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

J. Chen [a], Z. Qin [a], L. Wu [a], J.J. Noël [a], D.W. Shoesmith [a,b,*]

[a] Department of Chemistry, The University of Western Ontario, London, ON N6A 5B7, Canada
[b] Surface Science Western, The University of Western Ontario, London, ON N6G 0J3, Canada

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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.

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 (~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 5×10^{-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 5×10^{-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., 5×10^{-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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* Corresponding author at: Department of Chemistry, The University of Western Ontario, London, ON N6A 5B7, Canada. Tel.: +1 519 661 2111x86366; fax: +1 519 661 3022.

E-mail address: dwshoesm@uwo.ca (D.W. Shoesmith).

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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 2.4×10^{-2} m and a thickness of 6×10^{-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_2O_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 4.52×10^{-4} m^2, and the solution volume was 6.5×10^{-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 time [21], the Cu electrode was rotated at a low rate of 30 rpm (3.14 rad/s).

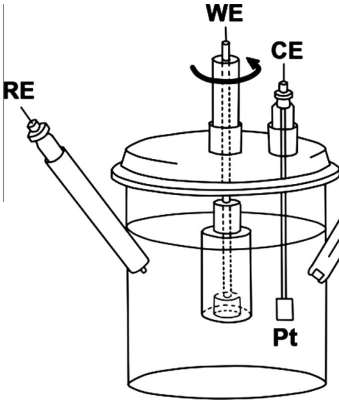

Fig. 1. Schematic of the electrochemical cell used in sulphide depletion experiments.

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 $\leqslant$4.2 mg/m^3, which includes the oxygen in both air and vapor. The actual oxygen content of the solution should be less than this value. Even though there is a trace amount of oxygen present, copper sulphide is more stable in sulphide solution than copper oxide based on thermodynamic data ($\Delta_f G^\circ = -101.46$ kJ/mol for the conversion from Cu_2O to Cu_2S 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 5×10^{-2} mol m^{-3} Na_2S + 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 ($Na_2S \cdot 9H_2O$, 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 5×10^{-2} mol m^{-3} Na_2S + 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)).