SEMICONDUCTOR ELECTROCHEMISTRY OF COAL PYRITE

Technical Progress Report

April - June 1992

by

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ABSTRACT

The work performed during this quarter focuses on the study of the reaction between aqueous sulfide ions and dissolved Fe(II) salts by using a stopped-flow spectrophotometric technique. At a wavelength of 500 nm, no absorption was observed with either aqueous sulfide or dissolved Fe(II) salt alone. However, when the two solutions were mixed, a strong absorbance appeared at the same wavelength. The absorbance-time curve showed that a black material formed at the first few seconds of the reaction, then this material decayed and changed gradually to a lighter dark material within the following several minutes. This processes were pH-dependent. It was more likely to form the black intermediate at the pH range from 7 to 8. This indicates that the reaction between Fe^{2+} and HS^- results in the formation of the black intermediate because in this pH range, both Fe^{2+} and HS^- are the predominant species. The absorbance varied linearly with the concentration of the reactant for the first step of the reaction. The absorptivity of the black intermediate was determined as 4800 l/mol/cm. By means of this spectrophotometric technique, the stoichiometry, the equilibrium constant and the rate constant of the reaction will be determined.

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 on the earth 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 and 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 some difficulties because this reaction is so fast that it not easy, with conventional techniques, to reach the intermediate steps experimentally. To solve this problem, Rickard (1989) designed an apparatus which consists of a T-tube where $\text{Fe}(\text{II})$ 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 $\text{Fe}(\text{II})$ and polysulfides. When excess polysulfides are present, a complex of form $[\text{Fe}(\text{SH})\text{S}_x]^-$ is produced.

Apparently, the processes of the formation of FeS are not well understood. In the present study, the reaction between aqueous sulfide and dissolved $\text{Fe}(\text{II})$ 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. $\text{Fe}(\text{II})$ 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 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 was measured immediately with a Model 701 A digital pH/mV meter (Orion Research) after the two solutions were mixed .

Spectra of Fe(II) solution, sulfide solution and the mixed solution of the two were determined by an HP 8451 A diode array spectrophotometer (HP Kewlett Packard) with a 1 cm quartz optical cell. 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 not especially controlled. However, the thermometer on the stopped-flow instrument showed the reaction temperature was $25 \pm 0.5^\circ \text{C}$.

RESULTS AND DISCUSSION

Spectral Analysis

The spectra of Fe(II) solutions were run for different Fe(II) concentrations at pH 2.0. The results, presented in Figure 1, show that a strong absorption occurs at a wavelength of 335 nm for the Fe(II) concentration of 1×10^{-1} mol/l, as also observed by Heinrich and Seward (1990); however, within the experimental range of Fe(II) concentration, no absorption occurs at wavelengths higher than 450 nm. The spectra of sulfide solutions for different sulfide concentrations at pH 12.4 are shown in Figure 2. It can be seen that HS^- ion exhibits strong ultra-violet absorption around a wavelength of 235 nm, a value similar to that reported by Chen and Morris (1971); in the concentration range reported, no absorption occurs at wavelengths higher than 350 nm.

The spectra showed significant changes when the two solutions reacted with each other. Figure 3 shows the spectra for the reaction between Fe(II) and sulfide solutions at pH 7.4, with both reactants at a concentration of 1×10^{-4} mol/l. Comparison of Figure 3 with Figures 1 and 2 indicates that at wavelengths higher than 250 nm, all the absorptions observed are due solely to the new species formed by the reaction between Fe(II) and sulfide solutions; neither Fe^{2+} nor HS^- contributes individually to the absorption. At 300 nm, the absorbance increases steadily with increase in time, until equilibrium is reached. However, a more interesting feature of the spectra appears at wavelengths higher than 400 nm. At 500 nm for example, the absorbance increases at first (note from Figures 1 and 2 that the absorbance is zero at zero time) and then decreases with time. This trend indicates that a new species forms in the initial stages of the reaction and then disappears as time increases; meanwhile another species

forms as shown by the absorption increases at 300 nm. It follows from these results that, by monitoring the time dependence of the absorption at 500 to 700 nm and at 300 nm, one can obtain useful information about the reaction of Fe(II) and sulfide solutions.

Pathways for the Formation of FeS

A typical absorbance-time behavior, based on the 500 nm wavelength, is shown in Figure 4. It can be seen clearly that the absorbance increases rapidly within the first few seconds (Figure 4A). This means that the black material forms as soon as the Fe(II) and sulfide solutions are mixed. The absorbance subsequently decreases slowly as the time increases (Figure 4B), which indicates that the black material formed initially is decomposed to form another species.

The results of the effect of pH on the reaction are shown in Figure 5 (preliminary results were presented in the previous progress report). The maximum absorbance indicates the maximum concentration of the black material formed initially. The data therefore show that the maximum formation of the black material occurs at about pH 7.5. Comparing Figure 5 with the speciation behavior of Fe(II) and sulfide, as shown in Figure 6, it can be seen that the formation of the black material is clearly due to the reaction between Fe^{2+} and HS^- ; in the pH range most favorable for the formation of the black material, both Fe^{2+} and HS^- are predominant. Based on this observation, 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.

Determination of the Absorptivity of $\text{Fe}(\text{HS})^{2-n_n}$

To determine the absorptivity of the black intermediate, the experiments were carried out by changing the concentration of Fe^{2+} and keeping the mole ratio of Na_2S to FeCl_2 at 10. Because the concentration of HS^- was in excess, the concentration of the product ($\text{Fe}(\text{HS})^{2-n_n}$) was approximately equal to the initial concentration of Fe^{2+} . As can be seen from Figure 7, the maximum absorbance varies linearly with Fe^{2+} concentration. From this measurement, the absorptivity of the intermediate product was determined as 4800 l/mol/cm. This indicates that the spectrophotometric technique can be used to study the reaction of Fe^{2+} and HS^- not only qualitatively, but also quantitatively. Therefore, by means of the spectrophotometric technique, the mechanisms of the reaction between aqueous sulfide and aqueous ferrous species can be studied. This aspect of the work is currently under investigation in our laboratory.

CONCLUSIONS

The reaction between aqueous sulfide and aqueous ferrous species can be studied by the stopped-flow spectrophotometric technique.

Wavelengths between 500 nm to 700 nm can be used to monitor this reaction because no absorption of sulfide or $\text{Fe}(\text{II})$ was observed at these wavelengths. 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 (from tens of milliseconds to several minutes).

The absorbance-time curves at 500 nm showed that on the way to FeS formation, a black intermediate material formed within the first few seconds of the reaction and this intermediate converted eventually to FeS and other species. The pH experiments and the speciation diagram of Fe(II) and sulfide suggest that the intermediate results from the reaction between Fe^{2+} and HS^- in the solution. The formation of the black intermediate is most likely to occur at a pH around 7.5 because under this condition, both Fe^{2+} and HS^- are predominant species.

The absorbance has a linear relation with the concentration of reactant Fe^{2+} when the concentration of HS^- is kept in excess. These measurements give the absorptivity of the black intermediate as 4800 l/mol/cm.

The spectrophotometric technique reported in this study is a useful method to study the reaction between aqueous sulfide and aqueous ferrous iron. By means of this technique, the thermodynamic and kinetic data for the formation of the black intermediate, such as stoichiometry, equilibrium constant and rate constant of the reaction, can be obtained, and the black intermediate formed initially can be identified. It is also possible to study the kinetics of the formation of FeS, and further the formation of FeS_2 by adding polysulfides or elemental sulfur in the system after the formation of FeS using sequential addition technique associated with the Sequential Stopped-Flow Spectrofluorimeter.

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FIGURE 1. Spectra of aqueous Fe^{2+} at pH 2.0.

FIGURE 2. Spectra of aqueous HS⁻ at pH 12.4.

FIGURE 3. Spectra of the reaction between FeCl_2 and Na_2S solutions (Reaction time was measured manually with a stop-watch).

FIGURE 4. Typical absorbance-time curve for the reaction between aqueous sulfide and ferrous iron. (A) is a part of (B) for the first 5 seconds of the reaction.

FIGURE 5. Absorbance vs pH after 5 seconds of the reaction.

FIGURE 6. Logarithmic concentration diagram for 5×10^{-4} M FeCl_2 and Na_2S . Equilibrium data from Boulegue et al.(1978) and Osseo-Asare(1981).).

FIGURE 7. Absorbance vs concentration of Fe^{2+} .

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