



Electrochemistry of Sulfides: Process and Environmental Aspects

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Abstract: One of the main sources of non-ferrous and precious metals is sulfide ores. This paper presents a review of the existing literature on the electrochemical properties of some of the most common industrial sulfides, such as pentlandite, chalcopyrite, sphalerite, galena, pyrrhotite, pyrite, etc. The study results of the surface redox transformations of minerals, galvanic effect, cathodic oxygen reduction reaction on the surface of sulfides are presented. The electrochemical properties of sulfide minerals are manifested both in the industrial processes of flotation and hydrometallurgy and in the natural geological setting or during the storage of sulfide-containing mining, mineral processing, and metallurgical industry waste.

Keywords: electrochemistry of sulfides; flotation; hydrometallurgy; mining waste



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1. Introduction

Sulfide minerals are an important group of ore minerals and a major source of nonferrous and precious metals. Sulfide minerals are known for high conductivity, which determines the abrupt change in the potential at the sulfide–solution interface [1–7]. Sulfides such as pentlandite ((Fe,Ni)₉S₈), covellite (CuS), galena (PbS), and pyrrhotite (Fe_{1-x}S) are close to metals in terms of conductivity. Semiconductor minerals with good conductivity include pyrite (FeS₂), bornite (Cu₅FeS₄), chalcosine (Cu₂S), chalcopyrite (CuFeS₂), arsenopyrite (FeAsS) [5].

A relevant research and practical task is to improve the contrast of the physicochemical and process properties of sulfide minerals to achieve high separation performance in ore concentration circuits. Multiple existing studies convincingly show that the sorption mechanism of the collector, sulfides flotation kinetics, and the interactions between the minerals in intergrowths have an electrochemical background [1–8]. Pioneering studies in this field include those by Plaksin et al. [1–3]. A comprehensive study of the process of interaction of sulfhydryl reagents with sulfides made it possible to discover a number of fundamentally new patterns in the mechanism of xanthate sorption on sulfide minerals. The effect of the electrochemical properties of minerals and the concentration of free electron vacancies on the distribution of the collector and the ratio of xanthate to dixanthogen on sulfide surfaces was experimentally established. By manipulating the state of the mineral surfaces through various physical and chemical impacts, it is possible to modify their electrochemical properties and, thereby, control the flotation of sulfides [1–10].

Currently, for the processing of low-grade sulfide ores and technogenic mineral resources (overburden, concentration tailings, and smelter slags), heap and bioleaching methods are increasingly being used [11]. The electrochemical properties of sulfides have a decisive influence on the leaching kinetics, the concentration of non-ferrous metals in pregnant solutions, and recovery [12–16]. It should be noted that the utilization of operando/in situ techniques, e.g., X-ray absorption and Raman spectroscopy, can more accurately track the phase, composition, local atomic coordination of sulfides during electrochemistry process.

In addition to process engineering challenges, the environmental aspect should also be taken into consideration (Figure 1).



Figure 1. Technological and environmental aspects of the electrochemistry of sulfides.

Sulfide-containing ore mining, mineral processing, and metallurgical wastes are known to be some of the most environmentally hazardous types of industrial waste [17,18]. During waste storage, sulfide minerals, in particular pyrite and pyrrhotite, oxidize forming sulfuric acid (acid mine drainage (AMD)), ferrous and non-ferrous sulfates. Chemical weathering of tailings proceeds much faster than in a natural geological environment. Oxidative dissolution of sulfides as a result of galvanic interactions is one of the most important agents of environmental pollution [17,19,20]. To better understand the nature and mechanisms of chemical weathering, studies of the physicochemical properties of minerals, including electrochemical properties, are needed.

This paper presents a brief review of the existing literature on the electrochemical behavior of some common industrially important sulfide minerals in aqueous solutions and the process of oxygen reduction on the surface of sulfide minerals, which ensures the occurrence of processes important for the processing of sulfide ores (oxidation and leaching reactions, chemisorption and oxidation of sulfhydryl collectors) and in processes weathering occurring in sulfide-containing wastes of mining enterprises. The results of studies of galvanic interactions of sulfides in technological processes—flotation and hydrometallurgy—and environmental aspects of studying the electrochemical properties of sulfide minerals, which must be taken into account to predict the processes of AMD generation and the transfer of heavy metals and other toxic elements to soil and surface water during the storage of mining waste, are also reflected.

2. Electrochemistry of Sulfides in Aqueous Solutions

2.1. Iron Sulfides

Iron sulfides are represented by such minerals as pyrite and marcasite (FeS₂), greigite (Fe₃S₄), pyrrhotite (Fe_{1x}S), mackinawite (FeS_{1-x}), and troilite (FeS). Pyrite and pyrrhotite are the most abundant minerals found in polymetallic ores.

The electrochemical properties of pyrite and pyrrhotite are presented in great detail in [21–27]. Cathodic and anodic decomposition of pyrite and pyrrhotite in acidic environments is discussed in [22,24,26] without consideration of intermediate reactions preceding decomposition processes. Surface redox transformations of pyrite and pyrrhotite in the stability region of minerals in a wide pH range were studied by cyclic voltammetry in [21]. The authors note that the surface of iron sulfide minerals, depending on pH, is covered with either sulfur or sulfur and iron(III) hydroxide; this film is quite porous and does not inhibit electrochemical dissolution. However, the anodic processes on sulfide electrodes as described in [21] mainly concern the electrochemical oxidation of the products of the preliminary cathodic polarization of these minerals.

Electrochemical oxidation of pyrite in 1 M of HCl was studied in [28] using a wide range of methods. It was found that oxidation includes a series of sequential and parallel reaction stages, as a result of which the

$$\label{eq:Fe2+} \begin{array}{l} Fe^{2+} \rightarrow Fe^{3+},\\ S \rightarrow S_2 O_3{}^{2-} \rightarrow HSO_4 \end{array}$$

processes were observed, depending on pH and potential.

The author considers the effect of a borate electrolyte (a $Na_2B_4O_7$ solution) on the kinetics of the electrochemical oxidation of pyrite in [29]. The borate electrolyte was used in most studies as a model buffer system inert with respect to minerals. According to the results obtained, the first stage of the interaction is the irreversible one-electron reaction of formation of a FeS₂…[B(OH)₄]_{ads}. complex.

Fourier-transform infrared spectroscopy (FTIR) spectra of the pyrite electrode–electrolyte interface were collected in situ and interpreted in [30] at a polarization of -0.5 to +0.9 V relative to the standard hydrogen electrode (SHE) and pH 9.2. An electrochemical model of pyrite oxidation in aqueous environments was proposed. The cathodic half-reaction proceeds in sulfur-deficient regions of pyrite or on FeS defects. The anodic half-reaction proceeds along the thiosulfate path in the areas of "ordinary" pyrite, due to the Fermi level in the upper part of the valence band. The main role of the oxidizing agent is to maintain a high potential on the anode sites. Direct (chemical) oxidation of pyrite is an indirect effect and consists in the interaction of the oxidizing agent with the products of the anodic reaction.

The effect of polysulfide formation on the kinetics of pyrite dissolution in a 1 M HCl solution was examined in [31]. Pyrite was oxidized electrochemically at various anodic dissolution potentials. Further, the thickness of the polysulfide layer was estimated by two methods: using X-ray photoelectron spectroscopy (XPS) and Raman spectroscopy. Both methods showed that the thickness of the polysulfide layer increases with increasing potential. At the same time, the current increases exponentially with increasing potential, which indicates the absence of the passivating effect of polysulfides.

Electrochemical properties of pyrrhotite were studied in the works by Chanturiya and Wigdergauz, Buckley, Woods, and other researchers [5,21,24]. The electrochemical behavior of natural pyrrhotite was studied in solutions of 1 M HCl and 0.05 M Na₂B₄O₇ using cyclic voltammetry and potentiostatic method [32]. It was found that the formation of a massive nonequilibrium metal-deficient layer on the mineral surface occurs in 1 M HCl in the potential range from 0.08 to 0 V relative to the silver–silver chloride reference electrode. In this case, the dissolution rate changes by about two orders of magnitude. On the cyclic voltammograms of pyrrhotite with a previously formed metal-deficient layer, an intense cathodic peak is recorded at -0.2 V, and several anodic waves are observed when the potential is reversed. It was found that the cathode peak corresponds to the reductive cleavage of polysulfide with the formation of monosulfide S_0^{2-} centers, which dissolve in acid to release H_2S . Three anodic peaks correspond to the association of S_0^{2-} with each other and with polysulfide clusters, oxidation of terminal sulfur atoms (S_1^{-}) with the association of chains into larger ones and the oxidation of residual S_1^{-} . The behavior of an electrode with a metal-deficient layer previously formed in hydrochloric acid and transferred to a borate solution is consistent with these suggestions. In the reactions of pyrrhotite without preliminary acid etching, the same centers participate at lower concentrations. Similar results were obtained by Mikhlin et al. in their study of the electrochemical oxidation of pyrrhotite in a sulfuric acid solution [33,34].

2.2. Copper Sulfides

Industrial minerals include chalcocite (Cu₂S), covellite (CuS), chalcopyrite (CuFeS₂), to a lesser extent bornite (Cu₅FeS₄) and cubanite (CuFe₂S₃). In recent years, a number of studies were conducted on the electrochemistry of a relatively rare sulfoarsenide mineral—enargite (Cu₃AsS₄).

As noted by Chanturiya and Wigdergauz [5], for copper sulfides, electroleaching processes—cathodic and anodic decomposition—are studied in more detail. The processes preceding decomposition are understood less fully.

One of the early works studied the anodic dissolution of Cu₂S in sulfate solutions with simultaneous precipitation of copper [35]. An intermediate product—digenite—was found on the anode surface:

$$Cu_2S \rightarrow Cu_{1.8}S + 0.2Cu^+ + 2e^-.$$

Then, due to a sharp increase in the potential of the electrode, digenite was transformed into covellite. The decomposition of covellite is also superimposed on that of digenite:

$$CuS \rightarrow Cu^{2+} + S + 2e^{-}$$

The structure was studied and the phase components of copper(I) sulfide synthesized by the authors were identified [36]. It was shown that crystallization of copper sulfide can lead to the formation of chalcocite (Cu₂S) and djurleite phases (Cu₃₁S₁₆), characterized by a deficiency of copper in the crystal lattice and a deviation from the stoichiometric composition. Electrochemical oxidation of the sample in a solution of sulfuric acid was carried out. It was established that at a current density of 1000 A/m² and a concentration of 100 g/dm³ H₂SO₄, electrochemical dissolution of copper sulfide proceeds with the formation of a passivating film of sparingly soluble products during the oxidation of copper(I) sulfide to copper(II) sulfide. Moreover, during the oxidation, intermediate nonstoichiometric sulfides were formed in the following sequence:

$$\operatorname{Cu}_2{\rm S}\left(\operatorname{Cu}_{31}{\rm S}_{16}\right) \to \operatorname{Cu}_{1.8}{\rm S} \to \operatorname{Cu}_{1.74}{\rm S} \to \operatorname{Cu}_{1.6}{\rm S} \to \operatorname{Cu}{\rm S} \to \operatorname{Cu}^{2+}_{1.8}{\rm S} \to \operatorname{Cu}_{1.8}{\rm S} \to \operatorname{Cu}_{1.8$$

The process was accompanied by the transition of copper cations into solution. With the accumulation of elemental sulfur and copper sulfides on the reaction surface of the sample, the rate of electrochemical oxidation decreased due to the difficult removal of products and supply of the reagent to the reaction zone.

The electrochemical behavior of chalcocite in a 0.05 M buffer borate solution (pH 9.2) was studied in [37]. During anodic scanning, the oxidation wave began at -0.1 V relative to the saturated calomel electrode and was accompanied by the transition of Cu²⁺ ions into solution. During reverse cathodic sweep, a wave of copper sulfide formation was recorded with a peak at ~ -0.1 V. Cathodic sweep to more negative potentials led to the emergence of a recovery wave that began at ~ -0.58 V with a soluble reduction product HS⁻. During reverse anode sweep, the HS⁻ ion, apparently interacting with Cu²⁺, formed copper sulfide with a peak at -0.6 V.

Anodic dissolution of covellite in hydrochloric acid solutions was studied in [38]. It was found that the dissolution rate depends on pH and the concentration of chloride ions. At a Cl⁻ concentration higher than 1 M, the dissolution of CuS is accelerated due to the formation of a CuCl₂⁻ complex as a result of the chemical reaction between Cu²⁺ and CuS.

In papers [39–41], the anodic decomposition of chalcopyrite in acidic solutions was discussed. It was shown that at a potential of +0.8 V relative to the silver–silver chloride electrode, selective dissolution of iron occurred with the oxidation of sulfide sulfur to elemental, and at potentials more positive than +1.1 V, sulfide sulfur oxidized to sulfate [37].

Surface redox transformations of chalcopyrite and chalcocite were studied in the region of mineral stability in a wide pH range [42]. Studies performed by cyclic voltammetry included the polarization of the sulfide electrode from the rest potential to the cathode

region and then to the anode region. Thus, the electrochemical oxidation of the products of cathodic polarization of chalcopyrite was actually studied.

According to [43], where the stationary polarization curve of chalcopyrite was studied in a 0.1 M Na₂B₄O₇ solution, at a potential greater than -0.044 V relative to a SHE, an iron-deficient layer formed on the surface of chalcopyrite, which passivated the mineral upon reaching a potential of 0.120 V. Transition to the active state occurred at a potential of 0.237 V. At a potential of 0.436 V, chalcopyrite was passivated by metal hydroxides, oxides, and sulfates. At potentials greater than 0.53 V, the mineral dissolved.

Somewhat different results were reported in [44,45]. During the anodic polarization of a mineral in a borate solution, two current maxima were observed, the first of which was associated with the formation of metastable CuS_2 and $CuFe_{1-x}S_2$ phases. With a further positive shift of the potential, these phases dissociated with the formation of oxides CuO, Fe_2O_3 , and sulfur.

The reaction of chalcopyrite dissolution in ammoniacal solutions (NH₄OH and (NH₄)₂SO₄ at a ratio of 1:1) was studied by potentiostatic and potentiodynamic methods [46]. It was found that the anodic current densities near the mixed potential increased with increasing total ammonia (NH₃ + NH₄⁺) concentration from 1 to 3M. It was established that the reaction with respect to ammonia was of the first order. The reaction was of zero order in terms of [OH⁻] at pH 9 to 10. Tafel equations showed that the average charge transfer coefficient was 0.61. The reaction was controlled by a one-electron charge transfer step. That formed an intermediate copper-depleted layer, which was rapidly oxidized in subsequent electron transfer reactions. The surface precipitate formed during the reaction did not passivate the mineral, but reduced the rate of its dissolution.

The same authors studied the cathodic reduction of copper(II) and oxygen on the surface of chalcopyrite in ammoniacal solutions using cyclic voltammetry and chronoamperometry [47]. It was established that the predominant cathodic reaction during the oxidative dissolution of chalcopyrite in ammonical solutions is the reduction of copper(II). The cathodic reaction rate was found to be inversely proportional to pH and total ammonia concentration. Although tetra-ammine copper(II) ion is the dominant ion, the tri-ammine complex is believed to be the most electrochemically active under these conditions. It was shown that both copper(II) reduction and copper(I) oxidation occur simultaneously at potentials close to the mixed potentials of chalcopyrite in these solutions. The reaction rate is controlled by mass transfer determined by the migration of Cu(I) ions from the surface of the mineral.

Nicol summarized the results of studies of anodic processes on chalcopyrite in alkaline hydroxide and carbonate solutions [48]. Anodic oxidation of chalcopyrite involves active oxidation at low potentials followed by a passivation region and transpassive oxidation at higher potentials. In this case, the formation of solid products of the passivating film does not prevent continued oxidation. The oxidation kinetics is activated with an increase in pH in both hydroxide and carbonate solutions. Coulometric measurements showed that thiosulfate and sulfate ions formed as a result of oxidation in sodium hydroxide solutions. Thiosulfate ion is the main product in carbonate and bicarbonate solutions.

Relatively few studies were focused on the electrochemical behavior of bornite. In one of the earlier papers [49], it was reported that during the anodic oxidation of bornite, an intermediate phase deficient in copper $Cu_{2.5}FeS_4$ formed. It was noted that at temperatures below 50 °C, the anodic dissolution of bornite was controlled by solid-phase diffusion. At temperatures above 65 °C, dissolution was controlled by a chemical reaction.

In a recent article by Chinese researchers, based on the cyclic voltammetry and XPS data, it was shown that the oxidation of bornite proceeds intensively at a potential of more than 0.3 V relative to the silver–silver chloride reference electrode [50]. The main intermediate phases on the surface of bornite during oxidation are elemental sulfur, FeOOH, and CuS.

One of the first studies of the process of electrochemical oxidation of enargite, a valuable but arsenic-containing mineral, usually found in intergrowths with common

copper sulfides, was carried out by Asbjornsson et al. [51]. In a hydrochloric acid solution, they observed a wave in the range from 0.2 to 0.6 V (relative to the SHE) with a maximum at 0.54 V. This wave was associated with the formation of elemental sulfur as a passivating layer. Other parallel reactions with the formation of sulfate ions and arsenic(III) or arsenic(V) were also suggested.

The mechanism of electrochemical oxidation of enargite in sulfuric acid with a concentration of 0.1 mol·L⁻¹ at room temperature was studied in detail by electrochemical and spectroscopic analysis methods [52]. Cyclic voltammetry, potentiodynamic polarization, electrochemical impedance spectroscopy, and the Mott–Schottky method were used. XPS with cold stage, Raman spectroscopy, and synchrotron X-ray absorption near edge structure (XANES) were used to identify product layers on the electrode surface after electrochemical dissolution. A region of passivation of the enargite electrode was found at potentials from 450 to 750 mV relative to the Ag/AgCl electrode. The decrease in the current density in this potential region is due to the formation of a surface layer of $As_{(1-y-z)}S_4$. Copper dissolved more readily than arsenic. The transpassive region with a window between 750 and 900 mV is associated with the partial dissolution of the sulfide sulfur of the passivating surface film to elemental sulfur.

Nicol et al. conducted fundamental studies of the electrochemical behavior of enargite in ammonium sulfate and ammonium chloride solutions in the pH range from 8 to 10 [53] and compared that with the behavior of chalcopyrite under similar conditions. Mixed potential measurements showed that copper(II) is an effective oxidizer of enargite in ammoniacal solutions. Voltammetry confirmed the occurrence of the process of partial passivation of the electrode in the studied solutions. In general, the anodic behavior of enargite in chloride and sulfate solutions is similar, with the main product of anodic oxidation being thiosulfate ion. The relative dissolution rates of chalcopyrite and enargite in ammoniacal solutions were estimated using the mixed potential theory. It was demonstrated that enargite dissolves in such systems faster than chalcopyrite.

Same authors studied cathodic processes [54]. The process of reduction of copper(II) to copper(I) on the surface of enargite in ammonium sulfate solutions proceeds at a high rate and is quasi-reversible. The reaction of the first-order in terms of the concentration of copper(II) ions and its rate is limited by mass transfer even at low overpotentials. The kinetics and mechanism of copper(II) reduction in chloride solutions are quantitatively similar to those occurring in sulfate solutions. The reduction rate decreases with increasing concentrations of ammonia and ammonium ions. According to the developed model, this rate is approximately proportional to the concentration of tri-ammine copper(II) species, whose concentration decreases as the concentrations of ammonia and ammonium ions increase.

2.3. Nickel Sulfides

Pentlandite ($(Fe,Ni)_9S_8$) is the main nickel mineral in sulfide copper and nickel deposits. Violarite ($(Fe,Ni)_3S_4$) is found in association with pyrrhotite and pentlandite. Nickel also forms several other natural sulfides: millerite (NiS), vaesite (NiS₂), heazlewoodite (Ni₃S₂), polydymite (Ni₃S₄), and godlevskyite (Ni₇S₆). These minerals are relatively rare in sulfide ores. At the same time, heazlewoodite is the main component of the copper–nickel concentrate smelting product—feinstein.

The electrochemical behavior of millerite and heazlewoodite was described in detail in [5,55–57]. Specifically, the anodic reactions of heazlewoodite are interpreted as mineral transformations $Ni_3S_2 \rightarrow Ni_{3-x}S_2$ up to 600 mV relative to the calomel reference electrode; at intermediate potentials of 700–1200 mV, elemental sulfur forms, and at potentials above 1300 mV, the mineral is decomposed with the formation of elemental sulfur and sulfate ion.

In a later paper, Aromaa investigated the anodic dissolution of synthetic heazlewoodite in 1 N sulfuric acid at 25 °C [58]. An analysis of the potentiostatic curves and cyclic voltammograms showed that the formation of intermediate sulfides continued even at high potentials, up to 1600 mV relative to the saturated calomel electrode. It was found that solely sulfur formed up to 900 mV. At a polarization potential of 1000 mV, 90% of elemental sulfur and 10% of sulfates form, at 1600 mV—10% of sulfur, and the rest are sulfate ions.

The electrochemical properties of pentlandite are studied in less detail [59]. In [5], the complex nature and abundance of redox processes on the surface of pentlandite, caused by phase transitions of the mineral, are discussed.

In [60], oxidative dissolution of pentlandite in iron(III) chloride solution was investigated by electrochemical methods, including potentiometry, cyclic voltammetry, galvanostatic polarization, chronopotentiometry, and chronoamperometry. The oxidation products were analyzed using reflected light microscopy, powder X-ray diffraction (XRD), and electron microprobe analysis. It was shown that pentlandite oxidizes directly to elemental sulfur without the formation of any intermediate phases. Violarite formation was not reported. Sulfur layers create obstacles for mass transfer, and the dissolution process is limited by the diffusion of metal atoms in the surface layer of the mineral.

The same authors proposed a similar mechanism for the oxidative dissolution of violarite in an acidified iron(III) chloride solution [61].

In [62], anodic processes on a pentlandite electrode in a carbonate solution were investigated. Anodic polarization of the mineral started at a stationary potential of -0.035 ± 0.010 V relative to Ag/AgCl electrode for various samples of naturally occurring minerals. At an electrode polarization rate of 0.02 V/s, waves were observed at potentials of +0.265 and +0.545 V. The potential of the first wave shifts in the positive direction with an increase in the polarization rate, while in the rate range of 0.02–2 V/s it did not depend on the sweep rate, thus the process was controlled by diffusion. Characteristically, the current-voltage curves did not show a decrease in the current at electrode polarization rates lower than 0.1 V/s. With the use of potentiostatic electrolysis at wave potentials and new phases diagnostics, reaction schemes were proposed. Anodic process at the first wave potential consists in a decrease in the Me:S ratio in the sulfide due to the oxidation of ferrous iron with the formation of X-ray amorphous Fe(III) hydroxides and metastable sulfide $Fe_{4.5-n}Ni_{4.5}S_8$. At the second wave potential, the metastable sulfide phase dissolves with the formation of elemental sulfur and ferric hydroxides. The concentration of nickel ions in the solution after electrolysis at the second wave potential exceeds the concentration of iron ions by approximately an order of magnitude. At more positive potentials, sulfate ions form.

2.4. Lead Sulfide (Galena)

Electrochemical properties of galena are described in a number of papers, mainly in relation to flotation processes [5,6,63–70]. It is noted that during the anodic polarization of galena in the pH range of 6.8–11, a layer of lead and sulfur oxide is formed, which inhibits the process of further oxidation [5]. It is emphasized that, according to a number of studies, the main product of galena oxidation in alkaline solutions is thiosulfate. Formation of $S_2O_3^{2-}$ ions was reported in [67,70]. Using FTIR spectroscopy, in situ surface compounds on galena at anodic polarization in the range from -0.5 to +0.7 V (relative to a SHE) in an oxygen-free solution of sodium tetraborate (pH 9.18) were identified in [64]. A conclusion was made about the formation of lead hydroxide on the surface of galena by the salt-film mechanism. At the next stage of oxidation lead thiosulfate and lead sulfite formed.

An electrochemical study of the surface of galena in solutions of various acids was carried out and it was shown that passivation is not associated with shielding of the electrode surface with sulfur, salts, and lead oxides, and that ligands are directly involved in electrochemical reactions [63].

A detailed study of the electrochemical behavior of galena in acidic media was undertaken by Mikhlin in [71]. The cyclic current–voltage curves of galena show that the shape of the anodic curves and the values of the oxidation currents are fundamentally different in different acids, and that in solutions of sulfuric and hydrochloric, perchloric and nitric acids, the values of the maximum anodic oxidation currents are pairwise comparable. A feature of the anodic curves, common for sulfate and perchlorate solutions, in contrast to chloride and nitric acid solutions, is a significantly lower oxidation rate at low potentials (less than 0.5 V). Unusually, in sulfuric acid, the maximum at a potential of 0.7–0.8 V is reproduced in the reverse section of the curve. The electrochemical behavior of PbS is affected even by small additions of ligands, which do not change the activity of other ions and the solubility of lead sulfate and its other salts. Specifically, a number of anions, including those that do not form stable complexes with lead, for example, perchlorate ions, first increase the anodic currents, and then cause them to drop (passivation) and rise again with a further increase in the concentration of ClO_4^- . The cathode branches of the curves in different electrolytes are more similar and are characterized by a small maximum near 0.2 V, a more intense near -0.2 V, and an increase in current at potentials below -0.4 V. Cathode current is not directly related to an increase in the time and amount of anode oxidation products; longer oxidation leads to a decrease in the reduction charge. Specifically, the charge that passes through a stationary PbS electrode during cathodic potential sweep (up to -0.35 V) after anodic polarization, carried out in the potentiostatic mode in the passivation region, has two maxima corresponding to sulfuric and perchloric acids-at pre-oxidation times of the order of 10^{-2} s and ~100 s, while there is only one in hydrochloric acid electrolyte, at 10–50 s. The processes taking place over a time of about 10 ms are associated with the probable reaction of the transition of lead into solution and depletion of the surface of the sulfide phase in lead:

$$PbS \rightarrow xPb^{2+} + Pb_{1x}S + 2e^{-}$$

and charging of the resulting defects [71].

2.5. Zinc Sulfide (Sphalerite)

Sphalerite is the most important zinc mineral, which contains various impurities. Common impurities in sphalerite are iron, lead, cadmium, and copper. Sphalerite is characterized by a high resistivity of $10^9-10^{12} \Omega \cdot \text{cm}$ [72]. To improve conductivity, carbon paste electrodes are often used in research. Impurities have a significant effect on the conductivity of a mineral.

A number of publications are devoted to the study of the electrochemical properties of sphalerite [72–78]. In particular, the anodic behavior of sphalerite is divided into two separate potential regions: dissolution in the passivation region and active dissolution. In the area of passivation, sphalerite is oxidized to zinc ions and elemental sulfur, which forms a passive layer on the surface of the mineral. In the active region, sphalerite dissolves without the formation of any passive layer.

In a later paper [79], dissolution of a sphalerite concentrate in a 0.5 M solution of sulfuric acid was studied using a carbon paste electrode at 22 °C. Various electrochemical methods were used, including cyclic voltammetry, chronoamperometry, and electrochemical impedance spectroscopy. In general, the study refines and updates the results obtained earlier. It was found that the oxidation of sphalerite proceeds in the range of anodic potentials up to 900 mV relative to the Ag/AgCl reference electrode. At low potentials (up to 400 mV), a sulfur-rich passive layer forms on the surface of the mineral. The predominant reaction on the electrode surface at 400 mV is the oxidative dissolution of sphalerite, in which zinc ions form as a result of an electrochemical reaction and a layer of elemental sulfur as a passive layer. As the potential increases to 550 mV, the passive layer partially dissolves. A further increase in the potential to 900 mV leads to the complete dissolution of the passive film and active dissolution of sphalerite.

Electrochemical behavior of natural polycrystalline sphalerite from the Zhairem deposit, which contained up to 4% iron in acid media and a borate buffer solution, was investigated in [71]. It was found that preliminary repeated acid etching of compact electrodes increases their conductivity and makes electrochemical experiments possible. The features of the current–voltage curves of sphalerite are a rapid increase in current with a cathodic potential shift and a slower one, often with a pronounced limiting current, with anodic polarization, which is typical for n-type semiconductors. In acid solutions, in some cases, there is a close to linear relationship between the anodic current and potential. Thus, based on the analysis of studies of the processes of electrochemical oxidation of minerals, it can be concluded that the main products of oxidation on the surface of sulfides are elemental sulfur, metal oxides, and hydroxides, while metal ions and various oxidized sulfur compounds, mainly thiosulfate and sulfate ions, pass into the aqueous solution.

3. Reduction of Oxygen on the Surface of Sulfides

A brief review of the existing literature on the cathodic reaction of oxygen reduction on the surface of sulfides, which is a central process during flotation, is presented below. The recognition of the electrochemical role and intensive electrochemical research into sulfide flotation began with the recognition of the role of oxygen [5]. Fundamental research by Plaksin et al. [80–83] showed that for effective flotation of various sulfides, each of these required optimal oxygen concentration in the slurry. It was observed that oxygen in the initial period of exposure contributes to the dehydration of the mineral surface, facilitates the penetration of xanthate molecules and their attachment. With prolonged exposure to oxygen, flotation properties demonstrated by sulfides deteriorate due to the formation of sulfates on their surfaces.

Recovering on the surface of sulfide minerals, oxygen ensures the occurrence of such important processes for the processing of sulfide ores as oxidation and leaching reactions, chemisorption and oxidation of sulfhydryl collectors [5–7,84].

In biohydrometallurgy, aeration of an ore heap (pile) or slurry is implemented as tank leaching of sulfide concentrates [11].

Oxygen is also of paramount importance in the processes of weathering and spontaneous combustion occurring in sulfide-containing mining waste. The activity of dissolved oxygen largely determines the kinetics of the processes of oxidation of sulfide minerals and the formation of AMD [17,20].

Australian researchers Bigler, Rand, and Woods studied the oxygen reduction reaction in nine sulfide minerals: galena, pyrrhotite, arsenopyrite, bornite, covellite, chalcopyrite, pentlandite, chalcosine, and pyrite [85–88]. The studies were carried out by voltammetry with a rotating disk electrode.

They found that the reduction reaction of molecular oxygen on pyrite developed in two parallel directions [5,89]: the four-electron process:

$$O_2 + 2H_2O + 4e^- = 4OH^-$$

or the two-electron process to yield hydrogen peroxide as an intermediate:

$$O_{2} + 2H_{2}O + 2e^{-} = H_{2}O_{2} + 2OH^{-}, H_{2}O_{2} + 2e^{-} = 2OH^{-}.$$
(1)

A similar effect of pH on the Tafel dependences of the oxygen reduction reaction on pyrite was established similar to the effect of pH on that reaction on platinum. However, while for platinum the proportion of the first reaction at all pH values did not exceed 10–15%, for pyrite it was 50% at pH = 13 and 75% at pH = 9.2. In terms of its behavior in the O₂ reduction reaction, pyrite lies between groups 1 (pyrocarbon, pyrographite) and 2 (platinum group metals) of electrode materials, where the difference between the kinetic parameters is in the $\partial E/\partial H$ slope (0 in group 1 and 2.3RT/F in group 2) [5]. Formation of H₂O₂ for the reaction of oxygen reduction on pyrite was observed by direct experiments using a rotating disk electrode with a ring [90]. In addition, that study showed that an oxidized pyrite surface coated with iron oxides and sulfoxides is less active than a reduced surface.

Reduction of oxygen on natural samples of bornite, chalcopyrite, and chalcocite in borate buffer solutions was studied in [91] by XPS and rotating disk voltammetry. It was established that on Cu_2S , CuS, and copper-rich bornite, the oxygen electroreduction reaction proceeds at much more positive potentials, i.e., there is a decrease in overvoltage compared to pyrite and chalcopyrite. Note that these results do not fully agree with the findings of [87], where this statement is valid only for chalcosine.

A conclusion was made in [91,92] that the electrochemical reduction kinetics of O_2 on iron- and copper-containing minerals are affected by the state of the mineral surface. It was found that active reaction centers in the case of pyrite and chalcopyrite were Fe²⁺ ions, in the case of covelline and chalcocite, Cu⁺ ions associated with sulfide sulfur, and in the case of bornite, Fe²⁺ and Cu⁺ ions.

The cathodic reduction of oxygen, peroxide, and hypochlorite on chalcopyrite as possible oxidizing agents in a two-stage heap leaching process under alkaline conditions was investigated by Nicol in [48]. Measurements of the mixed potential of chalcopyrite in alkaline solutions showed that the reactivity of the studied oxidizing agents descends according to the sequence:

hypochlorite > peroxide > oxygen >> chlorate.

It was found that the reduction rate of dissolved oxygen on enargite has two stages with the formation of hydrogen peroxide as an intermediate [54].

The equations that determine the currentless potential of the reactions of a number of sulfides, redox processes, which are the equations of cathodic and anodic reactions on the surface of minerals in a wide pH range (0.3–13), are presented in the monograph by Chanturiya and Vigdergauz [5].

4. Electrochemical Properties of Sulfides in Technological Processes

4.1. Electrochemical Properties of Sulfides in Flotation Processes

Electrochemical properties and galvanic interactions of sulfide minerals in flotation have been the subject of numerous studies [1-3,5,93,94]. Electrochemical processes during ore dressing are influenced by multiple factors of the flotation system: pH and pulp potential, concentration of dissolved O₂ and oxidizing agents, concentration of reducing agents, galvanic interactions between conductive grinding media and minerals at the grinding stage, etc., [95]. Studies of the flotation of sulfide minerals should combine theoretical and applied aspects of electrochemistry. Let us examine some examples.

In [8], it was found that in the presence of xanthate, the potential of pentlandite in a borate buffer solution (pH 9.2) is more significantly shifted to the negative region than the potential of pyrrhotite. Using FTIR spectroscopy, it was concluded that galvanic interactions in a mixed mineral pulp of pentlandite-pyrrhotite enhance the predominant formation of hydroxide on pyrrhotite (cathodic reduction of oxygen) and dixanthogen by the reaction:

$$2C_4H_9OCSS^- - 2e^- = (C_4H_9OCSS)_2$$

on pentlandite (anodic process). This results in increased floatability of pentlandite.

The influence of the galvanic interaction of pyrite and galena on the adsorption of xanthate on the surface of galena was studied using the density functional theory (DFT) and cyclic voltammetry [96]. The relationship between the intensity of galvanic interaction and the adsorption capacity of xanthate on the surface of galena was studied in detail. It was established that the galvanic interaction between pyrite and galena enhances the adsorption of xanthate on the surface of galena.

Selective flotation of pentlandite in the presence of non-magnetic (hexagonal) pyrrhotite has been a highly relevant research problem for a long time. In [97], the possibility was demonstrated of selective depression of non-magnetic pyrrhotite during flotation of pentlandite using H_2O_2 . H_2O_2 reactions with sulfide surface were studied by chronopotentiometry and by monitoring dissolved oxygen. Surface oxidation was diagnosed by studying surface composition depth profiles of XPS and time-of-flight secondary ion mass spectrometry (ToF-SIMS). For non-magnetic pyrrhotite, H_2O_2 reduction caused significant oxidation and rapid accumulation of oxide particles on its surface. H_2O_2 reduction on pentlandite was balanced by the oxidation of H_2O_2 to O_2 , which limited the oxidation of the mineral surface.

In connection with the high recovery of pyrite during the flotation of copper ores using sea water, the role of sodium metabisulfite, a widely used pyrite depressant, in suppressing the flotation of copper-activated pyrite was studied [98]. Metabisulfite was added prior to grinding and during pre-treatment prior to flotation. The electrochemical reactions of pyrite were studied using cyclic voltammetry. The state of the mineral surface was studied by XPS. It was established that in the absence of oxygen, metabisulfite did not suppress the flotation of copper-activated pyrite. On the contrary, in strongly reducing conditions, copper activation was observed on the pyrite surface. In the presence of oxygen, the combination of sulfite and oxygen ions can form the highly oxidizing radical SO_5^- , which is able to oxidize Cu(I)S, the product of copper activation on the surface of pyrite, with the formation of a hydrophilic $Cu(OH)_2/CuSO_4$ layer. This leads to pyrite depression during chalcopyrite flotation. The stronger depressant effect of metabisulfite when added to flotation rather than grinding is due to the greater exposure to oxygen during flotation.

Gold is often present in pyrite as micron and submicron inclusions, the so-called invisible gold [99,100]. Successful recovery of this gold requires a high level of pyrite recovery in flotation. Flotation of gold-bearing pyrite is carried out in a wide range of pH and collector concentration values with various types of grinding media. It was found that grinding media (forged steel, 15% chromium steel, and 30% chromium steel) affect pyrite flotation in different ways. At pH 5.0, both iron contamination from grinding media and xanthate oxidation played an important role in the pyrite flotation process. Iron particles on the surface of pyrite inhibit pyrite flotation. Oxidation of xanthate, on the contrary, promotes flotation. Therefore, the higher flotation activity of pyrite was observed when using chromium steel grinding media, compared to forged steel. The higher concentration of the collector also contributed to the flotation performance. At pH 7.0, pyrite flotation was mainly controlled by xanthate concentration. At low xanthate concentrations, pyrite oxidation was the predominant anodic reaction, and pyrite flotation was poor. At a high concentration of xanthate, the formation of dixanthogen predominated, which contributed to the flotation of the mineral [99]. At pH 8.5 and the same xanthate flow rate, the best pyrite flotation performance was achieved when forged steel was used as grinding media compared to 30% chromium steel, although the highest share of iron impurities was observed. At pH 8.5, pyrite oxidation predominates over xanthate oxidation, and the slurry potential plays a dominant role in mineral flotation. The high slurry oxidation-reduction potential (ORP) resulting from the chromium steel grinding media promoted pyrite oxidation, preventing xanthate oxidation. The low ORP of the slurry resulting from the forged steel grinding media still allowed xanthate oxidation, thus favoring pyrite flotation [100].

Carboxymethylcellulose (CMC) is a highly effective, non-toxic, and biodegradable depressant for Cu-Pb separation. For a wider use of the depressant, it is important to identify the mechanism of interaction between CMC and minerals. In [101], it was found that at pH above 10, galena was completely inhibited at a CMC flow rate of 250 mg·L⁻¹. The effect on chalcopyrite flotation was negligible. Zeta potential studies confirmed that CMC adsorbs much more easily on galena than on chalcopyrite. CMC adsorption kinetics on galena is described using a pseudo-second order model in which chemisorption predominates. In the presence of CMC on galena, more than 74% of the electrochemical reaction sites were inhibited. The resistance of the surface film of the galena electrode sharply increased in this case from 3838.7 to 17,547.5 Ω cm².

Some complex sulfide ores contain anglesite (PbSO₄), a relatively highly soluble mineral, which makes selective flotation difficult because Pb^{2+} is released when it dissolves, "activating" other sulfide minerals present, such as sphalerite. The effect of pyrite on the flotation activity of lead-activated sphalerite was investigated using flotation and electrochemical methods in combination with contact angle measurements [102]. In addition, the main factors behind the flotation performance of lead-activated sphalerite were investigated in detail using dissolution experiments and XPS. The paper proposed a mechanism for the depression of activated sphalerite upon interaction with pyrite. The contact angle of xanthate-treated galena in contact with pyrite was lower than that without contact, indicating desorption of xanthate and/or formation of Pb(OH)₂. Pyrite enhances the dissolution of galena as a result of galvanic interactions and the surface of galena becomes less hydrophobic due to the formation of hydrophilic surface phases Pb(OH)₂. The floatability of sphalerite activated with lead was suppressed directly due to galvanic interaction, which led to the dissolution of PbS-like phases with adsorbed xanthate, and indirectly due to the formation of hydrophilic Pb(OH)₂ on sphalerite.

The flotation performance of sulfide minerals in the presence of dithionite ions (sodium dithionite Na₂S₂O₄) was studied in [103]. It was shown that the flotation performance is affected by interactions in solutions between dithionites and xanthates and modification of the surface of sulfides with the help of derivatives of dithionite oxidation. Microflotation data showed a decrease in the recovery of chalcopyrite and galena in dithionite solutions even in the presence of xanthate. By measuring the zeta potential, it was found that the potential-determining effect of dithionites on the surfaces of sulfide minerals reduces the interaction of the collector and the mineral. Xanthate decomposition tests showed that more than half of the collector in solution decomposed in a 10 min interaction of xanthate (initial concentration 20 mg·L⁻¹) with dithionite (500 mg·L⁻¹). In addition, it was found that dithionite strongly affects the state of the surface of the studied minerals. For instance, the formation of lead sulfite on the surface of galena and iron oxides and hydroxides on chalcopyrite was observed. In the processing of massive sulfide ores, when circulated plant water is saturated with the thiosalt compounds in various concentrations, processing decisions should be taken considering many water quality parameters.

The effect of oxidative treatment using hydrogen peroxide (H_2O_2) on the flotation performance of copper sulfide minerals (chalcopyrite and bornite) and copper minerals containing arsenic (enargite and tennantite) was reported [104]. Enargite and tennantite exhibited higher floatability than chalcopyrite and bornite after oxidative treatment of the mineral mixture followed by the addition of potassium amyl xanthate (PAX). The flotation performance indicates the possibility of selective flotation of copper sulfides and copper minerals containing arsenic. Various oxidation products (CuO, Cu(OH)₂, CuSO₄, FeOOH and Fe₂(SO₄)₃) on the surface of each of the minerals are likely to be the reason for their behavior during flotation. In addition, the oxidation products can determine the adsorption of the collector on each mineral. It was found that PAX is better adsorbed on tennantite, bornite, and enargite compared to chalcopyrite. A possible mechanism explaining the behavior of a mixture of minerals during flotation is based on galvanic interactions.

The authors showed that galvanic interactions between galena and pyrite greatly enhance the dissolution of galena in [105]. This process is highly dependent on the pyrite content and the reaction time. The XPS method confirmed that the galvanic interaction between galena and pyrite enhances the oxidation of galena, which leads to an increase in oxysulfide and hydroxide compounds on the surface of the mineral. The activation of pyrite in the presence of galena is also enhanced by the migration and adsorption of lead ions on the pyrite surface. As a result, an increase in pyrite recovery was observed when butyl xanthate was used as a collector. In general, galvanic interaction changed the surface properties of galena and pyrite, which complicated the selection of minerals during flotation.

Pyrite is known to partially or completely oxidize during the storage of pyrite ores, which leads to poor performance of subsequent flotation. Potential-controlled sulfidization is used to convert the oxidized surface of the pyrite to the sulfide form prior to flotation. Huai and Peng showed that sulfidization with Na₂S at -200 mV (relative to a SHE) reduce the amount of iron hydroxide on the oxidized pyrite surface through the formation of elemental sulfur/polysulfide [106]. Iron sulfide particles formed on oxidized pyrite only after sulfidization at a potential below -300 mV. Sulfidized pyrite can react with PAX at

100 mV. However, newly formed particles with a higher reactivity than the bulk of pyrite began to oxidize at a potential of approximately -50 mV.

4.2. Galvanic Interactions of Sulfides in Hydrometallurgical Processes

Biohydrometallurgy (bioleaching) is considered a promising solution for processing low-grade ores considering its environmental and economic advantages over the conventional pyrometallurgy process [107]. Using biohydrometallurgy to recover metals from various types of mining waste is also gaining importance to support the transition to a circular economy.

The greatest challenge in the leaching of sulfides is the formation of passivating layers on the surface of minerals, consisting of poorly soluble metal-deficient polysulfides, hydroxides [Fe(OH)₂], and iron oxyhydroxides [FeO(OH) \cdot nH₂O], jarosite [KFe₃(SO₄)₂(OH)₆]. The electrical insulating properties of the deposited films significantly slow down the dissolution of sulfides. The formation of a passivating surface is influenced by various physical and chemical parameters of the system, including temperature, pH, and the redox potential of the leaching solution. To prevent the formation of passivating layers, various methods are used, for example, adjusting the redox potential of the solution, adding catalysts, conducting electrochemical leaching [9,10,39], the use of thermophilic iron- and sulfur-oxidizing microorganisms, etc., [108,109]. Some existing research on this issue is discussed below.

The largest number of studies of galvanic interactions of minerals in hydrometallurgical processes is focused on chalcopyrite. This is due to the fact that chalcopyrite is the most common, but also the most resistant copper sulfide in leaching processes [110,111]. The reasons for its refractory behavior include passivation and/or its semiconductor properties.

Considering the above, it is important to understand the mechanisms behind the processes of dissolution and passivation of chalcopyrite during bioleaching. In [112], the processes of dissolution and the mechanism of passivation during the bioleaching of chalcopyrite are summarized and discussed. Potential passivating particles are mainly sulfur-containing particles composed of polysulfide (S_n^{2-}), elemental sulfur (S_0), and undissolved sulfate (SO_4^{2-}). The effect of physicochemical properties of chalcopyrite and multiple factors on the mechanism of dissolution and passivation of chalcopyrite is summarized. The role of the redox potential in the bioleaching of chalcopyrite and methods for its control are discussed.

A detailed critical review of the existing ideas about the nature and mechanisms of the formation of passivating layers on chalcopyrite during leaching is offered by O'Connor and Eksteen [113].

Using a combination of scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS), transmission electron microscopy (TEM), focused ion beam (FIB), and XRD, they studied newly formed phases on the chalcopyrite surface during leaching in sulfate solutions in the presence of various additives [114]. The effect of such additives as ethylene glycol, wetting agent, and chloride ions both in the presence and in the absence of silver ions was studied. In the presence of silver ions and ethylene glycol, metallic silver was formed and deposited on the surface in the form of predominantly cubic nanoparticles up to 500 nm in size due to the reduction of silver ions with ethylene glycol in a sulfate environment. The deposition of metallic silver on the surface of chalcopyrite, in turn, enhanced the leaching of chalcopyrite by improving the surface conductivity. In the presence of low concentrations of chloride ions reduced the amount of sulfur formed. Layers of elemental sulfur formed in the presence of chloride ions were found to be porous. In the presence of a wetting agent, the formation of elemental sulfur was also observed both in the presence and in the absence of silver.

A combination of methods was applied to interpret the catalytic mechanism of Ag⁺ ions in the chalcopyrite–sulfuric acid-ferric sulfate system [115]. DFT calculations showed adsorption of Ag⁺ ions on the reconstructed surfaces (001)-S and (112)-S of chalcopyrite

and confirmed the possibility of the formation of silver sulfide and sulfur vacancies. XPS analysis also recorded the formation of silver sulfide on the surface of chalcopyrite. Electrochemical analysis showed that the dissolution of chalcopyrite is catalyzed by silver due to an increase in electrochemical activity. In addition, the introduction of silver atoms into the surface of chalcopyrite can cause serious distortions in its structure and increase the diffusion rate of copper atoms, mainly due to the fact that the ionic radius of Cu^+ is much smaller than the radius of Ag^+ . As a consequence, the accumulation of passivating particles was prevented and the adverse effect of the passivating layer, which consists mainly of metal polysulfides and oxides, was reduced, resulting in better dissolution kinetics. A model was proposed for interpreting the catalytic action of Ag^+ in the dissolution of chalcopyrite.

Chalcopyrite underwent hydrometallurgical processing by chemical leaching, electrochemical leaching, bioleaching, and electrobiological leaching in [109]. All bioleaching treatments were more successful than the abiotic leach experiments, however, overall copper recovery was low due to the refractory properties of chalcopyrite. Various electrochemical methods, such as cyclic voltammetry, potentiodynamic polarization, and electrochemical impedance spectroscopy, were applied to investigate differences in the surface properties of the mineral. Potentiodynamic polarization and cyclic voltammetry showed that any kind of leaching results in reduced dissolution and surface redox inactivation compared to unprocessed chalcopyrite. However, if chalcopyrite was constantly in direct contact with the active cathode electrode, its surface was activated and high oxidation currents were observed, and as a result, increased leaching. It was found that more easily leachable compounds, such as chalcocite, were formed on the surface of chalcopyrite. In addition, studies were carried out by electrochemical impedance spectroscopy in the presence of ferrous and ferric iron. No surface activation due to ferrous iron was observed. In contrast, ferric iron resulted in consistent passivation over time. Charge transfer resistance was the lowest for unprocessed chalcopyrite and surface reduced chalcopyrite, and the highest for chemically and electrochemically leached sulfide mineral. The results of this comparative electrochemical study confirm that passivation occurs to a greater extent during abiotic leaching (chemical and electrochemical leaching) compared to biotic leaching (bio-leaching and electro-bio-leaching).

The study of bioleaching at low temperatures is of practical interest. For instance, in [116], the authors examined the electrochemical behavior of chalcopyrite during bioleaching at 6 °C. Cyclic voltammetry, potentiodynamic polarization, and electrochemical impedance spectroscopy were used. SEM was used to study the phase composition of the surface. Chalcopyrite bioleaching experiments using *Acidithiobacillus ferrivorans* showed that the maximum cell density can reach 5.3×10^8 cells·mL⁻¹. A concentration of copper in the solution of about 2 g·L⁻¹ was achieved. Cyclic voltammetry showed that as the leaching time increases, the anode and cathode currents decrease, the anode peak gradually moves in the positive direction. With potentiodynamic polarization, an increase in the potential and a decrease in the corrosion current were observed. This is due to the passivation of the chalcopyrite surface. As a result of electrochemical impedance spectroscopy analysis, it was suggested that the impedance of the chalcopyrite electrode at low temperature is mainly related to the ion exchange impedance, rather than the passivation layer. This explains the difference between the low temperature process and bioleaching at normal or high temperature.

The effect of galvanic interaction between chalcopyrite (anode) and pyrite (cathode) was investigated by long-term electrochemical measurements of galvanic current and confirmed by chemical leaching and bioleaching [5,117]. For the first time, the results of measurements of galvanic corrosion (in the absence and presence of microorganisms) over several days were presented. Combined microbial and galvanic leaching of chalcopyrite showed increased copper recovery in the presence of pyrite. Corrosion led to the dissolution of minerals depending on multiple parameters (similar to the corrosion of metals). However, the dissolution of chalcopyrite during bioleaching was the highest in the presence of a

large cathode surface area of pyrite. The highest recovery of copper was observed when there were high rest potentials differences between galvanically coupled minerals (pyrite in combination with copper concentrate).

Bioleaching of chalcopyrite in combination with various pyrite grades in the presence of *Leptospirillum ferriphilum* was also studied [118]. It was established that the addition of pyrite significantly enhances the dissolution of chalcopyrite, especially when the mass ratio of pyrite and chalcopyrite is 3:1. In this case, the redox potential was maintained in the appropriate range of 350–370 mV relative to the silver–silver chloride electrode for 25 days. Pyrite played the role of an additional source of iron. The results of electrochemical tests showed that the addition of pyrite did not affect the mechanism of electrochemical dissolution of chalcopyrite. Although there was a galvanic effect in this process, it was not the main reason for the accelerated dissolution of chalcopyrite. The effect of pyrite was mainly associated with the regulation of redox potential and the formation of secondary sulfides (Cu₂S). As a result of the rapid dissolution of the formed chalcocite, a high recovery of copper (70%) was achieved.

Galvanic interactions between chalcopyrite and magnetite (Fe₃O₄) in an acidic microbial culture medium that is commonly used in bioleaching processes were investigated [119]. It was found that CuFeS₂ and Fe₃O₄ in intergrowth act as anode and cathode, respectively. Electrooxidation of CuFeS₂-Fe₃O₄ intergrowths in an acidic culture medium releases twice as many copper ions as pure chalcopyrite. This confirms that galvanic interactions prevent the formation of the typical passivating layers usually observed on the surface of chalcopyrite.

A number of interesting publications have been recently devoted to other copper sulfides.

The interactions of chalcocite and marmatite was studied in [120]. Given that the potential of marmatite is 39 mV lower, theoretically marmatite should react in this galvanic pair as an anode, thereby dissolving faster. However, the leaching results showed that the introduction of marmatite promotes the dissolution of chalcocite, and its own dissolution is hindered, despite the slight acceleration observed at an early stage in abiotic systems. It was concluded that solution factors, including redox potential, Fe³⁺ to Fe²⁺ ratio, and microbial activity may have a stronger effect than the galvanic effect. In mixed ore systems, the introduction of marmatite contributed to an increase in redox potential and the dissolution of chalcocite, while the inhibition of chalcocite during the dissolution of marmatite was due to excessive release of Cu^{2+} into solution. However, it was proved that suitable concentrations of Cu^{2+} (0.5 mg·L⁻¹ and 50 mg·L⁻¹ are optimal for biotic and abiotic systems, respectively) improve the dissolution of marmatite. A potential synergistic method of dissolution was used by controlling the mass ratios of marmatite and chalcocite. Optimal ratios were proposed equal to approximately 30:1 and 130:1 for biotic and abiotic systems, respectively. Intermediate species of elemental sulfur and "blaubleibender (blue-remaining)" covellite $(Cu_{1,2}S)$ were found after leaching, the latter being refractory and capable of preventing further dissolution of chalcocite in abiotic systems.

The synergistic effect of pyrite with different semiconductor properties on the acceleration of bioleaching of bornite was demonstrated in [121]. Hall effect tests, electrochemical studies, XRD and XPS combined with bioleaching experiments were conducted. In particular, bioleaching of mixed ore (a mixture of pyrite and bornite at a mass ratio of 3:1) was carried out. It was found that in sulfuric acid environments, the recovery of copper from mixed ore containing n-type pyrite is 10% higher than that from p-type pyrite ore. However, the difference is eliminated in the presence of *Leptospirillum ferriphilum* (*L. ferriphilum*), and eventually a copper recovery of 85% is achieved. The XRD and XPS results of the leached residues confirmed that pyrite with different semiconductor properties cannot change the mechanism of bornite dissolution. Large amounts of jarosite and elemental sulfur formed in the last stage of bioleaching are responsible for the passivation of bornite. Electrochemical measurements additionally confirmed the conclusion made on the basis of XRD tests and showed that n-type pyrite is better at intensifying the dissolution of bornite than p-type pyrite. Introducing additives into the pyrite system eliminates the limiting stage of the process and achieves a high recovery of copper during the leaching of copper–arsenic concentrates containing enargite in a sulfuric acid solution of $Fe_2(SO_4)_3$ [122]. It was found that the rate of dissolution of the mineral is not affected by the concentration of ferric ion and sulfuric acid, and the resulting elemental sulfur covers the surface of enargite with a porous layer, while the surface of pyrite remains clean. Arsenic dissolves similarly to copper and goes into solution mainly in the trivalent form. In general, the study demonstrated the possibility of complete dissolution of enargite under oxidizing conditions in a sulfuric acid environment, using crushed pyrite as a process catalyst. The new way of processing enargite allows copper–arsenic concentrates to be processed in leaching tanks at atmospheric pressure without calcination, ultrafine grinding, pressure treatment, or adding bacteria.

The galvanic interaction between enargite and pyrite in the process of bioleaching was studied in [123]. The experiment showed that the addition of pyrite significantly increases the enargite leaching rate due to the galvanic effect. However, the effect was reduced due to oxidation of the pyrite and reduction in the surface area of the pyrite during the bioleaching process. The rate of dissolution of enargite without pyrite was controlled by diffusion through the film of the passivating layer on the surface of enargite. The presence of pyrite changed the rate-limiting factor in the dissolution of enargite. Thus, the addition of pyrite eliminates the passivating effect. Electrochemical studies showed that the mixed potentials and dissolution current densities of enargite electrodes increase when enargite is in contact with a pyrite electrode and further increase with increasing surface area of the pyrite electrode. The effect of the surface area of the pyrite electrode on the dissolution of the enargite electrodes was quantified by the kinetics of semi-elemental reactions occurring in the pyrite-enargite galvanic pair at mixed potentials with oxygen and ferric ions as oxidizing agents. Studies of electrochemical impedance spectroscopy demonstrated a significant decrease in the charge transfer resistance and the resistance of the passivating film of the enargite electrode in contact with pyrite. Galvanically bonded pyrite continued to act as a cathode to enhance the oxidation of enargite with oxygen and ferric ions even after its passivation.

Cyanidation is one of the main hydrometallurgical processes. During cyanidation, galvanic interactions of gold and the mineral occur, which can prevent the dissolution of the metal [124]. Simulations were performed based on the DFT to reveal some important electronic features of gold/pyrite associations during cyanidation of gold. It was demonstrated that the preferential adsorption of cyanide on gold rather than on the pyrite surface is regulated by either galvanic interactions or gold oxidation, causing a higher electron deficit at the gold sites. Due to an increase in the electron deficit in Au atoms during oxidation, the interaction of gold with CN⁻ will increase and thus contribute to the dissolution of gold during the cyanidation process.

5. Oxidation of Sulfide Minerals during Mining Waste Storage

The electrochemical behavior of sulfides must be taken into account in order to predict AMD generation processes and the transfer of heavy metals and other toxic elements into soil and water during mining waste storage in overburden dumps, at concentration tailings and slag storage facilities [17,20,125]. Understanding the kinetics of these processes, taking into account the influence of galvanic interactions, is also useful in developing plans for the preservation and reclamation of storage sites [126–130].

Forecasting water quality in mines and open pits, taking into account the impact on the environment, is of great importance in the development of mineral deposits. AMD forms when sulfides are in contact with oxygen and water. At the same time, several parameters influence the quality of the final drainage. Galvanic interactions determine the reactivity of sulfide minerals. Therefore, galvanic interactions must be studied to predict the generation potential of AMD and to estimate the rate of transition of environmentally hazardous metals and metalloids into the environment [19,131].

Below, the results of some studies on galvanic interactions of sulfide minerals in relation to the storage conditions of mining waste are presented.

Five mixtures consisting of free grains of quartz/pyrite, quartz/chalcopyrite, quartz/sphalerite, quartz/pyrite/chalcopyrite, and quartz/pyrite/sphalerite underwent geochemical testing over 200 days [19]. The mixtures were leached twice a week. The filtrates were analyzed for pH, ORP, electrical conductivity, and sulfate and metal concentrations. The results of these tests confirmed the galvanic interactions of sulfides. At the same time, pyrite was galvanically protected during the entire test period in a mixture of quartz/pyrite/chalcopyrite, as well as Zn, Mn, and Cd from sphalerite, was accelerated in the presence of pyrite.

To understand the mechanisms of dissolution of sulfides, the heterogeneity of the composition and properties of the surface of minerals is of decisive importance [132]. Using synchrotron scanning photoelectron microscopy, fresh and partially dissolved chalcopyrite surfaces (HClO₄, pH 1.0, redox potential 650 mV, 75 °C) were studied. In all samples, S^{2-} (bulk), S_2^{2-} , and S_n^{2-} in various ratios were found. Oxidation occurred heterogeneously on a submicron scale. Compared to chalcopyrite, partially dissolved after 5 days, prolonged dissolution up to 10 days did not increase oxidation, but surface roughness increased noticeably. When 4 mM iron was added, S_0 , SO_4^{2-} were observed, but not SO_3^{2-} . This indicates that the higher activity/concentration of Fe³⁺ promotes heterogeneous oxidation of sulfur. Upon contact of pyrite with chalcopyrite, a significantly greater oxidation of the chalcopyrite surface was observed than in other studied systems. At the same time, S_0 , SO_3^{2-} , and SO_4^{2-} distributed non-uniformly over the surface were detected. It was suggested that the oxidative dissolution of chalcopyrite is enhanced by an increase in the cathode area of pyrite and an increase in the activity/concentration of Fe³⁺. Thus, the dissolution of chalcopyrite will be accelerated in contact with pyrite at solution redox potential intermediate between the rest potentials of chalcopyrite and pyrite (560 mV and 660 mV, respectively) and/or in acidic water with a high iron content, which in turn will lead to accelerated formation of supergene minerals and enhanced metalliferous drainage.

The galvanic effect of pyrite was studied on the transfer of As into solution as a result of the oxidation of arsenopyrite in circumneutral solutions under oxygen depletion and saturation conditions [133]. Oxidation experiments were carried out in a flow reactor in the absence of FeS₂ particles and at different contents of the sulfide. The results showed that constant physical contact between FeAsS and FeS₂ particles causes an increase in As accumulation in the solution, mainly under conditions of saturation with O₂. At 30% of FeS₂ mass, increase in arsenic concentrations compared to those without FeS₂ was 82% in solutions of depleted O₂ and 117% in solutions saturated with O₂. In steady state, As dissolution rate increased from $(4.9 \pm 0.5) \cdot 10^{-4} \,\mu \text{mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$ (0%wt. FeS₂) to $(1.1-1.9) \cdot 10^{-3} \,\mu \text{mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$ (5–30% wt. FeS₂) when saturated with O₂. An analysis of FeAsS samples after oxidation showed that the oxidized particles were partially or completely covered with precipitates of various sizes, shapes, and compositions (for example, As-S containing ferrihydrite, elemental sulfur, and As-O phases). A thin (3–4 nm) amorphous ferric oxyhydroxide layer containing S-As was also identified on oxidized FeAsS with Fe(III) and As(III) particles.

Experiments carried out by Japanese researchers confirmed the influence of galvanic interactions with pyrite on the kinetics of dissolution of sphalerite and galena in sea water [134]. Mixtures of hydrothermal sulfides with varying amounts of pyrite were reacted with artificial sea water for 144 h, then the dissolution rates of Zn and Pb were measured by extraction. The dissolution rate of sphalerite increased with increasing pyrite content. The lead concentration also increased when the pyrite-rich sample was dissolved. Zn dissolution rates for samples with high Fe/Zn molar ratio (>0.26) were (1.3–1.5)·10⁻¹⁰ mol·m⁻²·s⁻¹, which is about an order of magnitude higher than that of samples with a low Fe/Zn molar ratio (<0.002; (1.6–1.8)·10⁻¹ mol·m⁻²·s⁻¹). The dissolution rate of Pb from the sample with high pyrite content was about nine orders of

magnitude faster ($8.4 \times 10^{-10} \text{ mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$) than the dissolution rate of pure galena ($8.9 \times 10^{-19} \text{ mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$). It was shown that low electrode potential sulfide minerals such as sphalerite and galena can be selectively dissolved from a mixture of sulfides containing high potential minerals (e.g., pyrite). This fact has an impact on the geological, geochemical, and chemical processes in ore mining and other industrial operations.

The research goal of paper [135] was to determine the combined effect of galvanic interaction and the addition of silicate on the dissolution of pyrite, the main factor in AMD. Experiments with minerals (pyrite, sphalerite, and galena) and mixtures (pyrite–sphalerite and pyrite–galena) were carried out with the addition of 0.8 mM dissolved silicate (sodium metasilicate). The dissolution rate of pyrite was reduced by 98% with the addition of silicate at pH 7.4. When pH was lowered to 3.0 and 5.0, the effect was insignificant. The effect of galvanic interaction on the decrease in pyrite dissolution decreased with increasing pH and was greater in the presence of sphalerite than galena. In contrast, the effect of silicate addition increased with increasing pH and was greater in the presence of galena than sphalerite. The greatest combined effect was observed at pH 7.4, when leaching <0.1% pyrite in both bisulfide systems. The addition of silicate also significantly reduced the dissolution of sphalerite or galena (by 10–44%, except for the pyrite–sphalerite system at pH 3). The authors hypothesize that silicate addition may be applicable over a wide pH range in mixed sulfide systems to both reduce pyrite dissolution and reduce metalliferous drainage.

Thus, the analysis of the presented results indicates a significant effect of galvanic interactions of sulfides on the processes of their dissolution and the transfer of their reaction products into water bodies and soil. Fundamentally different conditions for the electrochemical oxidation of sulfides develop at storage tailings and tailings from current production facilities [17]. At storage tailings facilities, due to better aeration and saturation of pore solutions with oxygen, the mixed potentials of sulfide minerals shift to the anode region, which leads to an increase in the rate of sulfide oxidation products is controlled by hydrodynamic conditions, the concentration of oxygen, and ferric ions in solution.

6. Conclusions

Sulfide minerals of non-ferrous metals are conductors and/or semiconductors, which cause their oxidation by the mechanism of galvanic corrosion. Both anodic and cathodic regions are present on the mineral surface. Usually, the surface areas related to impurity atoms, dislocations, grain boundaries, etc., become anodic regions, and the rest of the surface becomes cathodic regions. The anodic regions dissolve, and the oxidizing agent is reduced in the cathodic regions. Sulfide minerals are characterized by the formation of intergrowth. The intergrowth in the electrolyte solution catalyzes the oxidation of the electronegative sulfide, while the rate of the electropositive mineral slows down.

The most important problem of electrochemical oxidation processes is the passivation of sulfides, caused by the screening of the surface by solid oxidation products—elemental sulfur, poorly soluble salts, metal oxides, and hydroxides. It has also been suggested that the surface metal-deficient structures formed during corrosion are responsible for the passivation. As a result of corrosion and violations of the stoichiometric composition, the properties of real surface layers of sulfides change significantly.

The electrochemical properties of sulfide minerals are manifested both in the industrial processes of flotation and hydrometallurgy and in the natural geological setting or during the storage of sulfide-containing mining, mineral processing, and metallurgical industry waste.

Data on the electrochemical properties of sulfides make it possible to scientifically substantiate and select optimal electrochemical treatments for mineral slurries to control the processes of adsorption of collectors during flotation [5,9].

Studies of the electrochemical behavior of sulfides in various electrolytes make it possible to determine the limiting stages of the processes of oxidation and dissolution, and

as a result, by controlling the process of pulp oxidation, to achieve the desired intensification effect on the leaching of sulfide ores and non-ferrous metal concentrates.

The electrochemical behavior of sulfides must be taken into account in order to predict AMD generation processes during mining waste storage in overburden dumps, at concentration tailings and slag storage facilities. Better understanding the role of galvanic interactions in geochemical testing and geochemical modeling will help develop effective environmental protection measures for the long-term preservation, reclamation, and decontamination of industrial sites containing sulfides.

The presented results of comprehensive studies substantiate the relevance of investigating the electrochemical properties of sulfides for optimizing industrial processes and ensuring the environmental safety in mining regions.

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References

- Plaksin, I.N.; Shafeev, R.S.; Chanturiya, V.A. The relationship between the energy structure of mineral crystals and their flotation properties. In Proceedings of the VIII International Mineral Processing Congress; Mekhanobr: Leningrad, Russia, 1969; Volume 2, pp. 235–245. (In Russian).
- 2. Plaksin, I.N.; Shafeev, R.S. Effects of some semiconductor properties of the surface on the interaction of xanthate with galena. *Dokl. Akad. Nauk. USSR* **1960**, *132*, 399–401. (In Russian)
- 3. Plaksin, I.N.; Shafeev, R.S. On the effects of the electrochemical potential on the distribution of xanthate across the surface of sulfides. *Dokl. Akad. Nauk. USSR* **1958**, *118*, 546–548. (In Russian)
- 4. Abramov, A.A.; Avdohin, V.M. Oxidation of Sulfide Minerals in Benefication Processes; Gordon and Breach Science Publishers: Philadelphia, PA, USA, 1997; 321p.
- 5. Chanturiya, V.A.; Vigdergauz, V.E. *Electrochemistry of Sulfides. Theory and Practice of Flotation*; Publishing House Ore and Metals: Moscow, Russia, 2009; 280p.
- Buckley, A.N.; Hamilton, I.C.; Woods, R. Flotation of sulphide minerals. In *Developments in Mineral Processing*; Forssberg, K.S.E., Ed.; Elsevier: Amsterdam, The Netherlands, 1985; pp. 41–115.
- Woods, R. Flotation of sulfide minerals. In *Reagents in Mineral Technology*; Somasundaran, P., Moudgil, B.M., Eds.; Marcel Dekker: New York, NY, USA, 1987; pp. 39–78.
- Bozkurt, V.; Xu, Z.; Finch, J.A. Pentlandite/pyrrhotite interaction and xanthate adsorbtion. *Int. J. Miner. Process.* 1998, 52, 203–214. [CrossRef]
- 9. Chanturiya, V.A. Scientific foundations of the electrochemical technology of mineral processing processes. *Vestn. Akad. Nauk. USSR* **1985**, *9*, 39–47. (In Russian)
- 10. Chanturiya, V.A.; Nazarova, G.N. Electrochemical Technology for Beneficiation and Hydrometallurgical Processes; Nauka: Moscow, Russia, 1977; 160p. (In Russian)
- 11. Watling, H.R. Review of biohydrometallurgical metals extraction from polymetallic mineral resources. *Minerals* **2015**, *5*, 1–60. [CrossRef]
- 12. Muñoz, A.; Bevilaqua, D.; Garcia, O., Jr. Leaching of Ni and Cu from mine wastes (tailings and slags) using acid solutions and *A. Ferrooxidans. Adv. Mater. Res.* **2009**, 71–73, 425–428. [CrossRef]
- Riekkola-Vanhanen, M.; Palmu, L. Talvivaara Nickel Mine–from a project to a mine and beyond. In Proceedings of the Symposium Ni-Co 2013, San Antonio, TA, USA, 3–7 March 2013; pp. 269–278.
- 14. Tanne, C.K.; Schippers, A. Electrochemical applications in metal bioleaching. Adv. Biochem. Eng. Biotechnol. 2017, 167, 327–359.
- 15. Tanne, C.K.; Schippers, A. Electrochemical process engineering in biohydrometallurgical metal recovery from mineral sulfides. *Solid State Phenom.* **2017**, *262*, 118–121. [CrossRef]

- 16. Holmes, P.R.; Crundwell, F.K. Kinetic aspects of galvanic interactions between minerals during dissolution. *Hydrometallurgy* **1995**, 39, 353–375. [CrossRef]
- 17. Kalinnikov, V.T.; Makarov, D.V.; Makarov, V.N. Oxidation sequence of sulfide minerals in operating and out-of-service mine waste storage. *Theor. Found. Chem. Eng.* 2001, 35, 63–68. [CrossRef]
- Parbhakar-Fox, A.; Lottermoser, B.; Bradshaw, D. Evaluating waste rock mineralogy and microtexture during kinetic testing for improved acid rock drainage prediction. *Miner. Eng.* 2013, 52, 111–124. [CrossRef]
- Chopard, A.; Plante, B.; Benzaazoua, M.; Bouzahzah, H.; Marion, P. Geochemical investigation of the galvanic effects during oxidation of pyrite and base-metals sulfides. *Chemosphere* 2017, *166*, 281–291. [CrossRef] [PubMed]
- 20. Kwong, Y.T.J.; Swerhone, G.W.; Lawrence, J.R. Galvanic sulphide oxidation as a metal-leaching mechanism and its environmental implications. *Geochem. Explor. Environ. Anal.* **2003**, *3*, 337–343. [CrossRef]
- Radyushkina, K.A.; Wigdergauz, V.E.; Tarasevich, M.R.; Chanturiya, V.A. Electrochemistry of sulfide minerals. Electrochemical processes on the surface of pyrite and pyrrhotite in aqueous solutions of electrolytes. *Elektrokhimjya* 1986, 22, 1394–1398. (In Russian)
- Chanturiya, V.A.; Makarov, V.N.; Makarov, D.V.; Vasil'eva, T.N.; Belyaevskii, A.T. Electrochemical oxidation of pyrrhotine in alkaline media. *Russ. J. Electrochem.* 1999, 35, 759–763.
- 23. Andriamanana, A.; Lamache, M. Etude electrochimique de la pyrite en milieu acide. Electrochim. Acta 1983, 28, 177–183. [CrossRef]
- Hamilton, I.C.; Woods, R. An investigation of surface oxidation of pyrite and pyrrhotite by linear potential sweep voltammetry. J. Electroanal. Chem. 1979, 101, 327–343. [CrossRef]
- Mischra, K.K.; Osseo-Asare, K. Aspects of the interfacial electrochemistry of semiconductor pyrite (FeS₂). J. Electrochem. Soc. 1988, 135, 2502–2509. [CrossRef]
- Moses, C.O.; Nordström, D.K.; Herman, J.S.; Mills, A.L. Aqueous pyrite oxidation by dissolved oxygen and by ferric ion. *Geochim. Cosmochim. Acta* 1987, 51, 1561–1571. [CrossRef]
- Yin, Q.; Kelsall, G.H.; Vaughan, D.J.; Welham, N.J. Rotating ring(Pt)-disc(FeS₂) electrode behavior in hydrocloric solutions. J. Colloid Interface Sci. 1999, 210, 375–383. [CrossRef]
- 28. Kelsall, G.H.; Yin, Q.; Vaughan, D.J.; England, K.E.R.; Brandon, N.P. Electrochemical oxidation of pyrite (FeS₂) in aqueous electrolytes. *J. Electroanal. Chem.* **1999**, *47*, 116–125. [CrossRef]
- 29. Wang, X.-H. Interfacial electrochemistry of pyrite oxidation and flotation. J. Colloid Interface Sci. 1996, 178, 628–637. [CrossRef]
- Chernyshova, I.V. Pyrite oxidation mechanism in aqueous solutions: An in situ FTIR study. Russ. J. Electrochem. 2004, 40, 69–77. [CrossRef]
- Holmes, P.R.; Crundwell, F.K. Polysulfides do not cause passivation: Results from the dissolution of pyrite and implications for other sulfide minerals. *Hydrometallurgy* 2013, 139, 101–110. [CrossRef]
- 32. Mikhlin, Y. Reactivity of pyrrhotite surfaces: An electrochemical study. Phys. Chem. Chem. Phys. 2000, 2, 5672–5677. [CrossRef]
- 33. Kuklinskii, A.V.; Mikhlin, Y.L.; Pashkov, G.L.; Kargin, V.F.; Asanov, I.P. Conditions for the formation of a nonequilibrium nonstoichiometric layer on pyrrhotite in acid solutions. *Russ. J. Electrochem.* **2001**, *37*, 1269–1276. [CrossRef]
- 34. Mikhlin, Y.L.; Kuklinskii, A.V.; Pashkov, G.L.; Asanov, I.P. Pyrrhotite electrooxidation in acid solutions. *Russ. J. Electrochem.* 2001, 37, 1277–1282. [CrossRef]
- 35. Habashl, F.; Torres-Âcuna, N. The anodic dissolution of copper(l) sulfide and the direct recovery of copper and elemental sulfur from white metal. *Trans. Metall. Eng. AIME* **1968**, 242, 780–787.
- 36. Nechvoglod, O.V.; Pikalov, S.M. Mechanism of passive layer formation during electrochemical oxidation of copper(I) sulfide. *Russ. J. Electrochem.* **2021**, *57*, 580–586. [CrossRef]
- O'Dell, C.S.; Walker, G.W.; Richardson, P.E. Electrochemistry of the chalcocite-xanthate system. J. Appl. Electrochem. 1996, 16, 544–554. [CrossRef]
- Ghali, E.; Lewenstam, A. Electrodissolution of synthetic covellite in hydrochloric acid. J. Appl. Electrochem. 1982, 12, 369–376. [CrossRef]
- 39. Wigdergauz, V.E.; Chanturiya, V.A.; Teplyakova, M.V. Potentiometric study of chalcopyrite electroleaching. In *Combined Ore Processing Methods*; IPKON, Academy of Sciences of the USSR: Moscow, Russia, 1988; pp. 13–22. (In Russian)
- 40. Biegler, T.; Swift, D.A. Anodic electrochemistry of chalcopyrite. J. Appl. Electrochem. 1979, 9, 545–554. [CrossRef]
- 41. Biegler, T.; Swift, D.A. The electrolytic reduction of chalcopyrite in acid solution. J. Appl. Electrochem. 1977, 6, 229–235. [CrossRef]
- 42. Radyushkina, K.A.; Wigdergauz, V.E.; Tarasevich, M.R.; Chanturiya, V.A. Electrochemistry of sulfide minerals. Surface redox transformations of chalcopyrite and chalcocite in aqueous solutions of electrolytes. *Electrochimiya* **1986**, *22*, 1491–1496. (In Russian)
- 43. Chander, S. Electrochemistry of sulfide flotation: Growth characteristics of surface coating and their properties, with special reference to chalcopyrite and pyrite. *Int. J. Miner. Process.* **1991**, *33*, 121–134. [CrossRef]
- Velásquez, P.; Gómez, H.; Ramos-Barrado, J.R.; Leinen, D. Voltammetry and XPS analysis of a chalcopyrite CuFeS₂ electrode. *Colloids Surf. A* 1998, 140, 369–375. [CrossRef]
- Velásquez, P.; Gómez, H.; Leinen, D.; Ramos-Barrado, J.R. Electrochemical impedance spectroscopy of chalcopyrite CuFeS₂ electrode. *Colloids Surf. A* 1998, 140, 177–182. [CrossRef]
- 46. Moyo, T.; Petersen, J.; Nicol, M.J. The electrochemistry and kinetics of the oxidative dissolution of chalcopyrite in ammoniacal solutions. Part I–Anodic reactions. *Hydrometallurgy* **2018**, *182*, 97–103. [CrossRef]
- 47. Moyo, T.; Petersen, J.; Nicol, M.J. The electrochemistry and kinetics of the oxidative dissolution of chalcopyrite in ammoniacal solutions. Part II–Cathodic reactions. *Hydrometallurgy* **2019**, *184*, 67–74. [CrossRef]

- 48. Nicol, M.J. The electrochemistry of chalcopyrite in alkaline solutions. Hydrometallurgy 2019, 187, 134–140. [CrossRef]
- 49. Price, D.C.; Chilton, J.P. The anodic reactions of bornite in sulfuric acid solution. Hydrometallurgy 1981, 7, 117–133. [CrossRef]
- 50. Zhao, H.; Huang, X.; Hu, M.; Zhang, C.; Zhang, Y.; Wang, J.; Qin, W.; Qiu, G. Insights into the surface transformation and electrochemical dissolution process of bornite in bioleaching. *Minerals* **2018**, *8*, 173. [CrossRef]
- Ásbjornsson, J.; Kelsall, G.H.; Pattrick, R.A.D.; Vaughan, D.J.; Wincott, P.L.; Hope, G.A. Electrochemical and surface analytical studies of enargite in acid solution. J. Electrochem. Soc. 2004, 151, E250–E256. [CrossRef]
- 52. Ma, Y.; Yang, Y.; Skinner, W.; Chen, M. Electrochemical and spectroscopic analysis of enargite (Cu₃AsS₄) dissolution mechanism in sulfuric acid solution. *Hydrometallurgy* **2020**, *194*, 105346. [CrossRef]
- Nicol, M.J.; Ruiz-Sanchez, A.; Senanayake, G.; Tjandrawan, V.; Lapidus, G.T. The electrochemical behaviour of enargite in ammoniacal solutions. I. Anodic reactions. *Hydrometallurgy* 2019, 188, 92–100. [CrossRef]
- Nicol, M.J.; Ruiz-Sanchez, A.; Senanayake, G.; Tjandrawan, V.; Lapidus, G.T. The electrochemical behaviour of enargite in ammoniacal solutions. II. Cathodic reactions. *Hydrometallurgy* 2019, 189, 105115. [CrossRef]
- 55. Buckley, A.N.; Woods, R. Electrochemical and XPS studies of the surface oxidation of synthetic heazlewoodite (Ni₃S₂). *J. Appl. Electrochem.* **1991**, *21*, 575–582. [CrossRef]
- 56. Power, G.P. The electrochemistry of the nickel sulfides. 1. NiS. Aust. J. Chem. 1981, 34, 2287–2291. [CrossRef]
- 57. Power, G.P. The electrochemistry of the nickel sulfides–2. Ni₃S₂. Electrochim. Acta 1982, 27, 359–364. [CrossRef]
- 58. Aromaa, J. Electrochemical dissolution of synthetic heazlewoodite (Ni₃S₂). *Physicochem. Probl. Miner. Processing* **2011**, *46*, 51–64.
- 59. Thornber, M.R. Mineralogical and electrochemical stability of the nickel –iron sulphides–pentlandite and violarite. *J. Appl. Electrochem.* **1983**, *13*, 253–267. [CrossRef]
- 60. Warner, T.E.; Rice, N.M.; Taylor, N. An electrochemical study of the oxidative dissolution of synthetic pentlandite in aqueous media. *Hydrometallurgy* **1992**, *31*, 55–90. [CrossRef]
- 61. Warner, T.E.; Rice, N.M.; Taylor, N. Electrochemical study of oxidative dissolution of synthetic violarite in aqueous media. In *Hydrometallurgy'94*; Springer: Berlin/Heidelberg, Germany, 1994; pp. 273–287.
- 62. Makarov, D.V.; Forsling, W.; Makarov, V.N. Electrooxidation of pentlandite in a carbonate solution. *Russ. J. Electrochem.* 2004, 40, 420–423. (In Russian) [CrossRef]
- 63. Mikhlin, Y.L.; Galkin, P.S.; Kopteva, S.A. Electrochemical study of galena surfaces in acid solutions. *Izv. Sib. Otd. Akad. Nauk. SSSR. Ser. Him.* **1988**, *2*, 11–17. (In Russian)
- 64. Chernyshova, I.V. In situ study of the oxidation of galenite (natural PbS) in alkaline media by FTIR spectroscopy: Anode processes in the absence of oxygen. *Russ. J. Electrochem.* **2001**, *37*, 579–584. [CrossRef]
- 65. Ahlberg, E.; Elfstrom, B.A. Anodic polarization of galena in relation to flotation. Int. J. Miner. Process. 1997, 33, 135–142. [CrossRef]
- 66. Cisneros-Gonzalez, I.; Oropeza-Guzman, M.T.; Gonzalez, I. Cyclic voltammetry applied to the characterisation of galena. *Hydrometallurgy* **1999**, *53*, 133–144. [CrossRef]
- 67. Gardner, J.R.; Woods, R. Study of surface oxidation of galena using cyclic voltammetry. J. Electroanal. Chem. 1979, 100, 447–459. [CrossRef]
- 68. Nicol, M.J.; Paul, R.L.; Diggle, J.W.; Saunders, A.P. The electrochemical behaviour of galena (lead sulphide): II. Catodic reduction. *Electrochim. Acta* **1978**, *23*, 635–639. [CrossRef]
- 69. Paul, R.L.; Nicol, M.J.; Diggle, J.W.; Saunders, A.P. The electrochemical behaviour of galena (lead sulphide): I. Anodic dissolution. *Electrochim. Acta* 1978, 23, 625–633. [CrossRef]
- 70. Pritzker, M.D.; Yoon, R.H. Thermodynamic calculation on sulfide flotation system. 2. Comparison with electrochemical experiments on the galena-ethylxanthate system. *Int. J. Miner. Process.* **1987**, *20*, 267–290. [CrossRef]
- Mikhlin, Y.L. State of the Real Surface and Features of the Kinetics of Dissolution and Oxidation of Metal Sulfides in Interaction with Acid Solutions. Extended abstract. Ph.D. Thesis, Institute of Chemistry and Chemical Technologies of the SB RAS, Krasnoyarsk, Russia, 2003; 40p. (In Russian).
- Ahlberg, E.; Asbjörnsson, J. Carbon paste electrodes in mineral processing: An electrochemical study of sphalerite. *Hydrometallurgy* 1994, 36, 19–37. [CrossRef]
- 73. Choi, W.K.; Torma, A.E.; Ohline, R.W.; Ghali, E. Electrochemical aspects of zinc sulphide leaching by Thiobacillus ferrooxidans. *Hydrometallurgy* **1993**, *33*, 137–152. [CrossRef]
- Lotens, J.P.; Wesker, E. The behaviour of sulphur in the oxidative leaching of sulphidic minerals. *Hydrometallurgy* 1987, 18, 39–54. [CrossRef]
- 75. Nava, J.L.; Oropeza, M.T.; Gonzalez, I. Oxidation of Mineral Species as a Function of the Anodic Potential of Zinc Concentrate in Sulfuric Acid. J. Electrochem. Soc. 2004, 151, B387–B393. [CrossRef]
- Narasagoudar, R.A.; Johnson, J.W.; O'Keefe, T.J. The anodic dissolution of ZnS electrodes in sulfuric acid solutions. *Hydrometallurgy* 1982, 9, 37–55. [CrossRef]
- 77. Srinivasan, G.N.; Iyer, S.V. Cyclic voltammetric studies on sphalerite electrodes. Bull. Electrochem. 2000, 16, 5–9.
- Urbano, G.; Meléndez, A.M.; Reyes, V.E.; Veloz, M.A.; González, I. Galvanic interactions between galena–sphalerite and their reactivity. *Int. J. Miner. Process.* 2007, 82, 148–155. [CrossRef]
- Karimia, S.; Ghahreman, A.; Rashchia, F.; Moghaddam, J. The mechanism of electrochemical dissolution of sphalerite in sulfuric acid media. *Electrochim. Acta* 2017, 253, 47–58. [CrossRef]

- 80. Plaksin, I.N.; Shafeev, R.S. Effect of electrochemical inhomogeneity of the surface of sulfide minerals on the distribution of xanthate under flotation. *Dokl. Akad. Nauk. USSR* **1958**, *121*, 145–146. (In Russian)
- 81. Plaksin, I.N.; Shafeev, R.S. Mechanism of occurrence of electrochemical inhomogeneity in the surface of sulfide minerals. *Dokl. Akad. Nauk. USSR* **1959**, *125*, 599–600. (In Russian)
- Plaksin, I.N.; Shafeev, R.S. Quantitative assessment of xanthate attachment depending on the surface properties of sulfide minerals. *Dokl. Akad. Nauk. USSR* 1959, 128, 777–780. (In Russian)
- 83. Plaksin, I.N.; Shafeev, R.S. Hydrophobic effect of oxygen on the surface of sulfide minerals. *Dokl. Akad. Nauk. USSR* **1960**, 135, 140–142. (In Russian)
- 84. Chander, S. Electrochemistry of sulfide mineral flotation. Min. Metall. Explor. 1988, 5, 104–114. [CrossRef]
- 85. Biegler, T. Oxygen reduction on sulphide minerals. 2. Relation between activity and semiconducting properties of pyrite electrodes. *J. Electroanal. Chem.* **1976**, *70*, 265–275. [CrossRef]
- 86. Biegler, T.; Rand, D.A.J.; Woods, R. Oxygen reduction on sulphide minerals. 1. Kinetics and mechanism at rotated pyrite electrodes. *J. Electroanal. Chem.* **1975**, *60*, 151–162. [CrossRef]
- 87. Biegler, T.; Rand, D.A.J.; Woods, R. Oxygen reduction on sulphide minerals. In *Trends in Electrochemistry*; Bockris, J.O.M., Ed.; Plenum Press: New York, NY, USA, 1977; pp. 291–302.
- Rand, D.A.J. Oxygen reduction on sulphide minerals. 3. Comparison of activities of various copper, iron, lead and nickel mineral electrodes. J. Electroanal. Chem. 1977, 83, 19–32. [CrossRef]
- 89. Doo, S.G.; Sohn, H.J. Electrochemical reduction of oxygen on a pyrite surface. Min. Metall. Explor. 1989, 6, 201–205. [CrossRef]
- Wigdergauz, V.E.; Radyushkina, K.A. Mechanism and kinetics of oxygen reduction on pyrite. In Achieving Complete Recovery of Valuable Components in Mineral Processing; IPKON, Academy of Sciences of the USSR: Moscow, Russia, 1986; pp. 8–20. (In Russian)
- Tarasevich, M.R.; Kudaikulova, G.A.; Radyushkina, K.A. Electroreduction of oxygen on copper-containing sulfide minerals. *Russ. J. Electrochem.* 2000, 36, 49–53. [CrossRef]
- Kudaykulova, G.A. Electrochemical Processes of Oxidation on the Surface of Sulfide Minerals in Aqueous and Aprotic Environments. Extended Abstract. Ph.D. Thesis, Institute of Electrochemistry, Academy of Sciences of the USSR, Moscow, Russia, 1990; 22p. (In Russian).
- Pozzo, R.L.; Malicsi, A.S.; Iwasaki, I. Pyrite-pyrrhotite-grinding media contact and its effect on flotation. *Min. Metall. Explor.* 1990, 7, 16–21. [CrossRef]
- 94. Rao, S.R.; Finch, J.A. Galvanic interaction studies on sulphide minerals. Can. Metall. Q. 1988, 27, 253–259. [CrossRef]
- 95. Hu, Y.; Wu, M.; Liu, R.; Sun, W. A review on the electrochemistry of galena flotation. *Miner. Eng.* 2020, 150, 106272. [CrossRef]
- 96. Ke, B.; Chen, J.; Li, Y.; Chen, Y. Galvanic contacting effect of pyrite on xanthate adsorption on galena surface: DFT simulation and cyclic voltammetric measurements. *Physicochem. Probl. Miner. Process.* **2018**, *54*, 826–836.
- 97. Qi, C.; Khalkhali, M.; Grundy, J.S.; Liu, B.; Wang, A.; Liu, Q. Unraveling H₂O₂-stimulated surface oxidation of non-magnetic pyrrhotite and pentlandite by underlying electronic structures. *Miner. Eng.* **2021**, *170*, 106964. [CrossRef]
- Mu, Y.; Peng, Y. The role of sodium metabisulphite in depressing pyrite in chalcopyrite flotation using saline water. *Miner. Eng.* 2019, 142, 105921. [CrossRef]
- Mu, Y.; Cheng, Y.; Peng, Y. The interaction between grinding media and collector in pyrite flotation at neutral and slightly acidic pH. *Miner. Eng.* 2020, 145, 106063. [CrossRef]
- 100. Mu, Y.; Cheng, Y.; Peng, Y. The interaction of grinding media and collector in pyrite flotation at alkaline pH. *Miner. Eng.* **2020**, 152, 106344. [CrossRef]
- 101. Xuemin, Q.; Hongying, Y.; Guobao, C.; Shuiping, Z.; Chuangkai, C.; Bibo, L. Inhibited mechanism of carboxymethyl cellulose as a galena depressant in chalcopyrite and galena separation flotation. *Miner. Eng.* **2020**, *150*, 106273. [CrossRef]
- 102. Aikawa, K.; Ito, M.; Segawa, T.; Jeon, S.; Park, I.; Tabelin, C.B.; Hiroyoshi, N. Depression of lead-activated sphalerite by pyrite via galvanic interactions: Implications to the selective flotation of complex sulfide ores. *Miner. Eng.* **2020**, *152*, 106367. [CrossRef]
- 103. Mhonde, N.; Johansson, L.-S.; Corin, K.; Schreithofer, N. The effect of sodium isobutyl xanthate on galena and chalcopyrite flotation in the presence of dithionite ions. *Miner. Eng.* **2021**, *169*, 106985. [CrossRef]
- 104. Suyantara, G.P.W.; Hirajima, T.; Miki, H.; Sasaki, K.; Kuroiwa, S.; Aoki, Y. Effect of H₂O₂ and potassium amyl xanthate on separation of enargite and tennantite from chalcopyrite and bornite using flotation. *Miner. Eng.* **2020**, *152*, 106371. [CrossRef]
- 105. Wang, X.; Qin, W.; Jiao, F.; Wu, J. The influence of galvanic interaction on the dissolution and surface composition of galena and pyrite in flotation system. *Miner. Eng.* **2020**, *156*, 106525. [CrossRef]
- 106. Huai, Y.; Peng, Y. The formation of iron sulphide on oxidised pyrite during sulphidisation and subsequent interactions with xanthate. *Miner. Eng.* **2020**, *157*, 106564. [CrossRef]
- Kaksonen, A.H.; Deng, X.; Bohu, T.; Zea, L.; Khaleque, H.N.; Gumulya, Y.; Boxall, N.J.; Morris, C.; Cheng, K.Y. Prospective directions for biohydrometallurgy. *Hydrometallurgy* 2020, 195, 105376. [CrossRef]
- Zhang, Y.; Zhao, H.; Qian, L.; Sun, M.; Lv, X.; Zhang, L.; Petersen, J.; Qiu, G. A brief overview on the dissolution mechanisms of sulfide minerals in acidic sulfate environments at low temperatures: Emphasis on electrochemical cyclic voltammetry analysis. *Miner. Eng.* 2020, 158, 106586. [CrossRef]
- Tanne, C.K.; Schippers, A. Electrochemical investigation of chalcopyrite (bio)leaching residues. *Hydrometallurgy* 2019, 187, 8–17.
 [CrossRef]

- 110. Tobolik, M.; Krinik, L. Electrolyzer for Anodic Dissolution of Conductive Materials. Patent 93102 PPR, MKI S25S7/00, 6 December 1973.
- 111. Morozov, A.F.; Morozova, V.P.; Mutylin, Y.V. Electrochemical treatment in the gravity flotation of tin-containing products. *Ore Benef. Irkutsk. Polytech. Inst.* **1988**, *4*, 88–92. (In Russian)
- 112. Zhao, H.; Zhang, Y.; Zhang, X.; Qian, L.; Sun, M.; Yang, Y.; Zhang, Y.; Wang, J.; Kim, H.; Qiu, G. The dissolution and passivation mechanism of chalcopyrite in bioleaching: An overview. *Miner. Eng.* **2019**, *136*, 140–154. [CrossRef]
- 113. O'Connor, G.M.; Eksteen, J.J. A critical review of the passivation and semiconductor mechanisms of chalcopyrite leaching. *Miner. Eng.* **2020**, *154*, 106401. [CrossRef]
- 114. Tapera, T.; Nikoloski, A.N. The effect of silver on the acidic ferric sulfate leaching of primary copper sulfides under recycle solution conditions observed in heap leaching. Part 3: Surface characterization. *Hydrometallurgy* **2019**, *183*, 130–141. [CrossRef]
- 115. Zhao, H.; Zhang, Y.; Sun, M.; Ou, P.; Zhang, Y.; Liao, R.; Qiu, G. Catalytic mechanism of silver in the oxidative dissolution process of chalcopyrite: Experiment and DFT calculation. *Hydrometallurgy* **2019**, *187*, 18–29.
- Zeng, W.; Peng, Y.; Peng, T.; Nan, M.; Chen, M.; Qiub, G.; Shen, L. Electrochemical studies on dissolution and passivation behavior of low temperature bioleaching of chalcopyrite by Acidithiobacillus ferrivorans YL15. *Miner. Eng.* 2020, 155, 106416. [CrossRef]
- 117. Tanne, C.; Schippers, A. Electrochemical investigation of microbially and galvanically leached chalcopyrite. *Hydrometallurgy* **2021**, 202, 105603. [CrossRef]
- 118. Hong, M.; Huang, X.; Gan, X.; Qiu, G.; Wang, J. The use of pyrite to control redox potential to enhance chalcopyrite bioleaching in the presence of Leptospirillum ferriphilum. *Miner. Eng.* **2021**, *172*, 107145. [CrossRef]
- 119. Saavedra, A.; García-Meza, J.V.; Cortón, E.; González, I. Understanding galvanic interactions between chalcopyrite and magnetite in acid medium to improve copper (Bio)Leaching. *Electrochim. Acta* 2018, 265, 569–576. [CrossRef]
- 120. Zhang, Y.; Zhao, H.; Zhang, Y.; Liu, H.; Yin, H.; Deng, J.; Qiu, G. Interaction mechanism between marmatite and chalcocite in acidic (microbial) environments. *Hydrometallurgy* **2020**, *191*, 105217. [CrossRef]
- 121. Hong, M.; Wang, X.; Yang, B.; Liu, S.; Lin, H.; Qiu, G.; Qin, W.; Wang, J. Effect of pyrite with different semiconducting properties on bornite bioleaching in the presence of Leptospirillum ferriphilum. *Hydrometallurgy* **2020**, *196*, 105414. [CrossRef]
- 122. Rivera-Vasquez, B.F.; Dixon, D. Rapid atmospheric leaching of enargite in acidic ferric sulfate media. *Hydrometallurgy* **2015**, 152, 149–158.
- 123. Ma, Y.; Yang, Y.; Gao, X.; Fan, R.; Chen, M. The galvanic effect of pyrite enhanced (bio)leaching of enargite (Cu₃AsS₄). *Hydrometallurgy* **2021**, 202, 105613. [CrossRef]
- 124. Azizi, D.; Larachi, F. DFT simulations of pyrite galvanic interactions with bulk, solid-solution and nanoparticle Au occurrences– Insights into gold cyanidation. *Miner. Eng.* **2020**, *149*, 106239.
- 125. Hofmann, T.; Schuwirth, N. Zn and Pb release of sphalerite (ZnS)-bearing mine waste tailings. *J. Soils Sediments* **2008**, *8*, 433–441. [CrossRef]
- Pabst, T.; Aubertin, M.; Bussière, B.; Molson, J. Experimental and numerical evaluation of single-layer covers placed on acidgenerating tailings. *Geotech. Geol. Eng.* 2017, 35, 1421–1438. [CrossRef]
- Benzaazoua, M.; Bouzahzah, H.; Taha, Y.; Kormos, L.; Kabombo, D.; Lessard, F.; Bussière, B.; Demers, I.; Kongolo, M. Integrated environmental management of pyrrhotite tailings at Raglan Mine: Part 1 challenges of desulphurization process and reactivity prediction. *J. Clean. Prod.* 2017, *162*, 86–95. [CrossRef]
- 128. Rey, N.J.; Demers, I.; Bussière, B.; Mbonimpa, M.; Gagnon, M. A geochemical evaluation of a monolayer cover with an elevated water table for the reclamation of the Doyon-Westwood tailings ponds, Canada. *Environ. Earth Sci.* **2020**, *79*, 58. [CrossRef]
- Rakotonimaro, T.V.; Guittony, M.; Neculita, C.M. Compaction of peat cover over desulfurized gold mine tailings changes: Arsenic speciation and mobility. *Appl. Geochem.* 2021, 128, 104923. [CrossRef]
- Perlatti, F.; Martins, E.P.; Pontes de Oliveira, D.; Ruiz, F.; Asensio, V.; Rezende, C.F.; Otero, X.L.; Ferreira, T.O. Copper release from waste rocks in an abandoned mine (NE, Brazil) and its impacts on ecosystem environmental quality. *Chemosphere* 2021, 262, 127843. [CrossRef]
- Qian, G.; Fan, R.; Huang, J.; Pring, A.; Harmer, S.L.; Zhang, H.D.; Rea, M.A.; Brugger, J.; Teasdale, P.R.; Gibson, C.T.; et al. Oxidative dissolution of sulfide minerals in single and mixed sulfide systems under simulated acid and metalliferous drainage conditions. *Environ. Sci. Technol.* 2021, 55, 2369–2380. [CrossRef]
- 132. Qian, Y.; Li, G.; Brown, P.L.; Gerson, A.R. Chalcopyrite dissolution: Scanning photoelectron microscopy examination of the evolution of sulfur species with and without added iron or pyrite. *Geochim. Et Cosmochim. Acta* **2017**, 212, 33–47.
- Ferreira, P.M.; Majuste, D.; Freitas, E.T.F.; Caldeira, C.L.; Dantas, M.S.S.; Ciminelli, V.S.T. Galvanic effect of pyrite on arsenic release from arsenopyrite dissolution in oxygen-depleted and oxygen-saturated circumneutral solutions. *J. Hazard. Mater.* 2021, 412, 125236. [CrossRef]
- Fuchida, S.; Kawachi, M.; Koshikawa, H. Kinetic investigation of galvanic dissolution of ZnS and PbS with FeS₂ from hydrothermal sulfides in seawater. *Appl. Geochem.* 2021, 129, 104963. [CrossRef]
- Qian, G.; Fan, R.; Short, M.D.; Schumann, R.C.; Pring, A.; Gerson, A.R. The combined effects of galvanic interaction and silicate addition on the oxidative dissolution of pyrite: Implications for acid and metalliferous drainage control. *Environ. Sci. Technol.* 2019, 53, 11922–11931. [CrossRef] [PubMed]