

Passivation of pyrite oxidation with metal cations

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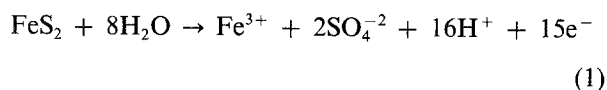
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Under the influence of anodic potentials greater than 0.5 V against SCE (saturated calomel electrode), pyrite slurried in acidic electrolytes is oxidized to water soluble ferric and sulphate ions. Experiments were conducted in a stirred Pyrex reactor provided with three electrodes, the anode being a platinum mesh. The rate of reaction of pyrite corrosion was observed to increase with electrolysis time. The autocatalytic reaction is brought about by the ferric ions produced during the course of the reaction. The rates of reaction, however, can be depressed by adding small quantities of copper and silver ions (both of these have lower redox potentials than that of the $\text{Fe}^{2+}/\text{Fe}^{3+}$ couple) to the electrolyte. It is suggested that addition of these cations results in the formation of an electrochemically inactive sulphur layer on the surface of pyrite particles.

1. Introduction

Pyrite, FeS_2 , is the most common of all sulphide minerals. It is frequently present in base metal sulphide deposits, in sulphide concentrates (generally as an impurity) produced by the grinding and flotation of sulphide ores, in the discarded overburden of open base metal mining operations and in coal [1]. In the USA it is estimated that the wet cleaning of over 300 million tons of coal per year leaves behind aqueous slurries of refuse containing at least 10 million tons of pyrite and some carbonaceous material. Thus pyrite oxidation is a common process in the mining and coal cleaning industries. Oxidation of pyrite results in sulphuric acid and ferric hydroxide formation in mine drainage waters, and this can present significant environmental problems [2, 3].

Although pyrite is not a very good electrical conductor, its oxidation is usually described in terms of electrochemical corrosion mechanisms developed for metals. Peters and Majima [4] studied the anodic dissolution of pyrite electrodes in 1 M HClO_4 and found a short ($\sim \frac{1}{2}$ to 1 decades) Tafel region of slope 130–160 mV, depending on the pyrite electrode history. Furthermore, product and coulometric analyses at anodic current density of 1 mA cm^2 and a potential of 1.05 V against SCE (saturated calomel electrode) indicated that the only electrode reaction is:



Anodic polarization studies of pyrite have also been reported by several investigators [1, 5–8]. Nagai *et al.* [9] studied pyrite electrochemically at elevated temperatures (up to 175°C). In another paper [10] they related the relative rates of elemental sulphur and sulphate formation from pyrite. Biegler *et al.* [11–13] found that the sulphate route (Equation 1) dominates

over the potential range accessible at ambient temperatures; and that sulphate yield increases with the potential and is independent of temperature at fixed potentials. They concluded that elemental sulphur is not an intermediate in the sulphate route. All the studies cited above were carried out at pyrite electrodes. In a recent paper Lalvani *et al.* [14] have utilized pyrite slurries as depolarizing agents for water in the production of hydrogen gas. We report in this paper, the results of the addition of certain cations of metals that result in the passivation of the oxidation of pyrite slurries.

2. Experimental procedure

Pyrite samples in the form of discs were obtained from the Franklin mine in Southern Illinois. The samples were ground, sieved and then dried in vacuum at 40°C for 12 h. Pyrite characterization by X-ray diffraction spectroscopy revealed over 99.9% sample purity with traces of aluminium. Aqueous electrolytes were prepared with Fisher analyzed reagents.

Pyrite slurries were electrolysed in stirred cells made of Pyrex. Three electrolysis cells with similar designs but different volumetric capacities were used. The large electrolysis cell has a volume of 500 ml, while the two smaller cells have a capacity of 175 ml each. A typical stirred electrolysis cell shown in Fig. 1 is divided into two parts: (i) The working electrode (anode) compartment where the pyrite is kept in suspension in an electrolyte by a magnetic stirrer. The anodes used in the study were made of platinum gauze supplied by Fisher Scientific Co. The anode compartment is also provided with a saturated calomel electrode. A thermometer is inserted in the electrolyte. (ii) The counter electrode (cathode) compartment is separated from the working electrode by a porous glass frit that confines the pyrite particles to the anode compartment. The cathode is a platinum mesh

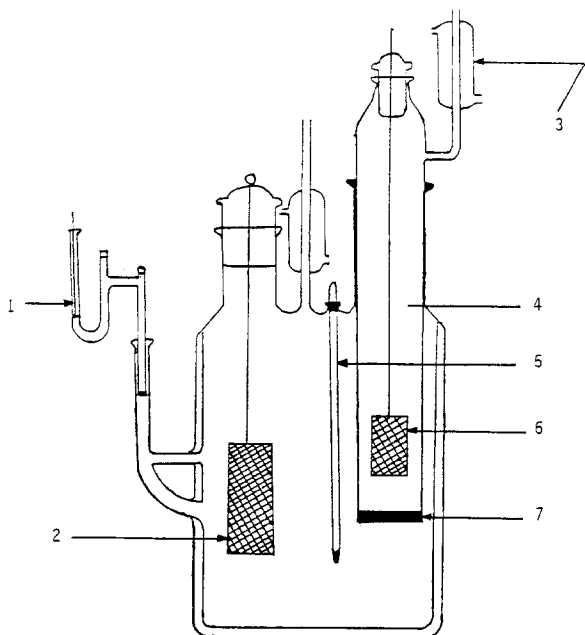


Figure 1 Pyrite electrolysis cell. 1, Calomel reference electrode; 2, working electrode; 3, condenser; 4, cathode compartment; 5, thermometer; 6, counter electrode; 7, frit.

electrode. Both anode and cathode compartments are provided with glass condensers through which the gases from the cell are collected separately. A hot water circulator provided with a temperature controller circulates water heated in a water bath through the glass jacket of the electrolysis cell.

Pyrite samples were first contacted with an electrolyte under nitrogen and brought to the desired temperature of reaction. Initial contact between the acid and pyrite produces H_2S gas. Contact between 15 g of pyrite with 400 ml of 1 M HCl at $60^\circ C$ released up to 36 ml of H_2S in 6 h. After about 5 to 7 h of contact between the acid and pyrite, H_2S production was observed to cease completely. A constant positive electrode potential was then applied to the cell using a PAR 371 potentiostat. The gases produced were collected and analysed by gas chromatography.

After electrolysis, the remaining pyrite slurry was filtered. The solid pyrite residue was washed several times with distilled water and then dried in a vacuum oven at $40^\circ C$ for 12 h. Experimental details are provided elsewhere [14].

3. Results and discussion

Fig. 2 shows a typical relationship between the corrosion rate and time of electrolysis for pyrite slurries oxidized anodically at a potential of 0.8 V against SCE and $60^\circ C$. The rates of reaction are observed to be somewhat low at the beginning of electrolysis. However, the rates increase monotonically with the time of electrolysis. This constant increase in the anodic current suggests that the reaction may be autocatalytic. We believe that ferric ions generated via Equation 1 catalyze pyrite oxidation. Chemical oxidation of pyrite by ferric ions is well known [15]. A straight-line relationship between the amount of hydrogen gas collected at the cathode and time of electrolysis is observed in Fig. 3. The following reaction chemistry is

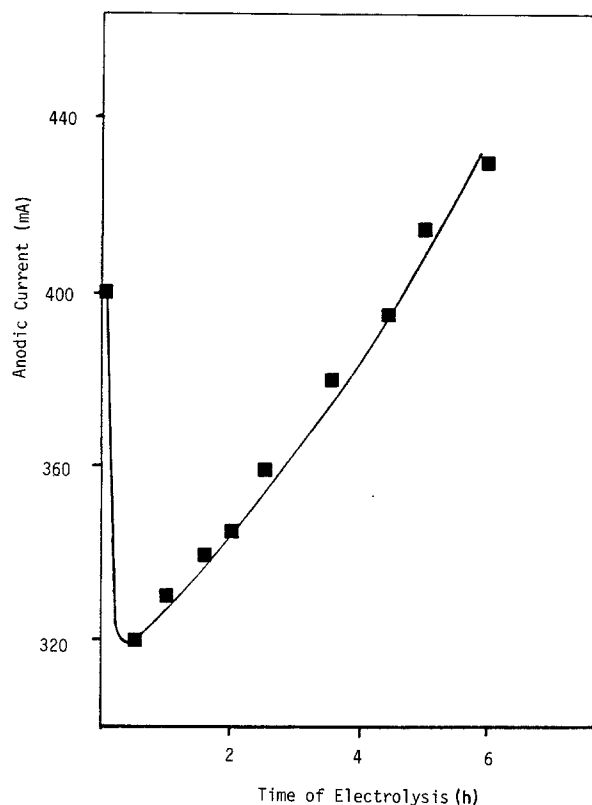


Figure 2 Current against time of electrolysis. 15 g of pyrite (106 to 125 μm) were electrolysed in 400 ml of 1 M HCl on 19.5 cm^2 Pt mesh anode at an applied potential of 0.8 V against SCE and $60^\circ C$.

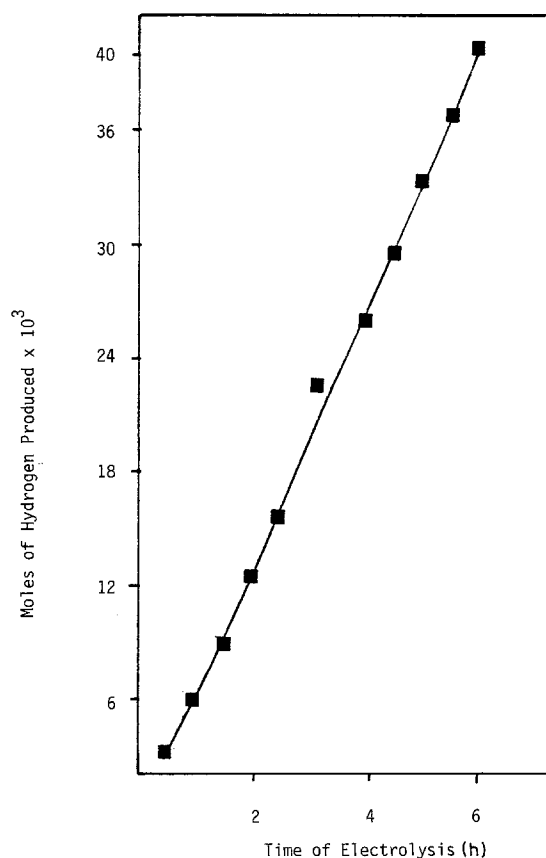


Figure 3 Hydrogen evolution against time of electrolysis. Experimental conditions as in Fig. 2.

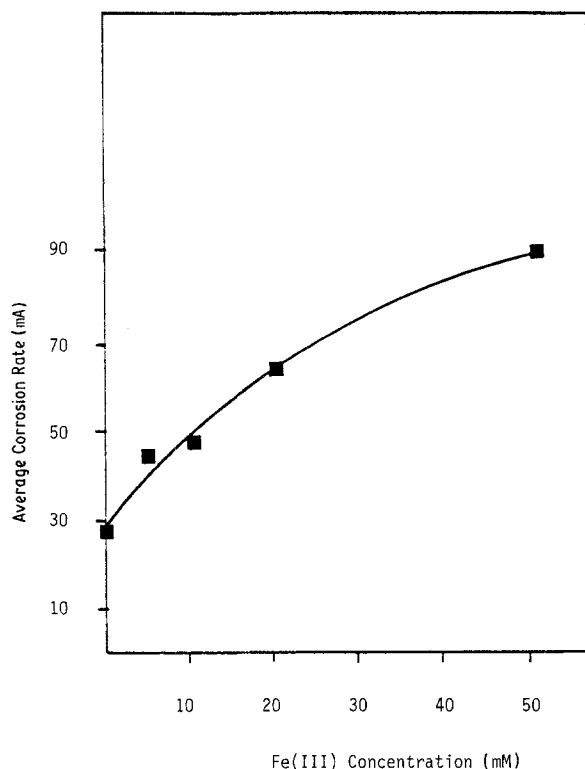


Figure 4 Average corrosion rate (mA) against Fe^{3+} concentration. 5.625 g of pyrite (106 to 125 μm) were electrolysed in 150 ml of 1 M HCl on 4 cm^2 Pt mesh anode for 3 h at an applied potential of 0.8 V against SCE and 60°C.

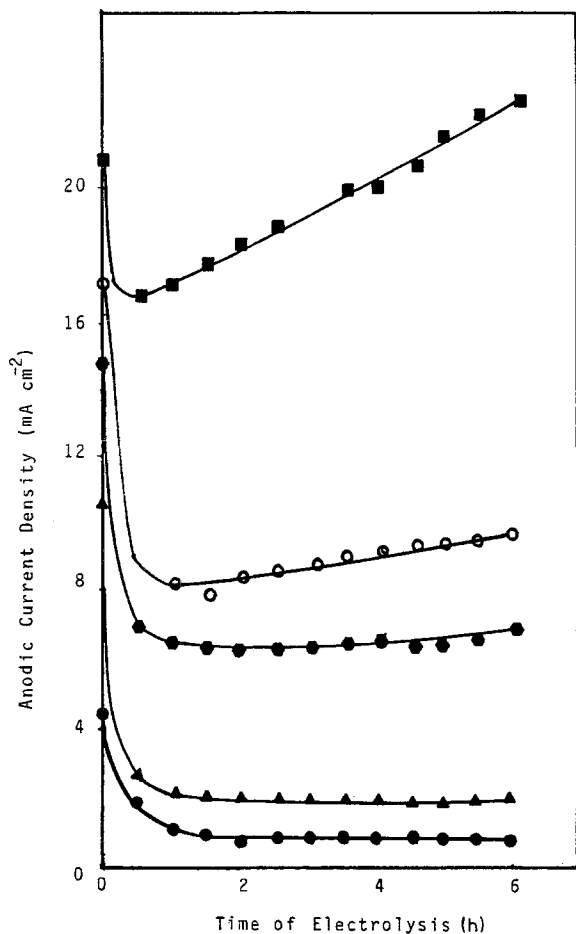
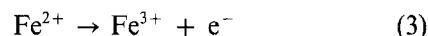
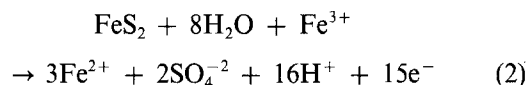


Figure 5 Influence of temperature on anodic current. 0.0375 g ml^{-1} of pyrite (106 to 125 μm) in 1 M HCl were electrolysed at 0.8 V against SCE using a Pt mesh of 19.5 cm^2 as a feeder anode. (●) 25°C; (▲) 30°C; (★) 45°C; (○) 50°C; (■) 60°C.

believed to occur in our experiments:

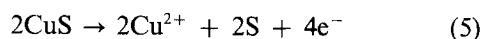
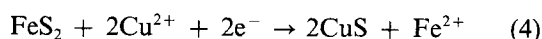


Ferrous ions produced via Equation 2 undergo further oxidation at the electrode to regenerate ferric ions (since in our experiments the electrode potential was kept more positive than the redox potential of $\text{Fe}^{2+}/\text{Fe}^{3+}$). Thus during the course of reaction, ferric ion concentration increases and as a result the pyrite corrosion rate increases with the electrolysis time. In one set of experiments, the cation of ferric was added to pyrite slurries prior to electrolysis. The slurries were then electrolysed at a potential of 0.8 V against SCE. The curve of the average corrosion rates (i.e. the average anodic current/total charge passed per unit time) against the concentration of iron added to the electrolyte is shown in Fig. 4. As expected, the rates are found to increase with the ferric concentration.

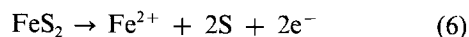
The effects of temperature were studied between 25 and 75°C on 15 g pyrite (106 to 125 μm) stirred in 400 ml of 1 M HCl, with an applied anode potential of 0.8 V against SCE. Fig. 5 shows the effect of temperature on the relationship between anodic current and time. Anodic current density increased with temperature. The rate of current increase was more rapid at higher temperatures. The apparent activation energy for the process, on the basis of temperature dependence of anodic currents, was found to be 61.9 kJ mol^{-1} .

3.1. Influence of Cu^{2+} addition

Fig. 6 shows the effect of the addition of ions of Cu^{2+} on the corrosion rates of pyrite slurries. The rates of reaction are observed to decrease with Cu^{2+} concentration. When no ion is added to the electrolyte, the average rate of reaction over a three-hour period is observed to correspond to approximately 53 mA, however, when Cu^{2+} concentration of 50 mM (milli-moles per litre) is maintained in the electrolyte under identical reaction conditions, the anodic current declines to about 26 mA. We believe that copper, which according to thermodynamic considerations is more electroactive than iron, in the presence of pyrite forms a sulphur layer on the surface of FeS_2 particles. This amorphous sulphur film renders pyrite electrochemically inactive thus resulting in lower corrosion rates. In one experiment, pyrite particles electrolysed with Cu^{2+} were leached with CS_2 to extract the elemental sulphur formed. Re-electrolysis of these particles resulted in essentially the same reaction rates as those obtained from the electrolysis of the pyrite slurries not contacted with Cu^{2+} . Nicol *et al.* [16] in a recent paper described the following chemistry for pyrite electrooxidation in the presence of Cu^{2+} :



with the net anodic process being



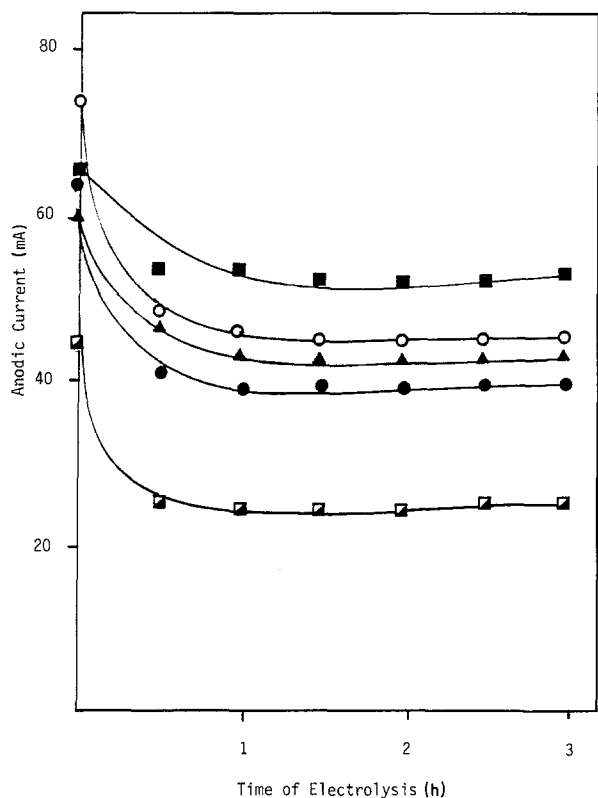
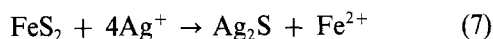


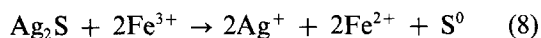
Figure 6 Influence of CuCl_2 addition on corrosion rate. Experimental conditions as in Fig. 4. CuCl_2 concentration (mM): (■) No catalyst; (○) 2; (▲) 5; (●) 10; (◼) 50.

3.2. Influence of Ag^+ addition

Pyrite slurries were electrolysed in 1 M H_2SO_4 (rather than the HCl used in other experiments) to avoid the precipitation of silver chloride upon the addition of silver nitrate. The addition of Ag^+ to the slurry resulted in deposition of a dark blue layer on the pyrite particles. Fig. 7 shows the influence of Ag^+ concentration on the pyrite corrosion rates at an anodic potential of 0.8 V against SCE. The rates of reaction were observed to decrease sharply with Ag^+ concentration. We suggest that formation of the silver sulphide layer on the pyrite particle depresses the rates of reaction. No literature exists on the oxidation of pyrite in presence of Ag^+ , however, guidance may be gleaned from the work on chalcopyrite oxidation by Miller and Portillo [17] who conclusively demonstrated the formation of a blue-black film of Ag_2S which was rendered inactive by ferric ions due to sulphur film formation on chalcopyrites. We believe in our experiments the following reactions take place:



although the surface films (dark-blue) of silver sulphide produced is a good conductor of electricity, the ferric ions (produced by oxidation of ferrous generated via above equation) oxidize the sulphide film and result in the formation of a passive sulphur layer:



Thus, the pyrite surface is completely passivated and the silver ion is regenerated in the electrolyte. More work is in progress on the characterization of sulphur layers formed on pyrite particles, results of which will be published at a later date.

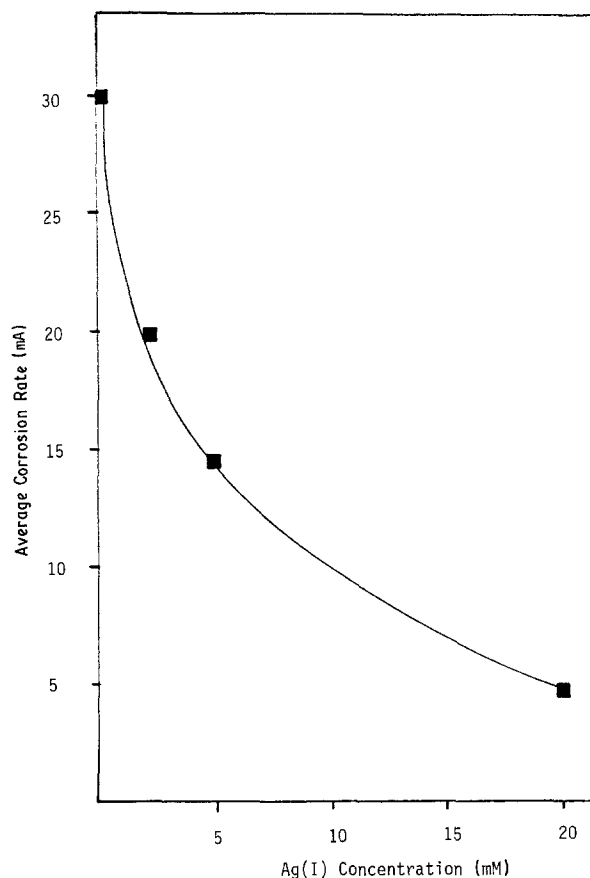


Figure 7 Average corrosion rate (mA) against Ag^+ concentration. 5.625 g of pyrite (90 to 106 μm) were electrolysed in 150 ml of 1 M H_2SO_4 on 4 cm^2 Pt mesh anode for 3 h at 0.8 V against SCE and 60°C.

4. Conclusions

Pyrite slurry electrooxidation results in dissolution of pyrite at the anode via autocatalytic reaction pathways. The rate of corrosion is enhanced by iron, however, the pyrite particles can be rendered electrochemically inactive by adding very small quantities of the metal cations of Ag^+ and Cu^{2+} to the supporting electrolytes. Passivation of the electrochemical oxidation of pyrite by addition of the metal cations with redox potentials less than that of the $\text{Fe}^{2+}/\text{Fe}^{3+}$ couple, is brought about by the formation of sulphur layer on pyrite particles. The maximum passivation of the oxidation of pyrite was accomplished by addition of Ag^+ to the pyrite slurry. One of the notable advantages of the process is that there is no net consumption of Ag ions.

Acknowledgements

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