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# The influence of sulphide transport on the growth and properties of copper sulphide films on copper

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### ABSTRACT

The kinetics of $Cu_2S$ (chalcocite) film growth on corroding copper surfaces were monitored by following the change in pH in anaerobic aqueous sulphide solutions. Under stagnant conditions film growth was controlled by $SH^-$ diffusion in solution, and the formation of a non-protective film allowed complete consumption of available $SH^-$. When accelerated by convection, film growth rapidly became controlled by $Cu^+$ transport through a coherent protective film and proceeded at a considerably slower rate.

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## 1. Introduction

Containers with an outer copper shell have been proposed and designed for high level nuclear waste disposal in Sweden, Finland and Canada [1–7]. For a Swedish repository, in the short term, while potentially oxidizing conditions prevail, corrosion will be supported by the reduction of oxygen trapped in the repository on sealing. The extent of corrosion due to this oxygen and to radiolytic corrosion is expected to be minimal ($\sim$0.08–0.09 mm) [4]. Once anaerobic conditions are established the major threat to the long-term durability of the container is corrosion by sulphide from mineral dissolution and/or microbial activity involving sulphate-reducing bacteria [6,8]. Microbial activity within the immediate vicinity of the copper container surface will be limited by a combination of water availability, temperature, radiation fields and limited pore space in the compacted clay barriers surrounding the container [6,8]. Consequently, sulphide must diffuse through the compact bentonite clay surrounding the container from remote locations in order to initiate corrosion. For Swedish repository conditions, sulphide concentrations are expected to be in the range from $10^{-4}$ mol m$^{-3}$ to 0.1 mol m$^{-3}$ [4]. Under these conditions, copper corrosion should be controlled either by $SH^-$ diffusion in solution/bentonite and/or by the properties of the sulphide film formed on the copper surface, both of which are expected to be dependent on the groundwater chemistry.

If the sulphide that diffuses through the compacted clay to the container surface is consumed in film formation under restricted mass-transport control, the flux of sulphide in a Swedish repository (i.e., at the Forsmark site) can be calculated as $\sim$10$^{-13}$ mol m$^{-2}$ s$^{-1}$, taking the diffusion coefficient of sulphide in the compacted clay to be around $10^{-11}$ m$^2$/s, the sulphide content to be $\sim$10$^{-2}$ mol m$^{-3}$, and the thickness of the compacted clay to be >0.35 m [9]. This value is several orders magnitude lower than sulphide fluxes generally observed in a laboratory experiment. For example, when the sulphide concentration is $5 \times 10^{-2}$ mol m$^{-3}$, the sulphide flux would be $\sim$10$^{-8}$ mol m$^{-2}$ s$^{-1}$, assuming the Cu corrosion process is primarily controlled by $SH^-$ transport in solution with a diffusion coefficient of $\sim$10$^{-9}$ m$^2$/s and with the length of the diffusion path >0.001 m [10].

The sulphide concentration used in our studies is usually in the range from $5 \times 10^{-2}$ mol m$^{-3}$ to 0.5 mol m$^{-3}$ [10–15]. This range allows us to focus on the effect of sulphide content on the structure and properties of the sulphide film formed on the Cu surface in anaerobic sulphide solutions. To achieve this, the sulphide concentration must be sufficient to avoid sulphide depletion and the effects of trace oxygen on the corrosion process. Our previous studies [10–15] demonstrated that the $SH^-$ concentration has a significant influence on the morphology and properties of the sulphide film formed. When the concentration is low (i.e., $5 \times 10^{-2}$ mol m$^{-3}$), the film develops a cellular structure and its growth kinetics appear to be linear and primarily controlled by $SH^-$ diffusion in aqueous solution. However, when the sulphide concentration is >0.5 mol m$^{-3}$, the film appears to be compact and follows a parabolic growth law. In this case, film growth is controlled by a combination of $Cu^+$ diffusion through the sulphide film and $SH^-$ diffusion in solution.

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While instructive, these studies do not confirm that SH$^-$ diffusion in solution will control Cu corrosion under repository conditions.

Under electrochemically polarized conditions, the film growth process of Cu in sulphide solutions has been shown to be under SH$^-$ transport control based on a Levich analysis of the limiting currents measured in polarization experiments [16]. Under natural corrosion conditions, however, a direct demonstration of diffusion-control is difficult via conventional electrochemical techniques. If corrosion is completely controlled by SH$^-$ diffusion in solution, the interfacial sulphide concentration at the sulphide film/electrolyte interface [15] should be zero, and a demonstration that this is the case would verify the assumption in the current container corrosion model [4].

In the absence of corrosion product deposits, the concentration gradient of reacting species can be determined using microelectrode probes [17], scanning electrochemical microscopy (SECM) [18], confocal resonance Raman microscopy [19] and digital holography [20]. However, in sulphide-containing solutions the contribution of SH$^-$ diffusion is significantly influenced by the properties of the sulphide films formed on the corroding surface [10,13–15]. This makes the direct monitoring of SH$^-$ concentration at the film/electrolyte interface difficult during the on-going growth of a sulphide film.

In this paper, a novel sulphide depletion experiment is described to determine the interfacial sulphide concentration at the corroding interface. Since the transport regime has a significant effect on film morphology, special attention has been paid to the control of this regime and to the morphology and structure of the sulphide film formed on the Cu surface.

## 2. Experimental

### 2.1. Sample preparation

Phosphorous-doped (30–100 mg/kg), oxygen-free copper (Cu–OF, purity: 99.99%) provided by the Swedish Nuclear Fuel and Waste Management Co. (SKB, Stockholm, Sweden) was used in all experiments. Working electrodes were Cu disks with a diameter of $2.4 \times 10^{-2}$ m and a thickness of $6 \times 10^{-3}$ m, threaded onto a stainless steel shaft. A non-conductive lacquer was painted on the sample to prevent contact of the Cu/steel junction with the aqueous electrolyte. After painting, samples and the Cu/steel junction were encased in cylindrical Teflon holders with epoxy resin, and then heated at 60 °C for 12 h to promote adhesion of the paint/epoxy resin to the sample/Teflon holder. Electrodes were ground successively with 240, 600, 800, 1000, 1200 grade SiC paper, and then polished to a mirror finish using 1 μm, 0.3 μm, and finally 0.05 μm Al$_2$O$_3$ suspensions. Prior to experiments, the electrodes were washed with Type I water (0.182 M Ω m), cleaned with methanol, washed again with Type I water, and finally dried using Ar gas.

### 2.2. Sulphide depletion experiments

To accelerate the sulphide depletion rate, an electrochemical cell with a large ratio of electrode surface area to electrolyte volume was designed, Fig. 1. The exposed area of the Cu electrodes was $4.52 \times 10^{-4}$ m$^2$, and the solution volume was $6.5 \times 10^{-5}$ m$^3$. A Pt plate and a saturated calomel reference electrode (SCE, 0.241SHE/V) were used in a standard 3-electrode arrangement. All potentials are quoted on the SCE scale. Since the SH$^-$/S$^{2-}$ couple acts as a buffer, the solution pH can be used as an indicator of the bulk sulphide concentration [10,13–15]. To control the diffusion layer thickness while minimizing sulphide film erosion that may arise due to the presence of forced convection over a long exposure
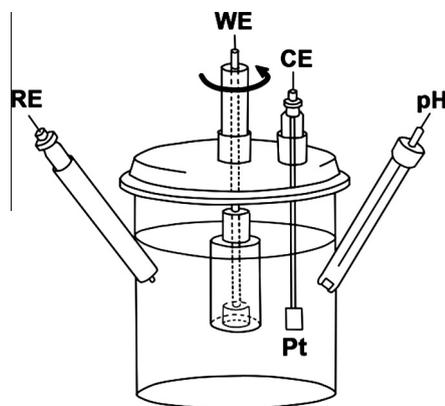


**Fig. 1.** Schematic of the electrochemical cell used in sulphide depletion experiments.

time [21], the Cu electrode was rotated at a low rate of 30 rpm (3.14 rad/s).

To ensure the maintenance of anoxic conditions, all experiments were performed in an Ar-purged anaerobic chamber (Canadian Vacuum Systems Ltd.), maintained at a positive pressure (2–4 mbar) by an MBraun glove box control system. The oxygen concentration in the chamber was analysed with an MBraun oxygen probe with a detection limit of 1.4 mg/m$^3$. The anaerobic chamber was maintained at a total oxygen concentration ⩽4.2 mg/m$^3$, which includes the oxygen in both air and vapor. The actual oxygen content of the solution should be less than this value. Even though there is a trace amount of oxygen present, copper sulphide is more stable in sulphide solution than copper oxide based on thermodynamic data ($\Delta_f G°$ = −101.46 kJ/mol for the conversion from Cu$_2$O to Cu$_2$S in sulphide solutions at 298 K [22]) and available literature [7,23–25].

Experiments were performed at an ambient temperature of 25 ± 1 °C. The $5 \times 10^{-2}$ mol m$^{-3}$ Na$_2$S + 100 mol m$^{-3}$ NaCl (pH = 9.56) and 100 mol m$^{-3}$ NaCl solutions were prepared with Type I water, reagent-grade sodium sulphide (Na$_2$S·9H$_2$O, 98.0% assay), and analytical-grade sodium chloride (NaCl, 99.0% assay). The sodium chloride was added to simulate the saline groundwater conditions anticipated in a repository, and also to improve solution conductivity.

Prior to a sulphide depletion experiment, the Cu electrode was cathodically cleaned in 100 mol m$^{-3}$ NaCl solution at −1.6 V/SCE for 2 min, and then at −1.15 V/SCE for 2 min to remove the oxides formed during polishing and sample transfer to the anaerobic chamber [12]. The subsequent steady-state corrosion potential ($E_{CORR}$) was independent of whether the electrode was cleaned in this manner indicating that any hydrogen uptake during cathodic cleaning had a negligible effect on the corrosion process. After cleaning, the electrodes were rinsed with Type I water, and immersed in an anaerobic $5 \times 10^{-2}$ mol m$^{-3}$ Na$_2$S + 100 mol m$^{-3}$ NaCl solution for various times under natural corrosion conditions. The $E_{CORR}$ was monitored, and the bulk solution pH measured intermittently over the full exposure period. Electrochemical impedance spectroscopy (EIS) measurements were performed at $E_{CORR}$ after sulphide depletion experiments. A sinusoidal potential perturbation with an amplitude (peak-to-zero) of 10 mV was applied over the frequency range from 10$^5$ Hz to 10$^{-3}$ Hz using a Solarton 1287 electrochemical interface and a Solarton 1255B frequency response analyser. Data were obtained at 10 frequencies per decade. The validity of the impedance spectra was checked using the Kramers–Kronig (K–K) transform [26] (an example of a K–K transform is shown in Fig. 7(b)).

## 2.3. Analysis of sulphide films

Electrodes removed from solution for surface analyses were rinsed with Type I water for 10 min and then dried in Ar gas. Analyses were performed after a minimum period of interim storage (<0.5 h). The surface morphologies of corroded specimens were observed using a Leo 1540 FIB/SEM microscope (Zeiss Nano Technology Systems Division, Germany), and the compositions of the sulphide films were qualitatively analysed by Energy Dispersive X-ray Spectroscopy (EDS) using a Leo 1540 FIB/SEM microscope (the oxygen detection limit is 1 at.%).

## 3. Theory

In sulphide-containing solutions, equilibrium is established by the coupling of sulphide hydrolysis (Eq. (1)) and bisulphide dissociation (Eq. (2)), and for a given total sulphide concentration, $[S]_T$, the equilibrium sulphide concentration ($[S^{2-}]$) can be determined from the dissociation equilibria:

$$S^{2-} + H_2O \xrightarrow{K_b} SH^- + OH^- \quad K_b = \frac{[SH^-][OH^-]}{[S^{2-}]} = \frac{[SH^-]^2}{[S^{2-}]} \quad (1)$$

$$SH^- \xleftarrow{K_a} S^{2-} + H^+ \quad K_a = \frac{[S^{2-}][H^+]}{[SH^-]} \quad (2)$$
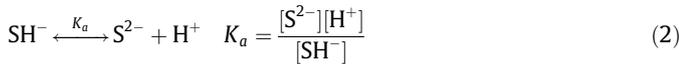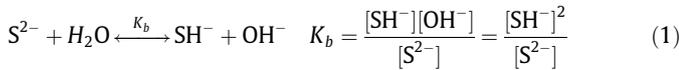
Since the value of $pK_a$ ($=-\log K_a$) is large (i.e., 11.96–19 at 298 K [27–32]), the bisulphide concentration ($[SH^-]$) will be much greater than that of sulphide and, hence, $[SH^-] \approx [S]_T$. In addition, Eqs. (1) and (2) also show that the solution pH is set by the $SH^-/S^{2-}$ buffer couple. During a depletion experiment, the bulk sulphide concentration is monitored by measuring the pH of the solution. From pH measurements and Eqs. (1) and (2), the bulk sulphide concentration can be calculated approximately using Eq. (3),

$$pH \approx 14 + \log C_{bulk} \quad (3)$$

or more accurately obtained by experimentally calibrating the pH as a function of sulphide concentration.

The steady-state flux of bisulphide to the sulphide film/electrolyte interface is given by Fick's first law,

$$J = -D\frac{\partial C}{\partial x} = D\frac{C_{bulk} - C_s}{\delta} \quad (4)$$

where $D$ is the diffusion coefficient of $SH^-$ in solution ($1.731 \times 10^{-9}$ m$^2$/s [32]), $C_{bulk}$ and $C_s$ are the bulk and interfacial $SH^-$ concentrations, respectively, and $\delta$ is the diffusion layer thickness. This flux is a measure of the bisulphide depletion rate ($-dC/dt$), and, thus, also the film growth rate, if all of the sulphide is consumed in film formation, Eq. (5),

$$J = \frac{V_{sol}}{A_e}\frac{dC}{dt} \quad (5)$$

where $A_e$ is the area of the Cu electrode, and $V_{sol}$ the solution volume.

The diffusion layer thickness is controlled using a rotating disk electrode (RDE), and is given by Eq. (6) [33],

$$\delta = \frac{1.61 v^{1/6} D^{1/3}}{\omega^{1/2}} \quad (6)$$

where $v$ is the kinematic viscosity of the solution ($9 \times 10^{-7}$ m$^2$ s$^{-1}$ for 100 mol m$^{-3}$ NaCl solution [34]), and $\omega$ the angular rotation rate of the RDE (3.14 rad/s).

According to Bard and Faulkner [33], the lower limit of rotation rate for the eligibility of Eq. (6) would be:

$$\omega > 2\pi \times \frac{10v}{r^2} = 0.3925 \text{ rad/s} \quad (7)$$

where $r$ is the radius of the rotated Cu electrode (0.012 m). As a consequence, Eq. (6) is valid at the rotation rate of 3.14 rad/s used in our experiments.

These calculations and measurements leave the interfacial concentration at the sulphide film/electrolyte interface as the only unknown in Eq. (4), and a combination of Eqs. 4–6 yields

$$C_s = C_{bulk} - \frac{V_{sol}}{A_e}\frac{dC}{dt}\frac{1.61 v^{1/6}}{D^{2/3}\omega^{1/2}} \quad (8)$$

This equation can then be used to evaluate the interfacial bisulphide concentration in sulphide depletion experiments.

## 4. Results and discussion

### 4.1. Calibration of the bulk solution pH as a function of sulphide concentration

A calibration curve of pH vs. $C_{bulk}$ is shown in Fig. 2, and clearly illustrates that Eq. (3) is closely followed for sulphide concentrations >$10^{-3}$ mol m$^{-3}$. The observed deviation between the theoretical prediction and the experimental data when the sulphide concentrations are <$10^{-3}$ mol m$^{-3}$ can be attributed to the approximation in the derivation of Eq. (3) and/or water hydrolysis which becomes significant for sulphide concentrations <$10^{-4}$ mol m$^{-3}$. For these reasons, the calibration curve was used in depletion calculations.

### 4.2. Sulphide depletion under stagnant conditions

Fig. 3 shows measured pH values and bisulphide concentrations (calculated using the calibration curve in Fig. 2) for a depletion experiment conducted in a stagnant anaerobic $5 \times 10^{-2}$ mol m$^{-3}$ Na$_2$S + 100 mol m$^{-3}$ NaCl solution. Under these conditions, bisulphide depletion occurred at a rate of $10^{-7}$–$10^{-6}$ mol m$^{-3}$ s$^{-1}$ over an exposure period of 11 h.

Using this depletion rate, $-dC/dt$, of $\sim 10^{-6}$ mol m$^{-3}$ s$^{-1}$, evaluated from the slope of Fig. 3, and assuming an interfacial $SH^-$ concentration close to zero, the diffusion layer thickness, $\delta_0$, is calculated to be $6 \times 10^{-4}$ m. Although the diffusion layer thickness cannot be determined under stagnant conditions, it can be reasonably expected to be >$\delta_0$, suggesting that the interfacial $SH^-$ concentration was close to zero in this experiment.

Previously it was shown [10] that the sulphide film formed on Cu after 1691 h of exposure to an anaerobic solution of this composition under stagnant conditions has a cellular structure and the
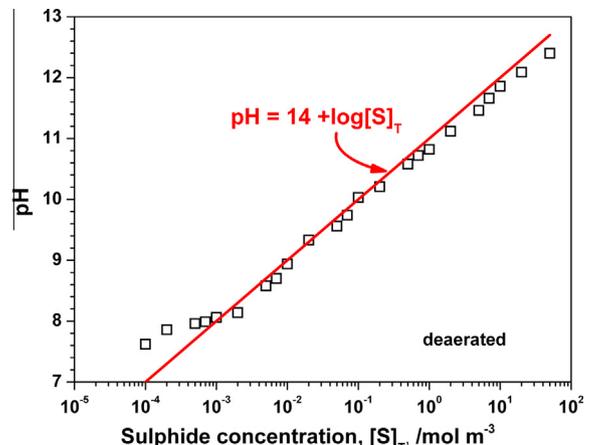


**Fig. 2.** Calibration curve showing the variation of the bulk solution pH as a function of the total sulphide concentration under anaerobic conditions.
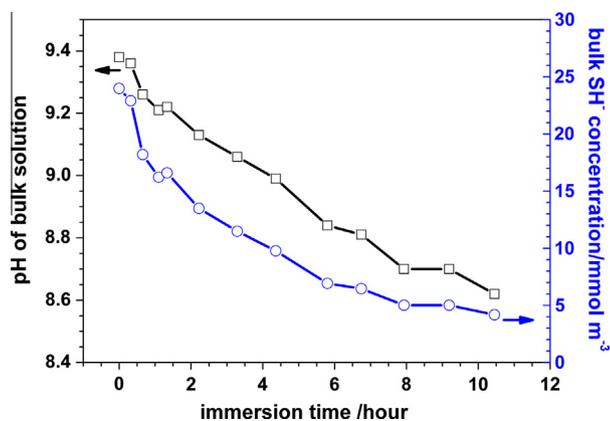
**Fig. 3.** Evolution of the bulk solution pH and SH$^-$ concentration with immersion time in a stagnant anaerobic sulphide solution (initial concentration: $5 \times 10^{-2}$ mol $\times$ m$^{-3}$ Na$_2$S + 100 mol $\times$ m$^{-3}$ NaCl).

corrosion process is controlled by SH$^-$ diffusion partially in film pores and partially in bulk solution. This observation also suggested that the SH$^-$ concentration at the film/electrolyte interface was effectively zero.

### 4.3. Sulphide depletion at an RDE

To control the diffusion layer thickness, a depletion experiment was conducted using an RDE at a rotation rate of 3.14 rad/s (30 rpm). Fig. 4 shows the variation in measured pH and $E_{CORR}$ of the rotated Cu electrode with time. Unlike in the stagnant experiment, when the pH continuously decreased, an initial drop in pH was arrested and an almost steady-state value obtained after ~2 h. This behaviour suggests a rapid initial depletion of bisulphide but only to an eventual steady-state concentration. This is demonstrated in Fig. 5 which shows the rate of depletion ($-$d$C$/d$t$) and the interfacial bisulphide concentration. The bisulphide depletion rate was obtained by differentiation of the bulk sulphide concentration against time since this concentration is a function of the solution pH (Eq. (3)). The interfacial bisulphide concentration was then calculated from Eq. (8).

For an exposure time <1 h, $-$d$C$/d$t$ is ~$10^{-6}$ mol m$^{-3}$ s$^{-1}$. According to Eq. (8), the interfacial SH$^-$ concentration ($C_s$) will be almost zero, confirming that film formation is dominated by SH$^-$ diffusion in solution. At this stage, the sulphide flux is about ~$10^{-7}$ mol m$^{-2}$ s$^{-1}$, which
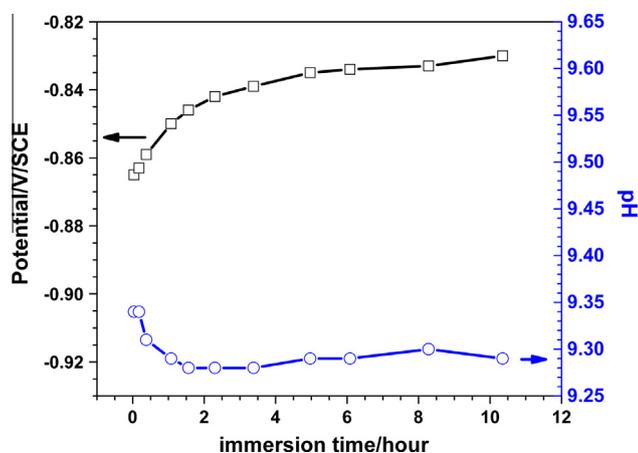


**Fig. 4.** Evolution of $E_{CORR}$ and the bulk solution pH with immersion time in an anaerobic sulphide solution (initial concentration: $5 \times 10^{-2}$ mol $\times$ m$^{-3}$ Na$_2$S + 100 mol $\times$ m$^{-3}$ NaCl) at an electrode rotation rate of 30 rpm.
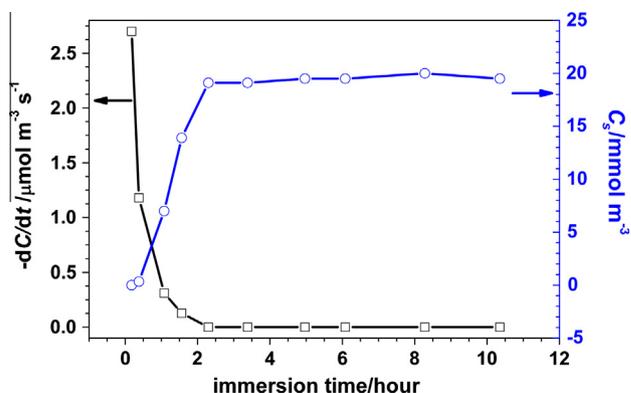


**Fig. 5.** Evolution of sulphide depletion rate ($-$d$C$/d$t$) and interfacial bisulphide concentration with immersion time in an anaerobic sulphide solution (initial concentration: $5 \times 10^{-2}$ mol $\times$ m$^{-3}$ Na$_2$S + 100 mol $\times$ m$^{-3}$ NaCl) at an electrode rotation rate of 30 rpm.

is about six orders magnitude higher than that anticipated in a Swedish repository (~$10^{-13}$ mol m$^{-2}$ s$^{-1}$). At longer times, the bisulphide depletion rate at the RDE surface approaches zero and the interfacial SH$^-$ concentration is calculated to approach the bulk concentration value. Clearly, at longer times, film formation is uninfluenced by the solution diffusion of SH$^-$ and, if growth continues, dominated by the transport properties of the surface film.

These observations and calculations are consistent with the observed changes in $E_{CORR}$, Fig. 4. The initial positive shift in $E_{CORR}$ indicates a decrease in sulphide concentration at the reacting Cu interface [16] as formation of the copper sulphide film progresses [10,13–15], while the later positive shift at a slower rate can be
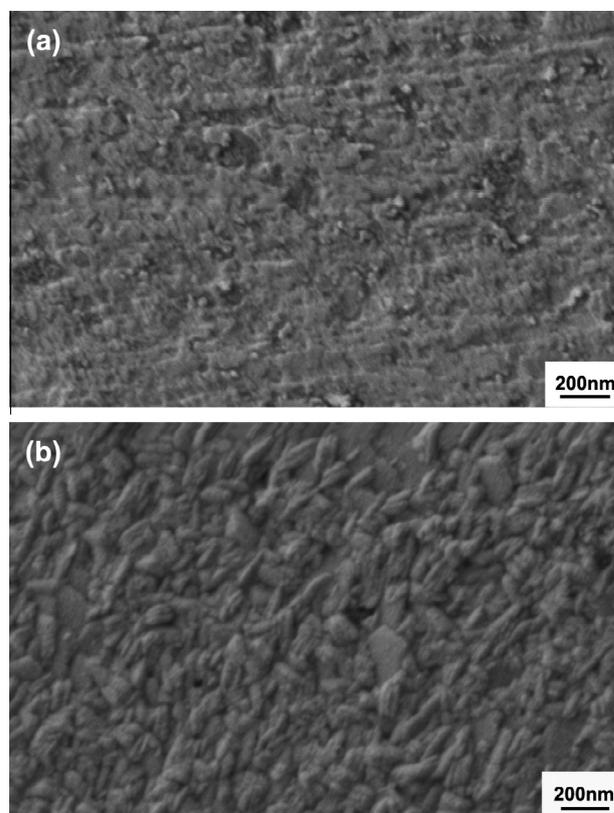


**Fig. 6.** Morphologies of the sulphide films formed on the rotated Cu surface after (a) 300 s and (b) 11 h immersion in an anaerobic sulphide solution (initial concentration: $5 \times 10^{-2}$ mol $\times$ m$^{-3}$ Na$_2$S + 100 mol $\times$ m$^{-3}$ NaCl).

attributed to the formation of either a coherent or a passive film. Previous results suggest that this change in $E_{CORR}$ behaviour indicates a switch from film formation under solution-diffusion control to control by the solid state diffusion of $Cu^+$. As calculated previously, the diffusion coefficient of $Cu^+$ in a $Cu_2S$ film is $\sim10^{-14}$ $m^2/s$ [13], much lower than that of $SH^-$ in solution ($\sim10^{-9}$ $m^2/s$) [32].

To determine the morphology of the sulphide film formed, the specimens were removed after depletion experiments performed using an RDE in anaerobic $5 \times 10^{-2}$ mol m$^{-3}$ $Na_2S$ + 100 mol m$^{-3}$ NaCl solution after either 300 s or 11 h. SEM micrographs recorded on these surfaces are shown in Fig. 6. The EDS analyses confirmed that both films are composed only of Cu and S. Though the exact crystal structure of the film cannot be determined by XRD because it is very thin (on the nanometer scale), our previous XRD analyses of films formed in a solution with the same sulphide concentration after long-term exposure under natural corrosion conditions confirmed the film was $Cu_2S$ (chalcocite) [13]. As shown in Fig. 6(a), the film formed after the short exposure period did not completely cover the whole Cu surface. At this stage, the Cu corrosion process is controlled by $SH^-$ diffusion in the solution [10]. After 11 h, the Cu surface is covered by a compact $Cu_2S$ layer, Fig. 6(b), consistent with a film whose growth is controlled by a solid state diffusion process.

When the sulphide concentration is >0.5 mol m$^{-3}$, the sulphide films formed on the Cu surfaces in anoxic sulphide solutions under stagnant condition are compact, grow predominantly by a solid state diffusion process [13–15], and look similar to that formed in anaerobic $5 \times 10^{-2}$ mol m$^{-3}$ $Na_2S$ + 100 mol m$^{-3}$ NaCl solution under rotation.

All of the EIS measurements were performed at the $E_{CORR}$ measured just prior to EIS measurement. Although the value of $E_{CORR}$ is not a constant during the EIS measurement, its rate of change is <2 mV/h (Fig. 4), which is considerably lower than the sinusoidal potential perturbation applied. Comparison of the EIS spectrum recorded on the RDE after 11 h in anaerobic $5 \times 10^{-2}$ mol $\times$ m$^{-3}$ $Na_2S$ + 100 mol $\times$ m$^{-3}$ NaCl solution to that of an electrode after 1691 h immersion in anaerobic 0.5 mol $\times$ m$^{-3}$ $Na_2S$ + 100 mol $\times$ m$^{-3}$ NaCl solution under stagnant conditions shows the impedance at the low frequency limit of the measurement ($10^{-3}$ Hz) is much higher for the film formed on the RDE, Fig. 7. This is consistent with the observations (above) that the film is more rapidly formed and more compact/protective when formed under forced convection conditions.

After rotation for 11 h, the RDE experiment was continued for an additional 10 h without rotation and an additional EIS spectrum recorded, Fig. 7. This spectrum exhibits a linear relationship between the real and imaginary impedances at low frequencies (Fig. 7(a)) and the phase angle approaches $-45°$ (Fig. 7(b)), an indication of the presence of a Warburg impedance [35] due to long-range diffusion. This change in EIS suggests a switch from short-range diffusion in the film, dominant under rotation, to long-range diffusion in solution, dominant under stagnant conditions. It also indicates the sulphide film continues to grow; i.e., the film formed initially under rotating conditions is coherent, but not passive. As the sulphide film continues to grow, sulphide will be consumed, leading to its further depletion. This will cause the positive shift in $E_{CORR}$ [12,36–42], and would account for the observation that $E_{CORR}$ did not vary significantly over the 11 h exposure period (Fig. 4).

## 5. Conclusions

A sulphide depletion experiment has been designed to investigate the influence of diffusive flux on the properties of $Cu_2S$ films grown on Cu in anaerobic sulphide solutions.

By controlling the diffusive flux at an RDE and calculating the bulk solution bisulphide concentration by measuring the pH, it was shown that growth of a non-protective film was controlled by $SH^-$ diffusion under stagnant conditions.

In the presence of accelerated sulphide transport, $Cu_2S$ growth initially proceeded via the same mechanism. However, the rapid formation of a coherent film led to a switch from growth controlled by $SH^-$ solution diffusion to growth controlled by the solid-state diffusion of $Cu^+$ in the film.

However, this film acted only as a partial corrosion barrier since its growth continued slowly in the sulphide-containing solution.

## Acknowledgements

**Fig. 7.** EIS spectra ((a) Nyquist plots and (b) Bode plots) measured on sulphide-covered Cu electrodes in: (□) anoxic $5 \times 10^{-2}$ mol $\times$ m$^{-3}$ $Na_2S$ + 100 mol $\times$ m$^{-3}$ NaCl after 11 h rotating; (○) anoxic 0.5 mol $\times$ m$^{-3}$ $Na_2S$ + 100 mol $\times$ m$^{-3}$ NaCl after 1691 h immersion under stagnant condition; (△) anoxic $5 \times 10^{-2}$ mol $\times$ m$^{-3}$ $Na_2S$ + 100 mol $\times$ m$^{-3}$ NaCl after 11 h rotating followed by 10 h stagnant.

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