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PYRITE SURFACE CHARACTERIZATION AND CONTROL FOR ADVANCED FINE COAL DESULFURIZATION TECHNOLOGIES

DOE Grant No: DE-FG22-90PC90295

Tenth Quarterly Technical Progress Report
(from Jan.1, 1993 to March 31, 1993)

by

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J. W. Leonard and B.K. Parekh (Co-PIs).
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SUMMARY

This is the 10th quarterly technical progress report for the project entitled "Pyrite surface characterization and control for advanced fine coal desulfurization technologies", DE-FG22-90PC90295. The work presented in this report was performed from Jan.1, 1993 to March 31, 1993.

The objective of the project is to conduct extensive fundamental studies on the surface chemistry of pyrite oxidation and flotation and to understand how the alteration of the coal-pyrite surface affects the efficiency of pyrite rejection in coal flotation. This report summarizes the studies in the following three aspects: (1) the effects of borate, used as pH buffer or electrolyte, on the pyrite surface oxidation and flotation; (2) the quantification of pyrite surface oxidation kinetics under different oxidation potentials; and (3) finding new coal-pyrite depressants. It has been demonstrated, for the first time, that borate, a pH buffer and electrolyte used by many previous investigators in studying pyrite oxidation, actively participates in the surface oxidation of pyrite. In high borate concentration solutions, the surface oxidation of pyrite is strongly enhanced. The anodic oxidation potential of pyrite is lowered by more than 0.4 volts. At low borate concentration, borate is chemisorbed on pyrite surfaces. In the intermediate concentration range, borate dissolves surface iron compounds. Consequently, the flotation of pyrite in borate solutions (using fuel oil as collector) displays depression-flotation-depression phenomena as the borate concentration is increased. The oxidation kinetics of pyrite surfaces has been determined by AC impedance spectroscopy. At low oxidation potentials, only capacitive behavior is observed. However, at high oxidation potentials, an inductive loop appears. The charge transfer resistance decreases with increasing potential, indicating that the oxidation rate increases with increasing potential. A chemical reagent has been found to be very effective in depressing the flotation of coal-pyrites

from different sources, while it has little effects on the flotation of coal. The surface chemistry involved in the selective pyrite depression by this new reagent has been investigated by electrochemical studies and contact angle measurements.

INTRODUCTION

Sodium borate (NaBO_4 or $\text{Na}_2\text{B}_4\text{O}_7$) is a pH buffer at $\text{pH}=9.2$. It has been widely used as the electrolyte by many previous investigators in studying the electrochemistry of sulfide minerals. Our literature survey show that over 95 percent of the publications on metal sulfide electrochemistry in alkaline solutions were performed in sodium tetraborate solutions. The concentration of sodium borate varied from 1×10^{-2} M to 1.0 M. In all the studies, borate was regarded as an inactive chemical, and its possible effects on the electrochemical oxidations of pyrite have been completely neglected. In our last report (No.9), it has been shown that sodium borate (or sodium tetraborate) is actively involved in the oxidation of pyrite and other sulfide minerals. The oxidation of pyrite is substantially enhanced when borate is present. Thus, it is of great importance to understand the detailed mechanisms of the interaction between borate and pyrite. During this reporting, the effects of varying borate concentration on pyrite surface oxidation and flotation have been systematically investigated. In addition, the quantification of the pyrite surface oxidation kinetics have been performed using AC impedance spectroscopy. We have also devoted considerable efforts into searching effective pyrite depressants.

Results And Discussion

I. The Effects of Borate on Pyrite Oxidation and Flotation

Figure 1 shows the cyclic voltammograms of pyrite in the presence of varying concentrations of sodium borate as a pH buffer. In the absence of sodium borate, only one anodic current rise (note: not a peak) is seen at potential above 0.4 Volt (vs

SCE), which is attributed to the oxidation of pyrite. In the presence of borate, an additional anodic peak (labelled as peak I in Fig.1) appears at a potential above 250 mV (vs SCE). Figure 2 shows the peak current, I_p , and the peak potential, E_p , as a function of borate concentration. Both the peak current and peak potential increase linearly with increasing the borate concentration. No corresponding reduction peak is observed. It was also observed that on a rotating electrode, the limiting current density is nearly a linear function of the square root of the rotation speed. These characteristic features demonstrate that borate species is involved in the pyrite oxidation process, and the oxidation process is irreversible. Furthermore, the Tafel plots show that the rate-determining step is a single-electron transfer reaction. Thus, the rate-determining step of pyrite oxidation in a borate solution can be described by the following reaction:

The solution chemistry of the borate-water and borate-iron systems has been investigated and reported in the previous report (No.9). It was shown that besides the protonation reactions of borate, borate undergoes polymerization under high concentrations to form a number of polymers, $\text{B}_3\text{O}_3(\text{OH})_4^-$, $\text{B}_3\text{O}_3(\text{OH})_5^-$, $\text{B}_4\text{O}_5(\text{OH})_4^{2-}$ and $\text{B}_5\text{O}_6(\text{OH})_4^-$. Furthermore, borate is a strong complexing agent for heavy metal ions such as Fe^{3+} , Pb^{2+} , and Cu^{2+} . It reacts with the heavy metal ions and forms both soluble and insoluble metal-borate compounds. For the borate-iron system, the following iron-borate complexes can be formed:

It has been shown that in the presence of borate, ferric hydroxide dissolves to form a number of ferric borate species. The precipitation pH of $\text{Fe}(\text{OH})_3(\text{s})$ shifts from pH=3 to pH=7--9. Therefore, it can be expected that in a borate solution, the highly complex pyrite oxidation processes will become more complicated.

Figure 3 shows the flotation recovery of ore-pyrite (from Peru) as a function of borate concentration in the presence of 50 mg/l fuel oil as collector. It can be seen that at lower borate concentration (below 10^{-4} M), the pyrite flotation decreases with increasing the borate concentration. In the intermediate concentration range (10^{-3} to 10^{-2} M), the flotation increases with increasing borate concentration, reaches a maximum and then decreases as the borate concentration further increases. At extremely high borate concentration, the pyrite flotation is completely depressed. Similar results have been obtained for the coal-pyrite (from Kentucky no.9 coal seam), as shown in Figure 4. The effects of borate on the flotation of the Kentucky No.9 coal has also been studied. For the coal-pyrite, the depression-flotation-depression phenomena is clearly observed as the borate concentration varies from low to high concentration.

From the electrochemical and flotation results, the interaction of pyrite with borate can be explained as follows. At low borate concentration, borate is chemisorbed on pyrite surfaces:

This renders the pyrite surfaces hydrophilic and thus causes depression. When the concentration of borate is increased, the dissolution of surface iron-hydroxide species takes place. As shown in the last report (No.9), iron hydroxide can be dissolved to form ferric borate complexes. Thus, borate, like other iron-complexing agents such

as EDTA, becomes a surface cleaning agent. Schematically, this may be illustrated using as follows:

where { } represents surface substances.

Then the pyrite will expose a sulfur-rich surface to the solution. Due to the depletion of the hydrophilic surface (hydr)oxide, the surface will be highly hydrophobic. At extremely high borate concentrations, the pyrite oxidation is greatly enhanced, as demonstrated by the electrochemical measurements. Consequently, the surfaces of pyrite will be severely oxidized and the pyrite flotation be eliminated. The enhancement of pyrite surface oxidation by borate species has also clearly been demonstrated by the AC impedance measurements. The Nyquist plots for pyrite at pH=9.2 in the absence and presence of varying borate show that the charge transfer resistance (R_{CT}) decreases with increasing borate concentration. Since the charge transfer resistance and the exchanging current density I_0 are related by the following equation:

$$R_{CT} = \frac{R T}{n F I_0}$$

where R is the gas constant, T is the temperature (K), F is the Faraday constant, and n is the number of electron transfer.

Thus, the charge transfer resistance (R_{CT}) is a measure of the rate of the electrode reaction. The smaller the R_{CT} is, the greater the surface oxidation rate is.

II. AC Impedance Studies of the Pyrite Oxidation Kinetics and Mechanisms

It has been shown that the oxidation of pyrite surfaces is extremely complex. Traditional research techniques, like cyclic voltammetry, steady-state polarization, mixed-potential measurements, solubility measurements, etc, can only provide very limited qualitative information on the processes. In order to quantitatively characterize the pyrite surface oxidation mechanisms and kinetics, we have applied AC impedance spectroscopy to the studies.

Figures 5 and 6 compare the impedance diagrams (Nyquist plots) of different ore- and coal-pyrite electrodes. It has been found that the ore-pyrite electrodes have much higher resistances at low frequencies than the coal-pyrite electrodes studied. Interestingly, KYPY1, which was made from a high-purity single crystalline coal-pyrite selected from a KY no.9 coal seam, has intermediate resistances (but more close to the ore-pyrite). This is in good agreement with our previous findings from the cyclic voltammetric measurements [report no.7 and 8). The impedance measurements at high frequencies can quantitatively determine the impurity concentrations in the electrodes. The studies are in progress. A comprehensive comparison of the impurity concentrations and semiconducting properties of the various electrodes will be reported in the next report.

The oxidation kinetics of pyrite under different oxidation potentials have been investigated by the impedance spectroscopy. For the simplicity, only the results obtained for the synthetic single pyrite crystal electrode (SYNPY) will be presented. Figure 7 shows the cyclic voltammogram obtained on a stationary electrode (SYNPY) at pH=8.5 in KClO_4 electrolyte solution. The features of the cyclic voltammograms are similar to that of the other ore-pyrite electrodes and have been interpreted in the previous reports. The AC impedance measurements have been made at ten potentials

and are shown in Fig.8, where A is at the mixed potential (ca. -100 mV vs SCE), B, C, ..., etc., are at 0, 100, 200, 300, 400, 500, 600, 700 and 800 mV (vs SCE) respectively. The AC impedance is measured in the frequency range of 1×10^4 to 10^{-2} Hz. It was attempted to measure at higher frequencies. However, there were problems with the FRA and potentiostat systems. The measurements at high frequencies are not reliable and will not be used.

It has been observed that in the potential range between -200 to 100 mV, the measured impedances are essentially indistinguishable. Figure 8 shows the Nyquist plots obtained at 100 mV (C), 200 mV (D), 300 mV (E) and 400 mV (F) respectively. It can be seen that as the oxidation potential increases, the impedances decrease. Above 200 mV (vs SCE), the semicircles can be clearly observed. Furthermore, when the potential increases, the radius of the semicircles decreases, as shown in Figs.9, 10 and 11. When the potential is above 400 mV, an inductive loop is obtained. As discussed above, the radius of the semicircle in the Nyquist represents the reaction charge transfer resistance. Therefore, the impedance measurements clearly demonstrate that the higher the oxidation potential is, the higher the oxidation rate is. Quantitative analysis of the kinetic rate constants are being investigated. Mathematical and chemical models are also being developed to describe the measured results. It is expected that such studies will be able to elucidate the detailed reaction mechanisms of pyrite oxidation.

III. Studies of Coal-Pyrite Depressants.

Very extensive effort has been devoted to search for effective pyrite depressants for efficient pyrite-coal separation using flotation. More than ten different chemicals have been investigated. One reagent was found to be very effective in depressing both coal-pyrite and mineral pyrite flotation. The reagent, coded as "STAOT" here, is mixture of three different chemicals. Figure 12 shows the

flotation recovery of the Kentucky No.9 coal-pyrite (KYPY) and coal as a function of the reagent dosage in the single mineral/coal flotation tests. It is interesting to note that at low concentrations, the coal flotation is somewhat depressed, while the flotation of pyrite is not affected. However, when the concentration is increased to above 30 ppm, the coal again becomes completely floatable, and the pyrite is completely depressed. The flotation results demonstrate that the reagent is highly selective in depressing the coal-pyrite at moderate concentrations (30-100 ppm). The electrochemical measurements show that the reagent is extremely effective in suppressing pyrite surface oxidation. Figures 13 and 14 shows the cyclic voltammograms of the PAPY electrode (i.e., the coal-pyrite from a Pittsburgh No.8 coal seam) under stationary and rotating conditions respectively. In the absence of STOAT, the coal-pyrite oxidation rate is extremely high. For example, at a potential of 500 mV (vs SCE), an oxidation current of 5 mA/cm² is obtained. This value is almost ten times of that of the ore-pyrite electrodes. On the second positive-going potential scan, an oxidation peak is observed at about -200 mV. This peak corresponds the oxidation of hydrogen sulfide (H₂S) to elemental sulfur. The peak current increases with increasing the positive-going potential limit, reaches a maximum at about 800 mV and then decreases with further increasing the potential. These results indicates that when the pyrite surface is oxidized under moderate oxidizing atmosphere, the surface will be covered by elemental sulfur and iron hydroxides. Then when the iron hydroxide is depleted from the surface by mechanical or chemical actions, the surfaces of pyrite will become more floatable. Interestingly, as shown in Fig.13, in the presence of 20 ppm of the new pyrite depressant, the surface oxidation of pyrite is decreased. When the concentration is increased to 100 ppm, the oxidation of pyrite is completely eliminated. The results thus indicate that suppression of pyrite surface oxidation is mainly responsible for the pyrite depression using this new reagents. Similar flotation and electrochemical results have been obtained for other coal- and ore-pyrites. For example, Figure 15

shows the cyclic voltammograms of the KYPY electrode in the absence and presence of STAOT. It can be seen that the surface oxidation of pyrite is completely depressed. These results suggest that this new reagent will be effective for depressing pyrite of different sources. Therefore, it will have great potential in coal depyritization using flotation.

Future Plan

We will continue the studies of the AC impedance measurements. The emphasis of the next phase research will be on the equivalent circuit analysis and mathematical modelling to obtain quantitative information on pyrite surface oxidation. Efforts will also be devoted to looking for new depressants and new methods for depressing pyrite oxidation.

Figure 1 Cyclic voltammograms of the ore-pyrite electrode (PUPY) in the presence of various borate concentrations.

Fig.2 The peak current and peak potential of the peak I (Fig.1) as a function of the borate concentration.

Fig. 3 Flotation recovery of ore-pyrite (PUPY) as a function of the borate concentration at pH=9.2 in the presence of 50 ppm fuel oil as collector.

Fig.4 Flotation recovery of the Kentucky No.9 coal and coal-pyrite as a function of borate concentration at pH=9.2 in the presence of 50 ppm fuel as collector.

Fig. 5 Impedance spectra (Nyquist plots) of various ore-pyrite electrodes in 0.1 M NaNO₃ electrolyte solution at pH=8.5.

Fig.6 Impedance spectra (Nyquist plots) of different coal-pyrite electrodes in 0.1 M NaNO_3 electrolyte solution at pH=8.5. Note the difference in the scale with Fig.5.

Fig.7 Cyclic voltammogram of the stationary synthetic single crystal pyrite electrode (SYNPY) in KClO₄ electrolyte solution at pH=8.5.

Fig. 8 Impedance spectra of the SYPY electrode at different oxidation potentials in 0.1 M NaNO₃ at pH=8.5. Oxidation potentials: 100 mV (C), 200 (D), 300 (E) and 400 mV vs SCE (F).

Fig. 9 Impedance spectra of the SYPY electrode under different oxidation potentials in NaNO₃ at pH=8.5. Oxidation potential: 400 mV (F), 500 mV (G) and 600 mV (H) vs SCE.

Fig. 10 Impedance spectra of the SYPY electrode under different oxidation potentials in NaNO₃ at pH=8.5. Oxidation potential: 500 mV (G), 600 mV (H) and 700 mV (I) vs SCE.

Fig. 11 Impedance spectra of the SYPY electrode under different oxidation potentials in NaNO₃ at pH=8.5. Oxidation potential: 600 mV (H), 700 mV (I) and 800 mV (J) vs SCE.

Fig.12 Flotation recovery of Kentucky No.9 coal and coal-pyrite as a function of the concentration of STOAT.

Fig.13 Cyclic voltammograms of the Pittsburgh No.8 coal-pyrite electrode (PAPY) in the absence and presence of 20 and 100 ppm STAOT at pH=3.0 under stationary condition.

Fig.14 Cyclic voltammograms of rotating-disc electrode of PAPY in the absence and presence of STAOT at pH=3.0. Rotation speed: 1000 RPM.

Fig.15 Cyclic voltammograms of stationary KYPY (Kentucky No.9 coal pyrite) electrode in the absence and presence of 100 ppm STAOT at pH=3.0.

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