SEMICONDUCTOR ELECTROCHEMISTRY OF COAL PYRITE

Final Technical Report

September 1990 - September 1995

by

K. Osseo-Asare and Dawei Wei

Metals Science and Engineering Program
Department of Materials Science and Engineering
The Pennsylvania State University
University Park, PA 16802

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Chapter 1

INTRODUCTION

1.1 Pyrite Aqueous Systems

The pyrite/aqueous interface features prominently in many aspects of coal mining, processing, and utilization (Meyers, 1977; Drzymala and Wheelock, 1993; Liu et al., 1993). Coals typically contain 1-4% sulfur, a major fraction of which may come from pyrite. Since the combustion of coal releases unacceptable quantities of sulfur-oxides into the atmosphere, coal-desulfurization is increasingly becoming a major component of coal processing technology (Meyers, 1977). Many of the current available or proposed coal cleaning and desulfurization methods (e.g. froth flotation, oil flotation, agglomeration, leaching) exploit physicochemical processes occurring at the pyrite/aqueous interface. In addition to the deliberate utilization of pyrite/aqueous interfacial interactions in these industrial processes, there is also the natural (but unwanted) interfacial process of dissolution of pyrite that leads to the serious environmental problem of acid-mine drainage (Nordstrom, 1982).

There have been numerous studies on the aqueous interfacial chemistry of pyrite, all aimed at understanding and controlling the behavior of this metal sulfide in various stages of coal and mineral processing, and excellent review articles have been written (Hiskey et al., 1982; Lawson 1982). In spite of the vast volume of the literature on pyrite aqueous chemistry, there is little agreement on the mechanisms of pyrite surface reactions. A proper

understanding of the fundamental chemistry of the pyrite/aqueous system is needed if improved strategies are to be devised for enhancing/suppressing pyrite reactions for commercial exploitation in coal cleaning and desulfurization or in controlling the environmental hazards associated with these reactions.

The conventional approach to pyrite electrochemistry is based on the metal electrode model (Peters and Majima, 1968; Biegler and Swift, 1979; Peters, 1992). Pyrite is treated as an electronic conductor and its oxidation is thought to proceed only through electron transfer. Although pyrite has been widely accepted as a semiconductor material (Bither et al., 1968; Gupta et al., 1980; Ennaoui et al., 1986; Liu et al., 1988), some early investigators (Springer, 1970; Biegler, 1975) found that n- and p-type pyrite exhibited very similar anodic and cathodic polarization curves. They concluded therefore that there was no significant relationship between the semiconductor properties of pyrite and the interfacial electrochemical reactions of this metal sulfide. However, more recent electrochemical and photoelectrochemical experiments (Mishra and Osseo-Asare, 1987, 1988a, 1992a; Ahmed and Giziewicz, 1992) have shown that the dissolution rate of pyrite increases under illumination. This indicates that both electrons and holes may participate in the interfacial electrochemical reactions during pyrite dissolution.

It is generally believed that the semiconductor dissolution process may involve electron or hole transfer routes (Vijh, 1973; Morrison, 1980). When the band gap of a semiconductor is larger than 0.66 eV, a hole transfer pathway will play a key role in the anodic dissolution process (Gerischer, 1969; Crundwell, 1988; Osseo-Asare, 1992). The solid-state properties of the semiconductor material, such as the bulk phase electronic structure, the band gap and the band edges, will affect the dissolution rate. The interfacial electrochemical processes associated with the electron and hole transfers between the solid surface and the redox couple in the aqueous solution will also influence the dissolution

process. However, only a small amount of work has been devoted to relating the semiconductor properties of pyrite to its dissolution mechanism. It is thus necessary to do more research on semiconductor electrochemistry to advance the fundamental understanding of the interfacial reactions at the pyrite/aqueous interface.

The conventional approach to the pyrite/aqueous interfacial studies is based on the use of a bulk pyrite specimen as an electrode for conducting electrochemical measurements (Peters and Majima, 1968; Woods, 1976; Mishra and Osseo-Asare, 1988a; Richardson et al., 1992). Because of the resulting small area of the pyrite/solution interface and the slow specific reaction rate, the response of the electrochemical reaction at the interface may not be strong enough to be detected and presented clearly by a given analytical instrument. The identification of the reaction products at the pyrite/aqueous interface is important for understanding the mechanism of pyrite dissolution. However, the small amount of reaction products on the pyrite surface makes direct analysis very difficult (Mycroft et al., 1990; Khan et al., 1992; Wang et al., 1992; Zhu et al., 1993). Therefore, in an effort to obtain a meaningful electrochemical response and more quantitative information about the reaction products, the use of pyrite in a highly divided form, as microelectrodes, would be advantageous because of the increase in the amount of reaction surface per given pyrite/solution mass ratio.

1.2 Research Objectives

This project seeks to advance the fundamental understanding of the physico-chemical processes occurring at the pyrite/aqueous interface, in the context of coal cleaning, coal desulfurization, and acid mine drainage. Central to this research is the use of synthetic microsize particles of pyrite as model microelectrodes to investigate the semiconductor

electrochemistry of pyrite. The research focuses on: (a) the synthesis of microsize particles of pyrite in aqueous solution at room temperature, (b) the formation of iron sulfide complex, the precursor of FeS or FeS₂, and (c) the relationship between the semiconductor properties of pyrite and its interfacial electrochemical behavior in the dissolution process.

A simple direct method for preparing microsize particles of pyrite is not available in the literature. In fact, the mechanism of pyrite formation is not well understood, although there are numerous publications on this subject (Berner, 1970,1984; Schooner and Barnes, 1991a,b; Drobner et al., 1990; Graham and Ohmoto, 1994). In Chapters 2, 3 and 4, a suitable protocol for preparing microsize particles of pyrite in aqueous solution is given, and the essential roles of the precursors elemental sulfur and "FeS" in pyrite formation are investigated. The iron sulfide complex formed initially from the reaction of ferrous and sulfide solutions is very important for understanding the mechanism of pyrite formation (Rickard, 1989; Luther, 1991; Luther and Ferdelman, 1993). In Chapter 5, the formation of iron sulfide complex prior to the precipitation of FeS or FeS₂ is investigated using a fast kinetics technique based on a stopped-flow spectrophotometer. The stoichiometry of the iron sulfide complex is determined, and the rate and formation constants are also evaluated. Chapter 6 provides a summary of the semiconductor properties of pyrite relevant to the present study. In Chapters 7 and 8, the effects of the semiconductor properties on pyrite dissolution are investigated experimentally, and the mechanism of pyrite dissolution in acidic aqueous solution is examined. Finally, a summary of the conclusions from this study and suggestions for future research are presented in Chapter 9.

Chapter 2

AQUEOUS SYNTHESIS OF FINELY DIVIDED PYRITE PARTICLES

Abstract

Pyrite (FeS_2) was synthesized by aqueous precipitation from the reaction between FeCl_3 and NaHS at room temperature and atmospheric pressure. The solid product was purified by means of solvent extraction for elemental sulfur removal. The synthetic pyrite particles were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX), X-ray photoelectron spectroscopy (XPS), surface area determination (BET), zeta potential measurements, and chemical analysis. The purified pyrite contained 99.46% FeS_2 with an average particle size of 1.5 μm and a standard deviation of 0.3, BET specific surface area of 4.1 m^2/g , and the isoelectric point (iep) at pH 2.3.

2.1 Introduction

The pyrite/aqueous interface is encountered in a wide variety of natural and technological systems. These include coal processing (Meyers, 1977; Drzymala and Wheelock, 1993; Liu et al., 1993), mineral processing (Woods, 1976; Chander, 1991; Witika and Dobias, 1995), hydrometallurgy (Peters, 1976, 1986, 1992; Osseo-Asare, 1992), geochemistry (Berner, 1970, 1984; Nordstrom, 1982; Morse et al., 1987; Schooner

and Barnes, 1991a,b), acid mine drainage formation and control (Aston, 1974; Ahmed and Giziewicz, 1992; Chander and Zhou, 1992, Osseo-Asare, 1993), toxic metal removal by sorption on pyrite fines (Zouboulis et al., 1992) and solar energy conversion (Jaegermann and Tributsch, 1983; Ennaoui et al., 1986; Tributsch, 1986; Alonso-Vante and Tributsch, 1990; Chen et al., 1991).

The conventional approach to pyrite/aqueous interfacial studies is based on the use of bulk natural or synthetic pyrite specimens, i.e., planar electrodes (Peters and Majima, 1968; Woods, 1976; Mishra and Osseo-Asare, 1988a,b; Richardson et al., 1992) or relatively large particles with a size range from 106 to 125 μm (Lalvani and Shami, 1986) or 106 to 150 μm (Ciminelli and Osseo-Asare, 1995). Because of the resulting limited area of the pyrite/solution interface, the response of electrochemical reaction at the interface may not be strong enough to be detected and characterized clearly by a given analytical instrument. The identification of the reaction products at the pyrite/aqueous interface is important for understanding the mechanism of pyrite dissolution (Buckley and Woods, 1984; Buckley et al., 1988; Mishra and Osseo-Asare, 1988, 1992; Mycroft et al., 1990; Wang et al., 1992; Zhu et al., 1993). However, the small amount of reaction products on pyrite surface makes direct analysis very difficult. Therefore, the use of pyrite in a highly divided form would be advantageous since, with fine particles, there would be an increase in the amount of reaction surface per given pyrite/aqueous mass ratio. More reaction products and stronger electrochemical response will be expected.

Pyrite has been synthesized in aqueous solutions at low temperatures and atmospheric pressure by a number of investigators (Berner, 1964, 1969; Sweeney and Kaplan, 1973; Rickard 1969; Roberts et al., 1969; Taylor et al., 1979; Luther 1991; Schoonen and Barnes 1991b). A summary of the selected results is shown in Table 2.1. It can be seen from Table 2.1 that there are basically two pathways to synthesize pyrite at low

TABLE 2.1. Summary of published data on FeS₂ formation at low temperature.

Starting materials	Temperature °C	pH	Aging time	Products [‡]	Ref.
FeCl ₂ + H ₂ S + S ⁰	25-60 °C	-	5 days	py	1
FeS + H ₂ S + S ⁰	65	7.9	14 days	py	2
FeS + S ⁰	40	8.0	-	py	3
FeS* + H ₂ S	35	-	3 days	gr, mk, py	4
FeS + Na ₂ S _n	25	7.0	-	py, mc, S ⁰	5
FeO.OH+H ₂ S	25	3.8	20 days	py, tetr FeS	6
FeSO ₄ + H ₂ S	40-42	3	25 days	py, mc	7†
FeSO ₄ + Na ₂ S _n	25	4.4-9.5	-	py, mc	5
Fe ^{2+***} + Na ₂ S ₅	25	5.8	4 hrs.	py	8
Fe ^{3+****} + Na ₂ S ₅	25	5.5	22 hrs.	py	8
Fe(NH ₄) ₂ (SO ₄) ₂ +Na ₂ S ₄	65	7.3-7.6	18 days	py	9

*FeS was pre-oxidized in air..

**Fe²⁺ sources are FeCl₂, FeSO₄ and Fe(NH₄)₂(SO₄)₂.

***Fe³⁺ sources are FeCl₃ and Fe(NO₃)₃.

†Air oxidation was not completely prevented.

‡py = pyrite; mk = mackinawite; gr = greigite; mc = marcasite.

1-Sweeney et al., 1973; 2-Berner, 1969; 3-Rickard, 1975; 4-Taylor et al., 1979;

5-Rickard, 1969; 6-Roberts et al., 1969; 7-Berner, 1964b; 8-Luther, 1991; 9-Schoonen et al., 1991.

temperature in aqueous solutions, i.e., (a) the reaction between FeS and elemental sulfur S^0 , where FeS is prepared by Fe^{2+} /sulfide reaction (Sweeney et al., 1973; Berner, 1969; Rickard, 1975), and the elemental sulfur may be either sulfur powder or the sulfur generated by Fe^{3+} /sulfide reaction (Roberts et al., 1969), and (b) the reaction between Fe^{2+} or Fe^{3+} and polysulfides S_n^{2-} (Rickard, 1969; Luther, 1991; Schoonen and Barnes, 1991b).

Most of the previous investigations have been preoccupied with the mechanisms of pyrite formation. However, relatively little attention has been paid to the examination of the properties of the pyrite product. In this chapter, the work focuses on the synthesis of fine particles (micron size) of pyrite in aqueous solution at room temperature and atmospheric pressure, with $FeCl_3$ and NaHS as starting materials. Purification of the pyrite product was achieved via solvent extraction for elemental sulfur removal. The pyrite particles were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX), X-ray photoelectron spectroscopy (XPS), surface area determination (BET), zeta potential measurements, and chemical analysis. The pyrite sample thus obtained is a useful model material for the investigation of pyrite/aqueous interfacial reactions (see Chapters 7 and 8).

2.2 Experimental

2.2.1 Materials

Ferrous chloride ($FeCl_2 \cdot 4H_2O$) and ferric chloride ($FeCl_3 \cdot 6H_2O$) were used as iron sources. Sodium sulfide ($Na_2S \cdot 9H_2O$) and sodium hydrosulfide ($NaHS \cdot xH_2O$) and sodium tetrasulfide (90 % Na_2S_4) from Alfa were used as sulfur sources. The respective

iron and sulfide solutions were prepared by dissolving the relevant chemicals in oxygen-free water. The oxygen-free water was prepared by bubbling prepurified N₂ in high purity water (18 MΩ-cm), which was obtained from a Millipore Milli-Q system, for at least 5 hours. The nitrogen gas was deoxygenated by flowing over a bed of copper filings at 450 °C. The pH of the reaction solution was adjusted by small additions of concentrated HCl or NaOH. Carbon disulfide (99.9% CS₂) was used as sulfur-extracting solvent. All the chemicals were of reagent grade and purchased from Aldrich except those specified otherwise, and were used without further purification.

2.2.2 Pyrite Synthesis

The synthesis experiments were carried out in 50 ml screwcapped vials in a glove box with a nitrogen pressure maintained at about 250 kPa (~2.5 atm). Iron and sulfide solutions in two separate uncapped vials were placed in the glove box for 2 hours to release possible oxygen content in the solutions. Then the two solutions were mixed in one vial, shaken vigorously by hand for a few seconds, and sealed in the glove box for aging. The pH of the reaction solution was measured in separate experiments. The temperature was maintained at 25 ± 0.5 °C.

2.2.3 Pyrite Purification

The pyrite synthesized from the reaction between aqueous sulfide and ferric ions was found to contain elemental sulfur (see below). A solvent extraction technique (Reilly et al., 1978, 1984; Filmer et al., 1979a,b) was used to remove the elemental sulfur. The extraction was conducted at 47°C in a Soxhlet apparatus with 270 mg solid and 60 ml CS₂.

The suspension was agitated with a magnetic stirrer for 2 hours. Following solid/liquid separation, the solvent was evaporated at room temperature to leave a sulfur residue. The purified pyrite particles were washed with carbon disulfide first, then with acetone, followed by several washings with oxygen-free water. To prevent oxidation of the sample, all the above steps were conducted in a nitrogen atmosphere.

2.2.4 Materials Characterization

The phases in the solid products were identified with X-ray diffraction (Rigaku Geigerflex). The surface chemistry of the purified pyrite particles was examined by X-ray photoelectron spectroscopy (Kraton XSAM model 800 spectrometer). The particle size was characterized with a Topcon SX-40A scanning electron microscope. Energy dispersive x-ray spectroscopy was used to detect the elemental components of the solid material under the SEM. The zeta potential of pyrite particles was determined with a model 501 Lazer Zee Meter (Pen Kem Inc., Bedford, New York). The ionic strength of the solutions for zeta potential measurements was maintained at 0.01 M KNO₃. Specific surface area was measured using the BET gas absorption method with a Quantasorb apparatus (Quantachrome Corporation, Greenvale, NY). Chemical compositional analysis was conducted by Galbraith Laboratories, Knoxville, TN.

2.3 Results and Discussion

2.3.1 Reaction Products

The nature of the solid products generated by the synthesis experiments and the corresponding iron and sulfur starting materials are summarized in Table 2.2. The related X-ray diffractograms are shown in Figure 2.1. It can be seen from Table 2.2 and Figure 2.1, that using Fe(II) as the iron source, mackinawite and mixtures containing pyrite were produced (Runs 15#, 67# and 51#), and the use of Na₂S₄ as sulfur source resulted in significant amount of elemental sulfur in the precipitates (Runs 51# and 57#). The reaction product of Fe(III) with Na₂S or NaHS was pyrite as identified by X-ray diffraction (Runs 17# and 58#), although these products contained elemental sulfur according to the chemical analysis, as can be seen later.

The precipitates (30 min) that resulted eventually in mackinawite and pyrite were initially X-ray amorphous materials (Runs 25# and 65# in Table 2.2). These materials were very sensitive to air oxidation. As can be seen from Figures 2.2 and 2.3, the X-ray amorphous precipitates were oxidized to lepidocrocite (γ -FeOOH) after 30 minutes exposure in air.

To examine the feasibility of the conversion of mackinawite to pyrite, the product yielded by the reaction of FeCl₂ with Na₂S was aged in O₂-free environment for 1 year. After 1 year, the reaction product was still mackinawite (Runs R-15#), no pyrite was observed. This indicates that mackinawite is an end product from the solution containing ferrous and sulfide ions in the absence of oxygen and elemental sulfur. This observation is consistent with the suggestion that pyrite formation must involve the precursors elemental

TABLE 2.2. Summary of the experimental results for pyrite synthesis at 25 °C.

Run	Source of Fe and conc., M	Source of S and conc., M	pH	Aging time	Product*
25#	FeCl ₂ , 0.05	Na ₂ S, 0.05	7.3	30 min.	amorphous
15#	FeCl ₂ , 0.05	Na ₂ S, 0.05	7.3	4 days	mk
R-15#	FeCl ₂ , 0.05	Na ₂ S, 0.05	7.3	1 year	mk
17#	FeCl ₃ , 0.05	Na ₂ S, 0.05	6.5	9 days	py
67#	FeCl ₂ , 0.033	NaSH, 0.067	4.0	4 days	mk, py
R-67#	FeCl ₂ , 0.033	NaSH, 0.067	4.0	1 year	mk, py
65#	FeCl ₃ , 0.033	NaSH, 0.067	3.6	30 min.	amorphous
58#	FeCl ₃ , 0.033	NaSH, 0.067	3.6	2 days	py
51#	FeCl ₂ , 0.067	Na ₂ S ₄ , 0.033	4.3	6 days	S ⁰ , py
R-51#	FeCl ₂ , 0.067	Na ₂ S ₄ , 0.033	4.3	1 year	S ⁰ , py
57#	FeCl ₃ , 0.067	Na ₂ S ₄ , 0.033	5.6	3 days	S ⁰

*The phases were determined only by X-ray diffraction; py = pyrite; mk = mackinawite;

S⁰ = elemental sulfur.

FIGURE 2.1. X-ray diffractograms for different reaction products (see Table 2.2).

FIGURE 2.2. X-ray diffractograms of (a) the initial precipitate of mackinawite, and (b) oxidation product of the initial precipitate.

FIGURE 2.3. X-ray diffractograms of (a) the initial precipitate of pyrite and (b) the oxidation product of the initial precipitate.

FIGURE 2.4. X-ray diffractograms showing pyrite formation at different aging stages.

sulfur or polysulfides (Berner 1970; Rickard 1975; Schoonen and Barnes 1991a,b; Luther, 1991).

The time evolution of pyrite formation, using FeCl_3 and NaHS as reactants, is illustrated by the X-ray diffractograms in Figure 2.4. It can be seen that as the reaction proceeded, pyrite was formed gradually from the initial X-ray amorphous material. The X-ray amorphous material was considered to be iron monosulfide, which is the precursor for forming pyrite (Berner, 1964, 1967; Rickard, 1969, 1975; Sweeney and Kaplan, 1973). The essential role of iron monosulfide in pyrite formation was demonstrated by Schoonen and Barnes (1991a,b) in an extensive laboratory study. Their work indicated that pyrite formation always involved an iron monosulfide precursor, and mackinawite was the first crystalline phase converted from amorphous FeS before pyrite formation. However, no significant crystalline FeS intermediate was formed during pyrite formation as can be seen from Figure 2.4. Therefore, it is believed that amorphous FeS (Berner, 1964, 1967; Rickard, 1969, 1975; Sweeney and Kaplan, 1973) or iron sulfide complexes, such as $\text{Fe}(\text{HS})^+$ (Luther, 1991; Luther and Ferdelman, 1993; see Chapter 5) or $\text{Fe}(\text{HS})_2$ (Richard, 1989) may serve as precursors for pyrite formation under the experimental conditions in this study.

Pyrite is more stable than mackinawite when the materials are contacted with air. Figure 2.5 shows the X-ray diffractograms for a mixture of mackinawite and pyrite with different lengths of exposure in air. It can be seen that all the peaks representing mackinawite (Figure 2.5a) were replaced by peaks of lepidocrocite ($\gamma\text{-FeOOH}$) after the sample was exposed in air for 30 minutes (Figure 2.5b). However, pyrite peaks did not experience any significant changes even after the material had been exposed in air for 5 days (Figure 2.5c). The reason why pyrite is more inert than mackinawite can be explained on the basis of the electronic structures of these materials. The $\text{Fe}(\text{II})$ ion has a high spin

FIGURE 2.5. X-ray diffractograms showing different oxidation behaviors for mackinawite and pyrite.

state ($t_{2g}^4 e_g^2$) in FeS, but has a low spin state (t_{2g}^6) in FeS₂ (Goodenough, 1978). The low spin state of Fe(II) makes pyrite more kinetically stable (Luther, 1991).

2.3.2 Pyrite Formation by Fe(III)-S(II) Reactions

It has been suggested that pyrite formation is a two step process (Berner 1969; Rickard 1975; Schoonen and Barnes 1991):

In the first step, an iron monosulfide precursor, FeS, forms via the reaction between aqueous sulfide and aqueous ferrous iron species (Equation 2.1). In the second step, the iron monosulfide precursor is converted to pyrite in the presence of elemental sulfur (Equation 2.2a) or polysulfide ions (Equation 2.2b). It can be seen from Equations 2.1 and 2.2 that the species needed in order to form pyrite in the solution are Fe^{2+} , HS^- and S^0 (or S_n^{2-}).

With Fe(III) as the iron source, a redox reaction occurs initially between the ferric ions and the sulfide ions to give the necessary ferrous iron and elemental sulfur (Roberts et al., 1969):

The presence of ferrous and sulfide ions and elemental sulfur in the aqueous system can result in the formation of pyrite according to the following reactions:

It is noted that the FeCl_3 -NaSH reaction pathway for pyrite formation is relatively straightforward and fast (see Table 2.2). It is believed that this is the simplest pathway to synthesize pyrite at room temperature in aqueous solution.

2.3.3 Pyrite Purification

In view of Equations 2.3 and 2.4, it is expected that a certain amount of elemental sulfur will be present in the precipitates produced by Fe(III)-S(II) reaction. Chemical analysis by Galbraith Laboratories showed that the products (Run 58# in Table 2.2) obtained from the reaction between FeCl_3 and NaHS solutions contained 29.56% elemental sulfur (based on calculation assuming the stoichiometry of pyrite as FeS_2). To remove the elemental sulfur from the pyrite-containing initial product, a solvent extraction technique (Reilly et al., 1978, 1984; Filmer et al., 1979a,b) was applied. The elemental sulfur was dissolved in the organic phase (CS_2) followed by solvent/solid separation and washing steps. The chemical analysis of the pyrite sample before and after purification is shown in Table 2.3. A purified pyrite sample containing 99.46% FeS_2 has been obtained from this extraction procedure.

TABLE 2.3. Chemical analysis of pyrite samples.

Material	Mass, mg	Composition		
		Fe%*	S%*	FeS ₂ %
Initial product	270	32.79	67.21	70.44
Purified material	185	46.30	53.70	99.46
Residue**	85	-	-	-

*Elemental analysis by Galbraith Laboratories

** After evaporation of CS₂

2.3.4 Material Characterization

The SEM micrographs of pyrite samples obtained before and after purification, and of the elemental sulfur derived from the organic solvent are shown in Figure 2.6. Corresponding EDX spectra are presented in Figure 2.7. It can be seen that the unpurified pyrite sample contains two kinds of particles, i.e., smaller and larger particles (Figure 2.6a). The whole-screen EDX spectra covering both small and large particles give a peak ratio S:Fe of 4.3 (Figure 2.7a), which is attributed to a mixture of pyrite and elemental sulfur. The small particles with a peak ratio of 2.5 (Figure 2.7b) are believed to be pyrite, and the larger particles with a high sulfur peak and a negligible Fe peak represent elemental sulfur. As can be seen from Figure 2.6b, following the purification step, the larger particles of elemental sulfur are absent and small uniform pyrite particles are highlighted. The EDX spectra of the purified pyrite sample give a peak ratio of 2.4 (Figure 2.7d). A magnification of the SEM micrograph of the purified pyrite particles is shown in Figure 2.8. The SEM micrograph of the solid derived from the CS₂-soluble extract is shown in Figure 2.6c. The organic-soluble material is identified as elemental sulfur by the EDX result shown in Figure 2.7e. It can be seen further from the X-ray diffractograms presented in Figure 2.9, that the sulfur in the initial pyrite sample (Figure 2.9a) is extracted into the organic solvent (Figure 2.9c), and a purified pyrite sample is obtained (Figure 2.9b).

Figure 2.10 shows the XPS spectra of the purified pyrite. The peaks at S 2p_{3/2} binding energy of 162.4 eV (Figure 2.10a) and at Fe 2p_{3/2} binding energy of 707.4 eV (Figure 2.10b) are attributed to pure pyrite (Wagner et al., 1979; Ennaoui et al., 1986; Mycroft et al., 1990). The small peak at S 2p_{3/2} binding energy of 168.6 eV may be due to the presence of iron sulfates on the pyrite surfaces (Frost et al., 1977; Wagner et al., 1979).

FIGURE 2.6. SEM micrographs of (a) pyrite sample before purification, (b) pyrite sample after purification, and (c) elemental sulfur obtained from organic extract.

FIGURE 2.7. EDX spectra of (a) whole screen of Figure 2.6a, (b) small particle in Figure 2.6a, (c) large particle in Figure 2.6a, (d) particles in Figure 2.6b, and (e) particles in Figure 2.6c.

FIGURE 2.8. SEM micrograph of the purified pyrite particles.

FIGURE 2.9. X-ray diffractograms of (a) pyrite sample before purification, (b) pyrite sample after purification, and (c) elemental sulfur obtained from organic extract.

FIGURE 2.10. XPS spectra of the purified pyrite.

The particle size histogram (Figure 2.11), obtained from the SEM micrograph of the purified particles presented in Figure 2.6b, shows an average pyrite particle size of 1.5 μm with standard deviation of 0.3. Thus more than 90% of the purified pyrite particles have diameters in the range of 1.0 to 2.0 μm . The formation of uniform particles of pyrite suggests that the mechanism of pyrite nucleation and particle growth may follow LaMer's theory (LaMer and Dinegar, 1950; Matijevic, 1981, 1985; Sugimoto, 1987) on the formation of monodispersed colloidal particles. A fast nucleation of pyrite may occur when the concentration of pyrite-forming precursors reaches a critical supersaturation condition, followed by a slow growth of the particles via monomer addition on the existing particles. Since all the nuclei of pyrite particles are generated at the same time, and the particles grow at the same rate, uniform particles of pyrite are produced.

The BET specific surface area for the purified pyrite particles was measured to be 4.10 m^2/g . Assuming that the pyrite particles are spherical, a specific area of 0.80 m^2/g was calculated, based on the average particle size of 1.5 μm and a density of 5.0 g/cm^3 (Deer et al., 1992). The comparatively high experimentally determined BET surface area (4.1 m^2/g) suggests that the pyrite particles have a porous structure or a rough surface as can be seen from Figure 2.8.

The zeta potential of the purified pyrite particles as a function of pH is shown in Figure 2.12. The dependence of the surface charge on pH indicates that H^+ and OH^- are the potential-determining ions. Like most of the metal sulfides (Park and Huang, 1987; Ronngren et al., 1991; Dekkers and Schoonen, 1994), hydrolysis of pyrite surface may lead to thiol groups ($\equiv\text{S-H}$) and metal hydroxide groups ($\equiv\text{Fe-OH}$). Therefore, the protonation of the pyrite surface at low pH gives a less negatively charged surface. On the other hand, deprotonation at high pH makes the pyrite surface more negatively charged.

FIGURE 2.11. Particle size histogram of purified pyrite particles.

FIGURE 2.12. Zeta potential of the purified pyrite particles as a function of pH.

The adsorption of the proton and hydroxyl ions on pyrite surfaces has also been found in the electrochemical studies of pyrite/aqueous interfaces (Mishra and Osseo-Asare, 1988b, Chen et al., 1991; Chapter 7 in this study). The isoelectric point (iep) for an extensively oxidized natural pyrite has been reported at pH 6.5 (Fornasiero et al., 1992) and 6.9 (Fuerstenau et al., 1968, 1990). The iep of minimally oxidized natural pyrite was found at pH 2.1 to 2.5 (Zouboubis et al., 1992; Kydros et al., 1993). Thus, the iep at pH 2.3 (Figure 2.12) indicates that the particulate pyrite prepared in this study has a minimally oxidized surface, as also can be seen from the XPS analysis (Figure 2.10).

2.4 Conclusions

Pyrite and mackinawite were synthesized in aqueous solution at room temperature from the Fe(III)/S(II) and Fe(II)/S(II) reactions respectively. In both cases, the initial products were X-ray amorphous FeS, which was easily oxidized to γ -FeOOH. Formation of pyrite required the presence of elemental sulfur or polysulfides. The reaction of mackinawite with sulfide could not produce pyrite even after aging for 1 year. Using Na₂S₄ as the source of sulfur, no mackinawite was observed under the experimental conditions, while pyrite was obtained with a significant amount of elemental sulfur in the products.

When using the Fe(III)/S(II) reaction to prepare pyrite, a redox reaction occurred between ferric and sulfide ions to form ferrous ions and elemental sulfur. The presence of Fe²⁺, HS⁻ and S⁰ in the system made pyrite formation feasible. Pyrite synthesized from ferric and sulfide solutions contained elemental sulfur, which could be removed by solvent extraction. The pyrite sample after purification contained 99.46% FeS₂ and had an average particle diameter of 1.5 μ m. More than 90% of the particles had diameters in the range of

1.0 to 2.0 μm . The uniform particle size suggests a possible role for the homogeneous precipitation mechanism for pyrite nucleation and particle growth. The needed supersaturation of the precursors for pyrite formation may result from the slow generation of Fe^{2+} from FeS precipitate and of polysulfides from the S^0 intermediate product.

Pyrite synthesis via the $\text{Fe}^{3+}/\text{HS}^-$ reaction is preferred because the starting materials are readily available, the method is relatively simple (e.g., FeS and S^0 are produced in-situ and therefore do not require separate synthesis steps), the reaction is relatively fast, and the particulate pyrite of uniform size is produced. The XPS analysis and electrokinetic mobility measurements indicate that the pyrite particles prepared in this study have clean surfaces. The electronic and electrochemical properties of the pyrite particles synthesized by the Fe(III)/S(II) reaction have also been investigated and the results are presented in Chapters 7 and 8.

Chapter 3

PYRITE SYNTHESIS IN A TWO-PHASE ORGANIC/AQUEOUS SYSTEM: AN INVESTIGATION INTO THE ROLE OF ELEMENTAL SULFUR

Abstract

The $\text{Fe}^{3+}/\text{HS}^-$ reaction has been investigated in aqueous solution with or without the addition of a sulfur-extracting organic phase (carbon disulfide, CS_2). In the absence of the organic phase, pyrite and elemental sulfur formed in aqueous solution. In the presence of the organic phase, no pyrite was observed when the organic phase was initially free of elemental sulfur. In this case, the elemental sulfur produced by the reaction was extracted into the organic phase. However, when the organic phase was presaturated with elemental sulfur, pyrite was produced. The experimental results indicate that the presence of elemental sulfur in aqueous solution is necessary for pyrite formation. The essential role of elemental sulfur was to generate polysulfides (S_n^{2-}) in aqueous solution. These dissolved forms of sulfur reacted with the freshly formed "FeS" to produce pyrite within 2 days in aqueous solution at 25 °C.

3.1 Introduction

Pyrite formation has been considered by many investigators as a two-step process (Berner, 1970; Sweeney and Kaplan, 1973; Luther, 1991, Schoonen and Barnes, 1991a,b):

In the first step, as shown in Equation 3.1, the reaction between Fe^{2+} and HS^- ions produces amorphous iron monosulfide, "FeS", with a chemical composition varying from $\text{Fe}_{0.87}\text{S}$ to $\text{FeS}_{1.1}$ (Berner, 1964, 1967; Rickard, 1969, 1975; Sweeney and Kaplan, 1973). In the second step, the monosulfide reacts with elemental sulfur S^0 (Equation 3.2a) or polysulfides S_n^{2-} (Equation 3.2b) to form pyrite in the presence of excess sulfide.

In apparent conflict with the above view, Drobner and co-workers (1990) reported that the presence of elemental sulfur was not necessary in the aqueous system for pyrite formation. They claimed that pyrite was produced from the reaction between amorphous FeS and aqueous H_2S at 100 °C under strictly oxygen-free conditions. The pyrite formation reactions were proposed as (Drobner and co-workers, 1990):

where H_2S served not only as a sulfur source, but also as an oxidizing agent.

Another pathway which bypasses the need for elemental sulfur has been offered by Furukawa (1994). It was suggested that the conversion of mackinawite (Fe_9S_8) to pyrite could occur through the loss of iron from the mackinawite lattice in the presence of an oxidant, because this process would be accompanied by a decrease in the total solid volume. The following two possible reactions were considered (Furukawa, 1994):

Calculation (Furukawa, 1994) showed that the sulfur addition pathway (reaction 3.5) resulted in a solid volume increase of 17%. However, the iron loss process (reaction 3.6) reduced the solid volume by 48%. It was also suggested that the role of elemental sulfur or polysulfides in Equation 3.2 is only to serve as oxidant rather than the source of sulfur (Furukawa, 1994).

Can pyrite form in the absence of elemental sulfur? This is the question that is addressed in this chapter. A novel experimental technique was utilized in which the $\text{Fe}^{3+}/\text{HS}^-$ reaction was allowed to proceed in a two phase organic/aqueous system based on a sulfur-extracting solvent. An insight into the role of elemental sulfur in pyrite formation was obtained by conducting the synthesis experiments with and without presaturation of the organic solvent with elemental sulfur.

3.2 Experimental

3.2.1 Solution Preparation

Reagent grade ferric chloride ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) and sodium hydrosulfide ($\text{NaHS} \cdot x\text{H}_2\text{O}$) were used as the reactants for synthesizing pyrite. Carbon disulfide (99.9% CS_2) was used as the sulfur-extracting solvent. All the chemicals were purchased from Aldrich and used without further purification. Ferric ion and sulfide solutions, both 0.1 M, were prepared separately by dissolving ferric chloride and sodium hydrosulfide respectively in oxygen-free water prepared by bubbling prepurified N_2 in high-purity water ($18\text{M}\Omega\text{-cm}$) for at least 5 hours. The high-purity water was generated from a Millipore

Milli-Q system, and the nitrogen was purified by flowing the gas over a bed of copper filings at 450 °C to remove oxygen. The organic solvent, with or without presaturating elemental sulfur, was used in the two phase organic/aqueous system. The sulfur-saturated solvent was prepared by adding elemental sulfur (99.999% S from Aldrich) in the CS₂ solvent until solid precipitates were found. The solvent was then passed through a 0.2 µm filter to remove solid sulfur, and used in the synthesis experiments. All solutions were prepared daily in a glove box with a nitrogen pressure maintained at about 250 kPa (~2.5 atm). The temperature of the synthesis experiments was 25±0.5 °C.

3.2.2 Experimental Procedure

An aqueous solution of NaSH (20 ml, 0.1 M) was combined with 10 ml of organic solvent (CS₂) in a 50 ml screwcapped vial followed immediately by addition of 10 ml of 0.1 M FeCl₃ solution. The initial concentrations of Fe³⁺ and HS⁻ were 0.033 and 0.067 M respectively in the resulting aqueous phase, with a pH of 4.0. The vial was then capped and sealed, and transferred to a wrist-action shaker. The vial was shaken for a certain number of days, following which the two liquid phases were allowed to separate spontaneously in the vial. When the solid product settled to the bottom of the aqueous phase, the liquid phase was decanted out from the vial. The solid products in the vial were then washed with acetone, and dried in a vacuum oven at room temperature. The organic phase was also collected for analysis when needed. In some cases, the dried solid particles were washed with carbon disulfide to remove elemental sulfur.

The phases in the solid reaction products were identified with X-ray diffraction (Rigaku Geigerflex). The particles of the product were observed with a Topcon SX-40A

scanning electron microscope (SEM). The Eh-pH diagrams for the S-H₂O systems were plotted using the DIAGRAM software (Osseo-Asare and Brown, 1979).

3.3 Results and Discussion

3.3.1 Reaction in the Absence of Organic Solvent

Figure 3.1 shows an SEM micrograph and the corresponding X-ray diffractogram of the solid products obtained by the reaction between Fe³⁺ and SH⁻ ions in the aqueous solution in the absence of the organic solvent. It can be seen that pyrite and elemental sulfur were produced from the reaction. It has been suggested that pyrite forms in the Fe³⁺/HS⁻ aqueous system at pH 4.0 according to the following reactions (see Chapter 2):

The first step produces Fe²⁺ and S⁰, and subsequently, pyrite forms from the solution containing amorphous FeS and polysulfide ions S_n²⁻. It is noted that the production of elemental sulfur is an important step in this pathway of pyrite formation.

FIGURE 3.1. (a) SEM micrograph, and (b) X-ray diffractogram of the solid product obtained from the reaction between Fe^{3+} and HS^- ions in the absence of organic phase (aging time = 25 days).

3.3.2 Reaction in the Presence of Organic Solvent Initially Free of Elemental Sulfur

To examine the role of elemental sulfur in pyrite formation, the sulfur-extracting organic phase (CS₂) was introduced into the reaction system. The SEM micrograph and the X-ray diffractogram of the solid reaction product are shown in Figure 3.2. It can be seen that in the presence of carbon disulfide, CS₂, the reaction product in the aqueous phase became greigite (Fe₃S₄), and not pyrite. After the reaction, the organic solvent was evaporated at room temperature, and yellow crystals of elemental sulfur were observed. This result suggests that immediately elemental sulfur was produced from reaction 3.7, it was transferred into the organic phase:

Therefore, no elemental sulfur was available for reactions 3.9 and 3.10 to take place in aqueous solution, and pyrite could not form. This observation provides a strong indication that the presence of elemental sulfur is essential for pyrite formation.

3.3.3 Reaction in the Presence of Organic Solvent Presaturated with Elemental Sulfur

To verify that the inhibition of pyrite formation is due to the unavailability of elemental sulfur rather than direct interference by the organic phase itself, the organic solvent was presaturated with sulfur before introduction into the reaction system. It can be seen from Figure 3.3 that pyrite formed when the organic phase was presaturated with

FIGURE 3.2. (a) SEM micrograph, and (b) X-ray diffractogram of the solid product obtained from the reaction between Fe^{3+} and HS^- ions in the presence of organic phase (25% CS_2) initially elemental-sulfur-free (aging time = 25 days).

FIGURE 3.3. (a) SEM micrograph, and (b) X-ray diffractogram of the solid product obtained from the reaction between Fe^{3+} and HS^- ions in the presence of organic phase (25% CS_2) presaturated with elemental sulfur (aging time = 25 days).

elemental sulfur. In this situation, the elemental sulfur produced from reaction 3.7 stayed in the aqueous phase, and pyrite formed by reactions 3.8 to 3.10.

3.3.4 Effects of Aging Time

Figure 3.4 shows the X-ray diffractogram of the solid products obtained by reaction of Fe^{3+} with HS^- in the presence of the organic phase, after two different aging times. In this experiment the organic phase was initially free of elemental sulfur. It can be seen that mackinawite (Fe_9S_8) formed after 5 days (Figure 3.4a), and the product after 25 days was greigite (Fe_3S_4) as indicated in Figure 3.4b. This product sequence is consistent with the findings of previous investigators (Schoonen and Barnes, 1991a,b) in connection with the $\text{Fe}^{2+}/\text{HS}^-$ reaction:

However, as can be seen from Figure 3.5, when the organic phase was presaturated with elemental sulfur, pyrite was produced following the initial formation of mackinawite. The corresponding reaction pathway may be expressed as follows:

The formation of pyrite from the reaction between mackinawite and elemental sulfur has been reported by several investigators (Berner, 1969; Sweeney and Kaplan, 1973; Rickard, 1975).

FIGURE 3.4. X-ray diffractograms of the reaction products in the aqueous/organic system containing 25% CS_2 initially elemental-sulfur-free, (a) aging time = 5 days, and (b) aging time = 25 days.

FIGURE 3.5. X-ray diffractograms of the reaction products in the aqueous/organic system containing 25% CS_2 presaturated with elemental sulfur, (a) aging time = 5 days, and (b) aging time = 25 days.

3.3.5 Reaction Mechanism

The experimental results presented above indicate clearly that pyrite could not form in the absence of elemental sulfur in aqueous solution. However, the question arises: what is the essential role of elemental sulfur in pyrite formation?

Based on a kinetic investigation of pyrite formation at neutral pH, Rickard (1975) suggested that both elemental sulfur and iron sulfide should dissolve in solution to form polysulfide ions and ferrous ions respectively, and the reaction between ferrous ions and polysulfide ions can produce pyrite from solution directly according to the reaction:

Pyrite formation via direct reaction of ferrous iron with polysulfide ions under the conditions where iron monosulfide was undersaturated was also reported by Howarth (1979), Howarth and Teal (1979) and Graham and Ohmoto (1994). However, in an extensive laboratory work, Schoonen and Barnes (1991a,b) demonstrated that instead of FeS_2 nuclei, the reaction of ferrous ions and polysulfides produced initially amorphous FeS . The subsequent sulfidation of the iron monosulfide precursor by polysulfides produced pyrite. Luther (1991) studied the reaction of ferrous ions with polysulfides at 25 °C, and found that the initial reaction products included FeS and $\text{Fe}(\text{HS})^+$. Either solid FeS or the soluble complex $\text{Fe}(\text{HS})^+$ could react with polysulfides to form pyrite (Luther, 1991).

Despite the disagreement on the role of the iron monosulfide precursor, the important role of polysulfides in pyrite formation has been recognized by many investigators (Rickard, 1975; Luther, 1991; Schoonen and Barnes, 1991a,b; Graham and

Ohmoto, 1994). In aqueous solution, the elemental sulfur can react with HS^- to form polysulfide ions, according to the following reaction (Millero, 1986; Morse et al., 1987):

The S_n^{2-} species can also undergo protonations to form H_2S_n and HS_n^- ions (Schoonen and Barnes, 1988):

Based on the thermodynamic data provided by Millero (1986) and Schoonen and Barnes (1988), an Eh-pH diagram for the S-H₂O system was generated as shown in Figure 3.6. It can be seen that elemental sulfur is the thermodynamically stable species at low pH. However, no polysulfides can be seen from this diagram. If reaction kinetics is considered, an assumption can be made that the polysulfides appear before the formation of the oxy-sulfur species. The Eh-pH diagram for the S-H₂O system with exclusion of oxy-sulfur species is shown in Figure 3.7. The polysulfide species, S_5^{2-} , S_4^{2-} and S_2^{2-} , are predominant above pH 9, and no significant hydropolysulfides are present in the system. Similar trends can also be observed from the speciation diagram as shown in Figure 3.8 (Morse et al., 1987).

Generally, pyrite formation through solid-solid reaction of iron monosulfide and elemental sulfur is a very slow process (Berner, 1969, 1970; Marnette et al., 1993). The rapid formation of pyrite in this study (2 days, see Chapter 2) indicates that pyrite formation through solid-solid reaction is not significant.

FIGURE 3.6. Eh-pH diagram for the S-H₂O system at 25 °C.

FIGURE 3.7. Eh-pH diagram for the S-H₂O system at 25 °C with exclusion of oxy-sulfur species.

FIGURE 3.8. Speciation diagram for the S-H₂O system at 25 °C (Morse et al., 1987).

It is proposed that polysulfides were responsible for the rapid formation of pyrite in this study. Although polysulfide species were not thermodynamically predominant (Figures 3.6 to 3.8), their concentration may, kinetically, be significant for pyrite formation. Furthermore, the concentration of polysulfides may be much higher in the solutions of this study due to the in-situ generation of elemental sulfur. When elemental sulfur was precipitated in aqueous solution, sub-colloidal particles of elemental sulfur were expected to form first. Because these tiny particles have large surface energies, they are relatively unstable. As a result, the solubility of these tiny particles will be much larger than the macroscopic particles. In other words, the concentrations of the dissolved polysulfide species (formed via Equation 3.15) will be higher. The concentration of the polysulfide ions near the surface of the sulfur particles is even higher, because the dissolution of elemental sulfur to release polysulfide ions occurs at the solid/aqueous interface. Thus, pyrite may form in the polysulfide-concentrated region near the elemental sulfur particles (Graham and Ohmoto, 1994). The reactions of the polysulfide ions with amorphous "FeS" or $\text{Fe}(\text{HS})^+$ complex to form pyrite may proceed as proposed by Luther (1991) (Equation 3.2b).

Another possibility for the rapid formation of pyrite is that the aqueous zero-valent sulfur species ($\text{S}(0)$) formed before the sulfur crystallization are the reactants for pyrite formation. These species may be in the form of atomic sulfur (S), molecular sulfur (S_x ($x \leq 8$)) or sulfur clusters ($n\text{S}_8$). Although the mechanism of elemental sulfur formation in aqueous solutions is not fully known, it is reasonable to expect that the precipitation of orthorhombic sulfur must be preceded by a series of reactions, including monomer formation, polymerization and crystallization. The importance of atomic sulfur in gas-phase reactions has been shown in the literature (Davis, 1968; Meyer, 1968). Similarly, atomic sulfur may also play an important role in aqueous reactions. Marcus and co-

workers (1984, 1989) suggested that adsorbed monoatomic sulfur on the metal/aqueous interface could activate metal dissolution. It has also been proposed by Macdonald (1992) that zero-valent sulfur may be the reactive intermediate responsible for metal dissolution in aqueous sulfide solutions. However, the possible role of atomic sulfur in metal dissolution, as in pyrite formation, has not yet been seriously investigated in the literature.

3.4 Conclusions

Investigations of the reaction between Fe^{3+} and HS^- ions in aqueous solution with or without the addition of a sulfur-extracting organic phase (CS_2) showed that: (a) in the presence of the organic phase, no pyrite formed because the elemental sulfur produced in the system was extracted into the organic phase, and (b) when the organic phase was presaturated with elemental sulfur, pyrite was produced.

The stability diagrams for the S- H_2O system showed that polysulfides were predominant above pH 9. At pH 4.0, elemental sulfur predominated in the aqueous system. However, kinetic considerations suggest that the concentration of the polysulfide ions S_n^{2-} may be high enough for pyrite formation. The reaction of the polysulfide ions with the freshly formed " FeS " or $\text{Fe}(\text{HS})^+$ resulted in the rapid formation of pyrite in aqueous solution at room temperature. In addition, the possible role of atomic sulfur, molecular sulfur and sulfur clusters as reactants in pyrite formation needs to be further examined.

Chapter 4

PYRITE FORMATION BY THE $\text{Fe}^{3+}/\text{HS}^-$ REACTION IN AQUEOUS SOLUTIONS: EFFECTS OF SOLUTION COMPOSITION

Abstract

Microsize particles of pyrite were synthesized by reaction of ferric ions with sulfide ions in aqueous solutions. The reaction products of the synthesis experiments were characterized by X-ray diffraction and electron-optical techniques. The formation of pyrite was affected strongly by the pH and redox potential (Eh) of the working solutions. Pyrite, with a mean particle diameter of 1.5 μm , formed in the pH range from 3.6 to 5.7 and Eh $\sim 0\text{V}$ (-0.05 to 0.01V). The intermediate products of elemental sulfur and FeS (or $\text{Fe}(\text{HS})^+$) were identified as essential precursors for pyrite formation. Eh-pH diagrams for the S- H_2O and Fe-S- H_2O systems indicated that the solid species FeS (or the soluble complex $\text{Fe}(\text{HS})^+$) and elemental sulfur are both thermodynamically stable under the conditions where pyrite forms. The inability to form pyrite below $\sim\text{pH}$ 3.6 is attributed to undersaturation of FeS or the absence of $\text{Fe}(\text{HS})^+$. On the other hand, the inhibition of pyrite formation above $\text{pH}\sim 5.7$ is ascribed to the corresponding Eh conditions which make FeS unstable relative to FeOOH . In addition, it was demonstrated that nanoparticles of pyrite could be obtained by lowering the concentrations of Fe^{3+} and HS^- in the early stages of the reaction.

4.1 Introduction

Experimental investigations and practical applications of finely divided pyrite particles have received growing attention in recent years. Because of the large specific surface area, particulate pyrite has been used as a model material for pyrite oxidation investigations (Lalvani and Shami; Ciminelli and Osseo-Asare, 1995). Fine particles of pyrite have also been used as carriers which can adsorb some toxic metal ions from wastewater (Zouboulis et al., 1992). Another application of pyrite particles is in lithium batteries as a cathodic active material (Knodler et al., 1979; Iwakura et al., 1983 a,b). It was found that the cathodic efficiencies of the Li/FeS₂ cells increase significantly with increase in the specific area of the pyrite particles (Iwakura et al., 1983a). Pyrite can also be used as a photoactive material in photoelectrochemical cells (PEC) (Ennaoui et al., 1986), because it has an energy gap $E_g=1\pm0.2$ eV (Gupta et al., 1980; Ennaoui et al., 1986; Liu et al., 1988), similar to the solar energy material silicon ($E_g=1.1$ eV). Pyrite particle suspensions may have potential PEC applications because of the increase in the reaction surface area (Chen et al., 1991).

Pyrite has been synthesized in aqueous solutions at low temperature and pressure by a number of investigators (Roberts et al., 1969; Berner, 1970; Rickard, 1975; Luther, 1991; Schoonen and Barnes, 1991b). Generally, it is believed that pyrite formation requires a precursor of iron monosulfide, obtained from the reaction between aqueous sulfide and ferrous ions. The precursor forms initially as an amorphous "FeS" with a chemical composition varying from Fe_{0.87}S to FeS_{1.1} (Berner, 1964b, 1967; Rickard, 1969, 1975; Sweeney and Kaplan, 1973). This precursor reacts subsequently with elemental sulfur S⁰ or polysulfides S_n²⁻ to form pyrite in the presence of excess sulfide (Berner, 1970; Sweeney and Kaplan, 1973; Luther, 1991, Schoonen and Barnes,

1991a,b). The critical role of iron monosulfide in pyrite formation was demonstrated by Schoonen and Barnes (1991a,b) in an extensive laboratory investigation. Their experimental results indicate that pyrite will not form when iron monosulfides are undersaturated and that pyrite formation always involves an iron monosulfide precursor.

In addition to iron monosulfide, FeS , the solid species $\text{Fe}(\text{HS})_2$ (Rickard, 1989), and soluble complexes, such as $\text{Fe}(\text{HS})^+$, $\text{Fe}_2(\text{HS})^{3+}$, or $[\text{Fe}(\text{HS})\text{S}_x]^-$ (Luther, 1991, Luther and Ferdelman, 1993; see Chapter 5) were also proposed as the initial products of the $\text{Fe}^{2+}/\text{HS}^-$ reaction and these may also play some role in pyrite formation. However, the exact roles of these species in pyrite formation have not been elucidated.

Another mechanism for pyrite formation is based on direct reaction of ferrous ions with polysulfides. Rickard (1975) proposed that both elemental sulfur and iron sulfide dissolve to form polysulfide ions and ferrous ions respectively. The reaction between ferrous ions and polysulfide ions then produces pyrite from solution directly. Pyrite formation via direct reaction of ferrous iron with polysulfide ions without monosulfide precursor under conditions where iron monosulfide was undersaturated was also observed by Howarth (1979) and Howarth and Teal (1979). Pyrite formation through the reaction of iron monosulfide and elemental sulfur is a very slow process (Berner, 1970). However, Howarth (1979) found that pyrite actually forms rapidly in nature under the condition when iron monosulfide was undersaturated. The fast formation of pyrite was attributed to the direct reaction of ferrous iron with polysulfide ions (Howarth, 1979; Howarth and Teal, 1979). It must be noted, however, that the proposed roles of ferrous and polysulfide ions as reactants in pyrite nucleation have not been demonstrated directly.

The previous study (see Chapters 2 and 3) has shown that pyrite can be synthesized (within a few days) from the reaction between FeCl_3 and NaHS in aqueous solutions at room temperature. In this chapter, the effects of solution composition (pH, reactant

concentrations and $\text{Fe}^{3+}/\text{HS}^-$ mole ratios) and redox potential (Eh) on pyrite formation were studied systematically. Thermodynamic stability diagrams (Eh-pH) were constructed in order to identify the predominant species in solution. The mechanism of pyrite formation by the $\text{Fe}^{3+}/\text{HS}^-$ reaction was examined.

4.2 Experimental

Reagent grade ferric chloride ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) and sodium hydrosulfide ($\text{NaHS} \cdot x\text{H}_2\text{O}$) from Aldrich were used as the iron and sulfur sources respectively. A solution of Fe(III) with a concentration of 0.1 M was prepared by dissolving the ferric salt in oxygen-free water containing 0.01 M HCl to prevent iron hydroxide precipitation. Sulfide solution with a concentration of 0.1 M was prepared by dissolving NaHS in oxygen-free water. These solutions were diluted further with oxygen-free water to obtain the required concentrations. The oxygen-free water was prepared by bubbling purified N_2 in high purity water ($18 \text{ M}\Omega\text{-cm}$) for at least 5 hours. Fresh ferric and sulfide solutions were prepared daily. The pH of the reaction solutions was controlled by small additions of concentrated HCl or NaOH. In separate experiments, the pH was measured with a Model 701 A digital pH/mV meter (Orion Research) immediately after the two solutions were mixed. The potentials, Eh, of the reaction solutions were measured with a platinum plate electrode referenced to a saturated calomel electrode (SCE). The potentials reported in this study were converted to the SHE scale ($\text{SHE(V)} = \text{SCE(V)} + 0.242$).

The synthesis experiments were carried out in 50 ml screwcapped vials in a glove box with nitrogen pressure maintained at 250 kPa (~ 2.5 atm). Iron and sulfide solutions in two separate vials without caps were placed in the glove box for 2 hours to release possible

oxygen content in the solutions. Then the two solutions were mixed in one vial. The vial was shaken manually for a few seconds, and then sealed and stored in the glove box for aging. The temperature of the reactions was 25 ± 0.5 °C.

Identification of the phases of the solid products was conducted by X-ray diffraction ($\text{Cu K}\alpha$ radiation; Rigaku Geigerflex). The characterization of the particles was performed with a Philips 420T transmission electron microscope (TEM) and a Topcon SX-40A scanning electron microscope (SEM). Before extracting a TEM sample from the aqueous solution, the sealed vial was shaken manually for 1 minute to suspend the particles. The vial was then opened, and a sample of the suspension was collected with a micropipette. With the micropipette, a droplet of suspension was deposited on a carbon-coated copper grid, and TEM examination was performed immediately. To prepare the SEM specimen, the precipitate in the vial was separated by centrifugation and then dried in a vacuum oven at room temperature. The dried solid material was then placed on a specimen mount and coated with gold. Energy dispersive X-ray (EDX) spectroscopy was used to detect the components of the material under the SEM. Potential-pH diagrams were plotted using the DIGRAM computer program (Osseo-Asare and Brown, 1979). The thermodynamic data were obtained from Naumov et al. (1974), Baes and Mesmer (1976), Smith and Martell (1977), Schoonen and Barnes (1988), and Chapter 5 in this study.

4.3 Results and Discussion

4.3.1 Reaction pH

Experiments were performed with 0.033 M FeCl_3 and 0.067 M NaHS at different pH values, with an aging time of 5 days. The experimental results are summarized in Table

4.1. Typical diffractograms for the solid reaction products and the SEM micrographs for the particle morphology are presented in Figures 4.1 and 4.2. As can be seen from Table 4.1 and Figure 4.1a, elemental sulfur was produced at pH 2.4. The SEM micrograph of the elemental sulfur particles is shown in Figure 4.2a. At pH 2.9, a mixture of elemental sulfur and pyrite was obtained (Table 4.1). The SEM micrograph of the mixture is shown in Figure 4.2b. The larger particles are elemental sulfur and the smaller ones are pyrite, on the basis of the EDX results shown in Figures 4.3a and 4.3b.

In the pH range from 3.6 to 5.7, pyrite was produced from the reaction, as can be seen from both the X-ray diffractogram (Figure 4.1b) and the EDX spectrum (Figure 4.3c). The pyrite particles formed under these conditions had an average particle size of 1.5 μm (Figure 4.2c). With further increase in pH to above 7.2, the X-ray diffractogram of the solid product lost the characteristic pyrite peaks, giving instead, weak peaks attributable to $\gamma\text{-FeOOH}$ (Figure 4.1c). Analysis of the solid material by EDX showed that it contained both sulfur and iron (Figure 4.3d). It is believed to be a mixture of amorphous FeS and $\gamma\text{-FeOOH}$. As discussed previously (see Chapter 2), amorphous FeS is readily oxidized to $\gamma\text{-FeOOH}$.

4.3.2 Eh-pH diagrams

Pyrite formation from the reaction between Fe^{3+} and HS^- in aqueous solution is via the following reactions (see Chapter 2):

TABLE 4.1. Effects of pH on pyrite formation.

Run#	pH	Eh, V	X-ray phase	Soluble in HCl*	Particle size, μm
220	2.4	0.13	S ⁰	No	~6
221	2.9	0.09	S ⁰ +pyrite	No	~6(S ⁰)+~1(pyrite)
222	3.6	0.01	Pyrite	No	~1.5
223	4.0	-0.01	Pyrite	No	~1.5
224	5.7	-0.05	Pyrite	No	~1.5
225	7.2	-0.12	Amorphous	Yes	/
226	9.8	-0.24	Amorphous	Yes	/
227	11.8	-0.33	Amorphous	Yes	/

*Concentrated HCl; 10 min.

FIGURE 4.1. X-ray diffractograms of the solid products formed at (a) pH 2.4, (b) pH 4.0, and (c) pH 7.2.

FIGURE 4.2. SEM micrographs of (a) elemental sulfur formed at pH 2.4, and (b) a mixture of sulfur and pyrite formed at pH 2.9.

(Figure 4.2 continued) (c) pyrite formed at pH 4.0, and (d) amorphous FeS formed at pH 7.2.

FIGURE 4.3. EDX spectra of the solid products formed at different pH values.

It can be seen that both elemental sulfur and iron monosulfides are essential for pyrite formation. The importance of elemental sulfur and iron monosulfides was also recognized by other investigators (Berner, 1970; Sweeney and Kaplan, 1973; Rickard, 1975; Luther, 1991; Schoonen and Barnes, 1991a,b; see Chapter 3).

An Eh-pH diagram is presented in Figure 4.4 for the S-H₂O system. Corresponding diagrams for the Fe-S-H₂O systems are given in Figures 4.5, 4.6 and 4.7. The Eh values measured in the reaction solutions are also indicated in these figures as square data points; the open squares identify conditions that resulted in pyrite formation. It can be seen from Figure 4.4 that, at pH 4 and Eh = -0.01 V (Run# 223, Table 4.1), elemental sulfur is available in the aqueous system. The thermodynamic feasibility of pyrite formation in the pH range of 3.6 to 5.7 is shown in the Eh-pH diagram presented in Figure 4.5. The Eh-pH diagram shown in Figure 4.6 was calculated with the exclusion of FeS₂ from this Fe-S-H₂O system in order to show the possible metastable field of FeS. It is observed that, at pH 4 and Eh = -0.01 V, iron monosulfide(FeS) exists as a metastable species before pyrite formation. Therefore, pyrite formation at pH 4 and Eh = -0.01 V is expected (Table 4.1), because both elemental sulfur and iron monosulfide are present in the aqueous system.

The formation of elemental sulfur at pH 2.4 and Eh = 0.13V (Table 4.1) would be expected, according to Figure 4.4. However, as can be seen from Figure 4.6, iron monosulfide is undersaturated at pH 2.4 and Eh = 0.13 V (Run# 220, Table 4.1); the soluble species Fe²⁺ is predominant in this low pH solution. The synthesis experiments showed that, when mixing Fe³⁺ with HS⁻ solution at pH 2.4, no black material was produced. The black materials of the form FeS (Berner, 1970), Fe(HS)₂ (Rickard, 1989) or Fe(HS)⁺ (Luther, 1991; Luther and Ferdelman, 1993; see Chapter 5) have been observed as the initial products and have been proposed as the precursors for pyrite

FIGURE 4.4. Eh-pH diagram for S-H₂O system at 25 °C with measured Eh; □, pyrite formed; ■, no pyrite formed.

FIGURE 4.6. Eh-pH diagram for Fe-S-H₂O system at 25 °C with exclusion of FeS₂;

□, pyrite formed; ■, no pyrite formed.

FIGURE 4.7. Eh-pH diagram for Fe-S-H₂O system at 25 °C with exclusion of FeS₂ and FeS; □, pyrite formed; ■, no pyrite formed.

formation. Therefore, the failure to make pyrite at low pH may be attributable to the undersaturation of the iron sulfide precursors.

At high pH, elemental sulfur is not thermodynamically stable in the aqueous system (Figure 4.4), although iron monosulfide may exist in the system (Figure 4.6). If Equation 4.3 represented a direct reaction path, then it could be argued that, even if FeS were available, the absence of elemental sulfur would preclude pyrite formation (as observed experimentally, Table 4.1). However, a solid-solid reaction such as Equation 4.3 is not likely to be kinetically significant at room temperature. It is likely that the essential role of elemental sulfur is to produce polysulfide ions, S_n^{2-} ($n=2$ to 6), which are the reactants for pyrite formation in aqueous solutions (Rickard, 1975; Luther, 1991):

It is known that polysulfide concentration increases with pH (Morse et al., 1987). Thus, the inability to form FeS_2 at pH 7.2 and higher (Table 4.1) cannot be attributed to a lack of the necessary sulfur precursor.

It is interesting to observe in Figure 4.6 that, even though there is a large FeS stability region that encompasses the pH range of 7.2 to 11.8 (see Table 4.1), the corresponding Eh values of the reaction media fall outside the FeS stability region. In particular, the experimental Eh values fall within the FeOOH stability region. It is therefore proposed here that for $pH \geq 7.2$, the current experiments did not produce pyrite because FeS formation could not compete successfully with FeOOH formation. The presence of γ -FeOOH in the pH 7.2 reaction product, as indicated by the X-ray diffractogram of Figure 1c, is supportive of this interpretation.

Further insight into the effects of solution composition may be gained by excluding both FeS₂ and FeS from the thermodynamic analysis of the Fe-S-H₂O system (Figure 4.7). The predominance field of the iron sulfide complex Fe(HS)⁺ was found in the pH range from 3.6 to 7.8 within a certain Eh range. It is also seen that the Eh and pH conditions leading to FeS₂ formation fall within the stability region of Fe(HS)⁺. Therefore, the possible pathways for forming pyrite may be expressed as follows (Luther, 1991):

or

4.3.3 Concentrations of Fe³⁺ and HS⁻

The effects of variations in reactant concentrations on the particle size of pyrite were examined by changing the concentration of FeCl₃ from 1.7x10⁻³ M to 6.7x10⁻² M and fixing the ratio of [FeCl₃] to [NaSH] as 1:2, and pH at 4.0±0.2. As shown in Figure 4.8, pyrite with an average particle size of 1.5 μm can be made within 2 days when the concentration of FeCl₃ is higher than 1.7x10⁻² M. The particle size can be reduced to about 50 nm when the concentration of FeCl₃ is less than 6.7x10⁻³ M. However, if the aging time is long enough, 5 days for example, the particle size of pyrite becomes 1.5 μm for any initial concentration of reactants (Figure 4.9). The particle size of pyrite as a function of reactant concentration for different aging times is shown in Figure 4.10. The results

FIGURE 4.8. TEM micrographs of pyrite formed from different concentrations of reactants for the aging time of 2 days. (a)-0.067 M FeCl_3 , 0.134 M NaHS; (b)-0.033 M FeCl_3 , 0.067 M NaHS; (c)-0.017 M FeCl_3 , 0.033 M NaHS; (d)-0.0067 M FeCl_3 , 0.0134 M NaHS; (e)-0.0033 M FeCl_3 , 0.0067 M NaHS; (f)-0.0017 M FeCl_3 , 0.0033 M NaHS.

FIGURE 4.9. TEM micrographs of pyrite formed from different concentrations of reactants for the aging time of 5 days. (a)-0.067 M FeCl_3 , 0.134 M NaHS; (b)-0.033 M FeCl_3 , 0.067 M NaHS; (c)-0.017 M FeCl_3 , 0.033 M NaHS; (d)-0.0067 M FeCl_3 , 0.0134 M NaHS; (e)-0.0033 M FeCl_3 , 0.0067 M NaHS; (f)-0.0017 M FeCl_3 , 0.0033 M NaHS.

FIGURE 4.10. Particle size as a function of reactant concentrations at different aging time.

indicate that the initial concentrations of the reactants do not affect the final particle size if the aging time is long enough. However, small particles can be obtained in the early stage of the reaction by lowering the initial concentrations of the reactants. This implies that if one can control the growth of the particles at a certain stage of the reaction, it may be possible to synthesize discrete nanosize particles.

The formation of uniform particles suggests that the mechanism of pyrite nucleation and particle growth may follow LaMer's theory (LaMer and Dinegar, 1950; Matijevic, 1981, 1985; Sugimoto, 1987). A fast nucleation of pyrite may occur when the concentration of pyrite-forming precursors reaches a critical supersaturation condition, followed by a slow growth of the particles via monomer addition on the existing particles. Since all the nuclei of pyrite particles are generated at the same time, and the particles grow at the same rate, uniform particles of pyrite are produced.

4.3.4 Mole Ratio of Fe^{3+} to HS^-

The effect of the $[\text{Fe}^{3+}]$ to $[\text{HS}^-]$ mole ratio on pyrite formation was examined by varying the volumes of Fe^{3+} solution (0.1 M) at 5, 10, 15 and 20 ml while fixing the volumes of HS^- solution (0.1 M) at 20 ml. Thus Fe^{3+} to HS^- mole ratios of 0.25:1, 0.5:1, 0.75:1 and 1:1 were obtained. The pH of the reaction was maintained at 4.0 ± 0.2 . The X-ray diffractograms of the solid products for different mole ratios are shown in Figure 4.11. It can be seen that pyrite is produced predominantly at the lowest ratio of Fe^{3+} to HS^- , and elemental sulfur dominates at the highest ratio. The measured Eh values at different Fe^{3+} to HS^- mole ratios are shown in Figure 4.12. It can be seen that the Eh increases gently with increase in Fe^{3+} to HS^- mole ratio. Referring to Figures 4.6 and 4.7, it can be seen that at pH 4.0 and Eh $\sim 0\text{V}$, a subtle increase in Eh can shift reaction conditions from the FeS (or

FIGURE 4.11. X-ray diffractograms of the solid products formed at different mole ratios of Fe^{3+} to HS^- (a) 0.25:1, (b) 0.5:1, (c) 0.75:1 and (d) 1:1 at $\text{pH } 4.0 \pm 0.2$.

FIGURE 4.12. The measured Eh of the solution as a function of Fe³⁺ to HS⁻ mole ratio.

$\text{Fe}(\text{HS})^+$) stability region (conducive to pyrite formation) into the Fe^{2+} stability region (which does not favor pyrite formation).

Another effect of the Fe^{3+} to HS^- mole ratio on pyrite formation concerns the effect of HS^- concentration. According to Equation 4.1, when the initial concentration of HS^- far exceeds that of Fe^{3+} , Fe^{2+} and S^0 can be produced while leaving enough HS^- in the aqueous system for making pyrite (via Equation 4.2). However, as the initial concentration of Fe^{3+} increases, most of the sulfide is converted to elemental sulfur, and there is not sufficient HS^- left in the system to go to the next step, i.e., FeS formation (Equation 4.2) and polysulfide formation (Equation 4.4). Hence, instead of pyrite, elemental sulfur forms from the reaction. It should be pointed out that although a low Fe^{3+} to HS^- mole ratio favors pyrite formation, the amount of the resulting product is small if the Fe^{3+} concentration is relatively low.

4.4 Conclusions

The effects of pH, redox potential (Eh), Fe^{3+} and HS^- concentrations, and the $\text{Fe}^{3+}/\text{HS}^-$ mole ratio on pyrite formation have been investigated in this study. Thermodynamic stability diagrams (Eh-pH) were used to elucidate the reaction pathways for pyrite formation.

The solution pH and Eh in the FeCl_3 and NaHS system control the final products of the reaction. Pyrite particles with a size of $1.5\ \mu\text{m}$ were produced in the pH range from 3.6 to 5.7. At pH 2.4, elemental sulfur was observed with an irregular shape and a size of $6\ \mu\text{m}$. A mixture of elemental sulfur and pyrite was obtained at pH 2.9. When pH was higher than 7.2, amorphous iron sulfides were produced. Pyrite formation requires both iron (II) monosulfide (or $\text{Fe}(\text{HS})^+$) and elemental sulfur (or polysulfide ions) as

precursors. At lower pH, monosulfide is undersaturated because of preferential stability of Fe^{2+} . On the other hand, at higher pH, Fe(II) is not available because of the competing reaction of Fe(III) oxyhydroxide formation.

Lowering of the concentrations of the reactants (FeCl_3 and NaHS) can decrease the particle size of pyrite only in the early stage of the reaction. The final particles have the same size for any initial concentration of the reactants tested in this study. This implies that extremely fine (nanosize) particles of pyrite may be obtained if one can control the growth (or aggregation) of the pyrite particles in the early stage.

The mole ratio of Fe^{3+} to HS^- affects the products of the reaction dramatically. A lower ratio is favorable for forming pyrite because a sufficiently low Eh is maintained and there is sufficient HS^- remaining in the system. On the other hand, a higher $\text{Fe}^{3+}/\text{HS}^-$ ratio leads to elemental sulfur formation.

Chapter 5

FORMATION OF IRON MONOSULFIDE: A SPECTROPHOTOMETRIC STUDY OF THE REACTION BETWEEN FERROUS AND SULFIDE IONS IN AQUEOUS SOLUTIONS

Abstract

The initial product from the reaction between ferrous and sulfide ions in aqueous solutions was studied by using a stopped-flow spectrophotometric technique. The absorbance-time curve showed that an intermediate product formed quickly within the first few seconds of the reaction; this material subsequently decomposed slowly to other species within the following several minutes. It was more likely to form the intermediate in the pH range from 7 to 8. This suggests that the reaction between Fe^{2+} and HS^- ions results in the formation of the intermediate product because both Fe^{2+} and HS^- are respectively the predominant Fe(II) and S(II) species in this pH range. The absorbance at a wavelength of 500 nm varied linearly with the concentration of the intermediate, the absorptivity of which was $4800 \text{ M}^{-1} \text{ cm}^{-1}$, as determined in this study. Stoichiometric experiments, based on the continuous variation method, gave the ratio of $[\text{HS}^-]$ to $[\text{Fe}^{2+}]$ as 1:1 for the formation of the intermediate, which is an iron bisulfide of the form $\text{Fe}(\text{HS})^+$. Analysis of the kinetic data showed that the rate of $\text{Fe}(\text{HS})^+$ formation was first order with respect to both Fe^{2+} and HS^- with a reaction rate constant of $10^{3.81} \text{ M}^{-1} \text{ sec}^{-1}$. The formation constant of

$\text{Fe}(\text{HS})^+$ was evaluated as $\log K = 4.34 \pm 0.15$ at 25°C and $I = 0$ from the thermodynamic analysis of the pertinent experimental data.

5.1 Introduction

The rejection or decomposition of pyrite (FeS_2) constitutes an essential step in many mineral, metal, and coal processing schemes (Hiskey and Schlitt, 1982; Nordstrom, 1982). This is because: (a) pyrite is the most abundant of the metal sulfides in nature, (b) it is distributed in a wide variety of geochemical settings, and consequently, it is found in association with many minerals and coal deposits, and (c) it is the source of both aqueous (acid mine drainage) and atmospheric (SO_2 emissions from coal combusters) pollution (Lowson, 1982; Nicholson et al., 1990; Chander and Zhou, 1992; Meyers, 1977). Recently pyrite has come under active investigation as a potential solar energy material (Tributsch, 1986), and it has been proposed as an anodic depolarizer for electrolytic hydrogen production (Lalvani and Shami, 1986).

In view of its importance in a wide range of natural and technological systems, the formation mechanism and interfacial reactivity of pyrite have attracted the attention of numerous investigators. It has been suggested by many studies that pyrite formation is a two-step process (Allen et al., 1914; Berner, 1964, 1967, 1969, 1970; Rickard, 1969, 1975; Roberts et al., 1969; Skripchenko, 1969; Sweeney and Kaplan, 1973; Goldhaber and Kaplan, 1974; Schoonen and Barnes, 1991a,b). In the first step (Equation 5.1), an iron monosulfide precursor, FeS , forms via the reaction between aqueous sulfide ion and aqueous ferrous ion. In the second step (Equation 5.2), the iron monosulfide precursor is converted to pyrite in the presence of element sulfur and excess hydrogen sulfide.

Therefore, the study of FeS formation in aqueous solution can provide useful information towards understanding the formation of pyrite. A further motivation for the study of FeS formation comes from recent investigations of the stoichiometry of pyrite. It appears that both natural and synthetic (CVD) samples are nonstoichiometric, being characterized by sulfur deficiencies of up to 7% (Fiechter et al., 1992). It has been suggested that the sulfur deficiency may be due to FeS centers built into pyrite crystals (Alonso-Vante et al., 1988) or it may be due to Schottky defects of S vacancies (Birkholz et al., 1991; Fiechter et al., 1992).

Iron monosulfide (FeS) can be produced in aqueous solution from reaction of sulfide with ferrous ions at room temperature. A black product is observed immediately when a sulfide containing solution is mixed with a ferrous solution. It has been suggested by a number of investigators (See review by Morse et al., 1987; Schoonen and Barnes, 1991a,b) that the black material is iron sulfide which is X-ray amorphous and has a chemical composition varying from $\text{Fe}_{0.87}\text{S}$ to $\text{FeS}_{1.1}$ (Berner, 1962, 1964, 1967; Rickard, 1969, 1975; Sweeney and Kaplan, 1973). However, some uncertainties still remain. Pohl (1953) postulated that the formation of FeS might be via an activated complex with a formula of $\text{Fe}(\text{HS})^+$. Baas Becking (1956) suggested that $\text{Fe}(\text{HS})_2$ is the first precipitated ferrous sulfide. Based on stereochemical arguments, Taylor (1980) proposed the formation of $\text{Fe}(\text{HS})^+$ as an intermediate in the formation of FeS.

The experimental verification of the above suggestions has encountered some difficulties because this reaction is so fast that it is not easy, with conventional techniques, to monitor the intermediate steps experimentally. To counteract this problem, Rickard

(1989) designed an apparatus which consists of a T-tube where Fe(II) and sulfide solutions can be introduced along two separate arms into a mixing chamber. The concentrations of dissolved sulfides are measured directly with silver-silver sulfide electrodes mounted along the chamber. By means of this apparatus, Rickard (1989) reported that the well known initial black precipitate is a neutral iron bisulfide ($\text{Fe}(\text{HS})_2$), but not FeS. Luther (1991), who utilized a polarographic technique, observed that the material initially formed from the reaction between Fe(II) and polysulfides consists of (a) a complex of the form $\text{Fe}(\text{HS})^+$ and (b) solid FeS. When excess polysulfides are present, a complex of the form $[\text{Fe}(\text{HS})\text{S}_x]^-$ is produced. Most recently, in a voltammetric study, Luther and Ferdelman (1993) concluded that $\text{Fe}(\text{HS})^+$ and $[\text{Fe}_2(\text{HS})]^{3+}$ complexes exist over the pH range 7 to 10 in solutions containing Fe(II) and sulfide, and over the pH range 3 to 6, the complex is in the form of $\text{Fe}(\text{H}_2\text{S})^{2+}$. In contrast to Rickard's observation (1989), Luther and Ferdelman (1993) found no evidence for the presence of the $\text{Fe}(\text{HS})_2$ precipitate in solutions containing Fe(II) and sulfide at neutral pH. Apparently, the process of the intermediate iron sulfide formation is not well understood.

It is interesting to note that Drobner and co-workers (1990) have proposed the formation of a bisulfide intermediate during pyrite formation under anaerobic conditions:

Thus, the $\text{Fe}(\text{II})/\text{HS}^-$ reaction may be important not only during FeS formation (Equation 5.1) but also during the subsequent reaction to pyrite. In this chapter, the reaction between aqueous sulfide and ferrous ions was examined by means of spectrophotometric technique. A stopped-flow spectrophotometer was used to monitor the reaction progress in the

millisecond to several minute time range. On the basis of the resulting experimental data, the stoichiometry of the intermediate species is identified, the relevant kinetic and thermodynamic parameters are derived, and the pathway of FeS formation is discussed.

5.2 Experimental

5.2.1 Reagents

Reagent grade ferrous chloride (FeCl_2) and sodium sulfide (Na_2S) were obtained from Aldrich. A stock solution of Fe(II) with a concentration of 0.1 M was prepared by dissolving FeCl_2 in oxygen-free water containing 0.01 M HCl to prevent $\text{Fe}(\text{OH})_2$ precipitation. A stock solution of S(II) with a concentration of 0.1 M was made with Na_2S and oxygen-free water. These solutions were diluted further to obtain the required concentrations. Both Fe(II) and S(II) stock solutions were prepared daily. The oxygen-free water was prepared by bubbling prepurified N_2 in high purity water ($18\text{M}\Omega\text{-cm}$) for at least 5 hours. The high purity water was obtained from a Millipore Milli-Q system. The nitrogen gas was deoxygenated by flowing over a bed of copper filings at 45°C . The pH of the working solution was adjusted by small additions of concentrated HCl or NaOH, and determined in separate experiments.

5.2.2 Spectrophotometric Technique

The spectra of the Fe(II) solution, the S(II) solution and the mixed Fe(II) and S(II) solution were determined by an HP 8451A diode array spectrophotometer (Hewlett Packard) with a 1 cm quartz optical cell. For determining the spectra of Fe(II) or S(II)

solution, the measurements were made 10 minutes after the solution was prepared. In this case, equilibrium conditions in the solutions could be assumed. For determining the spectra of the solution containing both Fe(II) and S(II), the measurements were made at different times after Fe(II) and S(II) solutions were mixed. The time was recorded by a stopwatch, thus these measurements yielded only preliminary results. The time-dependent absorption of the reaction mixture was determined by using a DX. 17 MV Sequential Stopped-Flow Spectrofluorimeter (Applied Photophysics) with a quartz spectrophotometric cell having an optical pathlength of 1 cm. This instrument allowed one to mix the Fe(II) and S(II) solutions from two separate syringes into the optical cell and the absorbance of the mixed solution was recorded as a function of time at a given wavelength. Oxygen-free water was taken as the reference solution in all spectrophotometric measurements and the zero absorbance was checked before each measurement. The average absorbance was determined from at least 5 measurements under the same conditions. The temperature of the experiments was controlled at $25 \pm 0.5^\circ\text{C}$.

5.3 Results And Discussion

5.3.1 Spectral Analysis

The spectra obtained with different Fe^{2+} concentrations at pH 2.0 are shown in Figure 5.1. A strong absorption occurs at a wavelength of 335 nm, as also observed by Heinrich and Seward (1990). The spectra of Fe(II) solutions, each at a total Fe(II) concentration of 1×10^{-4} M, were determined for different pH values as shown in Figure 5.2. Strong ultra-violet (UV) absorption occurs when pH is higher than 6.0. The increase in UV absorption at higher pH values is attributed to the presence of iron hydroxide species

FIGURE 5.1. Spectra of Fe^{2+} ion for different Fe(II) concentrations at pH 2.0.

FIGURE 5.2. Spectra of Fe(II) species at different pH.

FIGURE 5.3. Spectra of HS⁻ ions for different sulfide concentrations at pH 12.0.

FIGURE 5.4. Spectra of S(II) species at different pH.

FIGURE 5.5. Spectra of the reaction mixture of Fe(II) and S(II) solutions at pH 7.4.

formed in the solution. It can be seen further from Figure 5.2 that very low absorptions were obtained at wavelengths larger than 500 nm, even for high pH solutions.

The spectra of HS^- ion for different sulfide concentrations at pH 12.0 are shown in Figure 5.3. It can be seen that aqueous sulfide species exhibit strong UV absorption at a wavelength of 235 nm, a value similar to that reported by Chen and Morris (1971). The spectra of S(II) solutions for a total S(II) concentration of 1×10^{-4} M at different pH values are shown in Figure 5.4. It can be seen that, for a wide range of pH values, no absorption occurred at wavelengths beyond 300 nm.

Figure 5.5 shows the spectra for a solution containing 1×10^{-4} M Fe(II) and S(II) at pH 7.4. Significant changes in spectra were observed. Comparison of Figure 5.5 with Figures 5.2 and 5.4 indicates that the strong absorption observed at wavelengths higher than 300 nm is due to new species formed by the reaction between Fe(II) and S(II) solutions. At a wavelength of 500 nm, the absorbance increases at first (note that the absorbance at beginning of the reaction should be the one contributed by Fe(II) species only, so that the initial absorbance is about 0.02 as shown in Figure 5.2) and then decreases with time. This trend indicates that an initial reaction product forms in the early stages of the reaction and then transforms to other species as time increases. It follows from these results that the initial product can be detected by monitoring the time dependence of the absorption at 500 nm.

5.3.2 Pathway for the Formation of the Initial Product

A typical absorbance-time behavior, based on the 500 nm wavelength, is shown in Figure 5.6. It can be seen clearly that the absorbance increases rapidly within the first few seconds (Figure 5.6A). This means that a reaction product forms as soon as the Fe(II) and

FIGURE 5.6. Typical absorbance-time curve for the reaction between Fe(II) and S(II) solutions. (A) is a part of (B) for the reaction in the first five seconds.

FIGURE 5.7. Effect of pH on the formation of the intermediate product.

FIGURE 5.8. Logarithmic concentration diagram for 5×10^{-4} M Fe(II),
Equilibrium data from Baes and Mesmer (1976).

FIGURE 5.9. Logarithmic concentration diagram for 5×10^{-4} M S(II),
Equilibrium data from Schoonen and Barnes (1988).

S(II) solutions are mixed. The absorbance subsequently decreases slowly with increase in time (Figure 5.6B). This indicates that the initial product from the reaction is an intermediate species which reacts further to produce other species.

The maximum absorbance obtained from the absorbance-time experiments (Figure 5.6) corresponds to the highest concentration of the intermediate product. The effect of pH on the magnitude of the maximum absorbance is shown in Figure 5.7. The data show that the maximum formation of the intermediate occurs at pH about 7.4. Comparison of Figure 5.7 with the speciation behaviors of Fe(II) and S(II), as shown in Figures 5.8 and 5.9, suggests that the formation of the intermediate is attributable to the reaction between Fe^{2+} and HS^- ; in the pH range most favorable for the formation of the intermediate, both Fe^{2+} and HS^- are predominant. Based on this observation, the pathway of the reaction to form the intermediate can be postulated as:

where the iron sulfide complex $\text{Fe}(\text{HS})_n^{2-n}$ is the intermediate product formed in the initial stages of the reaction. This intermediate product is converted to FeS finally by some possible pathways to be discussed later.

5.3.3 Absorptivity of the Iron Sulfide Complex

For the reaction shown in Equation 5.5, Beer's law gives,

$$A - A_0 = \epsilon b [\text{Fe}(\text{HS})_n^{2-n}] \quad (5.6)$$

where A is the total absorbance contributed by $\text{Fe}(\text{HS})_n^{2-n}$, $\text{Fe}(\text{II})$ and $\text{S}(\text{II})$ species; A_0 the absorbance contributed by $\text{Fe}(\text{II})$ and/or $\text{S}(\text{II})$ species except $\text{Fe}(\text{HS})_n^{2-n}$; ϵ the absorptivity of $\text{Fe}(\text{HS})_n^{2-n}$ and b the pathlength of the optical cell (1 cm). To evaluate the values of A_0 , the absorbance as a function of pH for different concentrations of $\text{Fe}(\text{II})$ or $\text{S}(\text{II})$ was determined at a wavelength of 500 nm as shown in Figure 5.10. It can be seen that no absorption was observed for $\text{S}(\text{II})$ species at 500 nm within a wide range of pH, even at a high $\text{S}(\text{II})$ concentration of 1×10^{-2} M. However, some absorption was observed for $\text{Fe}(\text{II})$ species; the absorption increases with increasing pH and the concentration of $\text{Fe}(\text{II})$. At pH 7.4, the absorbance, A_0 , as a function of the concentration of $\text{Fe}(\text{II})$ is shown in Figure 5.11, from which A_0 can be estimated for various concentrations of $\text{Fe}(\text{II})$ at pH 7.4 and 500 nm.

To determine A , the absorbance-time curves, similar to that shown in Figure 5.6, were measured by means of the stopped-flow technique. The maximum absorbance in each curve was obtained as the value of A .

The experiments to evaluate the value of absorptivity of the intermediate were carried out by varying the concentration of Fe^{2+} and keeping the mole ratio of Na_2S to FeCl_2 at 10. Because the concentration of HS^- is in excess, the concentration of $\text{Fe}(\text{HS})_n^{2-n}$ can be assumed to be approximately equal to the initial concentration of Fe^{2+} , if the $\log K$ for the reaction is much greater than 1. This assumption is true for most transition metal sulfide complex systems (Dyrssen, 1988). The plot of $A - A_0$ vs the initial concentration of Fe^{2+} is shown in Figure 5.12, from which the absorptivity of the intermediate was determined as $4800 \text{ M}^{-1}\text{cm}^{-1}$, based on Equation 5.6. This implies that the spectrophotometric technique can be used to study the reaction of Fe^{2+} and HS^- not only qualitatively, but also quantitatively.

FIGURE 5.10. Absorption of different concentrations of Fe(II) or S(II) as functions of pH.

FIGURE 5.11. Absorbance as a function of Fe(II) concentrations at pH 7.4.

FIGURE 5.12. Absorbance, $A - A_0$, as a function of initial concentration of Fe^{2+} .

5.3.4 Stoichiometry of the Iron Sulfide Complex

Based on the fact that the absorbance of the intermediate product has a linear relationship with its concentration, the stoichiometry of the intermediate can be determined experimentally with the continuous variation method by fixing the total concentration of HS^- plus Fe^{2+} and varying the mole ratio of HS^- to Fe^{2+} (Job, 1928; Potts, 1987).

For the reaction shown in Equation 5.5, the formation constant can be expressed as:

$$K = \{ \text{Fe}(\text{HS})_n^{2-n} \} / (\{ \text{Fe}^{2+} \} \{ \text{HS}^- \}^n) \quad (5.7)$$

where $\{ \}$ represents the activities of the species. Since the experiments were conducted in solutions of relatively low ionic strength ($[\text{FeCl}_2] \leq 3.5 \times 10^{-4}$ and $[\text{Na}_2\text{S}] \leq 3.5 \times 10^{-3}$ M), the assumption was made that the activity coefficients for all soluble species in the system are unity, so that the activities can be represented by concentrations in the following discussions. The deviation from this assumption will be discussed later.

Suppose the total concentration of HS^- plus Fe^{2+} is C and the mole ratio of HS^- to Fe^{2+} is R, one then has:

$$C = [\text{Fe}^{2+}] + [\text{HS}^-] \quad (5.8)$$

$$R = [\text{HS}^-] / [\text{Fe}^{2+}] \quad (5.9)$$

and Equation 5.6 gives:

$$[\text{Fe}(\text{HS})_n^{2-n}] = (A - A_0) / \epsilon b \quad (5.10)$$

FIGURE 5.13. Absorbance, $A - A_0$, as a function of mole ratio (R) of HS^- to Fe^{2+} .

Substitution of Equations 5.8, 5.9 and 5.10 into Equation 5.7 gives:

$$A - A_0 = \epsilon b K (C / (1+R) - (A - A_0) / \epsilon b) (RC / (1+R) - n(A - A_0) / \epsilon b)^n \quad (5.11)$$

Measuring the absorbance of each solution with a certain mole ratio of HS^- to Fe^{2+} , and plotting absorbance, $A - A_0$, versus the mole ratio, R , the maximum absorbance occurs at $R = n$, a mole ratio corresponding to the combining ratio for the intermediate, $\text{Fe}(\text{HS})_n^{2-n}$.

The concentrations of HS^- and Fe^{2+} at a given pH and total $\text{Fe}(\text{II})$ or $\text{S}(\text{II})$ concentration were calculated based on corresponding dissociation constants selected from Baes et al.(1976) and Schoonen and Barnes (1988). The absorbance as a function of R for two different total concentrations is shown in Figure 5.13. It can be seen that the maximum absorbance occurs at $R = 1$. This means that the stoichiometric parameter n has a value of 1, and that the iron sulfide complex $\text{Fe}(\text{HS})_n^{2-n}$ is of the form $\text{Fe}(\text{HS})^+$.

5.3.5 Formation Constant of the Iron Sulfide Complex

For reaction 5.5, and recalling Equation 5.6, Beer's law can be expressed as:

$$\begin{aligned} A - A_0 &= \epsilon b [\text{Fe}(\text{HS})_n^{2-n}] \\ &= \epsilon b ([\text{Fe}^{2+}]_0 - [\text{Fe}^{2+}]) \end{aligned} \quad (5.12)$$

and

$$\begin{aligned} (A - A_0)_{\max} &= \epsilon b [\text{Fe}(\text{HS})_n^{2-n}]_{\max} \\ &= \epsilon b [\text{Fe}^{2+}]_0 \end{aligned} \quad (5.13)$$

where $[\text{Fe}^{2+}]_0$ is the initial concentration, $[\text{Fe}^{2+}]$ and $[\text{Fe}(\text{HS})_n^{2-n}]$ the concentrations at equilibrium, and $[\text{Fe}(\text{HS})_n^{2-n}]_{\text{max}}$ the concentration when all of Fe^{2+} is converted to $\text{Fe}(\text{HS})_n^{2-n}$. Hence, from Equations 5.7, 5.12 and 5.13, we have:

$$\begin{aligned} [(A-A_0) - (A-A_0)_{\text{max}}] / (A - A_0) &= - [\text{Fe}^{2+}] / [\text{Fe}(\text{HS})_n^{2-n}] \\ &= - K^{-1} / [\text{HS}^-]^n \end{aligned} \quad (5.14)$$

or

$$A - A_0 = (A - A_0)_{\text{max}} - K^{-1} (A - A_0) / [\text{HS}^-]^n \quad (5.15)$$

It is noted that:

$$\begin{aligned} [\text{HS}^-] &= [\text{HS}^-]_0 - n[\text{Fe}(\text{HS})_n^{2-n}] \\ &= [\text{HS}^-]_0 - n (A - A_0) / \epsilon b \end{aligned} \quad (5.16)$$

Equation 5.15 therefore becomes

$$A - A_0 = (A - A_0)_{\text{max}} - K^{-1} [(A - A_0) / ([\text{HS}^-]_0 - n (A - A_0) / \epsilon b)]^n \quad (5.17)$$

When $n = 1$, a plot of $(A-A_0)$ vs $[(A-A_0) / ([\text{HS}^-]_0 - (A-A_0)/\epsilon b)]$ should be a straight line with a slope of $(-K^{-1})$ and an intercept of $(A-A_0)_{\text{max}}$. The experiments for determining the formation constant were conducted by fixing the concentration of Fe^{2+} at 2.5×10^{-4} M at pH 7.4, and varying concentrations of HS^- from 1.5×10^{-4} to 3.5×10^{-3} M. The initial concentrations of Fe^{2+} and HS^- were calculated based on thermodynamic data available in the literature (Baes et al., 1976; Schoonen and Barnes, 1988). The plot of $(A-A_0)$ vs $[(A-A_0) / ([\text{HS}^-]_0 - (A-A_0)/\epsilon b)]$ is shown in Figure 5.14. The straight line indicates that the value of n is equal to 1, and the slope gives the formation constant as $\log K = 4.34 \pm 0.15$.

FIGURE 5.14. A plot of $(A - A_0)$ vs $[(A - A_0) / ([\text{HS}^-]_0 - (A - A_0) / \epsilon b)]$.

FIGURE 5.15. A plot of $A - A_0$ vs $\epsilon b [C / (1+R) - (A - A_0) / \epsilon b] [RC / (1+R) - (A - A_0) / \epsilon b]$.

The formation constant for reaction 5.5 can also be estimated from the experimental data as shown in Figure 5.13 (Job, 1928; Potts, 1987). According to Equation 5.11, a plot of $A - A_0$ versus $\epsilon b(C / (1+R) - (A - A_0) / \epsilon b) (RC / (1+R) - (A - A_0) / \epsilon b)$ will give a straight line when $n=1$, and the slope of the line will give the K value of the formation constant directly. Such a plot is shown in Figure 5.15, from which the stoichiometry ($n=1$) is confirmed and the formation constant is determined as $\log K = 4.33 \pm 0.10$ from the slope of the line. The value of $\log K = 4.33$ is consistent with the value of $\log K = 4.34$ determined above.

It should be point out that the formation constant evaluated above was based on the assumption that the ionic strength approaches zero. The deviation resulting from this assumption can be estimated by evaluating the activity coefficient γ based on the Davies Equation (Davies, 1962; Nancollas and Tomson, 1982):

$$\log \gamma = -0.5 z^2 [I^{1/2} / (1 + I^{1/2}) - 0.3 I] \quad (5.18)$$

where z is the charge of the ion, and I the molar ionic strength:

$$I = 1/2 \sum C_i z_i^2 \quad (5.19)$$

where C_i is the mole concentration of the i th ion. Under the experimental conditions ($[\text{FeCl}_2] \leq 3.5 \times 10^{-4} \text{ M}$ and $[\text{Na}_2\text{S}] \leq 3.5 \times 10^{-3} \text{ M}$ respectively), the ionic strength was calculated to be $I \leq 0.006 \text{ M}$, according to Equation 5.19. The deviation, σ , of the $\log K$ at $I=0.006 \text{ M}$ from that at $I=0$ can be expressed as:

$$\sigma = \log [\gamma_{\text{FeSH}^+} / (\gamma_{\text{Fe}^{2+}} \gamma_{\text{HS}^-})] \quad (5.20)$$

The activity coefficients for Fe^{2+} , HS^- and FeHS^+ were calculated respectively according to Equation 5.18 at $I = 0.006 \text{ M}$. A deviation of $\sigma = 0.14$ was obtained from Equation 5.20. Considering the deviations from the experimental errors (Figures 5.14 and 5.15) and the ionic strength variations, the formation constant of $\log K = 4.34 \pm 0.15$ at 25°C and $I = 0$ is proposed.

The reported formation constants for $\text{Fe}(\text{HS})^+$ and other related metal sulfide complexes, $\text{M}(\text{HS})^+$, are listed in Table 1. It can be seen that the $\log K$ value of 4.3 determined in this study is near the value of 5.5 obtained by Luther and Ferdelman (1993) using a voltammetric technique, but is much higher than the value of 1.4 estimated by Dyrssen (1988). The divalent transition metal ions, Co^{2+} and Ni^{2+} , have estimated formation constants of $10^{4.7}$ and $10^{3.8}$ respectively, which are similar to the value of $10^{4.3}$ for Fe^{2+} determined in this study.

TABLE 1. Formation constants of various metal sulfide complexes for the reaction $\text{M}^{2+} + \text{HS}^- = \text{M}(\text{HS})^+$, at 25°C .

Metal ions	Fe^{2+}	Co^{2+}	Ni^{2+}	Pb^{2+}	Zn^{2+}
$\log K$	1.4 ^a 5.50 (seawater) ^b 4.34 ($I=0$) ^d	4.7 ^a 5.7 ($I=0.1$) ^c	3.8 ^a	5.0 ^a	6.5 ^a

^aEstimated values from Dyrssen (1988),

^bDetermined experimentally by Luther and Ferdelman (1993),

^cNaumov et al., 1974.

^dFrom this study,

5.3.6 Formation Kinetics of the Iron Sulfide Complex

According to the absorbance-time behavior for the reaction between sulfide and ferrous ions in aqueous solution (Figure 5.6), an intermediate species forms rapidly within the first few seconds and then decomposes slowly as the reaction progresses. The pathway of the reactions can be postulated as:

Based on Equations 5.21 and 5.22, the rate law for $\text{Fe}(\text{HS})_n^{2-n}$ formation can be written as:

$$d[\text{Fe}(\text{HS})_n^{2-n}]/dt = k_1[\text{Fe}^{2+}]^\alpha[\text{HS}^-]^\beta - k_2[\text{Fe}(\text{HS})_n^{2-n}]^\gamma \quad (5.23)$$

where α , β and γ are the reaction orders with respect to Fe^{2+} , HS^- , and $\text{Fe}(\text{HS})_n^{2-n}$, while k_1 and k_2 are the rate constants for the first and second reaction steps respectively. Because reaction 5.21 is much faster than reaction 5.22, $k_1 \gg k_2$, Equation 5.23 can be modified as:

$$d[\text{Fe}(\text{HS})_n^{2-n}]/dt = k_1[\text{Fe}^{2+}]^\alpha[\text{HS}^-]^\beta \quad (5.24)$$

By using the pseudo-order method (Katakis and Gordon, 1987), with $[\text{HS}^-]_0 \gg [\text{Fe}^{2+}]_0$ and therefore $[\text{HS}^-] \approx [\text{HS}^-]_0$, Equation 5.24 becomes:

$$d[\text{Fe}(\text{HS})_n^{2-n}]/dt = k[\text{Fe}^{2+}]^\alpha \quad (5.25)$$

where

$$k = k_1[\text{HS}^-]_0^\beta \quad (5.26)$$

or

$$\log k = \log k_1 + \beta \log [\text{HS}^-]_0 \quad (5.27)$$

If the experiments are carried out with different concentrations of Fe^{2+} and HS^- at a fixed pH, always maintaining $[\text{HS}^-]_0 \gg [\text{Fe}^{2+}]_0$, then the reaction order α with respect to Fe^{2+} and pseudo rate constant k can be obtained from Equation 5.25. Furthermore, a plot of $\log k$ vs $\log [\text{HS}^-]_0$ will be a straight line according to Equation 5.27; the slope of the line is β , the order with respect to HS^- , and the intercept is $\log k_1$.

A typical curve, used to evaluate the reaction order α and the pseudo rate constant k , is shown in Figure 5.16. A mathematical expression of the absorbance as a function of time was obtained by a curve-fitting procedure. The absorbance of $\text{Fe}(\text{HS})_n^{2-n}$, $A - A_0$, can be expressed as:

$$A - A_0 = (A - A_0)_{\max} (1 - e^{-kt}) \quad (5.28)$$

According to Equation 5.6, we have,

$$[\text{Fe}(\text{HS})_n^{2-n}] = [\text{Fe}(\text{HS})_n^{2-n}]_{\max} (1 - e^{-kt}) \quad (5.29)$$

FIGURE 5.16. Determination of reaction order with respect to Fe^{2+} and pseudo rate constant of k .

FIGURE 5.17. Determination of reaction order with respect to HS^- and the rate constant of k_1 .

It must be noted that

$$[\text{Fe}(\text{HS})_n^{2-n}] = [\text{Fe}^{2+}]_0 - [\text{Fe}^{2+}] \quad (5.30)$$

Therefore, since $[\text{HS}^-]_0 \gg [\text{Fe}^{2+}]_0$, it follows that :

$$[\text{Fe}(\text{HS})_n^{2-n}]_{\text{max}} = [\text{Fe}^{2+}]_0 \quad (5.31)$$

Accordingly, Equation 5.29 can be rewritten as:

$$[\text{Fe}^{2+}] = [\text{Fe}^{2+}]_0 e^{-kt} \quad (5.32)$$

The rate law is then:

$$-d[\text{Fe}^{2+}]/dt = d[\text{Fe}(\text{HS})_n^{2-n}]/dt = k [\text{Fe}^{2+}] \quad (5.33)$$

Comparison of Equations 5.25 and 5.33 indicates that the reaction is first order with respect to Fe^{2+} (i.e. $\alpha = 1$), with a pseudo rate constant of k .

A series of experiments was conducted in which different initial concentrations of HS^- were used, while keeping $[\text{HS}^-]_0 \gg [\text{Fe}^{2+}]_0$. All the results followed the first order expression (Equation 5.28), but gave different k values. This indicates that the reaction remains first order with respect to Fe^{2+} irrespective of the initial HS^- concentration. A plot of $\log k$ vs $\log[\text{HS}^-]_0$ was then obtained, as shown in Figure 5.17. Based on Equation 5.27, the slope of the line gives the reaction order with respect to HS^- as $\beta=1$, while the x-

axis intercept of the line gives the rate constant as $k_1=10^{3.81} \text{ M}^{-1}\text{sec}^{-1}$. The rate law for the reaction shown in Equation 5.24 was then obtained as:

$$d[\text{Fe}(\text{HS})^+]/dt = 10^{3.81} [\text{Fe}^{2+}] [\text{HS}^-] \quad (5.34)$$

The results presented in this study are in agreement with the previous suggestions (Pohl, 1953; Taylor, 1980; Luther, 1991, Luther and Ferdelman, 1993) that $\text{Fe}(\text{HS})^+$ is the intermediate species formed initially from the reaction between ferrous and sulfide ions in aqueous solutions. The complex $\text{Fe}(\text{HS})^+$ may decompose to form FeS via the following reaction:

It is also possible that the complex further reacts with HS^- to form $\text{Fe}(\text{HS})_2$, and then decomposes to FeS , as suggested by Baas Becking (1956) and Rickard (1989):

In either case, the complex $\text{Fe}(\text{HS})^+$ is the intermediate species formed initially from the $\text{Fe}(\text{II})$ - $\text{S}(\text{II})$ reaction.

5.4 Conclusions

The work reported here demonstrated that the reaction between aqueous sulfide and ferrous ions can be studied by the stopped-flow spectrophotometric technique at a wavelength of 500 nm. The absorbance-time curves obtained by the stopped-flow technique can provide useful information relevant to the mechanisms of the reaction because the absorbance corresponding to the reaction product can be recorded within a short time. The absorbance-time curves at 500 nm showed that on the way to making FeS, an intermediate formed initially within the first few seconds of the reaction and this intermediate converted eventually to other species. The use of the spectrophotometric technique is also based on the fact that the absorbance changes linearly with the concentration of the intermediate. The absorptivity of the intermediate was determined as $4800 \text{ M}^{-1} \text{ cm}^{-1}$.

The relevant thermodynamic and kinetic experiments show that the intermediate species initially formed from the reaction of Fe^{2+} with HS^- in aqueous solution is a complex of the form $\text{Fe}(\text{HS})^+$. This stoichiometry of the intermediate was determined by several methods and consistent results were obtained. The experiments also provided the formation constant for $\text{Fe}(\text{HS})^+$ as $\log K = 4.34 \pm 0.15$ at 25°C and $I = 0$. The rate law for the formation of $\text{Fe}(\text{HS})^+$ was determined experimentally as $d[\text{Fe}(\text{HS})^+] / dt = 10^{3.81} [\text{Fe}^{2+}][\text{HS}^-]$.

The experimental evidence presented here for the formation of $\text{Fe}(\text{HS})^+$, coupled with the proposals previously offered in the literature concerning the possible existence of $\text{Fe}(\text{HS})_2$ (Rickard, 1989), $\text{Ni}(\text{HS})_2$ and $\text{Co}(\text{HS})_2$ (Joris, 1969), suggest that the formation of metal sulfides may proceed via mechanisms that parallel those associated with metal hydroxides, and oxides. It is well documented in the literature that the precipitation of a

metal oxide generally involves an intermediate stage in which a metal hydroxide forms, and the final oxide product is the end result of a series of processes, including hydrolysis, polymerization, oxolation, nucleation, growth and aggregation (Dousma and de Bruyn, 1976; Matijevic, 1992; Sugimoto et al., 1993). The corresponding processes in sulfide systems have so far received little attention in the literature (Joris, 1969; Chiu and Meehan, 1974; Wilhelmy and Matijevic, 1985; Williams et al., 1985; Chou and Wu, 1991; Dalas et al., 1991). A further implication of this work lies in the area of surface chemistry (Williams and Labib, 1985; Park and Huang, 1989; Ronngren et al., 1991) and dissolution of metal sulfides (Wadsworth, 1984; Peters, 1986; Dutrizac, 1992; Osseo-Asare, 1992). For example, surface metal-hydrogen-sulfide complexes, formed via surface protonation reactions, may be responsible for important, but as-yet-unrecognized, interfacial ionization and ligand-exchange reactions.

Chapter 6

SEMICONDUCTOR PROPERTIES OF PYRITE

6.1 Introduction

It is generally believed that semiconductor dissolution processes may involve electron transfer (conduction band) or hole transfer (valence band) routes (Vijh, 1973; Morrison, 1980). When the band gap of a semiconductor is larger than 0.66 eV, a hole transfer pathway will play a key role in the anodic dissolution process (Gerischer, 1969; Crundwell, 1988; Osseo-Asare, 1992). Pyrite is a semiconductor material with a band gap of 1 ± 0.2 eV (Bither et al., 1968; Gupta et al., 1980; Ennaoui et al., 1986; Liu et al., 1988). Therefore, pyrite dissolution process would be affected by its semiconductor properties. In this chapter, the semiconductor properties of pyrite relevant to the present study, such as the electronic structure, the energetics of the solid, and the interfacial electrochemistry, are summarized in order to have a better understanding of the interfacial reaction at the semiconductor pyrite/aqueous interface.

6.2 Crystalline Structure of Pyrite

The structure of pyrite, as shown in Figure 6.1, is cubic, similar to the structure of NaCl (Vaughan, 1980; Ennaoui et al., 1986; Kjekshus, 1969). The iron atoms, occupying the Na positions, lie at the corners and face centers of the cubic unit cell, while the 'dumb-

FIGURE 6.1. (a) The crystalline structure of pyrite, (b) the nearest neighbor coordination of the sulfur molecule, and (c) the nearest neighbor coordination of the metal atom. after Ennaoui et al. (1986).

bell' shaped disulfide atoms, S_2^{2-} , are located at the center of the cube and the mid-points of the cube edges like Cl atoms in the NaCl structure. The S_2^{2-} pairs are oriented such that their axes are parallel to four body diagonals of the cube and thus give pyrite hemihedral symmetry. The crystal structure of pyrite consists of an octahedral coordination of a central iron atom (Fe^{2+} : $1s^2 2s^2 2p^6 3s^2 3d^6 4s^0 4p^0$) to six sulfur atoms (S^{2-} : $1s^2 2s^2 2p^6 3s^2 3p^6$). Each sulfur atom is in tetrahedral coordination with one sulfur and three iron atoms, based on the interaction of 3s and three 3p orbitals of sulfur atom to give four hybrid sp^3 orbitals (eight electrons in one s and three p orbitals have a distribution in space that is the same as that obtained by treating the electrons as occupying four equivalent hybrid orbitals).

6.3 Molecular Orbital Model of Pyrite

The molecular orbital model of pyrite is illustrated in Figure 6.2 (Vaughan and Craig, 1980; Osseo-Asare, 1992). The FeS_2 molecular orbitals are formed by the interaction between iron 3d, 4s, and 4p orbitals and six sp^3 hybrid orbitals from six sulfur atoms (there are four sp^3 hybrid orbitals in each sulfur atom; one interacts with the iron atom shown in the figure, one interacts with another sulfur atom, and the other two orbitals interact with two other iron atoms). The 4s, three 4p orbitals ($4p_x$, $4p_y$, $4p_z$) and two 3d e_g group orbitals (d_{z^2} and $d_{x^2-y^2}$) of the iron atom are aligned with the Cartesian axes (x, y, z). Thus there is an overlap with the atomic orbitals of ligands, as shown in Figure 6.3a, to form six sigma bonding molecular orbitals ($1\sigma_s$, $3\sigma_p$, and $2\sigma_d$) and six sigma antibonding molecular orbitals ($1\sigma_s^*$, $3\sigma_p^*$, and $2\sigma_d^*$ or e_g^*), as shown in Figure 6.2. The iron 3d t_{2g} orbitals (d_{xy} , d_{xz} , and d_{yz}) are not directly aligned towards the ligands, as shown in Figure 6.3b, and therefore they do not participate in σ bonding. These bonds are termed nonbonding orbitals and their energies remain unchanged. The e_g^* and t_{2g}

FIGURE 6.2. Relation between molecular orbitals model and band model of pyrite.

FIGURE 6.3. Interaction between iron 3d and sulfur sp^3 orbitals.

molecular orbitals are separated by an energy difference denoted as Δ . As shown in Figure 6.2, the bonding molecular orbitals represent the maximum positive overlap between atomic orbitals, and are more stable than the component atomic orbitals of metal or ligand. The corresponding antibonding orbitals are less stable than the component atomic orbitals.

6.4 Band Model of Pyrite

The band model of solids is based on the concept of molecular orbitals. When a large number of atoms or molecules are combined to form a solid, the individual energy levels (orbitals) will be so closely spaced that the discrete energy levels will be broadened into bands. The bands are filled with electrons, starting from the lowest energy band. The electrons in a filled band can not move up into an unoccupied band at a higher energy level, unless they obtain enough energy. The uppermost of these filled bands is called the valence band, and the lowest of these unoccupied bands is termed the conduction band. The energy difference between the conduction and valence bands represents the energy gap, E_g . As shown in Figure 6.4, for metals, the uppermost band is only partially filled by electrons, so that the electrons can move around freely within the band by a small excitation. However, for semiconductors and insulators, the valence bands are completely filled so that the electrons must be excited to jump up from valence bands into conduction bands for conducting electricity. Semiconductors have energy gaps of less than 2 eV generally, and the energy gap is greater than 2 eV for insulators.

In a solid FeS_2 material, the interaction of the iron 4s, 4p, and e_g orbitals with sulfur sp^3 hybrid orbitals produces bonding orbitals which contribute to the valence band, and antibonding orbitals which are responsible for the conduction band. The energy gap ($E_g \sim 1$ eV) of pyrite is represented by the separation between the antibonding e_g^* orbitals

FIGURE 6.4. Schematic band model of solids.

and non-bonding t_{2g} orbitals, as shown in Figure 6.2b (Vaughan and Craig, 1980; Osseo-Asare, 1992).

6.5 Photoeffects

For the electron transfer between solids and aqueous species, the electrochemical potential of the electrons in the solid must be equal to that in the solution when the solid and the aqueous species are in equilibrium (Crundwell, 1988; Osseo-Asare, 1992). That is, the Fermi energy of the solid must be equal to the equilibrium potential of the redox couple in the solution:

$$E_F = E_{\text{redox}}^{\text{eq}} \quad (6.1)$$

where the Fermi energy, E_F , represents the electrochemical potential of the electrons in a solid (Vijh, 1973; Morrison, 1980). The Fermi level is located in different positions for different semiconductor materials, as shown in Figure 6.5. For an intrinsic semiconductor at room temperature, the Fermi level may lie essentially midway between the conduction band and the valence band within the band gap, when the density of states of holes at the top of the valence band is the same as the density of states of electrons at the bottom of the conduction band. For n-type semiconductors, at room temperature, E_F lies slightly below the conduction band, while for p-type semiconductors, E_F lies just above the valence band (Vijh, 1973; Morrison, 1980; Bard and Faulkner, 1980).

However, when a semiconductor is illuminated by light with an energy greater than its band gap, electrons will be excited into the conduction band and holes will be created in the valence band, leading to an excess of electrons and holes. Considering that n_0 and p_0

are the equilibrium concentrations of electrons in the conduction band and of holes in the valence band respectively, and Δn and Δp are the excess concentrations generated by illumination, the change in free energy associated with illumination can be expressed as (Gerischer, 1966; Ward et al., 1983):

$$\Delta\mu_e = {}_nE_F - E_F = kT \ln (1 + \Delta n/n_0) \quad (6.2)$$

$$\Delta\mu_p = {}_pE_F - E_F = -kT \ln (1 + \Delta p/p_0) \quad (6.3)$$

where ${}_nE_F$ and ${}_pE_F$ are defined as quasi-Fermi energies, which describe the concentration of the electrons in the conduction band and of holes in the valence band respectively at non equilibrium conditions. If $(E_c - E_F)$ or $(E_F - E_v)$ exceeds $2kT$, the Fermi -Dirac function can be simplified and we have:

$$n_0 = N_c \exp [-(E_c - E_F)/kT] \quad (6.4)$$

and

$$p_0 = N_v \exp [-(E_F - E_v)/kT] \quad (6.5)$$

where N_c and N_v are the effective densities of energy levels in the conduction and valence bands respectively. Thus we obtain:

$$n_0 p_0 = N_c N_v \exp (-E_g/kT) \quad (6.6)$$

where E_g is the band gap, $E_g = E_c - E_v$.

FIGURE 6.5. Fermi energy levels for different semiconductors.

FIGURE 6.6. Quasi-Fermi energy levels for different semiconductors under illumination.

Equation 6.6 shows that for a given semiconductor at equilibrium, n_0 and p_0 cannot both be large; if one is large, the other must be small. Hence, it can be seen from Equations 6.2 and 6.3 that the change in free energy under illumination is much greater for minority carriers than for majority carriers. In other words, the concentration of majority carriers is not appreciably increased by illumination. Therefore, the quasi-Fermi energy for majority carriers is almost the same as the equilibrium Fermi energy. However, the quasi-Fermi energy for the minority carriers can be changed substantially. For example, an n-type semiconductor has electrons as majority carriers and holes as minority carriers with the equilibrium Fermi energy near the conduction band. Under illumination, the concentration of the holes may increase many orders of magnitude, so that pE_F will decrease dramatically. In fact, pE_F may be near the valence band of the semiconductor. On the other hand, the effect of illumination on electron concentration is not much for an n-type semiconductor, thus nE_F increases only a little and is still located near the conduction band. The quasi-Fermi energies for intrinsic, n-type and p-type semiconductors are illustrated in Figure 6.6.

6.6 Energetics of Pyrite

As noted above, pyrite is a semiconductor with a band gap of about 1 ± 0.2 eV. The band positions of pyrite in aqueous solution shift with the solution pH due to the adsorption of H^+ , OH^- and SH^- ions on the particle surface. The pH-dependent Fermi level (in terms of potential (E_h , V)) of pyrite can be expressed as (Chen et al., 1991):

$$E_F = 0.18 - 0.059 \text{ pH} \quad (6.7)$$

FIGURE 6.7. Energy diagram of semiconductor pyrite.

FIGURE 6.8. Reactions of electrons in CB and holes in VB with environments.

FIGURE 6.9. Energetics of pyrite with potentials of redox couples in solution.

For an n-type pyrite, it can be assumed that under illumination the conduction band edge, E_c , is near the Fermi level, E_F , so that the band positions can be estimated by Equation 6.7 (Chen et al., 1991).

For the purpose of studying electrochemical reactions at the interface between a semiconductor solid and a liquid, it is useful to relate the energetics of the solid with the electrochemical potentials of the redox couples in solution. Conventionally, the energy levels are expressed in units of electron volts (eV), which take the energy of a free electron at infinity (vacuum) as the reference. On the other hand, the redox couples are characterized conventionally by electrochemical potentials (V); the reference state may be taken as the potential of either the standard hydrogen electrode (SHE) or the saturated calomel electrode (SCE). The relationship between the energy level (E , eV) and the electrochemical potential (E_h , V), taking SHE as reference, is given by (Morrison 1980; and Osseo-Asare, 1992):

$$E(\text{eV}) = -eE_h(\text{V}) - 4.5 \quad (6.8)$$

Based on Equations 6.7 and 6.8, the energy level diagram of pyrite can be constructed as shown in Figure 6.7, where E_c and E_v refer to the bottom of the conduction band and the top of the valence band respectively.

The energy level diagrams of semiconductor materials are very useful for examining the mechanisms involved in the reaction systems. For example, the band gap (E_g) of 1 eV for pyrite indicates that visible light, which has energies from 1.7 eV to 3.1 eV, can excite electrons from the valence band to the conduction band, leaving holes in the valence band. There are at least three possible ways for the electron-hole pairs to react further, as shown in Figure 6.8: (a) the electrons excited may recombine with the holes; (b) the electron-hole

pairs may interact with species in the aqueous solution; and (c) the holes may oxidize the lattice atoms of the solid. Figure 6.9 compares the band edges of pyrite with the energy levels of several redox couples (Osseo-Asare, 1993). It can be seen that the corresponding oxidants can be divided into two groups, i.e., those which are most likely to accept conduction band electrons ($E_{\text{redox}}(\text{V}) < E_{\text{v}}$: O_2 , Fe^{3+}) and those which are most likely to inject holes into the valence band ($E_{\text{redox}}(\text{V}) > E_{\text{v}}$: H_2O_2 , Cl_2).

It will be seen later in Chapters 7 and 8 that some of these properties discussed above can affect the electrochemical behavior of pyrite.

Chapter 7

SEMICONDUCTOR ELECTROCHEMISTRY OF PARTICULATE PYRITE: DISSOLUTION VIA HOLE AND ELECTRON PATHWAYS

Abstract

Electrochemical and photoelectrochemical experiments were conducted to investigate the pyrite/aqueous interface reaction by using microparticles of synthetic pyrite as electrodes. The potential of the conduction band edge of pyrite as a function of pH was estimated to be $E_c = 0.34 - 0.059 \text{ pH}$ in volts vs. SCE. The open circuit potential of pyrite electrode in 1 M HNO_3 solution was 0.38 V(SCE). Illumination of pyrite microelectrodes increased both the anodic current and the dissolution rate dramatically, but had little effect on the cathodic current and the cathodic dissolution. These results indicate that pyrite, as an n-type semiconductor, dissolves anodically through a hole transfer (valence band) pathway, while cathodic dissolution only involves electron reaction (conduction band).

7.1 Introduction

The electrochemical properties of the pyrite-aqueous system are important in many engineering applications. These include coal processing (Meyers, 1977; Ogunsola and Osseo-Asare, 1986; Drzymala and Wheelock, 1993; Liu et al., 1993), mineral processing (Woods, 1976; Chander et al., 1993; Witika and Dobias, 1995), hydrometallurgy (Peters,

1976, 1986, 1992; Wadsworth, 1984; Osseo-Asare, 1992), environmental engineering (Aston, 1974; Ahmed and Giziewicz, 1992; Chander and Zhou, 1992; Osseo-Asare, 1993), geochemistry (Berner, 1970, 1984; Nordstrom, 1982; Morse et al., 1987; Schooner and Barnes, 1991a,b), and photovoltaic applications (Jaegermann and Tributsch, 1983; Ennaoui et al., 1986; Tributsch, 1986; Alonso-Vante and Tributsch, 1990; Ferrer and Sanchez, 1992). Pyrite oxidation or dissolution in aqueous solutions is of particular significance to the various engineering applications cited above. As a result, many investigations on pyrite oxidation abound in the literature, but surprisingly little agreement exists on the oxidation mechanism.

Pyrite is widely recognized as an electronic conductor and its oxidation has been described by the metal corrosion model for many years (Peters and Majima, 1968; Biegler and Swift, 1979; Peters, 1992). Some earlier studies (Springer, 1970; Biegler, 1975; Biegler and Swift, 1979) showed that n- and p- type pyrite exhibited very similar anodic and cathodic polarization curves under acidic conditions. These investigators therefore concluded that the semiconductor properties of natural pyrite do not influence its electrochemical behavior, and that these properties do not play a significant role in pyrite oxidation and dissolution reactions. Biegler and Swift (1979) suggested that as a good electronic conductor, pyrite oxidation could be described by the metal corrosion model where the hole transfer (valence band) process is not relevant.

However, electrochemical and photoelectrochemical experiments conducted in this laboratory (Mishra and Osseo-Asare, 1987, 1988a, 1992a) showed that pyrite dissolution rate increased under illumination. This suggests that both electrons and holes may participate in the dissolution reactions. Based on the semiconductor dissolution model, Mishra and Osseo-Asare (1988a, 1992a) and Osseo-Asare (1992, 1993a) proposed that

semiconductor properties may play an important role in the physicochemical processes of pyrite dissolution.

The semiconductor dissolution process can, in principle, involve both electron and hole transfer routes. However, when the band gap of a semiconductor is larger than 0.66 eV, the hole transfer pathway will play a key role in the anodic dissolution process (Gerischer, 1969; Crundwell, 1988; Osseo-Asare, 1992). The solid state properties of the semiconductor material, such as its structure, band gap, band edges, the nature of surface states and the surface charge region, and the quasi-Fermi-energy caused by illumination, will definitely affect the dissolution rate. The interfacial electrochemistry concerning the electron and hole transfers between the solid surface and the redox couples in the solution will also influence the dissolution processes.

Pyrite, like many metal sulfides, is a semiconductor material; its band gap is 1 ± 0.2 eV (Bither et al., 1968; Gupta et al., 1980; Ennaoui et al., 1986; Liu et al., 1988). However, as noted above, the semiconductor dissolution model for pyrite has not been widely accepted. Little systematic work has been done on the effects of semiconductor properties of pyrite on its dissolution behavior (Springer, 1970; Biegler, 1975; Biegler and Swift, 1979). In this study, electrochemical and photoelectrochemical experiments are conducted using synthetic pyrite as microelectrodes to explore the relationship between the semiconductor properties of pyrite and the interfacial electrochemical behavior of this metal sulfide. The use of pyrite in a highly divided form offers some advantages because the amount of reaction surface per given pyrite/aqueous mass ratio is increased. Therefore, stronger electrochemical responses and an increase in reaction products would be expected.

7.2 Experimental

7.2.1 Materials

Reagent grade ferric chloride ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), sodium hydrosulfide ($\text{NaHS} \cdot x\text{H}_2\text{O}$), nitric acid (HNO_3), sodium hydroxide (NaOH), and potassium nitrate (KNO_3) were obtained from Aldrich. Carbon disulfide (CS_2 , 99.9%) also came from Aldrich. High purity water (18 MW-cm) was generated from a Millipore Milli-Q system. Oxygen-free water was prepared by bubbling prepurified N_2 through the water for at least 5 hours. The nitrogen gas was deoxygenated by flowing the gas over a bed of copper filings at 450 °C.

7.2.2 Microelectrodes Preparation

Synthetic pyrite particles were used as microelectrodes in the electrochemical and photoelectrochemical measurements and in the dissolution experiments. Pyrite was synthesized by reacting ferric and sulfide ions in aqueous solution at room temperature (see Chapter 2). A batch of pyrite samples was made in 50 ml vials in a glove box filled with nitrogen. Each vial contained a mixture of 10 ml 0.1 M FeCl_3 and 20 ml 0.1 M NaSH solutions at pH 4.0. These were allowed to age for a period of 5 days, after which pyrite was well formed and precipitated in the bottom of the vials. The pyrite particles were separated from the solution by decanting the liquid, then the solids were washed with O_2 -free water several times, and dried in a vacuum oven at room temperature. The pyrite sample synthesized using this method contained elemental sulfur, thus requiring further purification. This was done by solvent extraction (Reilly et al., 1978, 1984; Filmer et al., 1979a,b) at 47°C in a Soxhlet apparatus using 270 mg solid and 60 ml CS_2 . The

suspension was agitated with a magnetic stirrer for 2 hours. After solid/liquid separation, the purified pyrite particles were washed first with carbon disulfide, then with acetone, and finally with oxygen-free water. To prevent oxidation of the sample, all the processes were conducted in nitrogen atmosphere. Typically, a 180 mg pyrite sample was obtained after purification. An SEM micrograph of the pyrite particles is shown in Figure 7.1. The particles had an average diameter of 1.5 μm . The purity of the pyrite sample was 99.46% FeS_2 .

7.2.3 Apparatus

The experiments described below were based on the current collection technique developed by Bard and coworkers (Chen et al., 1991; Ward et al., 1983) for semiconductor particle suspensions. The apparatus used in the electrochemical and photoelectrochemical experiments is shown in Figure 7.2. The 100 ml Pyrex H-cell consisted of two chambers separated by a fine porosity glass frit. This set-up confined the pyrite particles to the main chamber. A platinum grid inert electrode with an area of 2 cm^2 and a saturated calomel reference electrode (SCE) was located in the main chamber, and a platinum grid counter electrode was in the other chamber. On the wall of the main chamber there was a flat window which allowed the light to go into the cell directly. The light source was an Oriel 250 W halogen lamp. A water bath with a 14 cm length was placed between the cell and the light source to remove the heat. Before introducing the pyrite sample into the electrochemical cell, a prepurified nitrogen stream was bubbled through a 100 ml electrolyte in the cell for 1 hour. The pyrite sample was then added into the electrolyte through the sample gate. Nitrogen was bubbled continuously over the duration of the experiment. A magnetic stirrer was used to bring the pyrite particles, which act as

FIGURE 7.1. SEM micrograph of pyrite particles synthesized by Fe(III)-S(II) reaction in aqueous solution.

FIGURE 7.2. Setup of the electrochemical cell.

microelectrodes, into contact with the inert electrode. The platinum electrodes were treated in concentrated HNO_3 for 1 minute then washed with distilled water before experiments. A model 273 Potentiostat /Galvanostat (EG&G Princeton Applied Research) controlled by a computer with a model 352 corrosion analysis software was used to make the electrochemical measurements. The potentials reported in this work are in SCE scale unless otherwise specified.

7.2.4 Determination of Conduction Band Edge

The potential of the conduction band edge of the synthetic pyrite was estimated using an onset potential method (Chen et al., 1991; Richardson et al., 1992). The experiments were carried out using a 90 mg pyrite sample in 100 ml 1M KNO_3 solutions in the Pyrex H-cell. The pH of the solutions was controlled by NaOH and HNO_3 . The suspension was agitated for 1 hour under illumination before the measurements. Then the current density was recorded as a function of time for different given potentials at the inert electrode. The decay of the current generally took 5 to 10 minutes. The illumination continued throughout the duration of the experiments.

7.2.5 Determination of Open Circuit Potential

The open circuit potential of the synthetic pyrite was estimated by measuring the potential of the inert platinum electrode in contact with the suspended particles. The experiments used 90 mg pyrite samples in 100 ml 1 M KNO_3 solutions with different pH values. The suspension was agitated in the Pyrex H-cell for 15 minutes before the measurements. The experiments were conducted in the dark.

7.2.6 Photocurrent Collection Experiments

The photocurrent collection experiments were conducted using 180 mg pyrite in 100 ml 1 M KNO_3 solution. Illumination was applied to the system to investigate the effects of irradiation on the anodic and cathodic currents collected on the inert electrode. The anodic current was collected by applying to the inert electrode a potential of 0.75 V(SCE), which was more positive than the conduction band edge. On the other hand, the cathodic current was measured by applying a potential (0.15 V(SCE)) more negative than the conduction band edge. The current was recorded as a function of time. For the first 30 minutes, the experiments were conducted in the dark. Then the light was turned on for 60 minutes. Finally, the light was switched off and the experiments were continued for another 30 minutes.

7.2.7 Dissolution Experiments

The dissolution experiments were carried out in the electrochemical cell as described above. A given potential was maintained during the dissolution experiment while the electrode current was recorded as a function of time. At regular intervals, a 2 ml liquid sample was taken from the reaction solution with a syringe connected to a 0.2 mm filter. The concentration of the dissolved Fe in solution was determined by atomic absorption spectroscopy (AA).

7.3 Results And Discussion

7.3.1 Conduction Band Edge

The electrochemical behavior of semiconductor pyrite is dependent on the energetics, especially the band gap and the energy levels of the band edges, of the solid. As illustrated in Figure 7.3a, when the electrode potential, E , is more negative than the conduction band edge, E_c , electrons will be injected into the conduction band, resulting in cathodic current on the electrode. On the other hand, if E is more positive than E_c (Figure 7.3b), the electrode will accept electrons from the conduction band, and an anodic current will be produced. When the electrode potential is more positive than the valence band edge, E_v (Figure 7.3c), the electrode will extract electrons directly from the valence band resulting in an anodic current on the electrode and the injection of holes into the valence band. Therefore, a knowledge of the conduction band position of pyrite is important for understanding the electrochemistry of this metal sulfide.

The band gap of pyrite has been evaluated at 1 ± 0.2 eV (Bither et al., 1968; Gupta et al., 1980; Ennaoui et al., 1986; Liu et al., 1988). However, the conduction band edge potential, E_c , has been assigned widely different values (Figure 7.4) by various authors (Chen et al., 1991; Richardson et al., 1992; Ahmed et al., 1992). Because of the large disagreement, it is necessary to evaluate the E_c values for the synthetic pyrite used in this study.

The conduction band edge potential can be estimated by measuring the quasi-Fermi level of a semiconductor under illumination (Chen et al., 1991; Richardson et al., 1992). Since illumination can increase the electron concentration in the conduction band, the Fermi level will be moved near the conduction band edge. Figure 7.5 shows the i - t transient

FIGURE 7.3. Illustration of electron transfers between inert electrode and solid semiconductor.

FIGURE 7.4. Conduction band edge potential of pyrite determined by different investigators.

FIGURE 7.5. Chronoamperometric transients of pyrite at pH 10.8 under illumination.

features of the pyrite microelectrodes under illumination at pH 10.8 and at different potentials. It can be seen that the current changes from cathodic to anodic at an onset potential of -0.3 V(SCE). This value corresponds to the quasi-Fermi level of pyrite at pH 10.8. Therefore, the potential of the conduction band edge at pH 10.8 for the pyrite sample can be taken to be -0.3 V(SCE). Using the same approaches, the values of E_c for pyrite at pH 14 and pH 3.0 were estimated at -0.49 V(SCE) and 0.15 V(SCE) respectively. A plot of the E_c values against pH gives a straight line with a slope of -0.059. This is consistent with the observation made by Chen and co-workers (1991). The shift of the band position with pH was attributed to the adsorption of ions (e.g. H^+ , OH^-) on the semiconductor particle surface (Rouse and Weininger, 1966; Chen et al., 1991). A slope of -0.059 indicated the adsorption of protons and hydroxyl ions on pyrite surfaces. Therefore, the potential of the conduction band edge, E_c , of the synthetic pyrite in this study can be expressed as:

$$E_c = 0.34 - 0.059 \text{ pH V(SCE)} \quad (7.1)$$

7.3.2 Open Circuit Potential

For an electrode in the dark, the anodic and cathodic reactions will depend on whether the potential is more positive or negative than the open circuit potential (OCP) of the electrode. Therefore, the OCP of a semiconductor should be somehow related to the energy levels of the band edges. The open circuit potentials for the synthetic pyrite particles are shown in Figure 7.6; also included in this figure are data reported by other investigators (Sato, 1960; Peters and Majima, 1968; Springer, 1970; Biegler and Swift, 1979; Meyer, 1979; Hamilton et al., 1981; Ahmed and Giziewicz, 1992; Mishra and

FIGURE 7.6. Open circuit potentials reported by different investigators.

FIGURE 7.7. Comparison of conduction band edge potential with open circuit potential.

Osseo-Asare, 1992; Richardson et al., 1992; Wang et al., 1992). It can be seen that the reported data are widely scattered. The observed variations in the OCP values may result from the use of samples from different sources and the use of different methods in sample preparation. However, it is generally believed that the OCP at pH 0 is close to 0.38 V(SCE) for both n- and p-type pyrite (Springer, 1970; Biegler and swift, 1979; Meyer, 1979; Mishra and Osseo Asare, 1992). Comparison of OCP and E_c (Figure 7.7) shows that they have similar values at a given pH. This indicates that like most synthetic pyrite (Tributsch, 1986; Morse et al., 1987), the pyrite used in this study is an n-type semiconductor, because illumination cannot increase the electron concentration in the conduction band significantly. The slight shift of the E_c to negative potentials is due to the small increase in electron concentration in the conduction band.

7.3.3 Photocurrent Collection

The results of the photocurrent collection experiments are shown in Figure 7.8. The current responses in the absence of pyrite are also plotted in the figure to demonstrate that the observed currents are due only to the reactions of pyrite microelectrodes in the solutions. The potential of the inert electrode was held at 0.75 V(SCE). It can be seen from Figure 7.8 that in the presence of pyrite, a small anodic current is observed in the dark. However, when the light is switched on, the anodic current increases dramatically, and then decreases when the light is turned off. The increase of anodic current under illumination is attributed to the photoeffect on the semiconductor pyrite electrodes.

The processes of photocurrent generation are illustrated in Figure 7.9; E refers to the potential of the inert electrode. At pH 0, E_c is 0.34 V(SCE) according to Equation 7.1. Since the potential of the inert electrode (0.75 V (SCE)) is more positive than E_c , the

electrons in the conduction band of pyrite can be transferred to the inert electrode, resulting in anodic current. When the light, which has an energy higher than the band gap of pyrite, is incident on the surface of the particles, it excites electrons in the valence band to jump into the conduction band and leave holes in the valence band. The electrons in the conduction band are collected by the inert electrode, resulting in an observed increase in anodic current. On the other hand, in the absence of electroactive species in the aqueous solution, the holes in the valence band may react with the lattice atoms on the solid surface according to the following overall oxidation reactions:

In this case, the rate of pyrite dissolution will be proportional to the photocurrent observed on the inert electrode.

The effect of illumination on the cathodic current is shown in Figure 7.10. Comparison of Figures 7.8 and 7.10 shows that illumination increases the anodic current dramatically, but it does not affect the cathodic current significantly. Similar photoeffect phenomena have been widely reported in the literature (Flynn, 1958; Efimov and Erusalimchik, 1963; Memming and Schwandt, 1968). This behavior indicates that the anodic reaction at the pyrite/aqueous interface involves hole transfer processes, the cathodic reaction mainly electrons, and that the pyrite sample used is an n-type semiconductor.

The dissolution kinetics of a semiconductor material, unlike a metal, may depend on the rate of electron or hole transfer from the bulk to the surface of the semiconductor. Therefore, the rate of the reaction may be limited by the supply of minority carriers to the

FIGURE 7.8. Effect of illumination on the anodic current of pyrite microelectrodes at E = 0.75 V(SCE).

FIGURE 7.9. Illustration of photocollecting experiments.

FIGURE 7.10. Effect of illumination on the cathodic current of pyrite microelectrodes at E = 0.15 V(SCE).

surface, assuming that the minority carriers are consumed in the reaction. The anodic oxidation of a semiconductor may occur through either a hole pathway or an electron pathway (Gerischer and Mindt, 1968, Osseo-Asare, 1992). According to Gerischer and Mindt (1968), the rate of the reaction via the hole pathway (R_h) and the rate of the reaction via the electron pathway (R_e) are related as:

$$R_h/R_e \propto \exp(E_g/kT) \quad (7.5)$$

where E_g is the difference between the energy levels of E_c and E_v . From Equation 7.5 it can be seen that the hole transfer pathway will predominate as the energy gap of the semiconductor increases. In fact, when $E_g \geq 0.66$ eV, the hole transfer pathway will be dominant (Gerischer, 1969; Crundwell, 1988; Osseo-Asare, 1992). Therefore, the anodic oxidation of pyrite ($E_g=1.0$ eV), which is expected to involve holes, will be promoted under illumination only for an n-type pyrite. This is because illumination can only increase the concentration of minority carriers substantially (Vijh, 1973; Gerischer, 1966; Osseo-Asare, 1992). On the other hand, the cathodic dissolution of n-pyrite, which occurs through electron transfer, will not be affected by illumination.

7.3.4 Anodic and Cathodic Dissolution

The thermodynamic feasibility of anodic and cathodic dissolution of pyrite is illustrated in the Eh-pH diagram presented in Figure 7.11 for the Fe-S-H₂O system. When the starting point is at O, the route O→A represents anodic oxidation, and the route O→B cathodic dissolution.

FIGURE 7.11. Eh-pH diagram for Fe-S-H₂O system (thermodynamic data from Naumov et al., (1974), Baes et al., (1976) and Smith et al., (1977)).

FIGURE 7.12. Effect of illumination on the anodic dissolution rate of pyrite.

FIGURE 7.13. Effect of illumination on the cathodic dissolution rate of pyrite.

The effect of illumination on the anodic dissolution of pyrite is shown in Figure 7.13, where the potential of the inert electrode was maintained at 1.0 V (SCE) in 1 M HNO₃ solution. It can be seen that the dissolved Fe concentration under illumination is higher than that in the dark. This indicates that anodic dissolution of pyrite involves hole reactions because illumination, which creates holes in the valence band of the solid, can increase the dissolution rate. The mechanism of pyrite oxidation through a hole pathway are discussed elsewhere (see Chapter 8). Figure 7.14 shows the effect of illumination on the cathodic dissolution of pyrite in 1 M HNO₃ solution, with the potential of the inert electrode potential set at -0.1 V(SCE). It can be seen that illumination does not affect the cathodic dissolution. This is because the cathodic dissolution of pyrite is a conduction band electron transfer process:

The cathodic dissolution of pyrite via an electron pathway is commonly accepted (Peters and Majima, 1968; Meyer, 1979).

7.4 Conclusions

The results from the electrochemical and photoelectrochemical experiments presented here indicate that the semiconductor properties of pyrite affect its dissolution behavior. The photocurrent experiments showed that when the inert electrode potential was at a value more positive than E_c , an anodic current was produced at the inert electrode. This current increased dramatically upon illuminating the pyrite particles in the suspension. However, illumination had little effect on the cathodic current of pyrite microelectrodes

when the inert electrode potential was at a value more negative than E_c . These results confirm that the pyrite synthesized in this study is an n-type semiconductor. The anodic dissolution involves a valence band hole transfer process, while the cathodic dissolution involves a conduction band electron transfer reaction. The dissolution experiments showed that the dissolved Fe concentration from anodic dissolution under illumination was higher than that in the dark. Illumination does not change the dissolved Fe concentration for cathodic dissolution, which is consistent with the results from photocurrent experiments.

In addition, the potential of the conduction band edge (E_c) of pyrite as a function of pH was estimated at $E_c = 0.34 - 0.059 \text{ pH}$ in volts vs. SCE. The value of E_c is a little more negative than that of open-circuit potential. This suggests that the pyrite synthesized in this study is an n-type semiconductor, because illumination does not increase the electron concentration in the conduction band significantly.

Chapter 8

SEMICONDUCTOR ELECTROCHEMISTRY OF PARTICULATE PYRITE: MECHANISMS AND PRODUCTS OF DISSOLUTION

Abstract

Pyrite dissolution in acidic solution was found to occur via both electrochemical oxidation and chemical decomposition. The mechanism of chemical decomposition of pyrite in acidic solution may involve surface complexation of hydrogen ions. The anodic current of pyrite was observed to be of negligible magnitude in non-aqueous solution compared with that in aqueous solution, which indicated that direct reaction of the holes with S_2^{2-} in the pyrite lattice was not significant and that the dissolution of pyrite required the presence of water. The anodic dissolution products of pyrite in acidic aqueous solution included elemental sulfur which was detected by X-ray diffraction.

8.1 Introduction

There have been numerous studies on pyrite dissolution in the literature (see reviews: Hiskey and Schlitt, 1982; Lowson, 1982; Nordstrom, 1982, Peters, 1992). It is generally accepted that pyrite dissolution in acidic and oxidative conditions is an electrochemical process. This process can be described according to the following

reactions (Sato, 1960; Peters and Majima, 1968; Bailey and Peters, 1976; Biegler and Swift, 1979; Hamilton and Woods, 1981; Morse et al., 1987):

It is noted from Equation 8.2 that oxidation of pyrite to sulfate involves 15 electron transfers for the overall reaction. Since electron transfer reactions are generally limited to one, or at most two electrons, the overall reactions must involve several steps that require sulfur species of intermediate oxidation states.

Some of the investigators (Hamilton and Woods, 1981; Peters, 1984) proposed that elemental sulfur formed initially as an intermediate species of pyrite oxidation (Equation 8.1), and was subsequently oxidized to sulfate. Another proposed mechanism for pyrite oxidation suggests that the formation of elemental sulfur and sulfate are independent processes. That is, the sulfur produced during the anodic dissolution of pyrite is a stable end product, but not an intermediate species in the sulfate reaction pathway (Biegler and Swift, 1979). Other investigators have suggested that the end products of elemental sulfur and sulfate may be produced via intermediate sulfoxy anions, such as sulfite, SO_3^{2-} , thiosulfate, $\text{S}_2\text{O}_3^{2-}$, and polythionates, $\text{S}_n\text{O}_6^{2-}$ ($n = 4, 5, \text{ and } 6$) (Conway et al., 1980; Goldhaber, 1983; Morse et al., 1987). Buckley and Woods (1984) and Buckley et al. (1988) postulated that instead of elemental sulfur, an iron deficient pyrite ($\text{Fe}_{1-x}\text{S}_2$) was produced as a metastable product. Electrochemical experiments conducted by Mishra and Osseo-Asare (1988, 1992) showed that no significant anodic current was observed on pyrite electrode in a non-aqueous solvent. The authors concluded that reaction 8.1 does not take place as an elementary reaction during pyrite decomposition in aqueous solution. The

reason elemental sulfur cannot be produced directly during pyrite decomposition was discussed on the basis of the solid-state chemistry of pyrite, and a hydroxide radical activation model was proposed (Mishra and Osseo-Asare, 1988, 1992). However, direct evidence to show the presence or absence of elemental sulfur was not provided.

The presence of elemental sulfur on the pyrite surface is not only important for understanding the dissolution mechanism of the mineral, but also important for practical applications, such as mineral processing, hydrometallurgy, and acid mine drainage (AMD) control systems. The collectorless flotation of pyrite is attributed to the hydrophobicity of the elemental sulfur produced from a slight oxidation of pyrite (Ahlberg et al., 1990; Chander et al., 1993). From a hydrometallurgical extraction standpoint, the production of elemental sulfur from a metal sulfide leaching process is preferred because elemental sulfur is directly marketable (Peters, 1986, 1992). It is generally believed that a surface film of elemental sulfur on pyrite can hinder the mineral dissolution (Hiskey and Schlitt, 1982; Lawson, 1982; Peters, 1984). Therefore, AMD prevention may be achieved by forming a passive film of elemental sulfur on the pyrite surface.

Direct detection of the dissolution products, especially for the intermediate species, is frequently difficult due to the inherent limitations of the specific analytical instruments, and the low stability and the small amount of the reaction products. Surface analysis by X-ray photoelectron spectroscopy (XPS) showed that the reaction products of pyrite dissolution involved species such as elemental sulfur (Mycroft et al., 1990; Wang et al., 1992), polysulfides (Mycroft et al., 1990), and iron and sulfur oxides (Frost et al., 1977; Ennaoui et al., 1986; Khan et al., 1992; Wang et al., 1992). Raman spectra collected by Mycroft et al. (1990) and Zhu et al. (1993) showed that both elemental sulfur and polysulfides formed on the surface of oxidized pyrite.

Elemental sulfur is kinetically stable at room temperature, although its oxidation should occur spontaneously from a thermodynamic point of view (Habashi and Bauer, 1966; Biegler and Swift, 1979). Hence, if elemental sulfur is an intermediate species, it should be detectable directly, provided enough reaction products can be obtained.

In this study, microelectrodes of pyrite were used to investigate the mechanism of pyrite dissolution. It was expected that the use of microelectrodes would provide more information on the dissolution mechanism of pyrite, by yielding stronger electrochemical responses and more reaction products. Electrochemical measurements and dissolution experiments were carried out to determine the contributions of electrochemical and chemical reactions in pyrite dissolution processes. Electrochemical measurements were performed in both aqueous and non-aqueous (acetonitrile) solutions to probe the pathways for the anodic dissolution of pyrite. Reaction products were analyzed directly using X-ray diffraction techniques.

8.2 Experimental

8.2.1 Materials

Reagent grade ferric chloride ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), sodium hydrosulfide ($\text{NaHS} \cdot x\text{H}_2\text{O}$), nitric acid (HNO_3), sodium hydroxide (NaOH), and potassium nitrate (KNO_3) were obtained from Aldrich. Carbon disulfide (CS_2) from Aldrich contained 99.9% CS_2 . Acetonitrile (99.5% CH_3CN) and tetra-n-butylammonium perchlorate, $(\text{C}_4\text{H}_9)_4\text{NClO}_4$ were purchased from Alfa. High purity water ($18 \text{ M}\Omega\text{-cm}$) was generated from a Millipore Milli-Q system. The water was deoxygenated by bubbling nitrogen. The nitrogen was prepurified by flowing the gas over a bed of copper filings at 450°C to remove oxygen.

8.2.2 Pyrite Preparation

Synthetic pyrite particles were used as microelectrodes in the electrochemical and photoelectrochemical measurements and in the dissolution experiments. Pyrite was synthesized by reacting ferric and sulfide ions in aqueous solution at room temperature. The details of pyrite synthesis are described elsewhere (see Chapter 2). Generally, a batch of pyrite samples was made in 50 ml vials. Each contained 10 ml 0.1 M FeCl_3 and 20 ml 0.1 M NaSH solutions at pH 4.0. After aging the solutions for 5 days, pyrite was well formed and precipitated in the bottom of the vials. The pyrite particles were separated from the solution by decanting out the liquid. The particles were then washed several times with O_2 -free water and then dried in a vacuum oven at room temperature. Each vial contained 45 mg solid material. The pyrite sample thus prepared was purified further by solvent extraction to remove elemental sulfur (Reilly et al., 1978, 1984; Filmer et al., 1979a,b). The extraction was conducted at 47°C in a Soxhlet apparatus with 270 mg solid and 60 ml CS_2 . The suspension was agitated with a magnetic stirrer for 2 hours. Following solid/liquid separation, the purified pyrite particles were washed with carbon disulfide first, then with acetone and oxygen-free water. To prevent oxidation of the sample, all the above processing was conducted in a nitrogen atmosphere. Typically, a 180 mg sample of pyrite was obtained after purification. The pyrite sample contained 99.46% FeS_2 with an average particle diameter of $1.5\ \mu\text{m}$.

8.2.3 Electrochemical and Dissolution Measurements

The electrochemical and dissolution experiments were carried out in an electrochemical cell as used in Chapter 7. The 100 ml Pyrex H-cell consisted of two

chambers separated by a fine porosity glass frit, as used by Ward et al.(1983). This arrangement confined the pyrite particles to the main chamber. A platinum grid inert electrode with an area of 2 cm^2 and a saturated calomel reference electrode (SCE) were in the main chamber and a platinum grid counter-electrode was in the other chamber. The current density reported in this work was based on the area of the inert platinum electrode. A flat optical window, located on the wall on the main chamber, allowed light to go directly into the cell. The light source was an Oriel 250 W halogen lamp.

A model 273 Potentiostat /Galvanostat (EG&G Princeton Applied Research), controlled by a computer with a model 352 corrosion analysis software, was used to conduct the electrochemical measurements. In the dissolution measurements, a constant potential was maintained during the experiment and the electrode current was recorded as a function of time. At timed intervals, a liquid sample of 2 ml was taken from the reaction solution with a syringe connected to a $0.2\text{ }\mu\text{m}$ filter. The concentration of the dissolved Fe in solution was determined by atomic absorption spectroscopy (AA).

8.2.4 Non-Aqueous Solution Experiments

Acetonitrile, CH_3CN , and tetra-n-butylammonium perchlorate, $(\text{C}_4\text{H}_9)_4\text{NClO}_4$, were used as the non-aqueous solvent and an electrolyte, respectively. Acetonitrile solutions with different water contents were prepared by mixing certain volumes of 1 M HNO_3 solutions with acetonitrile solvent. The final solutions contained 0.1 M $(\text{C}_4\text{H}_9)_4\text{NClO}_4$ electrolyte. Electrochemical measurements carried out in the electrochemical cell were performed using the same procedure described previously.

8.2.5 Characterization of Reaction Products

The reaction products were analyzed and characterized with X-ray diffraction (Rigaku Geigerflex) and a Topcon SX-40A scanning electron microscope (SEM). The samples for X-ray diffraction and SEM were prepared by collecting the solid products from the electrochemical cell after reaction. The solids were then separated from the liquids and dried in a vacuum oven at room temperature.

8.3 Results And Discussion

8.3.1 Electrochemical and Chemical Dissolution

The effect of illumination on the anodic dissolution of pyrite in 1 M HNO_3 solution at a potential of 1.0 V(SCE) is shown in Figure 8.1. It is observed that the dissolved Fe concentration under illumination is higher than that in the dark. The effect of illumination on the anodic current under the same conditions is shown in Figure 8.2. An increase in anodic current was also observed under illumination. The pyrite synthesized by the $\text{Fe}^{3+}/\text{HS}^-$ reaction is an n-type semiconductor, and the anodic dissolution of pyrite involves the valence band hole reaction (see Chapter 7). Illumination enhances the concentration of the minority carriers (holes) in the valence band of the solid, thus promoting the anodic dissolution rate of pyrite.

The current density shown in Figure 8.2 can be converted to the dissolved Fe concentration. Assuming that the overall electrochemical oxidation of FeS_2 by holes

FIGURE 8.1. Dissolved Fe concentrations as functions of reaction time in 1 M HNO₃ solution at E=1.0 V(SCE).

FIGURE 8.2. Anodic currents as functions of time in 1 M HON₃ solution at E=1.0 V(SCE).

involves a two-electron transfer process (reactions involving more electrons will be discussed later):

and the rate of electron transfer from the conduction band of pyrite to the inert electrode is the same as that of the hole reaction with the pyrite lattice, then the total charge, Q in coulombs, from reaction 8.3 is given by Faraday's law as:

$$Q = z \cdot F \cdot W_{\text{Fe}} / M \quad (8.4)$$

where F is the Faraday constant, M the molecular weight of Fe , W_{Fe} the weight of dissolved Fe in grams and z the number of electrons involved in the reaction. The total charge, Q , for a given time, t in seconds, can be calculated by:

$$Q = S \int i(t) dt \quad (8.5)$$

where $i(t)$ is the measured current density in A/cm^2 and S the area of the inert electrode in cm^2 . The dissolved Fe concentration, $[\text{Fe}]$ in mg/l , in 100 ml solution can be expressed as:

$$[\text{Fe}] = W_{\text{Fe}} \times 10^4 \quad (8.6)$$

From Equations 8.4, 8.5 and 8.6, we have:

$$[\text{Fe}] = M \cdot S \cdot 10^4 / (z \cdot F) \int i(t) dt \quad (8.7)$$

The current density as a function of time was obtained by curve-fitting the data in Figure 8.2. In this particular case, $M=55.85 \text{ g mol}^{-1}$, $S=2 \text{ cm}^2$, $z=2$, and $F=96500 \text{ C mol}^{-1}$, the dissolved Fe concentration contributed by electrochemical reaction 8.3 was calculated according to Equation 8.7. The results, along with the dissolved Fe concentration from direct measurements are shown in Figure 8.3. It can be seen that the dissolved Fe concentrations both under illumination and in the dark are lower than the corresponding Fe concentrations that were measured directly. To further confirm this dissolution behavior, an inert electrode potential of 0.8 V(SCE) was applied to conduct the experiments. The current density as a function of time is shown in Figure 8.4. A comparison of the calculated and measured Fe concentrations is shown in Figure 8.5. The same trend was observed as shown in Figure 8.3.

It must be pointed out that the assumed reaction (Equation 8.3) involved the transfer of two electrons. If the overall electrochemical oxidation of pyrite involves more electrons (e.g., Equation 8.2), the dissolved Fe concentration calculated from Equation 8.7 will be even smaller. This strongly suggests that the dissolution of pyrite in aqueous solution involves not only an electrochemical process, but also a chemical process. Semiconductor dissolution may involve both chemical and electrochemical reactions. In a recent study, Allongue and co-workers (1993) found that chemical and electrochemical reactions coexist in the oxidation of n-type silicon.

A possible mechanism for pyrite dissolution by a non-electrochemical pathway may involve surface complexation of hydrogen ions. The adsorption of hydrogen ions on the pyrite surface may break the Fe-S bond and subsequently dissolve pyrite according to the following reactions:

Data from "C-1/PH0/E1.0-DATA" i-C/E1.0-F

FIGURE 8.3. Comparison of dissolved Fe concentrations calculated from current density and measured from AA ($E=1.0$ V(SCE)).

FIGURE 8.4. Anodic currents as functions of time in 1 M HON₃ solution at E=0.8 V(SCE).

FIGURE 8.5. Comparison of dissolved Fe concentrations calculated from current density and measured from AA (E=0.8 V(SCE)).

The surface hydropolysulfide may decompose to form elemental sulfur (Equation 8.10) or, by further reaction, produce polysulfides (Equation 8.11).

Therefore, it is important to recognize that the elemental sulfur and polysulfides observed by some investigators (Mycroft et al., 1990; Zhu et al., 1993) may come not only from the electrochemical processes, but also from the chemical dissolution processes as shown in Equations 8.8 to 8.11.

Chemical dissolution via surface protonation of hydrogen ion has been well established in the dissolution studies of metal oxides and silicates (Schindler, 1981; Schindler and Stumm, 1987; Stumm et al., 1970, 1976, 1980, 1987; Wieland et al., 1988, 1992). However, the surface complexation modeling of metal sulfide dissolution system has received little attention so far (Wadsworth, 1984; Osseo-Asare, 1992), despite the extensive studies on the non-oxidative dissolution of metal sulfides, such as sphalerite (ZnS), galena (PbS) and pyrrhotite (Fe_{1-x}S) (Subramanian et al., 1972; Nicol and Scott, 1979; Awakura et al., 1980; Majima et al., 1981). The non-oxidative dissolution of pyrite via surface complexation may be one of the pathways to produce elemental sulfur and polysulfides as described in Equations 8.10 and 8.11.

From Figure 8.3, it is also evident that in the dark, electrochemical reaction yields about 50% of the dissolved Fe in solution. However, the contribution of electrochemical reaction to pyrite dissolution increases substantially under illumination. In this case,

illumination creates holes in the valence band of pyrite, favoring electrochemical reaction (Equation 8.3). This further confirms that anodic dissolution of pyrite involves hole reactions. Comparison of Figures 8.3 and 8.5 shows that the chemical dissolution predominates at lower electrode potential (Figure 8.5). Obviously, the applied potentials control the electrochemical oxidation, but do not affect the chemical dissolution.

8.3.2 Autocatalysis of Electrochemical Reaction

Figures 8.2 and 8.4 show that the anodic current increases with reaction time. A maximum current is observed followed by a decrease in current. This behavior indicates that an autocatalysis reaction occurs during the anodic dissolution of pyrite. The autocatalytic process is illustrated in Figure 8.6, where E_c and E_v refer to the bottom of the conduction band and the top of the valence band of pyrite, respectively. When the potential of the inert electrode (Pt) was maintained at a more positive value than E_c ($E_c = 0.34$ V(SCE) at pH 0 (see Chapter 7)), pyrite dissolved to release Fe^{2+} ions in aqueous solution. The ferrous ions would be oxidized to Fe^{3+} at the inert electrode/solution interface. The ferric ions then acted as an oxidant for pyrite by receiving electrons from the conduction band, and were reduced to Fe^{2+} . In other words, the Fe^{2+}/Fe^{3+} couple worked as an electron transfer medium between the inert electrode and the pyrite particles, when the pyrite particles were not in contact with the electrode. As the reaction proceeded, the concentration of Fe^{2+} increased. As a result, the anodic current increased with the time. On the other hand, the depletion of the pyrite sample would cause a decrease in the current as the dissolution reaction proceeded. This autocatalysis behavior in the pyrite oxidation system was also observed by Lalvani (1986).

FIGURE 8.6. Illustration of autocatalysis process during pyrite dissolution.

8.3.3 Pyrite Dissolution in Acetonitrile Solutions

The polarization curves of pyrite in non-aqueous solutions with and without illumination are shown in Figures 8.7 and 8.8, respectively. It can be seen that small anodic currents were generated in the absence of water in the solutions. However, when the solutions contained 20% aqueous 1 M HNO₃, large anodic currents were observed. The small current generated in the absence of water indicates that reaction 8.3 does not proceed at a significant rate in the absence of water. The essential role of water in the process of electrochemical dissolution of pyrite has been stressed by Mishra and Osseo-Asare (1988). According to their theory, pyrite dissolution involves several steps. In the first step, pyrite reacts with water via the interaction of iron 3d states with OH⁻ ions in the aqueous phase:

In the second step, the OH groups are rearranged on the pyrite surface and move next to the S₂²⁻ sites in the pyrite lattice:

Finally, the complete hydroxylation of the surface, followed by oxidation of S₂²⁻ takes place according the following reactions:

FIGURE 8.7. Polarization curves of pyrite microelectrodes in acetonitrile under illumination.

FIGURE 8.8. Polarization curves of pyrite microelectrodes in acetonitrile in the dark.

FIGURE 8.9. Effect of illumination on the anodic current in acetonitrile containing 20% aqueous 1 M HNO₃.

FIGURE 8.10. Effect of illumination on the anodic current in acetonitrile.

FIGURE 8.11. Anodic currents as functions of time under illumination at E=1.0 V(SCE).

FIGURE 8.12. Anodic currents as functions of time in dark at E=1.0 V(SCE).

Thiosulfate may either be oxidized further to sulfate through a series of sulfur oxyanions or it may decompose to produce elemental sulfur and bisulfate (Mishra and Osseo-Asare, 1988). However, it is also possible that following reaction 8.13, the polysulfide, S_2^{2-} , may be oxidized directly by the hydroxyl radical, OH, to form elemental sulfur:

Further insight into the effects of illumination and water on the anodic currents may be gained by replotting the data of Figures 8.7 and 8.8, as indicated in Figures 8.9 and 8.10. It is obvious that the increase in anodic current under illumination in the presence of 20% aqueous 1 M HNO_3 (Figure 8.9) is much larger than that in the absence of water (Figure 8.10). This indicates that the water and holes are both essential elements for anodic dissolution of pyrite. The experimental data are consistent with Equation 8.12. The anodic currents are shown as a function of time in Figures 8.11 and 8.12. It can be seen that the anodic current increases dramatically in the aqueous solution. The currents observed in non-aqueous solutions were of negligible magnitude compared with the current in aqueous solution.

8.3.4 Dissolution Products

One of the advantages of using microelectrodes (as opposed to planar electrodes) to study pyrite dissolution is that more products will form from the reaction because of the overall enlarged interface between solid and solution. The solid products from pyrite

dissolution can be analyzed by X-ray diffraction technique, and observed directly from SEM photographs.

The X-ray diffractograms of the solid products from the reaction in aqueous solution are shown in Figure 8.13 for different acidities. It is observed that elemental sulfur forms at pH 0.3 (Figure 8.13a). However, no elemental sulfur was observed at pH 13.7 (Figure 8.13c). The X-ray diffractograms of the reaction products from non-aqueous solution experiments are shown in Figure 8.14. No elemental sulfur was produced in the absence of water in the solutions, while elemental sulfur was observed when the solution contained 20% aqueous 1 M HNO_3 . The X-ray diffractograms have clearly shown that elemental sulfur is one of the products from anodic dissolution of pyrite in aqueous solution at low pH. As discussed previously, pyrite dissolution in aqueous solutions at low pH may involve at least two processes; the chemical dissolution via the surface complexation of the proton, and electrochemical oxidation via hole reactions. It is postulated that the hydropolysulfide, HS_2^- , produced from the pyrite surface protonation by hydrogen, is further decomposed to form elemental sulfur via the chemical reactions as shown in Equations 8.8 to 8.10. Formation of elemental sulfur from the electrochemical reaction may be a result of the hole oxidation of lattice S_2^{2-} (Equation 8.3). The holes must be transferred by the hydroxyl radical, OH , from the Fe 3d state to the S_2^{2-} sites. Alternatively, elemental sulfur could form by the decomposition of thiosulfate as proposed by Mishra and Osseo-Asare (1988).

The SEM micrographs (Figure 8.15) show that the dissolution of pyrite produces porous surfaces on the pyrite particles (Figure 8.15b). When the reaction time is long enough, elemental sulfur becomes the main solid product from the dissolution process (Figure 8.16).

FIGURE 8.13. X-ray diffractograms of the solid reaction products for different acidities.

FIGURE 8.14. X-ray diffractograms of the solid reaction products obtained from acetonitrile-based experiments.

FIGURE 8.15. SEM micrographs of the pyrite particles. (a) original sample, and (b) treated in 1 M HNO₃ at E=1.0 V(SCE) for 4 hours.

FIGURE 8.16. (a) SEM micrograph and (b) X-ray diffractogram of the solid reaction products treated in 1 M HNO_3 at $E=1.0$ V(SCE) for 3 days.

8.4 Conclusions

The anodic dissolution of pyrite in acidic solution was studied using microsize particles of pyrite as electrodes. The electrochemical and dissolution experiments showed that pyrite dissolution in acidic solution involved both electrochemical and chemical processes. Under illumination at a high potential, electrochemical oxidation predominates in the overall dissolution process. This is because more holes are created in the valence band of the pyrite by photo excitation. The electrochemical oxidation of pyrite is believed to occur via the hole reaction, unlike chemical dissolution which may take place via the surface complexation of hydrogen ions to break Fe-S bonds.

Pyrite dissolution requires the presence of water. The direct reaction of S_2^{2-} with holes in the pyrite lattice is not significant in the overall oxidation process. The essential role of water in pyrite dissolution can be attributed to the hydroxyl ions (Mishra and Osseo-Asare, 1988). Their role, as an intermediate, enables the transfer of the holes from pyrite non-bonding orbitals to the S_2^{2-} sites, resulting in oxidation of the sulfides. On the other hand, the lack of hydrogen and/or hydroxyl ions in non-aqueous solution depresses the chemical dissolution process.

Elemental sulfur was directly determined through X-ray diffraction to be a dissolution product of pyrite in acidic solution. Elemental sulfur may be produced both from electrochemical and from chemical reaction.

Chapter 9

RESEARCH SUMMARY

Particulate pyrite was synthesized from the $\text{Fe}^{3+}/\text{HS}^-$ reaction in aqueous solutions at room temperature. A redox reaction occurred initially between Fe^{3+} and HS^- ions to form Fe^{2+} and elemental sulfur:

Further reactions in the presence of Fe^{2+} and HS^- ions, and elemental sulfur form pyrite:

The essential role of elemental sulfur in the formation of pyrite was investigated by exclusion of elemental sulfur from the reaction systems. This was accomplished by introducing a sulfur-extracting organic solvent (Carbon disulfide, CS_2) into the experimental system. It was expected that the elemental sulfur would be extracted into the organic phase immediately upon formation from reaction 9.1, so that reactions 9.2b and 9.2c would be suppressed. The experimental results showed that pyrite could not form in the presence of the organic solvent. The importance of elemental sulfur was further

investigated by using the organic solvent presaturated with sulfur. In this case, the elemental sulfur produced in reaction 9.1 was expected to stay in the aqueous solution. The experimental results indicated that pyrite did form in the presence of an organic solvent that was presaturated with elemental sulfur.

Elemental sulfur can be in equilibrium with polysulfides in the aqueous solution:

The analysis of the equilibrium aqueous speciation for the S-S_n²⁻-H₂O system showed that polysulfides, such as S₅²⁻, S₄²⁻ and S₂²⁻, predominate at pH above 9, and elemental sulfur dominates in acidic solution. However, the concentration of the polysulfide ions (S_n²⁻) may be much higher in the system of this study because the subcolloidal particles of elemental sulfur produced initially from the Fe³⁺/HS⁻ reaction have a larger solubility than the macroscopic sulfur particles. The reaction of the dissolved sulfur species with the freshly formed "FeS" or Fe(HS)⁺ resulted in the rapid formation of pyrite in aqueous solution at room temperature.

The pH and Eh of the solutions determined the reaction products. It was found that under the conditions where pyrite formed, both elemental sulfur and "FeS" (amorphous FeS or Fe(HS)⁺) were available in the solution. The suitable pH range for making pyrite was from 3.6 to 5.7. At higher pH, the experimental Eh was such that FeOOH formed instead of "FeS". At lower pH, on the other hand, "FeS" was undersaturated. Under these conditions, pyrite was not produced. Therefore, it was concluded that the precursors of sulfur species and "FeS" are necessary for pyrite formation.

Synthetic pyrite obtained by the Fe³⁺/HS⁻ reaction contained elemental sulfur. Pyrite was purified by solvent extraction to remove the elemental sulfur. The purified

pyrite sample contained 99.64% FeS₂ with an average particle diameter of 1.5 μm , and a specific surface area of 4.1 m²/g.

The formation of an iron sulfide complex intermediate from the Fe(II)/S(II) reaction in aqueous solution was studied using stopped-flow spectrophotometry, a fast kinetics technique. The successful use of this technique was based on the fact that this instrument could monitor the reaction progress in the millisecond to minute time range. In addition, the absorbance was observed to have a linear relationship with the concentration of the intermediate. The absorptivity of the intermediate was determined to be 4800 M⁻¹cm⁻¹ at 500 nm. The stoichiometry of the Fe(III)/S(II) reaction was determined by using Job's continuous variation method as:

The rate law for the formation of Fe(HS)⁺ was obtained as:

$$d [\text{Fe}(\text{HS})^+] / dt = 10^{3.81} [\text{Fe}^{2+}][\text{HS}^-] \quad (9.5)$$

The formation constant of Fe(HS)⁺ was determined to be 10^{4.34±0.15} at 25 °C and I=0, which is similar to the estimated values for other transition metal sulfide complexes, such as 10^{4.7} for Co(HS)⁺, and 10^{3.8} for Ni(HS)⁺ (Dryssen, 1988). It is also interesting to note that the formation constant of Fe(OH)⁺ is 10^{4.5} (Smith and Martell, 1976), very near the value of 10^{4.3} for Fe(HS)⁺.

Identification of the intermediate species is very important in understanding pyrite formation. The mechanism for pyrite formation may involve a reaction between Fe(HS)⁺ and polysulfides via the following reaction:

Pyrite formation may also include reaction between polysulfides and the iron monosulfide produced from Fe(HS)^+ :

In either case, Fe(HS)^+ is the initial product in the process of pyrite formation.

Pyrite decomposition was investigated by electrochemical, photoelectrochemical and dissolution experiments using synthetic pyrite particles as microelectrodes. The experimental results showed that illumination increased both the anodic current and the dissolution rate dramatically. However, illumination had no effect on the cathodic current and the dissolution rate. These results indicated that the synthetic pyrite used in this study was an n-type semiconductor, and the electrochemical dissolution of pyrite involved both electron and hole pathways. The anodic oxidation of pyrite involved the hole reaction :

The cathodic dissolution of pyrite involved electron reaction:

Illumination can increase the concentration of the minority carriers (holes), so that the anodic oxidation which involves holes will be enhanced under illumination. Obviously, the electronic properties of pyrite affect its dissolution processes.

Pyrite dissolution has been considered as an electrochemical processes (see reviews: Hiskey and Schlitt, 1982; Lawson, 1982; Peters, 1992). However, the experimental results in this study have shown that pyrite dissolution in an acidic solution may involve both electrochemical oxidation and chemical (i.e., non-electrochemical) decomposition. Under illumination, electrochemical oxidation is predominant in the dissolution process because more holes are created by photo excitation. The chemical dissolution of pyrite may be through the surface complexation of hydrogen ions which break the Fe-S bond and cause pyrite decomposition.

Electrochemical experiments were also conducted in acetonitrile solutions to examine whether pyrite can be decomposed in the absence of water. The results showed that the anodic current observed in a non-aqueous solution was of negligible magnitude compared with the current in an aqueous solution. This indicates that pyrite dissolution requires the presence of water, and the direct reaction of S_2^{2-} with holes is not significant in the overall oxidation process. The essential role of water in pyrite dissolution can be attributed to the role of hydroxyl ions as an intermediate for transferring the holes from the pyrite non-bonding orbital to the S_2^{2-} sites, resulting in oxidation of the sulfide (Mishra and Osseo-Asare, 1988). On the other hand, the exclusion of water can also suppress the chemical decomposition process of pyrite.

It is expected that the use of microelectrodes will produce more reaction products for analysis because of the larger interface between solid and solution. Elemental sulfur as a dissolution product in acidic solution was detected by X-ray diffraction. It is postulated

that the hydropolysulfide, HS_2^- , produced from the chemical reaction, may decompose further to produce elemental sulfur according to the following reaction:

In the process of electrochemical oxidation of pyrite, elemental sulfur may form through the decomposition of thiosulfate produced from reaction 9.9 (Mishra and Osseo-Asare, 1988):

In this study, pyrite dissolution in acidic solution was found to involve a chemical decomposition process. The mechanism for the chemical dissolution of pyrite needs to be further investigated. The kinetic studies of some metal sulfides (e.g. PbS , ZnS and FeS) have related the chemical dissolution rate with the concentration of hydrogen ions in the bulk solution (Subramian et al., 1972; Nicol and Scott, 1979; Awakura et al., 1980; Majima et al., 1981). However, the studies of metal oxides and silicates have demonstrated that the dissolution rate is dependent primarily on the concentration of hydrogen ions adsorbed on the solid surfaces (Schindler, 1981; Schindler and Stumm, 1987; Stumm et al., 1970, 1976, 1980, 1987; Wieland et al., 1988, 1992). It should be possible to determine the mechanism for chemical dissolution of pyrite by examining the surface concentration of hydrogen ions and establishing the relationship between the surface concentration of protons and the dissolution rate. Determination of the concentration of hydrogen ions on solid surfaces by potentiometric titration has been demonstrated in the literature (Schindler, 1981; Wieland and Stumm, 1982; Stumm, 1986; Ronngren et al., 1991; Sun et al., 1991).

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Appendix A

SELECTED X-RAY DIFFRACTION PATTERN

Figure A-1. Standard X-ray diffraction patterns from JCPDS.

Appendix B

SELECTED THERMODYNAMIC DATA

TABLE B-1. Standard free energies of formation for iron species, ΔG°_f (kcal/mol) at 25°C.

Species	ΔG°_f	Ref.	Species	ΔG°_f	Ref.
Fe ²⁺	-22.05	1	FeS, precipitate	-21.3	3
Fe ³⁺	-4.27	1	FeS, mackinawite	-22.3	3
FeO	-58.59	1	FeS, pyrrhotite	-24.2	3
Fe ₂ O ₃	-177.44	1	FeS ₂ , pyrite	-38.3	3
Fe ₃ O ₄	-242.70	1	Fe ₃ S ₄ , reigite	-69.4	3
FeOOH	-117.20	1	FeSO ₄	-202.83	4
Fe(OH) _{2(s)}	-117.84	1	FeSO ₄ ⁺	-184.70	4
Fe(OH) _{3(s)}	-170.80	1	Fe(SO) ₂ ⁻	-364.40	4
FeOH ⁺	-64.0	2			
Fe(OH) _{2(l)}	-105.6	2			
Fe(OH) ₃ ⁻	-148.1	2			
Fe(OH) ₄ ²⁻	-184.3	2			
Fe(OH) ₂ ²⁺	-56.2	2			
Fe(OH) ₂ ⁺	-108.2	2			
Fe(OH) _{3(l)}	-156.2	2			
Fe(OH) ₄ ⁻	-199.8	2			

1 - Naumov et al., 1974, 2 - Baes et al., 1976, 3 - Berner, 1967, 4 - Smith et al., 1977.

TABLE B-2. Standard free energies of formation for sulfur species, ΔG°_f (kcal/mol) at 25°C.

Species	ΔG°_f	Ref.	Species	ΔG°_f	Ref.
H ₂	0	1	HS ₂ ⁻	6.029	3
O ₂	0	1	H ₂ S ₂	-0.951	3
H ₂ O(l)	-56.690	1	HS ₃ ⁻	7.258	3
H ⁺	0	1	H ₂ S ₃	1.368	3
OH ⁻	-37.595	1	HS ₄ ⁻	7.535	3
			H ₂ S ₄	2.195	3
S ₂ ²⁻	19.749	1	HS ₅ ⁻	7.479	3
S ₃ ²⁻	17.968	1	H ₂ S ₅	2.599	3
S ₄ ²⁻	16.615	1			
S ₅ ²⁻	15.689	1	S ₅ O ₆ ²⁻	-228.22	1
S ₆ ²⁻	16.04	1	S ₄ O ₆ ²⁻	-244.30	1
S ²⁻	20.5	2	S ₂ O ₄ ²⁻	-138.00	1
HS ⁻	2.88	2	HS ₂ O ₄ ⁻	-141.40	1
H ₂ S(l)	-6.66	2	S ₃ O ₆ ²⁻	-229.00	1
S ₂ O ₃ ²⁻	-122.80	2	S ₂ O ₆ ²⁻	-231.00	1
HS ₂ O ₃ ⁻	-125.15	2	S ₂ O ₈ ²⁻	-262.00	1
H ₂ S ₂ O ₃	-125.97	2			
SO ₃ ²⁻	-116.30	2			
HSO ₃ ⁻	-126.15	2			
H ₂ SO ₃	-128.56	2			
SO ₄ ²⁻	-177.78	2			
HSO ₄ ⁻	-180.48	2			
H ₂ SO ₄	-128.56	2			

1- Pourbaix et al., 1992, 2- Naumov et al., 1974, 3- Schoonen et al., 1988.

TABLE B-3. Selected equilibrium constants for the S-H₂O system at 25 °C.

Reaction	logK	Ref.
$\text{HS}^- = \text{S}^{2-} + \text{H}^+$	-18.51	1
$\text{H}_2\text{S} = \text{S}^{2-} + 2\text{H}^+$	-25.56	1
$\text{HS}_2^- + 2\text{e} = 2\text{S}^{2-} + \text{H}^+$	-32.59	1
$\text{HS}_3^- + 4\text{e} = 3\text{S}^{2-} + \text{H}^+$	-46.27	1
$\text{HS}_4^- + 6\text{e} = 4\text{S}^{2-} + \text{H}^+$	-64.25	1
$\text{HS}_5^- + 8\text{e} = 5\text{S}^{2-} + \text{H}^+$	-79.92	1
$\text{S}_2^{2-} + 2\text{e} = 2\text{S}^{2-}$	-22.53	2
$\text{S}_3^{2-} + 4\text{e} = 3\text{S}^{2-}$	-38.41	2
$\text{S}_4^{2-} + 6\text{e} = 4\text{S}^{2-}$	-57.59	2
$\text{S}_5^{2-} + 8\text{e} = 5\text{S}^{2-}$	-73.90	2
$\text{S}_6^{2-} + 10\text{e} = 6\text{S}^{2-}$	-89.89	2
$\text{S}^0 + 2\text{e} = \text{S}^{2-}$	-16.20	3
$\text{SO}_3^{2-} + 6\text{e} + 6\text{H}^+ = \text{S}^{2-} + 3\text{H}_2\text{O}$	24.41	3
$\text{HSO}_4^- + 8\text{e} + 7\text{H}^+ = \text{S}^{2-} + 4\text{H}_2\text{O}$	18.91	3
$\text{SO}_4^{2-} + 8\text{e} + 8\text{H}^+ = \text{S}^{2-} + 4\text{H}_2\text{O}$	20.90	3
$\text{S}_2\text{O}_3^{2-} + 8\text{e} + 6\text{H}^+ = 2\text{S}^{2-} + 3\text{H}_2\text{O}$	4.60	3

1 - Schoonen et al., et al., 1988; 2 - Millero, 1986; 3 - Naumov et al., 1974.

TABLE B-4. Selected equilibrium constants for the Fe-S-H₂O system at 25 °C.

Reaction	logK	Ref.
$\text{Fe} = \text{Fe}^{2+} + 2\text{e}$	16.17	1
$\text{Fe}_2\text{O}_3 + 2\text{e} + 6\text{H}^+ = 2\text{Fe}^{2+} + 3\text{H}_2\text{O}$	26.93	1
$\text{FeOOH} + \text{e} + 3\text{H}^+ = \text{Fe}^{2+} + 2\text{H}_2\text{O}$	13.37	1
$\text{Fe}_3\text{O}_4 + 2\text{e} + 8\text{H}^+ = 3\text{Fe}^{2+} + 4\text{H}_2\text{O}$	36.81	1
$\text{FeO} + 2\text{H}^+ = \text{Fe}^{2+} + \text{H}_2\text{O}$	14.77	1
$\text{Fe}(\text{OH})_2 + 2\text{H}^+ = \text{Fe}^{2+} + 2\text{H}_2\text{O}$	12.90	1
$\text{Fe}(\text{OH})_3 + \text{e} + 3\text{H}^+ = \text{Fe}^{2+} + 3\text{H}_2\text{O}$	15.63	1
$\text{Fe}_2(\text{SO}_4)_3 + 26\text{e} + 24\text{H}^+ = 2\text{Fe}^{2+} + 3\text{S}^{2-} + 12\text{H}_2\text{O}$	89.75	1
$\text{FeSO}_4 + 8\text{e} + 8\text{H}^+ = \text{Fe}^{2+} + \text{S}^{2-} + 4\text{H}_2\text{O}$	22.76	1
$\text{FeSO}_4 \cdot 7\text{H}_2\text{O} + 8\text{e} + 8\text{H}^+ = \text{Fe}^{2+} + \text{S}^{2-} + 11\text{H}_2\text{O}$	17.61	1
$\text{FeS} = \text{Fe}^{2+} + \text{S}^{2-}$	-14.76	1
$\text{FeS}_2 + 2\text{e} = 2\text{S}^{2-} + \text{Fe}^{2+}$	-44.75	1
$\text{Fe}^{3+} + \text{e} = \text{Fe}^{2+}$	13.04	1
$\text{FeOH}^+ + \text{H}^+ = \text{Fe}^{2+} + \text{H}_2\text{O}$	9.5	2
$\text{Fe}(\text{OH})_2(\text{l}) + 2\text{H}^+ = \text{Fe}^{2+} + 2\text{H}_2\text{O}$	20.6	2
$\text{Fe}(\text{OH})_3^- + 3\text{H}^+ = \text{Fe}^{2+} + 3\text{H}_2\text{O}$	31.0	2
$\text{Fe}(\text{OH})_4^{2-} + 4\text{H}^+ = \text{Fe}^{2+} + 4\text{H}_2\text{O}$	46.0	2
$\text{Fe}(\text{OH})_2^{2+} + \text{e} + \text{H}^+ = \text{Fe}^{2+} + \text{H}_2\text{O}$	15.23	2
$\text{Fe}(\text{OH})_2^+ + \text{e} + \text{H}^+ = \text{Fe}^{2+} + 2\text{H}_2\text{O}$	18.71	2
$\text{Fe}(\text{OH})_3(\text{l}) + \text{e} + 3\text{H}^+ = \text{Fe}^{2+} + 3\text{H}_2\text{O}$	25.04	2
$\text{Fe}(\text{OH})_4^- + \text{e} + 4\text{H}^+ = \text{Fe}^{2+} + 4\text{H}_2\text{O}$	34.64	2
$\text{FeSO}_4^+ + 9\text{e} + 7\text{H}^+ = \text{Fe}^{2+} + \text{S}^{2-} + 4\text{H}_2\text{O}$	29.03	3
$\text{FeSO}_2^- + 17\text{e} + 16\text{H}^+ = \text{Fe}^{2+} + 2\text{S}^{2-} + 8\text{H}_2\text{O}$	47.72	3
$\text{FeSO}_4(\text{l}) + 8\text{e} + 8\text{H}^+ = \text{Fe}^{2+} + \text{S}^{2-} + 4\text{H}_2\text{O}$	17.83	3

1 - Naumov et al., 1974; 2 - Baes et al., 1976; 3 - Smith et al., 1977.

Appendix C

CONVERSION OF CURRENT DENSITY TO DISSOLVED Fe CONCENTRATION

Suppose that the overall anodic dissolution of pyrite proceeds via the following reaction:

The total charge, Q in C, from reaction C-1 is given by Faraday's law:

$$Q = z \cdot F \cdot W_{\text{Fe}} / M \quad (\text{C-2})$$

where F is Faraday constant, M the mole weight of Fe, W_{Fe} the weight of dissolved Fe in grams and z the number of electrons involved in the reaction. The total charge, Q , for a given time, t in seconds, can be calculated by:

$$Q = S \int i(t) dt \quad (\text{C-3})$$

where $i(t)$ is the measured current density in A/cm^2 and S the area of the inert electrode in cm^2 . The dissolved Fe concentration, $[\text{Fe}]$ in mg/l , in 100 ml solution can be expressed as:

$$[\text{Fe}] = W_{\text{Fe}} \times 10^4 \quad (\text{C-4})$$

FIGURE C-1. Curve fitting for the data in Figure 8.2 , (a) in dark and (b) under illumination.

FIGURE C-2. Curve fitting for the data in Figure 8.4 , (a) in dark and (b) under illumination.

From Equations C-2 to C-4, we have:

$$[\text{Fe}] = M \cdot S \cdot 10^4 / (z \cdot F) \int i(t) dt \quad (\text{C-5})$$

The current density as a function of time was obtained by a curve fitting method as shown in Figures C-1 and C-2. The expressions were obtained for Figure C-1:

$$\begin{aligned} i(\text{light}) = & 2.44 \times 10^{-6} t - 2.56 \times 10^{-10} t^2 \\ & + 2.55 \times 10^{-14} t^3 - 1.07 \times 10^{-18} t^4 \end{aligned} \quad (\text{C-6})$$

$$\begin{aligned} i(\text{dark}) = & -1.63 \times 10^{-7} t + 3.16 \times 10^{-10} t^2 - 5.75 \times 10^{-14} t^3 \\ & + 4.45 \times 10^{-18} t^4 - 1.26 \times 10^{-22} t^5 \end{aligned} \quad (\text{C-7})$$

and for Figure C-2:

$$\begin{aligned} i(\text{light}) = & 4.03 \times 10^{-7} t - 1.49 \times 10^{-10} t^2 \\ & + 3.18 \times 10^{-14} t^3 - 2.68 \times 10^{-18} t^4 + 7.64 \times 10^{-23} t^5 \end{aligned} \quad (\text{C-8})$$

$$\begin{aligned} i(\text{dark}) = & 2.49 \times 10^{-7} t - 7.49 \times 10^{-11} t^2 \\ & + 1.39 \times 10^{-14} t^3 - 1.04 \times 10^{-18} t^4 + 2.75 \times 10^{-23} t^5 \end{aligned} \quad (\text{C-9})$$

In this particular case, $M=55.85$, $S=2$, $z=2$, and $F=96500$, the dissolved Fe concentration contributed by electrochemical reaction C-1 can be calculated according to Equation C-5.