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Electrochemical study of surface oxidation and collectorless flotation of arsenopyrite

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The surface oxidation of arsenopyrite in alkaline solutions has been studied by cyclic voltammetry. The initial oxidation of arsenopyrite surface produces ferric hydroxide and a realgar-like compound according to the following rection:

$$FeAsS + 3H_2O \Longleftrightarrow Fe(OH)_3 + AsS + 3H^+ + 3e^-$$

At higher potentials, the oxidation of arsenopyrite results in elemental sulphur and arsenate according to the following overall reaction:

$$FeAsS + 7H_2O \longrightarrow Fe(OH)_3 + HAsO_4^{2-} + S^0 + 10H^+ + 8e^-$$

Ferric hydroxide is precipitated and arsenate stays on the surface. Both elemental sulphur and realgar (AsS) are retained on the arsenopyrite substrate. Oxidation of arsenopyrite surfaces is not affected by potential cycling or by the presence of arsenic or sulphide species. The oxidation of hydroxyl ions takes place simultaneously with the arsenopyrite oxidation. Flotation tests demonstrated that freshly ground arsenopyrite is non-floatable in the absence of xanthate as collector. Good flotation was obtained for both freshly ground and aged arsenopyrite in the presence of EDTA. The flotation results support the reactions for arsenopyrite oxidation drawn from the electrochemical studies.

1. Introduction

It is well known that gold and silver usually occur in association with arsenopyrite. At present, the processes of recovering gold and silver contained in arsenopyrite are extremely complex. Various methods have been studied, including roasting of arsenopyrite followed by cyanide leaching of the roasted products, direct cyanidation of arsenopyrite, oxidation of arsenopyrite matrices by bacterial oxidation, as well as pressure oxidation of arsenopyrite under high oxygen pressure in nitric acid, etc. [1, 2]. The desired prior upgrading procedures for all the techniques are the separation of arsenopyrite from other sulphides, usually by flotation. When arsenopyrite is not associated with gold and silver, it is usually a hazard impurity. Complete removal of arsenopyrite is desired. In the conventional method of separation of arsenopyrite from other sulphide minerals by flotation, the temperature of flotation pulp is increased to about 40° C in the alkaline solutions (usually at pH 11) [3]. Arsenopyrite is then depressed or floated by adding collector and other chemicals, depending on the economic importance of arsenopyrite. Although this processing technique has been patented for more than twenty years, the underlying principles are not yet understood. This is not surprising, since the chemistry of arsenopyrite in relation to flotation and leaching, and its electrochemistry in particular, has received very little attention. Numerous investigations have been performed on the other sulphides, however, and a number of reviews have been published [4–8].

Rand [9] investigated the oxygen reduction activity at a rotating-disc arsenopyrite electrode. Compared with other sulphide minerals, it was found that the oxygen reduction activity on arsenopyrite is smaller than that of pyrite and chalcopyrite, but higher than that of the other sulphides. Vreudge [10]. Beattie and Poling [11] studied arsenopyrite oxidation by using cyclic voltammetry and ESCA spectroscopy. They

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Table 1. Chemical analysis of the arsenopyrite sample

Element	*Wt. %*
Fe	32.2
As	44.4
S	18.7
Pb	0.74
Sb	0.64
Ni	0.24
Co	0.22
Cu	0.069
Zn	0.013
SiO_2	0.55

showed that the arsenopyrite is oxidized according to the following reaction:

$$\mathrm{FeAsS} + 11\mathrm{H_2O} \longrightarrow \mathrm{Fe(OH)_3(s)} + \mathrm{HAsO_4^{2-}} + \mathrm{SO_4^{2-}} + 18\mathrm{H^+} + 14\mathrm{e^-} \quad (1)$$

Sulphate diffuses into the solution while arsenate is adsorbed on the electrode surface, and $Fe(OH)_3$ is precipitated on the surface. Chemisorption and oxidation of xanthate are inhibited by the surface oxide films. The oxidation of arsenopyrite commences at lower potentials than that of pyrite. This shows that arsenopyrite is more readily oxidized than pyrite. The flotation separation of arsenopyrite from pyrite is explained by selective oxidation of arsenopyrite surfaces [10, 11]. Sanchez and Hiskey [12] recently investigated the surface oxidation of arsenopyrite. They suggested that the following overall reactions are responsible for the surface oxidation of arsenopyrite.

$$\mathrm{FeAsS} + 10\mathrm{H_2O} \longrightarrow \mathrm{Fe(OH)_3(s)} + \mathrm{H_2AsO_3^-} + \mathrm{SO_4^{2-}} + 15\mathrm{H^+} + 12\mathrm{e^-} \quad (2)$$

and

$$\mathrm{H_2AsO_3^-} + \mathrm{H_2O} \longrightarrow \mathrm{HAsO_4^{2-}} + 3\mathrm{H^+} + 2\mathrm{e^-} \quad (3)$$

However, these reactions cannot explain the good floatability exhibited by arsenopyrite in the absence of collectors.

In the present paper, the surface oxidation of arsenopyrite is studied by cyclic voltammetry. Collectorless flotation of arsenopyrite was investigated in EDTA solutions. The products and mechanisms of the surface oxidation of arsenopyrite are discussed.

2. Experimental details

The arsenopyrite electrode was prepared from a natural massive specimen whose chemical composition is shown in Table 1. The mineral specimen was attached to a brass rod using conductive carbon glue. The electrode was then embedded in epoxy resin with only one side exposed to the solution. The geometric area of the electrode was $0.2\,\mathrm{cm}^2$ and this value was used to calculate the current density. Before each experiment, the electrode was wet ground with silicon carbide paper (1000 and 4000 grid), rinsed with ethonal and de-ionized water. It was then immediately inserted into the electrochemical cell.

Apart from sodium sulphide, all chemicals used in the experiments were of analytical grade. Sodium sulphide was prepared in the laboratory before the experiments were conducted. High purity hydrogen sulphide gas ($H_2S(g)$) was passed into 5.0 M NaOH solution until yellowish colloids appeared. The solution was filtered and diluted to the desired concentration. Milli-Q de-ionized water was used throughout.

The experimental setup for cyclic voltammetry has been described in detail by Ahlberg and Frie [13]. The potentials were measured and quoted against a sodium saturated calomel electrode (SSCE). All the experiments reported in this paper were performed in 1.0 M $NaClO_4$ + 1.0×10^{-3} M NaOH solutions at ambient temperature. The pH value of the solutions was 11. The solutions were purged with high purity nitrogen gas for at least 60 min before the experiments were started. A nitrogen gas flow was maintained above the solution surface during the experiments to prevent the possible return of oxygen to the system.

Experimental techniques for flotation tests and sample preparation have been described elsewhere [14, 15]. The mineral sample used for flotation tests was the same as for the electrode. A size fraction of 38 – 75 μm was used.

3. Results

The open circuit potential (o.c.p.) of a freshly polished arsenopyrite electrode was found to shift negatively by about 50 mV within the first 20 s in contact with the solution and reach a steady state value of −475 (± 10) mV in about 5 min. The reproducibility was fairly good. An initial value of −375 mV was obtained for a freshly polished arsenopyrite, with the variation less than 10 mV. Fairly good reproducibility was also obtained in a parallel study of pyrite surface oxidation [14]. Previous investigators [16] reported that freshly ground iron sulphide surfaces did not give good reproducibility and its o.c.p. varied widely. The large discrepancies were attributed to the thickness of the iron (hydr)oxide film [14]. The negative shift in the open circuit potential of a freshly polished arsenopyrite probably suggest that the thickness of the iron hydroxide film grows very rapidly upon contact with the solution.

Figure 1 shows typical cyclic voltammograms of the arsenopyrite electrode with the initial potential sweep going in the negative direction. The starting potential of the potential sweeps shown in Fig. 1 is about 400 mV more positive than the o.c.p. of the freshly polished arsenopyrite electrode surface. However, it was found that the reduction peak current and the calculated charges under the peak are nearly the same if the potential sweeps were initiated from the o.c.p., indicating that the arsenopyrite electrode surface is not affected significantly by the prehistory indicated in Fig. 1. As shown in Fig. 1, when a potential sweep is scanned negatively from 0 mV, the surface film formed

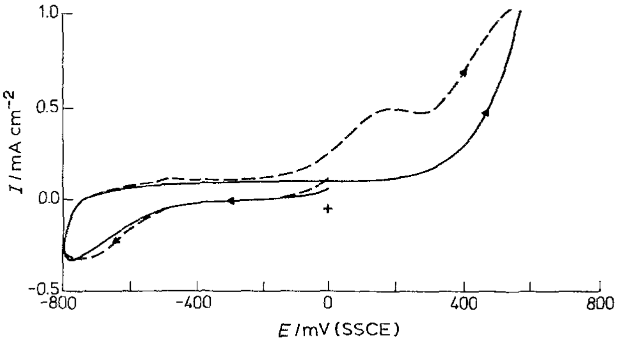

Fig. 1. Cyclic voltammograms of a freshly polished arsenopyrite electrode with a first negative-going potential sweep initiated at 0 mV/SCE. (——) Stationary electrode and (- - -) rotating-disc electrode at 30 r.p.s. Sweep rate: 20 mV s^{-1}. pH 11.0.

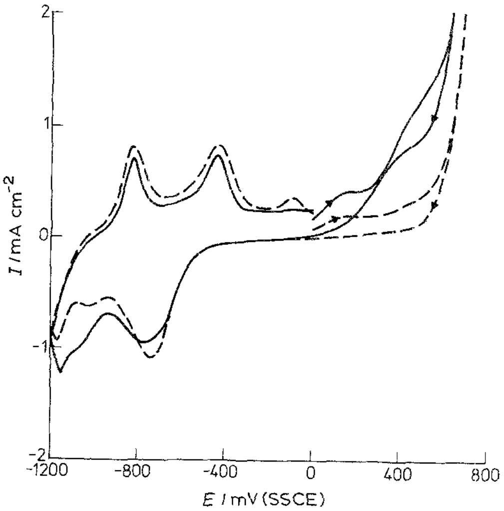

Fig. 3. Multiple cyclic voltammograms of a rotating-disc arsenopyrite electrode with the first potential sweep started at 0 mV/SCE in positive-going direction. Sweep rate: 20 mV s^{-1}. Rotation speed: 30 r.p.s. pH 11.0. (——) 1st cycle, (- - -) 2nd cycle.

during polishing is reduced. The reduction process is nearly independent of the rotation conditions. Unlike pyrite, no significant anodic oxidation of the corresponding reduced oxide is observed on the return scan for the arsenopyrite electrode. The anodic behavior of the electrode on the second scan is nearly identical to that of the initial anodic scan of freshly polished arsenopyrite. This suggests that arsenopyrite is probably regenerated during the initial cathodic reduction. Furthermore, our studies (Figs 2, 3 and 4, and others not presented here) demonstrate that the initiating potential and sweep direction exert little effect on the oxidation behavior of arsenopyrite. The cyclic voltammograms of the arsenopyrite surface oxidation are identical provided the initial potential sweep is started in the potential range ~ −800–50 mV.

Figure 2 shows the cyclic voltammograms of stationary and rotating-disc arsenopyrite electrodes with the potential sweep initiated positively from −800 mV, which is more negative than the open circuit potential of a freshly polished arsenopyrite surface. Great differences are observed for the voltammograms of a stationary and a rotating-disc electrode. For ease of discussion in this paper, the peaks will be numbered, I, II, . . . , XI, according to the potential sequence of the peaks. As shown in Fig. 2 for the stationary electrode, starting the potential scans positively from −800 mV, an anodic current commences at about 200 mV and increases rapidly as the potential increases. On the return (negative-going) scan, a peak (VII) appears at a potential of about 200 mV. In the potential range of −400 mV to −1200 mV, several cathoic peaks are observed. On the second positive going sweep, a sharp and symmetric peak (III) appears at a potential of about −150 mV. The voltammograms of the subsequent cycles are nearly identical to that of first cycle. The peak current for peak III, however, decreases as the number of cycles increases. For a rotating-disc electrode, on the first anodic-going scan, at least three anodic processes (IV, V, VI) are observed. Peak IV is not significant on a stationary electrode. On the return (negative-going) scan, a plateau can be observed. The two cathodic peaks observed at 200 mV (VII) and 400 mV (VIII) on the stationary electrode disappear. Instead, additional peaks are observed at higher

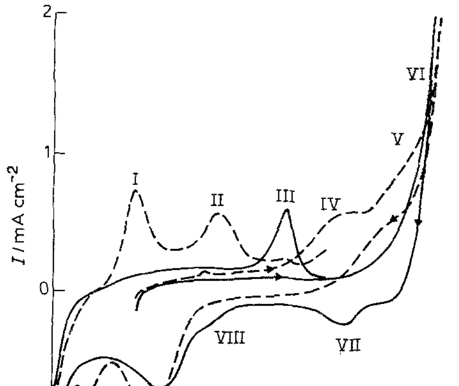

Fig. 2. Cyclic voltammograms of a freshly polished arsenopyrite electrode with a first positive-going potential sweep initiated at −800 mV/SCE. (——) Stationary electrode and (- - -) rotating-disc electrode at 30 r.p.s. Sweep rate: 20 mV s^{-1}. pH 11.0.

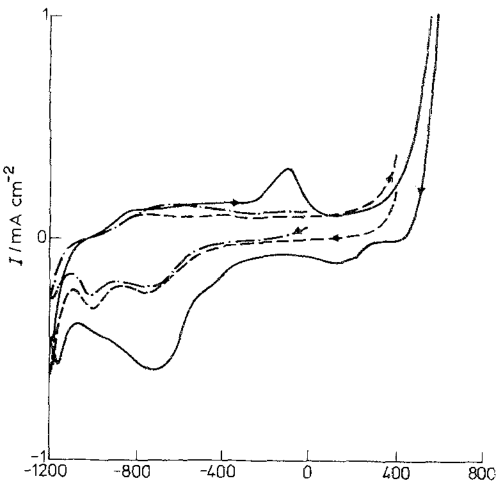

Fig. 4. Effect of the positive sweep potential limit on the cyclic voltammograms of a stationary arsenopyrite electrode. (-·-·-·-) 0, (- - -) 400 and (——) 800 mV/SCE. Potential sweeps started at 0 mV in positive-going direction, only the 2nd and 3rd sweeps are shown. Sweep rate: 20 mV s^{-1}. pH 11.

reduction potentials. On the second positive-going scan, two peaks (I and II) are obtained. These peaks were not observed on a stationary electrode. Depending on the rotation speed, peak (III) observed at a stationary electrode decreases or completely disappears. On the multiple cyclic voltammograms, as shown in Fig. 3, the anodic plateau (V) is no longer observed on the second and subsequent cycles, while peaks IV and VI remain. In principle, the behaviour of the anodic plateau IV is identical to that oberved on the pyrite disc [14]. Interestingly, peak III is again observed on the second and subsequent cycles.

The effect of the sweep potential limits on the cyclic voltammetry of the arsenopyrite electrode was studied. It was observed that if the sweep potental limits are between − 800 mV and 0 mV, no significant difference in the anodic current is shown in the first potential cycle and the subsequent cycle, regardless of whether the sweep is started positively or negatively. Furthermore, on the second and subsequent negative-going sweep, no reduction peak as observed on the first sweep (see Fig. 1) is shown. These results indicate that no oxidation or reduction products have accumulated on the arsenopyrite surface. Arsenopyrite has most likely been regenerated during the recycling processes, as has been shown in Fig. 1 and discussed above.

The effect of increasing positive potential limit on the voltammograms of a stationary electrode is shown in Fig. 4. It can be seen that peak III appears on the subsequent anodic-going scan only when the electrode has previously been subjected to oxidation at potentials higher than 400 mV/SCE. It was found that the peak current for peak III increases as the anodic potential is increased. The peak current of peak III increases with increasing sweep rate. Furthermore, the peak potential of peak III shows no shift with an increase in sweep rate. On a rotating electrode, the effect of the positive reversing potential on the voltammograms is very small. The higher the positive potential limit, the higher the peak current for peaks I, II and IX–XI.

Studies on the effect of electrode rotation enables us to distinguish the reaction originating from the soluble species from those where only insoluble species are involved. For a stationary electrode, dissolved products remain in the vicinity of the surface and may participate in further electrochemical reactions. When the electrode is rotated, the soluble products will be partially or completely dispersed into the soluton. The potential limit dependence and rotating dependence of the voltammograms suggested that soluble products of arsenopyrite oxidation/reduction must have participated in the subsequent electrochemical reactions. Peak III clearly originates from a soluble species of arsenopyrite oxidation and reduction. Under such a solution condition, a soluble species may be a soluble arsenic species, or sulphur species or even the hydroxyl ion. Thus the effect of adding soluble arsenic and sulphur species to the solution on the voltammograms has been studied and compared with the electrochemical behavior of the soluble arsenic or sulfur on a gold electrode.

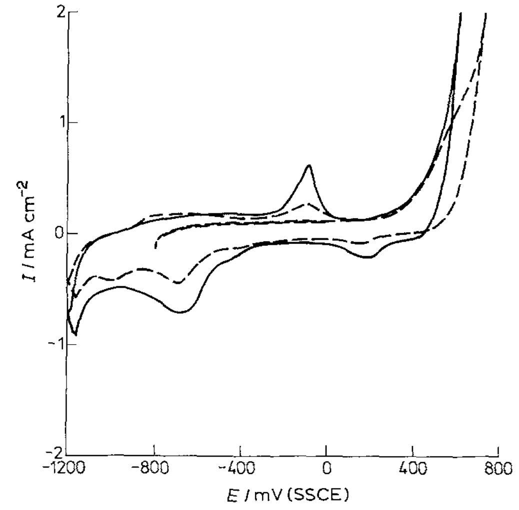

Fig. 5. Cyclic voltammograms of a stationary arsenopyrite electrode in the absence (——) and presence of 1.0 × 10^{-4} M $NaAsO_2$ (– – –). First sweep started at − 800 mV/SCE. Sweep rate: 20 mV s^{-1}. Rotating disc: stationary. pH 11.

The results of the cyclic voltammetry study on arsenite and arsenate oxidation/reduction on a gold electrode will be reported elsewhere [17]. It was found that arsenite can be electrochemically oxidized to arsenate or reduced to elementary arsenic. The process of arsenite oxidation to arsenate is irreversible, that is, no reduction of arsenate to arsenite takes place, while the reduction of arsenite to arsenic is reversible. The oxidation of arsenite to arsenate follows an AE mechanism:

$$AsO_2^- \longrightarrow AsO_{2,ads}^- \qquad A \qquad (4)$$

$$AsO_{2,ads}^- + 2OH^- \longrightarrow HAsO_4^{2-} + H^+ + 2e^- \qquad E \qquad (5)$$

Arsenite is strongly adsorbed on the gold electrode surface and the oxidation of gold is completely inhibited. Figs. 5 and 6 show the effect of the presence of arsenite in solution on voltammograms for a stationary electrode and a rotating electrode, respectively.

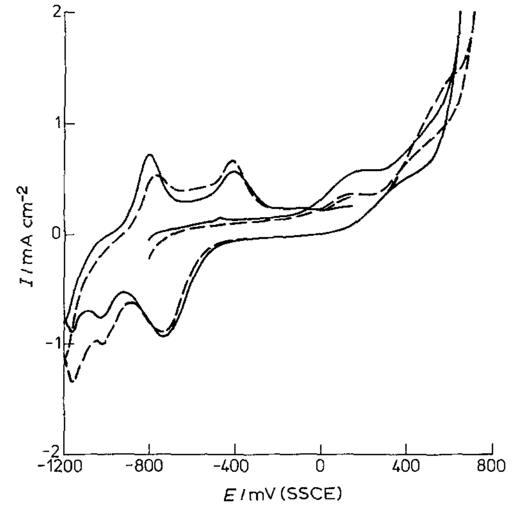

Fig. 6. Cyclic voltammograms of a rotating arsenopyrite electrode in the absence of (——) and presence of 1.0 × 10^{-4} M $NaAsO_2$ (– – –). First sweep started at − 800 mV/SCE. Sweep rate: 20 mV s^{-1}. Rotation speed: 30 r.p.s. pH 11.

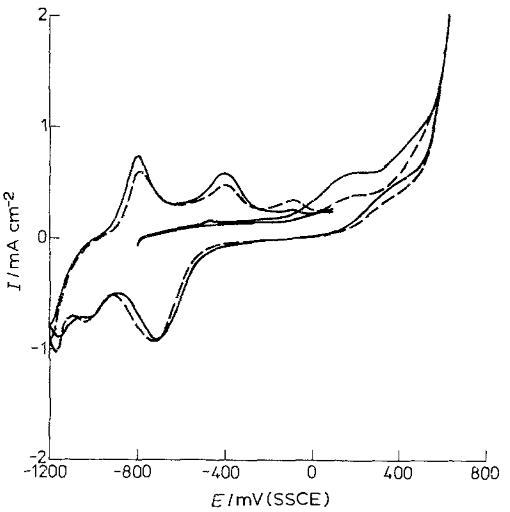

Fig. 7. Cyclic voltammograms of a rotating arsenopyrite electrode in the absence of (a) and presence of 1.0×10^{-4} M Na_2HAsO_4. (b) First sweep started at −800 mV/SCE. Sweep rate: 20 mV s^{-1}. Rotation speed: 30 r.p.s. pH 11.

On a stationary electrode, the peak current for all the peaks decreased in the presence of 1.0×10^{-4} M arsenite. For a rotating electrode, peak IV is suppressed, but the plateau has a nicer shape. Similarly, in the presence of arsenate (Fig. 7), peak V is suppressed. The results indicate that soluble arsenic species affect (in a complex manner) the anodic oxidation process on an arsenopyrite disc. However, it can be concluded that peak III does not originate from the soluble arsenic species.

The electrochemical behaviour of the sulphur system on a gold electrode was also studied. The results were similar to those published in the literature [18–21]. It was found that underpotential deposition of elemental sulphur occurs at a highly negative potential (−0.9 V/SCE), gold sulphide was probably formed. Polysulphide ions were formed during the reduction of elemental sulphur to sulphide. The cyclic voltammogram of arsenopyrite in the presence of 1.0×10^{-3} M sodium sulphide is shown in Fig. 8. It can be seen that a wide peak is obtained near peak III. Compared with the cyclic voltammograms obtained in the absence of bulk hydrogen sulphide, the peak current commences at more negative potentials than is the case for peak III, probably overlapped by several peaks. The amplitude of cathodic peak IX increases significantly. This indicates that hydrogen sulphide ion reacts with iron hydroxide produced during the oxidation of arsenopyrite and forms iron sulphide on the surface, as is the case with pyrite [14] and other sulphides [20, 21]. Note that the oxidation behaviour at high potentials is essentially unchanged by the presence of hydrogen sulphide. However, the amplitude of cathodic peak (VII) was decreased. It was found that the peak potential and also the peak shape for peak III are identical to that of the oxidation of hydrogen sulphide ions on the gold electrode. These results indicate that peak III originates from the oxidation of hydrogen sulphide produced during the reduction of the oxidation products of arsenopyrite.

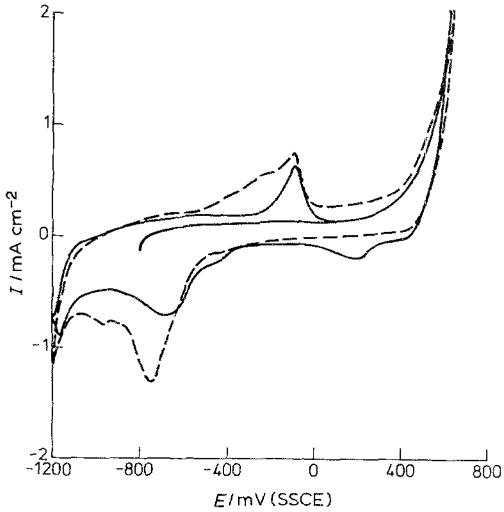

Fig. 8. Effect of the presence of Na_2S on the cylic voltammograms of a stationary arsenopyrite electrode. (——) No Na_2S. First potential sweep started at −800 mV/SCE. (- - -) 1.0×10^{-3} M Na_2S. First potential sweep started at −1100 mV/SCE in positive-going direction. Sweep rate: 20 mV s^{-1}. Rotation speed: 30 r.p.s. pH 11.

The flotation tests demonstrated that freshly ground arsenopyrite is non-floatable in the absence of xanthate as a collector. In the presence of EDTA, however, both freshly ground and aged arsenopyrite show fairly good floatability in the pH range 6–10 (Fig. 9). In general, the aged arsenopyrite exhibited a higher floatability in EDTA solution. Figure 10 shows the flotation recovery of a freshly ground arsenopyrite and the total concentration of released iron as a function of EDTA concentration at pH 8.5 ± 0.5. It can be seen that at a medium concentration of EDTA, the flotation recovery of arsenopyrite exhibits a plateau. However, a further increase in the EDTA concentration above 10^{-2} M significantly decreases arsenopyrite flotation. Similar results were obtained for the other sulphide minerals [14, 15, 44].

The thermodynamic stabilty diagrams for the Fe–As–S–H_2O system are shown in Fig. 11. The thermodynamic data for the substances considered were described elsewhere [43]. All the solids and soluble species having reliable thermodynamic data were

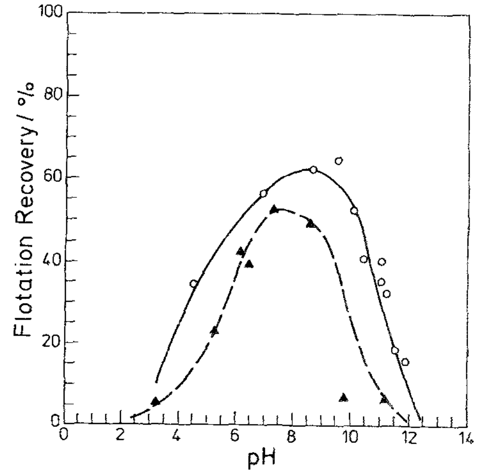

Fig. 9. Flotation recovery of freshly ground (▲) and 10 months aged (○) arsenopyrite (−7.5 + 40 μm) as a function of solution pH in the presence of 5.0×10^{-4} M and 1.0×10^{-3} M EDTA, respectively. Flotation time: 5 min.

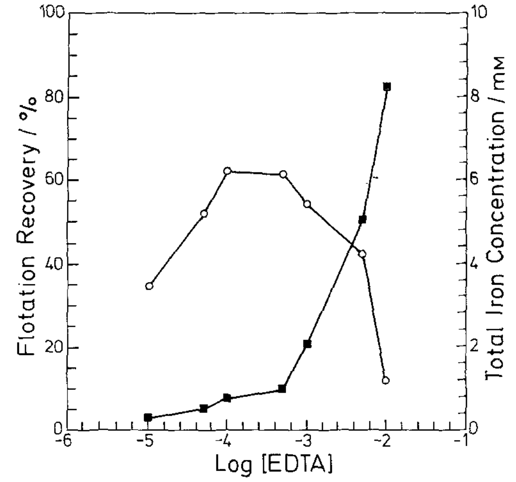

Fig. 10. (○) Flotation recovery of arsenopyrite (−74 + 40 μm) and (■) the total concentration of released iron as a function of EDTA concentration. Test pH 8.5. Flotation time: 5 min. Dissolution time: 20 min. All under nitrogen atmosphere.

considered in the calculations of the stability diagrams. It can be seen that thermodynamically the oxidation products of arsenopyrite can be $FeS_2(s)$, $AsS(s)$, $Fe_3(AsO_4)_2(s)$, $HAsO_4^{2-}$, $Fe(OH)_3(s)$ and finally SO_4^{2-}.

Discussion

The cyclic voltammetric results suggest that the products of the initial oxidation of arsenopyrite surfaces are insoluble species. The following reaction is consistent with the cyclic voltammetric studies:

$$FeAsS + 3OH^- \rightleftharpoons Fe(OH)_3 + AsS + 3e^- \qquad (6a)$$

Thermodynamically, it is possible that arsenopyrite oxidizes by Reaction 6a, as demonstrated by the *pe*–pH stability diagrams. Reaction 6a is probably reversible, that is, arsenopyrite is regenerated from its initial oxidation products by Reaction 6a during the reduction. Reaction 6a also predicts that the electrode potential of arsenopyrite shifts 59 mV/pH. This was observed experimentally by Sanchez and Hiskey [12]. The consideration of pyrite as an intermediate of arsenopyrite oxidation in alkaline solution [12], however, is believed to be very unrealistic. The behaviour of arsenopyrite oxidation can be readily understood by considering the structural chemistry of the mineral. In an ionic approximation, the arsenopyrite formula could be written as $Fe^{3+}(AsS)^{3-}$ [24]. The arsenic and sulphur are covalently bonded directly to each other. The separation of the arsenic from the sulphur is more difficult than the separation of the iron from the arsenic–sulphur group [25, 26]. The oxidation of the AsS group therefore requires a high oxidizing potential. The above interpretation is also supported by the thermodynamics. The reversible potential for Reaction 6a is more than 200 mV more negative than that of the preferential oxidation of arsenic component by the following reaction as suggested by other investigators [12, 22]:

$$FeAsS + 2H_2O \longrightarrow FeS + AsO_2^- + 4H^+ + 3e^-$$

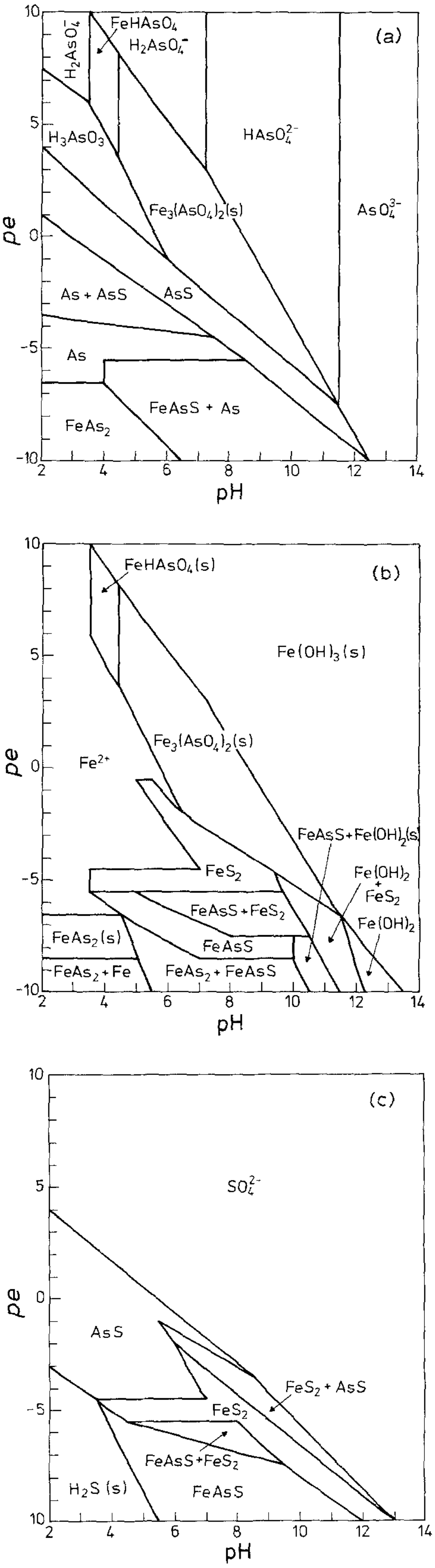

Fig. 11. *pe*–pH predominance diagrams for the Fe–As–S–H_2O system at total concentration of [Fe] = [As] = [S] = 1.0 × 10^{-3} M. (a) Stability domains of arsenic species, (b) stability domains of iron species and (c) stability domains of sulphur species.

The electrochemical regeneration of the metal-sulphides from their initial oxidation products has also been reported for the other metal sulphides [21, 27–29]. It was proposed the initial oxidation reaction involves the migration of metal atoms from the surface layers, leaving a sulphide lattice essentially unaltered from that in the original minerals [27–29]. The regeneration of the metal-sulphide could then take place readily [28].

Analysis of the experimental data indicates that as with the pyrite electrode [14], the oxidation of hydroxyl ions most probably takes place simultaneously with the addition of arsenopyrite. Thus, Reaction 6 probably occurs through the following step:

$$\mathrm{FeAsS + OH^- \longrightarrow FeAsS[OH]_{ads} + e^-} \quad (6b)$$

This gives the anodic plateau (V) on the rotating electrode. Although the much lower potential for the commencement of the hydroxyl ion oxidation than that of oxygen evolution from water seems to be very unrealistic, as was stated earlier for the case of the pyrite electrode [14], it was shown recently by a number of investigators [45, 46] that oxidation of water indeed occurs at these potentials on pyrite surfaces. However, after the first step, the surface corrodes to iron oxide and sulphate. Furthermore, it was shown that the oxidation of arsenite to arsenate takes place through adsorption of arsenite and discharge of hydroxyl ions [30, 31]. One possibility, therefore, is that the oxidation of arsenic to arsenate catalyzes the process for hydroxyl oxidation. It can be seen from Fig. 3 that the oxidation of hydroxyl ions is suppressed on the second cycle. The oxidation of the mineral surface is essentially unaffected by potential cycling, by the rotation condition, or by the presence of soluble arsenic or sulphide species.

The cyclic voltammetric results indicate that peak III corresponds to the oxidation of a reduced species derived from the oxidation of arsenopyrite. Considering the rotating dependence and potential limit dependence, we have attributed peak III to oxidation of hydrogen sulphide to elemental sulphur by the following reaction:

$$\mathrm{HS^- \longrightarrow S^0 + H^+ + 2e^-} \quad (7)$$

Note that peak III was not observed for a freshly polished arsenopyrite disc if the initial anodic sweep potential limit was below 400 mV. This indicates that no HS^- is formed from the reduction of arsenopyrite itself and its initial products. It can therefore be concluded that HS^- was generated during reduction of the oxidation products of arsenopyrite formed at highly positive potentials. Note that the oxidation of sulphur and sulphide to sulphoxy ions is completely irreversible, that is, the reduction of sulphoxy ions to elemental sulphur or sulphide is electrochemically impossible. Therefore, the final product of sulphur component in arsenopyrite oxidation must have been elemental sulphur. The quantity of sulphate or other sulphoxy products formed is probably insignificant, although thermodynamically all sulphur should be oxidized into sulphate at the potentials studies. These results agree with the finding from XPS studies [22, 23].

The oxidation of an arsenopyrite surface at high potentials can therefore be described by the following reaction:

$$\mathrm{FeAsS + 7H_2O \longrightarrow Fe(OH)_3(s)}$$
$$\mathrm{+\ S + HAsO_4^{2-} + 10H^+ + 8e^-} \quad (8)$$

The thermodynamics and the results of arsenite oxidation on a gold electrode demonstrate that the arsenic should be oxidized to arsenate at these potentials. This also agrees with other studies for the oxidation of arsenic mineral [10–12, 32, 33]. Buckley and Walker [22] showed, however, that most of the arsenic had the oxidation state III rather than V. This was propably because the oxidizing potential of an air-saturated solution is not so high.

The observed current peaks in the cyclic voltammograms are interpreted as follows. On a stationary electrode, the arsenate formed stays on the electrode surface. On the cathodic scan, ferric hydroxide is reduced to ferrous hydroxide according to the following reaction:

$$\mathrm{Fe(OH)_3(s) + e^- \Longrightarrow Fe(OH)_2(s) + OH^-} \quad (9)$$

Ferrous hydroxide then combines with arsenate to form ferrous arsenate:

$$\mathrm{3Fe(OH)_2(s) + 2HAsO_4^- + 4H^+}$$
$$\mathrm{\Longrightarrow Fe_3(AsO_4)_2(s) + 6H_2O} \quad (10)$$

The *pe*–pH stability diagrams indicate that the above reaction is thermodynamically favorable under the experimental conditions. The ferrous arsenate formed cannot be reduced further. This explains the absence of anodic peaks for the oxidation of reduced iron and iron hydroxide (Fig. 2). For a rotating electrode, the arsenate is dispersed into the solution. Thus, ferric hydroxide is first reduced to ferrous hydroxide and then to metallic iron. The reverse reactions take place on the return potential scan, and peaks I and II are then observed (Fig. 2). These results agree well with those published for an iron electrode in alkaline solution [34] and with those for precipitated iron oxide on a platinum electrode [35].

The elemental sulphur formed is reduced to hydrogen sulphide ion according to the following reaction:

$$\mathrm{S^0 + H_2O + 2e^- \longrightarrow HS^- + OH^-} \quad (11)$$

This process takes place with the formation of polysulphide ions as intermediate products, as is the case with the sulphur reduction on a gold electrode [18–21]. On a stationary arsenopyrite electrode, the hydrogen sulphide ions formed stay in the vicinity of the electrode. On the second anodic-going sweep, therefore, hydrogen sulphide is oxidized into elemental sulphur according to Reaction 7. This gives peak III. On a rotating electrode, the hydrogen sulphide formed is dispersed into the solution. Thus peak III cannot be obtained on the returning anodic-going scan. It is further believed that on a stationary electrode, the preferential combination of iron hydroxide with arsenate into ferrous arsenate, because arsenate is more closely bound to the iron hydroxide than the elemental sulfur is. On a rotating electrode, both arsenate and hydrogen sulfide are dispersed into solution.

However, the above interpretation is not very satisfactory. On studying the surface oxidation of other iron sulphides like pyrite and pyrrhotite, previous investigators (for example [36, 37]) have demonstrated that, during the reduction, a monosulphide of iron is formed from the oxidation products according to the following reaction:

$$Fe(OH)_3(s) + S^0 + 3e^- \longrightarrow FeS(s) + 3OH^- \quad (12)$$

Therefore, it is possible that Reaction 12 occurs on the arsenopyrite electrode. However, our cyclic voltammograms do not completely support the above reaction having occurred at the arsenopyrite surface. Since, first, if this is the case, then peak III should be due to the oxidation of iron sulphides, FeS, to elemental sulphur by:

$$FeS + 2H_2O \longrightarrow Fe(OH)_2(s) + S + 2H^+ + 2e^- \quad (13a)$$

or

$$FeS + 2H_2O \longrightarrow Fe(OH)_3(s) + S + 2H^+ + 3e^- \quad (13b)$$

because the formation of HS^- from the reduction of FeS takes place at potentials far below -600 mV which is the potential for peak III to occur at the reverse scan. Second, if Reactions 12 and 13 have occurred, then peak III would show no rotation dependence; this means that peak III should be observed on the rotating-disc electrode. Of course, it may be assumed that Reaction 12 proceeds stepwise through the following reactions:

$$S^0 + H_2O + 2e^- \longrightarrow HS^- + OH^- \quad (14a)$$

$$Fe(OH)_3(s) + HS^- + e^- \longrightarrow FeS + H_2O + 2OH^- \quad (14b)$$

with Reaction 14a occurring at a higher potential. It was observed that the oxidation of FeS and that of HS^- on Fe or iron hydroxide electrode proceed by rather complex steps and show no single and sharp peak like peak III, since Reactions 13a and 13b will by no means take place by a single step. This can be clearly seen from the results presented in Fig. 8.

The cathodic peak appearing at about 200 mV (VI) is probably due to the desorption of an adsorbed species. This peak appears only when the anodic sweep potential is above 600 mV. It disappears at a rotating electrode and in the presence of soluble arsenic and sulphur species. The exact nature of the peak, however, cannot yet be identified.

In general, the above cycle voltammetric studies indicate that surface oxidation of arsenopyrite leads to the formation of either hydrophobic realgar or elemental sulphur, together with hydrophilic ferric hydroxide deposits and probably arsenate, depending on the oxidizing potentials. It is very likely that elemental sulphur and realgar are closely bound to the arsenopyrite lattices. The nature of such an oxidized surface is hydrophilic. Thus it is expected that freshly ground arsenopyrite is non-floatable in the absence of xanthate as collector or before the hydrophilic layers are removed by complexing agents. This is in good agreement with flotation results. Addition of small amounts of EDTA, a strong complexing agent for iron (III), immediately leads to fairly good flotation of arsenopyrite. A maximum flotation is achieved at a moderate concentration range (from 1.0×10^{-6} M to 1.0×10^{-3} M). It was found that, thermodynamically, iron hydroxides are unstable in the presence of EDTA, they are dissolved by EDTA and form iron-EDTA complexes [15, 38, 44]. Thus, in the presence of EDTA, the surface oxides and hydroxides formed on arsenopyrite during grinding and storage are dissolved to form Fe–EDTA complexes and removed from the surface into solution. A hydrophobic surface, either realgar or elemental sulphur, is then exposed to the solution. It was shown that under the experimental conditions, the adsorption of EDTA and iron–EDTA complexes on the surface of iron oxides is negligible [39–42]. Thus good flotation is obtained. The aged arsenopyrite gives a higher flotation recovery. This is probably because further oxidation reaction has occurred during storage. As shown by the cyclic voltammograms, a further quantity of elemental sulphur is formed when arsenopyrite is subject to oxidation at more positive potentials. Aged arsenopyrite may possess much more elemental sulphur covered on the surface than is the case for the freshly ground arsenopyrite. A further increase in EDTA concentration, however, reduces arsenopyrite flotation, while the total released iron increases in amounts that approach the EDTA concentration. This shows that excess EDTA wil leach the mineral itself and therefore will very likely destroy the hydrophobic surface. However, the reduced flotability in the presence of excess EDTA can also be due to several other reasons, for example, the adsorption of some EDTA or iron–EDTA complexes, possible extremely large repulsion between the mineral surface and gas bubbles which prevent the particle-bubble attachment, etc. At present, it has not been possible to identify the exact cause of the phenomenon. Direct analysis of the surface chemical composition using techniques such as ESCA and AES is needed in order to understand the flotation results.

5. Conclusions

In alkaline solution (pH 11), the initial oxidation of arsenopyrite surfaces produces ferric hydroxide, $Fe(OH)_3(s)$, and realgar (AsS). Arsenopyrite can be regenerated during the negative potential scan. At higher potentials, the oxidation of arsenopyrite surface takes place with the concurrent oxidation of hydroxyl ions. The products of arsenopyrite surface oxidation are mainly elemental sulphur and arsenate. Both elemental sulphur and realgar are closely bound to the arsenopyrite surface. Arsenate stays on the arsenopyrite surface, and most likely adsorbs on the surface deposits of the ferric hydroxide. The oxidation of arsenopyrite is unaffected by either potential cycling or by the presence of arsenite, arsenate or hydrogen sulphide. Freshly ground arsenopyrite is non-floatable in the absence of collectors. In the presence of EDTA, good flotation is exhibited by freshly ground and aged arsenopyrite, with higher floatability for the aged samples. The good flotation induced by EDTA is due to the removal of hydrophilic surface ferric hydroxide films by the formation of iron–EDTA complexes and exposure of a hydrophobic realgar-like or elemental sulphur surface to the solution. The flotation results obtained provide strong support for the conclusions drawn from the electrochemical studies.

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