ADSORPTION MECHANISMS OF HS⁻IONS ON

SULPHIDE MINERAL SURFACES RELATED

TO Na₂S-INDUCED FLOTATION[①]

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ABSTRACT

The adsorption mechanisms of HS⁻ions existing in air-saturated alkaline solutions on sulphide minerals (including pyrite, arsenopyrite, chalcopyrite and galena) were investigated. The measurement of adsorption density, solvent extraction-chemical analysis of neutral sulphur at the surfaces, measurements of pulp potential and voltammogram, and flotation tests were done. Both the electrochemical and non-electrochemical adsorption models of HS⁻ions were established. The former was observed and resulted in the formation of neutral sulphur (S°) when the pyrite and arsenopyrite were chosen, and hence renders the surfaces hydrophobic and induced the two minerals flotation. It is called Na₂S-induced flotation. On the other hand, the latter took place and did not produce S° when the chalcopyrite and galena were selected, and hence depresses the collectorless flotation of the two minerals. The adsorptions of HS⁻ions were mainly influenced by potentials, pH and the electron structures of the mineral surfaces.

Key words: HS⁻adsorption   sulphide minerals   Na₂S-induced flotation

1 INTRODUCTION

Recent work reported that after pyrite was conditioned in air-saturated alkaline solutions containing HS⁻ions, its surface was changed from a hydrophilic condition into a hydrophobic condition and the collectorless flotation of the mineral was observed[1-2]. The similar fact has been also observed in the case of arsenopyrite[3]. It has been found that the Na₂S-induced flotation of the pyrite and arsenopyrite was associated with the adsorption and oxidation of HS⁻ions on the mineral surfaces[1-8], which are greatly influenced by the electrochemical properties of sulphide minerals[9,10]. The anodic oxidation of HS⁻ions on chalcopyrite was different from that on pyrite because the rest potential of the pyrite is higher than that of the chalcopyrite.

Our work are aimed to investigate the adsorption mechanisms of HS⁻ions on the four minerals using the several techniques and to discuss the influence of HS⁻adsorption on the collectorless flotation of the four minerals.

2 EXPERIMENTAL

2.1 Flotation Procedures

The samples of pure pyrite, arsenopyrite, chalcopyrite and galena were taken from four different mines of China. They were ground in ceramic mills under atmosphere. The particles of 0.053～0.152mm size were chosen for flotation tests, which were conducted in a common small organic glass cell with a volume of 30mL for 4min under atmosphere. The weight of feed is 2.0 g. The mineral surfaces were cleaned with an ultrasonic generator prior to the flotation

to remove the possible oxidation films. Polyglycol ester (PGE) was selected as flotation frother, and its dosage is 10 mg/L.

2. 2　Analyses of Concentrations of HS⁻ ions and Amount of Neutral Sulphur Extracted

After the mineral particles of $0.053 \sim 0.152$ mm size were conditioned in air-saturated solutions containing HS^- ions, the separation of the solid and liquid was conducted. Then, the concentration of HS^- ions in the filtrate and the amount of neutral sulphur on the solid also were determined respectively. Dionex-2020 ion chromatography meter was used to analyze the concentration of HS^- ions. The adsorption density of HS^- ions on the mineral surface was calculated as following:

$$\Gamma_{HS^-} = \frac{C_0 - C_1}{m} \times \frac{V}{1000} \quad (mol/g)$$

where C_0 and C_1 are initial and residual concentrations(mol/L)of HS^- ions respectively; m is the weight(g) of the mineral particles; and V is the volume(mL) of the solution.

The mineral particles after condition and filtration were washed repeatedly with distilled water untill HS^- ions adsorbed on the surfaces were completely removed.

After that, they were dried in a vacuum-desicating box. CCl_4 was chosen to extract the neutral sulphur from the surfaces. Then, the neutral sulphur extracted was oxidized into SO_4^{2-} ions. Finally, the concentraions of SO_4^{2-} ions were analyzed using the Dionex-2020 ion chromatography meter.

3　ADSORPTION MECHANISMS OF HS⁻ IONS EXISTING IN AIR- SATURATED SOLUTION ON MINERAL SURFACES

3. 1　Pyrite and Arsenopyrite

Fig. 1 presents the effects of HS⁻ ion

concentrations on pulp potential and adsorption density of HS⁻ ions on pyrite as well as the effects of HS^- ions adsorption on amount of neutral sulphur extracted from the surface and collectorless flotation rate of the mineral in a buffer solution of pH 11. 0. After the pyrite was conditioned in an air- saturated buffer solution containing HS^- ions, the pulp potential declines slowly and still remains higher values enough to meet the need of HS^- ions oxidation on the surface. Therefore, HS^- ions can be adsorbed as the following model:

$$HS^-_{(aq)} \rightleftharpoons HS^-_{(ad)} \tag{1}$$

$$HS^-_{(ad)} \rightleftharpoons S^\circ_{(ad)} + H^+ + e(FeS_2) \tag{2}$$
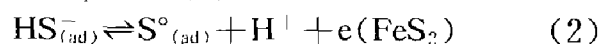
Equation (1) is supported by the fact that the adsorption density of HS^- ions increases with the concentrations of HS^- ions. Similarly, equation(2) is confirmed by the fact that the amount of neutral sulphur extracted increases with the adsorption density of HS^- ion. Equation (2) indicates that the
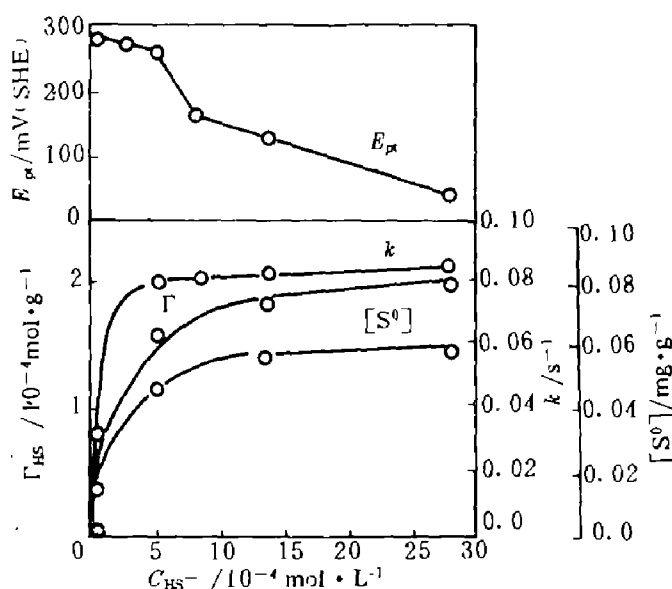

Fig. 1　Effects of HS⁻ ion conentrations on pulp potential(E_{pi}) and adsorption density(Γ) of HS⁻ ions on pyrite as well as effects of HS⁻ ion adsorption on amount of neutral sulphur extracted([S°]) and collectorless flotation rate constant(k) of the mineral in an air- saturated buffer solution of pH11. 0

HS⁻ion adsorbed is oxidized into neutral sulphur.

The formation of neutral sulphur by the oxidation of HS⁻ions results in the change of pyrite surface from hydrophilicity to hydrophobicity and the increase of flotation rate constant in the first 20 seconds. Therefore, Na_2S can induce the collectorless flotation of pyrite, which is also called Na_2S- induced flotation.

The pyrite and the arsenopyrite under investigation are P- type semiconductors and have similar electrochemical properties. Therefore, the adsorption model of HS⁻ions on the arsenopyrite surface is the same as that on the pyrite surface, as follows:

$$HS^-_{(aq)} \rightleftharpoons HS^-_{(ad)} \tag{1}$$
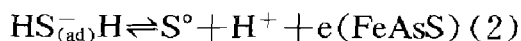$$HS^-_{(ad)}H \rightleftharpoons S^° + H^+ + e \, (FeAsS) \tag{2}$$

Fig. 2 presents the experimental results confirming equations(1) and (2). The HS⁻ ions adsorbed on the arsenopyrite surface can be oxidized into neutral sulphur. The formation of the neutral sulphur renders the mineral surface hydrophobic and induces mineral flotation.

3. 2　Chalcopyrite and Galena

In the case of chalcopyrite and galena, the adsorption mechanisms of HS⁻ ions on the two mineral surfaces are very different from those on the pyrite and arsenopyrite surfaces. Fig. 3 shows that when the concentrations of HS⁻ ions increases, the pulp potential controlled by HS⁻ ions declines rapidly and the adsorption density of HS⁻ions on the chalcopyrite surface increases rapidly. The lower values of pulp potential prevent the formation of neutral sulphur by the oxidation of HS⁻ions on the surface and by the oxidation of the mineral itself. Therefore, the amount of neutral sulphur extracted from the surface decreases with increasing concentration and

adsorption density of HS⁻ions, which is confirmed by the experimental results presented in Fig. 3. This indicates that the HS⁻ions adsorbed on the mineral can not be oxidized into the neutral sulphur. The HS⁻ions are adsorbed on the sufrace through the following way.

$$mHS_{(aq)} \overset{CuFeS_2}{\rightleftharpoons} mHS^-_{(ad)} \tag{3}$$

It can be seen from Fig. 3 that the decrease in amount of neutral sulphur extracted and the hydrophilicity produced by HS⁻ adsorbed make the collectorless flotation rate constant in the first 20s of the chalcopyrite descend. This reveals that the addition of Na_2S can depress the collectorless flotation of the mineral in air-saturated solutions.
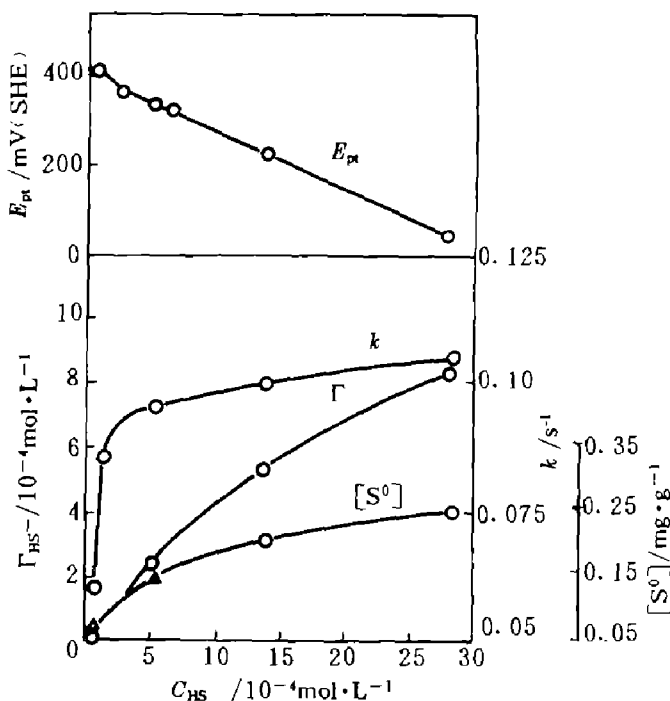

Fig. 2　Effects of adsorption of HS⁻ ions at arsenopyrite surface on amount of neutral sulphur extracted from the surface and collectorless flotation of the mineral in an air-saturated buffer solution of pH8. 4

The galena and chalcopyrite are N — type semiconductors. It may be suggested that the galena is similar to the chalcopyrite
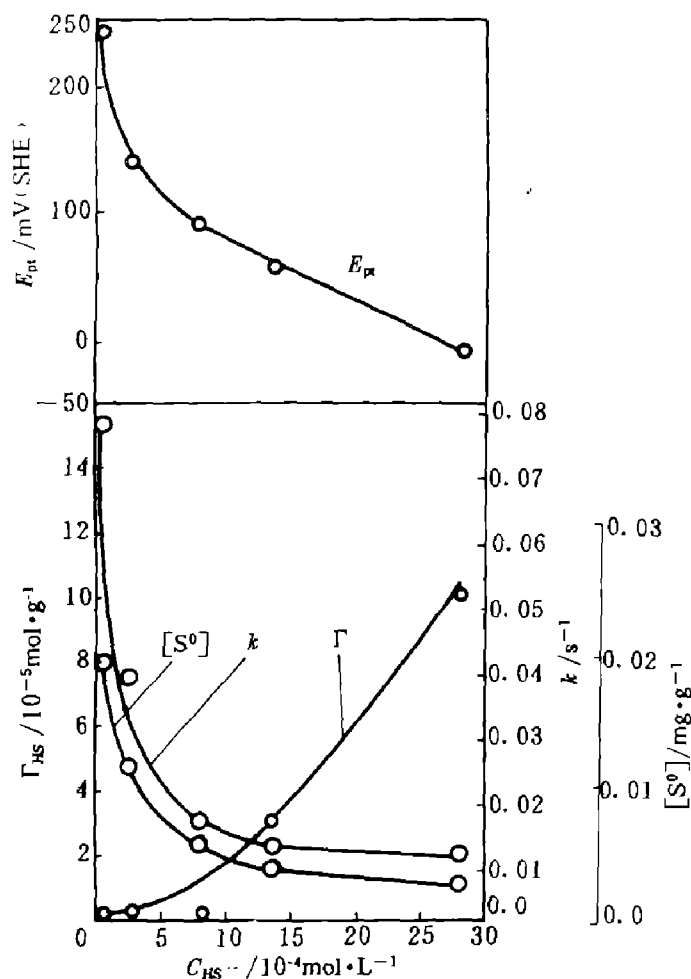
Fig. 3   Effects of HS⁻ concentrations on pulp potential(E_{pt}) and adsorption density(Γ) of HS⁻ ion at chalcopyrite surface as well as effects of HS⁻ adsorption on amount of neutral sulphur extracted([S°]) and collectorless flotation rate constant(k) of the mineral in an air- saturated buffer solution of pH11. 0

The adsorption of HS⁻ ions increases the hydrophilicity of the galena and reduces the amount of neutral sulphur extracted, and hence decreases the collectorless flotation rate. This indicates that the existence of more HS⁻ ions can depress the collectorless flotation of the galena in air-saturated solutions.

in the electrochemical properties. when the concentrations of HS⁻ ions are greater than 5 $\times 10^{-4}$mol/L, the open-circuit potentials of platinum electrode in the galena pulp containing HS⁻ ions decline rapidly (See Fig. 4). It corresponds to the cd part of the adsorption-isotherm in Fig. 4. The adsorption model of HS⁻ ions on the galena surface is the same as that on the chalcopyrite surface and is

$$m\text{HS}_{(aq)} \overset{\text{PbS}}{\rightleftharpoons} m\text{HS}^-_{(ad)} \qquad (4)$$

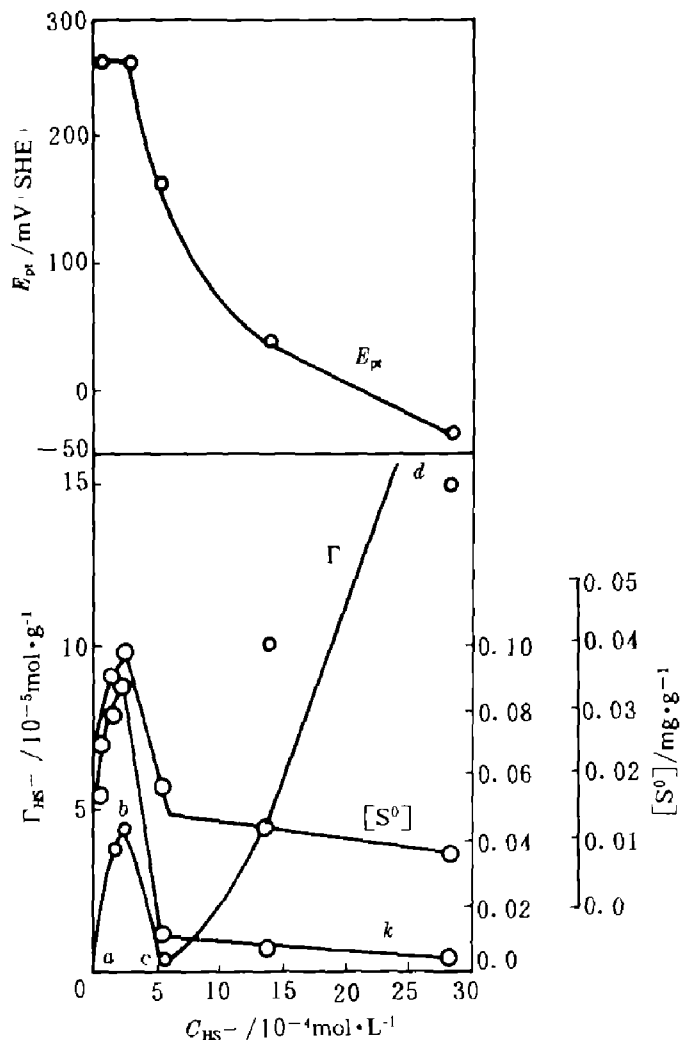The HS⁻ ions adsorbed cannot be oxidized into the hydrophobic neutral sulphur.

Fig. 4   Effects of HS⁻ ions adsorption at galena surface on amount of neutral sulphur extracted from the surface and collectorless flotation of the mineral in an air-saturated buffer solution of pH11. 0

4 VOLTAMMOGRAMS OF ELECTRODES IN DEAERATED BUFFER SOLUTIONS CONTAINING HS⁻ IONS

4. 1   Platinum Electrode

Fig. 5 presents the voltammograms of platinum electrode in a 0.05 mol/L $Na_2B_4O_7$ solution containing different concentrations of HS^- ions. If no HS^- ions in the buffer solution of pH9.2(curve 1), anodic of cathodic current is not observed in the entire sweep range of $-0.64 \sim +0.6$ V. This indicates the electrode reactions of producing oxygen and hydrogen do not take place.
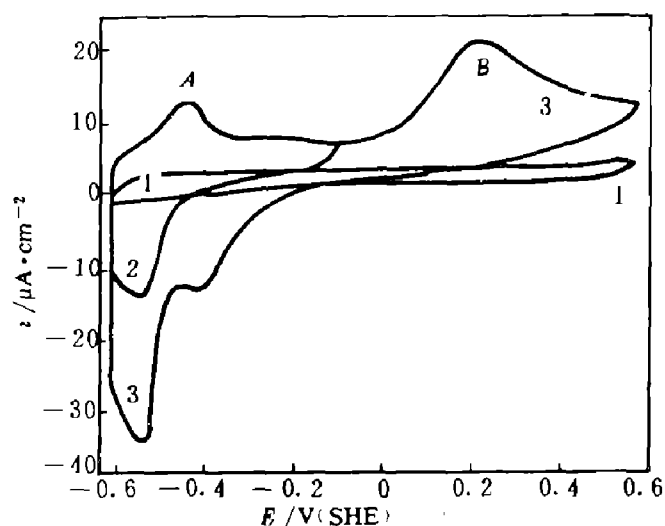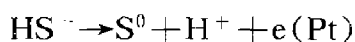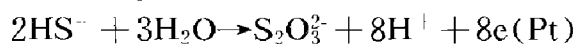

Fig. 5　Voltammograms of platinum electrode in a deaerated 0.05 mol/L $Na_2B_4O_7$ solution containing different concentrations of HS^- ions

sweep rate: 40 mV/s; HS concentrations: curve 1—0 mol/L, curves 2 and 3—1.5×10^{-4}mol/L

In the presence of HS^- ions of 1.5×10^{-4} mol/L(curves 2 and 3), two anodic current peaks are observed in the positive sweep process. Peak A commences at -0.5 V and peak B at 0.2 V. Peak A is attributed to the following oxidation reaction in which HS^- ions are converted into neutral sulphur that renders the electrode surface hydrophobic.

$$HS^- \rightarrow S^0 + H^+ + e(Pt)$$

Peak B corresponds to the reaction of

$$2HS^- + 3H_2O \rightarrow S_2O_3^{2-} + 8H^+ + 8e(Pt)$$

A greater oxidation overpotential exists in the oxidation process in which the HS^- ions are changed into the $S_2O_3^{2-}$ ions. This means that if the electrode potentials are controlled within the range of $-0.5 \sim +0.2$ V, the neutral sulphur can exist stably on the platinum electrode surface and is not oxidized further into $S_2O_3^{2-}$ ions.

4.2　Pyrite Electrode

Fig. 6 are the voltammograms of pyrite electrode in a 0.05 mol/L $Na_2B_4O_7$ solution containing different concentrations of HS^- ions. Because the sweep process is carried out at a rather slower rate of 2 mV/s, the anodic oxidation of the electrode itself in the absence of HS^- ions(dashed curve) is not observed in the entire sweep range of $-0.8 \sim +0.4$ V. The electrode reactions of producing oxygen and hydrogen do not take place also.

In the presence of HS^- ions of 0.01 mol/L, an anodic current peak is observed and commences at -0.25 V in the positive sweep process. It is corresponding with the following oxidation reaction.

$$HS^- \rightarrow S^0 + H^+ + 2e(FeS_2)$$
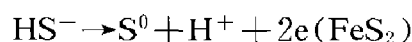
This indicates that the HS ions can be oxidized into neutral sulphur which renders the pyrite electrode surface hydrophobic. But in contrast to the platinum electrods, the commencing potential of the above reaction on the pyrite electrode has a positive shift of ~ 0.25 V. If the commencing potential(-0.5 V) on the platinum electrode is considered as a reference value, there is an oxidation "overpotential" of 0.25 V when HS ions are converted into S^0 on the pyrite electrode. This reveals that the property of electrode itself has a great effect on the oxidation of HS ions. Generally speaking, if an electrode has a higher open-circuit potential, the oxidation of HS ions on the electrode takes place more easily.

4.3　Chalcopyrite Electrode

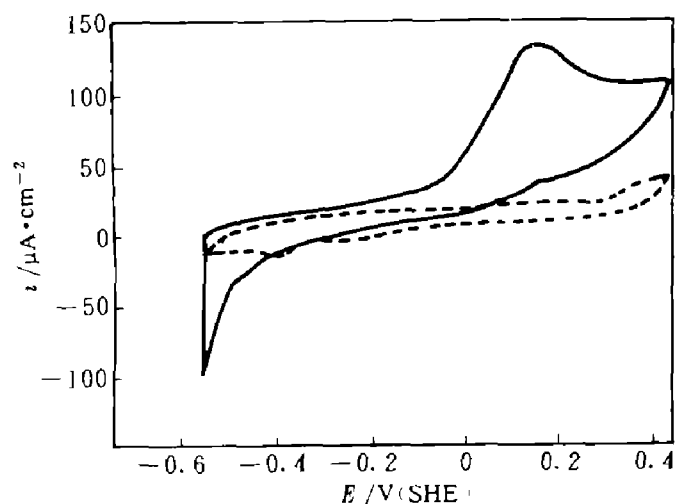Fig. 7 shows the voltammograms of

Fig. 6   Voltammograms of pyrite electrode in a deaerated 0. 05 mol/L Na₂B₄O₇ solution containing different concentrations of HS⁻ ions

Sweep rate: 2 mV/s; HS⁻ concentrations: dashed line—0, solid line—0. 01 mol/L

chalcopyrite electrode in a 0. 05mol/ L Na₂B₄O₇ solution (dashed curve) and in a 0. 05 mol/ L Na₂B₄O₇ solution containing 0. 01 mol/L HS⁻ ions(solid curve). The oxidation of the electrode itself may be not considered because of a rather lower sweep rate of 2 mV/s. In the presence of 0. 01 mol/L HS⁻ ions, when the potential is positively swept to about 0. 0V, an anodic current peak occurs. It arises from the oxidation of HS⁻ ions on the chalcopyrite electrode. The reaction is as follows.

$$HS^- \longrightarrow S^0 + H^+ + 2e \, (CuFeS_2)$$
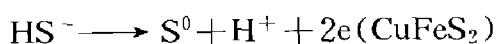
In contrast to the platinum and the pyrite electrodes, the commencing potential of the oxidation reaction on the chalcopyrite electrode have a positive shifts of 0. 5V and 0. 25 V respectively. There is an oxidation "overpotential" of 0. 5V.

On the chalcopyrite and pyrite electrode surfaces, the HS⁻ ions are anodically oxidized into the neutral sulphur, but the commencing potential .of the oxidation on the

chalcopyrite electrode is 0. 25 V higher than that on the pyrite electrode. This indicates that the oxidation of HS⁻ ions on the former is more difficult than that on the latter. The results are in agreement with those reported by Hamilton and Woods[5].
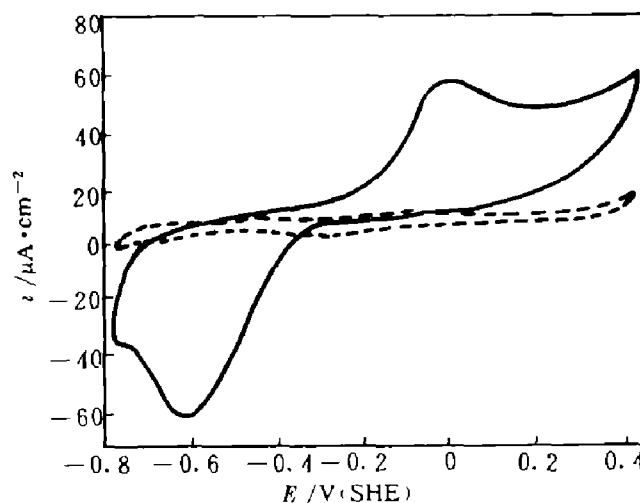

Fig. 7   Voltammograms of chalcopyrite electrode in a 0. 05mol/L Na₂B₄O₇ solution (dashed line) and in a 0. 05 mol/ L Na₂B₄O₇ solution containing0. 01 mol/L HS⁻ ion(solid line)

sweep at a rate of 2mV/s

5   CONCLUSIONS

(1) At open- circuit potentials controlled by HS⁻ ions, the HS⁻ ions dissolved in air-saturated alkaline solutions are adsorbed on the pyrite and arsenopyrite surfaces through the electrochemical adsorption mechanism, and on the chalcopyrite and galena surfaces through the non-electrochemical adsorption mechanism.

Electrochemical adsorption madel:

$$HS_{(aq)}^- \rightleftharpoons HS_{(ad)}^- \rightarrow S_{(ad)}^0 + H^+ + 2e$$

Non-electrochemical adsorption model:

$$mHS_{(aq)}^- \rightleftharpoons mHS_{(ad)}^-$$
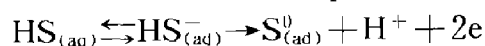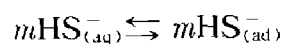
The electrochemical adsorption of HS⁻ ions results in the formation of neutral sulphur through the oxidation of HS⁻ions. The neutal sulphur renders the pyrite and arsenopyrite surfaces hydrophobic and induces the two minerals flotation. On the other

hand, the non-electrochemical adsorption of HS⁻ ions cannot cause the oxidation of HS⁻ ions into neutral sulphur and the makes the chalcopyrite and galena surfaces more hydrophilic and depresses the collectorless flotation of the two minerals.

(2) At polarizing potentials controlled by a potentiostat, the HS⁻ ions dissolved in a deaerated alkaline solution can be anodically oxidized into neutral sulphur on the pyrite and chalcopyrite electrodes. But the commencing potential of the oxidaton on the chalcopyrite electrode is 0. 25 V higher than that on the pyrite electrode.

(3) The potentials across a mineral-solution interface control the adsorption mechanisms of HS⁻ ions on the mineral. When the potentials are changed from higher values to lower values, the adsorption mechanism of HS⁻ ions on the mineral may be changed from the electrochemical one to the non-electrochemical one.

REFERENCES

1 Trahar, W J. In: Jones, M H and Woodcook, J T (Eds), Principles of Mineral Flotation, The Wark Memorial Volume, Australia, 1983. 117—135.

2 Sun, Shuiyu et al. J Cent South Inst Min Metall, 1991, 3(Suppl): 43—48.

3 Sun, Shuiyu et al. J Cent South Inst Min Metall, 1990, 5: 178—484.

4 Hamilton, I C and Woods, R. J Appl Electrochem, 1983, 13:783—792.

5 Hamilton, I C and Woods, R. In: Richardson, P E and Woods, R (Eds), Proc Int Symp Electrochemistry in Mineral and Metal Processing (I), Electrochemical Soc, 1984. 259—281.

6 Walke, G W and Richardson, P E. In: Richardson, P E and Woods, R(Eds), proc Int Symp Electrochemistry in Mineral and Metal Processing(I), Electrochemical Soc, 1984. 54—56.

7 Walk, G W et al. Int J Miner Process, 1986, 18: 119—137.

8 Woods, R et al. Int J Miner process, 1989, 27: 309—326.

9 Wang, Dianzuo et al. Transactions of NF soc, 1991, 1: 20—27.

10 Sun, Shuiyu et al. In: Richardson, P E and Woods, R(Eds), Proc Int Symp Electrochemistry in Mineral and Metal Processing (Ⅲ), Electrochemical Soc, 1992. 280—292.