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The interaction of iron species with pyrite surfaces

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The development of iron oxide films on pyrite has been investigated using linear potential sweep voltammetry. Voltammograms for a fresh pyrite surface indicated the presence of an iron(II) hydroxy-oxide. After brief exposure to air, the surface layer oxidized to iron(III) hydroxy-oxide. Immersion in iron(II) solutions containing small amounts of iron(III) resulted in an increase in the thickness of the oxide layer to a limiting value; the oxide was present mainly in the iron(III) state. An iron hydroxy-oxide also developed on gold during immersion in iron(II) solution. A pyrite surface abraded on iron powder in deoxygenated water also became coated with iron hydroxy-oxide. Immersion of pyrite in cyanide solution resulted in a decrease in the quantity of oxide on the surface.

1. Introduction

Pyrite (FeS_2) occurs widely in ore-bodies of commercial interest. It is present in sulphide mineral assemblages in conjunction with non-ferrous metals, is an important constituent of gold-bearing deposits, and is a major sulphur-bearing impurity in coals. In each of these systems, the valuable minerals are separated from the unwanted components by flotation processes. Pyrite may be the mineral floated or it may be depressed and other sulphides selectively recovered. The surface characteristics of pyrite are important in determining interactions with flotation collectors and the modification of flotation of the mineral by depressant action. Pyrite flotation and depression have been the subject of extensive investigations, that have included the application of electrochemical techniques [1–14].

The development of an iron oxide layer on pyrite surfaces after exposure to air or oxidizing aqueous environments has been established by electrochemical [7, 8, 11] and electron spectroscopic [9, 14, 15] methods. It has been shown [7, 11] that the nature and extent of this iron oxide layer can be determined from the characteristics of the redox reactions of the iron(III)/iron(II) hydroxy-oxide couple on linear potential sweep voltammograms.

Interactions between minerals in flotation pulps are known to influence flotability and selectivity. The high electrocatalytic activity of pyrite for oxygen reduction [6] leads to this mineral having a high potential in pulps, and galvanic action can enhance the oxidation of other metal sulphides and a loss of selectivity [4]. The potential dependence of the flotation of chalcocite and pyrite was found to be different in mixtures than in single mineral systems [17] and this suggested that exchange of cations between the two sulphides had occurred. Interaction between minerals and grinding media also affects flotation recovery [13, 18–20]. Iron ions released by the corrosion and erosion of steel grinding media result in a coating of iron hydroxy-oxides on sulphide minerals that interferes with collector adsorption and impairs flotation [18–20]. In addition, steel debris in the form of metallic particles can inhibit the flotation of pyrite and pyrrhotite through galvanic action holding the mineral potential below the value required for flotation [13]. Trahar and co-workers [21, 22] found that some components of complex sulphide ores did not float under conditions that single mineral studies had shown self-induced flotation to be effective. The loss of flotability was identified with interferences from the hydroxides of metals derived from the ore itself. Flotation characteristics of the complex ore led these authors to suggest that the function of added collector in the particular circumstances could be as much to overcome the effects of the hydroxides as to increase the hydrophobic character of the floating minerals.

It is evident that an understanding of practical flotation systems requires a knowledge of the mode of interaction between minerals as well as between minerals and collectors. In the present publication, results of investigations are presented of the pyrite/iron oxide system. This system was selected for study because of the ubiquitous presence of pyrite in sulphide ores, and the ability to identify and quantify iron oxides on the mineral surface by voltammetry.

2. Experimental details

The pyrite electrodes were prepared from a massive cubic specimen of the mineral originating from Navajun, La Rioja, Spain. Rectangular slabs, approximately $5 \times 5 \times 2\,mm^3$, were cut from the massive mineral

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and attached to a copper rod with conducting silver epoxy cement. Before applying the silver epoxy, the pyrite surface was ground to minimize contact resistance. The copper rod was threaded at one end to attach to the electrode contact. The mineral and rod were encapsulated in Araldite D epoxy and, after curing, the face machined to expose a 5 × 5 mm^2 surface of pyrite. The electrode surface was prepared before each experiment by abrading on 400 or 600 grade silicon carbide paper.

A gold electrode was constructed in a similar manner to that for pyrite. The surface was cleaned before each run by rising with hydrochloric acid solution.

Investigations were also carried out with iron and magnetite electrodes, the former in the form of powder incorporated into a Metrohm carbon paste electrode. The magnetite originated from Biggenden, Queensland, and a single mineral electrode was fabricated from a rectangular shaped specimen cut from this mineral.

Electrochemical investigations were carried out at 25° C in 0.05 M sodium tetraborate solution (pH 9.2). Experiments were carried out to determine the influence of pretreatment with (i) aqueous solutions of ferrous sulphate, (ii) aqueous solutions of sodium cyanide and (iii) an acetate buffer of pH 4.6 containing 0.5 M sodium acetate and 0.5 M acetic acid. All reagents were prepared from BDH or AR grade chemicals and doubly distilled water. The solutions were deoxygenated with high purity nitrogen.

A Utah Electronics Model 0152 potentiostat programmed with a Utah Model 0151 sweep generator was used to control the electrode potential. Currents were recorded with a Rikadenki XY recorder. Potentials were measured against a saturated calomel electrode (SCE) and converted to the standard hydrogen electrode (SHE) scale assuming the SCE has a potential of 0.245 V with respect to the SHE [23].

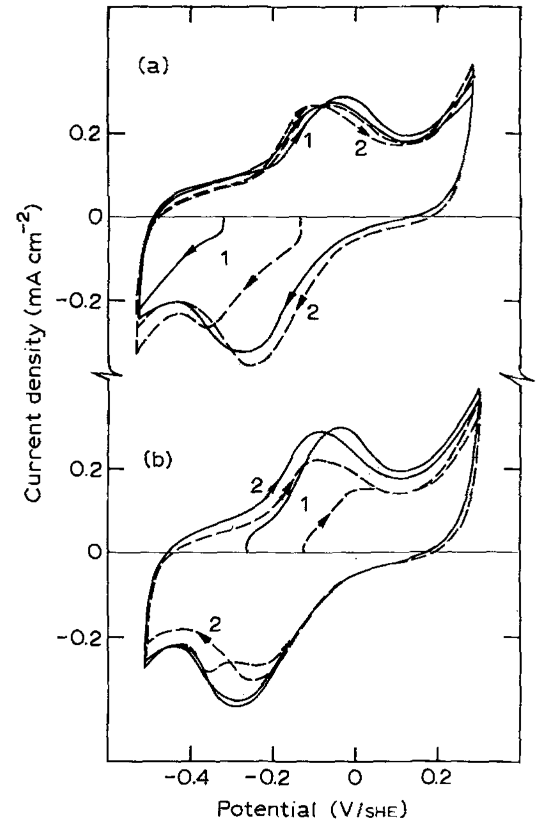

Fig. 1. Voltammograms for pyrite in pH 9.2 solution after abrading under deoxygenated water (——) and this treatment followed by exposure to air for 5 s (– – –). Scan taken initially in (a) negative-going and (b) positive-going direction from the open circuit potential. Scan rate 20 mV s^{-1}.

3. Results and discussion

3.1. *Effect of surface preparation*

Voltammograms for a pyrite electrode in pH 9.2 solution are presented in Fig. 1. It is possible to interpret these curves in terms of redox reactions involving the iron(II)/iron(III) hydroxy-oxide couple without any significant involvement of pyrite itself.

An anodic peak at ~ -0.1 V has been identified with the reaction

$$Fe(OH)_2 + OH^- = Fe(OH)_3 + e^- \qquad (1)$$

and a cathodic peak at ~ -0.25 V with the reverse process [7, 8, 11].

The solid curves in Fig. 1 were obtained with an electrode that had been introduced into the cell immediately after the surface had been abraded in running deoxygenated water. It can be seen that there was negligible cathodic current on the initial scan taken in the negative-going direction (Fig. 1a). Thus, in contrast to pyrite abraded in water in equilibrium with air [7, 8], there was no evidence for the presence of iron(III) hydroxy-oxide. However an anodic peak appears on the reverse scan that is consistent with the presence of iron(II) hydroxy-oxide on the surface. A similar peak was observed when the initial scan was taken in the positive-going direction (Fig. 1b). The anodic charge on the second positive-going scan was the same as that on the first, and the anodic and cathodic charges were approximately equal, as expected for reversible redox processes.

The dashed curves in Fig. 1 were recorded after the electrode was exposed to air for 5 s following the generation of a fresh surface by abrasion under deoxygenated water. The initial scan in the negative-going direction (Fig. 1a) then displayed a cathodic peak indicating that some iron(III) hydroxy-oxide was present on the surface. An anodic peak still appeared on the initial scan taken in the positive-going direction (Fig. 1b) and thus the surface layer contained both iron(II) and iron(III) species. More extended exposure to air gave a voltammogram that was characteristic of the presence of iron(III) hydroxy-oxide alone. The charges observed after both surface treatments in Fig. 1 were essentially the same, and this supports the conclusion [7] that the difference between the two surfaces lay solely in the valence state of the surface oxide and not in the extent of oxidation.

The voltammograms in Fig. 1 are not consistent with the anodic peak arising from pyrite oxidation to iron oxide and a soluble sulphur species on the positive-going scan,

$$FeS_2 + 11H_2O = Fe(OH)_3 + 2SO_4^{2-} + 19H^+ + 15e^- \qquad (2)$$

The reduction of iron(III) to iron(II) hydroxy-oxide on the subsequent negative-going scan is a one electron process and hence the cathodic charge should be only 1/15 that of the anodic but the charges for the anodic and cathodic peaks in Fig. 1 were approximately equal.

The charge balance could be explained in terms of pyrite oxidation if the reactions giving rise to the anodic and cathodic peaks were, respectively, the forward and reverse of the reaction,

$$FeS_2 + 3xH_2O = Fe_{1-x}S_2 + xFe(OH)_3 + 3xH^+ + 3xe^- \qquad (3)$$

Investigations were also carried out in which the electrode surface was abraded in an acidic solution. Iron oxides are soluble in such media and hence should not remain on the mineral surface. Voltammograms recorded after abrasion under a deoxygenated acetate buffer solution of pH 4.6 are presented in Fig. 2. The initial scan in either direction showed no evidence of the presence of iron hydroxy-oxide on the electrode surface and this supports the hypothesis that the peaks in Fig. 1 correspond to iron hydroxy-oxide reactions. However, anodic oxidation gave rise to a significant current and reduction of the oxidation products resulted in a cathodic peak of charge similar to that in Fig. 1, although the peak potential was at a less negative potential. The anodic and cathodic charges in this case could arise from Reaction 3. The increasing cathodic current at the negative potential limit of the cycle, and the anodic charge at the beginning of the return scan, can be explained by loss of iron by oxidative dissolution during the abrasion procedure to leave excess sulphur [11]. The respective charges in the low potential region would then arise from the forward and reverse of the process

$$S + H^+ + e^- = HS^- \qquad (4)$$

It is not possible to arrive at an unequivocal conclusion whether the voltammetric peaks in Fig. 1 derive from Reaction 1 or 3. However, the authors consider the evidence favoured the first process. The iron hydroxy-oxide layer would develop during the preparation of surface and its valence state would depend on the oxidizing potential of the environment. This is consistent with the observation that pyrite surfaces prepared under stringent anaerobic conditions [11] did not show this charge transfer peak. X-ray photoelectron spectroscopic (XPS) investigations of pyrite [16] indicated the presence of an appreciable amount of oxygen-containing species on a freshly fractured sur-

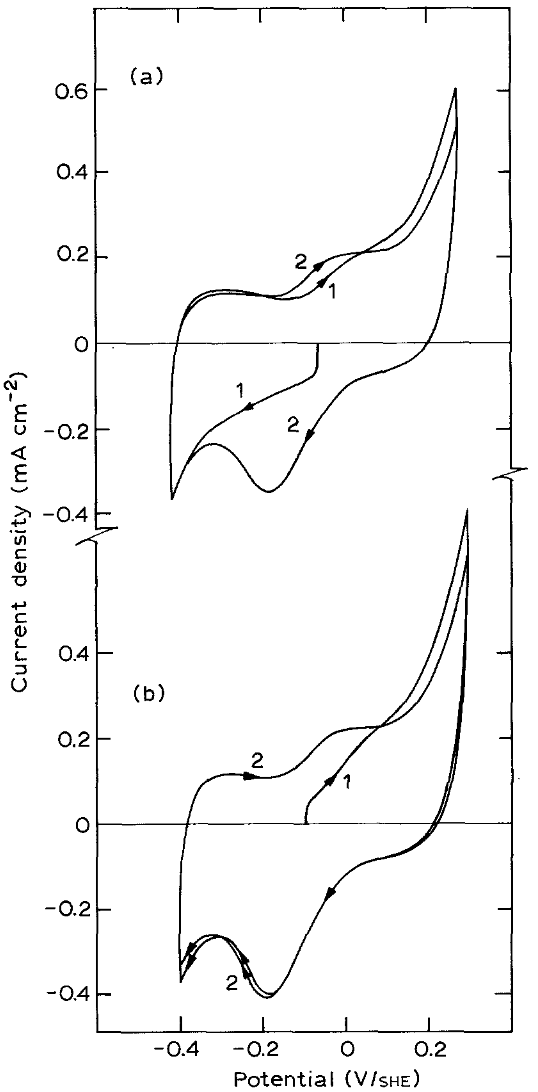

Fig. 2. Voltammograms for pyrite in pH 9.2 solution after abrading under deoxygenated pH 4.6 solution. Scan taken initially in (a) negative-going and (b) positive-going direction from the open circuit potential. Scan rate 20 mV s^{-1}.

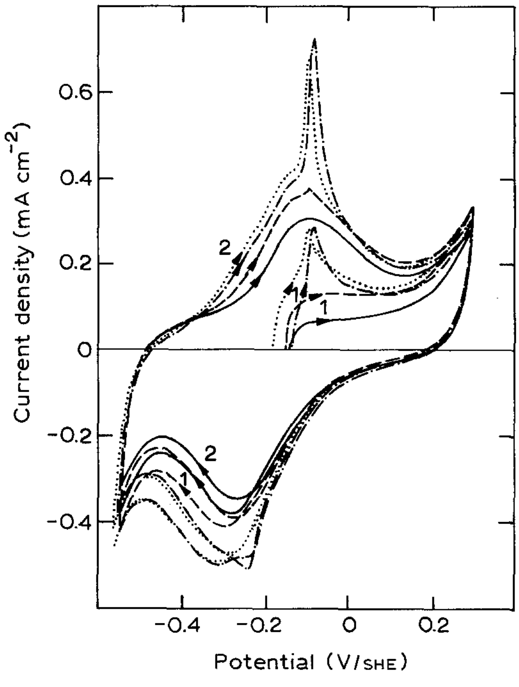

Fig. 3. Voltammograms for pyrite in pH 9.2 solution after treatment in deoxygenated solution of pH 4.6 that was (——) 0.058; (– – –) 0.12; (· · ·) 0.23; (—·—) 0.46 M in iron(II). Electrode washed for 20 s in deoxygenated pH 9.2 solution before insertion into the cell. Scan taken initially in the positive-going direction from the open circuit potential. Scan rate 20 mV s^{-1}.

face that had the minimum exposure to air. The O(1s) binding energy did not correspond to an oxide phase but was consistent with hydroxide species.

The layer thickness calculated from the charge associated with the peaks in Fig. 1, was ~3 nm applying the approach adopted for anodically formed iron oxide films on platinum [24]. This indicated that only the order of a monolayer of oxide was present under these conditions, a conclusion that was in agreement with previous studies on pyrite surfaces [9, 11].

3.2. *Interaction with iron(II) solutions*

The pyrite electrode was abraded and immersed in iron(II) sulphate solutions at pH 4.6 for varying times. The electrode was then washed in pH 9.2 solution for 20 s before being transferred to the cell. A comparison of the voltammograms in Figs 1 and 3 show that there was a significant increase in current at ~ −0.1 V which was attributed to iron hydroxy-oxide on the pyrite surface following treatment in iron(II) solutions.

The total quantity of iron hydroxy-oxide on the surface is given by the total anodic or cathodic charge on a complete cycle whereas the anodic charge on the initial positive-going scan from the rest potential is a measure of the iron(II) constituent (Fig. 3). The total oxide and the ratio of the iron(II) to iron(III) components is presented in Fig. 4. It can be seen that the adsorbed total iron increased and the fraction present as iron(II) hydroxy-oxide decreased with increasing iron(II) concentration to a limiting value.

The appearance of a limiting value for the total iron adsorbed on the surface in Fig. 4 supports the view that the iron was not simply deposited by precipitation when the electrode was washed in pH 9.2 solution. To explore this aspect further, voltammetry was carried out in which the electrode was washed in pH 4.6 solution for 20 s following immersion in the iron(II) solution. For example, the charge when immersed in 0.46 M iron(II) was 4.5 mC cm^{-2} when the electrode was washed at pH 4.6 compared with 5.8 mC cm^{-2} when washed at pH 9.2. Thus, the surface iron species largely remained on the surface during treatment in the iron-free acid medium.

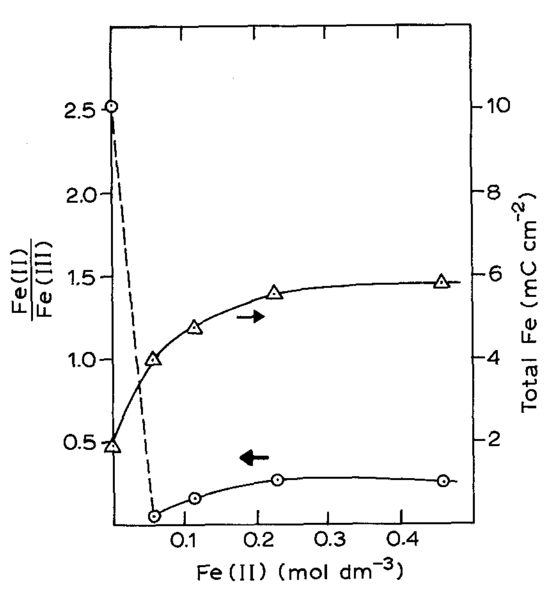

Fig. 4. Dependence of the charges corresponding to the total iron oxide present on pyrite surface, and the iron(II)/iron(III) ratio, on the concentration of iron(II) employed in the treatment stage.

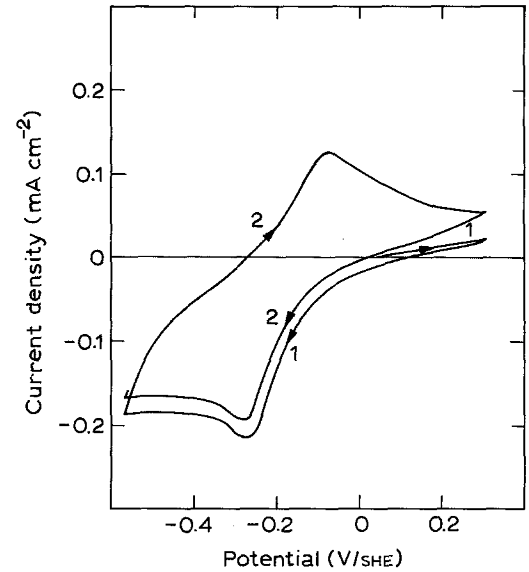

Fig. 5. Voltammograms for gold in pH 9.2 solution after treatment in deoxygenated solution of pH 4.6 containing 0.46 M iron(II). Electrode washed for 20 s in deoxygenated pH 9.2 solution before insertion into the cell. Scan taken initially in the positive-going direction from the open circuit potential. Scan rate 20 mV s^{-1}.

A gold electrode was treated in iron(II) solutions in the same manner as for pyrite. Voltammograms for gold in pH 9.2 solution after immersion in 0.46 M iron(II) at pH 4.6, and washing for 20 s in pH 9.2 solution, are presented in Fig. 5. It can be seen that peaks characteristic of the iron(II)/iron(III) hydroxy-oxide were present. From the initial potential scans, it was apparent that the iron was present in the iron(III) valence state. The total iron adsorbed was equivalent to a charge for Reaction 1 of 2.5 mC cm^{-2}. This value is of the same order as that for pyrite and the difference could be accounted for by differences in surface roughness.

These investigations demonstrated that iron can be adsorbed by surfaces in contact with iron-containing solutions. The iron(II) concentrations used here were much greater than would be experienced in flotation situations. However, the voltammograms indicate that an iron(III) rather than an iron(II) species was adsorbed. The reactivity of iron(II) with traces of oxygen in solution would ensure the presence of some iron(III) species. There is evidence [25] that the active species that adsorbs on oxide minerals are the first hydroxy complexes. For iron(III), the adsorbing species would be $FeOH^{2+}$ ions. The equilibrium concentration of $FeOH^{2+}$ ions at pH 4.6 is 10^{-7} M at pH 4.6 [26], but this complex could be present at higher concentrations under the metastable conditions of the solutions used in the present experiments. Similar concentrations of this and other iron(III) hydroxy complexes would be present in flotation pulps, being formed by oxidation of grinding media and iron minerals.

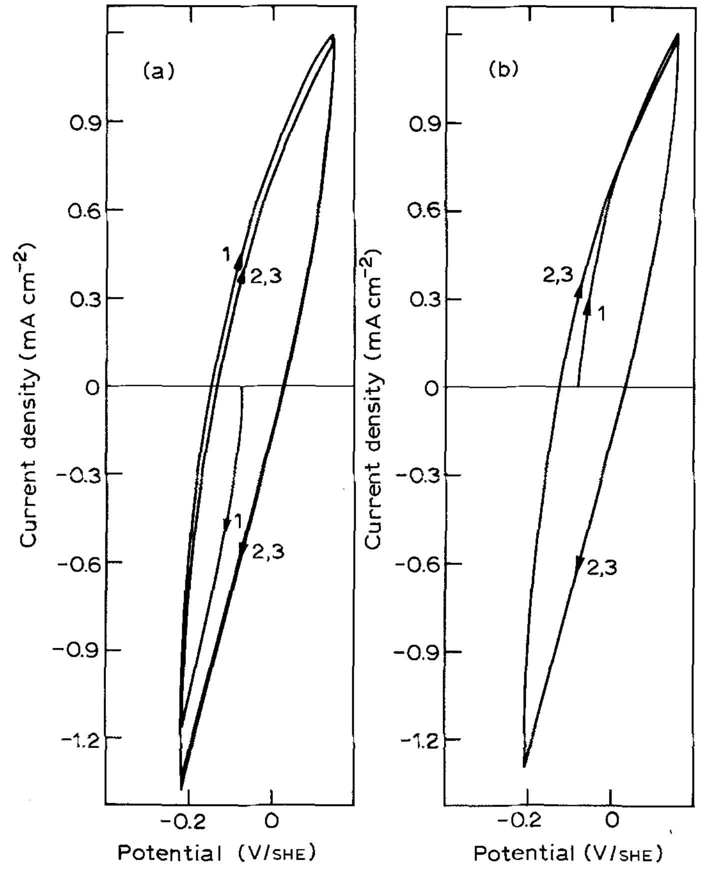

Fig. 6. Voltammograms for magnetite in pH 9.2 solution. Scan taken initially from the initial open circuit potential for a freshly abraded surface to increasing negative value in Curve a and increasing positive value in Curve b. Scan rate 20 mV s^{-1}.

The broad voltammetric peaks observed for the iron(II)/iron(III) hydroxy-oxide system suggest that the reactions proceed through a series of intermediate mixed valence oxides. The voltammograms in Fig. 3 show additional sharp peaks at ~0.1 V for the higher coverages. Such features are indicative of the development of a stable phase. Since it appears in the middle of the broad peak, it could have a stoichiometry close to that of magnetite (Fe_3O_4). The behaviour of pure magnetite at pH 9.2 is shown in the voltammograms in Fig. 6. It can be seen that within a narrow potential range close to −0.1 V, the oxide on a surface freshly abraded in deoxygenated water can be reduced on scans commencing from the initial rest potential to lower potentials and oxidized on scans taken to higher potential values. The shape of the voltammograms (curves A and B) indicates the highly reversible nature of these reactions. This observation supports the hypothesis that the sharp peaks in Fig. 3 correspond to a magnetite-type phase. Presumably, a certain oxide thickness was required before the magnetite structure could develop.

3.3. *Interaction with grinding media*

A freshly abraded pyrite surface was gently rubbed on iron powder that was slurried in deoxygenated water and then the electrode was inserted into the cell. The resulting voltammograms are presented in Fig. 7. It is apparent that significant quantities of iron were adsorbed on the mineral surface. The open circuit potential of −0.51 V, observed after treatment with iron powder, was about 0.26 V lower than that found for freshly abraded pyrite. This can be explained by galvanic interaction between metallic iron and pyrite. Thus, iron cathodically protects pyrite from oxidation, but iron species resulting from corrosion of the metal are adsorbed on the mineral surface.

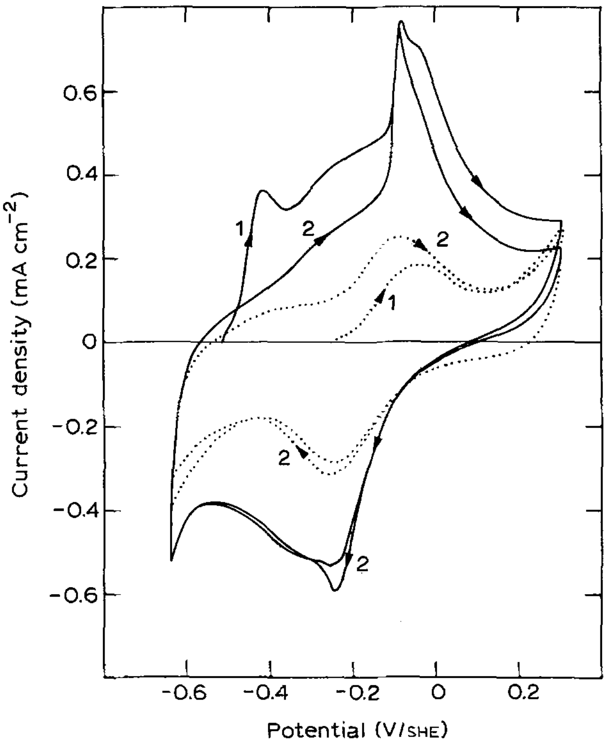

Fig. 7. Voltammograms for pyrite in pH 9.2 solution: (——) after abrading on iron powder under deoxygenated water; (····) freshly abraded surface. Scan taken initially in the positive-going direction from the open circuit potential. Scan rate 20 mV s^{-1}.

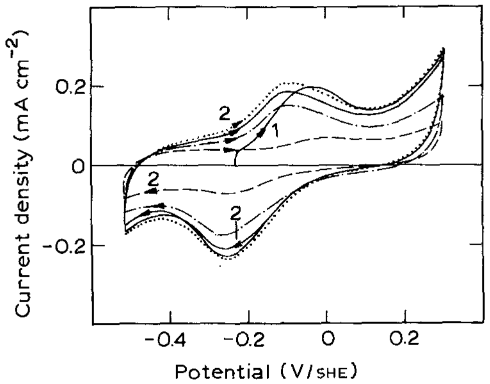

Fig. 8. Voltammograms for pyrite in pH 9.2 solution after treatment in deoxygenated solution containing (——) 0; (···) 10^{-3}; (—·—) 10^{-2} and (- - -) 10^{-1} M sodium cyanide. Electrode washed for 20 s in deoxygenated pH 9.2 solution before insertion into the cell. Scan taken initially in the positive-going direction from the open circuit potential. Scan rate 20 mV s^{-1}.

Investigations were also carried with a gold electrode aimed at determing if iron species were adsorbed from metallic iron and from pyrite slurries. The presence of iron on the gold surface was observed, but the voltammograms were indicative of the incorporation of the iron and the pyrite into the gold surface rather than of an adsorbed species. Incorporation is much more likely to occur in the relatively soft gold surface than in pyrite, which is hard and brittle.

3.4. *The influence of cyanide*

In flotation practice, cyanide is often used as a depressant for pyrite. The mechanism of depressant action with this system was identified [1] as the formation of an adsorbed iron(III) ferrocyanide that imparts a greater degree of hydrophilicity to the mineral surface. The observation [7] that the anodic oxidation of ethyl xanthate on pyrite was inhibited when cyanide was present in solution supports this viewpoint. The presence of cyanide also diminished the voltammetric peaks due to the iron(II)/iron(III) couple [7]. This result has been confirmed in the present study. Voltammograms for a pyrite electrode after conditioning in sodium cyanide solutions for 60 s are shown in Fig. 8. As found previously [7], the iron hydroxy-oxide peaks were decreased as the cyanide concentration was increased. Figure 8 also indicates that the oxidation of pyrite was inhibited by the presence of cyanide since the anodic current at the upper-potential limit of the scan was decreased. This is evidence in support of the iron hydroxy-oxide being replaced by a surface cyanide species.

4. Conclusions

An experimental technique involving abrasion of the sulphide surface under carefully controlled conditions has been developed to simulate the behaviour of mineral during grinding.

The results indicate that a thin hydroxy-oxide film is formed rapidly on pyrite on exposure to solutions containing trace amounts of oxygen. Multilayer quantities of oxide/hydroxide are rapidly adsorbed on pyrite when the mineral is immersed in solutions containing dissolved iron. Oxidation and reduction of the iron oxide/hydroxide species give rise to characteristic peaks on voltammograms. When thick layers are present on a pyrite surface, sharp voltammetric features are observed and these have been identified with progression of the oxide/hydroxide through a magnetite-like phase.

Cyanide ions can largely replace the hydroxy-oxide film.

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