Cd	5	*102*	*22*	*7.1*	*11.3*	0.37	0.24	0.22	0.23
Cr	100	16.6	<1	1.3	1.4	<1	1.2	<1	3
Cu	1000	6.5	6.2	31	2.9	1.2	6.5	1.4	0.6
F	4000	ND	ND	ND	ND	ND	ND	ND	ND
Pb	15	*390*	*305*	*350*	*16*	5.7	1.2	2.3	*215*
Hg	2	ND	ND	ND	ND	ND	ND	ND	ND
Se	50	3.9	3.3	2.6	1.8	<1	<1	<1	1.5
Tl	2	0.2	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.2
	Secondary Standard								
Al	200	129	138	89	*446*	*440*	*492*	87	<2
Cl	250000	NA	NA	NA	NA	NA	NA	NA	NA
Fe	300	*23400*	*51100*	*64700*	*338*	176	201	236	<50
Mn	50	*123*	*165*	*88*	2.8	2.1	2.3	4.2	*54*
pH	6.5-8.5	NA	NA	NA	NA	NA	NA	NA	NA
Ag	100	<3	<3	3.7	3	<3	3	3	<3
SO4	250000	13000	20000	37000	<1600	11800	13300	*257000*	5000
TDS	500000	NA	ND	ND	ND	ND	ND	ND	ND
Zn	5000	*118000*	*103000*	*64200*	*66000*	*10400*	*10000*	*13100*	3920

All values (except pH) in micrograms/liter. MCL = maximum contaminant level. NA = not analyzed or not applicable; ND = not determined.

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