

Key parameters determining structure and properties of sulphide films formed on copper corroding in anoxic sulphide solutions

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The corrosion behaviour of copper was studied in anoxic solutions containing different concentrations of sulphide (10^{-5} – 10^{-3} mol L⁻¹) and chloride (0.1–5 mol L⁻¹) under stagnant and controlled convective conditions. The main determinants of the structure and properties of the copper sulphide (Cu₂S) films formed are the rate of sulphide transport to the surface relative to the rate of its interfacial reaction with copper, and competition between sulphide and chloride for surface adsorption sites. When sulphide diffusion is rate limiting, the sulphide film formed is porous and non-protective, whereas when film growth is not limited by mass transport of sulphide, the sulphide film is compact and protective. The results indicate that, under Swedish repository conditions, the film formed on copper will be porous and non-protective and its growth diffusion controlled.

Keywords: Copper, Sulphide, Corrosion, Film, Nuclear waste disposal

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Introduction

Because of its high corrosion resistance and thermodynamic stability in the anoxic saline groundwater anticipated in a Swedish nuclear waste repository, copper is the chosen material for the fabrication of high level nuclear waste containers.^{1–7} Once oxygen trapped in the repository on sealing is consumed by microbial activity and oxidation of container, attack by sulphide derived from mineral dissolution and/or microbial activity such as sulphate reducing bacteria^{6,8} is the main corrosion threat to a copper container surrounded by compacted bentonite. In sulphide solutions, copper corrosion is driven by the formation of a copper sulphide film supported by water or proton (from SH⁻ dissociation) reduction. Previously^{9–12} it has been shown that the structure and properties of this sulphide film have a significant influence on both the mechanism and the rate limiting step of the corrosion process, and that the structure and properties of the film appear to be dependent on sulphide concentration.^{9–12}

In a geologic repository, the measured sulphide and chloride concentrations in the anticipated groundwaters will be in the range of 10^{-7} – 10^{-4} mol L⁻¹ and 0.1–0.5 mol L⁻¹ respectively,² and container corrosion is assumed to be limited by the rate of supply of sulphide to the container surface.^{2–4} Chloride, a key constituent of the groundwater, has also been shown to influence the Cu corrosion process by changing the film structure and properties.¹³ The primary aim of this paper is to clarify the relative importance of the various parameters in

controlling the structure and properties of the sulphide film expected under the anticipated anoxic repository conditions.

Experimental

Sample preparation

Phosphorous doped (30–100 ppm), oxygen-free copper 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 1 cm (for long-term exposure tests) or 2.4 cm [for rotating disk electrodes (RDE)] and a thickness of 0.6 cm, threaded onto a stainless steel shaft. A non-conductive lacquer was painted on the electrodes to prevent contact of the Cu/stainless steel junction with the aqueous electrolyte. Subsequently, the electrodes were encased in cylindrical Teflon holders using an epoxy resin. These electrode assemblies were 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 finally polished to a mirror finish using 1 μm, 0.3 μm, and finally 0.05 μm Al₂O₃ suspensions. Prior to the experiments, the electrodes were washed with Type I water (high purity water with a resistivity >18.2 MΩ·cm as defined in ASTM D1193-91), cleaned with methanol, washed again with Type I water, and finally dried using a stream of Ar gas.

Long term exposure and sulphide depletion experiments

To ensure the maintenance of anoxic conditions (oxygen concentration ≤3 ppm), all experiments were performed in an Ar purged anaerobic chamber (Canadian Vacuum Systems Ltd.), maintained at a positive pressure (2–4 mbar)

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by an MBraun glove box control system. The oxygen concentration in the chamber was analysed with an MBraun oxygen probe.

Experiments were performed at ambient temperature ($25 \pm 1^\circ\text{C}$). The sulphide solutions (1×10^{-5} – 1×10^{-3} mol L⁻¹) containing chloride (0.1–5 mol L⁻¹) were prepared with Type I water, reagent grade sodium sulphide (Na₂S.9H₂O, 98.0% assay), and reagent grade sodium chloride (NaCl, 99.0% assay).

A standard three-electrode cell was employed with a Pt plate as the counter electrode and a saturated calomel electrode (SCE, 0.241SHE/V) as the reference electrode. All potentials are quoted on the SCE scale. Since the SH⁻/S²⁻ couple acts as a buffer, the solution pH can be used as an indicator of the bulk sulphide concentration.^{9–12} For the long term exposure experiments, the exposed area of the Cu electrodes was 0.785 cm² and the solution volume was 1 L. For sulphide depletion experiments, an electrochemical cell with a large ratio of electrode surface area to solution volume was designed to accelerate the sulphide depletion rate. The exposed area of the Cu electrodes was 4.52 cm², and the solution volume was 65 mL. When required, the Cu electrode was rotated at a low rate of 30 rev min⁻¹ (3.14 rad s⁻¹) to control the diffusion layer thickness while avoiding sulphide film erosion.

Prior to experiments, the Cu electrode was cathodically cleaned at -1.6 V(SCE) for 2 min, and then at -1.15 V(SCE) for 2 min as a standard procedure⁷ to remove the oxides formed during polishing. The 2 min period at -1.15 V(SCE) was to facilitate the detachment of hydrogen bubbles produced on the electrode surface at the more negative potential. The electrodes were then rinsed with Type I water, and immersed in anoxic solutions containing different sulphide and chloride concentrations for various times under natural corrosion conditions. The corrosion potential (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 – 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 data was checked using the Kramers–Kronig transform.

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 examined 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-%).

Results and discussion

Influences of solution chemistry, chloride/sulphide concentration ratio and sulphide flux

Our previous work^{9–12} showed that the corrosion product is a single layer Cu₂S film, formed by an outward growth

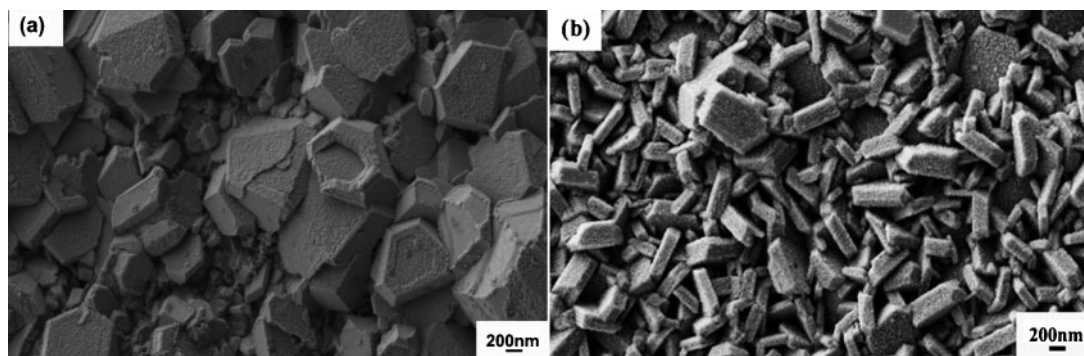
mechanism controlled by a combination of Cu⁺ diffusion in the film and SH⁻ diffusion in solution. When the sulphide concentration is low (i.e. 5×10^{-5} mol L⁻¹), the film has a cellular structure and its growth kinetics are linear. The film growth process is controlled primarily by SH⁻ diffusion in the aqueous solution, implying that the sulphide film is not protective under these conditions up to an exposure time of ~ 4000 h. However, when the sulphide concentration is $\geq 5 \times 10^{-4}$ mol L⁻¹, the film appears compact, and its growth obeys a parabolic law. In this case, film growth is controlled mainly by Cu⁺ diffusion in the sulphide film indicating the film is protective under these conditions.

When the chloride concentration is low (i.e. 0.1 mol L⁻¹), it does not appear to significantly influence the sulphide film growth process. However, when the chloride concentration is > 0.5 mol L⁻¹, EIS spectra exhibit three time constants indicating a detectable influence on the sulphide film properties. The detection of a high frequency response, not seen at lower chloride concentrations, implies that a rapid charge transfer process occurs at the copper/solution interface. While this could indicate the occurrence of localized corrosion, no obvious pits were found in subsequent surface analyses. At extremely high chloride concentrations (i.e. 5 mol L⁻¹), the film grows out from the copper surface in the form of thin flat plates separated by open spaces. The well defined high frequency impedance response clearly indicates that the film is non-protective for exposure periods up to 1691 h (~ 71 days). Under these conditions, it is proposed that the film growth process is controlled by a combination of SH⁻ diffusion in the bulk of the aqueous solution and CuCl₂⁻ diffusion in the spaces between the plates.

Since the properties of the sulphide film depend on the solution concentrations of both sulphide and chloride^{9–12} and the concentration of these ions in groundwaters can vary with repository location², copper corrosion was investigated in anoxic solutions containing sulphide and chloride in the ranges of 5×10^{-5} mol L⁻¹ to $\sim 1 \times 10^{-3}$ mol L⁻¹ and 0.1 mol L⁻¹ to ~ 5 mol L⁻¹ respectively. The surface morphology and cross-sectional structure of the films formed was subsequently characterized using SEM and focused ion beam (FIB) sectioning.

Table 1 summarises the relationship between film properties determined after corrosion under stagnant conditions and the sulphide and chloride contents of the exposure solutions. The structure of the sulphide film was found to change from compact to porous when the ratio of chloride to sulphide concentration is ≥ 1000 . These results suggest that the ratio of chloride and sulphide concentration might be a factor influencing the properties of the sulphide film.

However, if, over a total immersion time of 1691 h, the electrolyte was magnetically stirred for 3 h at a constant rate of 80 rev min⁻¹ (8.37 rad s⁻¹) every 168 h with the interim periods remaining stagnant, E_{CORR} shifted to a more negative potential during the stirred intervals.¹² This indicates an increase in sulphide flux to the film/electrolyte interface,¹² which led to an increase in film growth rate and a change in film structure and morphology compared to the film grown under continuous stagnant conditions^{9,12} (Fig. 1). It can be concluded that either the ratio of chloride and sulphide concentrations or the sulphide flux is probably the key parameter determining the structure and properties of the sulphide film.



1 Surface morphology of sulphide covered Cu electrode after 1691 h exposure in anoxic $5 \times 10^{-4} \text{ mol L}^{-1} \text{ Na}_2\text{S} + 0.1 \text{ mol L}^{-1} \text{ NaCl}$ solution under natural corrosion conditions: *a* after corrosion under completely stagnant conditions⁹ and *b* after corrosion for total immersion time of 1691 h in which sequence of 168 h stagnant periods were interspersed with periods employing magnetic stirring (80 rev min^{-1}) for 3 h

Competition between interfacial reaction rate and diffusive sulphide flux

The steady state flux of sulphide to the sulphide film/solution interface is given by Fick's first law

$$J = -D \frac{\partial C}{\partial x} = D \frac{C_{\text{bulk}} - C_s}{\delta} \quad (1)$$

where D is the diffusion coefficient of SH^- in solution ($1.731 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$),¹⁴ C_{bulk} and C_s are the bulk and interfacial SH^- concentrations respectively, and δ is the diffusion layer thickness. The value of C_s is determined by the competition between the interfacial reaction rate to form the copper sulphide film and sulphide diffusion to the film/solution interface to support corrosion. If the interfacial reaction rate is much faster than sulphide diffusion, $C_s = 0$. For this diffusion controlled process, the diffusive flux is defined by

$$J_{\text{diff}} = D \frac{C_{\text{bulk}}}{\delta} \quad (2)$$

A well defined diffusion layer with a thickness of $\sim 100 \mu\text{m}$ was established using a RDE at a rotation rate of 30 rev min^{-1} .¹⁵ Under stagnant conditions, mass transport also occurs primarily by diffusion, although the thickness of the diffusion layer is less well defined but will be larger than that for the rotating electrode. For calculations of the diffusive flux for the stationary electrode, therefore, we have assumed a steady state diffusion layer thickness of 1 mm .¹⁰

In this closed system, the bulk concentration of sulphide will change with time as the consequence of its reaction with Cu. If all the sulphide is consumed in film formation (assumed to occur uniformly), the interfacial reaction rate, R_{SH^-} ($\text{mol cm}^{-2} \text{ s}^{-1}$), can be estimated using equation (3)

$$R_{\text{SH}^-} = \frac{V_{\text{sol}}}{A_{\text{el}}} \cdot \frac{\Delta C}{\Delta t} \quad (3)$$

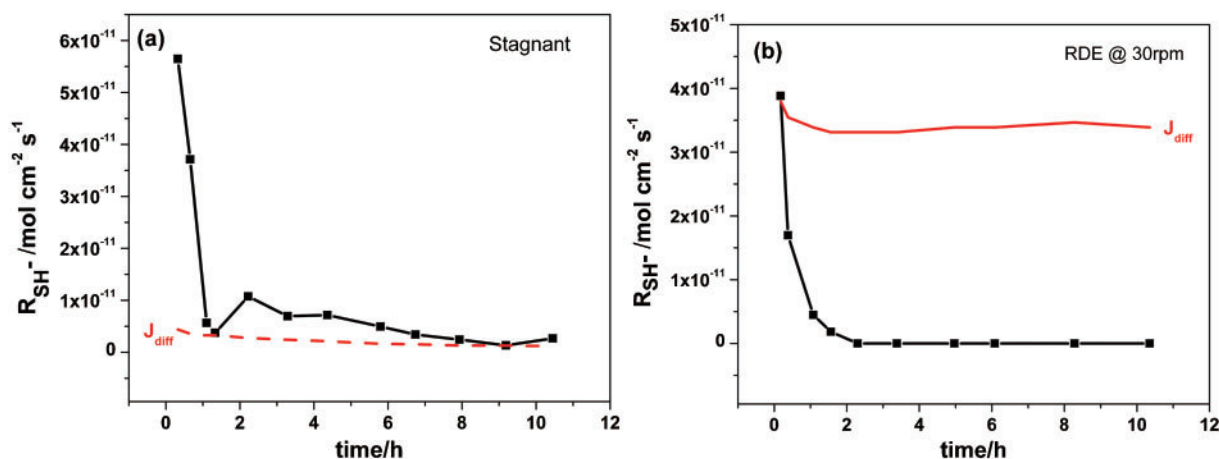
where V_{sol} is the solution volume (65 mL), A_{el} the electrode surface area (4.52 cm^2), and $\Delta C/\Delta t$ the rate of the change of bulk sulphide concentration (ΔC) during a time interval (Δt), which is determined by the measured time dependent $[\text{SH}^-]$ of the bulk solution.

Figure 2 compares the interfacial reaction rate with the calculated diffusive sulphide flux for both stationary and RDE electrodes in anoxic $5 \times 10^{-4} \text{ mol L}^{-1} \text{ Na}_2\text{S} + 0.1 \text{ mol L}^{-1} \text{ NaCl}$ solution as a function of immersion time. Under stagnant conditions (Fig. 2*a*), the initial interfacial reaction rate exceeds the calculated diffusive sulphide flux ($\sim 10^{-11} \text{ mol cm}^{-2} \text{ s}^{-1}$) because sulphide transport occurs rapidly under transient diffusive conditions as the interfacial diffusion layer becomes depleted. Subsequently, the interfacial reaction rate becomes comparable to the diffusive flux indicating a diffusion controlled film growth process. Previous long term exposure tests¹⁰ showed that the sulphide film formed after 1691 h of stagnant anoxic exposure to a solution with this composition has a cellular structure with corrosion controlled partially by SH^- diffusion in film pores and partially by its diffusion in bulk solution. Under the diffusion controlled conditions of this experiment, the SH^- concentration at the film/solution interface would be effectively zero.

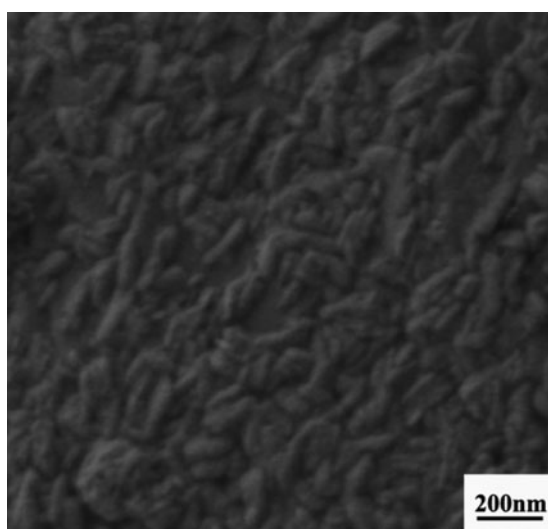
The behaviour under convective conditions is different (Fig. 2*b*). When a higher rate of mass transport is employed, the interfacial reaction rate is always lower than the available diffusive sulphide flux, indicating that the corrosion process is controlled by either the interfacial reaction rate or by solid state diffusion. After 2 h of exposure, the interfacial reaction rate is effectively zero,

Table 1 Film properties after corrosion in anoxic sulphide solutions containing different chloride contents under stagnant condition

Experimental condition	Film morphology	$[\text{SH}^-]/\text{mol L}^{-1}$	$[\text{Cl}^-]/\text{mol L}^{-1}$	$[\text{Cl}^-]/[\text{SH}^-]$
$5 \times 10^{-4} \text{ mol L}^{-1} \text{ Na}_2\text{S}$, 1691 h, natural corrosion	Compact	5×10^{-4}	0	0
$1 \times 10^{-3} \text{ mol L}^{-1} \text{ Na}_2\text{S} + 0.1 \text{ mol L}^{-1} \text{ NaCl}$, 1691 h, natural corrosion	Compact	1×10^{-3}	0.1	100
$5 \times 10^{-4} \text{ mol L}^{-1} \text{ Na}_2\text{S} + 0.1 \text{ mol L}^{-1} \text{ NaCl}$, 1691 h, natural corrosion	Compact	5×10^{-4}	0.1	200
$1 \times 10^{-3} \text{ mol L}^{-1} \text{ Na}_2\text{S} + 0.5 \text{ mol L}^{-1} \text{ NaCl}$, 1691 h and 3000 h, natural corrosion	Compact	1×10^{-3}	0.5	500
$1 \times 10^{-3} \text{ mol L}^{-1} \text{ Na}_2\text{S} + 1.0 \text{ mol L}^{-1} \text{ NaCl}$, 1691 h and 3000 h, natural corrosion	Porous	1×10^{-3}	1.0	1000
$5 \times 10^{-5} \text{ mol L}^{-1} \text{ Na}_2\text{S} + 0.1 \text{ mol L}^{-1} \text{ NaCl}$, 1691 h and 4000 h, natural corrosion	Porous	5×10^{-5}	0.1	2000
$1 \times 10^{-3} \text{ mol L}^{-1} \text{ Na}_2\text{S} + 5.0 \text{ mol L}^{-1} \text{ NaCl}$, 1691 h, natural corrosion	Porous	1×10^{-3}	5.0	5000



2 Evolution with immersion time of interfacial reaction rate for Cu_2S film growth on Cu in anoxic $5 \times 10^{-4} \text{ mol L}^{-1} \text{ Na}_2\text{S} + 0.1 \text{ mol L}^{-1} \text{ NaCl}$ solution: a stagnant conditions and b convective conditions; line marked J_{diff} shows rate achievable if diffusion control prevails



3 Morphology of sulphide covered Cu electrode after 14 h exposure to anoxic sulphide solution (initial concentration: $5 \times 10^{-5} \text{ mol L}^{-1} \text{ Na}_2\text{S} + 1.0 \text{ mol L}^{-1} \text{ NaCl}$) at electrode rotation rate of 30 rev min^{-1}

suggesting a protective copper sulphide film is formed. A micrograph of this electrode surface (after corrosion for 11 h) (Fig. 3) shows that the electrode surface is covered by a compact Cu_2S layer (as analysed by EDS), consistent with a film whose growth was controlled by a solid state diffusion process. This film formed under convective conditions is similar to the compact sulphide films formed on Cu in anoxic sulphide solutions ($>5 \times 10^{-4} \text{ mol L}^{-1}$) under stagnant conditions, whose growth was shown to be dominated by a solid state diffusion process.⁹⁻¹²

To confirm that the structure and properties of the sulphide films formed are determined by a competition between interfacial reaction rate and sulphide diffusion in solution, experiments under convective conditions (30 rev min^{-1}) were conducted in solutions containing a wide range of sulphide and chloride concentrations. Table 2 summarises the relationships observed between solution chemistry and film properties. It is clearly demonstrated that rotating the electrode changes the morphology of the sulphide film from porous to compact even when the chloride to sulphide ratio is ≥ 1000 . In all the experiments using the rotating electrode, the interfacial reaction rate is less than the available diffusive sulphide flux, indicating that this competition could be the inherent condition that determines the film structure and properties.

For a Swedish repository (i.e. at the Forsmark site), if the sulphide diffusing through the compacted clay to the container surface is consumed in film formation under restricted mass transport control, the calculated sulphide flux will be $\sim 10^{-17} \text{ mol cm}^{-2} \text{ s}^{-1}$, taking the diffusion coefficient of sulphide in the compacted clay to be around $10^{-7} \text{ cm}^2 \text{ s}^{-1}$, the sulphide content in bulk groundwater surrounding the bentonite to be $\sim 10^{-5} \text{ mol L}^{-1}$, and the thickness of the compacted clay to be $\geq 35 \text{ cm}$.¹⁶ Thus, the steady state flux of SH^- to the canister surface would be over ~ 6 orders of magnitude lower than the diffusive sulphide flux ($\sim 10^{-11} \text{ mol cm}^{-2} \text{ s}^{-1}$) available under the stagnant conditions employed in our experiments. This suggests that the corrosion rate of the canister in saturated bentonite will be limited by mass transport of SH^- and the sulphide film formed will be porous.

Table 2 Film properties after corrosion in anoxic sulphide solutions containing different chloride contents at rotation rate of 30 rev min^{-1}

Experimental condition	Film morphology	$[\text{SH}^-]/\text{mol L}^{-1}$	$[\text{Cl}^-]/\text{mol L}^{-1}$	$[\text{Cl}^-]/[\text{SH}^-]$	Condition
$1 \times 10^{-3} \text{ mol L}^{-1} \text{ Na}_2\text{S} + 0.1 \text{ mol L}^{-1} \text{ NaCl}$, 11 h, natural corrosion	Compact	1×10^{-3}	0.1	100	$R_{\text{SH}^-} < J_{\text{diff}}$
$5 \times 10^{-5} \text{ mol L}^{-1} \text{ Na}_2\text{S} + 0.1 \text{ mol L}^{-1} \text{ NaCl}$, 11 h, natural corrosion	Compact	5×10^{-5}	0.1	2000	$R_{\text{SH}^-} < J_{\text{diff}}$
$1 \times 10^{-5} \text{ mol L}^{-1} \text{ Na}_2\text{S} + 0.1 \text{ mol L}^{-1} \text{ NaCl}$, 11 h, natural corrosion	Compact	1×10^{-5}	0.1	10 000	$R_{\text{SH}^-} < J_{\text{diff}}$
$5 \times 10^{-5} \text{ mol L}^{-1} \text{ Na}_2\text{S} + 1.0 \text{ mol L}^{-1} \text{ NaCl}$, 11 h and 24 h, natural corrosion	Compact	5×10^{-5}	1.0	20 000	$R_{\text{SH}^-} < J_{\text{diff}}$
$1 \times 10^{-5} \text{ mol L}^{-1} \text{ Na}_2\text{S} + 1.0 \text{ mol L}^{-1} \text{ NaCl}$, 14 h, natural corrosion	Compact	1×10^{-5}	1.0	100 000	$R_{\text{SH}^-} < J_{\text{diff}}$

Conclusions

1. The growth of sulphide films on a Cu surface under anoxic conditions is influenced by the solution sulphide and chloride concentrations, their ratio, and the sulphide flux at the film/solution interface.

2. The structure and growth kinetics of the sulphide film is governed by the competition between the interfacial reaction rate and sulphide diffusion in solution.

3. When the interfacial reaction rate is smaller than the available diffusive sulphide flux, corrosion proceeds under interfacial reaction control and a compact, protective film is formed. When corrosion proceeds under sulphide diffusion control a porous and non-protective film is formed.

4. In a Swedish repository the diffusive flux will be extremely low and our results support the assumption²⁻⁴ that corrosion should proceed under diffusion control since porous, non-protective sulphide films should be formed.

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