SEMICONDUCTOR ELECTROCHEMISTRY OF COAL PYRITE

Technical Progress Report

July - September 1992

by

K. Osseo-Asare and Dawei Wei

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

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ABSTRACT

The kinetics of the formation of $\text{Fe}(\text{HS})^{2-n_n}$, the intermediate in the formation of FeS (from the reaction between aqueous sulfide ions and dissolved Fe(II) salts) was studied with a stopped-flow spectrophotometric technique. As described in the previous report, the absorbance-time curve indicated that a black substance formed within the first few seconds of the reaction; this material subsequently decomposed gradually to give a lighter dark product within the following several minutes. It was proposed that an intermediate species, $\text{Fe}(\text{HS})^{2-n_n}$, was formed initially from the reaction between Fe^{2+} and HS^- ions in aqueous solution and this intermediate was converted to FeS finally. The kinetic experiments showed that the rate of formation of $\text{Fe}(\text{HS})^{2-n_n}$ was first order with respect to both Fe^{2+} and HS^- , with a rate constant of $10^{3.81} \text{ (mol/l)}^{-1}\text{sec}^{-1}$. These results suggest that the black intermediate is FeHS^+ .

PROJECT 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. A novel approach to the study of pyrite aqueous electrochemistry is proposed, based on the use of both synthetic and natural (i.e. coal-derived) pyrite specimens, the utilization of pyrite both in the form of micro (i.e. colloidal and subcolloidal) and macro (i.e. rotating ring disk) electrodes, and the application of in-situ direct electroanalytical and spectroelectrochemical characterization techniques. Central to this research is the recognition that pyrite is a semiconductor material. (Photo) electrochemical experiments

will be conducted to unravel the mechanisms of anodic and cathodic processes such as those associated with pyrite decomposition and the reduction of oxidants such as molecular oxygen and the ferric ion.

STATEMENT OF WORK

The experiments to be conducted fall into two main groups, depending on whether the pyrite specimens are used in the form of (a) nanoparticle microelectrodes, or (b) planar surface macroelectrodes. In the first case, synthetic pyrite microelectrodes will be used in the form of nanoparticles and the in-situ observation of the evolution of particle size and reaction products will be accomplished via photon correlation, absorption, and fluorescence spectroscopy techniques. In the second case, the experimental system will be based on a rotating ring disk electrode (RRDE) assembly, with coal pyrite serving as the disk and a Pt (or Ag, Cu) ring electrode permitting direct in-situ electroanalytical determination of reaction products.

DESCRIPTION OF TECHNICAL PROGRESS:

INTRODUCTION

Pyrite synthesis is of interest in many diverse fields, such as geology, fuel processing technology, chemistry, metallurgy, materials science, and so on. Based on fundamental studies of this process, the formation mechanisms of this important sulfide in geochemical systems can be better understood. The studies can also help us to better understand the surface chemistry and electrochemistry of pyrite, thereby assisting in the

development of more efficient processes for removal of the sulfide from coal.

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, Feld, 1977; Schoonen and Barnes, 1991b). In the first step, an iron monosulfide precursor, FeS, forms via the reaction between aqueous sulfide and aqueous ferrous iron species. In the second step, 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.

Iron sulfide (FeS) can be formed by the reaction between aqueous sulfide and dissolved Fe(II) salts. A black precipitate was observed immediately when the two solutions were mixed. It was demonstrated in a number of studies (See review by Morse et al., 1987; Schoonen and Barnes, 1991a, 1991b, 1991c) that the black material is iron sulfide which is X-ray amorphous, with the 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).

Is FeS the initially formed black material from the reaction between aqueous sulfide and aqueous ferrous iron species? Some arguments still exist. Pohl (1953) postulated that the formation of FeS might be via the activated complex with a formula of $(\text{FeSH})^+$. Baas Becking (1956) suggested that $\text{Fe}(\text{SH})_2$ was the first precipitated ferrous sulfide. Subsequently, Taylor (1980) suggested the formation of FeSH^+ as an intermediate, based on stereochemical arguments. The experimental

confirmation of these suggestions has encountered some difficulties because the initial reaction is extremely fast. Thus it is not easy, with conventional techniques, to monitor the intermediate steps experimentally. To solve this problem, Rickard (1989) designed an apparatus which consists of a T-tube where Fe(II) solution and sulfide solution can be brought along two separate arms to 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, 1991) reported that the well known initial black precipitate is a neutral iron bisulfide ($\text{Fe}(\text{HS})_2$) intermediate but not FeS. Luther (1991), by means of a polarographic technique, proposed that the FeS initially formed consists of (1) a complex of the form $\text{Fe}(\text{SH})^+$ and (2) solid FeS for the reaction between Fe(II) and polysulfides. When excess polysulfides are present, a complex of the form $[\text{Fe}(\text{SH})\text{S}_x]^-$ is produced.

Apparently, the processes associated with the formation of FeS are not well understood. In the present study, the reaction between aqueous sulfide and dissolved Fe(II) salt was studied by means of a spectrophotometric technique. A stopped-flow spectrofluorimeter was used to monitor the reaction progress in the millisecond to second time range.

EXPERIMENTAL

Reagent grade ferrous chloride (FeCl_2) and sodium sulfide (Na_2S) were obtained from Aldrich. Fe(II) stock solution with a concentration of 0.1 mol/l was made by dissolving FeCl_2 in oxygen-free distilled water containing 0.1 N HCl to prevent $\text{Fe}(\text{OH})_2$ precipitation. Sulfide stock solution with a concentration of 0.1 mol/l was made with Na_2S and oxygen-free distilled water. These solutions were diluted further to obtain the

required concentrations. The oxygen-free distilled water was prepared by bubbling purified N₂ in distilled water for at least 5 hours. Both Fe(II) and sulfide stock solutions were prepared daily. The pH of the reaction between the two solutions was controlled by adjusting the pH of either the Fe(II) or sulfide solution via small additions of concentrated HCl or NaOH. In the case of pH > 7, NaOH was added to the sulfide solution, while for pH < 7, HCl was added to the Fe(II) solution. The pH of the reaction mixture was measured immediately with a Model 701 A digital pH/mV meter (Orion Research) after the two solutions were mixed .

Kinetic measurements (the absorbance-time curves) were obtained by using a DX. 17 MV Sequential Stopped-Flow Spectrofluorimeter (Applied Photophysics) with an optical pathlength of 1 cm. This instrument allowed one to mix the Fe(II) and sulfide solutions from two separate syringes into an optical cell and the absorbance of the mixed solution was recorded as a function of time. Oxygen-free distilled water was taken as the reference solution and the zero absorbance was checked before each measurement. Average absorbance was made from at least 5 measurements. The temperature of the experiments was controlled at $25 \pm 0.5^\circ \text{C}$.

RESULTS AND DISCUSSION

As shown in the previous report (Osseo-Asare and Dawei, 1992), the typical absorbance-time behavior at a wavelength of 500 nm indicated that the absorbance increases rapidly within the first few seconds (Figure 1A). This means that the black material forms as soon as the Fe²⁺ and HS⁻ ions react in the solution. The absorbance subsequently decreases slowly as the time increases (Figure 1B), which indicates that the black material formed

initially is decomposed to form another species. Based on this observation and the other experiments, the pathway of the reaction can be postulated as

where $\text{Fe}(\text{HS})^{2-n_n}$ is the complex intermediate. This complex intermediate should be the black material formed in the initial stages of the reaction.

Based on Equations 1 and 2, the rate law for $\text{Fe}(\text{HS})^{2-n_n}$ can be written as:

$$d[\text{Fe}(\text{HS})^{2-n_n}]/dt = k_1[\text{Fe}^{2+}]^\alpha[\text{HS}^-]^\beta - k_2[\text{Fe}(\text{HS})^{2-n_n}] \quad (3)$$

Because reaction 1 is much faster than reaction 2, $k_1 \gg k_2$, Equation 3 can be modified to give the rate of formation of $\text{Fe}(\text{HS})^{2-n_n}$ as:

$$d[\text{Fe}(\text{HS})^{2-n_n}]/dt = k_1[\text{Fe}^{2+}]^\alpha[\text{HS}^-]^\beta \quad (4)$$

where α and β are the reaction orders with respect to Fe^{2+} and HS^- respectively and k_1 is the rate constant of reaction 1.

By using the pseudo order method, with $[\text{HS}^-]_0 \gg [\text{Fe}^{2+}]_0$ and therefore $[\text{HS}^-] \approx [\text{HS}^-]_0$, Equation 4 becomes:

$$d[\text{Fe}(\text{HS})^{2-n_n}]/dt = k[\text{Fe}^{2+}]^\alpha \quad (5)$$

where

$$k = k_1[\text{HS}^-]_0^\beta \quad (6)$$

or

$$\log k = \log k_1 + \beta \log [\text{HS}^-]_0 \quad (7)$$

The experiments were carried out with different concentrations of Fe^{2+} and HS^- at pH 7.4, always maintaining $[\text{HS}^-]_0 \gg [\text{Fe}^{2+}]_0$. The reaction order α with respect to Fe^{2+} and pseudo rate constant k can be obtained from Equation 5. Furthermore, a plot of $\log k$ vs $\log [\text{HS}^-]_0$ should be a straight line according to Equation 7; the slope of the line is β , the order with respect to HS^- , and the intercept is $\log k_1$.

Determination of the reaction order, α , with respect to Fe^{2+} and the pseudo rate constant k

A typical result is shown in Figure 2, with a mathematical expression of the absorbance as a function of time obtained by a curve-matching procedure. The absorbance, A , is expressed as

$$A = A_{\max}(1 - e^{-kt}) \quad (8)$$

Based on Beer's law,

$$A = \epsilon [\text{Fe}(\text{HS})^{2-n_n}] \quad (9)$$

where ϵ is the absorptivity of $\text{Fe}(\text{HS})^{2-n_n}$. Equation 8 therefore becomes:

$$[\text{Fe}(\text{HS})^{2-n_n}] = [\text{Fe}(\text{HS})^{2-n_n}]_{\max}(1 - e^{-kt}) \quad (10)$$

It must be noted that,

$$[\text{Fe}(\text{HS})^{2-n_n}] = [\text{Fe}^{2+}]_0 - [\text{Fe}^{2+}] \quad (11)$$

and,

$$[\text{Fe}(\text{HS})^{2-n_n}]_{\max} = [\text{Fe}^{2+}]_0 \quad (12)$$

Therefore Equation 10 can be rewritten as:

$$[\text{Fe}^{2+}] = [\text{Fe}^{2+}]_0 e^{-kt} \quad (13)$$

The rate law is

$$-d[\text{Fe}^{2+}]/dt = d[\text{Fe}(\text{HS})^{2-n_n}]/dt = k[\text{Fe}^{2+}] \quad (14)$$

Comparison of Equation 14 with Equation 5 indicates that the reaction is first order with respect to Fe^{2+} (i.e, $\alpha = 1$), with a pseudo rate constant of k .

Determination of the reaction order, β , with respect to HS^- and the rate constant k_1

Based on Equation 7 and the relevant experimental data, a plot of $\log k$ vs $\log[\text{HS}^-]_0$ was obtained, as shown in Figure 3. The slope (β) of the straight line is 1, which means that the reaction is first order with respect to HS^- . The intercept of the line is 3.81, which gives the rate constant for the reaction (Equation 1) as, $k_1 = 10^{3.81} \text{ (mol/l)}^{-1} \text{sec}^{-1}$. Therefore, Equation 1 can be written as

and the corresponding rate law is given by:

$$d[\text{Fe}(\text{HS})^+]/dt = 10^{3.81} [\text{Fe}^{2+}][\text{HS}^-] \quad (16)$$

Accordingly, the pathway for the formation of FeS can be proposed as

The results presented here suggest the previous suggestions (Pohl, 1953; Taylor, 1980; Luther, 1991) that FeHS^+ is the intermediate black material formed initially from the reaction between aqueous sulfide ions and dissolved Fe(II) salts.

CONCLUSIONS

Based on the results and the discussion presented above, the following conclusions can be forwarded:

1. The pathway of FeS formation follows the sequence:

2. The black material formed initially from the reaction between aqueous sulfide ions and dissolved Fe(II) salts is the FeHS^+ intermediate.

3. The rate law for the formation of FeHS^+ is

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

To further confirm this mechanism, additional experiments aimed at establishing the complex stoichiometry are currently in progress in our laboratory.

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FIGURE 1. Typical absorbance-time curve.

FIGURE 2. Determination of reaction order with respect to Fe^{2+} .

FIGURE 3. Determination of reaction order with respect to HS⁻ and the rate constant.

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