BASELINE LABORATORY STUDIES OF SPHALERITE (ZnS) DISSOLUTION: EFFECTS ON AQUEOUS METAL CONCENTRATIONS AND SOLUBILIZATION RATES[1]

Mark R. Stanton[2]

Abstract. The geochemical behavior of sphalerite (ZnS) under conditions where acid drainage is generated is well-documented. However, the rates of solubilization of major and trace metals, and their subsequent geochemical pathways after release from sphalerite, have been less well-studied. 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. Although pyrite (FeS_2) weathering usually dominates aqueous chemistry under acidic conditions, in metal-mining waste where pyrite is low in abundance or metals content, dissolution of ore minerals like ZnS might contribute significant amounts of dissolved metals to effluent waters.

Experimental leaching of sphalerite in acid chloride solution releases several major and trace elements into the aqueous phase. The concentrations produced depend on the original geochemical composition of the ZnS and gangue material, and the rate at which the mineral dissolves (a function of grain size/surface area). A fine-grained, high-iron sphalerite (12.1 wt. %) leached at pH 2-3 (25° C) produces dissolved iron and zinc concentrations approaching 50 and 180 mg/L, respectively, within one week of reaction. Copper and lead measure 3 g/L and 250 g/L, respectively, by the end of the week-long run. At higher pH (>4) using the fine-grained sample, longer reaction times (≤2 months) are needed before metal concentrations reach levels similar to those at low pH (<4).

At pH 4.0, coarse-grained, high-iron sphalerite produces much lower metal concentrations compared to the fine-grained sample, even after several months of reaction. Dissolved iron and zinc are about 400 and 6 times lower, respectively, compared to leachate from the fine-grained sample. Nonetheless, after 8 months of continuous reaction, the texture and color of the original coarse-grained crystalline sphalerite strongly resembled a ZnS-rich mine waste that had been weathering in the subsurface (3 meters) of a waste pile for more than 70 years.

Low-iron sphalerite (0.2 wt. %) produces Zn concentrations similar to the high-iron sample at pH 2.0 but lower Zn concentrations at pH 4.0. At both pH values, aqueous iron is about 100 times lower than the high-iron sample. Other metals (Cu, Pb, etc.) show a range of concentrations that depend on their original abundance in the solid and their solubilities in the solutions.

These data indicate sphalerite can act as a major source of metals when low-pH weathering of mineralized waste rock occurs. The results reinforce previously-established concepts that remediation of mine-related sites should take into account the potential metal contribution of non-pyritic minerals such as sphalerite, including the mineralogy, composition, and grain size of the mine waste, as well as oxidation-reduction and pH conditions, and hydrology and geochemistry of the site.

Additional Key Words: acid drainage, aqueous chemistry, sulfide minerals, mine wastes

---

[1] Paper was presented at the 2005 National Meeting of the American Society of Mining and Reclamation, June 19-23, 2005. Published by ASMR, 3134 Montavesta Rd., Lexington, KY 40502

[2] Mark R. Stanton, Research Geologist, U.S. Geological Survey, Denver, CO 80225

Proceedings America Society of Mining and Reclamation, 2005 pp 1155-1165
DOI: 10.21000/JASMR05011155
https://doi.org/10.21000/JASMR05011155

Introduction and Background

Mining wastes pose several challenges to storage or remediation because it can be difficult and expensive to isolate the wastes from on-site factors that may chemically affect the wastes. These factors include surface and groundwater flow (for example, percolation of meteoric water to the subsurface), and establishment of variable redox and pH conditions (Krause and Dwire, 1999). Mining wastes contain relict ore-grade solids whose mineralogy varies according to the type of deposit from which they were mined. Hardrock metal-mining wastes may consist of widely-contrasting mineralogies and compositions, such that pyrite might be the dominant metal-bearing sulfide mineral, a metal-deficient phase, or present in high or low abundance.

Monosulfide ore minerals such as sphalerite (ZnS) can be relatively common in mine-related remediation sites. Many aspects of the the geochemical behavior of sphalerite under conditions where acid drainage may be generated are well-known (Salmon and Malmstrom, 2004; Nordstrom and Southam, 1997), but less is known about the pathways of major and trace metals associated with ZnS. For example, how fast are metals solubilized from ZnS, and what are the potential pathways for these metals after being released? Because the aggregate neutralization and acid generation potentials (acid-base accounting) of an entire metal-mining waste is usually the focus of remediation plans (Scharer et al., 2000), metals or acidity that might be derived from weathering of individual ore minerals such as sphalerite, galena, and chalcopyrite are sometimes overlooked when designing remediation plans.

The contributions of non-pyritic ore minerals to dissolved metal loads can be underestimated because when highly-metallized pyrite weathers, it is the dominant source of acidity (H^+) and a major source of dissolved metals. On the other hand, in waste rock where pyrite is weakly-metallized, dissolution of ore minerals like sphalerite might contribute significant quantities of dissolved metals to effluent waters issuing from reactive metal-mine wastes.

The data presented here are part of a larger project to systematically investigate the dissolution of monosulfide minerals (ZnS, CuS, Cu_2S, and PbS) of variable compositions over a broad range of geochemical conditions. The goal of the larger project is to obtain fundamental data on the behavior of monosulfides and their associated metals under a variety of weathering conditions, some of which are encountered in mine wastes or remediation undertakings. A wide range of parameters and potential reactions that ZnS may undergo will be considered, including the presence/absence of microbes, different acid systems, changes in isotopic composition, role of intermediate sulfur species, and the presence/absence of aqueous species such as chloride, carbonate, and iron (II and III). This future work will focus on abiotic and microbially-mediated ZnS dissolution in the more-prevalent acid sulfate systems.

This paper reports the preliminary findings on ZnS dissolution and resulting aqueous metal concentrations from an abiotic acid chloride system. The primary purpose of the acid chloride experiments is to provide and assess baseline data from an initially sulfate-free system where early formation of solid sulfates that coat reactive mineral surfaces (Rimstidt et al., 1994) could be minimized. Rates of Zn and metal solubilization from this baseline system will be used to compare rates of ZnS dissolution in more-complex environments where reactions involving other major anions (such as carbonate and sulfate) are occurring.

An additional objective of these lab studies is to examine conditions that affect the evolution of solid metal-mine wastes (and waters); an example is the Mayday mine near Silverton, Colorado. At this site, a 0.5m-thick layer of weathered waste material rich in sphalerite (40-50%) and amorphous ferric-sulfate salts (50%), but low in pyrite (5-10%) is present at a depth of 3.0-3.5m. Although most of the sphalerite has been surficially altered, it has not been completely consumed during the more than 70 years of burial at the site. By following changes in composition and texture of ZnS over time, the experiments will attempt to record stages in the evolution of metal-mine wastes; some preliminary results are presented in the paper.

Experimental Methods

Sample Characterization and Preparation

Two sphalerite samples representing end-member compositions with respect to iron content were used in the dissolution experiments. The samples are from the Winston Lake deposit, Ontario, Canada (sample WL-01) and the Gordonsville mine, central Tennessee mining district, USA (sample CT-01; C. Taylor, USGS, pers. comm., 2001). Selected major and trace element abundances for bulk samples determined by ICP-MS (inductively coupled plasma - mass spectrometry) are summarized in table 1. Laser ablation analysis of the high-iron sphalerite WL-01 (12.1 wt % iron) showed microscale alternating bands of minor pyrite and major iron-rich sphalerite. Semi-quantitative X-ray diffraction (XRD) of a bulk sample detected only sphalerite, quartz, and a trace accessory mineral tentatively identified as pyrrhotite ($Fe_{x-1}S_x$). Because pyrite was not detected by XRD, it indicates FeS_2 was present at abundances of <5 volume percent in the bulk sample. The overall lack of pyrite suggests that most iron is substituted in the sphalerite or present in pyrrhotite, rather than in pyrite. Sample CT-01 is a low-iron sphalerite; neither pyrite nor pyrrhotite were detected by XRD and the total iron content is 0.2 wt. %.

Table 1. Selected major and trace element composition of Winston Lake (WL-01) and central Tennessee (CT-01) sphalerites.

	Ag	As	Cd	Co	Cu	Fe*	Mn	Pb	Sb	Sn	Zn*
WL-01	10	6.6	1000	170	380	12	760	1400	1.7	7.2	63
CT-01	0.24	6.1	2200	2.6	470	0.2	<2	9.7	0.5	<0.5	76

*Iron and zinc in weight percent (wt %); all others in parts per million (ppm).

The bulk WL-01 sample was ground in a ceramic mortar and pestle, sieved to recover grain sizes from <30 to >60 mesh, then split into two aliquots. One aliquot was set aside as the coarse-grained sample for reaction; the other aliquot was "micronized" in a ball mill to produce average particle sizes of approximately 10 μm ("fine-grained" sphalerite). These two grain sizes were used to examine dissolution of endmember particle sizes that might be present in metal-mine wastes. Both aliquots were rinsed in reagent-grade acetone to remove oxidation products (such as S°) that might have been present, then dried prior to use in the experiments. The surface area of each aliquot was measured by the three-point N_2 BET method. The <30 to >60 mesh sample has a small surface area, <0.7 m^2/g; the micronized aliquot surface area is higher at 2.08 m^2/g.

Sample CT-01 was characterized and pretreated for reaction as WL-01 but prepared only as a micronized aliquot (surface area=3.08 m^2/g).

Experimental Conditions

Both pH-stat and free-drift 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 grain size and pH. The results focus on experiments at pH 4.0 or less which produced higher metal concentrations over shorter time periods. 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 having a top fitted with ports for the pH electrode, titrant addition (0.1 N HCl), sampling, and temperature monitoring was used in all experiments. The vessel was cleaned three times with aqua regia (3 conc. HNO3: 1 conc. HCl) then rinsed 3 times with deionized water prior to usage in an experiment.

An initial ratio of 400 g (mL) solution: 1 g solid was used in all experiments but one. The solid was added to the pH-adjusted solution (time=0) and rapid magnetic stirring was begun 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). Solid residues were saved for examination by SEM, microscopic, and microprobe analyses. Total elemental sulfur (S°) is determined by cyanolysis in acetone (Bartlett and Skoog, 1954) to form the $(Fe^{3+}SCN)^{2+}$ complex. The concentration is determined at 465 nm using a spectrophotometer and standards containing 1, 5, 10, 20, and 25 ppm reagent-grade S°. Total solution sulfide ($H_2S_{(aq)} + HS^-$) is quantified using a methylene blue spectrophotometric method (Hach Chemical Co., 1996).

Results

Aqueous Metal Concentrations from Dissolution of Fine-Grained Sphalerite

Experimental leaching of the WL-01 fine-grained sphalerite in acid chloride solution releases several major and trace elements into the aqueous phase. Selected metals and their concentrations in Figure 1 show the leach at pH 2-3 (unstatted) produces dissolved zinc and iron concentrations approaching 180,000 and 50,000 μg/L, respectively, within one week of reaction. Trace metals such as copper and lead measure 3 μg/L and 250 μg/L, respectively, by the end of the week-long run. The solution: solid ratio in this experiment was 200, that is, 2 times the mass of solid than in other experiments. (The resulting iron and zinc concentrations are at least 2 times higher than in experiments with lower added solid). In higher pH experiments (pH >4) using the fine-grained sample, longer reaction times (up to 2 months) are needed before metal concentrations reach levels similar to those at low pH.

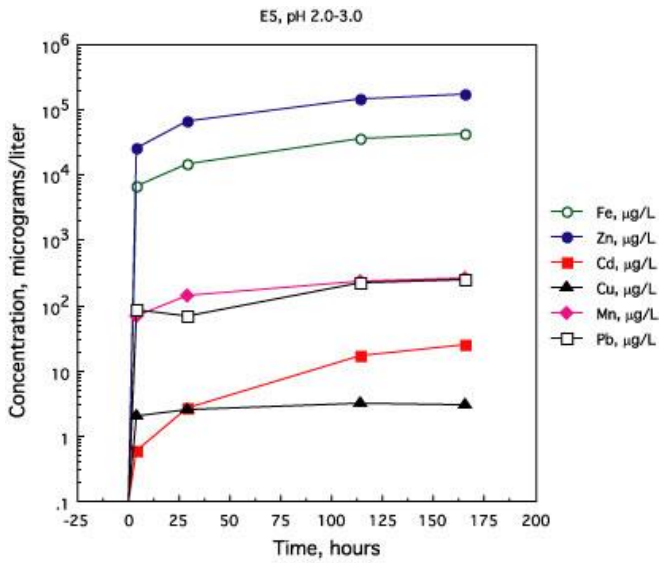
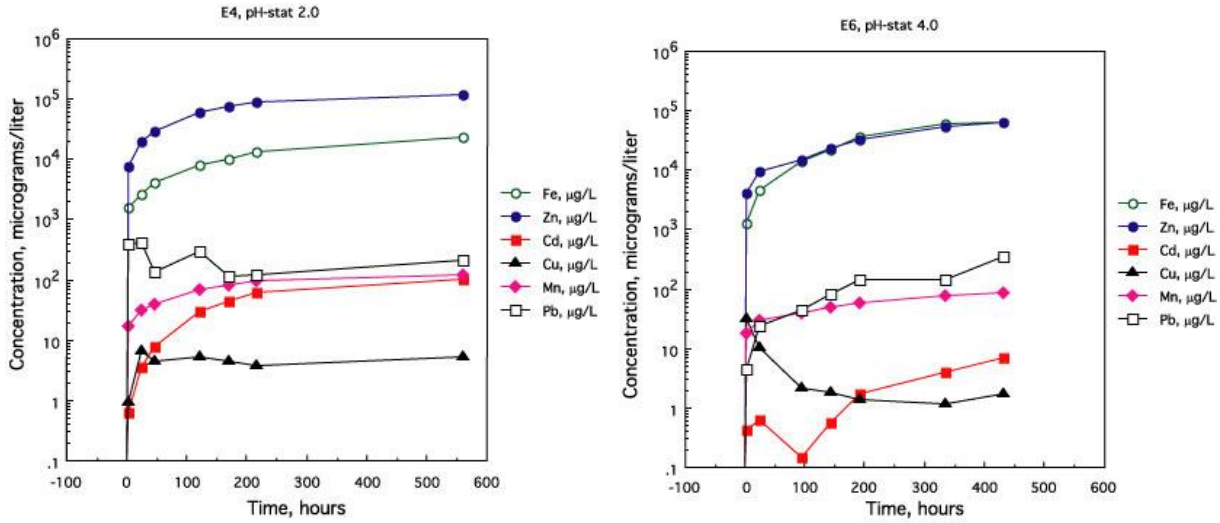


Figure 1. Aqueous metal concentrations resulting from the dissolution of fine-grained sphalerite in a non-pH-stat (free-drift) reaction. The pH varied from 2.0 to 3.0 during the run.

Fig. 2a and 2b illustrate metal concentrations obtained from experiments at pH 2.0 and 4.0, respectively. Zinc, iron, and manganese 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. Modeling indicates that $PbSO_4$ (anglesite) becomes saturated and precipitates at pH 2.0. At pH 4.0, lead continues to increase over time, indicating lead and sulfate concentrations are insufficient to produce saturation with anglesite.

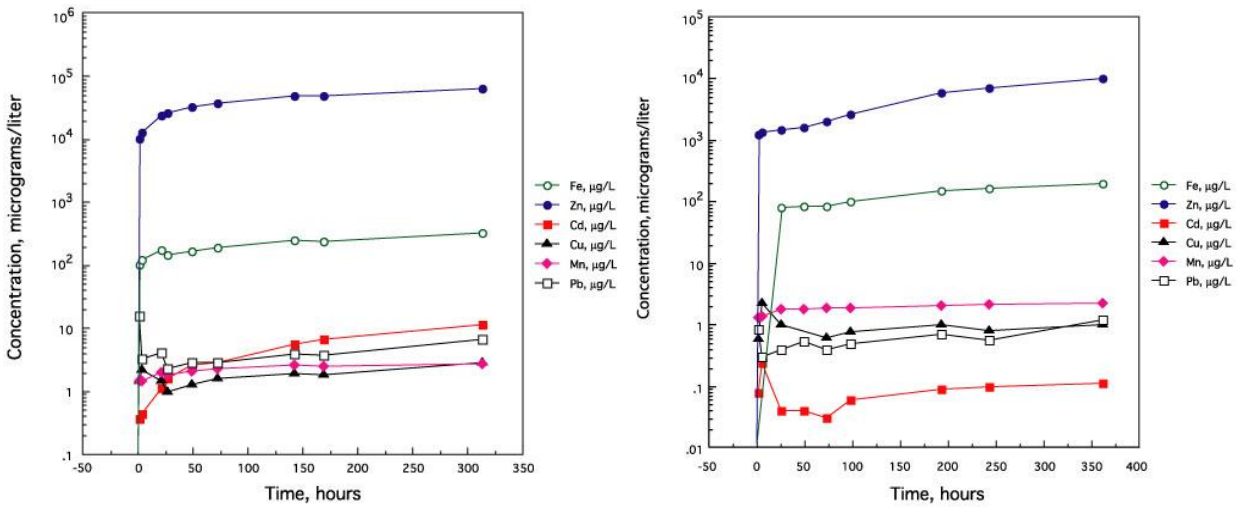


a) b)

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

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

CT-01 produces zinc concentrations at pH 2.0 similar to WL-01 (Fig. 3a and 3b). However, maximum iron concentrations are 50 times less compared to WL-01. At pH 4.0, zinc from CT-01 is about 10 times lower than WL-01; zinc concentrations are 10 times lower from the dissolution of CT-01 at pH 4.0 compared to pH 2.0.



a) b)

Figure 3. Aqueous metal concentrations resulting from the dissolution of fine-grained, low-iron sphalerite CT-01 at a) pH 2.0 and b) pH 4.0.

Aqueous Metal Concentrations from Dissolution of Coarse-Grained Sphalerite

Under otherwise similar conditions (pH 4.0), coarse-grained WL-01 produces much lower metal concentrations compared to the fine-grained sample, even after several months of reaction (Fig. 4). By the end of the experiment, dissolved iron and zinc remain about 400 and 6 times lower, respectively, compared to the final leachate from the fine-grained sample (Fig. 2b).

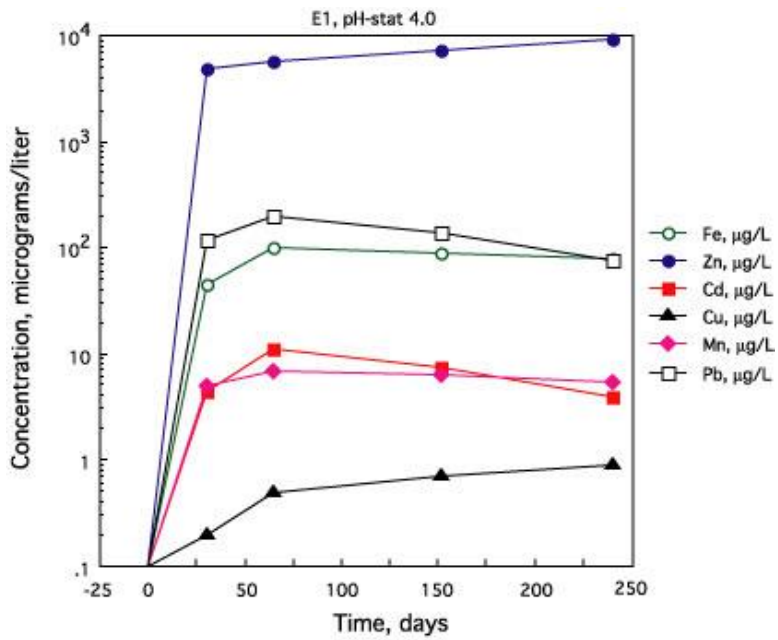


Figure 4. Aqueous metal concentrations resulting from the dissolution of coarse-grained sphalerite WL-01 at pH 4.0.

Formation of Sulfur Species and Solid Reaction Products

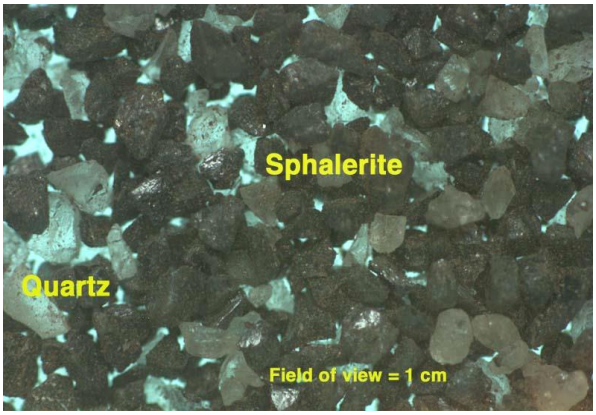
Elemental sulfur was a product of the reaction at low pH (<4.0). With increasing pH and reaction time, elemental sulfur became a more abundant product. The highest total sulfide concentrations were formed in the first 8 hours of reaction, and ranged from 1.35 to 1.96 mg/L at pH 2.0 for CT-01 and WL-01, respectively. In most experiments, sulfate was not detectable until near the end of the run, indicating a slow rate of conversion (oxidation) of sulfide to SO_4. Sulfur 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.

Upon allowing a filtered aliquot of the (WL-01, pH 4.0) solution to evaporate, amorphous ferric oxyhydroxide was produced. This has important consequences for the continued dissolution of ZnS in waste piles as the iron solids could store and later provide metals and acidity upon resolubilization (Desborough et al., 1999). Ferric oxyhydroxide did not form from lower pH solutions, rather, metal-rich evaporite salts were precipitated.

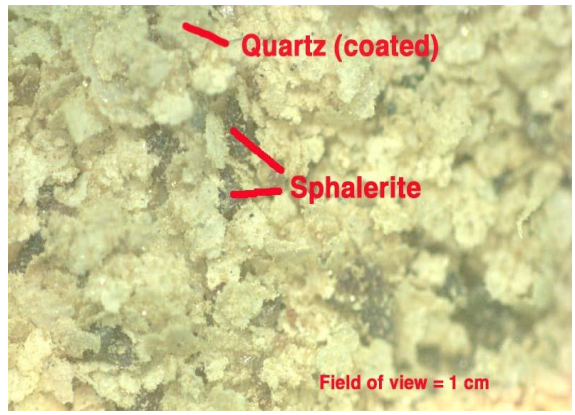
Color and Texture of Reacted Sphalerite

After 8 months of continuous reaction, the texture and color of the original coarse-grained crystalline sphalerite (Fig. 5a) resembled the ZnS-rich mine waste that had been weathering in the Mayday mine waste pile (Fig. 5c). Coatings on the sphalerite and quartz grains (Figs. 5b and 5c) are noncrystalline iron- and sulfate- rich phases.

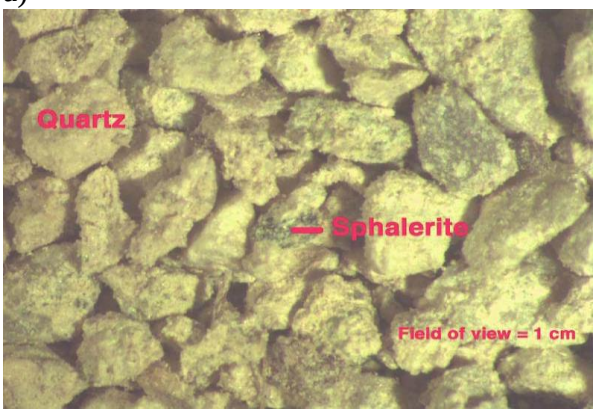
The relict ZnS is present within a matrix of yellow-gray, fine-grained, X-ray amorphous solids and silicate gangue minerals. It is unknown if FeS_2 was initially abundant in the waste rock or has been fully weathered away, or if there was low FeS_2 in the original material.



a)



b)



c)

Figure 5. a) Unreacted WL-01 ZnS (dark grains; grain diameters approximately 1 mm), and b)WL-01 after 8 months of reaction. c) Weathered ZnS mine waste from the Mayday mine near Silverton, CO.

Monitoring wells at the Mayday site were generally dry at the level where the ZnS waste is located except during a 2-week period in the spring. Surface flow is similarly restricted by location of the waste away from the low-discharge stream exiting the mine adit. The most likely source of moisture to the ZnS waste material is percolation of meteoric water or snowmelt to depth during unusually wet years. The ZnS likely undergoes brief periods of water saturation, and this is when the most effective weathering (solubilization) occurs.

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

Because the sphalerites are impure, a rate specific for ZnS dissolution cannot be derived. However, the rate of production of aqueous zinc can be used as an estimate of ZnS decomposition. For WL-01 at pH 2.0, the Zn solubilization rate is 2.16 $x10^{-9}$ m-l Zn^{2+}/sec and at pH 4.0, the rate is 6.75 $x10^{-10}$ m-l Zn^{2+}/sec. The rate at pH 2.0 is about 3 times faster than at pH 4.0. For CT-01 at pH 2.0, the Zn solubilization rate is 1.48 $x10^{-9}$ m-l Zn^{2+}/sec and at pH 4.0, the rate is 1.17 $x10^{-10}$. Thus, the rate at pH 2.0 is about 12 times faster than at pH 4.0. These Zn solubilization rates are in general agreement 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 ZnS via oxidation by ferric iron at pH 2.0 and 40° C.

At pH 2.0, the rate of Zn solubilization for WL-01 is about 1.5 times faster than CT-01. In addition, at pH 2.0, the iron solubilization rate for WL-01 (3.28×10^{-10} m-l Fe/sec) is approximately 2 orders of magnitude greater than for CT-01 (7.06×10^{-12} m-l Fe/sec). The faster dissolution rate for WL-01 at pH 2.0 may partially result from the action of oxidized iron on the ZnS (Salmon and Malmstrom, 2004), but the specific role of iron has not been resolved.

Implications for Weathering and Remediation of Sulfide Mine Wastes

The results show that sphalerite can be a significant source of metals when low-pH weathering of mineralized waste rock occurs. Although the zinc and iron contents were different in the two sphalerite samples, the rate of Zn solubilization was similar at pH 2.0, yet the rate of Fe solubilization differed by 2 orders of magnitude. This suggests the composition and mineralogy of a metal-mine waste should be considered an important component in remediation strategies. Grain size is also a critical factor in the rate of ZnS decomposition (Rimstidt et al., 1994); mill wastes are often fine-grained whereas ore wastes are usually coarser-grained. Thus, plans for cleanup or remediation of metal-mine wastes should take into account the type of waste, with respect to grain size, to be treated or stored. Remediation of mine-related sites or materials also should take into account the oxidation-reduction and pH conditions, and geochemistry and hydrology of the site.

Several factors that affect sphalerite dissolution should be addressed when considering waste site location and (or) remediation options:

1) Location of ZnS waste relative to groundwater or surface water flow. Although constant water saturation as in the experiments is not likely at most remediation sites, ZnS dissolution is rapid at low pH, and only a short time would be needed for weathering to take place once the waste is saturated. While many sites are located in dry climates with little groundwater flow and only intermittent surface flow or precipitation, the ZnS waste should be isolated from any water source. Use of a liner or similar barrier to inhibit shallow groundwater from entering the site, and a surface cover to repel precipitation, would be recommended.

2) Composition of ZnS in the mine waste. Compositional information combined with leach studies could be useful in predicting the contribution of metals and acidity by ZnS to the aqueous phase at a particular pH. This information could be used to determine a target pH to be maintained that limits the rate of metal solubilization from ZnS at the remediation site.

3) Grain size of waste ZnS. Larger grain sizes weather more slowly than finer grains. However, grain size of the waste material is generally not under the control of the remediation operator. Again, it would be preferred to isolate the waste, whether coarse or fine grained, from any water source.

4) The absence or presence of oxygen (O_2) at depth in waste sites will be a strong controlling factor in the degree to which oxidative weathering will occur. Measures to limit diffusion of oxygen to the ZnS should be employed.

5) The absence or presence of bacteria that might inhibit or accelerate ZnS decomposition is another factor that may need to be controlled. Although bacterial experiments have not yet

been undertaken, limitation of water and oxygen would prevent most bacteria (such as acidithiobacilli) from participating in oxidative weathering of ZnS.

6) The use of amendments (lime, e.g.) to maintain pH at relatively higher values (>pH 5), where ZnS solubilization was slower, could slow down the rate of ZnS dissolution and metal solubilization, although not necessarily prevent dissolution processes from occurring (Donovan et al., 2000).

Conclusions and Future Work

These preliminary results show that dissolution of metal-bearing ZnS can be rapid at low pH in an acid chloride system. The concentrations produced will depend primarily on the original geochemical composition of the sphalerite and the rate at which the mineral dissolves. Evolution of ZnS-bearing metal-mine waste solids appears to depend on multiple factors, such as rates of dissolution, chemical composition, duration of periods of saturation or dryness, agitation, and variations in pH and redox potential.

As noted, further study of ZnS decomposition will employ an acid sulfate system to mimic geochemical conditions most likely to exist at mine waste sites. Additionally, iron- and sulfur-oxidizing bacteria (Acidithiobacillus) will be used to determine how these organisms might promote or inhibit dissolution of sphalerite. Finally, analysis for low-level concentrations of intermediate sulfur species (for example, thiosulfate) will be integrated into the sampling scheme.

Literature Cited

Bartlett, J.K., and Skoog, D.A. 1954. p. 1008-1011. Colorimetric determination of elemental sulfur in hydrocarbons. Analytical Chemistry, v. 26. http://dx.doi.org/10.1021/ac60090a014.

Desborough, G.A., Leinz, R.W., Smith, K.S., Hageman, P.L., Fey, D.L., and Nash, T.J. 1999. Acid generation and metal mobility of some metal-mining related wastes in Colorado. U.S. Geological Survey Open-File Report 99-322, 18 p.

Donovan, J.J., Frazier, J., Ziemkiewicz, P.F., Daly, M., Black, C., and Werner, E. 2000. Experimental injection of alkaline lime slurry for in situ remediation of an acidic surface-mine aquifer. p. 1001-1015. *In*: Proceedings from the 5th International Conference on Acid Rock Drainage (ICARD), Denver, CO, May, 2000. Society for Mining, Metallurgy, and Exploration (SME).

Hach Chemical Company. 1996. Procedures Manual for DR/2010 Spectrophotometer, Loveland, Colorado, 824 p.

Krause, A.J., and Dwire, D.L. 1999. Site selection approach for mine tailings. p. 99-106. *In*: Proceedings of 6th International Conference on Tailings and Mine Waste, Ft. Collins, CO. Balkema Publishers, Rotterdam, Netherlands.

Lamothe, P.L., Meier, A.M., and Wilson, S.A. 2002. The determination of forty-four elements in aqueous samples by inductively coupled plasma-mass spectrometry. p. H1-H11. *In*: Taggart, J.E., Jr., ed., Analytical methods for chemical analysis of geologic and other materials. U.S. Geological Survey Open-File Report 02-0223.

Nordstrom, D.K., and Southam, G.K. 1997. Geomicrobiology of sulfide mineral oxidation. p. 361-390 (Chapter 11). *In*: Banfield, J.F., and Nealson, K.H., eds. Geomicrobiology: Interactions between microbes and minerals. Rev. Mineralogy, Min. Soc. America, Washington, D.C.

Rimstidt, J. D., Chermak, J.A., and Gagen, P.M. 1994. Reactions of minerals with Fe(III) in acidic solutions. p. 1-13. *In*: Alpers, C.N., and Blowes, D.W., eds. Environmental Geochemistry of Sulfide Oxidation. ACS Symposium Series, Am. Chem. Soc., Washington, D.C.

Salmon, S.U., and Malmstrom, M.E. 2004. Geochemical processes in mill tailings deposits: modeling of groundwater composition. p. 1-17. Applied Geochemistry, v. 19. http://dx.doi.org/10.1016/S0883-2927(03)00129-X

Scharer, J.M., Bolduc, L., Pettit, C.M., and Halbert, B.E. 2000. Limitations of acid-base accounting for predicting acid rock drainage. p. 591-601 *In*: Proceedings from the 5th International Conference on Acid Rock Drainage (ICARD), Denver, CO, May, 2000. Society for Mining, Metallurgy, and Exploration (SME).