

The surface oxidation of pyrite in alkaline solution

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Received 27 January 1989; revised 2 January 1990

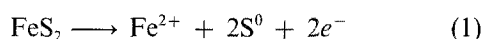
The collector-less flotation of pyrite has been studied by conventional techniques and is correlated to the electrochemical behaviour of pyrite in alkaline solution (1 M NaClO₄, pH 11). It was concluded that the initial oxidation of pyrite produces a hydrophobic sulphur rich surface together with hydrophilic iron hydroxide species. Also upon grinding, the surface is covered by hydrophilic species and therefore no significant flotation was obtained in the absence of a collector. However, collector-less flotation was readily obtained in an iron complexing solution like EDTA. This indicates that the remaining sulphur-rich layer is responsible for the floatability of pyrite under these conditions.

1. Introduction

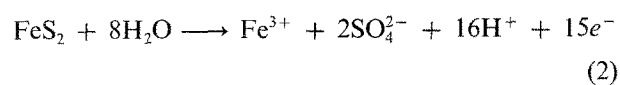
The electrochemistry of pyrite has been extensively studied, since the knowledge of its behaviour in aqueous solutions is important for many applications; for example, the separation of pyrite from complex sulphide ores by flotation and leaching of pyrite. Pyrite is the most noble sulphide mineral and can thus influence other sulphide minerals through galvanic couplings. In these interactions pyrite will be the cathode and thus enhance oxidation of the other minerals. Since most sulphide minerals form a hydrophobic sulphur layer upon oxidation the galvanic interaction between pyrite and the other sulphide minerals will lead to non-selective flotation. A number of excellent reviews have been published on the electrochemistry of pyrite [1-7]. The anodic dissolution behaviour of pyrite has been investigated by using various techniques, such as linear potential sweep voltammetry, coulometry at constant potential, reaction stoichiometry from the analysis of the products in solution using radiotracers and examination of the surface products by XPS [8-10].

It is generally accepted that the oxidation of pyrite can be described by the following overall reactions [11-16]:

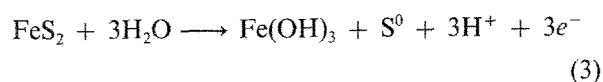
In acidic solutions



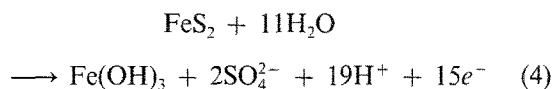
and at higher overpotentials



In alkaline solution ferric ions precipitate on the surface as ferric hydroxide. Thus,



and



However, the detailed mechanism for pyrite oxidation is not well established. Some problems have been particularly focused upon and a general agreement is not yet achieved [17]. These problems are: (i) whether elemental sulphur is involved as an intermediate during the formation of sulphate, and (ii) which component is oxidized preferentially. Peters and Majima [11], Bailey and Peters [12] and Hamilton and Woods [13] showed that elemental sulphur was the major product of the anodic oxidation in acidic solutions; that is, reaction (1) dominates the pyrite oxidation. They also claimed that the formation of sulphate takes place via elemental sulphur as an intermediate. Peters [14, 15] attributes the passivation behaviour during the acidic leaching of pyrite to the formation of elemental sulphur on the pyrite surface. However, Biegler and Swift [16] suggested that the sulphate route dominates over the potential range accessible at ambient temperature. Furthermore they concluded that elemental sulphur is not an intermediate in the sulphate route. Hamilton and Woods [13] showed that the sulphate route is the dominating reaction in alkaline solutions and that the formation of elemental sulphur is restricted to the order of a monolayer at pH 9.2 and 13.

The other most controversial aspect is regarding the oxidation process of the components. Two mechanisms have been proposed and can be described as follows: (a) *the preferential release of sulphur atoms from pyrite*. Goldhaber [18] proposed that the sulphur component in pyrite is first released and oxidized to sulphate. Hydroxide ions then go to the surface to react with iron sites to form an iron hydroxide layer.

(b) *the preferential removal of iron from the pyrite surface.* Sato [19] and Peters [14, 15] proposed that the oxidation of pyrite occurs first at the iron sites. Iron is released into the solution or precipitated on the surface as hydroxide, leaving a reacted layer of elemental sulphur. Recently Buckley *et al.* [9, 10, 20–25] carried out studies by using electrochemical and surface spectroscopic techniques. Their result show that the initial oxidation of sulphide minerals in general proceeds through a progressive removal of metal atoms and leaves the sulphur lattice largely unaltered. Also, in other investigations the formation of a sulphur-rich surface was postulated in the initial oxidation phase [26–28].

Collectorless flotation has been reviewed recently [17] and it was stated that the precise nature of the hydrophobic species is not known. Furthermore, oxidizing conditions are necessary for most of the sulphide minerals. However, severe oxidation results in hydrophilic surfaces due to the formation of oxidic species.

In this paper, the surface oxidation of pyrite is studied in a non-complexing electrolyte, sodium perchlorate, by using cyclic voltammetry. Collectorless flotation of pyrite was studied in an alkaline EDTA solution and the results are compared with the voltammetric data. The oxidation processes are discussed.

2. Experimental details

2.1. Cyclic voltammetry

The pyrite electrode was prepared from a natural massive specimen, which was attached to a brass rod using a conducting carbon glue. The electrode was moulded in epoxy, exposing only one side to the solution. The geometrical area was 0.09 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 mesh), rinsed with ethanol and milli-Q deionized water. The electrode was immediately put into the electrochemical cell.

Sodium sulphide was prepared in the laboratory before the tests. High purity hydrogen sulphide gas was passed into 5 M sodium hydroxide solution until yellowish colloids appeared. The solution was filtered and diluted to the desired concentration. All other chemicals used were of analytical grade. Milli-Q deionized water was used throughout.

A detailed description of the experimental setup has been given elsewhere [29]. The potentials were measured and quoted against a sodium saturated calomel electrode (SSCE), $E = 0.236 \text{ V}$ with respect to SHE. All the electrochemical experiments reported in this paper were performed in solutions composed of 1.0 M sodium perchlorate with $1.0 \times 10^{-3} \text{ M}$ sodium hydroxide and at room temperature. The pH of such a solution was defined to be 11. The electrolyte was purged with high purity nitrogen for at least 60 min

before the experiment was started. A nitrogen gas flow was maintained above the solution during the experiment, to prevent the possible return of oxygen to the system.

2.2. Collectorless flotation

The pyrite sample used for flotation was obtained from Wards Science Establishment, USA. The sample was first crushed by hand and quartz particles were removed. Strongly magnetic particles were removed by means of an electrical magnetic separator. The chemical analysis of the pyrite sample is shown in Table 1. The sample was ground with a micro centrifugal ball mill, where both the balls and the mill were made of zirconium oxide. The two size fractions $-120 + 75 \mu\text{m}$ and $-75 + 40 \mu\text{m}$ were used for flotation tests. All the flotation tests were performed with a Labor-Flotation machine, made by Clausthal University, West Germany. 5 g of pyrite was added to 150 ml solution. The pH of the solution before and after the flotation was measured and the tailing pH is referred to as the flotation pH. The total iron concentration was analysed by Atomic Absorption Spectrometry (AAS).

3. Results

3.1. Open circuit potential

The open circuit potential of a freshly polished pyrite electrode was found to shift in the negative direction reaching a steady state value of $-310 \pm 10 \text{ mV}$ in about 5 min. Some investigators [16] have observed previously that freshly polished pyrite surfaces gave no good reproducibility and that the rest potential varied widely, usually over 100 mV. However, with the pretreatment used in the present work fairly good reproducibility was obtained for the same sample. It is well known that a thin oxide film is formed on pyrite in air and by wet grinding [9, 10, 13]. The thickness of this film may well influence the rest potential of the system. In Fig. 1 a voltammogram at a rotating pyrite electrode is shown. The surface oxide film is reduced and the charge passed was calculated to be about 1.3 mC cm^{-2} . This corresponds to a maximum of two mono layers of iron oxide. The sweep is reversed at -800 mV and the corresponding oxidation takes place. The anodic charge consumed is approximately the same as the cathodic, which indicates that the total process is reversible. This process can be written schematically

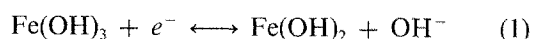


Table 1.

Element	Fe	S	Cu	Pb	Zn	Ni	SiO ₂
weight %	43.6	52.5	0.031	0.075	0.47	0.01	0.25

Sb, Co and As were below the limit of detection.

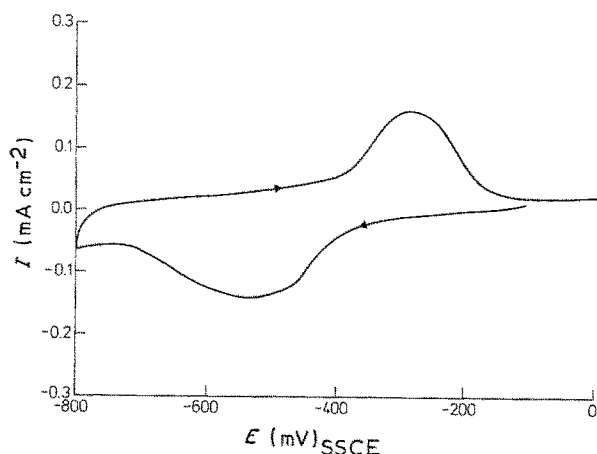


Fig. 1. Cyclic voltammogram of a freshly polished pyrite electrode in 1 M NaClO₄, pH = 11. The sweep is started in the negative-going direction. Sweep rate = 20 mV s⁻¹ and rotation speed = 30 r.p.s.

with an E_{rev} value of about -405 mV. This is in agreement with voltammetric studies of iron in alkaline solutions [30] and of iron hydroxide layers precipitated on platinum electrodes [31].

3.2. Cyclic voltammetry

Multiple cyclic voltammograms are shown in Fig. 2 for a stationary pyrite electrode and in Fig. 3 for a rotating electrode. The first cycle corresponds to a freshly polished surface. The sweeps were initiated in the negative-going direction at a potential of -100 mV, which is somewhat more positive than the open circuit potential. It can be seen that six anodic peaks and at least three cathodic peaks are obtained. These peaks are numbered I–IX and will be referred to in the following discussion.

Starting in the negative direction, Fig. 2, the reduction (VII) of oxidic species on the surface takes place. At more negative potentials both pyrite and iron (II) hydroxide can be reduced (IX), forming elemental iron on the electrode and hydrosulphide ions in the solution. The potential is reversed at -1200 mV and a large rather sharp anodic peak appears (I), which can be attributed to the oxidation

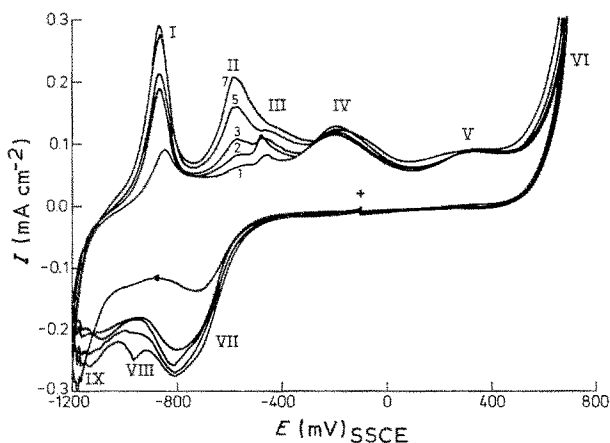


Fig. 2. Multiple cyclic voltammograms at a stationary pyrite electrode in 1 M NaClO₄, pH = 11. The numbers indicate the scan number. Sweep rate = 20 mV s⁻¹.

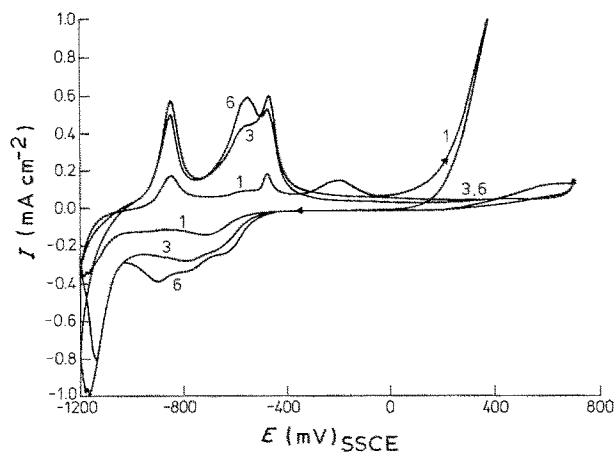


Fig. 3. Multiple cyclic voltammograms for a rotating pyrite electrode in 1 M NaClO₄, pH = 11. The numbers indicate the scan number. Sweep rate = 20 mV s⁻¹ and rotation speed = 30 r.p.s.

of iron. As elemental iron is oxidized in the presence of hydrosulphide ions, iron sulphide may be formed [32]. Peaks II and III correspond to the oxidation of iron (II) hydroxide and peak IV can be attributed to the oxidation of FeS, formed at peak I. However, hydrosulphide ions can also be oxidized in this potential region, forming elemental sulphur on the surface. The oxidation of pyrite itself starts at about 0 V with a small peak (V) and at higher anodic potentials further increase in the current appears (VI). On the subsequent sweeps there is a general increase of the current for peaks I, II, VII and IX, while peaks IV and V remain constant in size.

On the negative-going scan the increase in the current is dependent on the reduction of a larger amount of iron hydroxide on the surface and on reduction of sulphur species formed during the oxidation of the mineral. At the rotating disc electrode, Fig. 3, the voltammograms have the same appearance in the cathodic region. It is also evident that approximately the same amount of the solid oxidation products are formed in this case. However, two main differences between the voltammograms at the stationary and the rotating electrodes should be noticed. Firstly, the peak (IV), which corresponds to the oxidation of iron sulphide, disappears at the rotating electrode after the first cycle. Secondly, the oxidation at low overpotentials is largely inhibited on subsequent sweeps of the rotating electrode. On starting the sweeps in the positive-going direction similar results were obtained.

The large difference between the voltammetric response for the oxidation of pyrite at a stationary compared to rotating electrode made us look for a rotation dependence of the current, Fig. 4. In Fig. 4a voltammograms for three different rotation speeds are shown. All three voltammograms are the first in a series and thus are run on a freshly polished surface. A plot of the limiting current as a function of the square root of the rotation velocity yields a straight line, indicating diffusion control. Furthermore by plotting the $\log(I \cdot I_{lim} / (I_{lim} - I))$ as a function of potential a Tafel slope of about 120 mV was obtained.

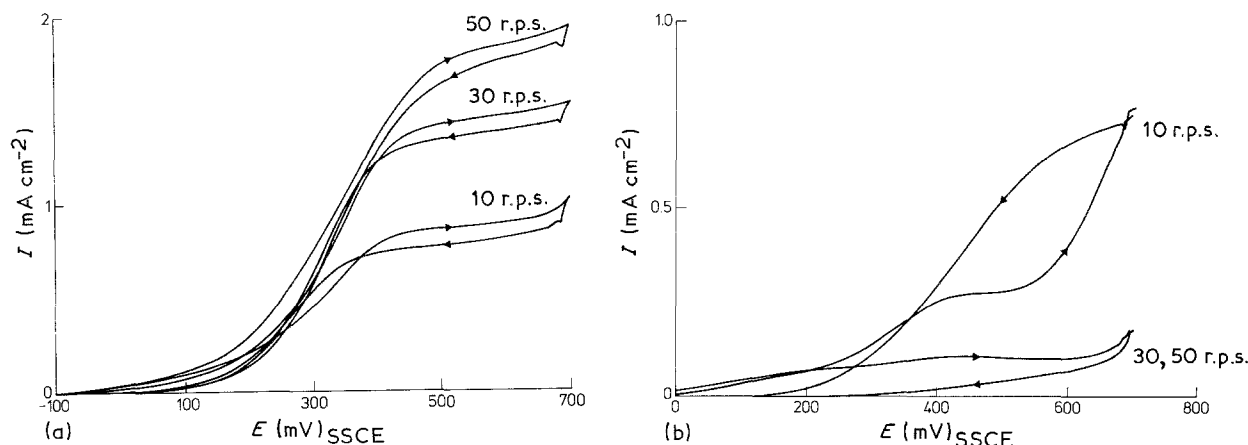


Fig. 4. The effect of rotation speed on the oxidation of pyrite in 1 M NaClO₄, pH = 11. (a) First scan, run on a freshly polished electrode. (b) Second scan. Sweep rate = 20 mV s⁻¹. The rotation speed is indicated in the figure.

This indicates an irreversible one electron transfer reaction as rate determining in this potential region. In Fig. 4b the second scan in the series are plotted as a function of rotation speed. It is evident that upon oxidation a surface film is formed, which influences the subsequent oxidation in this region. A passivated pyrite electrode was removed from the electrochemical cell and washed in acidic solution, in order to dissolve the iron hydroxide product layer, Fig. 5. The oxidation after the acid treatment is less inhibited, indicating that the passivating layer contains iron hydroxide. The fact that the inhibition is preserved suggests that the surface still contains inhibiting species like sulphur or a metal deficient sulphur layer. Similar results have been obtained with arsenopyrite [27].

In Fig. 6 the effect of sulphide ions on the voltammetry of pyrite is shown. As the oxidic species are reduced an iron sulphide is probably formed, which does not reduce further to elemental iron, to the same extent as pyrite. Thus the peak corresponding to the oxidation of iron (I) is almost absent and also the oxidation of iron hydroxide is largely diminished. The deposition of sulphur seems to be complex and probably overlaps with the oxidation of the iron sulphide formed during the reduction. At more positive

potentials the voltammogram looks much the same as in the absence of hydrosulphide ions in solution.

3.3. Collectorless flotation

A series of flotation tests were performed with freshly ground pyrite. It was found that in the absence of other agents, pyrite did not show any floatability. In the presence of EDTA, however, pyrite shows good floatability. This is in agreement with the results reported by Shannon and Trahar [33]. In Fig. 7 the flotation recovery of two size fractions of pyrite as a function of pH and in the presence of 5×10^{-4} M EDTA is shown. It can be seen that there is a pH range where a maximum flotation recovery is achieved for both size fractions. The difference of the maximum flotation recovery between the two size fractions can be explained as an effect of the particle size. In Fig. 8 the flotation recovery of pyrite and the total iron concentration in the pulp are shown as a function of the EDTA concentration. It can be seen that even for very low concentrations (1.0×10^{-5} M) of EDTA a considerable amount of pyrite will float. Note that the actual floatability of pyrite may be higher, since a certain number of large particles have settled at the bottom of the flotation cell. However, in the presence of very high concentrations of EDTA, the flotation of

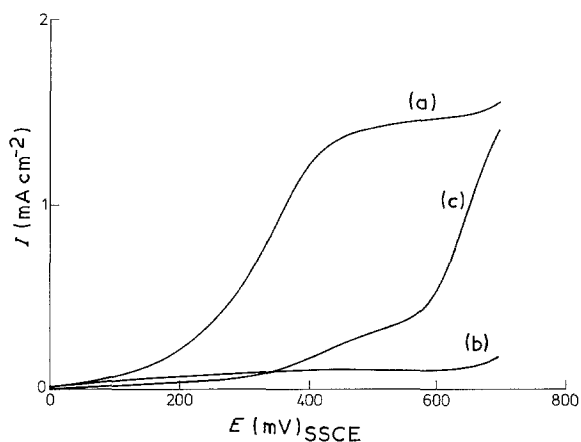


Fig. 5. The effect of acid treatment of a passivated pyrite electrode. (a) First scan, run on a freshly polished electrode. (b) Second scan. (c) After treating the electrode with 1 M perchloric acid for two minutes. Sweep rate = 20 mV s⁻¹ and rotation speed = 30 r.p.s.

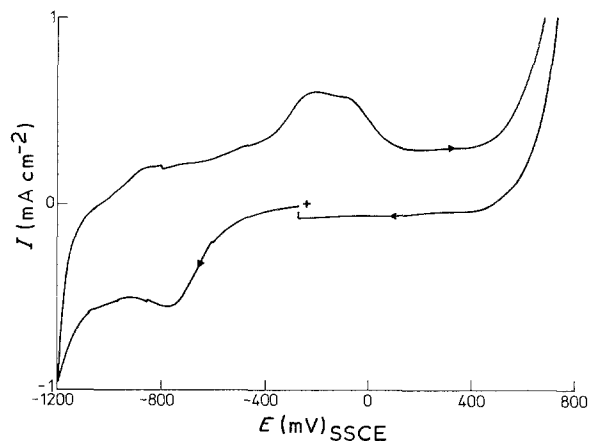


Fig. 6. The effect of hydrosulphide ions (1 mM) on the electrochemical behaviour of pyrite in 1 M NaClO₄, pH = 11. Sweep rate = 20 mV s⁻¹ and rotation speed = 30 r.p.s.

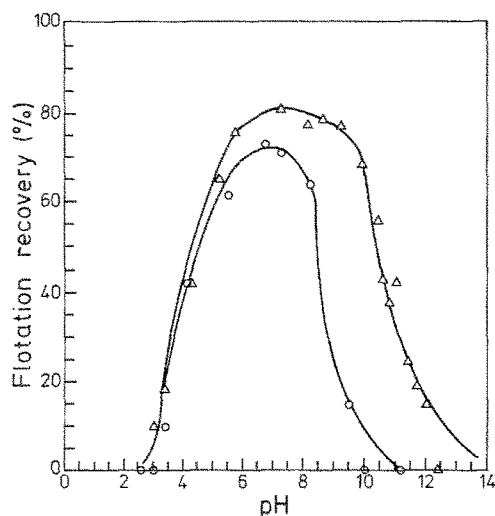


Fig. 7. Flotation recovery of pyrite as a function of pH in the presence of 5×10^{-4} M EDTA. No frother. Conditioning time 5 min. Flotation time 5 min. (O) $-120 + 75 \mu\text{m}$; (Δ) $-75 + 40 \mu\text{m}$.

pyrite reduces. The total iron concentration was shown to be a linear function of the EDTA concentration. The results are similar to those obtained for arsenopyrite [27].

4. Discussion

4.1. Open circuit potential

The reproducibility of the rest potential and the voltammetric sweep is very good if the same electrode is used. However, changing to another pyrite specimen also changes the rest potential and the first reduction scan. We found that for some pyrite electrodes hardly any iron hydroxide was formed on the surface during the pre-treatment procedure. This difference might be due to exposure of different crystallographic planes or to differences in the stoichiometry and impurity content of the various pyrite samples.

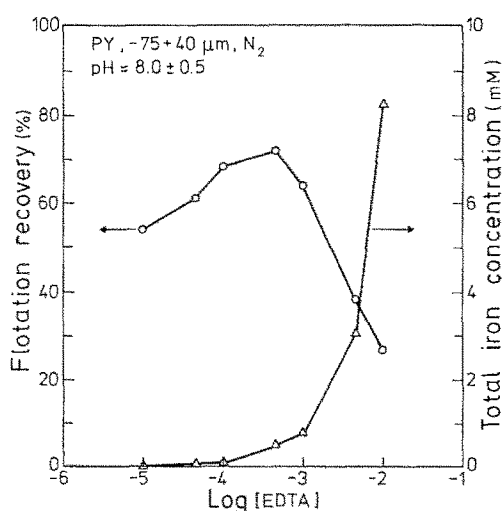


Fig. 8. Flotation recovery and the total iron concentration in the pulp as a function of the concentration of EDTA. (O) recovery; (Δ) iron concentration.

4.2. Cyclic voltammetry

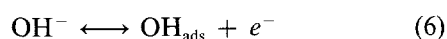
The voltammetry of pyrite in alkaline solution is very complex with several competing reactions that are not well separated. In the initial stage of oxidation a current appears, which depends on the mass transport conditions in solution. The value of the limiting current corresponds to a millimolar concentration of the soluble species. In order to explain this mass transport limiting process let us first consider the anodic dissolution of pyrite. It is generally agreed that the dissolution of pyrite in alkaline solution can be expressed by the overall Reactions (3) and (4). Iron (III) hydroxide is precipitated on the surface and no solution soluble species are indicated. In order to explain the mass transport limiting current we have to assume that either a soluble Fe(II) or Fe(III) species is formed when pyrite is oxidized. However, according to the thermodynamics of the hydrolysis of iron ions [34] at pH = 11 the maximum concentration available will be in the order of $1 \mu\text{m}$ for an Fe(II) species and several order of decades lower if a soluble Fe(III) species is assumed. This is of course true only at equilibrium and it might be possible that a meta stable substance can be formed in close vicinity of the electrode. Furthermore it is well known that super saturation is possible due to nucleation difficulties.

The mass transport process can, however, also be explained by the oxidation of hydroxyl ions in solution. A similar explanation has been given by Meyer [7]. He concluded that the limiting current was directly proportional to the hydroxyl ion concentration for the two pH values used (11 and 12). Thermodynamically it would be possible to have hydroxyl ion oxidation in the actual potential region, but comparing with other materials it seems somewhat unrealistic. For example Arvia *et al.* [31] reported the oxidation of hydroxyl ions on iron hydroxide, which was precipitated on a platinum electrode. The oxidation starts at about 0.9 V (with respect to SHE) and becomes diffusion limited at higher potentials. Similar results were obtained for the oxygen evolution reaction from OH^- at a nickel hydroxide covered platinum electrode [32]. Assuming a mass transport limiting oxidation of OH^- means that the surface concentration of OH^- is zero in that potential region. Thus the pH at the electrode is not defined. From the bulk solution through the diffusion layer a gradual decrease in the pH will appear as a function of the distance from the electrode. Outside the well defined diffusion layer the pH will be the same as in the bulk of the solution. Arvia *et al.* [31] also discussed the local decrease in pH as the oxidation of hydroxyl ions became diffusion limited, and attributed certain effects to this decrease in pH.

For the dissolution of pyrite a simultaneous oxidation of hydroxyl ions and dissolution of pyrite might facilitate the formation of soluble iron species close to the electrode surface. The oxygen evolution in alkaline solution is an electrocatalytic process, which is highly dependent on the material of the working electrode. Bright nickel is one of the most efficient

materials for this reaction [35]. However, upon oxidation the nickel electrode passivates and the oxidation of hydroxyl ions takes place at higher anodic potentials. Nickel hydroxide is a good electrocatalyst for the oxygen evolution in alkaline solution and the potential is about 0.6 V (with respect to SHE) at pH 12 [36]. On pyrite however, the oxidation starts at about 0.4 V (with respect to SHE) and thus this material seems to be a good electrocatalyst for the oxygen evolution in alkaline solutions. It is also well known that pyrite is a good electrocatalyst for the oxygen reduction reaction [37–39]. Even though the oxidation of hydroxyl ions seems to be unrealistic in the actual potential region a better explanation cannot be given at the present time, since the formation of soluble iron species of mM concentration is unlikely at the pH value used. Further studies are in progress in which a RRDE will be used to investigate the possibility of forming soluble iron species.

The oxidation has the properties of an irreversible one electron transfer reaction (Tafel slope 120 mV), which suggests that the rate determining step is the discharge of the hydroxyl ion



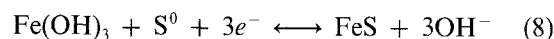
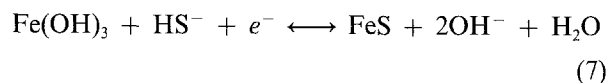
However, the coverage by OH_{ads} is low, since the current becomes mass transport controlled at high overpotentials. Upon adsorption of hydroxide the formation of iron hydroxide is probably facilitated. On the subsequent sweeps this oxidation reaction is largely inhibited, Fig. 5, suggesting that the surface composition changes during the potential cycling. The inhibition efficiency is dependent on the mass transport conditions. As the rotation speed is diminished the inhibition is not so severe, Fig. 4b. Also if the potential is raised into the region where sulphur and sulphide are oxidized to sulphate, the electrode becomes largely activated. In Fig. 4a a difference in the limiting current is observed, depending on the direction of the sweep. This can be explained by a parallel oxidation of pyrite and hydroxyl ions. When the latter oxidation is inhibited on the subsequent sweeps, the slight oxidation of pyrite is observable. This process seems to be unaltered by the potential cycling of the electrode.

At high anodic potentials pyrite is oxidized to sulphate and a large increase in the current occurs. This process seems not to be influenced by the pre-history of the electrode. For example, upon oxidation in the presence of hydrosulphide ions, deposition of sulphur will take place. This sulphur layer does not seem to alter the oxidation characteristics at high overpotentials (VII). This indicates that the oxidation process takes place on a sulphur rich surface and that the formal charge, whether elemental sulphur or metal deficient sulphur layer, has minor significance. Upon oxidation some iron hydroxide precipitates on the surface, but does not seem to inhibit the further oxidation of pyrite. This was also found by AC impedance measurements on pyrite [28].

The reduction of the iron hydroxide and the sulphur

species formed on the surface largely overlap and are difficult to separate. The increase in the cathodic current on subsequent sweeps, Figs 2 and 3, can thus be attributed to both reduction reactions. Peak (I), attributed to the iron oxidation, is also enhanced during cycling, indicating a larger extent of iron hydroxide. The oxidation of iron takes place in the presence of a small amount of hydrosulphide ions, formed during the reduction, and at least at the stationary electrode the formation of FeS is possible [32]. In the presence of hydrosulphide ions in the solution, peak IV also contains a contribution from the deposition of elemental sulphur on pyrite. This agrees well with the studies of Woods *et al.* on the oxidation of hydrosulphide ions on gold and sulphide minerals [23, 40, 41].

An interesting point is that in the presence of hydrosulphide ions (1 mM), the iron oxidation peak (I in Fig. 2) is absent, Fig. 6. This indicates that upon reduction of iron hydroxide and the surface sulphur species an iron sulphide is formed according to Equations (7) and (8), which is not reduced further to elemental iron in the potential region is used in this study.



4.3. Collectorless flotation

From the above electrochemical results, it can be concluded that the initial oxidation of pyrite produces a sulphur rich surface and an iron hydroxide species. It is obvious that the surface will be covered, more or less with hydrophilic species upon grinding. Therefore no significant flotation occurs in the absence of a collector. When EDTA is added to the pulp, it reacts with the iron hydroxide on the pyrite surface, to form soluble Fe(III)-EDTA complexes [42]. These species are dispersed into the bulk solution during conditioning. The pyrite surface is thus cleaned of hydrophilic substances and collector-less flotation is readily obtained. The adsorption of EDTA on iron oxides has been studied by several research groups [43–46]. They found that EDTA is strongly adsorbed on iron oxide in acidic solutions, but that the adsorption decreases with increasing pH and becomes negligible above pH 8. In the pH range 6–11, a considerable dissolution of iron oxide was observed. The maximum dissolution range was found to be dependent on the nature of the iron oxide. However, if an excess of EDTA is added, EDTA continues to leach the mineral itself. The sulphur layer is then destroyed and thus the flotation recovery decreases. Thus it can be concluded that the adsorption of EDTA or iron-EDTA complexes on the pyrite surface in acidic solutions can cause the depression, while the good floatability of pyrite achieved in the pH range 6–11 can be explained by the removal of hydrophilic metal oxide overlayers by EDTA, thus exposing a hydrophobic sulphur-rich layer to the solution.

The good floatability for pyrite shown above and for arsenopyrite as well as for other minerals [33] induced by the addition of EDTA, suggests that the role of conventional collectors needs to be re-examined, at least in some aspects. It has also been shown by Heyes and Trahar [47] that pyrite and pyrrhotite can be equally effectively induced to float by the addition of sodium sulphide as by xanthates. Note that xanthate, sulphide and EDTA differ completely in their chemical structures. It is thus believed that the most important role of all these chemical reagents is to counteract or remove the hydrophilic effects of iron hydroxide and other metal hydroxides that are produced during crushing and grinding. Electrochemically, the effect of hydrosulphide ions was shown to be a reduction of the iron hydroxide to an iron sulphide of unknown composition, most likely some kind of FeS. Thus the subsequent oxidation will be the same as for pyrrhotite, which is in agreement with the flotation measurements [33].

5. Conclusions

(i) The initial oxidation of pyrite takes place parallel to the oxidation of hydroxyl ions. This probably facilitates the formation of iron hydroxide on the surface.

(ii) The oxidation of pyrite at high overpotentials seems to be independent of the pre-history of the electrode, for the example whether elemental sulphur has been deposited on the surface prior to the oxidation or not.

(iii) Collector-less flotation of pyrite can be obtained by addition of a complexing agent such as EDTA. This suggests that the hydrophobic species, necessary for flotation, is a sulphur rich layer.

6. Acknowledgements

The authors would like to express their thanks to the members in the Electrochemistry group in Göteborg for valuable discussions. This work was financially supported by the Swedish National Board for Technical Development (STU).

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