SEMICONDUCTOR ELECTROCHEMISTRY OF COAL PYRITE

Technical Progress Report

October - December 1992

by

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ABSTRACT

The kinetic study of the reaction between sulfide and ferrous ions in solution suggested that the black species formed initially is $FeHS^+$ intermediate. To further confirm this mechanism, the experiments aimed at establishing the stoichiometry for the intermediate were carried out thermodynamically with a stopped-flow spectrophotometric technique. The results showed that the mole ratio of HS^-/Fe^{2+} is 1 to 1 for the intermediate product, which is in good agreement with the kinetic results previously obtained. Furthermore, the equilibrium constant for the reaction $Fe^{2+} + HS^- = FeHS^+$ was determined as $K = 10^{4.34}$. The forward rate constant is $10^{3.81}$ $(mol/l)^{-1}sec^{-1}$ and the backward rate constant is $10^{-0.53}$ $(mol/l)^{-1}sec^{-1}$.

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

The study of FeS formation in aqueous solution is very useful for understanding the mechanisms of pyrite formation. FeS can be formed by the reaction between aqueous sulfide and dissolved Fe(II) salts. A black precipitate is observed immediately when the two solutions are mixed. It

has been suggested 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 $Fe_{0.87}S$ to $FeS_{1.1}$ (Berner, 1962, 1964, 1967; Rickard, 1969, 1975; Sweeney and Kaplan, 1973).

However, some arguments still exist. What is the black species initially formed from this reaction? Pohl (1953) postulated that the formation of FeS might be via the activated complex with a formula of $(FeSH)^+$. Baas Becking (1956) suggested that $Fe(SH)_2$ was the first precipitated ferrous sulfide. Subsequently, Taylor (1980) suggested the formation of $FeSH^+$ as an intermediate, based on stereochemical arguments. Rickard (1989, 1991) studied this process experimentally and reported that the well known initial black precipitate is a neutral iron bisulfide $(Fe(HS)_2)$ intermediate but not FeS. Luther (1991), by means of a polarographic technique, found that the sulfide product initially formed consists of (1) a complex of the form $Fe(SH)^+$ and (2) solid FeS for the reaction between Fe(II) and polysufides.

Apparently, the processes associated with the formation of FeS are still not well understood. Most recently Osseo-Asare and Wei (1992b) reported that the black intermediate formed initially is $FeHS^+$ intermediate, based on a kinetic study using a stopped-flow spectrophotometer. It was proposed that the pathway of FeS formation follows the sequence of Fe^{2+} + HS^- --> $FeHS^+$ --> $FeS + H^+$. To further confirm this mechanism, the thermodynamic study of this process, aimed at establishing the intermediate stoichiometry was done and the thermodynamic parameters were obtained for this reaction.

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 $Fe(OH)_2$ 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 N_2 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 . The absorbance was measured by using a DX. 17 MV Sequential Stopped-Flow Spectrofluorimeter (Applied Photophysics) with an optical pathlength of 1 cm. The temperature of the experiments was controlled at $25 \pm 0.5^{\circ}$ C.

In the experiments for determining the stoichiometry of the intermediate, the total concentration of HS^- plus Fe^{2+} was maintained constant, while the mole ratio of HS^- to Fe^{2+} was changed between 0.1 and 10. The absorbance was measured as a function of the variation of the mole ratio.

In the experiments for determining the equilibrium constant, the concentration of Fe^{2+} was fixed at 2.5×10^{-4} M at pH 7.4, while the absorbance measurements were made for changing concentration of HS^-.

RESULTS AND DISCUSSION

Determination of Stoichiometry

The absorbance of the black species has a linear relationship with the concentration of Fe^{2+} when the mole ratio of Na_2S to $FeCl_2$ is kept at 10 as shown in Figure 1. The absorptivity of the intermediate such determined is 4800 $(mol/l)^{-1}cm^{-1}$ (Osseo-Asare and Wei, 1992a). Based on this fact, the stoichiometry of the intermediate can be determined experimentally by fixing the total concentration of HS^- plus Fe^{2+} and changing the mole ratio of HS^- to Fe^{2+}.

Consider the reaction:

$$Fe^{2+} + nHS^- \longrightarrow Fe(HS)^{2-n}_n \tag{1}$$
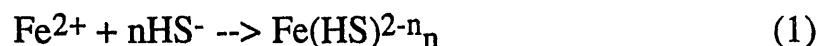
$$K = [Fe(HS)^{2-n}_n] / ([Fe^{2+}][HS^-]^n) \tag{2}$$

We can write:

$$[Fe(HS)^{2-n}_n] = A / \varepsilon \tag{3}$$

where A is the absorbance and ε the absorptivity. Supposed the total concentration of HS^- plus Fe^{2+} is C and the ratio of HS^- to Fe^{2+} is R, one has:

$$C = [Fe^{2+}] + [HS^-] \tag{4}$$

and $$R = [HS^-] / [Fe^{2+}] \tag{5}$$

Substitution of Equations 3 , 4 and 5 into 2 gives:

$$A = \varepsilon \, K \, C^{n+1} \, R^n \, / \, (1+R)^{n+1} \qquad (6)$$

It can be proved that the maximum of A will occur at n = R.

The variation in the absorbance as a function of R for two different total reactant concentrations is shown in Figure 2. It can be seen that the maximum absorbance occurs around R = 1. This means that the stoichiometry of n should be 1 and consequently, Equation 1 can be rewritten as:

$$Fe^{2+} + HS^- \rightarrow Fe(HS)^+ \qquad (7)$$

This result is consistent with the findings made previously in our laboratory on the basis of kinetic investigations (Osseo-Asare and Wei, 1992b).

Determination of Equilibrium Constant

For the reaction shown in Equation 1, the equilibrium constant, K, can be expressed as shown in Equation 2. Based on Beer's law, the absorbance can be writen as:

$$A = \varepsilon \, [Fe(HS)_n^{2-n}]$$
$$= \varepsilon \, ([Fe^{2+}]_0 - [Fe^{2+}]) \qquad (8)$$

and

$$A_\infty = \varepsilon \, [Fe(HS)_n^{2-n}]_\infty$$
$$= \varepsilon \, [Fe^{2+}]_0 \qquad (9)$$

where ε is the absorptivity (4800 $(mol/l)^{-1}cm^{-1}$)(Osseo-Asare and Wei, 1992a), $[Fe^{2+}]_0$ is the initial concentration of Fe^{2+}, and A_∞ is the absorbance when all of Fe^{2+} converts to $Fe(HS)_n^{2-n}$. Hence,

$$(A - A_\infty)/A = - [Fe^{2+}]/[Fe(HS)_n^{2-n}]$$
$$= - K^{-1}/[HS^-]^n \qquad (10)$$

or

$$A = A_\infty - K^{-1} A/[HS^-]^n \qquad (11)$$

Noting that

$$[HS^-] = [HS^-]_0 - n[Fe(HS)_n^{2-n}]$$
$$= [HS^-]_0 - n A/\varepsilon \qquad (12)$$

Equation 11 becomes

$$A = A_\infty - K^{-1}A/([HS^-]_0 - n A/\varepsilon)^n \qquad (13)$$

When $n = 1$, a plot of A vs $A/([HS^-]_0 - A/\varepsilon)$ should be a straight line with a slope of $-K^{-1}$ and an intercept of A_∞.

As shown in Figure 3, the straight line indicates that the value of n is equal to 1. The slope of -4.85×10^{-5} gives the equilibrium constant $K = 10^{4.34}$. Because the forward rate constant, k_1, is $10^{3.81}$ s^{-1}, the reverse rate constant, k_{-1}, can be calculated as k_1/K, which gives $k_{-1} = 10^{-0.53}$ s^{-1}.

CONCLUSIONS

The results presented above show that the black material initially formed from the reaction between Fe^{2+} and HS^- in solution is $FeHS^+$

intermediate. The stoichiometry of the intermediate was determined by several methods and consistent results were obtained. The thermodynamic and kinetic parameters for the reaction of forming the intermediate were determined by means of spectrophotometric techniques. The equilibrium constant is $K = 10^{4.34}$; the forward rate constant $k_1 = 10^{3.81}$ s^{-1} and the reverse rate constant $k_{-1} = 10^{-0.53}$ s^{-1}.

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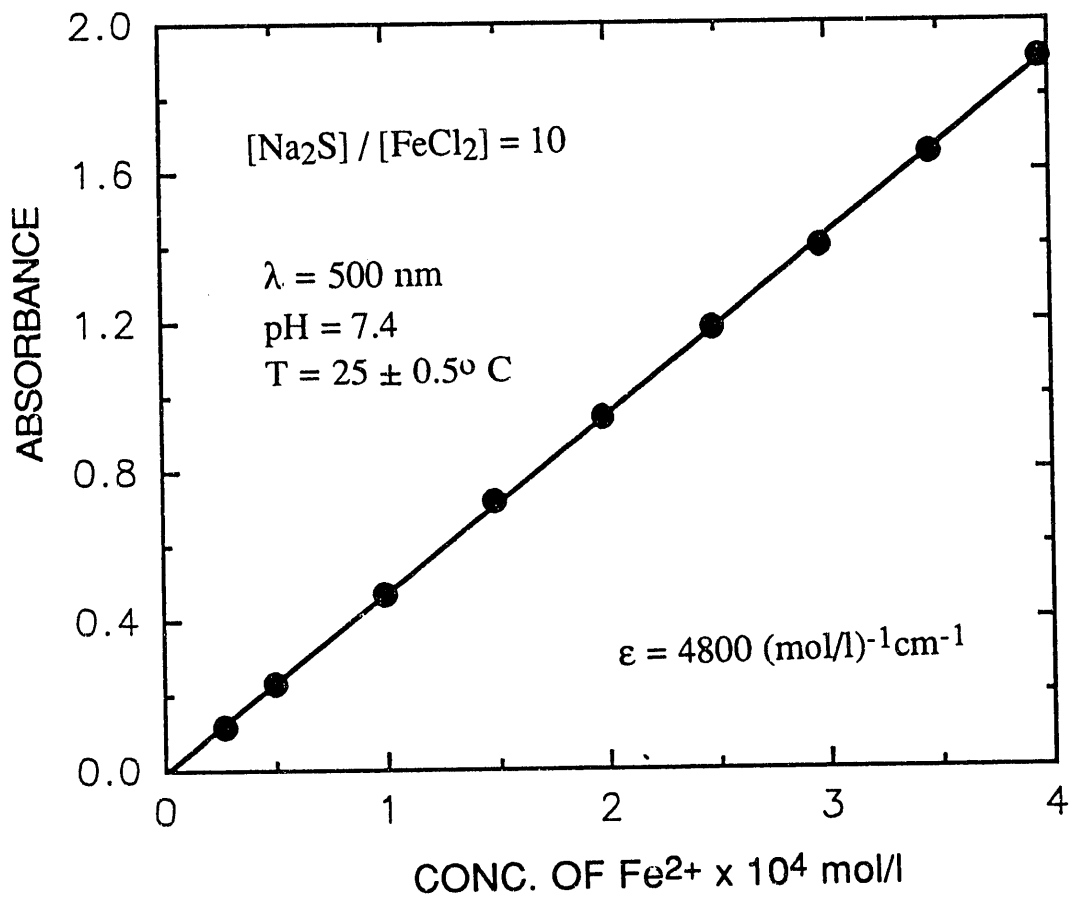
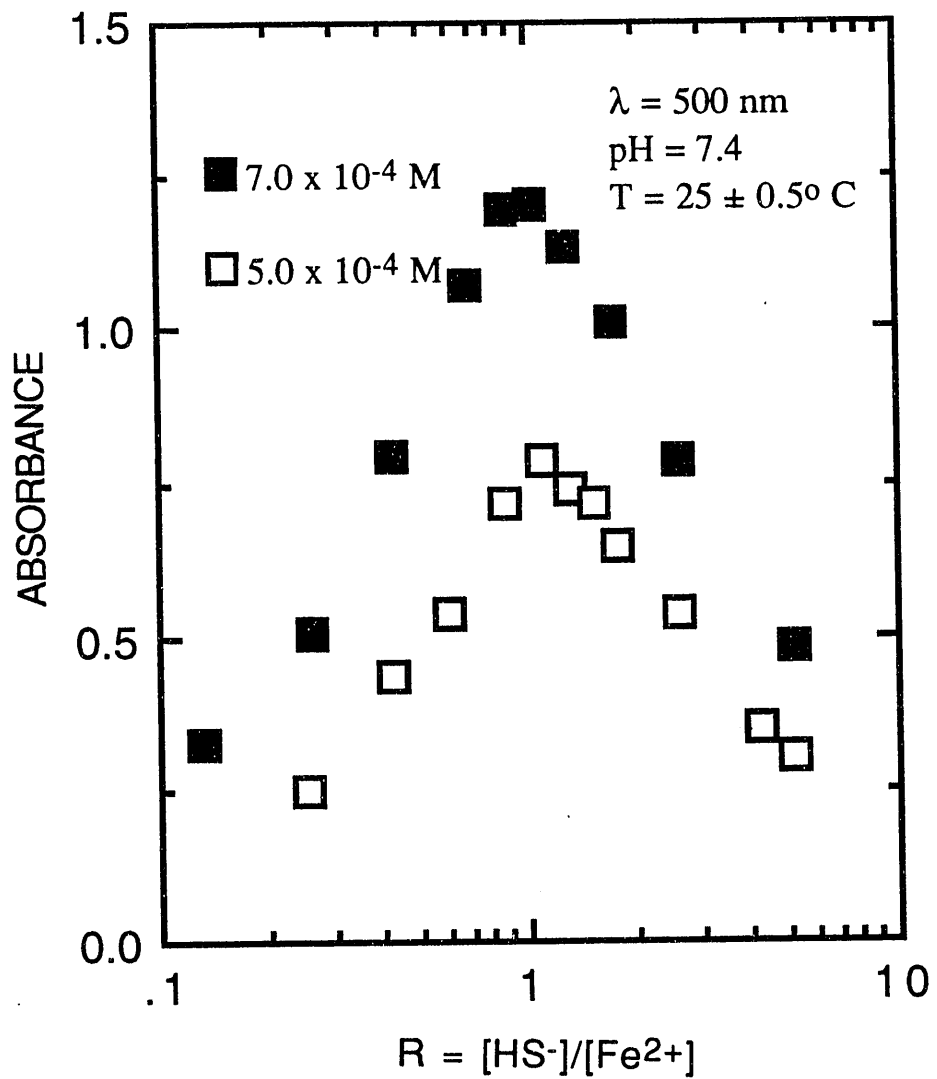FIGURE 1. Absorbance vs concentration of Fe^{2+}.

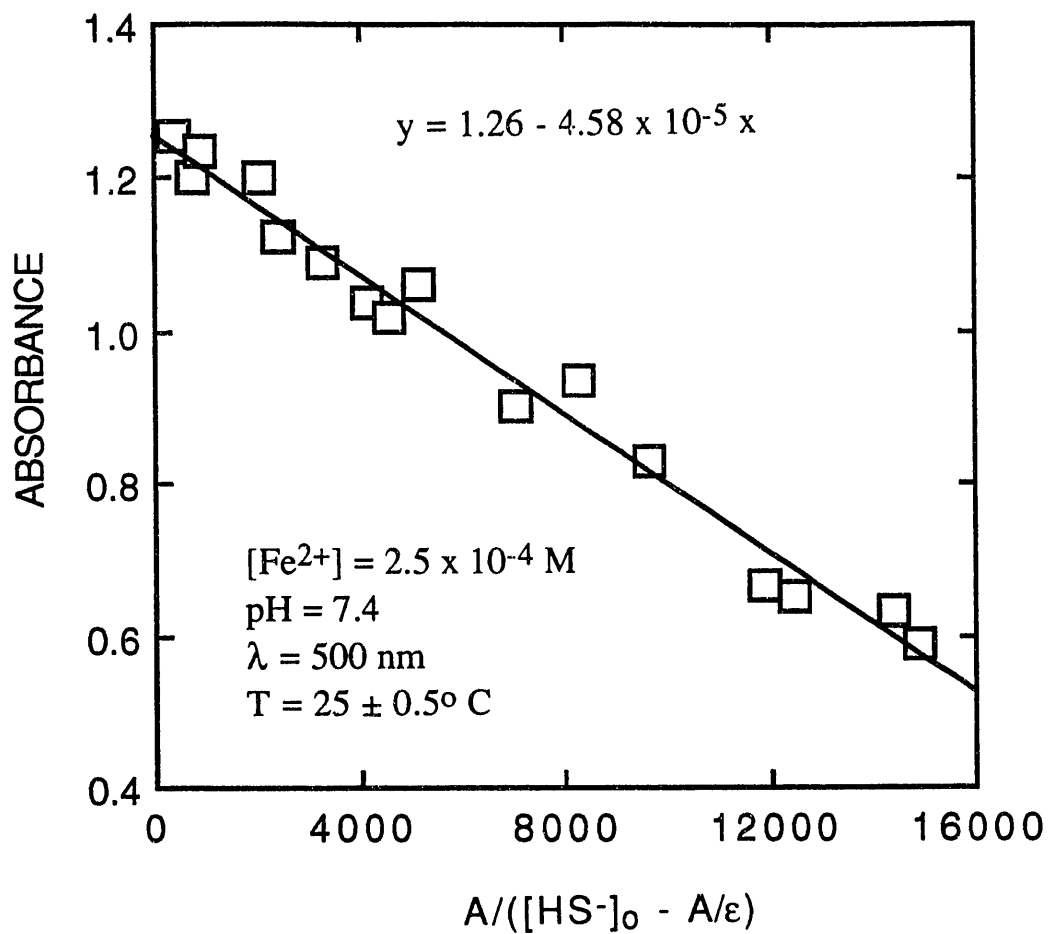FIGURE 2. Stoichiometry determination for the reaction of Equation 1.

FIGURE 3. Equilibrium constant determination
for the reaction of Equation 7.

The figure shows a plot of ABSORBANCE (y-axis, ranging from 0.4 to 1.4) versus $A/([HS^-]_0 - A/\varepsilon)$ (x-axis, ranging from 0 to 16000). The linear fit equation shown is:

$$y = 1.26 - 4.58 \times 10^{-5} x$$

Conditions listed:

$[Fe^{2+}] = 2.5 \times 10^{-4}$ M
pH = 7.4
$\lambda = 500$ nm
T = $25 \pm 0.5°$ C

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