

Electrodissolution of synthetic covellite in hydrochloric acid

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A systematic study has been undertaken to investigate the anodic dissolution characteristics of impure commercial and synthetic covellite. It has been observed that the dissolution is strongly influenced by the pH and chloride concentration and also shows a typical active-passive type of behaviour with production of elemental sulphur. The rate of the dissolution process is accelerated by the formation of a CuCl_2 complex at high chloride concentrations whereas at lower concentrations of hydrochloric acid the electrochemical oxidation to sulphate is predominant.

1. Introduction

Details about the leaching of CuS are given by Thomas and Ingraham [1], and Dutrizac and MacDonald [2]. They discuss the leaching of covellite in ferric sulphate solutions acidified with sulphuric acid. These authors worked with natural and synthesized copper (II) sulphide discs and found that CuS is oxidized by Fe^{3+} ions in the chemical reaction: $\text{CuS} + 2\text{Fe}^{3+} \rightarrow \text{Cu}^{2+} + \text{S} + 2\text{Fe}^{2+}$. The sulphur is preferentially produced at selected areas of the electrode surface in an amorphous form. A tendency to form pits has also been observed. The rate of covellite dissolution increases with increasing disc porosity which influences the pit propagation mechanism for dissolution. The sulphur produced is not found to build up as a protective layer at the electrode surface and, therefore, linear kinetics of dissolution have been observed. However, it has been mentioned that the CuS dissolution kinetics in oxygenated sulphuric acid have a parabolic form as a result of sulphur blockage [3, 4].

The published data on the electro-oxidation of CuS concerns mostly the experiments conducted in a sulphuric acid medium. Etienne [5] studying the behaviour of covellite (83% relative density)

anodes by galvanostatic polarization with current densities below 2.26 mA cm^{-2} has shown that in sulphuric acid CuS is oxidized by the reaction: $\text{CuS} \rightarrow \text{Cu}^{2+} + \text{S} + 2\text{e}^-$. As a result of this reaction, orthorhombic sulphur forms a fine porous network on the surface of the disc. A large increase in anodic potential after some period of polarization with current densities greater than 2 mA cm^{-2} has been observed by Etienne [5]. According to Peters [6] the polarization observed at low current densities is due simply to the concentration polarization whereas for high current densities it is a result of sulphur covering the surface. Koch [7] has also mentioned that the retardation of CuS oxidation may be attributed to the formation of surface films of sulphur. Recently MacKinnon [8] reported a sharp rise in potential after a time lapse accompanied by oxygen evolution. Similar potential rises during galvanostatic polarization of CuS have also been observed by Kato and Oki [9]. Based on the dissolution studies of Cu_2S many [10, 11] authors have proposed that solid state diffusion of copper is responsible for such a potential jump.

It is known that the change from H_2SO_4 to HCl results in a dramatic change of Cu_2S polarization [7]. The anodic behaviour of CuS in hydro-

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chloric acid medium has not yet been established even though this medium is attractive for leaching and electrolysis due to the high solubility of copper (II) chloride and expected low overvoltages associated with Cl^- ions. With this background an attempt has been made to examine the electro-dissolution of copper (II) sulphide in hydrochloric acid as a function of different parameters, for example, HCl and Cl^- concentrations, pH, polarization, oxygen, temperature, porosity and purity of the electrode.

2. Experimental procedure

Two types of copper (II) sulphide have been used. One is a commercial variety supplied by Ventron Corporation (denoted by the symbol V in the text) and the other one was synthesized by us (symbol L). X-ray diffraction analysis of V shows the presence of not more than 3 wt % Cu_7S_4 and L does not show any such impurity. The CuS electrodes were made using the method described by Dutrizac and MacDonald [12] in which sulphur (at 450°C) is allowed to distil slowly over pre-reduced copper (at 450°C) under vacuum. Once the distillation was finished, which takes approximately 48 h, the synthetic CuS was slowly cooled at a rate of 25°C per day. After cooling to room temperature it was powdered and pelletized using hydrostatic or mechanical compression techniques. The highest pressure applied was 1.23 GPa. This enabled us to produce electrodes of relative densities from approximately 82 to 96%. The electrodes used here were of 92 to 96% relative density unless mentioned otherwise. The electrical contacts were made by soldering a copper wire to the copper or silver print applied on the surface of the electrode. Only one face of the electrode was exposed to the solution, the remainder was embedded in epoxy resin. The electrodes are polished successively on emery papers from 240 to 600 grit followed by a final polishing on a diamond paste of $1\ \mu\text{m}$. The electrodes were then thoroughly cleaned with distilled water.

Pure copper foil was supplied by Fisher Scientific Company and 99.999% pure sulphur was supplied by Cerac Pure Inc. The chemicals used in these studies were of Baker Analytical grade quality. The gases (O_2 and Ar) used were of zero

grade quality supplied by Air Products Inc. A Tacussel PRT 20-2X potentiostat with a PAR 175 programmer was used for electrochemical studies. A graphite auxiliary electrode and a saturated calomel reference electrode were used. The Orion chloride 94-17A and copper ion selective electrodes (prepared at the University of Warsaw [13]) were used for the analysis of chloride and/or copper ion concentrations, and a Perkin-Elmer 603 Atomic Absorption Spectrometer was used for copper ions. A Philips X-ray diffractometer was used for X-ray diffraction analysis and a Hitachi Model S500 scanning electron microscope for SEM studies. The temperature was controlled by a thermostat ($\pm 1^\circ\text{C}$). The solutions were purged with the appropriate gas for 1 h before each experiment and then during the experiments. Magnetic agitation of the electrolyte was used except for cyclic voltammetric studies.

3. Results

3.1. Potentiodynamic studies in $1\ \text{mol dm}^{-3}$

The potential-sweep curves for electrode V with various scan rates are shown in Fig. 1. At all scan rates the shape of the curves is the same with a parabolic part coupled with a potential independent current plateau at higher polarization. It is found that there is a linear correlation between the peak current density and square root of the scan rate. The successive voltammetric curves are presented in Fig. 2. This shows a clear decrease in current in the positive going sweep of each subsequent cycle. The cathodic half cycles show no distinct peaks. It is observed by scanning electron microscopy that even after one anodic polarization amorphous sulphur is formed on the electrode surface (Fig. 3). Energy dispersion analysis confirmed the presence of sulphur.

The potentiodynamic curves for CuS having different porosities were studied. It is found that the higher the porosity, the higher the accompanying anodic dissolution current. However, the curves are generally of the same shape. The peak current is doubled from 96 to 86 relative density of the electrode and that of 86% is almost doubled again when the relative density dropped to 82%. The parabolic aspect of the anodic curve and the active-passive behaviour are very clear

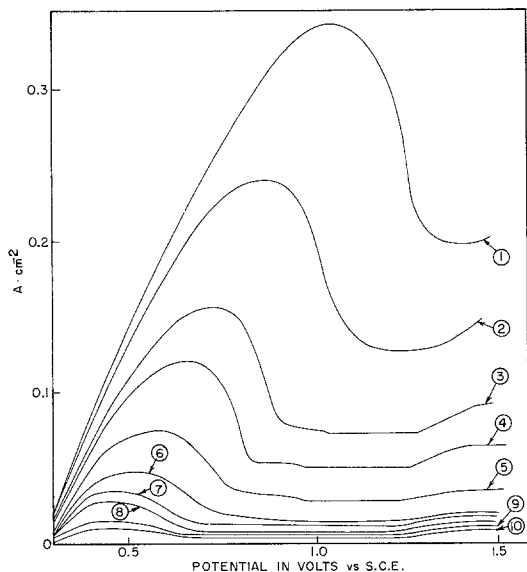


Fig. 1. Potentiodynamic curves for electrode V in 1 mol dm⁻³ HCl. Scan rates: 1. 100 mV s⁻¹; 2. 50 mV s⁻¹; 3. 20 mV s⁻¹; 4. 10 mV s⁻¹; 5. 5 mV s⁻¹; 6. 2 mV s⁻¹; 7. 1 mV s⁻¹; 8. 0.5 mV s⁻¹; 9. 0.2 mV s⁻¹; 10. 0.1 mV s⁻¹.

and nearly the same for electrodes with relative densities of 92 and 96% [14]. The change of HCl concentration has a great impact on the cyclic voltammetric behaviour of CuS as shown by Fig. 4. At lower HCl concentration (10⁻² mol dm⁻³) the current density diminishes whereas with 10⁻¹ mol dm⁻³ the perfect parabolic behaviour mentioned previously is observed showing a significant increase in the dissolution of CuS. It could be added that for 1.0 mol dm⁻³ of chloride ions in solution, the dissolution rate (Fig. 5, curve 2) is smaller than in 1 mol dm⁻³ (Fig. 4, curve 1)

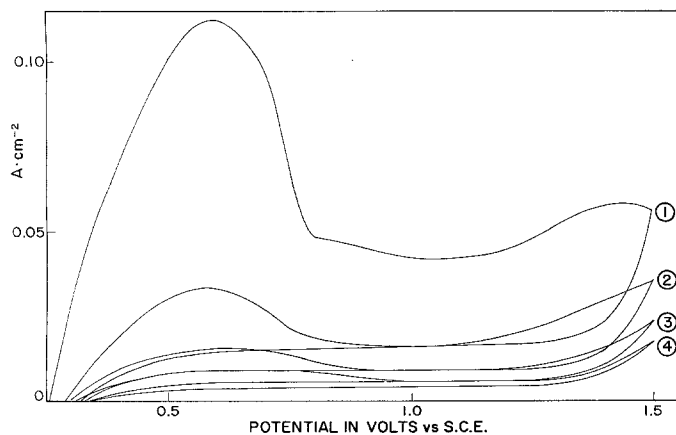


Fig. 2. Cyclic voltammograms for electrode V at a scan rate of 10 mV s⁻¹. 1. First cycle; 2. second cycle; 3. fifth cycle and 4. tenth cycle.

thus indicating a decrease in the attack with an increase in the pH.

The influence of Cu²⁺ on the current-voltage characteristics is studied. As CuCl₂ is added to increase the copper concentration in 1 mol dm⁻³ HCl, a small decrease in the current value is observed although the entire shape of the curve remains the same [14]. With an increase in temperature the rate of dissolution increases, as could be expected. However, oxygen plays a very minor role at lower temperatures, compared with 75°C where there is some increase in the dissolution rate. The results are summarized in Fig. 6.

Apparently the purity of the electrode strongly influences the anodic behaviour of CuS in 1 mol dm⁻³ HCl. Figure 7 (curves 1, 2), shows that the anodic current is smaller for pure synthetic material than for commercial material, which has been found to contain some Cu₇S₄ as an impurity. However, an active-passive behaviour for electrode L is seen on the cyclic voltammetric curves shown in Fig. 8, which are similar to those of V shown in Fig. 2. In 10⁻² mol dm⁻³ HCl the dissolution of both V and L CuS is the same (Fig. 7, curves 3, 4) and does not indicate an active-passive behaviour.

3.2. Current-time studies

The current-time curves were obtained at the peak potential (+0.6 V vs SCE). In 1 and 10⁻² mol dm⁻³ HCl containing 1 mol dm⁻³ KCl the dissolution is far greater at the beginning and decreases with time. In the case of 10⁻² mol dm⁻³ HCl there is very little change in current with time

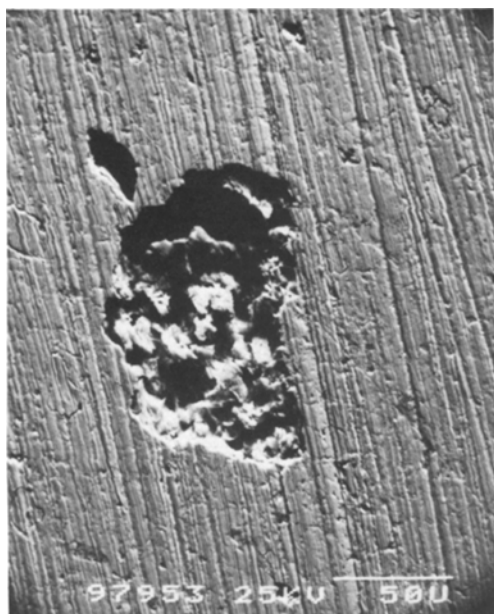


Fig. 3. Scanning electron microscope picture ($\times 272$) of CuS surface after first potentiodynamic half-cycle (anodic) in 1 mol dm^{-3} HCl. Electrode V, scan rate: 10 mV s^{-1} .

and the current at the beginning of the experiment is far smaller compared to the others. The exponential type decay of the current in the first two cases appears to coincide with the formation of elemental sulphur on the surface as confirmed by scanning electron microscopy and energy dispersion analysis. In the last case ($10^{-2} \text{ mol dm}^{-3}$ HCl) elemental sulphur is not found.

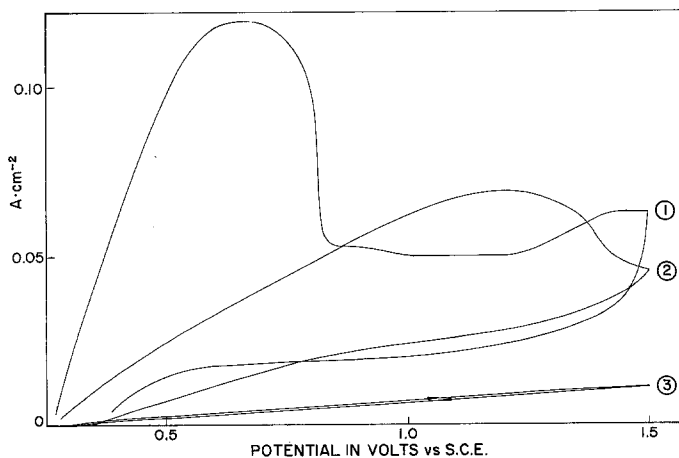


Fig. 4. Influence of HCl concentration on cyclic voltammograms of electrode V at 10 mV s^{-1} ; 1. 1.1 mol dm^{-3} HCl; 2. 0.1 mol dm^{-3} HCl; and 3. 0.01 mol dm^{-3} HCl.

4. Discussion

The potentiodynamic behaviour of CuS in 1 mol dm^{-3} HCl (Fig. 1) indicates an active-passive type of behaviour. As the copper salts associated with the dissolution of CuS in HCl are highly soluble, this passivation behaviour could not be attributed to them. The other main product during the dissolution of CuS is elemental sulphur according to the anodic reaction $\text{CuS} \rightarrow \text{Cu}^{2+} + \text{S}^0 + 2\text{e}^-$. Accumulation of elemental sulphur on the surface of the electrode can reduce the dissolution rate. SEM studies of the electrode surface after anodic polarization indicate the presence of elemental sulphur (Fig. 3). This has been established further by cycling the electrode successively. Figure 2 shows that the peak current diminishes progressively with successive cycling. Such behaviour probably results from the successive formation of a barrier-like film of sulphur imposing transport limitations in the vicinity of the electrode surface.

On analysing Fig. 1 there is almost a linear relationship between the square root of the scan rate and the peak current. This normally suggests diffusion control but there is no clear-cut dependence of the rotation rate (from 250 to 2500 rpm) of the electrode on the electrochemical behaviour of CuS [14], so that the possibility of diffusion control must be ruled out. The linear relationship is due mainly to the irreversible electrochemical reaction of CuS [15].

Theoretical support for the dissolution process could be obtained from the potential-pH diagrams.

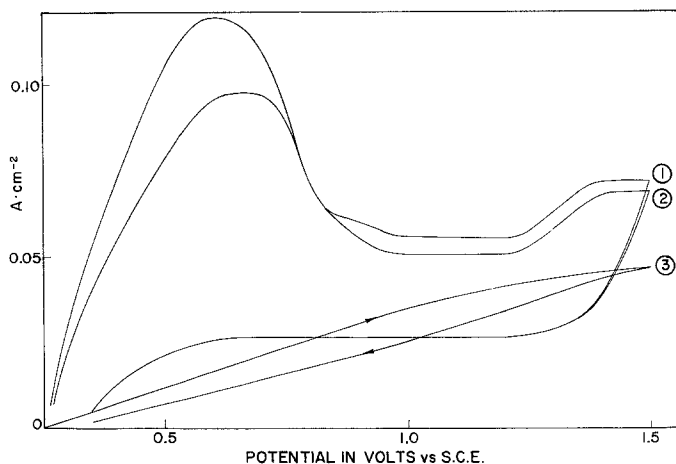


Fig. 5. Influence of hydrogen and chloride ion concentration on the voltammetric behaviour of electrode V at 10 mV s^{-1} . 1. 0.1 mol dm^{-3} + 1 mol dm^{-3} ; 2. 0.01 mol dm^{-3} HCl + 1 mol dm^{-3} KCl; 3. 0.01 mol dm^{-3} HCl + 0.01 mol dm^{-3} KCl.

The potential-pH (E -pH) diagram for the CuS- H_2O system at 25°C has been drawn based on the thermodynamic data in the literature [16] (Fig. 9). This predicts a wide range of pH at low concentrations of copper (II) ions for the dissolution of CuS with the production of elemental sulphur (Fig. 9, solid lines). Only crystalline sulphur formation occurs in this domain.

Amorphous sulphur, which is normally formed during anodic dissolution of CuS, will have a wider range than that calculated here. This possibility has been considered, therefore, in the interpretation of the results. When the concentration of copper (II) ions increases in the vicinity of the interface of CuS the anodic dissolution of this compound would be accompanied by the production of HSO_4^- and/or SO_4^{2-} ions if there was no increase of H^+ concentration in the above region (Fig. 9, dashed lines). This appears to be the case for the

dissolution process in $10^{-2} \text{ mol dm}^{-3}$ HCl as there is negligible formation of elemental sulphur and no active-passive type of behaviour (Fig. 7). However, when KCl is added to $10^{-2} \text{ mol dm}^{-3}$ HCl the active-passive type of behaviour reappears along with the formation of elemental sulphur. This suggests that the concentration of either the chloride ions or the copper ions, or both, strongly influences anodic dissolution. In order to establish the nature of the influence of these two ions on the anodic dissolution of CuS, experiments were conducted separately. Our studies indicate that increasing the concentration of copper (II) ions eventually decreases the dissolution rate. However, as mentioned previously the influence of chloride is more striking (Fig. 5). This can be attributed to the formation of copper (I) chloride complexes. Formation of such complexes is already known [17] and the form-

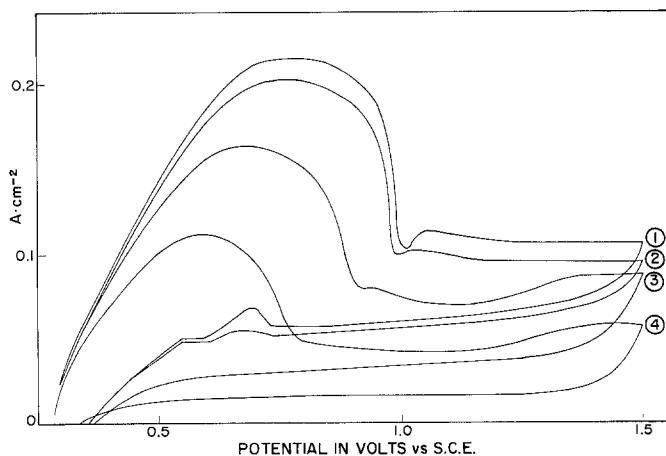


Fig. 6. Influence of temperature and oxygen on voltammetric behaviour in 1 mol dm^{-3} HCl. 1. 75°C , oxygen; 2. 75°C , argon; 3. 50°C , argon (and oxygen); and 4. 25°C , argon (and oxygen). Electrode V, scan rate: 10 mV s^{-1} .

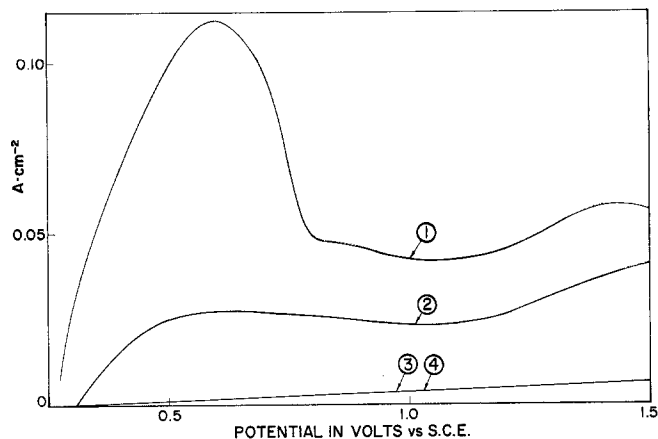
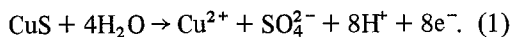
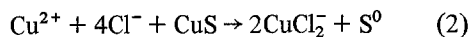


Fig. 7. Potentiodynamic curves for V and L. 1. V CuS in 1 mol dm⁻³ HCl; 2. L CuS in 1 mol dm⁻³ HCl; 3. V CuS in 10⁻² mol dm⁻³ HCl; and 4. L CuS in 10⁻² mol dm⁻³ HCl. Scan rate: 10 mV s⁻¹.

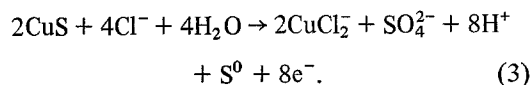
ation of a complex of the type CuCl_2^- having a high rate of formation constant in the following reaction, $\text{Cu}^{2+} + 4\text{Cl}^- + \text{CuS} = 2\text{CuCl}_2^- + \text{S}^0$, would be predicted. In our case formation of such a complex could arise by the same reaction with the copper (II) ions being supplied by the initial anodic dissolution of CuS. Westall *et al.* [17] have reiterated that this reaction could even proceed quantitatively towards the right at high chloride concentrations. This supports the argument about the nature of the influence observed here. Analyses of plots from potentiostatic work along with the measurement of total concentrations of copper ions dissolved during polarization indicates that the following reactions are possible. In 10⁻² mol dm⁻³ HCl alone the main product is the formation of sulphate through the following reaction, as also predicted by the E -pH diagram (Fig. 9):



The efficiency of this reaction has been found from potentiostatic studies to be $85 \pm 3\%$. When KCl is added to 10⁻² mol dm⁻³ HCl to reach a concentration of 1 mol dm⁻³ chloride the dissolution is accelerated through the additional reaction:



and the net reaction could be written as:



Considering this net reaction, the current efficiency, based on potentiostatic studies [14], has been found to be $99 \pm 3\%$.

As mentioned earlier the formation of the complex is always a fast step indicating that Equation 1 is the rate controlling step.

In a similar fashion the dissolution of CuS in 1 mol dm⁻³ HCl could be explained through the

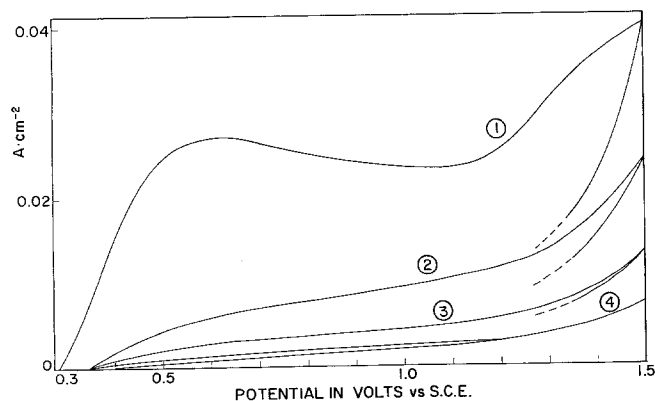


Fig. 8. Cyclic voltammograms of electrode L at 10 mV s⁻¹. 1. First cycle; 2. second cycle, 3. fifth cycle and 4. tenth cycle (cathodic going parts are not fully presented for 1, 2 and 3 to avoid confusion).

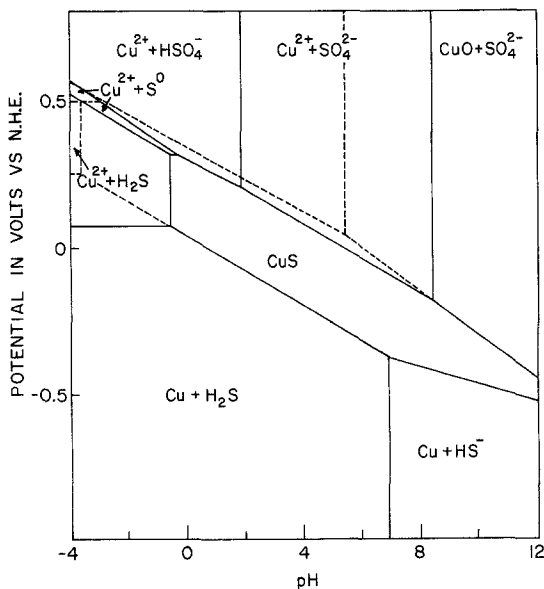
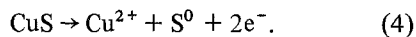
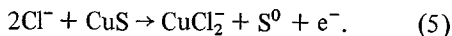


Fig. 9. E -pH diagrams for the $\text{CuS-H}_2\text{O}$ system at 25°C .
 - $[\text{Cu}^{2+}] = 10^{-9} \text{ mol dm}^{-3}$, $[\text{HSO}_4^-] = [\text{SO}_4^{2-}] =$
 $[\text{H}_2\text{S}] = [\text{HS}^-] = 10^{-5} \text{ mol dm}^{-3}$.
 --- $[\text{Cu}^{2+}] = 10^{-3} \text{ mol dm}^{-3}$, $[\text{HSO}_4^-] = [\text{SO}_4^{2-}] =$
 $[\text{H}_2\text{S}] = [\text{HS}^-] = 10^{-5} \text{ mol dm}^{-3}$.

formation of the above complex (Equation 2) with a simultaneous anodic dissolution of CuS as given below:



Such an anodic reaction is predicted from the E -pH diagrams (Fig. 9) at low concentrations of copper (II). The concentration of copper (II) ions is maintained at this low level by continuous fast formation of the complex. The potentiostatic studies show an efficiency close to 100% for the net reaction:



This high efficiency indicates that the reaction of formation of sulphate has not completely disappeared. Also, in the same manner, the reaction for forming sulphur is not excluded from dilute solutions.

Thus it could be mentioned at this stage that the principal product during the anodic dissolution of CuS is elemental sulphur which could, either on its own or coupled with some additional factors, be responsible for the observed active-passive type of behaviour. According to Peters [6], sulphur would normally nucleate and grow heterogeneously to provide porosity and access of the solution to

the covellite surface. But, he continues, at high current densities the sulphur might coat covellite protectively as a passivating process. Since high current densities are obtained in all the experiments reported here (far higher than those reported by Etienne [5] and Peters [6]), galvanostatic experiments were carried out at various current densities ranging from 2 to 300 mA cm^{-2} in a chloride media ($1 \text{ mol dm}^{-3} \text{ HCl}$ or $1 \text{ mol dm}^{-3} \text{ KCl} + 0.01 \text{ mol dm}^{-3} \text{ HCl}$), to compare the results obtained by others in sulphuric acid [5, 8]. No such abnormal increase in potential has been observed by us [18] even at the highest current density tried. However, it should be added that at 300 mA cm^{-2} with electrode V, there was a substantial increase in the voltage (8–9 V) after 20 min of polarization but it remained steady at this value during further polarization. It is possible that the mechanism of the passivation in chloride medium may not only be due to the formation of elemental sulphur but also due to some additional factors. Two causes, pore diffusion and stoichiometric changes at the active sites, can be considered for their effective role played in the passivation process. In the pore diffusion model the rate limiting process is the diffusion of copper or copper chloride complex dissolved in the electrolyte which fills the pores and cracks in the reaction products. This porosity is a result of the shrinkage accompanied by the dissolution of CuS in the reaction $\text{CuS} \rightarrow \text{Cu}^{2+} + \text{S}^0 + 2\text{e}^-$ (24 vol %). If there is a blockage of the above diffusion due to some changes in stoichiometry (to be discussed below) at the active site-electrolyte interface, especially at the bottom of the pores, this will influence the observed phenomena further. Physicochemical changes, such as changes in the stoichiometry at the electrode-electrolyte interface is possible when covellite becomes depleted in copper [19], e.g. $\text{CuS} \rightarrow \text{Cu}_{1-x}\text{S} + x\text{Cu}^{2+} + 2\text{xe}$ and $\text{Cu}_{1-x}\text{S} \rightarrow (1-x)\text{CuS} + x\text{S}^0$ etc. This reaction will then be due to concentration polarization. As there is no linear Tafel behaviour, such a concentration polarization may possibly occur. Thus it could be said that the passivation phenomenon observed here could be due principally to elemental sulphur coupled with pore diffusion blockage and/or stoichiometric changes at the active site-electrolyte interface.

The temperature (Fig. 6) does not seem to influence the pattern except to increase the rate of dissolution as would be expected. Similarly, high porosity in the material does not affect the reactions but is always accompanied by larger current values which is the behaviour normally observed for various sulphides [20]. The lowering of the current with purer materials (Fig. 7) could be attributed to either of the two following reasons. We know that noble metals or compounds with noble potentials generally have no, or a low, corrosion rate depending on the energetic level of the cathodic depolarization reaction. The effects of impurities which are generally more reactive, accelerate the rate of corrosion. It could also be attributed to the uniform nature of the surface which enhances the adhesion of the elemental sulphur produced. This forms a barrier-like film helping the surface to act like a passivated one. This is further supported by the observation that there is absolutely no difference in the anodic characteristics of CuS of different purities in 10^{-2} mol dm⁻³ HCl, where there is no formation of elemental sulphur as discussed earlier.

Acknowledgements

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