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Insights of sphalerite weathering under simulated acidic, circumneutral and alkaline conditions to account for mineral activity and potential Zn release

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Abstract

The present study combines surface analyses of pristine and leached low Fe-bearing and Pb-bearing sphalerite (PbS-ZnS) samples including XPS, GDOES, Raman spectroscopy, SEM and AFM, along with chemical evolution of leachates after 24 h of contact with 0.1 M NaOH, 0.1 M NaNO₃, 0.1 M H₂SO₄ or 0.1 M HClO₄ solution. A comprehensive electrochemical analysis using Cyclic voltammetry, Chronopotentiometry, Chronoamperometry, Linear sweep voltammetry and Tafel plots of PbS-ZnS and marmatite-like sphalerite (FeZnS) are conducted to compare its oxidation activities. Mineral characterizations reveal sluggish weathering linked to inhomogeneous and minor secondary polysulfides (S_n^{2-}) surface compounds distribution, thus defining bare modifications of surface-activity relationships. The occurrence of secondary Zn-bearing compounds was not identified on altered samples, which suggests that this heavy metal diffuses into the bulk-solution. Electrochemical assessments confirm sluggish sphalerite oxidation mainly composed by two subsequent stages, where the highest mineral activity was obtained in NaOH conditions. It was found that the sphalerite oxidation is more active in the presence of Pb, while the activity of sphalerite gradually decreases when it is a mineral rich in Fe probably associated with progressive accumulation of S_n^{2-}/S^0 compounds. We suggest general oxidation mechanisms for sphalerite, and their environmental implications are discussed.

Key words: Sphalerite oxidation; Structure-activity relationships; Oxidation mechanisms; Simulated weathering; Non-conventional Tafel analysis; Marmatite-like sphalerite.

1. Introduction

Mining industry is still a global source of air, water and soil pollution since it typically generates important amounts of waste (i.e., tailing impoundments, dumps and hard rock deposits), without an apparent control of spillage (Zhao et al. 2020; Myagkaya et al. 2021). Mining waste usually contains significant amounts of metal sulfide (MS) grains, which are present as free and/or occluded minerals in bulk, whence they are easily dispersed by eolic and/or pluvial processes highlighting environmental and health risks due to release of potentially toxic elements (i.e., As, Pb, Cr, Co, Ni, Zn, Cu, Hg) (Punia 2021; Myagkaya et al. 2021). Among the main MS causing these problems are pyrite (FeS_2), pirrothite (Fe_{1-x}S), sphalerite (ZnS), galena (PbS), chalcopyrite (CuFeS_2), and arsenopyrite (FeAsS) (Scoble et al. 2003; Lottermoser 2010). To this concern, arsenopyrite and galena have been mostly evaluated due to potential toxicity, and evident role in As and/or Pb mobility during environmental mineral weathering (Lu et al. 2011; Gamiño-Gutiérrez et al. 2013). In contrast, among the least studied MS is sphalerite, exhibiting diversity of mineral ZnS phases with varied Fe amounts (i.e., marmatite-like) and impurities (i.e., galena). These changes in structure significantly modify mineral weathering and the resulting Zn release with bare understanding of the reaction pathways, translocation of mobile Zn from soil to biomass and environmental distribution behavior (Robson et al. 2014; Shabbir et al. 2021). Examples of industrial, urban, forest and agricultural sites (and regions) with impacts generated by the occurrence of sphalerite spillage include Mexico, The USA, North China, West and Central Europe, among others, presenting different type of soil (i.e., saline, alkaline or acidic) and climatic conditions (Hita and Torrent 2005; Acero et al. 2007; Álvarez-Ayuso et al. 2013; Gamiño-Gutiérrez et al. 2013; Voldrichova et al. 2014; Li et al. 2014; Lu et al. 2019). Sphalerite oxidation is then global pollution problem for sites affected by mining waste alteration or spillage to soil, which threatens the sustainability of the local environment and human health.

Low-Fe bearing (~4.5 %) sphalerite samples present high-electrical resistivity ($\sim 10^{10} \Omega$) (Ahlberg and Ásbjörnsson 1994; Crundwell 2021), which hamper the analysis of their redox behavior using electrochemical methods, whereby its study is typically limited to chemical and mineralogical analysis. An indirect way of studying this type of sphalerite has been through the study of samples that presents reactive impurities such as galena or high Fe content in structure (Giudici et al. 2002; Da Silva et al. 2003; Urbano et al. 2007). The study of environmental sphalerite oxidation has been focused mainly towards understanding the weathering process when it is contained in acidity-generating Zn-bearing mining wastes (Langman and Moberly 2018; Bao et al. 2021), when it is altered in an environment where it is easily disturbed by the (bio)oxidation of mining wastes (Chen et al., 2009; Langman and Moberly, 2018), or when fine-particulate Zn-bearing minerals are generated increasing incidental ingestion and/or inhalation exposure (Thomas et al., 2018). Additionally, neutralization and precipitation processes, dissolution of gangue materials, uncontrolled dissolution reactions of concomitant MS, the progressive modification of chemical environment and/or the occurrence of significant amounts of PTEs in systems, among others, have hampered a comprehensive assessment of the interfacial mechanisms of sphalerite. For this reason, the interfacial insights of sphalerite oxidation are not yet well known, as well as the stages that make them up, or considering the effect of different types of sphalerite (i.e., marmatite-like, low-Fe and Pb-bearing specimens) on the stability of the oxidation products and the relationships that these processes have with its oxidation capacity, thus improving our knowledge of processes controlling the release of Zn in crops, mining, forest regions, urban and farming areas due to oxidation of primary sources of Zn (Razo et al. 2004; Hofmann and Schuwirth 2008; Gamiño-Gutiérrez et al. 2013; Lu et al. 2019).

The aim of the present study is to describe interfacial insights and activity regarding sphalerite oxidation to elucidate the main weathering mechanisms under typical environmental conditions (i.e., H_2SO_4 , NaNO_3 , NaOH , HClO_4), the role of secondary products (i.e., ZnO_2 , S_n^{2-} , S^0), and surface-activity relationships, among others. In order to achieve this goal, a combination of spectroscopic (Raman Spectroscopy, X-ray Diffraction Patterns (XRD), Glow Discharge Optical Emission Spectroscopy (GDOES), X-ray Photoelectron Spectroscopy(XPS)) and microscopic (Scanning Electron Microscopy (SEM), 2D-3D, Atomic Force Microscopy(AFM)) techniques along with chemical analysis of leachates (sulfates, ORP, pH and Zn, Cd, Fe determinations) are carried out using PbS-ZnS samples. A comprehensive electrochemical assessment (Cyclic voltammetry, Chronoamperometry, Chronopotentiometry, Linear sweep voltammetry, Tafel plots) is also conducted to simulate charge transfer and oxidation processes of PbS-ZnS and marmatite-like sphalerite during weathering. We expect these findings contribute to better understand the complex sphalerite oxidation and reactions, to improve the accuracy of predictions about the environmental fate of Zn due to primary sources oxidation, and the design of more efficient restoration methods (and mining practices) in benefit of urban, forest regions and agricultural polluted areas with Zn occurrence, distribution and release in the environment.

2. Materials and methods

2.1. Mineral samples

Sphalerite massive samples were obtained from different sites to cover most important sphalerite specimens. A low Fe-bearing and Pb-bearing sphalerite sample referred as ZnS-PbS samples was purchased from Excalibur minerals Corp. (Charlottesville, VA, USA) (Electronic Supplementary Material, ESM, Fig. S1a). Additionally, a marmatite-like sphalerite referred as FeZnS sample was obtained from the mining district of Charcas (San Luis Potosí, Mexico; ESM, Fig. S1b).

After careful selection, sphalerite crystals were reduced to 3-5 mm size. Grains were then rinsed with an acidic solution (HCl, 3 % v/v), washed with deionized water, and dried with direct N₂ current. The samples were also stored in a N₂ atmosphere until they were grinded using an agate mortar and sieved to fraction size <106 µm under inert conditions for mineralogical and electrochemical studies. X-ray diffraction patterns (Rigaku DMAX 2200, 2θ=0.02, from 10° to 90°, using Cu-Kα radiation) and elemental chemical analysis using atomic emission spectroscopy (Agilent MP-AES-4100 atomic emission spectrometer) were measured to verify the mineralogical identity and composition of the samples. Selected PbS-ZnS crystals were used for the construction of rectangular mineral pieces (dimensions 0.4 cm width, 0.6 cm length, 0.4 cm depth) to analyze with AFM and GDOES techniques.

2.2. Electrochemical study

PbS-ZnS and FeZnS samples were used during electrochemical assessment using carbon paste electrodes (CPE). These CPE were constructed and utilized as indicated elsewhere (Svancara et al. 2001). Mineral grains of PbS-ZnS and FeZnS samples were characterized using a SP-150 Biologic potentiostat/galvanostat system coupled to a personal computer. A three-electrode cell system was used: a carbon paste electrode which contains PbS-ZnS and/or FeZnS particles (50/50 wt. %) as the working electrode, a graphite rod (AlfaAesar, 99.9995 % purity) as the counter electrode, and a saturated calomel electrode (SCE) as the reference (0.244 V vs. SHE). The amount of sphalerite selected is based on achieve an adequate electrical percolation process of the sphalerite-bearing carbon paste system (Ahlberg and Ásbjörnsson 1994; Giudici et al. 2002; Da Silva et al. 2003). Different solutions were tested during electrochemical experiments to simulate typical environment weathering conditions, which were prepared using analytical grade

reagents (JT Baker) and mili-Q deionized-water ($18.2 \text{ M}\cdot\text{cm}^{-1}$). These solutions are 0.1 M H_2SO_4 (pH= 1.4), 0.1 M NaOH (pH= 13.3), 0.1 M NaNO_3 (pH= 6.6) and 0.1 M HClO_4 (pH= 1.6).

Cyclic voltammetry (CV) was then initiated in the positive and negative direction at $5 \text{ mV}\cdot\text{s}^{-1}$. Additionally, a study of the variation of the positive potential limit ($E_{\lambda\pm}$) was carried out to evaluate the stages of the corresponding oxidation process. Chronoamperometry (CA) and/or Chronopotentiometry (CP) were carried out using most significant anodic potentials or currents in agreement with the CV; in order to apply potential (E_a) and/or current (I_a) pulses during 600 s. Tafel plots (TP) were obtained using linear sweep voltammetry scans (LSV) using RDE Pine system at $1 \text{ mV}\cdot\text{s}^{-1}$ and stirring conditions of 300 rpm. TP were carried out using a stainless steel electrode jacketed with Teflon to generate a hole, where the carbon paste containing PbS-ZnS and/or FeZnS was placed (ESM, Fig. S2). The open circuit potential ($\text{OCP}_{i=0}$) was monitored before CV, CA, CP, TP and LSV studies which was situated within $\pm 20 \text{ mV}$ in all conditions tested (i.e., after $\sim 400 \text{ s}$ for $\text{OCP}_{i=0}$ stabilization under 0.1 M HClO_4). The effect of the altered mineral surfaces (i.e., secondary products) on the PbS-ZnS and FeZnS activities was also evaluated. These experiments consisted of applying $E_a = 1.2 \text{ V/SCE}$ during 1 and/or 2 h to the pristine samples to generate secondary compounds layers, which was followed by LSV on the positive direction at $20 \text{ mV}\cdot\text{s}^{-1}$ using all tested solutions. The comparison between LSV curves from pristine and oxidized samples, allowed inferring about evolution of mineral activity (i.e., oxidation capacity).

2.3. Sphalerite weathering process

Leaching devices were used to promote a simplified PbS-ZnS oxidation process under simulated weathering conditions (Schippers et al. 2019). PbS-ZnS grains were selected in the present study due to mineral availability: 10 g of PbS-ZnS grains (i.e., <106 μm) were placed in Erlenmeyer flasks containing in each case 250 mL of the same 0.1 M H_2SO_4 , 0.1 M NaOH, 0.1 M NaNO_3 or 0.1 M HClO_4 solution during 24 h at 30 rpm (ambient conditions). Experiments were carried out at duplicate. 5 mL of leachates were obtained from each leaching device every 3 h to determine pH, oxidation-reduction potential (ORP), sulfates (i.e., SO_4^{2-}), and total Zn, Fe or Cd concentrations. A sample of leached mineral was taken after 24 h, dried with direct current of N_2 and kept under vacuum for mineralogical characterizations. Additionally, a leaching experiment of sphalerite in 0.1 M H_2SO_4 conditions was carried out after 240 h to obtain a more altered sample aimed at one of the studied systems to further analyze with XPS for comparison purposes.

2.4. Chemical analyses of leachates

The total Zn, Fe and Cd were analyzed using atomic absorption spectroscopy with graphite furnace (AAS-GF, Perkin Elmer 3100 atomic absorption spectrometer) with a detection/quantification limit of 0.1/0.15, 0.1/0.15 and 0.05/0.1 $\text{mg}\cdot\text{L}^{-1}$, respectively. As a quality control, SRM 1643D (NIST, USA) trace element in water standard reference material was used. The percentage recovery values were better than 95% in all cases. Calibration of instruments, blank correction, matrix effects, sample manipulation, and operating conditions met national and international criteria (Eaton et al. 1995; DOF 2007). Sulfate determinations were carried out using turbidimetric method with BaCl_2 and an UV-1900 UV-Vis Agilent spectrophotometer, according to SW-846-9038 test method (USEPA 1986). The pH and ORP were measured using a Hanna HI-2211 pH-meter.

2.5. Surface analyses

Pristine and leached PbS-ZnS samples were characterized using microscopic (SEM, AFM) and spectroscopic techniques (XPS, GDOES, XRD and Raman). Scanning electron microscopy was conducted using a JEOL JSM-6610LV with an energy dispersive detector Oxford X-MAX for chemical analysis (SEM-EDS). XRD was carried out using a Rigaku DMAX 2200, ($2\theta=0.02$, from 10° to 90°) using Cu-K α radiation. Raman spectra were recorded with a Horiba XploRATM PLUS spectrometer coupled with a SWIFTTM v2 confocal imaging module which used a solid-state laser beam ($\lambda=532$ nm). A Si wafer disc (i.e., 521 cm^{-1}) was used for calibration purposes. At least 10 Raman spectra were collected for each sample. The X-ray photoelectron spectroscopy (XPS) analysis was performed using a KRATOS Axis Ultra (Kratos Analytical, UK) spectrometer equipped with a monochromatized Al K α X-rays source ($h\nu=1486.6$ eV) running at a power of 150 W. The pristine samples were milled and prepared under an argon atmosphere, whereas the leached samples were prepared under ambient exposure. The basic pressure in the analytical chamber was about 10^{-9} mbar. Spectra were collected at a normal take-off angle (90°) and the analysis area was $700\times300\text{ }\mu\text{m}^2$. XPS survey spectra were recorded with 1.0 eV step and 160 eV analyzer pass energy, while narrow scans were recorded with 0.05 eV step and 20 eV pass energy. XPS spectra were then analyzed by the Vision software from Kratos (Vision 2.2.0) after subtraction of the background (Shirley baseline). Typical Gaussian-Lorentzian (70/30) functions were used for peak decomposition. Charge correction was carried out using the C 1s core line, setting the adventitious carbon signal (H/C signal) to 284.6 eV. AFM study was carried out using a Nanosurf easy scan AFM 2 system using contact mode. AFM images (topographic and deflection modes) of at least 10 regions per surface were obtained. The silicon cantilever showed a free resonance frequency between 13 and 15 kHz and a constant of 0.2 N m^{-1} during these experiments. Average roughness (R_a , nm) and root mean square roughness (R_q , nm) of

each altered surface were also evaluated to obtain topographic information associated with secondary compounds (Table 1). GDOES analyses were performed using a glow discharge optical emission spectrometer Horiba Scientific GD profiler 2 using a current of 50 mA and 1000 W (140 °C) under vacuum conditions ($\sim 10^{-5}$ Torr). The spectrometer had a focal length of 1000 nm and configured with 40 simultaneous detectors for the different atomic emission lines. The analytical area was 4 mm in diameter. 700 Volts and 20 mA were chosen for the excitation and sputtering processes, respectively. Note that the use of this technique to investigate sphalerite samples (i.e., intensity vs. erosion time profiles) is unprecedented to our current state of knowledge. Therefore, it could provide a new perspective to account for the role of sphalerite oxidation indicating specific modifications of the surface-bulk mineral structure (i.e., structure-activity relationships).

2.6 Pourbaix-type diagrams

This diagram was calculated using the chemical equilibrium software package Medusa®, which is based on free energy minimization algorithms reported by Eriksson (1979). The reactions and equilibrium constants required by the software to calculate these diagrams are available in the HYDRA database within the Medusa® software package (Puigdomenech 2015). Note that the experimental data (i.e., equilibrium constants) used to calculate this diagram have not been validated (i.e., speciation, solubility), since this is a very demanding work which is beyond the scope of the present study. Therefore, this thermodynamic information is herein used as a rapid and predictive tool to evaluate the stability of released and/or oxidized species when the pH is varied as a function of potential (Fig. S14).

3. Results

3.1. Mineralogical characterization of pristine samples

Chemical analysis of the pristine PbS-ZnS and FeZnS samples were carried out (Figs. S1a, S1b), revealing 97 % (± 0.2) wt. % sphalerite, 1.8 (± 0.3) wt. % galena and 1.2 (± 0.3) wt. % quartz (SiO_2) for the PbS-ZnS sample. Additionally, this PbS-ZnS sample contained ~4.5 wt. % Fe in crystals, in agreement with SEM-EDS (data not shown). The presence of galena mainly as free grain particles was confirmed as main impurity in this sample (Figs. S1c, S1d). The presence of Cd, Ni, Pb and Mn traces was determined by atomic absorption spectroscopy. Mineral identity of the PbS-ZnS sample corresponded to the XRD pattern JCPDS card no. 77-2110. On the other hand, chemical analysis of the pristine FeZnS sample showed 99.6 (± 0.1) wt. % sphalerite, and 0.4 (± 0.2) wt. % chalcopyrite (CuFeS_2). This sample also contain ~20 wt. % Fe in crystals, in agreement with SEM-EDS (data not shown). The pure FeZnS sample corresponded to the XRD pattern JCPDS card no. 89-4939. The presence of Cd, Ni, Mn and Cu traces was also determined by atomic absorption spectroscopy.

3.2. Chemical evolution of leachates

Fig. 1 shows the pH (Fig. 1a), ORP (Fig. 1b), sulfates (Fig. 1c), total Zn, Fe and Cd concentrations (Figs. 1d, 1e and 1f, respectively) during evolution of leachates. Chemical evolution of pH and ORP suggest minor variations for sphalerite weathering in NaOH, HClO_4 and H_2SO_4 solutions (Figs. 1a and 1b, respectively), which was attributed to bare sphalerite weathering capacity. In contrast, evolution of pH was enhanced for the NaNO_3 system after 15 h whence pH changes are more evident (Fig. 1a, curve blue). Circumneutral conditions of the NaNO_3 system are significantly more prone to modification of pH whereby changes of this parameter can occur due to equilibrium changes (Heidel et al. 2013). Zn dissolution was

enhanced in HClO_4 , H_2SO_4 and NaOH solutions, while this process was lower in the NaNO_3 system (Fig. 1d). A similar dissolution behavior was identified for Fe and Cd in all tested solutions (Figs. 1e and 1f). In general, these results reveal the first insights of sphalerite weathering indicating a sluggish sphalerite oxidation in all tested conditions, which are consistent with other observations describing that dissolution rate of sphalerite (i.e., low-Fe bearing sample) depends mainly on pH, temperature and size of particle, among others, thus generating low concentrations of Zn and sulfates in these systems (Weisener et al. 2003; Malmström and Collin 2004; Acero et al. 2007).

3.3. Mineralogical analysis of samples

Fig. 2 shows 2D and 3D AFM images obtained from sphalerite weathering system after 24 h in 0.1 M NaOH (Figs. 2b and 2b', respectively), 0.1 M NaNO_3 (Figs. 2c and 2c', respectively), 0.1 M HClO_4 (Figs. 2d and 2d', respectively) and 0.1 M H_2SO_4 (Figs. 2e and 2e', respectively) solutions. The 2D and 3D images for the pristine sample were also included for comparison purposes (Fig. 2a and 2a', respectively). Table 1 shows a comparison of roughness (R_a , nm) and Root mean square (R_q , nm) parameters for a complete description of the surface processes. Figs. 1a and 1a' and Table 1 exhibited in general smooth-flat surface corresponding to typical non-altered mineral surfaces. In contrast, Figs. 2b' to 2e' and Table 1 showed clear evidence for sphalerite weathering under all tested conditions. A varied grade of surface alteration consisting of surface pitting, dissolution patterns and formation of sub-micro sized secondary structures was observed (Figs. 2b-b' to 2e-e', Table 1). The formation and evolution of sub-micro sized surface secondary structures has been typically attributed to sphalerite oxidation under different weathering conditions (Giudicci et al. 2002; Tauson et al. 2010), but the report of the formation of dissolution patterns on the mineral surface was unprecedented with AFM. Note that highest R_a

(nm) and R_q (nm) parameters was determined for samples in 0.1 M H_2SO_4 solution revealing that sphalerite oxidation occurring in these conditions are more prone to generate and accumulate secondary compounds on altered surfaces (Fig. 2e and 2e', Table 1). On the other hand, the occurrence of mineral dissolution patterns indicated a different reactive behavior for the samples obtained in 0.1 M NaOH (Fig. 2b'), 0.1 M $NaNO_3$ (Fig. 2c') or 0.1 M $HClO_4$ (Fig. 2d') solution (Table 1). These behaviors confirm a sluggish sphalerite weathering process in agreement with Fig. 1; however, there surface processes develop with minor accumulation of sub-micro sized secondary products (Fig. 2e', Table 1) and the establishment of dissolution patterns on altered sphalerite samples (Figs. 2b' to 2c', Table 1).

Fig. 3 shows 2D SEM images obtained from pristine (Fig. 3a) and leached PbS-ZnS samples in 0.1 M NaOH (Fig. 3c), 0.1 M $NaNO_3$ (Fig. 3d), 0.1 M $HClO_4$ (Fig. 3e) and 0.1 M H_2SO_4 (Fig. 3f) conditions. Additionally, a 3D SEM image is included from leached samples obtained in NaOH solution (Fig. 3b). Identification of secondary phases was carried out based on EDS analysis ($n=10$ points). Fig. S3 includes the rest of 3D SEM images obtained from leached samples treated with $NaNO_3$, $HClO_4$ or H_2SO_4 solution. 3D images show in general a similar surface behavior as illustrated in Fig. 3b, confirming a sluggish weathering processes of sphalerite samples whence it was not identified homogeneous or visible alteration of mineral surfaces to form clusters with secondary compounds in all tested solutions. However, SEM-EDS 2D images of leached samples indicate that the weathering trend of the sphalerite occurs mainly with the modification of the surface-bulk structure (i.e., surface-structure relationships) forming mineral rimmed particles with different degree of alteration with the formation of $Zn_{1-x}S$ -like structures (Figs. 3c to 3f). The best developed mineral rimmed particles were observed for the samples treated with 0.1 M NaOH and 0.1 M H_2SO_4 solution. The findings presented in Figs. 1 to 3 clearly indicate that

sphalerite oxidation involves sluggish surface weathering with the formation of minor and not-homogenously sub-micro sized secondary compounds distributed allowing scant surface-reactivity relationship in all tested systems (i.e., rimmed grain particles, surfaces with sub-micro sized secondary phases or well defined dissolution patterns).

Fig. 4a shows the Raman spectrum of the pristine sphalerite sample with typical peaks reported at 180, 220, 298, 330 and 349 cm^{-1} (Kharbish 2007; Osadchii and Gorbaty 2010; Buzatu et al. 2013). A summary of the typical transitions described for Raman transitions of S and Zn was given in Table S1, and they can be used for secondary compounds identification in the present study. Raman peak obtained at 521 cm^{-1} for Si-wafer disc was included to illustrate optimal conditions during collection of Raman peaks (Fig. 4b). Raman spectra obtained for leached samples obtained in 0.1 M NaOH, 0.1 M NaNO₃, 0.1 M HClO₄ or 0.1 M H₂SO₄ solution are illustrated in Figs. 4c, 4d, 4e and 4f, respectively. These spectra showed additional peaks ranging from 465 to 474 cm^{-1} ; which revealed the clear formation of polysulfides (i.e., S_n^{2-}) (Table S1). Additionally, the absence of Raman peaks around 980 cm^{-1} was identified for leached samples, indicating the minor or null formation of Zn-bearing compounds for all tested conditions (i.e., Zn(OH)₂, ZnSO₄, ZnCO₃, Table S1). The findings presented in Fig. 4 suggested the occurrence of polysulfides (i.e., S_n^{2-}) as main secondary surface products under all tested conditions. Interestingly, the presence of anglesite (PbSO₄)-like phase was identified on galena free-particles obtained from the recovered samples treated in 0.1 M H₂SO₄ condition. This result supports evidence regarding the formation of secondary compounds on the main sulfide impurity of sphalerite samples (i.e., galena, Fig. S4, Table S1).

330 The chemical bonding and composition of sulfur and zinc species on sphalerite samples were
331 further examined using XPS. Fig. 5 shows the high-resolution spectra ($\text{Zn}2p$ and $\text{S}2p$) for pristine
332 and leached samples after 24 h in 0.1 M NaOH, 0.1 M NaNO_3 , 0.1 M HClO_4 or 0.1 M H_2SO_4
333 solutions. Additionally, Figs. S5a and S5b exhibits respectively $\text{S}2p$ and $\text{Pb}4d$ spectra obtained
334 from leached sample after 240 h in 0.1 M H_2SO_4 0.1 M solution for comparison purposes. The
335 corresponding fitting parameters are given in Table 2, and a summary of typical binding energies
336 reported in the literature for main sulfur and zinc species are also given in Table S2. The $\text{Zn}2p$
337 spectrum of pristine sample presents one strong peak at 1021.28 eV that typically corresponds to
338 Zn(II)-S^{2-} species in pristine lattices (Fig. 5, Tables 2 and S2). The absence of carbonate (from
339 $\text{C}1s$ not shown) and sulfoxy-compounds (Fig. 5) suggests negligible occurrence of solid Zn-
340 bearing secondary compounds (i.e., ZnO_2 , Zn(OH)_2 , ZnCO_3 , ZnSO_4), in agreement with SEM-
341 EDS (Fig. 3) and Raman (Fig. 4) studies. The $\text{S}2p$ spectrum in the pristine sample showed a
342 major doublet, with a $2p_{3/2}$ component located at 161.4 eV, commonly assigned to S^{2-} species in
343 mineral lattices (Fig. 5, Tables 2 and S2). A second minor doublet with $2p_{3/2}$ component arising
344 at 162.9-163.3 eV was attributed to polysulfide species (i.e., S_n^{2-}), particularly for samples
345 recovered in 0.1 M NaOH and 0.1 M H_2SO_4 systems (Fig. 5, Tables 2 and S2), thus, confirming
346 the results obtained during the Raman study (Fig. 4, Table S1). Note that $\text{S}2p$ spectrum in Fig.
347 S5a clearly indicated a more advanced oxidation state for sulfur species since this spectrum was
348 obtained from the leached sample obtained after 240 h in 0.1 M H_2SO_4 solution, which reveals a
349 surface enrichment with $\text{S}_n^{2-}/\text{S}^0$ compounds for a more advanced alteration stage of sphalerite
350 samples. It is important to highlight the absence of advanced oxidation states of the sulfur species
351 to form sulfoxy-compounds (i.e., SO_4^{2-} , SO_x^{2-} , $\text{S}_2\text{O}_3^{2-}$) retained on leached surfaces for all tested
352 conditions (Fig. 5, Table S2), which was consistent with numerous studies of altered sphalerites
353 samples treated under different conditions (Acero et al. 2007; Harmer et al. 2008; Mikhlin et al.
354 2016). However, the reasons why sulfoxy-compounds are not retained on altered sphalerite

surfaces remains unknown and beyond the scope of the present study. Complementary to Fig. 5, Pb4d spectrum of the Fig. S5b provided supplementary evidence regarding concomitant galena oxidation in the simulated sphalerite weathering system (i.e., 0.1 M H₂SO₄), whereby the occurrence of altered concomitant galena was identified to form anglesite-like secondary compounds. The findings presented in Figs. 4 and 5 confirm the clear occurrence of polysulfides (i.e., S_n²⁻), as main secondary products, during the simulated weathering of sphalerite; whence a significant galena oxidation was also identified to form anglesite-like secondary compounds on altered galena surfaces associated to the PbS-ZnS grain particles system.

Fig. 6 shows the intensity vs erosion time profiles obtained during GDOES analysis of the pristine and leached samples to illustrate specific structure-reactivity relationships (i.e., S, Zn, Fe and Cd chemical behavior). The composition changes with depth (i.e., erosion times). The comparison between intensities of sulfur and Zn profiles for pristine and leached samples indicate a cyclic evolution of sulfur compounds with depletion-enrichment processes (Fig. 6a, i.e., > 6 sec). Likewise, in Fig. 6a it is observed that the mineral surface (i.e., shorter erosion times) contain high concentrations of sulfur when was treated with 0.1 M NaOH or 0.1 M NaNO₃ solutions. These results confirm what was observed by XPS (Fig. 5). It was observed that the lowest intensity of Fe corresponds to the mineral treated with 0.1 M NaOH solution (Fig. 6c). While the highest intensity of Fe corresponds to the mineral treated with 0.1 M H₂SO₄ solution (erosion times greater than 4 sec.). Finally, Cd profiles show highest intensity for samples treated with H₂SO₄ solution while highest depletion is identified for samples treated with NaNO₃ after 7 sec (Fig. 6d). Note that GDOES analysis has been typically used to characterize the variation in the composition of metals in the layer of alteration products, as a function of the thickness in the structure of materials (i.e., wt. % vs μm) (Yang et al., 2018). However, when the occurrence of

alteration products layer does not present a homogeneous distribution pattern on surfaces, the use of intensity profiles vs. erosion time is then used, which allows identifying at which point of the product structure occurs the greatest proportion of metals (Hoffmann et al. 2003). The findings presented in Fig. 6 suggest the occurrence of an inhomogeneous distributed layer of secondary products (i.e., S_n^{2-}) on altered sphalerite surfaces, whence the presence of non-stoichiometric metal-deficient layers ($Zn_{1-x}S_{1-y}$ -like structures) involves dynamic variations of sulfur, Zn, Fe and Cd elements to exhibit specific structure-activity relationships, in agreement with previous results (Figs. 2 to 5, Tables 1, S1, S2).

3.4. Electrochemical assessment

Voltammetry is commonly used to define regions of potential where the current flows as a response of certain electrochemical process (i.e., sphalerite interface/electrolyte solution). In the present study, this technique was utilized to analyze particularly the oxidation processes of pristine FeZnS and PbS-ZnS samples under conditions used in the simulated weathering process (See Section 2.3). This approach was also performed to elucidate the energetics and the reactions of sphalerite surfaces after 24 h of leaching. Altered PbS-ZnS samples were mineralogically characterized in “Section 3.3”; however, the energetics and kinetics processes were not properly assessed with this approach, whence an electrochemical evaluation was carried out (i.e., oxidation potential). Note that a comprehensive electrochemical assessment comparing CPE-PbS-ZnS and CPE-FeZnS samples has not been reported to our current state of knowledge; therefore, the experimental evidences provided here allowed a broaden understanding of the sphalerite weathering and mineral activity under simulated weathering conditions.

Fig. 7 shows cyclic voltammograms conducted on CPE-PbS-ZnS (curves identified as i) and CPE-FeZnS samples (curves identified as ii) in 0.1 M NaOH (Fig. 7a), 0.1 M NaNO₃ (Fig. 7b), 0.1 M HClO₄ (Fig. 7c) or 0.1 M H₂SO₄ (Fig. 7d) solutions. The CPE with 100 % graphite, which is inert to sphalerite and electrolytes composed of conductive carbon phase, was also included for comparison purposes (curves identified as iii). A complementary comparison between positive scans (black curves, curves identified as i) and negative scans (red curves, curves identified as ii) was included for CPE-marmatite-like systems (Figs. S6 and S7). According to Fig. 7 and the corresponding $E_{\lambda\pm}$ study (data not shown), the sphalerite oxidation is complex, progressive and several stages can be elucidated from these voltammograms. Three main oxidation processes (O1 from $OCP_{i=0}$ to ~0.5 V, O2 from ~0.5 to ~0.75 V, and after ~0.75 V) are defined during the positive scans of the PbS-ZnS sample in 0.1 M NaOH (Fig. 7a, curve i) and 0.1 M NaNO₃ (Fig. 7b, curve i) conditions. In contrast, a slow process followed by single-enhanced oxidation was clearly observed in 0.1 M HClO₄ (Fig. 7c, curve i) and 0.1 M H₂SO₄ (Fig. 7d, curve i) conditions (O2 and O3). The first O1 and O2 processes for the PbS-ZnS sample (mainly treated with NaOH and NaNO₃) can be associated with the first (incipient) weathering process of the concomitant galena impurity to form Pb-bearing secondary compounds (Wang et al. 2021). This establishes mineral oxidation due to galvanic interaction processes with sphalerite leading to the potential formation of the anglesite-like compound (i.e., 0.1 M H₂SO₄ and other conditions, Fig. S4) (Urbano et al. 2007; Wang et al. 2021), thus, indicating that the highest degree of sphalerite weathering occurs long-place term under environmental weathering conditions. Regarding the oxidative processes of the FeZnS sample, a very slow oxidation process (O1, from $OCP_{i=0}$ to 0.75 V/SCE) which was followed by progressive and highlighted oxidation process was in general observed under all tested conditions (involving potential region of O2 and O3, after 0.75 V/SCE, Figs. 7, S6 and S7). While the FeZnS oxidation in 0.1 M NaOH solution was more prone

to increase mineral oxidation regarding the other tested conditions (Fig. S6), indicating the release of soluble Zn in alkaline weathering conditions (i.e., Zn(OH)_3^- , Fig. S14).

All the findings presented here were disclosed in Figs. 7, S6 and S7 exhibiting general comparison to illustrate differences regarding the weathering processes of the PbS-ZnS and FeZnS samples, according to the following order of mineral activity in systems: $\text{NaOH} > \text{NaNO}_3 > \text{HClO}_4 > \text{H}_2\text{SO}_4$. Oxidation processes are in general lower for PbS-ZnS and FeZnS samples including at least two major stages (i.e., O1 and O2-O3) to constitute sluggish oxidation processes, in agreement with mineralogical observations (Figs. 2 to 6) and chemical evolution of leachates (Fig. 1). Regarding the reduction processes, some of them are identified during the reversed positive scans on voltammograms (Figs. 7, S6 and S7), which were mainly associated with the reduction of the secondary phases generated during oxidation of the samples as well as the intrinsic reduction of the pristine mineral structures as described elsewhere (Ahlberg and Ásbjörnsson 1994; Chen and Yoon 2000; Urbano et al. 2007; Wang et al. 2013; Karimi et al. 2017). Note that literature regarding the electrochemical oxidation of sphalerite samples is not recent but scarce and sparsed (Choi et al. 1993; Ahlberg and Ásbjörnsson 1994; Chen and Yoon 2000; Srinivasan and Iyer 2000; Da Silva 2004). The electrochemical behavior of the sphalerite samples presented in Fig. 7 shows oxidation processes for FeZnS and PbS-ZnS samples under tested conditions but involving comprehensive and unprecedented comparisons. While galena oxidation is predominant for the PbS-ZnS samples oxidation up to potentials close to 0.8 V/SCE revealing that weathering process of this sample occurs with several stages. Major findings provided in Fig. 7 also aim to complement understanding of the environmental sphalerite oxidation since diversity of impurities or varied Fe content modify mineral activity or oxidation capacity with potential release of Zn (Babedi et al. 2021).

The different energetic and kinetic stages of the sphalerite oxidation trends were further evaluated by chronoamperometry and chronopotentiometry under all tested conditions. Figs. S8 to S10 show obtained curves (I_s vs. E) describing electrochemical behavior of the PbS-ZnS and FeZnS samples, complimentary to Figs. 7 and S6. According to Fig. S8, the occurrence of at least two main oxidative complex mechanisms are identified under all tested conditions, in agreement with CV study. Additionally, Figs. S9 and S10 indicated a not-time dependent oxidation for PbS-ZnS and FeZnS treated with 0.1 M NaNO₃ or 0.1 M HClO₄ solution. These curves suggested a rapid increment of the oxidative current whence intensity of the mineral weathering depended mainly on the potential reached in systems ($0.8 > E_a > 0.6$ V/SCE). In contrast, I_s vs E curves revealed significant time-dependent oxidation for the PbS-ZnS and FeZnS sample treated with 0.1 M NaOH or 0.1 M H₂SO₄ solution ($E_a > 0.8$ V/SCE). The dependence of time in oxidation processes would imply that once certain overpotentials have been reached during weathering conditions (i.e., $E_a > 0.8$ V/SCE), there would be a significant oxidation where the release of Zn and sulfur soluble species occur leading to the progressive accumulation of secondary compounds on surfaces promoting progressive (potential) mineral passivation (Figs. S9 and S10). All these findings generally explain why the oxidation of sphalerite is sluggish process, whereby there is a need to establish important overpotentials (i.e., energetic conditions) for a significant weathering process to occur, in agreement with Fig. 1 and mineralogical characterizations (Figs. 2 to 4, S5 to S7).

Tafel analysis is typically used to quantify the kinetics of the rate-determining steps in systems, since it estimates the voltage that needs to be applied to increase the current by one order of magnitude. Tafel plots can then be then used to better understand the kinetics behavior of the PbS-ZnS samples and FeZnS weathering under all tested conditions. Note that most studies using

Tafel plots for materials are based on obtaining parameters such as the exchange current density since this parameter is drawn on well-defined reactions and mechanisms (Meng et al. 2019; Zhang et al. 2020); however, such approach requires a precise reaction mechanism for a given potential region, which is very difficult to achieve in the case of the MS oxidation due to imprecision of defining exact reactions occurring during oxidation. An additional approach that does not depend on the exchange current density is then required for the present assessment, for instance, using the potential of corrosion (E_{corr}) or oxidation, which can be easily determined during the electrochemical oxidation of sphalerite samples (Figs. 7 and S6). In this study, a modified Butler-Volmer equation in terms of E_{corr} was used for obtaining electrochemical kinetics parameters (Figs. 8, S11 to S13, Eqs. 1 to 3, Table 3):

$$i_0 = nFk_f * C_R^b \exp\left(\frac{\alpha_A nF}{RT} E\right) \quad \alpha_A = 1 - \alpha_C \quad (1)$$

$$i_0 = nFk_f * C_R^b \exp\left(\frac{\alpha_A nF}{RT} E_{eq}\right) = -nFk_b * C_O^b \exp\left(\frac{-\alpha_C nF}{RT} E_{eq}\right) \quad (2)$$

$$I = nFk_f * C_R^b \exp\left(\frac{\alpha_A nF}{RT} E\right) - nFk_b * C_O^b \exp\left(\frac{-\alpha_C nF}{RT} E\right) \quad (3)$$

Where i_0 is exchange current, η , overpotential, $\alpha_{A,C}$, transfer charge coefficients for anodic or cathodic branches, n , transferred electron number for the limitant step, C_R^b , bulk concentration of reduced species, C_O^b , bulk concentration of oxidized species, k_f , rate constant for oxidation, F , Faraday number and k_b , rate constant for reduction. The details and further considerations for the present approach are given in ESM section (Figs. S11 to S13). Fig. 8 confirms the complex nature of the oxidation processes (i.e., anodic branches) in all tested solutions, whereby reduction

processes were associated mainly with medium evolving to produce $H_{2(g)}$, as indicated in literature (Ahlberg and Ásbjörnsson 1994; Karimi et al. 2017, Karimi et al. 2018). As observed in Table 3, the least negative E_{corr} is obtained for NaOH followed very close by $HClO_4$ and $NaNO_3$, and after H_2SO_4 . This indicates that less electric work (energetics) needs to be applied to oxidize the PbS-ZnS and FeZnS samples in 0.1 M NaOH, while the medium with a lower oxidation is H_2SO_4 . This result confirms the evidence above described in the Cyclic Voltammetry analysis (Fig. 7), Chronoamperometry (Figs. S9 and S10) and Chronopotentiometry (Figs. S8). The fact that PbS-ZnS and FeZnS present a higher activity in NaOH is also corroborated in the rate constants for oxidation (Table 3) which are three and one order of magnitude, respectively, higher compared to the other solutions. Likewise, the $k_f^*C_R^b$ value in general reveals that FeZnS oxidation is slightly more prone to occur than the PbS-ZnS sample; although both processes are slow as previously described (i.e., Tafel slopes located between 100 and 150 mV dec⁻¹). Accordingly, it was also observed that the oxidation of the PbS-ZnS sample proceeded first than the FeZnS sample in all tested systems, particularly under the 0.1 M NaOH conditions, which was associated with enhanced sphalerite oxidation due to galvanic interactions with galena (Urbano et al. 2007; Srinivasan and Iyer 2000; Karimi et al. 2018; Table 1, Fig. 5). The Tafel plots are found to vary from 0 to 1.2 V/SCE. The form of Tafel plots at high potentials has found to vary depending on the alteration degree and surface composition (Ahlberg and Ásbjörnsson, 1994; Meng et al. 2019; Schippers et al. 2019). Accordingly, Tafel plots ranging from ~0.1 to ~0.8 V/SCE described most significant stages for mineral weathering whereby the most possible explanation is the progressive surface modifications to evolution of inhomogeneous polysulfide compounds layers (and eventually S^0 compounds in the FeZnS sample) and the development of additional secondary compounds (i.e., anglesite ($PbSO_4$)-like due) to galvanic interactions with galena in the PbS-ZnS sample (Figs. 4, S4 and S5b), in agreement with E_{corr} and K_f constants

(Table 3). The shift in the Tafel curves after ~0.8 V/SCE was then attributed to different charge transfer kinetics of the enhanced sphalerite dissolution to form sulfoxy-compounds (i.e., Zn^{2+} , $\text{S}_2\text{O}_3^{2-}$, SO_4^{2-}), in agreement with chronopotentiometric and chronoamperometric assessments describing at least two major stages for the weathering processes (Figs. S6 to S12, Table 3).

3.5. Reactivity assessment

The evolution of electrochemical reactivity of altered mineral surfaces can be used to predict changes of the oxidation capacity of the PbS-ZnS and FeZnS samples, as a function of the secondary compounds development (Cruz et al. 2001). The progress of secondary compounds was achieved by applying anodic pulses ($E_a = 1.2$ V/SCE) during 1 and/or 2 h using the same electrolytes for characterization purposes (See section 2.2). According to Fig. 9, the voltammetric behavior of PbS-ZnS and FeZnS samples are clearly affected by the simulated weathering process. In general, FeZnS samples showed the progressive surface passivation most probably due to secondary compounds accumulation (i.e., at high potentials, Fig. 9a to 9d). In contrast, the mineral activity of the PbS-ZnS samples indicated alternating passivation-oxidation stages, in all tested solutions, whence secondary compounds seems to promote a delayed surface passivation regarding FeZnS samples (Fig. 9a' to 9d'). These results agree with the leachates analysis, mineralogical characterizations and electrochemical assessments of pristine PbS-ZnS and FeZnS samples (Figs. 1, 4, 5 and S4), and indicate that the sphalerite weathering follows a mechanism similar to that of sphalerite electrochemical oxidation under simulated weathering conditions.

4. Discussion

The chemical analysis of leachates generated during simulated sphalerite (i.e., PbS-ZnS) weathering processes indicated limited Zn, Fe, Cd and sulfates ions dissolution (Fig. 1). Additionally, mineralogical analysis of these mineral samples confirmed that the polysulfides (i.e., S_n^{2-}) are the main sulfur compounds during weathering processes for all tested conditions. The progressive enrichment of altered samples with S_n^{2-}/S^0 compounds can also occur for a more extend weathering process (Fig. S5a). It was not identified Zn-bearing secondary compounds (i.e., $ZnSO_4$, $Zn(OH)_2$) on altered mineral surfaces (according to XPS study), suggesting a rapid diffusion of just Zn^{2+} release into bulk-solution systems (i.e., stirring conditions). These findings suggested that solid secondary compounds are bare during environmental weathering of the low-Fe and Pb-bearing sphalerite samples (i.e., PbS-ZnS) to form mainly soluble sulfur and Zn compounds (i.e., Zn^{2+} , SO_4^{2-}) in the systems. This same observation is possible based on extensive electrochemical assessments (i.e., Figs. S8 to S12, 7 to 9) for the marmatite-like samples (i.e., FeZnS), and according to literature illustrating the progressive surface S^0/S_n^{2-} enrichment after 24 of leaching in acidic or circumneutral solutions (Acero et al. 2007; Harmer et al. 2008; Schippers et al. 2021; Babedi et al. 2021). Therefore, the results presented in this work complement the existing reports for the oxidation of Fe-rich sphalerite samples at short intervals of alteration, particularly when sphalerite weathering occurs in mining waste environments (Bao et al. 2021).

On the basis of the experimental evidence presented here, equilibrium data from literature (i.e., Bobeck and Su, 1985) and/or equilibrium data calculated in Fig. S14, the following weathering mechanisms are suggested to describe major sphalerite oxidation process (i.e., PbS-ZnS and FeZnS samples) under most typical weathering environments (i.e., NaOH, $NaNO_3$, $HClO_4$ or

H₂SO₄). The initial stage of the sphalerite oxidation seems to be the same under all tested conditions, regarding sulfur bulk-species (i.e., S²⁻), which is attributed to the bare capacity of the PbS-ZnS sample to oxidize, thus involving sluggish weathering to form non-stoichiometric metal-deficient-like layers mainly composed of polysulfides (i.e., Zn_{1-x}S-like structures); these mechanisms also involve bare Zn²⁺ release, according to the next simplified reactions for acidic (Eq. 4), circumneutral (Eq. 5) and alkaline (Eq. 6) conditions:

If Fe content is considered, an alternative reaction scheme could then involve the Fe²⁺ release from the FeZnS structure (Babedi et al. 2021; Crundwell 2021), in agreement with the following simplified general process:

These weathering reactions suggest specific sphalerite activity, despite of weathering reactions occurring in typical acidic (0.1 M H₂SO₄), acidic-saline (0.1 M HClO₄), circumneutral (0.1 M NaNO₃) and alkaline (0.1 M NaOH) saturated conditions. However, pH, ORP, sulfates and Zn

measurements along with AFM (Fig. 2) and SEM-EDS (Figs. 3 and S3) studies highlight general sluggish oxidation mechanisms, in agreement with Eqs. 4 to 6. Additionally, Raman spectroscopy and XPS indicate the formation of i.e., $\text{Zn}_{1-x}\text{S}_{1-y(s)}$ secondary compounds for later stages of mineral weathering involving inhomogeneous distribution of secondary compounds on altered surfaces (Figs. 5 and 6). Concomitant galena weathering was also identified on free-altered galena particles associated with the PbS-ZnS grain particles system (i.e., 0.1 M H_2SO_4 conditions) to form an anglesite (PbSO_4)-like compound (Figs. S4 and S5b). Considering the potential formation of this compound due to galvanic interaction between galena and the sphalerite sample (Urbano et al. 2007; Srinivasan and Iver 2000); the following reaction scheme is also suggested to accompaniment of Eqs. 4 to 6 for the case of the PbS-ZnS sample:

The effect of the concomitant galena oxidation is strongly suggested by the literature (Urbano et al. 2007; Srinivasan and Iver 2000; Karimi et al. 2018), and our Raman study (Fig. S4). Accordingly, this oxidative behavior is determined by electrochemical assessment of the PbS-ZnS sample in 0.1 M H_2SO_4 solution helping to disclose stages associated with this synergistic weathering mechanism (Figs. S4 and S5b). Additionally, the corresponding depletion of Fe, Zn and Cd in the PbS-ZnS samples (Figs. 1 and 6), together with varied formation of inhomogeneous secondary compounds, leaded to the progressive passivation of the samples, as indicated by Figs. 7, 9, and S6, enhancing the production of mainly soluble but also surface compounds (i.e., SO_4^{2-} , $\text{S}_2\text{O}_3^{2-}$, Zn^{2+}), according to the next simplified global scheme:

This same weathering process can be suggested for the case of the FeZnS sample, where electrochemical studies (Figs. 7, S6 to S12) indicated the progressive enrichment of sulfur compounds ($\text{S}_n^{2-}/\text{S}^0$) through a two main stage oxidative process, even for the PbS-ZnS sample (Figs. 7, S6 to S12). The progressive enrichment of $\text{S}_n^{2-}/\text{S}^0$ compounds is well documented in elsewhere for a long pH range describing oxidation of Fe-rich sphalerite specimens (Acero et al. 2007; Harmer et al. 2008; Schippers et al. 2021; Babedi et al. 2021). The continuous bare production and oxidation of polysulfides (and likely S^0) to form sulfoxy-compounds (i.e., $\text{S}_2\text{O}_3^{2-}$, SO_4^{2-}) allows equilibrium of mineral activity, which occur indirectly after transpassive oxidation of PbS-ZnS (i.e., anglesite-like compound) and directly oxidation of the FeZnS sample (i.e., after formation and accumulation of $\text{S}_n^{2-}/\text{S}^0$ compounds), according to the following scheme:

Complex kinetic mechanisms were enhanced for the PbS-ZnS and FeZnS samples in 0.1 M NaOH solution, which suggested that sphalerite weathering was favored in alkaline conditions (Figs. 7, 8, S6 to S12); however, the rest of the tested systems revealed similar kinetic processes among them, even under acidic conditions of the 0.1 M H_2SO_4 system (Fig. 8). This fact was associated with the enhanced release of Zn to bulk-system (Fig. 1d), avoiding more accumulation of sub-micro sized secondary compounds regarding the other tested systems (Figs. 2 and 3, Table 1).

The pollution process for Zn release in soils has been studied under different climate and weathering conditions (i.e., alkaline or acidic soils) whereby Zn (and other heavy metals) behavior was associated to the weathering of primary Zn-bearing phases in regions affected by mining waste spillage with significant impacts to the environment (i.e., FeZnS, PbS-ZnS, Razo et al. 2004; Jaquiat et al. 2008; Navarro et al. 2008; Jalali and Khanlari 2008; Jalali and Moradi 2013). Most of these studies were conducted considering sphalerite weathering in the context of physicochemical reactions occurring in mining waste environments with significant production of acid solutions (Bao et al. 2021). The results presented in the present work improve the scientific perspective of the reactions and stages of alteration of different forms of sphalerite, and offer kinetic calculations with an adequate methodological approach, helping to better elucidate the interfacial phenomena and providing a thorough assessment of the reaction mechanisms controlling the release of Zn from mine wastes and their mobilization and attenuation in environment. To this context, there are also scenarios where the study of the alteration of the sphalerite is unprecedented, as is the case of the alteration of sphalerite in simulated calcareous (alkaline) soils conditions. This information is relevant since prospective findings helps to better understand the impact and mobility processes of Zn, accounting for relevant aspects of the stability and activity of sphalerite and the corresponding secondary compounds in such conditions (Navarro et al. 2008; Álvares-Ayuso et al. 2013), which can be helpful for further establishment of legal and efficient designing of mining practices and for urban planning, among others, in benefit of environmental and health risk issues.

5. Conclusions

A comprehensive methodology of chemical analysis of leachates along with mineralogical and electrochemical assessments were carried out to describe the main weathering process of sphalerite under simulated environmental conditions, revealing the following findings:

(1) The sphalerite weathering process is in general sluggish involving the occurrence of minor, sub-micro sized and non-homogeneously distributed polysulfides compounds on altered surfaces.

(2) The weathering processes occur mainly with the modification of the surface-bulk structure (i.e., surface-activity relationships), to form mineral rimmed particles with different degree of alteration under all tested conditions. The presence of anglesite (PbSO_4)-like compound is identified on galena free-particles, revealing the concomitant weathering of galena, which is associated with the PbS-ZnS system; this result supports extra experimental evidence regarding the formation of secondary compounds on the main sulfide impurity of sphalerite samples under simulated environmental weathering conditions. Additionally, the weathering of sphalerite led to the main production of soluble secondary phases (i.e., ZnOH^+ , $\text{S}_2\text{O}_3^{2-}$, SO_4^{2-}) while not Zn-bearing secondary compounds is identified on altered surfaces.

(3) The kinetic sphalerite oxidation process is enhanced in 0.1 M NaOH conditions, while this oxidation is similar for the rest of tested conditions involving the following activity order: $\text{NaOH} > \text{NaNO}_3 > \text{HClO}_4 > \text{H}_2\text{SO}_4$. The electrochemical oxidation processes

includes two main stages at least, where the establishment of the corresponding specific structure-activity relationships are illustrated with spectroscopic techniques (GDOES, Raman, XPS). Additionally, a clear weathering trend involving the progressive passivation of the FeZnS samples is revealed during mineral activity evolution assessment. While an alternated passive to transpassive oxidation stage is then observed for the PbS-ZnS sample during mineral activity evolution.

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Statements and declarations

Competing interests

Authors declare no competing or financial interest

Ethical Approval

Not applicable

Author contributions

Fabiola S. Sosa-Rodríguez and **René H. Lara** contributed as follows: Methodology, Resources, Funding, Investigation and Conceptualization, Writing and Review Analysis, Project administration. **Jorge Vazquez-Arenas:** Resources, Funding, Formal Analysis, Software and Validation, Writing and Review Analysis. **Patricia Ponce Peña, Antonio Aragón-Piña, Martine Mallet, Gabriel Trejo-Córdova, Diola M. Núñez-Ramírez and Miguel A. Escobedo-Bretado:** Methodology, Investigation, Supervising and Formal Analysis

Consent to participate

Not applicable

Consent to publish

All authors consent publication of the present submission

Availability of data and materials

The data and materials report in the present submission are available on request

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Figure legends

Fig. 1. Chemical leachates evolution during oxidation of the PbS-ZnS sample under simulated weathering conditions: pH (a); oxidation-reduction potential (ORP) (b); sulfates (c), Zn (d), Fe (e) and Cd (f). The standard deviations in the measurements of the present figure are within 15%.

Fig. 2. Typical AFM 2D and 3D obtained images during analysis of the pristine (a) and leached PbS-ZnS surfaces in 0.1 M NaOH (b), 0.1 M NaNO₃ (c), 0.1 M HClO₄ (d) or 0.1 M H₂SO₄ solution (e). Contact mode.

Fig. 3. SEM 2D images obtained during surface analysis of the pristine (a) and leached PbS-ZnS samples in 0.1 M NaOH (c), 0.1 M NaNO₃ (d), 0.1 M HClO₄ (e) or 0.1 M H₂SO₄ (f) solution. This Figure includes SEM 3D image for leached samples in 0.1 M NaOH conditions, for instance of similar mineral behavior (b). Secondary phases identification is carried out under EDS basis (analyses, $n=10$). ZnS= Sphalerite; Zn_{1-x}S_{1-y}= Non-stoichiometric-like layers; PbS= Galena.

Fig. 4. Raman spectra obtained during surface analysis of pristine (a) and leached PbS-ZnS samples in 0.1 M NaOH (c), 0.1 M NaNO₃ (d), 0.1 M HClO₄ (e) or 0.1 M H₂SO₄ solution (f). Calibration of Si-disc wafer was included for calibration purposes (b). Main Raman peaks are illustrated on the figure.

Fig. 5. Zn2p and S2p XPS narrow spectra obtained for pristine and after 24 of leaching PbS-ZnS samples in 0.1 M NaOH, 0.1 M NaNO₃, 0.1 M HClO₄ or 0.1 M H₂SO₄ solution.

Fig. 6. GDOES spectra for pristine and leached PbS-ZnS samples under different simulated weathering conditions for sulfur (a), Zn (b), Fe (c) and Cd (g) elements. The erosion time is indicated in the Figure.

Fig. 7. Cyclic voltammograms initiated into the positive direction using CPE-PbS-ZnS sample (curves i, fuchsia) and CPE-FeZnS (curves ii) in 0.1 M NaOH (a, red), 0.1 M NaNO₃ (b, blue), 0.1 M HClO₄ (c, green) or 0.1 M H₂SO₄ solution (d, black). Scan rate of 5 mV·s⁻¹. The inert response of the CPE without mineral samples (100 % graphite) is included for comparison purposes (intermittent curves iii, gray). Carbon paste and mineral sample contain is 50 wt. %. Ambient conditions. Quiescent systems.

Fig. 8. Tafel plots obtained using CPE-PbS-ZnS (50 wt. %) and FeZnS samples (50 wt. %) under different simulated weathering conditions: 0.1 M NaOH (a), 0.1 M NaNO₃ (b), 0.1 M HClO₄ (c) or 0.1 M H₂SO₄ (d) solution. Scan rate of 1 mV·s⁻¹. Ambient conditions. Stirring conditions of 300 rpm.

Fig. 9. Linear sweep voltammetric responses in the positive direction obtained for CPE-FeZnS (a to d) and CPE-PbS-ZnS (a' to d') samples in 0.1 M NaOH, 0.1 M NaNO₃, 0.1 M HClO₄ or 0.1 M H₂SO₄ solution, respectively. Applied anodic pulse (E_a) is of 1.2 V/SCE during 1 and/or 2 h. Scan rate of 20 mV·s⁻¹. Ambient conditions. Quiescent systems.

Table captions

Table 1. Root mean square (Rq) and Roughness (Ra) values collected from different altered sphalerite areas.

Table 2. Binding energy (BE), FWHM (Full width at half-maximum), peak areas and chemical state for Zn2p_{3/2} and S2p_{3/2}* spectra of pristine and leached sphalerite samples (i.e., PbS-ZnS).

Table 3. Kinetic oxidation parameters of the Tafel plots analysis regarding sphalerite oxidation processes in 0.1 M NaOH, 0.1 M NaNO₃, 0.1 M HClO₄ or 0.1 M H₂SO₄ solution.

Figures

Figure 1

Chemical leachates evolution during oxidation of the PbS-ZnS sample under simulated weathering conditions: pH (a); oxidation-reduction potential (ORP) (b); sulfates (c), Zn (d), Fe (e) and Cd (f). The standard deviations in the measurements of the present figure are within 15%.

Figure 2

Typical AFM 2D and 3D obtained images during analysis of the pristine (a) and leached PbS-ZnS surfaces in 0.1 M NaOH (b), 0.1 M NaNO₃ (c), 0.1 M HClO₄ (d) or 0.1 M H₂SO₄ solution (e). Contact mode.

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Figure 4

Raman spectra obtained during surface analysis of pristine (a) and leached PbS-ZnS samples in 0.1 M NaOH (c), 0.1 M NaNO_3 (d), 0.1 M HClO_4 (e) or 0.1 M H_2SO_4 solution (f). Calibration of Si-disc wafer was included for calibration purposes (b). Main Raman peaks are illustrated on the figure.

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Zn2p and S2p XPS narrow spectra obtained for pristine and after 24 of leaching PbS-ZnS samples in 0.1 M NaOH, 0.1 M $NaNO_3$, 0.1 M $HClO_4$ or 0.1 M H_2SO_4 solution.

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Linear sweep voltammetric responses in the positive direction obtained for CPE-FeZnS (a to d) and CPE-PbS-ZnS (a' to d') samples in 0.1 M NaOH, 0.1 M NaNO₃, 0.1 M HClO₄ or 0.1 M H₂SO₄ solution, respectively. Applied anodic pulse (E_a) is of 1.2 V/SCE during 1 and/or 2 h. Scan rate of 20 mV·s⁻¹. Ambient conditions. Quiescent systems.

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