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Electrochemical and Corrosion Examination of Copper under Deep Geologic Conditions for the Application of Nuclear Waste Containers

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Abstract

Copper is the selected material for the fabrication of nuclear fuel waste containers in Sweden, Finland and Canada due to its corrosion resistance in the anoxic aqueous environments, anticipated in deep geological repositories. A potential oxidant for copper is bisulphide produced either by the dissolution of minerals or by sulphate-reducing bacteria. The primary goals of this thesis were to determine the mechanism of corrosion of copper in bisulphide environments and to investigate the chemistry of the bentonite porewater that will ultimately be in contact with the copper container.

The mechanism of sulphide film growth and the details of copper corrosion in anoxic aqueous bisulphide solutions in the presence of various groundwater anions have been investigated electrochemically. The chalcocite films were analyzed via voltammetry, electrochemical impedance spectroscopy and surface analysis. Under these conditions, growth of a coherent film occurred initially but the development of interfacial stresses led rapidly to film fracture. Upon fracture, a resistive outer chalcocite deposit formed with continued growth governed by the mass transport of bisulphide. Specific anion effects were observed with chloride, a common groundwater ion, found to maintain porosity in the chalcocite film while the oxyanions, sulphate and bicarbonate were found to suppress film growth.

At high bisulphide concentrations and positive potentials growth of the outer deposit caused an apparent partial passivation of the surface, which theoretically could lead to localized film breakdown and pitting. However, the required high bisulphide concentrations are not attainable in a deep geologic repository and pitting should not occur.
Bentonite porewater chemistry was successfully monitored using a novel experimental set-up. Electrochemical sensors monitoring pH, chloride concentration and the copper corrosion potential were placed both on the surface and inside of a bentonite clay disk. The results showed that the bentonite acted like a pH buffer and chloride from bulk solution adsorbed onto the montmorillonite structure. Corrosion potential measurements suggested that corrosion likely occurred via formation of a copper chloride complex or growth of a cuprite film. Data collected from these studies will be used directly by SKB via incorporation into models.

**Keywords:** Copper, Sulphide, Bisulphide, Chloride, Corrosion, Electrochemistry, Film Growth, Mechanism, Bentonite, Nuclear Waste Disposal
Co-Authorship Statement

This thesis includes published data in Chapters 4 and 5.

Chapter 4: Dr. D. W. Shoesmith assisted with editing.

Chapter 5: Corrosion experiments were completed by Dr. J. Chen and Dr. D. W. Shoesmith assisted with editing.

Chapter 6: EIS data was collected by Dr. J. Smith but I performed the analysis and fitting. Dr. D. W. Shoesmith assisted with editing.

Chapter 7: Dr. D. W. Shoesmith assisted with editing.

Chapter 8: Dr. J. J. Noël assisted with experimental design and editing.
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This thesis is dedicated to my parents,
Pasquale and Nancy Martino

And my grandparents,
Elmiro and Angela Martino

and

Robert and Natta Todd
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<th>Description</th>
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<tbody>
<tr>
<td>AES</td>
<td>Auger electron spectroscopy</td>
</tr>
<tr>
<td>AFM</td>
<td>atomic force microscopy</td>
</tr>
<tr>
<td>CPE</td>
<td>constant phase element</td>
</tr>
<tr>
<td>CV</td>
<td>cyclic voltammetry</td>
</tr>
<tr>
<td>DGR</td>
<td>deep geologic repository</td>
</tr>
<tr>
<td>EDX</td>
<td>energy-dispersive X-ray spectroscopy</td>
</tr>
<tr>
<td>EIS</td>
<td>electrochemical impedance spectroscopy</td>
</tr>
<tr>
<td>EQCM</td>
<td>electrochemical quartz crystal microbalance</td>
</tr>
<tr>
<td>EXAFS</td>
<td>extended X-ray absorption fine structure</td>
</tr>
<tr>
<td>FIB</td>
<td>focused ion beam</td>
</tr>
<tr>
<td>ICP-AES</td>
<td>inductively coupled plasma atomic emission spectroscopy</td>
</tr>
<tr>
<td>RDE</td>
<td>rotating disk electrode</td>
</tr>
<tr>
<td>SCE</td>
<td>saturated calomel electrode</td>
</tr>
<tr>
<td>SEM</td>
<td>scanning electron microscopy</td>
</tr>
<tr>
<td>SHE</td>
<td>standard hydrogen electrode</td>
</tr>
<tr>
<td>SRB</td>
<td>sulphate reducing bacteria</td>
</tr>
<tr>
<td>TEM</td>
<td>transmission electron microscopy</td>
</tr>
<tr>
<td>XAS</td>
<td>X-ray absorption spectroscopy</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray photoelectron spectroscopy</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
</tr>
</tbody>
</table>
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<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>surface area of the electrode</td>
</tr>
<tr>
<td>C</td>
<td>capacitance</td>
</tr>
<tr>
<td>$c_b$</td>
<td>bulk solution concentration</td>
</tr>
<tr>
<td>$C_{dep}$</td>
<td>outer deposit capacitance</td>
</tr>
<tr>
<td>$C_{dl}$</td>
<td>double layer capacitance</td>
</tr>
<tr>
<td>$C_{film}$</td>
<td>combination of $C_{dl}$, $C$ of adsorbed species and $C$ of the film</td>
</tr>
<tr>
<td>$C_{int}$</td>
<td>interfacial capacitance</td>
</tr>
<tr>
<td>$c_s$</td>
<td>surface concentration</td>
</tr>
<tr>
<td>D</td>
<td>diffusion coefficient</td>
</tr>
<tr>
<td>E</td>
<td>applied potential</td>
</tr>
<tr>
<td>$\Delta E^\circ$</td>
<td>potential difference under standard conditions</td>
</tr>
<tr>
<td>$E_{corr}$</td>
<td>corrosion potential</td>
</tr>
<tr>
<td>$E^e$</td>
<td>equilibrium potential</td>
</tr>
<tr>
<td>F</td>
<td>Faraday’s constant (96485 C/mol)</td>
</tr>
<tr>
<td>$\Delta G^\circ$</td>
<td>Gibbs free energy change under standard conditions</td>
</tr>
<tr>
<td>$I_a$</td>
<td>anodic current density</td>
</tr>
<tr>
<td>$I_c$</td>
<td>cathodic current density</td>
</tr>
<tr>
<td>$I_{corr}$</td>
<td>corrosion current density</td>
</tr>
<tr>
<td>$I_{net}$</td>
<td>current density which would be measured if $E$ was not equal to $E_{corr}$</td>
</tr>
<tr>
<td>$I_o$</td>
<td>exchange current density</td>
</tr>
<tr>
<td>J</td>
<td>flux</td>
</tr>
<tr>
<td>k</td>
<td>reaction rate constant for a reaction at a specific temperature</td>
</tr>
</tbody>
</table>
n    number of electrons
Q    admittance
R    gas constant (8.314 J/K·mol)
R    resistance
R_{ct}  charge transfer resistance
R_{dep}  outer deposit resistance
R_{int}  interfacial resistance
R_{pore}  pore resistance
R_s    solution resistance
T    temperature
W    Warburg impedance
Z    impedance

\alpha  transfer coefficient
\delta  Nernst diffusion layer thickness
\eta  overpotential
\eta_a  anodic overpotential
\theta  phase angle
\nu  kinematic viscosity
\sigma_w  Warburg coefficient
\tau  time constant
\omega  angular rotation rate
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1

Introduction

1.1 Nuclear Waste Disposal Scenario: The Multi-BARRIER System

Countries around the world rely on nuclear power to provide a reliable, inexpensive and environmentally friendly source of electrical energy. A key requirement for the continued use of nuclear power is the successful management of the spent nuclear fuel. One approach under development in many countries, including Canada, Sweden and Finland, is a multi barrier system design illustrated in Figure 1.1, including engineered barriers such as the used fuel itself, a specially designed waste container, and the bentonite backfill, as well as the chosen geologic location for the deep geologic repository (DGR) [1].

![Figure 1.1: Schematic of the multi-barrier approach to nuclear waste disposal](image)

In such disposal facilities the spent fuel would be sealed in containers, specifically designed to avoid both corrosion and mechanical failure. Depending on the repository location, these
containers could have a design life of 100,000 years. The proposed spent fuel container, for the Swedish repository is shown in Figure 1.2, and is composed of two components; a cast iron inner vessel for structural integrity, and a 5 cm thick outer shell of Cu to provide corrosion resistance.

**Figure 1.2: Schematic of a Swedish high-level nuclear waste repository**

Cu was first selected in 1978 as a response to the 1977 Nuclear Stipulation Act which required that a safe method for disposing of spent fuel must be proposed before further fuelling of nuclear power plants could occur [2]. Cu was a viable candidate since it should be stable in the anoxic environments anticipated in a DGR. Thermodynamic studies completed in 1978, and reassessed in 2001, found the only significant oxidants to be atmospheric oxygen (O₂) and bisulphide (SH⁻). Lifetime assessments based on general corrosion were performed using the mass balance approach for O₂, and assuming transport control by SH⁻ produced remotely by the action of SO₄²⁻ reducing bacteria and, possibly, the dissolution of pyrite present in the geological environment [2]. It is proposed that these containers be buried
500 to 1000 m below the surface where geological properties and events are predictable and groundwater has little movement.

The container will be exposed to an evolving environment after burial, Figure 1.3, and, thus, will be susceptible to various corrosion processes. During the early period of emplacement the container will experience a warm oxidizing environment with temperatures of up to 90 °C [3]. During this stage the Cu container is vulnerable to corrosion via oxidants such as O₂ (trapped in the repository on sealing), and possibly radiolytically produced species such as HNO₃. Over the first few hundred years, there is a gradual shift in the environment to a cool, anoxic, reducing condition when the major available oxidant for Cu will be remotely-produced SH⁻. Over the long term, SH⁻ induced corrosion is the dominant threat to the durability of the container and is the focus of this thesis.

![Figure 1.3: Schematic qualitative illustration of the evolution in anticipated conditions in a DGR as a function of time.](image)

Another key barrier in the multi-barrier sequence is the bentonite clay buffer. The DGR will be backfilled with at least a 35 cm barrier of bentonite clay. Upon saturation with
groundwater, the clay will swell and the container will become sealed [4]. This is advantageous for many reasons; (i) it will inhibit the transport of reactants to, and corrosion products away from, the container surface; (ii) it will limit the amount of atmospheric O₂ initially trapped in the repository and hence available to react with the container; and (iii) due to the small pore size when fully saturated, it will prevent microbial activity close to the container surface [1, 2]. It also has post closure failure functions as it limits the transport of released radionuclides by providing a slow transport medium and possesses the ability to capture cationic radionuclides by ion exchange processes [5].

The final barrier is the geological repository, which must conform to strict regulations regarding stability. The general principle behind choosing a repository is summarized in Figure 1.4. The selected repository must be geologically stable, possess clearly identifiable

![Figure 1.4: Schematic of the general principle behind choosing a DGR](image)
advantageous features that must not be destroyed by the excavation/waste package emplacement process, and its evolution from the excavated or disturbed state must be predictable with acceptable certainty [1, 4]. In Canada, Sweden and Finland the preferred locations are in hard rock in which it can be demonstrated that, although there is a high density of intersecting rock fractures at shallow depths into the rock, there is only a low density at planned repository depths (500 to 100 m). While surface waters may be dilute, oxidizing, and mobile, those at planned DGR depths will have a low mobility and will be anoxic and likely saline [6].

1.2 Thermodynamics of Aqueous Corrosion Processes

Processes that occur in nature spontaneously are associated with a negative change in Gibbs free energy, since the stability of the products is greater than that of the reactants. In electrochemical terms the Gibbs free energy can be defined in terms of the change in energy of a charge as it moves reversibly under the influence of a potential [7],

\[ \Delta G^\circ = -nF\Delta E^\circ \]  \hspace{1cm} (1.1)

where \( \Delta G^\circ \) is the free energy change under standard conditions, \( n \) is the number of electrons transferred, \( F \) is Faraday’s constant (96485 C/mol) and \( \Delta E^\circ \) is the potential difference under standard conditions. Therefore, the thermodynamics of an electrochemical reaction can be expressed as a reversible, or equilibrium, potential under standard conditions and evaluated versus the Standard Hydrogen Electrode (SHE). However, deviations from standard conditions, such as those enforced by temperature and the concentration of redox species, change the equilibrium potential and the Nernst equation is used to describe the influence of these factors. For the following general reaction,
\[ aA + bB \rightleftharpoons cC + dD \]  \hspace{1cm} (1.2)

the equilibrium potential \((E^o)\) can be calculated from the Nernst equation,

\[
E^e = E^o - \frac{RT}{nF} \ln \left( \frac{[D]^d[C]^c}{[A]^a[B]^b} \right) \hspace{1cm} (1.3)
\]

where \(T\) is the temperature in K, \(R\) is the gas constant \((8.314 \text{ J/(K·mol)})\), and \([X]^x\) is the concentrations of species \(X\) to the power of its stoichiometric coefficient \(x\).

The aqueous corrosion of a material (commonly a metal) is a spontaneous process in which oxidation of the metal and reduction of an available oxidant in the solution occurs simultaneously at the metal/solution interface. The simplest anodic reaction is dissolution of the metal to yield a soluble species,

\[ M \rightarrow M^{n+} + ne^- \]  \hspace{1cm} (1.4)

The coupled cathodic reaction is often, but not limited to, the reduction of protons, water or dissolved oxygen, given here in the generalized form,

\[ \text{Ox} + ne^- \rightarrow \text{Red} \]  \hspace{1cm} (1.5)

The sum of these two half reactions yields the overall corrosion process,

\[ M + \text{Ox} \rightarrow M^{n+} + \text{Red} \]  \hspace{1cm} (1.6)

A common way to graphically represent all the thermodynamically possible reactions involved in a specific corrosion system is to use a Pourbaix diagram. Marcel Pourbaix first summarized thermodynamic data in the form of a Pourbaix diagram in 1945. Such a diagram is the plot of the equilibrium potentials, and solubility and complexation constants for a metal in an aqueous solution as a function of pH and, when necessary, temperature and the concentration of complexing species. These diagrams are defined by the Gibbs free energies of the species involved by the spontaneous directions of all the possible reactions [7]. Pourbaix diagrams contain three types of lines: horizontal lines that represent reactions only dependent on changes in potential; vertical lines that describe reactions only dependent on
pH; and angled lines that are characteristic of reactions that are both potential and pH dependent. The Pourbaix diagram describing the Cu/H\textsubscript{2}O anoxic system is shown in Figure 1.5, with the H\textsubscript{2}O stability region defined by the area between the two dashed lines. The dashed line at more positive potentials is the reversible oxygen line representative of the H\textsubscript{2}O/O\textsubscript{2} equilibrium potential as a function of pH. The dashed line at more negative potentials is the reversible hydrogen line representative of the H\textsubscript{2}O/H\textsubscript{2} equilibrium potential as a function of pH. Inspection of the Pourbaix diagram in Figure 1.5, shows that the stability region for Cu metal lies within the stability region of water, thus indicating Cu is thermodynamically stable in H\textsubscript{2}O in anoxic conditions. The solid lines define the stability regions for the solid (Cu\textsubscript{2}O, CuO) and solution soluble species (Cu\textsuperscript{2+}).

![Pourbaix Diagram for Cu](figure.jpg)

Figure 1.5: Pourbaix diagram for Cu at 25°C in H\textsubscript{2}O containing [Cl\textsuperscript{-}] = 10\textsuperscript{-3} mol/dm\textsuperscript{3} and [Cu\textsubscript{(aq)}\textsubscript{tot}] = 10\textsuperscript{-6} mol/dm\textsuperscript{3}: (a) The equilibrium line for H\textsubscript{2}O/H\textsubscript{2}; (b) the equilibrium line for H\textsubscript{2}O/O\textsubscript{2} [8].

Corrosion is the spontaneous coupling of an anodic half reaction of a metal with a cathodic half reaction, generally for a redox reaction involving species in the electrolyte solution in aqueous corrosion. When coupling occurs each reaction is polarized away from its equilibrium potential and as a consequence of overpotential a current is generated. Each half reaction is polarized to a magnitude which enables mass balance to be achieved. This is
attained at a potential known as the corrosion potential, $E_{\text{corr}}$, which must lie between the equilibrium potentials for the two half reactions. At $E_{\text{corr}}$, a positive current is generated for the anodic reaction and a negative current for the cathodic reaction. These current densities for the anodic and cathodic half reactions are equal but opposite in sign,

$$I_{\text{corr}} = |-I_c| = I_a$$

where $I_{\text{corr}}$ is the corrosion current density, $I_c$ is the cathodic current density and $I_a$ is the anodic current density, as depicted graphically in Figure 1.6.

![Figure 1.6: Schematic showing the coupling of a metal oxidization reaction with an oxidant reduction reaction to yield an overall corrosion process at $E_{\text{CORR}}$.](image)

**1.3 Kinetics of Aqueous Electrochemical and Corrosion Reactions**

At equilibrium, the potential and the ratio of the oxidized/reduced species involved in an electron transfer reaction are dictated by the Nernst equation (Equation 1.3). This equilibrium can be considered dynamic, with the current densities associated with the forward and reverse reactions being equal.
For reaction 1.5, the kinetics can be specified by equation 1.8 if the reaction is first order,

\[ R = k[Ox] \]  \hspace{1cm} (1.8)

where \( R \) is the rate of the reaction, \( k \) is the rate constant for the reaction at a specific temperature and \([Ox]\) is the concentration of the reactant. Since the reaction is electrochemical in nature, the rate is defined as a current density, \( I \), and the rate equation can be represented as,

\[ I = -nFk[Ox] \]  \hspace{1cm} (1.9)

where \( A \) is the surface area of the electrode. Since the reaction is an electron transfer reaction the rate constant is potential dependent and defined as,

\[ k = k^\circ \exp \left( \frac{-\alpha nF\eta}{RT} \right) \]  \hspace{1cm} (1.10)

where \( k^\circ \) is the standard rate constant, \( \alpha \) is the transfer coefficient (0.5 for simple electron transfer reactions), \( \eta \) is the overpotential \((E - E_{eq})\) which is a measure of how far the reaction is from equilibrium, where \( E \) is the applied potential. Equation 1.9 can now be written as,

\[ I = -nF[Ox]k^\circ \exp \left( \frac{-\alpha nF\eta}{RT} \right) \]  \hspace{1cm} (1.11)

At equilibrium the currents for the forward and reverse reactions are the same and equal to the exchange current density, \( I_o \). The overall reaction is the sum of the forward (anodic) and reverse (cathodic) currents and is given by the Butler-Volmer relationship which describes the current as a function of applied potential [9]:

\[ I = I_o \exp \left[ \frac{\alpha nF(E-E_{eq})}{RT} \right] - I_o \exp \left[ -\frac{(1-\alpha)nF(E-E_{eq})}{RT} \right] \]  \hspace{1cm} (1.12)

and can be simplified to:

\[ I = I_o \left[ \exp \left( \frac{\alpha nF(\eta)}{RT} \right) - \exp \left[ -\frac{(1-\alpha)nF(\eta)}{RT} \right] \right] \]  \hspace{1cm} (1.13)
The Butler-Volmer relationship is represented graphically in Figure 1.7. When a large anodic overpotential ($\eta_a$) is applied, the term describing the cathodic current density tends toward zero and only an anodic current density ($I_a$) is observed. Similarly, for a large cathodic overpotential, the anodic term approaches zero and only a cathodic reaction would be observed.

The kinetics of a corrosion reaction can be described in a similar way, but requires the coupling together of the anodic and cathodic portions of the two different coupled half reactions. Each half reaction is polarized away from its equilibrium potential to the corrosion potential, $E_{corr}$, where a mass balance condition is achieved.

![Figure 1.7: The Butler-Volmer relationship for a redox active species](image)

At this potential the anodic current is equal to the cathodic current and since the reactions are occurring on the same surface a direct measurement of the corrosion current density ($I_{corr}$) cannot be made. Adding the anodic and cathodic terms for the two half reactions, and defining the overpotential as the difference between the applied potential and $E_{corr}$, yields the Wagner-Traud relationship [9],
\[ I_{\text{net}} = I_{\text{corr}} \left[ \exp \left( \frac{\alpha_a n F (E - E_{\text{corr}})}{RT} \right) - \exp \left( - \frac{\alpha_c n F (E - E_{\text{corr}})}{RT} \right) \right] \] (1.14)

where \( I_{\text{net}} \) is the current density which would be measured if \( E \) was not equal to \( E_{\text{corr}} \). This relationship is graphically portrayed in Figure 1.8.

In contrast to the Butler-Volmer relationship, two different reactions can contribute to the current at either positive or negative overpotentials. However, at large anodic overpotentials (\( \eta_a > \sim 50 \text{ mV} \)) the cathodic current tends towards zero, and only the anodic current for metal dissolution is observed. Similarly for large cathodic overpotentials the anodic current approaches zero, and the current contribution is solely from the reduction reaction. Thus, for a large anodic polarization equation 1.14 becomes:

\[ I_{\text{net}} = I_{\text{corr}} \left[ \exp \left( \frac{\alpha_a n F (\eta_a)}{RT} \right) \right] \] (1.15)

where \( \eta_a \) is given by \( E - E_{\text{corr}} \). This relationship can be rearranged to yield the corresponding Tafel equation [7],

\[ \eta_a = \frac{2.3RT}{anF} \log \left( \frac{I_{\text{net}}}{I_{\text{corr}}} \right) \] (1.16)

which, on extrapolation to \( E_{\text{corr}} \) (\( \eta_a = 0 \)), yields a value of the corrosion current density, \( I_{\text{corr}} \). A similar Tafel relationship can be expressed and extrapolated for the cathodic half reaction.

The slope of each line provides insight into the kinetics and mechanism of the two half reactions.
1.3 Materials

1.3.1 SKB Cu

The container shell is designed to be 50 mm thick and fabricated from O-free, P-doped Cu. Initially the container experiences a warm, oxic period and pressures in the DGR are low. However, as temperatures decrease, H₂O returns to saturate the clay and the bentonite surrounding the container swells, exerting pressures > 15 MPa, leaving the Cu shell susceptible to creep deformation [11]. Removing the oxygen and doping with small concentrations of P (30 to 100 ppm) improves the creep strength of Cu thereby limiting the physical deformation of the container [12]. Recent studies show that P forms stabilizing atmospheres (Cottrell atmospheres) around dislocations and grain boundaries in the Cu.
These high-energy sites must break away from the P clouds in order to cause deformation [13].

1.3.2 Bentonite Clay

Bentonite clay is used in the DGR for two applications: a high grade bentonite is used as a buffer material in direct contact with the containers and a medium grade bentonite, possibly mixed with soil or non-swelling clays, is used as a backfill material for sealing the disposal vault after container/buffer emplacement. Bentonite contains expandable 2:1 (one octahedral sheet of Al$_2$O$_3$ between two tetrahedral sheets of SiO$_2$) phyllosilicate mineral layers that have a permanent layer charge. This layer charge arises from cation substitutions in either the octahedral or tetrahedral sheet, with the result of each substitution being an overall negative charge over the sheet surface. As shown in Figure 1.9, this net negative charge layer is then neutralized via H$_2$O molecules that accumulate around cations which causes an increase in their hydration shells. This neutralization via hydration causes the layers to expand and thus the clay to swell [14].

The difference between the two grades of clay is that the high grade is Na-based and the medium grade is Ca-based. For the Na-based clay, the electrical interactions between the Na$^+$ and the negatively charged platelets is relatively weak and an abundance of H$_2$O molecules can enter the interlayer allowing the clay to absorb 500% to 700% of H$_2$O relative to its weight. With respect to the Ca-based clay, the Ca$^{2+}$ interacts more strongly with the negative sheets thus allowing fewer H$_2$O molecules to penetrate the interlayer causing this clay to absorb only 150% to 200% H$_2$O with respect to its weight. Ca-based clay can be
converted to Na-based clay via “soda activation” which leads to an exchange of Ca$^{2+}$ cations for Na$^+$ [14].

Figure 1.9: Schematic of the swelling of both Ca and Na bentonite clay upon hydration of the interlayer [14]
1.4 Destabilization of Cu in Chloride and Sulphide Solutions

The thermodynamic data for Cu under anticipated repository conditions has been extensively studied [15] and is typically presented in the form of potential-pH (Pourbaix) diagrams. Various groundwater species have been studied, in particular Cl\(^-\) and SH\(^-\).

Cl\(^-\) is important since it is present in appreciable levels in groundwater and can accelerate the corrosion of Cu under oxidizing conditions by the formation of a Cu\(^+\) complex. Cl\(^-\) can cause film formation and accelerate metal dissolution. Figure 1.10 shows that, in the absence of dissolved O\(_2\), Cu is thermodynamically stable in moderately concentrated Cl\(^-\) solutions over a large pH range.

![Pourbaix diagram](image)

Figure 1.10: Pourbaix diagram for Cu at 25°C in H\(_2\)O containing [Cl\(^-\)] = 0.1 mol/dm\(^3\) and [Cu\(_{aq}\)]\(_{tot}\) = 10\(^{-6}\) mol/dm\(^3\). The stability region for H\(_2\)O is that between the two dashed lines [8].

For sufficiently positive potentials (e.g. when O\(_2\) is present and corrosion possible) various Cu(I) chloride species can form as the [Cl\(^-\)] increases. Lee and Nobe [16] found a sequence of Cu chloride species is produced as the [Cl\(^-\)] is increased,

\[
\text{Cu}^+ + 2\text{Cl}^- \rightleftharpoons \text{CuCl}_2^- + \text{Cl}^- \rightleftharpoons \text{CuCl}_3^{2-} + \text{Cl}^- \rightleftharpoons \text{CuCl}_4^{3-} \quad (1.17)
\]
For neutral to alkaline conditions when O\textsubscript{2} is present, corrosion can lead to a thin Cu(I) oxide film (~2.5 nm thick) which can form via a hydrolysis reaction [17],

$$
2 \text{CuCl}_2^− + 2 \text{OH}^− \rightleftharpoons \text{Cu}_2\text{O} + \text{H}_2\text{O} + 4 \text{Cl}^− \quad (1.18)
$$

with the stability of the oxide being inversely proportional to the [Cl\textsuperscript{−}]. Anodic dissolution of Cu in Cl\textsuperscript{−}-containing solutions proceeds via the following sequence of reactions [18],

$$
\text{Cu} + \text{Cl}^− \rightleftharpoons \text{CuCl}_{(ads)} + \text{e}^− \quad (1.19)
$$

$$
\text{CuCl}_{(ads)} + \text{Cl}^− \rightleftharpoons \text{CuCl}_2^−(\text{surface}) \quad (1.20)
$$

$$
\text{CuCl}_2^−(\text{surface}) \rightarrow \text{CuCl}_2^−(\text{bulk}) \quad (1.21)
$$

The rate of anodic dissolution will increase with increasing potential and will depend on mass transport conditions. As the rate of dissolution increases there will be an increase in the surface concentration of CuCl\textsubscript{2}^− and an increase in the flux of Cu chloride species away from the electrochemically dissolving surface.

Since any O\textsubscript{2} trapped on sealing the DGR will be rapidly consumed (Figure 1.3), the greatest threat to the thermodynamic stability of Cu under the eventually established anoxic conditions in a DGR is sulphide (SH\textsuperscript{−}). Figure 1.11 shows the Pourbaix diagram for Cu in equilibrium with an aqueous Cl\textsuperscript{−} solution containing SH\textsuperscript{−}. In the presence of SH\textsuperscript{−}, the equilibrium line for water is in the stability region for Cu\textsubscript{2}S showing that the Cu is unstable with respect to Cu\textsubscript{2}S in an aqueous solution. Under these conditions, Cu corrosion is supported by the cathodic reduction of the proton from H\textsubscript{2}O or SH\textsuperscript{−}. The proposed anodic reaction for Cu in the presence of SH\textsuperscript{−} is as follows [19],

$$
\text{Cu} + \text{SH}^− \rightarrow \text{Cu(SH)}_{(ads)} + \text{e}^− \quad (1.22)
$$

$$
\text{Cu} + \text{Cu(SH)}_{(ads)} + \text{SH}^− \rightarrow \text{Cu}_2\text{S} + \text{H}_2\text{S} + \text{e}^− \quad (1.23)
$$

with the supporting cathodic reaction being either,

$$
2 \text{H}_2\text{O} + 2 \text{e}^− \rightarrow \text{H}_2 + 2 \text{OH}^− \quad (1.24)
$$
or the reduction of the proton associated with \( \text{SH}^- \),

\[
2 \text{SH}^- + 2 \text{e}^- \rightarrow \text{H}_2 + 2 \text{S}^{2-}
\]  \hspace{1cm} (1.25)

The \( \text{Cu}_x\text{S} \) product formed is highly insoluble with solubility constants of \( 2 \times 10^{-47} \) and \( 8.5 \times 10^{-45} \) for \( \text{Cu}_2\text{S} \) and \( \text{CuS} \), respectively [20]. The driving force for the formation of \( \text{Cu}_2\text{S} \) is large making the corrosion reaction described by the coupling of equations 1.23 and 1.24/1.25 thermodynamically feasible over the full pH range for the redox and chemical conditions anticipated in a DGR.

![Pourbaix diagrams for the Cu/Cl\(^-\)/S\(^2-\)/H\(_2\)O system at 25 °C containing [Cl\(^-\)] = 10\(^{-3}\) mol/dm\(^3\), [SH\(^-\)] = 10\(^{-3}\) mol/dm\(^3\) and [Cu\(_{\text{aq}}\)]\(_{\text{tot}}\) = 10\(^{-6}\) mol/dm\(^3\). The stability region of \( \text{H}_2\text{O} \) is that between the two dashed lines [21].](image)

Under natural corrosion conditions a number of different \( \text{Cu}_x\text{S} \) films can form including non-stoichiometric phases. In addition to the stoichiometric phases, chalcocite (\( \text{Cu}_2\text{S} \)) and covellite (\( \text{CuS} \)), non-stoichiometric phases include: djurleite (\( \text{Cu}_{1.96}\text{S} \)), dijenite (\( \text{Cu}_{1.8}\text{S} \)) and anilite (\( \text{Cu}_{1.75}\text{S} \)). Each of these film types will be thermodynamically favorable depending on the potential and pH. For the proposed SKB DGR site the anticipated redox potential range is \(-200\) to \(-400\) mV/SHE within which chalcocite, \( \text{Cu}_2\text{S} \), would be the thermodynamically stable phase [15].
The total S content in a Swedish DGR could be up to 0.011 mol/kg. Specifically, \([\text{SH}^-]s\) are expected to be approximately \(3.0 \times 10^{-4}\) M upon closure and \(3.0 \times 10^{-5}\) M after 10,000 years [15]. This difference between S and \(\text{SH}^-\) content is due to the fact that metal sulphides present in host rock, such as pyrite (FeS\(_2\)), have a very low solubility. Another appreciable source of \(\text{SH}^-\) comes from microbial reactions involving sulphate-reducing bacteria (SRB). Since DGR concentrations of \(\text{SO}_4^{2-}\) are likely to range from \(6 \times 10^{-3}\) M at repository closure to \(4.2 \times 10^{-3}\) M after 10,000 years, this \(\text{SH}^-\) source cannot be discounted. Bi-products from the action of SRBs, are S species of lower oxidation state including sulphite (SO\(_3^-\)), elemental S, dithionite (S\(_2\)O\(_4^{2-}\)), thiosulphate (S\(_2\)O\(_3^{2-}\)), and sulphide (SH\(^-\)) [15]. However microbial activity near the container surface should be effectively suppressed due the presence of highly compacted bentonite clay, which will be emplaced with a dry density > 1600 kg/m\(^3\). At this density the swelling pressure achieved upon saturation will exceed 2 MPa and the activity of water will be reduced to < 0.96. These values are the critical values below which microbial activity at the container surface should be prevented [8, 22]. Consequently, only \(\text{SH}^-\) produced outside the compacted bentonite layer, which can diffuse to the container surface, needs to be considered as a potential oxidant.

1.5 Thesis Objectives

The primary goals of this thesis are the following:

- To electrochemically determine the effect of \([\text{SH}^-]\) and mass transport processes on the structural properties of anodically-formed Cu\(_x\)S films.
• To clarify the nature of the Cu$_x$S film grown at applied potentials positive to the corrosion potential, and to determine whether or not electrochemically grown films are representative of those formed under corrosion conditions.

• To determine whether or not SH$^-$-induced pitting of Cu is possible under DGR conditions, and, if it is, what the consequences would be for a Cu container in a DGR.

• To identify the effects of various groundwater anions, in particular Cl$^-$, on Cu$_x$S film formation under electrochemical and corrosion conditions.

• To develop an experimental method to measure bentonite pore and container surface water chemistry in order to better understand the exposure environment of the Cu waste container.

1.6 References


2

Literature Review

2.1 Corrosion Studies of Cu in Aqueous Sulphide Solutions

An extensive amount of research has been performed on sulphide-induced Cu corrosion in seawater for marine applications, when conditions can switch frequently between oxic and anoxic. Mor and Beccaria [1] investigated the effects of small concentrations of sulphide (50 – 30 ppm) on Cu corrosion in artificial seawater for both aerated and deaerated conditions in the pH range 6.5 to 8.6. Weight loss studies showed the extent of corrosion decreased with increasing pH when sulphide was absent but the reverse occurred when sulphide was present. It was claimed, over the pH range investigated, the [SH\(^-\)] remained the same while the [S\(^2-\)] changed 1000 fold over time. Thus, they attributed the observed increase in corrosion rate to the aggressiveness of the S\(^2-\) ion. The destabilizing effect of the sulphide was attributed to a decrease in \(E_{\text{corr}}\), and no appreciable change in \(E_{\text{corr}}\) was observed when SH\(^-\) and O\(_2\) were simultaneously present. It was found that an initial layer of Cu\(_2\)S developed over 2 hours, followed by the growth of a more complex second layer comprised of CuS, Cu\(_2\)O and CuO, as indicated by potential-pS plots and confirmed by X-ray diffraction (XRD). It was proposed that this second layer grew via S\(^2-\) diffusion through the porous Cu\(_2\)S base layer.

Corrosion rate measurements recorded under stagnant and rotating disk electrode (RDE) conditions were performed by Syrett [2] in order to investigate whether or not the presence of sulphide and/ or oxygen had a significant effect on Cu corrosion. The corrosion rates in anoxic sulphide solutions were found to be similar to those measured in oxic,
sulphide free solutions. However when both oxidants were present in the same solution, the corrosion rate increased substantially. This synergistic effect was attributed to the enhancement of the anodic reaction by oxygen reduction. XRD confirmed the growth of a chalcocite, Cu$_2$S, film that was thought to prevent the formation of a protective Cu oxide.

The effects of sulphide in aerated saline solutions (3% NaCl) were investigated by Rahmouni et al. [3] using $E_{\text{corr}}$, electrochemical impedance spectroscopy (EIS) and galvanostatic stripping measurements. $E_{\text{corr}}$ measurements suggested that, without the addition of sulphide, a protective Cu oxide covered the surface. However, upon the addition of sulphide (at a concentration as low as $3.2 \times 10^{-5}$ M) $E_{\text{corr}}$ promptly shifted to a more active value. EIS data collected in the presence of sulphide was fitted to a two time constant equivalent circuit, indicative of a film that is porous in nature, thus providing evidence that the initially grown protective oxide film had been breached. Polarization resistance values decreased with time which suggested an increase in corrosion rate accompanied by the thickening of the sulphide film. When the experiment was finished galvanostatic stripping yielded a plot with 2 potential plateaus attributed to the reduction of both Cu$_2$O and Cu$_2$S. It was suggested that the corrosion rate was accelerated when OH$^-$ and SH$^-$ were simultaneously present [3].

Abd Hallem et al. [4] studied Cu corrosion in aerated NaOH solutions in the absence and presence of sulphide. It was found that, in the absence of sulphide, Cu acts as a metal/metal oxide electrode, and while in the presence of $\leq 10^{-4}$ M sulphide, the formation of the Cu oxide was still favoured. When the sulphide was increased to intermediate concentrations ($10^{-3}$ M), $E_{\text{corr}}$ was found to fluctuate between active and passive potentials, while a further increase in sulphide concentration to $>10^{-3}$ M led to the formation of the non-protective
Cu_2S. Electrodes subjected to highly concentrated sulphide solutions reached a steady state $E_{corr}$ with a $-60$ mV/dec dependence on [S^{2-}]:

$$E = E^\circ - 0.059 \log[\text{S}^{2-}]V_{SCE}$$ (2.1)

This suggests that the $E_{corr}$ is determined by the redox potential for the reaction between Cu/Cu_2S. Gennero De Chialvo and Arvia [5] came to a similar conclusion in their study but suggest the $E_{corr}$ was determined by the equilibrium potentials ($E_e$) for the reaction,

$$2 \text{Cu} + \text{S}^{2-} \rightleftharpoons \text{Cu}_2\text{S} + 2 \text{e}^-$$ (2.2)

$$E = -1.13 V - 0.030 \log[S^{2-}]V_{SCE}$$ (2.3)

for Cu_2S covered surfaces and

$$2 \text{Cu} + \text{S}^{2-} \rightleftharpoons \text{CuS} + 2 \text{e}^-$$ (2.4)

$$E = -0.94 V - 0.030 \log[S^{2-}]V_{SCE}$$ (2.5)

for CuS covered surfaces. In contrast to these findings, MacDonald et al. [6] published a study that found the $E_{corr}$ was dependent on the [SH\textsuperscript{-}] but claimed it was a mixed potential not an equilibrium potential.

Many studies on Cu related to the corrosion of nuclear waste containers performed in simulated groundwater or saline solutions have shown that the addition of sulphide destabilized Cu. Escobar et al. [7], studied Cu corrosion in simulated groundwater solutions that contained sulphide over a temperature range from 15 to 90 °C. The low $E_{corr}$ values indicated Cu destabilization in the presence of sulphide and a Tafel analysis showed that the corrosion current density, and thus the corrosion rate increased as the sulphide concentration and temperature were increased.

King and Stroes-Gascoyne [8] performed a simulation of Cu corrosion in Cl\textsuperscript{-} and sulphide taking into account the changing repository conditions. A shift in $E_{corr}$ to a less noble potential was first observed as conditions evolved from oxic to anoxic. A second
negative shift was observed upon the addition of \( \text{SH}^- \) when \( E_{\text{corr}} \) dropped to \(-0.80\) V/SCE to \(-1.00\) V/SCE depending on the sulphide concentration. Results obtained for a clay-covered electrode yielded similar \( E_{\text{corr}} \) values, after a delay in electrode response due to the slow mass transport of sulphide in the bentonite buffer. Taniguchi and Kawasaki [9] performed experiments under similar conditions on both bare and clay-covered electrodes. They also observed an increase in corrosion rate as the sulphide concentration was increased in both saline solution and in environments with a bentonite/sand mixture. Immersion tests were conducted for up to 730 days in 0.1 M and \( 10^{-3} \) M Na\(_2\)S solutions at an elevated temperature of \( 80^\circ\)C to simulate container conditions. It was found that the corrosion products were more strongly adhered when exposed to solution rather than covered with bentonite. In all tests a Cu\(_2\)S corrosion product was formed but a larger crystalline structure was observed in the bentonite case. It was concluded that corrosion was likely governed by \( \text{SH}^- \) supply to the surface, with mass transport in bentonite controlled by diffusion. Corrosion was uniform and proceeded at a rate of \(< 0.6 \) and \( 10^{-15} \) \( \mu \)m/a in \( 10^{-3} \) M and 0.1 M Na\(_2\)S, respectively.

Chen et al. [10-16] have extensively studied the corrosion of Cu in sulphide and Cl\(^-\) solutions under completely anoxic conditions (i.e., in an anaerobic chamber). The growth of sulphide films was analyzed using \( E_{\text{corr}}, \) EIS, scanning electron microscopy (SEM), focused ion beam (FIB) and energy dispersive X-ray spectroscopy (EDX) measurements in 0.1 M NaCl solutions containing \( 5\times10^{-5} \) and \( 5\times10^{-4} \) M Na\(_2\)S. It was found that, in the \( 5\times10^{-5} \) M solution, corrosion proceeded via the formation of a cellular, non-protective chalcocite (Cu\(_2\)S) film which lead to the depletion of \( \text{SH}^- \) at the Cu surface with film growth proceeding at a constant rate [11]. It was proposed that growth occurred at the film/ solution interface by transport of Cu\(^+\) through the cellular film possibly as a CuCl\(_2^-\) complex. The constant, linear film growth rate indicated that further corrosion was likely governed by \( \text{SH}^- \) diffusion in the
cellular matrix of the Cu$_2$S film followed by diffusion in the bulk once sulphide became depleted at the film/solution interface [12]. Similar experiments were conducted at a rotated electrode to control the SH$^-$ flux. When depletion of sulphide at the Cu surface was avoided in this manner, a coherent film was formed with growth governed by solid-state Cu$^+$ transport [14]. At the higher sulphide concentration of 5×10$^{-4}$ M, film growth began as a single Cu$_2$S layer composed of fine particulates that did not fully cover the surface but over time developed into a thicker, more compact film with a larger crystalline structure [10]. Film growth was found to follow a parabolic growth law with growth likely governed by Cu$^+$ diffusion along grain boundaries in the Cu$_2$S matrix [12].

Chen et al. determined that whether a porous or passive film would form was dependent upon three critical factors: the SH$^-$ and Cl$^-$ concentrations, their ratio, and the flux of SH$^-$ to the Cu surface [13]. The film morphology and growth kinetics were governed by the competition between the interfacial reaction rate and the rate of SH$^-$ diffusion. When the interfacial reaction was rate determining, the Cu sulphide film was compact and protective, and when SH$^-$ diffusion dominated the film was porous and non-protective. It was determined that when the ratio [Cl$^-$]/[SH$^-$] was ≥ 1000, a switch from a compact to a porous film was observed. The effect of Cl$^-$ on Cu$_2$S film growth was also explored for a solution containing 10$^{-3}$ M Na$_2$S and [Cl$^-$] ranging from 0.1 M to 5.0 M [15]. It was proposed that Cl$^-$ had two main effects on Cu sulphide film growth: (i) it competed with SH$^-$ for surface adsorption sites thereby partially suppressing the first critical step in sulphide-induced Cu corrosion; (ii) it maintained porosity in the film allowing transport of Cu$^+$ to the film growth site at the Cu$_2$S/solution interface. Protective films with a parabolic growth law were observed at low Cl$^-$ concentrations but a switch to porous film growth occurred as the Cl$^-$ concentration was increased. At 5.0 M NaCl the film developed extensive porosity and it was
suggested that growth was controlled by SH\(^{-}\) diffusion in the bulk solution and of Cu\(^+\) species (Cu(SH)\(_2\)^{-}, Cu\(_3\)S\(_3\)) diffusion in the pores. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) determined Cu was released to the bulk solution at this high Cl\(^{-}\) concentration. These findings are similar to those of Srivastava and Balasubramaniam [17] who found the Cu was least protected at high sulphide and Cl\(^{-}\) concentrations, but their study was under aerated conditions.

More recently it has been shown that micro-galvanic coupling occurred when Cu corrosion occurred in solutions with high sulphide concentration (\(\geq 5\times 10^{-4}\) M) with growth of cathodic locations generated by Cu\(^+\) transport from adjacent corroding anodes [16]. The areas covered by a thin, non-protective film experience an increase in corrosion rate and became local anodes while the portion of the surface covered by a thicker, protective film acted as the cathode and accumulated deposited Cu\(_2\)S.

### 2.2 Electrochemical Studies of Cu in Aqueous Sulphide Solutions

Gennero De Chialvo and Arvia [18] characterized the behaviour of Cu in deaerated sulphide solutions in an extensive electrochemical study using potentiostatic polarization measurements and cyclic voltammetry under stagnant and RDE conditions. It was shown that, in the presence of sulphide, the potential for Cu oxide formation was shifted to more positive potentials, allowing the sulphidization and oxidation processes to be more readily separated. Sulphide film formation (Cu\(_2\)S/CuS) occurred at potentials close to the equilibrium potentials for their corresponding reactions, and it was claimed that the potential was controlled by the Cu/Cu\(_I\) and Cu/Cu\(_II\) redox couples when sulphide was present. Based only on voltammetric data it was claimed the initial film formed was non-stoichiometric Cu\(_{1.8}\)S.
(~0.4 nm thick), followed by the formation of Cu$_2$S at the Cu interface, and ultimately CuS when the overpotential was increased further, thus resulting in a bi-layer film. However no supporting phase analysis was provided. It was claimed that Cu sulphide film growth occurred in 2 stages; (i) SH$^-$ adsorption resulting in monolayer growth of Cu$_2$S, which current-time transients suggest occurred via a nucleation process; and, (ii) subsequent oxidation leading to the formation of a thick CuS homogeneous layer.

Vasquez Moll et al. [19] obtained similar voltammetric data in deaerated alkaline sulphide solutions. The two voltammetric anodic peaks observed were attributed to the formation of Cu(I) and Cu(II) sulphides resulting in a poorly adherent thick black film. The region of oscillating current observed following film formation was attributed to film breakdown and pitting and as the overpotential was increased the formation of Cu oxide was observed. It was found that as the sulphide concentration was increased the charge associated with Cu$_2$S film formation was significantly enhanced, and in addition, the film breakdown potential shifted to a more negative value. Potentiostatic current-time transients were used to determine the mechanism of film formation. An initial decrease in current was attributed to the initial formation of a Cu$_2$S film. The current then increased over time to a maximum current value, $j_m$, at time, $t_m$. As the applied potential approached the film breakdown potential $t_m$ decreased while $j_m$ increased. This behaviour was attributed to the nucleation and growth of CuS, thought to occur at the base of pores in the initially-grown Cu$_2$S film leading to passivation. Under potentiostatic conditions, film breakdown occurred at potentials more negative than the breakdown potential defined by voltammetric methods. This is commonly observed since breakdown potentials measured voltammetrically are commonly dependent on the scan rate [20].
The film growth mechanism was further studied by Smith et al. [21] in deaerated 0.1 M NaCl solution containing sulphide concentrations ranging from $10^{-5}$ to $10^{-3}$ M. XRD showed that the Cu sulphide film formed under corrosion conditions was composed mainly of chalcocite ($Cu_2S$) and some digenite ($Cu_{1.8}S$), with the cathodic reaction assumed to be the reduction of $H_2O$. Using potentiostatic measurements, EIS and cyclic voltammetry it was shown that growth occurred rapidly on the bare Cu surface and was controlled by the mass transport of $SH^-$ to the electrode surface. At the highest sulphide concentration it was claimed that film growth could proceed via two distinct pathways; the initial film which grew via $Cu^+$ transport through the film could either remain intact, and thus become limited by a steady state thickness, or the film could undergo fracture, due to the growth of interfacial stresses, which would then lead to the growth of a thicker outer deposit.

Abd El Haleem and Abd El Aal. [22] studied the electrochemical behaviour of Cu in 0.1 M NaOH solutions containing sulphide. Galvanostatic polarization of the Cu electrode was performed in solutions with sulphide concentrations ranging from $10^{-6}$ to $5 \times 10^{-3}$ M. For sulphide concentrations $\leq 5 \times 10^{-5}$ M, the potential vs. time profiles were identical to those collected in the absence of sulphide, and based on reduction potentials, $Cu_2O$, CuO and/or $Cu(OH)_2$ were thought to be formed. This suggested that there was a sulphide concentration threshold below which $Cu_2S$ formation was kinetically hindered. Cyclic voltammograms, collected in 0.1 M NaOH and $10^{-2}$ M Na$_2$S solution, exhibited three distinct peaks on the anodic branch and a number of overlapping cathodic peaks. The anodic peak at $-0.90$ V/SCE was attributed to $Cu_2S$ formation by reaction of adsorbed sulphide with Cu with the corresponding reduction peak appearing at $-1.25$ V/SCE. Oxidation peaks observed at more positive potentials, corresponding to additional reduction peaks, were attributed to the formation and reduction of CuO and CuS, although no analytical evidence was offered.
De Tacconi et al. [23] completed a similar set of experiments in N$_2$ purged 0.1 M NaOH containing various sulphide concentrations. If voltammetric scans were limited to an anodic limit of $-0.5$ V/Ag/AgCl, Cu oxide and hydroxide formation was avoided. In solutions containing $5\times10^{-3}$ M sulphide two anodic peaks were observed. The first peak, whose size depended on sulphide concentration, at $-1.1$ V/Ag/AgCl, was attributed to the underpotential deposition of hydrosulphide. The second anodic peak, observed at $\sim -0.8$ V/Ag/AgCl was attributed to a combination of stoichiometric and non-stoichiometric Cu sulphide films formed over a potential range of $\sim 200$ mV. For corrosion in $5\times10^{-4}$ M Na$_2$S, the single cathodic stripping peak observed after corrosion was attributed to the reduction of Cu$_2$S. When the potential was held at $E_{\text{corr}} +10$ mV cathodic stripping yielded this peak and an additional peak at more negative potentials, attributed to the reduction of a mixture of stoichiometric and non-stoichiometric films formed on top of the initial Cu$_2$S film.

A combination of electrochemical quartz crystal microgravimetric (EQCM) measurements and x-ray photoelectron spectroscopy (XPS) suggested this bi-layer film was comprised of an inner layer of Cu$_2$S which became non-stoichiometric with distance from the Cu surface culminating in an outer surface that was CuS (covellite) in composition.

Smith et al. [24] and Hollmark et al. [25] studied the conversion of Cu oxides to sulphides on exposure to deaerated sulphide solutions. Smith et al. studied the effect of $3\times10^{-5}$ M Na$_2$S on Cu oxides potentiostatically grown in 0.1 M NaOH, using EIS and cathodic stripping voltammetry. The conversion from Cu$_2$O to Cu$_2$S began immediately at the film/solution interface, and proceeded via a pore opening process as the SH$^-$ penetrated into the oxide leading finally to its conversion to Cu$_2$S. Upon sulphide exposure, the $E_{\text{corr}}$ evolved through three stages; (i) a Cu/Cu$_2$O redox couple; (ii) the penetration of SH$^-$ into the oxide; (iii) complete conversion to Cu$_2$S. In a similar study Hollmark et al. [25] grew oxide films
with various oxidation states (Cu(I) and Cu(II)) and then exposed them to solutions of $10^{-3}$ and 0.1 M Na$_2$S for 8 hours. Using x-ray absorption spectroscopy (XAS) they observed the penetration of the sulphide conversion deep into the bulk oxide, but suggested the process proceeded inhomogeneously since a small fraction of the oxide still persisted. This finding suggested that the sulphide films formed were not coherent layers. In agreement with Smith et al. they concluded the conversion occurred, via either direct chemical conversion [24]:

$$\text{Cu}_2\text{O} + \text{SH}^- \rightarrow \text{Cu}_2\text{S} + \text{OH}^- \quad (2.6)$$

or by galvanic coupling to the Cu substrate:

$$\text{Cu}_2\text{O} + 2 \text{e}^- + \text{H}_2\text{O} \rightarrow 2 \text{Cu} + 2 \text{OH}^- \quad (2.7)$$

$$2 \text{Cu} + \text{SH}^- \rightarrow \text{Cu}_2\text{S} + \text{H}^+ + 2 \text{e}^- \quad (2.8)$$

While these studies showed that Cu(I) oxides were ultimately converted to sulphides, the evidence for the conversion of Cu(II) oxide/hydroxide was less convincing. The implication of these observations was that neither Cu$^{2+}$ or Cu$^{1+}$ preformed oxides would likely prevent Cu corrosion by sulphide at least at the high sulphide concentrations employed in these studies.

Several studies have reported that sulphide induced pitting can occur on Cu in deaerated sulphide solutions when [Na$_2$S] = $2 \times 10^{-4}$ M [20, 26]. Based on potentiodynamic polarization curves, Mao et al. claimed that Cu$_2$S films on Cu were passive and experienced breakdown at large overpotentials with the critical breakdown potential decreasing as the [Cl$^-$] increased [26]. In a complimentary study, Dong et al. [20] studied the effect of elevated temperatures on the critical breakdown of these supposedly passive Cu$_2$S films, with the breakdown potential decreasing as the temperature increased. EDS mapping revealed Cl$^-$ accumulation at the Cu/Cu$_2$S interface once the critical breakdown potential was exceeded. This was attributed to the collection of Cl$^-$ in the newly formed pits formed as a consequence
of film breakdown. It was predicted that the pitting potential would experience a negative shift (making pitting easier to initiate) during the early warm repository period, with the probability of pitting decreasing as the repository cooled.

Kong et al. recently published a series of studies analyzing the breakdown of what they claim are passive Cu$_2$S films [27-30]. In 0.1 M NaCl solutions with sulphide concentrations ranging from $5 \times 10^{-5}$ M to $1 \times 10^{-2}$ M, it was claimed that, CV and XPS measurements showed that a passive film comprised of Cu$_2$S and CuS formed on the electrode surface and that its resistance decreased with increasing sulphide concentration. EIS and atomic force microscopy (AFM) measurements were used to demonstrate the effect of sulphide concentration on the passive film properties. It was claimed that, as the concentration of Cl$^-$ increased, the barrier layer thickness decreased (accounting for the decrease in film resistance) and a more porous outer layer formed [27]. P-type semiconductor properties were claimed to prevail over the entire passive range, and the number of defects to increase with increasing sulphide concentration. This would account for the higher growth and dissolution rates of the film. Sulphide film properties were investigated in a wider range of Cl$^-$ concentrations, 0.1 to 1 M, using polarization scans, EIS, SEM and XPS. An active to passive transition was observed in potentiodynamic scans but it was found that pits could be repassivated by OH$^-$ [28]. However, if both the Cl$^-$ and sulphide concentrations were high, a second passivation was not observed and the film underwent anodic dissolution. Contrary to the findings of Dong et al. [20], the pitting potential increased with increasing temperature which resulted in the growth of a thicker oxide film on the surface. In a solution containing 0.1 M NaCl and $2 \times 10^{-4}$ M Na$_2$S, the authors found that the total impedance first decreased with increasing temperature but then experienced an increase followed by a final decrease [29]. This complicated result was attributed to the nucleation and growth of deposits on the
Cu surface. Based on XPS measurements it was claimed that the sulphide films were composed of Cu$_2$S and CuS with the fraction of CuS increasing with increasing temperature, despite the fact XPS cannot distinguish between these two phases.

2.3 Corrosion of Cu Containing Alloys in Sulphide Polluted Environments

Cu-Ni alloys are commonly used for marine applications since their corrosion resistance in saline environments makes them ideal materials for piping, condensers and heat-exchange tubing for naval ships. Sulphide, is commonly found as a pollutant in seawater from various sources such as decaying vegetation or industrial waste discharge [31]. Sulphide typically reacts with dissolved oxygen in the water which ultimately creates an anoxic environment. However this change is not long lasting as tidal flows regenerate an O-rich environment. As a consequence, many studies have focused on the switching between oxidizing and reducing environments.

These alloys have a high corrosion resistance due to the formation of a thin passive film of Cu$_2$O that forms in the first few months of service [32, 33]. Awad et al. [34] found that the alloying element Ni increased the corrosion resistance of the alloy because the bivalent cation segregated into the defective lattice of the protective Cu oxide. The corrosion resistance was jeopardized upon exposure to sulphide, which caused disruption of the passive oxide film. Various studies [35, 36] used polarization resistance, CV and corrosion rate measurements to analyze the effect of sulphide on the corrosion resistance of 90:10 Cu:Ni alloys. An increase in corrosion rate was only observed once the sulphide-polluted environment was replaced by an aerated, unpolluted one. It was found that sulphide “pre-conditioned” the surface by disrupting the on-going growth of the passive Cu$_2$O film. Upon
exposure to anoxic sulphide conditions an outer layer of Cu$_2$S and Cu$_{1.8}$S was formed on top of the initial Cu$_2$O layer. It was found that the Cu$_{x}$S layer compromised the passive oxide by increasing its electrical and ionic conductivity while the mismatch in crystal structure lead to a porous film which allowed for mass transport of sulphide to the alloy surface. It was proposed that the reaction rate was limited by the transport of H$^+$ to cathodic sites at the Cu$_2$O/Cu$_{x}$S interface, with subsequent film thickening via Cu$^+$ migration through the Cu$_{x}$S film. However, when the environment was switched to aerated the outer Cu$_{x}$S film was converted to Cu$_2$O. The cathodic reaction changed from H$^+$ to O$_2$ reduction and, since this was kinetically faster, the corrosion reaction was accelerated.

Using a rotating electrode, Kumar et al. studied the effect of hydrodynamics on the corrosion of 90:10 Cu:Ni alloys in sulphide contaminated marine environments [37]. Based on EIS data they claimed that the addition of sulphide lead to pit formation. An increase in electrode rotation rate caused an increase in charge transfer resistance but a decrease in film resistance. A shift in $E_{\text{corr}}$ to more negative values in potentiodynamic scans as the rotation rate was increased was taken to indicate deterioration of the alloy on addition of sulphide ions leading to localized attack.

Yuan and Pehkonen studied the corrosion of 70:30 Cu:Ni alloys in simulated seawater containing 10 ppm Na$_2$S [38], and observed an increase in corrosion resistance over a 10 day period due to the formation of a passive layer of Cu$_2$O. This was indicated by an increase in Tafel slope from 70 to 120 mV/dec in 191 days. By contrast, the cathodic Tafel slopes appeared almost independent of exposure time which was attributed to the fact that O$_2$ reduction on the thin passive oxide did not alter much over the duration of the experiment. Sulphide was quickly depleted upon addition with EIS measurements indicating a low charge transfer resistance. This low value was maintained indicating the corrosion rate remained
high during the 10-day exposure period. This was attributed to degradation of the passive oxide by sulphide which also prevented oxide re-growth. An extensive XPS study showed that, upon exposure to sulphide, the film changed from Cu$_2$O and CuO to a more complex mixture of CuCl, Cu$_2$S, NiS, Cu$_2$O and NiO. After sulphide depletion the film was composed mainly of Cu$_2$O, CuO and NiO.

Experiments on the Cu-Ni alloys in flowing seawater, over both short and long times [39, 40], showed $E_{\text{corr}}$ shifted to more negative (active) potentials when dissolved sulphide was present and increased again when sulphide was depleted [39]. It was found that, in both time frames, as in previous studies, the corrosion rate upon exposure to sulphide was actually lower than the rate in an initially aerated environment but was accelerated by a factor of up to 1.4 when again exposed to aerated conditions after exposure to anoxic sulphide. A change from general corrosion to pitting was observed once the alloy was exposed to an aerated sulphide condition. The pit propagation rate was 19 mm/a [39] and the total extent of corrosion increased with increases in both sulphide concentration and time [40].

Patil and Tupkary used potentiodynamic polarization measurements, XRD and SEM to analyze the benefits of alloying elements in Cu in sulphide-polluted synthetic seawater containing 5.4 ppm of dissolved oxygen [41]. They compared the corrosion resistance of Cu-Ni-Zn and Cu-Ni-Zn-Mn alloys to that of the traditional Cu-Ni alloy. Anodic and cathodic polarization tests were performed on both bare and ‘filmed’ electrodes after 15 days of exposure to sulphide-polluted seawater, and, as expected, the corrosion rate of all alloys increased after exposure to sulphide. Multi-phase films comprising of Cu$_2$O, Cu$_2$S and ZnS were formed in the case of the Zn containing alloys. The alloys containing Zn showed the greatest corrosion resistance which was attributed to the formation of the ZnS film, a non-conductor that does not allow ionic or electronic conduction. It was observed that the
alloying elements of Ni, Fe and Mn form Ni$^{2+}$, Fe$^{2+}$, Fe$^{3+}$, Mn$^{2+}$ and Mn$^{3+}$ ions, which are able to migrate though the film to the film/solution interface and be incorporated into the film lattice. This improved the ionic and electronic resistance of the alloy, with the trivalent ions having a larger effect as they are able annihilate additional cation vacancies and electron holes in the film. The study concluded that Cu-10Ni-29Zn-1Fe and alloys containing 3% or 5% Mn showed a higher corrosion resistance than traditional Cu-Ni alloys and are a cost effect substitute.

Studies on these alloys in purely anoxic sulphide environments without prior and post exposure to aerated environments [6, 32, 42], showed that the presence of even small amounts of sulphide ($\leq 0.85$ mg/L) greatly increased their corrosion rate, an effect which increased with an increase in sulphide concentration. However the corrosion rate (as indicated by $R_p$ values) became independent of sulphide concentration once 0.85 mg/L was exceeded. EIS measurements showed that the Cu$_2$S film formed had a greatly reduced resistance to the passage of charge compared to that of the initially formed passive oxide. XRD showed the Cu sulphide films to be primarily composed of Cu$_2$S but peaks for Cu$_{1.8}$S were also present. The overall corrosion mechanism for the Cu-Ni alloy proved identical to that reported for pure Cu in aqueous anoxic sulphide solutions, with the formation of the Cu sulphide corrosion product shifting $E_{corr}$ to a more negative value allowing corrosion to be supported by proton reduction. A study by Alhajji and Reda [42] showed that, upon exposure to sulphide, corrosion became anodically controlled with the Tafel slopes increasing from 40 mV/decade to approximately 500 mV/decade. This was attributed to the formation of a porous, non-protective Cu$_x$S layer, which acted as a diffusion barrier to sulphide under stagnant conditions. A mechanism by which the anodic reaction proceeded via adsorption of
SH⁻ followed by dissolution of Cu⁺, which subsequently reacted with SH⁻ and was deposited on the surface, was proposed.

### 2.4 Properties of Cu Sulphide Films

The Cu sulphide system has many stable and metastable phases ranging from Cu rich to S rich. Thermodynamic studies have shown that stability regions exist for chalcocite (Cu₂S), djurleite (Cu₁.₉₆S), digenite (Cu₁.₈S), anilite (Cu₁.₇₅S), geerite (Cu₁.₆S), spionkopite (Cu₁.₄S), yarrowite (Cu₁.₁₂S) and covellite (CuS) [43-47]. Of these phases the structures of geerite, spionkopite and yarrowite have yet to be resolved [43] and studies by Zhao et al [48] have shown that digenite is the most thermodynamically stable species under ambient conditions.

Studies using XPS and extended X-ray absorption fine structure (EXAFS) have determined that Cu(I) exists in almost all forms of Cu sulphide from Cu₂S to CuS [49-51]. Although oxidized to Cu(II) in species such as covellite, the presence of the strong oxidant SH⁻ is known to cause charge transfer thus creating Cu(I) and various polysulphide species [46]. Using XPS it was found that the Cu(2p) binding energies corresponding to a Cu monovalent species were identical in all CuₓS samples. This is supported by the absence of both satellite peaks and peak broadening which would be expected for divalent Cu, thus confirming that no Cu(II) or mixed Cu(I)/Cu(II) species were present. However due to slight shifts in binding energies, alternate formula for CuS have been proposed as Cu⁺₃(S₂)²⁻S⁻ and Cu⁺₃(S₂)⁻S²⁻. Therefore any increase in complexity of the Cu(2p) peak confirms that Cu₂S contains only the S²⁻ ligand while CuS contains both S²⁻ and S₂²⁻ [49].
The crystal structure of Cu sulphide is complex as it varies with changing stoichiometry. The crystal structures of the Cu$_x$S species can be divided into three types; cubic close packed (anilite and digenite), hexagonal close packed (djurleite and chalcocite) and integration of hexagonal close packed with covalently bonded S atoms (covellite) [52]. Chalcocite, djurleite and digenite are found to have a monoclinic crystal structure at room temperature [53]. Covellite, CuS, consists of alternating layers; a layer of trigonal CuS$_3$ in between two layers of tetrahedral CuS$_4$ held together with a S-S covalent bond [54, 55].

Cu sulphide films are known to be ionically conductive, which is typical of crystals that contain large anions (S$^{2-}$) and relatively small cations (Cu$^+$) with either the Cu or defect vacancy being the mobile species [56, 57]. Studies by Cassaignon et al. [58] used EIS to measure Cu diffusion in various Cu sulphide films, both stoichiometric and non-stoichiometric. It was observed that Cu diffusion through Cu sulphide films likely occurred via vacancy diffusion. While vacancy concentrations in the Cu sulphide films were found to be on the order of magnitude of $10^{-3}$ to $10^{-2}$ mol/cm$^3$, they suggested only a small fraction of these vacancies contribute to diffusion processes. Diffusion coefficients of $3 \times 10^{-8}$ cm/s and $2.5 \times 10^{-12}$ cm/s for Cu$_2$S and CuS, respectively, were reported [58].

Electrical conductance has also been observed in Cu sulphide with electrons being 1000-times more mobile than cations [59]. The electrical conductance of Cu sulphide was strongly dependent on the defects and disorder present in the crystal lattice. Cu$_2$S, Cu$_{1.96}$S and Cu$_{1.8}$S contain structures with relatively short Cu-Cu bonds (similar to metallic bonding) and Cu-S bonds leading to a high electrical conductivity [60]. In Cu$_{2-x}$S phases the highest levels of the valence band are occupied by extra holes due to Cu vacancies and the energy band gap increased with increasing Cu deficiency. As the value of x increased, holes formed near the valence band caused a shift in the lowest occupied energy level and a change in band
gap energy was observed [48, 60]. The band gap energy values for Cu$_2$S, Cu$_{1.8}$S and CuS are 1.2 eV, 1.5 eV and 2.0 eV, respectively [48].

2.5 References


Experimental Techniques and Details

3.1 Experimental Design

The experimental design described in this section applies to all data chapters excluding Chapter 8.

3.1.1 Electrochemical Cell Arrangement and Instrumentation

All electrochemical data was collected using a conventional three-electrode electrochemical glass cell. A Pt sheet was used as the counter electrode and connected to external circuitry by a Pt wire. A saturated calomel reference electrode (SCE, 0.242 V/SHE) was used in all experiments, and was periodically checked against a reference SCE. For short-term bench top experiments two types of three-electrode electrochemical cells were used; a single compartment cell with the counter and reference electrodes not separated from the working electrode, and a second cell in which the working electrode was housed in a main compartment with the reference and counter electrodes separated in side arms from the main compartment by glass frits. The reference electrode in this second cell type was connected to the main compartment via a Luggin capillary to minimize any potential drop across the cell due to solution resistance. The cell was fitted with a glass dispersion tube with a fritted end to deaerate the solution with Ar.

For all experiments the electrochemical cell was housed inside a Faraday cage to reduce electrical noise from external sources. Electrochemical measurements were made
using either a Solartron 1287 potentiostat with CorrWare software, a Solartron Analytical Modulab with Modulab XM ECS software, or an analog to digital (ADC) converter for open circuit potential (corrosion) measurements.

### 3.1.2 Cu Working Electrode Composition and Preparation

O-free, P-doped Cu provided by the Swedish Nuclear Fuel & Waste Management Co. (SKB), Solna, Sweden was machined into Cu disks. Ti rods were threaded into the back of the disks and the disks were set into either a Teflon holder using an epoxy resin or painted with Amercoat resin. Only a single flat Cu face, with a surface area of 0.785 cm$^2$, area was exposed to solution. Prior to an experiment the Cu electrode was first polished with a sequence of SiC papers with grit sizes: 180, 600, 800, 1000, 1200, and 4000. Then, to achieve a mirror finish, the electrode was polished with a series of Al$_2$O$_3$ suspensions with decreasing suspension size (1 μm, 0.3 μm, and 0.05 μm). The electrode was then rinsed thoroughly with Type-1 water to remove any polishing residue and dried in a stream of ultrapure Ar gas. Once immersed in solution, the Cu electrode was cathodically cleaned to remove any air formed oxides, first for 60 s at −1.5 V/ SCE, and then at −1.15 V/ SCE for 60 s.

### 3.1.3 Solution Preparation

Electrolyte solutions were prepared with ultra pure Type-1 water (resistivity of 18.2 MΩ·cm) obtained using a Milli-Q® Millipore system. All water was purged with ultra-high purity (UHP) Ar gas for a minimum of 30 min prior to the preparation of solutions.
containing sulphide species. Since Na$_2$S is stored in the hydrated form, the crystals were dried thoroughly before being weighed in the preparation of stock solutions. For bench top experiments once the solution was in the electrochemical cell, it was sparged with Ar gas for a minimum of 30 min before an experiment to ensure anoxic conditions. During an experiment, the solution was continuously sparged with a stream of Ar gas.

3.2 Electrochemical Techniques

3.2.1 Corrosion Potential ($E_{corr}$) Measurements

The corrosion potential ($E_{corr}$) is the potential measured between the working and reference electrodes in the absence of an applied potential. $E_{corr}$ is the open circuit potential for a corroding system. Prior to $E_{corr}$ measurements, the electrode was cathodically cleaned at $-1.5$ V/SCE to remove air-formed oxides, and then at $-1.15$ V/SCE for a further 60 s to remove excess H$_2$ bubbles which may have formed on the surface at the more negative potential. The potential was measured between the Cu working and the SCE reference electrodes.

3.2.2 Basics of Cyclic Voltammetry

Cyclic voltammetry (CV) is an electrochemical technique in which a cyclic potential scan is imposed on an electrode and the current response is measured as a function of the applied potential. The current provides information on the kinetics and mechanism of electrochemical/chemical reactions occurring as a result of heterogeneous electron transfer [1]. A CV is recorded by scanning the potential at a constant rate from an initial potential
(E_{initial}) to a specified potential limit (E_{switch}), and then back to a final potential (E_{final}) which is typically the same as E_{initial}, as shown in Figure 3.1a. For a reversible reaction involving soluble species, a CV has the form shown in Figure 3.1b, with oxidation occurring on the forward scan (E_{initial} to E_{switch}) and reduction on the reverse scan. Based on the shapes and sizes of the anodic and cathodic peaks observed, film properties, and possibly even film growth mechanisms, can sometimes be deduced.

![Figure 3.1: Illustration of the potential-time input and current-potential output profiles in a CV experiment.](image)

### 3.2.2.1 CV Experimental Details

Prior to performing a CV the electrode was cathodically cleaned using the procedure described in Section 3.2.1. CVs were scanned from either −1.5 V/SCE or −1.35 V/SCE to various anodic limits at a scan rate of 2 mV/s. An RDE (discussed in section 3.2.3) was used with electrode rotation rates ranging from 0 to 25 Hz.
3.2.3 Rotating Disk Electrode (RDE)

A rotating disk electrode (RDE) can be used to control the mass transport of solution soluble species involved in an electrochemical reaction to and from the electrode surface. A species reacting at the electrode/solution interface will become depleted at a sufficiently high applied potential. The use of an RDE allows this species to be replenished and for a steady-state concentration gradient to be established at the electrode surface. According to Fick’s first law of diffusion, the rate of mass transport, i.e., the flux of a reactant to, or product from, an electrode surface, is proportional to the concentration gradient [2],

\[ J = -D \frac{\partial C}{\partial x} \]  

(3.1)

where \( J \) is the flux, \( D \) is the diffusion coefficient (m\(^2\)/s), \( C \) is the concentration (mol/m\(^3\)), and \( x \) is the distance from the electrode (m). Under controlled convective conditions (e.g. at an RDE) the concentration gradient can be approximately taken as linear, and the Nernst diffusion layer defined. This diffusion layer approximately describes the distance between the electrode surface and the point beyond which the undisturbed bulk solution concentration is established. Equation 2.1 can then be approximated to

\[ J = -\frac{D}{\delta} (c_b - c_s) \]  

(3.2)

where \( \delta \) is the Nernst diffusion layer thickness (m) (distance from the electrode surface to the transition point), \( c_b \) is the species concentration in the bulk solution and \( c_s \) is the concentration at the electrode surface.

As the rotation rate of the electrode is increased \( \delta \) decreases, as depicted in Figure 3.2. For a sufficiently high rotation rate, \( c_s \) begins to increase while for a sufficiently fast electrode reaction \( c_s \) becomes zero. The use of an RDE allows the thickness of the diffusion layer to be controlled, and, hence, the flux of the species to and from the electrode [2],
\( v \) is the kinematic viscosity (m\(^2\)/s), and \( \omega \) is the rotation rate of the electrode (rad/s).

Equation 3.3 shows that the diffusion layer thickness is independent of electrode surface area. Using this definition of \( \delta \), the limiting current for an electron transfer reaction proceeding under diffusion control at the electrode surface (i.e., \( c_s = 0 \)) can be described by the Levich equation,

\[
i_L = 0.62nFAD^{2/3} \omega^{1/2}v^{-1/6}c_b
\]  

(3.4)

where \( n \) is the number of electrons transferred and \( A \) is the electrode surface area (m\(^2\)).

Commonly, under many experimental conditions, reactions are governed by a combination of kinetics and mass transport control. However, it is possible to extract the kinetic current, corrected for any contribution from mass transport, by measuring the current as a function of \( \omega \) and using the Koutecky-Levich extrapolation [2]:

\[
\frac{1}{i_M} = \frac{1}{i_K} + \frac{1}{0.6 \alpha^{1/2} v^{-1/6} c_b \omega^{1/3} a^{2/3}}
\]

(3.5)

where \( i_M \) is the current measured under mixed kinetic/mass transport control, and \( i_K \) is the kinetic current free of transport effects. Plotting \( 1/i_M \) versus \( \omega^{-1/2} \) should yield a straight line,
which can be extrapolated to $\omega = \infty$ (or $\delta = 0$) to obtain $i_K$. Values of $\log(i_K)$ determined at a series of applied potentials can then be plotted to yield Tafel slopes which are important in the determination of reaction mechanisms and corrosion rates.

3.2.4 Potentiostatic and Galvanostatic Polarization

Potentiostatic polarization is a technique in which a constant potential is applied between the working and reference electrodes for a specified amount of time while the resulting current is monitored between the working and the counter electrodes. By selecting a potential more positive or negative than the $E_{corr}$, the anodic and cathodic reactions can be accelerated, respectively. When the applied potential is positive to $E_{corr}$ the current is a measure of the rate of the oxidation reaction occurring on the working electrode. This is commonly due to the dissolution of the material and/or the formation of surface films and deposits. When the applied potential is negative to $E_{corr}$ the current is a measure of the rate of the cathodic reaction.

Galvanostatic polarization is a technique in which a constant current is applied between the working and counter electrodes while the resulting potential is monitored between the working and reference electrodes. Depending on the sign of the applied current either the anodic or cathodic reaction is stimulated on the electrode surface.

These methods were employed largely to fabricate electrodes with specific properties and experimental details will be discussed in the respective data chapters.
3.2.5 Electrochemical Impedance Spectroscopy (EIS)

EIS is an in-situ technique that can be applied to the study of corrosion processes to yield insight on the chemical/physical evolution of the corroding surface with respect to time. In EIS a small sinusoidal potential excitation, usually ± 10 mV, is applied to an electrode (or corroding surface) over a wide range of frequencies, typically $10^6$ to $10^{-3}$ Hz, and the sinusoidal current response is measured, as illustrated in Figure 3.3. A small potential perturbation is used to avoid irreversible changes to the surface during the course of the measurement. Depending on the electrical characteristics of the electrode/solution interface and the frequency of the sinusoidal potential input the resulting sinusoidal current output will be partially, or entirely in or out of phase with the input signal, with $\theta$ being the phase angle difference, Figure 3.3. The output signal allows the determination of the electrical properties of the interface, often the metal/film interface, by fitting to electrical circuits comprised of resistors and capacitors in different configurations. However, since many equivalent circuits can be proposed, a physical understanding of the system is necessary.

Figure 3.3: Schematic of the potential perturbation applied during an EIS experiment and the resulting AC current response. Change in phase angle shown by $\theta$. 
A simple circuit with a resistor and capacitor in parallel, in series with solution resistance \(R_s\), is shown in Figure 3.4 and will be used to illustrate this technique. In this circuit the capacitor could represent the double layer capacitance, \(C_{dl}\), which arises due to the movement of ions into and out of the interfacial region at the electrode surface in response to the charging and discharging of the electrode surface by the sinusoidal applied potential. The resistor represents the charge transfer resistance, \(R_{ct}\), which arises when electron/ion transfer takes place across the electrode/solution interface. A system with this combination of capacitance and resistance can be said to have a time constant \(\tau\) which is the product of a resistor \(R\) and capacitor \(C\). When the system is perturbed, the applied potential, \(E(\omega)\), can be related to the current response by an AC equivalent of Ohm’s law,

\[
E(\omega) = i(\omega)Z(\omega) \tag{3.6}
\]

where \(\omega\) is the angular frequency and \(Z\) is the impedance, which relates the input perturbation to the output response and is a consequence of the restriction of current flow due to the presence of \(R\) and \(C\). When in parallel, as in Figure 3.4, the impedance can be expressed as,

\[
Z(\omega) = \left(\frac{R}{1 + \omega^2 C^2 R^2}\right) - j \left(\frac{\omega C R^2}{1 + \omega^2 C^2 R^2}\right) \tag{3.7}
\]

where \(j\) is the imaginary unit \((j^2 = -1)\) and is composed of a real and imaginary part. To determine the total impedance response the solution resistance can simply be added in series with the real contribution.

Figure 3.4: Equivalent circuit representing a metal surface covered with an oxide film
The response, or impedance, of the system can be plotted in two different ways; either as a Nyquist or a Bode plot. A Nyquist plot, Figure 3.5a, is a plot of $Z_{\text{imaginary}}$ vs. $Z_{\text{real}}$ and can be used to determine both ($R_s$) and ($R_{ct}$), and highlights the low frequency region of the overall EIS spectrum. A Bode plot is a plot of log|$Z|$ and the phase angle ($\theta$) vs. log frequency. As shown in Figure 3.5b, the horizontal components of the total impedance plot represent a resistive response while the angled portion represents a capacitive response. The phase angle plot yields information regarding the number of time constants ($\tau = RC$) as well as the frequency regions within which the response is purely resistive or capacitive, with resistors being in phase ($\theta = 0$) and capacitors exhibiting a phase shift ($\theta = 90^\circ$). The Nyquist and Bode plots shown in Figure 3.5 are those expected for the one time constant circuit shown in Figure 3.4.

Commonly corroding material/solution interfaces are inhomogeneous and do not exhibit uniform properties. As a consequence the capacitance(s) may be non-ideal and fits to a capacitance in an equivalent circuit lead to unreliable results. In order to improve the

$$Z(\omega) = \left(R_s + \frac{R}{1+\omega^2 C R^2}\right) - j\left(\frac{\omega C R^2}{1+\omega^2 C^2 R^2}\right)$$

Figure 3.5: Graphical representation of; a) a Nyquist plot, and b) a Bode plot containing one time constant.
quality of the fit a capacitance can be replaced by a constant phase element or CPE, which is defined by the mathematical expression,

\[ Z(\omega) = \frac{1}{Q(j\omega)^\alpha} \]  

(3.9)

where \( Q \) has the numerical value of the admittance [3] and \( \alpha \) allows one to determine how close the element is to a pure capacitance. For \( \alpha = 1 \), the CPE acts as a pure capacitance while for values \( \alpha < 1 \) the capacitance becomes non-ideal, and ultimately, for \( \alpha = 0 \) is representative of a resistance. When \( \alpha = 0.5 \) the CPE is representative of an element known as a Warburg impedance (W). This type of impedance is observed in EIS experiments when the current is partially controlled by diffusion of species involved in the corrosion reaction. An example would be the diffusion of the oxidant involved in the corrosion process in the pores of a corrosion product deposit. The Warburg impedance element can be observed in the Nyquist plot as a 45° line at low frequency and as a phase angle of 45° in a Bode plot. The diffusion of a redox species from the bulk solution to either the electrode/film or the film/solution interface can be replaced by an infinite Warburg element [4]. The Warburg coefficient, \( \sigma_W \), which relates the movement of ionic species in solution to the Warburg impedance element, can be mathematically defined by,

\[ \sigma_W = \frac{RT}{\sqrt{2n^2F^2cs\sqrt{D}}} = \frac{1}{\sqrt{2(CPE-T)}} \]  

(3.10)

where \( CPE-T \) is a parameter obtained from fitting the impedance data to an appropriate electrical equivalent circuit.

It is however important to note that EIS gives a general surface response and is not site-specific, meaning it can detect features such as porosity but cannot distinguish whether porosity is comprised of a small number of large pores or a large number of small pores [5].
3.2.5.1 EIS Experimental Details

EIS experiments were conducted using a Solartron potentiostat equipped with CorrWare software and a Solarton 1255B frequency response analyzer (FRA) with Zplot software. A sinusoidal potential perturbation of ±10 mV was applied while holding various applied potentials. The corresponding current response was measured over a frequency range from $10^5$ Hz to $10^{-3}$ Hz with 11 data points recorded per decade. Kramers-Kronig transformations were applied to all EIS data to confirm their validity.

3.3 Surface Analysis Techniques

3.3.1 Scanning Electron Microscopy (SEM)

Scanning electron microscopy (SEM) is an analytical tool used to study surface topography. SEM probes the sample surface with a beam of high-energy electrons referred to as primary electrons, to obtain a high-resolution image. These electrons are generated by thermionic emission from a metal filament such as W. After emission the electrons are passed through a set of condenser lenses to the objective lens which focuses the electron beam to a very small diameter (ranging from 10 to 1 nm depending on the primary source). This diameter defines the spatial resolution, as the resolution cannot exceed the incident-probe diameter [6]. This finely focused electron beam is then rastered over the sample surface leading to various electronic interactions between the probe and the sample. The most common products of these interactions are secondary electrons, backscattered electrons, Auger electrons and X-rays, as summarized in Figure 3.6.
Secondary electrons arise due to inelastic interactions of the primary electrons with the sample. During inelastic collisions a portion of the energy from the primary electrons is transferred to electrons in the atoms of the sample. When the transferred energy is greater than the work function of the material the emitted electrons can escape the sample. These “secondary” electrons can be used to characterize the topography of the surface [7]. Most of the detected secondary electrons come from a shallow location on the sample surface. These electrons have a high probability of reaching the detector and thus appear brighter in the SEM image. Electrons from deeper locations on the sample surface are fewer and thus appear darker in the image.

Backscattered electrons are electrons elastically scattered with no loss of kinetic energy. This process involves a small amount of energy exchange so the backscattered electrons escape the sample with energies similar to those of the primary electrons. The images produced yield chemical information, since the probability of backscattering
increases with atomic number of the element from which they are scattered. Consequently, heavier atoms appear lighter in the backscattered images since they enhance elastic scattering due to larger electron clouds associated with these atoms.

3.3.2 Energy Dispersive X-ray Spectroscopy (EDX)

X-rays can also arise when primary electrons undergo inelastic collisions. When the primary incident beam of electrons causes the ejection of an inner shell electron it leaves behind a vacancy. An electron from a higher energy level can relax to fill this vacancy and the energy released upon de-excitation is emitted as a characteristic x-ray photon, as illustrated in Figure 3.7. The energy of the emitted x-ray is defined by the difference in binding energy between the upper and lower energy orbitals. Since the energy of an x-ray is defined by the binding energy differences between orbital levels and of the atomic structure of the element, the emitted x-ray photons can be used to determine elemental composition [6]. Site-specific spectra can be obtained by scanning a specific area to generate EDX maps. It is important to note that this technique is only element specific and is unable to distinguish between various
elemental oxidation states and thus cannot differentiate between various phases present in a corrosion product deposit on a corroding surface.

### 3.3.3 Auger Electron Spectroscopy and Depth Profiling

The third type of electron that can be emitted when a surface is bombarded with a primary electron beam is an Auger electron. This type of electron spectroscopy provides both quantitative elemental and chemical state information, making it especially useful in corrosion science since it provides information on the composition of corrosion product deposits. When the primary electron beam is sufficiently high in energy (1 to 20 keV), inner core electrons can be excited and ejected from the atom. As a result, an electron from an outer orbital will relax to fill the inner shell void. The energy released by this relaxation can be transferred to another electron that in turn is ejected from the sample, as illustrated in Figure 3.8. This second ejected electron is known as an Auger electron [8], and has a characteristic energy that corresponds to the binding energy of the element from which it was emitted. Since Auger electrons can only escape from the top ~5 nm of the surface, this technique is surface sensitive.

Auger spectroscopy can be coupled with primary particle sputtering to obtain quantitative compositional depth profiling. This technique uses an ion beam (commonly Ar⁺) with an energy ranging from 0.1 to 5 keV, which induces erosion of the sample surface via ejection of secondary particles [8]. Continuing bombardment of the sample allows for the determination of an element specific depth profile.
Figure 3.8: Schematic of the ejection of an Auger electron as a result of the interaction with a high-energy primary electron beam.

3.3.4 Focused Ion Beam (FIB) Milling

Focused Ion Beam (FIB) systems can be used for various applications including milling, ion implantation and/or deposition, and are often used in conjunction with SEM for the imaging of such processes. FIB milling is used extensively in corrosion science to obtain cross-sections of naturally and electrochemically grown films and deposits in order to gain insight into important oxide properties, most notably the presence of porosity and film/deposit thickness. Small scale probe sputtering is attainable via the use of a liquid metal ion source (LMIS), which has the ability to yield an ion source approximately 5 nm in diameter. Gallium is currently the most widely used LMIS as it has a low melting point of 28.9°C, a low volatility at the melting point allowing for a long source life, and a low vapour pressure which allows for the ion to be used in its pure form with a long life-time as the beam is not very susceptible to evaporation [9].

The Ga⁺ ion beam is obtained via the flow of liquid Ga to a heated W needle where it is ultimately passed through an electric field that ionizes the liquid. This point source is first accelerated through a condenser lens, which forms the probe followed by an objective lens
that focuses the beam. After the ion probe is defined it passes through a set of apertures with various diameters which further help to define the beam size and also enable a distribution of ion currents that allow one to vary sample-sputtering rates [9]. Upon bombardment of the sample with the Ga⁺ ion beam, different sputtered products are collected including atoms, molecules, secondary electrons and secondary ions. For the analysis of film cross-sections an area of the sample is selected for sputtering and FIB milling is carried out in a slice-by-slice manner eventually resulting in a trench. The cross-section of the trench can then be imaged using the SEM portion of the instrument provided the sputtering has formed a trench with sufficient depth.

3.4 References


4

Mechanisms of Film Growth on Copper in Aqueous Solutions Containing Sulphide and Chloride under Voltammetric Conditions¹

4.1 Introduction

A key requirement for the continued use of nuclear power is the successful management of the spent nuclear fuel. One approach under study in many countries, including Sweden, Finland and Canada, is permanent disposal of the spent fuel in a deep geological repository (DGR). In such disposal facilities the spent fuel would be placed in canisters, specifically designed to avoid both corrosion and mechanical failure. The container will be fabricated with a carbon steel insert, and an outer shell of copper. It is proposed that these containers be buried in crystalline rock approximately 500 m below the surface and the excavated boreholes backfilled with bentonite clay [1]. Cu is chosen since it should be inert to corrosion in the anoxic environments anticipated in a DGR [1–7]. The Cu layer would be about 50 mm thick and the metal would be O-free and P-doped. Removing the O and doping with small concentrations of P (30 to 100 ppm) improves the creep resistance, thereby limiting the possibility of physical deformation of the container after emplacement [8]. Although Cu is chosen for its thermodynamic resistance to corrosion in anoxic environments, Swedish repositories are known to contain SH⁻, produced in the groundwater as a consequence of

SO₄²⁻ reducing bacteria and mineral dissolution [9]. This is potentially detrimental to the container since \( \text{SH}^- \) can act as an oxidant for Cu. Container corrosion in the groundwaters anticipated in a repository would also be complicated by the presence of high concentrations of Cl⁻. Previous studies have proposed that Cu corrosion begins with the adsorption of an anion [10] and corrosion in aqueous \( \text{SH}^- \) solutions involves a similar first step [9],

\[
\text{Cu} + \text{SH}^- \rightarrow \text{Cu(SH)}_{\text{ads}} + e^-
\]  

(4.1)

followed by a slow reaction step involving Cu to produce a \( \text{Cu}_2\text{S} \) film, the overall process being supported by \( \text{H}^+ \) or \( \text{H}_2\text{O} \) reduction [9],

\[
\text{Cu} + \text{Cu(SH)}_{\text{ads}} + \text{SH}^- \rightarrow \text{Cu}_2\text{S} + \text{H}_2\text{S} + e^-
\]  

(4.2)

In long-term experiments under these conditions a \( \text{Cu}_2\text{S} \) film (chalcopyrite) was formed. Since \( \text{Cu}_2\text{S} \) formed at a constant rate, the film can be considered only partially protective, and corrosion may also be facilitated by the complexation and solubilization of Cu(I) by Cl⁻ [11],

\[
\text{Cu(SH)}_{\text{ads}} + 2 \text{Cl}^- \rightarrow \text{CuCl}_2^- + \text{SH}^-
\]  

(4.3)

Since the solubility product of \( \text{Cu}_2\text{S} \) is very small [9], any dissolved Cu(I) would be expected to eventually precipitate as \( \text{Cu}_2\text{S} \).

\[
2 \text{CuCl}_2^- + \text{SH}^- \rightarrow \text{Cu}_2\text{S} + 4 \text{Cl}^- + \text{H}^+
\]  

(4.4)

Kinetic studies revealed two types of growth process dependent on \( [\text{SH}^-] \). At \( [\text{SH}^-] = 5.0\times10^{-4} \) M growth follows a parabolic law and is governed by the transport of the \( \text{Cu}^+ \) ion through the \( \text{Cu}_2\text{S} \) matrix or along grain boundaries in the \( \text{Cu}_2\text{S} \) film [9,12]. However, when the \( [\text{SH}^-] \) is lower \( (5.0\times10^{-5} \) M), film growth is controlled by \( \text{SH}^- \) diffusion, and the kinetics follow a linear growth law leading to a porous non-protective film [12]. A remaining question is whether or not, given that the [Cl⁻] is expected to be high, pitting can occur in saline groundwaters containing \( \text{SH}^- \). For this to occur the surface film must be generally passivating with local breakdown sites, and the cathodic reaction, in this case \( \text{SH}^- \) or \( \text{H}_2\text{O} \)
reduction, must be sustained on the passive surface outside the pitting area. In this paper, a series of voltammetric experiments (alternatively called polarization experiments) were performed in solutions containing a range of \([\text{SH}^-]\) and \([\text{Cl}^-]\). These studies serve two functions: (i) they provide information on the sulphide film growth process on Cu; and (ii) they enable us to determine when passivation occurs and whether or not this can lead to film breakdown and the initiation of pitting.

### 4.2 Experimental

#### 4.2.1 Electrochemical Cell and Instrumentation

All electrochemical data were collected using a conventional three-electrode electrochemical glass cell. A Pt sheet rolled into a cylinder was used as the counter electrode and connected to external circuitry by a Pt wire. A saturated calomel electrode (SCE, 0.242 V/SHE) was used as the reference electrode for all experiments. The cell was housed inside a Faraday cage to reduce electrical noise from external sources. All experiments were conducted using a rotating disc working electrode. The electrode rotation rate was controlled by a Pine Instrument Company Analytical Rotator Model AFA86 Serial 882, and electrochemical measurements were made using a 1287 Solartron potentiostat connected to a computer equipped with CorrWare software.

#### 4.2.2 Cu Composition and Preparation

O-free, P-doped Cu provided by the Swedish Nuclear Fuel & Waste Management Co. (SKB), Solna, Sweden, was machined into Cu disks. Ti rods were threaded into the back of
the discs and the Cu was set into a Teflon holder using an epoxy resin. Only a single flat Cu face with a surface area of 0.785 cm$^2$ was exposed to solution. Prior to an experiment, the Cu electrode was first ground with a sequence of SiC papers with grit sizes: 1000, 1200, and 4000. Then, to achieve a mirror finish, the electrode was polished with Al$_2$O$_3$ suspensions with decreasing suspension size (1 μm, 0.3 μm, and 0.05 μm). The electrode was then rinsed thoroughly with Type-1 water (resistance: 18.2 M Ω·cm) to remove any polishing residue and dried in a stream of ultrapure Ar gas.

### 4.2.3 Solutions

Electrolyte solutions were prepared with Type-1 water obtained using a NANOPure system. Chemicals were reagent-grade and purchased from Caledon Laboratories Ltd. All water was purged with Ar gas for one hour prior to the preparation of solutions. The actual [SH$^-\$] used were higher than those anticipated in a repository. The [Cl$^-\$] were representative of the range of groundwater concentrations anticipated. The NaCl and Na$_2$S·9H$_2$O concentrations used are listed in Table 4.1. Since Na$_2$S was stored in the hydrated form, the crystals were dried before being weighed to minimize error in calculated concentrations. Once in the electrochemical cell, the solution was purged for a minimum of 45 min before an experiment to ensure an anoxic environment. Subsequently, the solution was continuously purged with a stream of Ar gas.
**Table 4.1: NaCl and Na₂S concentrations**

<table>
<thead>
<tr>
<th>[NaCl] (M)</th>
<th>[Na₂S] (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>5×10⁻³</td>
</tr>
<tr>
<td>0.5</td>
<td>1×10⁻⁴</td>
</tr>
<tr>
<td>1.0</td>
<td>5×10⁻⁴</td>
</tr>
<tr>
<td>3.0</td>
<td>1×10⁻³</td>
</tr>
<tr>
<td>5.0</td>
<td>2×10⁻³</td>
</tr>
</tbody>
</table>

**4.2.4 Cyclic Voltammetry (CV)**

Cyclic voltammetry (CV) was used to investigate the mechanism of sulphide film formation. Prior to applying a voltammetric scan, the electrode was cathodically cleaned at −1.5 V/SCE to remove air-formed oxides, and then at −1.15 V/SCE for a further 60 s. Voltammetric scans were performed from an initial potential in the range −1.15 V/SCE to −1.5 V/SCE to various anodic limits at a scan rate of 2 mV/s. The choice of starting potential had no influence on the subsequent electrochemical behavior.

**4.2.5 Scanning electron microscopy (SEM)**

Surface imaging was performed using a LEO (Zeiss) 1540XB FIB/SEM equipped with an Energy Dispersive X-ray Spectroscopy (EDX) analyzer to elucidate the elemental composition of the surface. Analyses were performed at the Western Nanofabrication Facility. Focused ion beam (FIB) cross-sections were prepared using a Ga ion beam. The sample was not pre-coated before a cut was made.
4.3 Results and Discussion

CVs were performed in solutions with various [Cl\(^-\)] and [SH\(^-\)] and at various electrode rotation rates from 0 to 25 Hz. The anodic and cathodic current responses varied with solution composition, electrode rotation rate, and the anodic potential limit of the voltammetric scan. The results can be grouped into three distinct types of behaviour defined by the characteristics of the copper sulphide film.

4.3.1 Type I – Single layer porous Cu\(_2\)S film

Type I films were observed at the two lowest [SH\(^-\)] (5.0×10\(^{-5}\) M and 1.0×10\(^{-4}\) M) irrespective of changes in [Cl\(^-\)] and mass transport conditions. A similar Type I film was produced at 0.1 M Cl\(^-\) in the [SH\(^-\)] range from 5.0×10\(^{-5}\) M to 2.0×10\(^{-3}\) M, and also at 0.5 M and 1.0 M Cl\(^-\) providing the [SH\(^-\)] was in the range 5.0×10\(^{-5}\) M to 5.0×10\(^{-4}\) M, and providing the solution was stagnant or the rotation rate was low (i.e., 1.67 Hz).

At a stationary electrode, Figure 4.1, the shape of the anodic current peak for Cu\(_2\)S formation suggests film formation was diffusion controlled. On the reverse cathodic scan, a single, almost symmetrical peak for the reduction of Cu\(_2\)S was observed at -1.15 V/SCE. When the electrode was rotated, Figure 4.2, the flux of SH\(^-\) to the electrode surface was accelerated and the presence of an anodic current plateau, with the current dependent on electrode rotation rate, confirms that film growth was dominantly a diffusion-controlled process. On the reverse scan the anodic current retraced its original path, confirming that film growth was reversible and that the sulphide film did not passivate the Cu surface. The size of the single reduction peak increased with rotation rate, and integration of the anodic and cathodic sections of the curve showed the total charge consumed in film growth was
recovered in film reduction. The current at the negative potential limit on both the forward and reverse scans was due to H₂O reduction.

![Graph with CV recorded on a stationary electrode in 0.1 M Cl⁻ + 1.0×10⁻³ M SH⁻ solution.]

To maintain a diffusion controlled growth process the film must be porous allowing rapid transport of Cu⁺ cations from the metal surface to the film/solution interface where it can combine with SH⁻ from solution leading to film growth. In order to maintain film growth at the film/solution interface, growth within the pores must be limited in order to avoid blockage and a switch to control of growth by transport through the film. Figure 4.3 illustrates this mechanism schematically, although the dimensions of the porous network were much tighter than illustrated.

Figure 4.4 shows SEM images of the film surface and of a FIB cut cross-section in the film. The film had a small granular structure. Since the Cu/film interface was clearly visible, the film could be shown to have an average, and generally uniform, thickness of ~ 60 nm. This film was difficult to image since it almost instantaneously decomposed in the electron beam. This was apparent in the FIB image in which the cross section was not a sharp
cut but almost a bubbled edge. However, close inspection shows the individual Cu$_2$S crystals were $\sim$ 20 nm in lateral dimension and the porous network was very fine and uniformly distributed across the electrode surface. There was no indication of localized behavior.

Figure 4.2: CVs showing the formation of a Type I Cu$_2$S film at various electrode rotation rates: a) 0.1 M Cl$^-$ + 5.0\times10^{-5} M SH$^-$; b) 1.0 M Cl$^-$ + 5.0\times10^{-5} M SH$^-$; c) 5.0 M Cl$^-$ + 5.0\times10^{-5} M SH$^-$; d) 0.1 M Cl$^-$ + 5.0\times10^{-4} M SH$^-$. 
Figure 4.3: Schematic illustrating the growth of a compact Cu₂S film at the film solution interface by transport of SH⁻ through a network of fine pores in the film. The relative dimensions of the films and pores are not to scale.

Figure 4.4: a) SEM micrograph of a Cu₂S film; and b) FIB cross-section of the porous Cu₂S film. The film was grown in a 0.1 M Cl⁻ + 5.0×10⁻⁵ M SH⁻ solution at a rotation rate of 25 Hz during a CV that was terminated at the anodic potential limit.

4.3.2 Type II – Porous dual layer Cu₂S film

Type II films were formed at the lowest [Cl⁻] (Table 4.1) in the [SH⁻] range of 5.0×10⁻⁴ M to 2.0×10⁻³ M provided the electrode rotation rate was ≥ 1.67 Hz. These [SH⁻] were higher than those leading to the formation of the single layer porous Type I film as
described in section 4.3.1. Similar Type II films were observed in solutions with mid to high [Cl\(^-\)] (0.5 M to 5.0 M), and [SH\(^-\)] between 5.0\(\times\)10\(^{-4}\) M and 2.0\(\times\)10\(^{-3}\) M. At a [Cl\(^-\)] of 0.5 M and 1.0 M at the lowest [SH\(^-\)] this type of film was produced only when the rotation rate was \(\geq 1.67\) Hz. However for a [Cl\(^-\)] of 3.0 M and 5.0 M at similar [SH\(^-\)], porous dual layer films formed at all rotation rates, and at the highest [SH\(^-\)] for [Cl\(^-\)] of 0.5 M to 5.0 M, Type II films were observed only at rotation rates \(\leq 8.33\) Hz.

The voltammetric behaviour observed when a Type II film was formed is shown in Figure 4.5. In the CV, a small anodic pre-plateau was commonly observed, which sometimes appeared as a peak. This was indicated by an arrow and numbered 1 in Figure 4.6. Subsequently, the current rose to the main current plateau region (2 in Figure 4.6). As for Type I films the plateau, or limiting current, at the most anodic potentials was dependent on rotation rate confirming there was a major contribution of mass transport to the film growth process. As for Type I films the anodic current retraced its original path on the reverse scan indicating film growth was reversible and that passivation did not occur.

Two reduction peaks were observed when Type II films were grown as opposed to one for Type I films. Gradually increasing the anodic potential limit in the CV, Figure 4.7, shows that the first reduction peak was associated with the first anodic oxidation process (1). The current associated with this first anodic process was small compared to the final plateau current (2). Also, its size was not particularly influenced by electrode rotation rate. Similarly, the current and charge associated with the peak for its reduction changed only marginally with electrode rotation rate. The size of the second reduction peak (2’ in the cathodic scan, Figure 4.7) was governed by the plateau current achieved (2 in the anodic scan, Figure 4.7). The anodic plateau current increased with electrode rotation rate which lead to an increase in size of cathodic reduction peak 2, indicating this film grew in a similar manner to the Type I
film. Integration of the anodic and cathodic sections of the CVs showed all the oxidation charge again went to film growth with no detectable loss by dissolution. The presence of two reduction peaks indicated that two distinct films were formed: (i) one which grew initially but to a limited thickness (anodic reaction (1)); and (ii) a second film (anodic reaction (2)), which grew at higher potentials and whose thickness increased with increased anodic current, and possessed similar characteristics to a Type I film.

It is proposed that, at these higher [SH\textsuperscript{-}], coherent film growth could occur at the Cu/film interface providing a reasonable SH\textsuperscript{-} flux was maintained by electrode rotation. This would be expected to lead to a thin passive film with growth controlled by transport
processes within the film. However, growth at this interface was limited by the build up of interfacial stress leading to film fracture, the Pilling-Bedworth ratio for Cu$_2$S on Cu being 2. This attempt to passivate followed by breakdown would account for the shoulder (1 in Figure 4.6) in the anodic section of the voltammetric profile. Following breakdown of this potential barrier layer rapid transport of Cu$^+$ to the film solution interface became possible leading to the growth of a Type II porous film (2 in Figure 4.6). Film growth at the film/solution interface did not cause a build up of interfacial stress and growth of the outer Cu$_2$S layer (peak 2) continued unimpeded at a rate at least partially controlled by SH$^-$ diffusion to the film/solution interface.

It is clear from Figure 4.5 that Cl$^-$ had an important effect on film growth behaviour and the structure of the Cu$_2$S film. As [Cl$^-$] was increased from 0.1 M (Figure 4.5a) to 5.0 M (Figure 4.5d) the anodic plateau current decreased and the two reduction peaks became much more distinct, suggesting chloride played a role in the film growth/fracturing at the

Figure 4.6: A section of the anodic scan of a CV recorded in 3.0 M Cl$^- + 5.0 \times 10^{-4}$ M SH$^-$ solution at a rotation rate of 8.33 Hz.
Figure 4.7: CVs to various anodic limits obtained in 5.0 M Cl\(^-\) + 2.0 \times 10^{-3} \text{ M } SH^- \text{ solution and 1.67 Hz.}

Cu/film interface. A possibility is that Cl\(^-\) enforced a more open porous structure when present at very high concentrations.

Figure 4.8 shows a schematic of the dual Cu (I) sulphide film (Type II) where (A) was the initial compact and coherent film (which started to grow in the pre-plateau region 1,
Figure 4.6) and (B) was the thicker, more porous, Cu₂S film grown in plateau region 2, Figure 4.6. An SEM image of this film, Figure 4.9a, shows that the Cu₂S crystals were much larger (~100 nm) than for Type I films (~20 nm). The FIB cross section clearly shows the Cu/film interface, Figure 4.9b, and shows the film grew to a thickness, although uneven, in the range of 160 to 180 nm, compared to only ~60 nm for Type I films. This increased film thickness is consistent with the higher [SH⁻] present when Type II films were formed. Two distinct layers cannot be distinguished, which is not surprising since Figure 4.5 shows the amount of charge associated with process 1 was small compared to that associated with process 2. It is also possible that some decomposition of the film in the ion beam obscured the boundary between the two layers. As for Type I films, the porous network of the film was generally fine (on the scale of the crystals) and uniformly distributed, although a number of larger pores were also present. Inspection of the Cu/film interface showed no evidence of pitting. This is consistent with the presence of a uniformly distributed porous outer layer (Type II film) and confirms that anodic dissolution did not occur locally at pit locations including at locations where larger individual pores were present in the film, Figure 4.9.

![Figure 4.9: a) SEM image of a porous Type II Cu₂S film surface; and b) FIB cross section of the film. The film was grown in a 1.0 M Cl⁻ + 1.0×10⁻³ M SH⁻ solution at an electrode rotation rate of 8.33 Hz.](image-url)
4.3.3 Type III – Partially-passivating film

The formation of Type III film was limited to the two highest [SH\(^-\)] studied: 1.0×10\(^{-3}\) M and 2.0×10\(^{-3}\) M. For 1.0×10\(^{-3}\) M SH\(^-\) the formation of a partially passivating film was observed only at high [Cl\(^-\)] (3.0 M and 5.0 M) and high electrode rotation rates. At lower [Cl\(^-\)], but the same [SH\(^-\)] and electrode rotation rates, the anodic current for film growth at positive potentials became considerably lower than the theoretical diffusion limited current for SH\(^-\), suggesting film growth became partially chemically-controlled. However, passivation did not occur (i.e. the current did not decrease to a lower value). At the highest [SH\(^-\)] (2.0×10\(^{-3}\) M) partial passivation occurred at high electrode rotation rates (≥ 8.33 Hz) irrespective of the [Cl\(^-\)].

These features can be seen in the voltammetric behaviour, Figure 4.10. As expected, the anodic currents were considerably higher than those observed at lower [SH\(^-\)], Figure 4.10a, but separation into two distinct films (as indicated by two distinct reduction peaks) was poor at low [Cl\(^-\)]. As the positive anodic limit was approached, instead of rising to a plateau, as observed for Type I and Type II films, the current tended to peak. At high [SH\(^-\)] and low [Cl\(^-\)], Figure 4.10b, the current fell immediately to almost zero when the potential scan was reversed as opposed to retracing the forward scan as observed for Type I and II films. This fall in current indicated that film growth could only be sustained by the increasing electric field across the film imposed by the increasing potential. Once the potential was reversed this field became insufficient to drive the transport processes within the film required to maintain growth. At high [Cl\(^-\)], when the film was expected to be porous, partial passivation was observed as a drop in current at positive anodic potentials, Figure 4.10d. When this drop was observed, the cathodic scan showed the presence of a third film reduction peak, 3 in Figure 4.10c.
This behaviour can be summarized as follows, Figure 4.11. In anodic region 1, the surface attempted to passivate, as observed for Type II films and the reduction of this film occurred at cathodic peak 1, Figure 4.10c. As discussed above, this film rapidly fractured leading to the large increase in current in region 2. This Type II film was subsequently reduced at cathodic peak 2, Figure 4.10c. In region 3, the decrease in anodic current leading to partial passivation generated reduction peak 3 in the reverse scan, Figure 4.10c. The sites for Cu oxidation leading to the outer layer film (2 in Figure 4.11 and 4.10c) were at the base of pores in the initially formed thin base layer. The SEM and SEM-FIB images, Figure 4.12, showed the surface of the Cu when partial passivation had occurred and a Type III film was present.
The film had a uniform thickness of ~ 230 nm and was apparently less porous than Type II films, Figure 4.9. While some localized corrosion of the Cu interface was apparent in the cross-section image, Figure 4.12, there was no evidence for widespread development of pits.

A schematic of a Type III film is shown in Figure 4.13, with passivation indicated to occur by blockage of the pores in the film at the Cu/film interface. It is possible that passivation was more widespread and involved conversion of the Cu$_2$S to CuS [13] (or Cu$_x$S with compositions in the range Cu$_{1.98}$S to Cu$_{1.75}$S [14–17]) across the film/solution interface. If so, this universally passivating layer would have to have been very thin since the charge associated with its reduction (proportional to the area under reduction peak 3, Figure 4.10c) was small. However the minimum area that must be passivated was that at the base of pores.

![Figure 4.11: Section of the anodic scan of a CV recorded in 3.0 M Cl$^-$ + 2.0 × 10$^{-3}$ M SH$^-$ solution at 25 Hz. The numbers indicate three distinct regions of behaviour.](image)

in the initially grown Type I film. A key point is that the initially grown Cu$_2$S film (1 in Figure 4.11) did not lead to passivation and substantial growth of the outer layer film (2 in Figure 4.11) occurred before partial passivation was observed at considerably more positive potentials (3 in Figure 4.11).
Figure 4.12: a) SEM image of a passive copper sulphide film surface; b) FIB cross section of a passive copper sulphide film. The film was grown in a 5.0 M Cl⁻ + 2.0×10⁻³ M SH⁻ solution at a rotation of 25 Hz.

Figure 4.13: Schematic showing the formation of a passive CuS layer (designated C) at the base of pores in a Type II Cu₂S film.

Figure 4.14 attempts to summarize the various conditions under which the three types of films were formed, as a function of [SH⁻] and [Cl⁻] and electrode rotation rate. The latter parameter was included since, as indicated by the dependence of anodic film growth on electrode rotation rate, the flux of SH⁻ to the electrode surface was important in determining the kind of film formed. From this figure it is clear that the key features dictating the nature
of the film were the bulk $[\text{SH}^-]$ and the electrode rotation rate. At low $[\text{SH}^-]$ ($\leq 1.0 \times 10^{-4}$ M) porous Type I films were formed irrespective of the $[\text{Cl}^-]$ or electrode rotation rate. Additionally, as the $\text{SH}^-$ flux to the electrode surface decreased (i.e., the rotation rate approached 0) porous Type I and II films were always found irrespective of the $[\text{SH}^-]$ and $[\text{Cl}^-]$. Partially passive Type III films were formed only at high $[\text{SH}^-]$ although the threshold $[\text{SH}^-]$ for their formation was decreased providing the flux of $[\text{SH}^-]$ was increased to maintain a high interfacial $[\text{SH}^-]$.

![Figure 4.14: 3D Plot displaying various film types at different [SH⁻], [Cl⁻] and electrode rotation rates.](image)

It can be concluded that passive films which could lead to the conditions which could support pitting, were only formed for $[\text{SH}^-] \geq 5.0 \times 10^{-4}$ M and then only at high $\text{SH}^-$ fluxes (proportional to the rotation rate) when depletion of $\text{SH}^-$ at the Cu surface would be minimized, and the generally formed porous Types I and II films avoided. No clear influence of $[\text{Cl}^-]$ was apparent in this figure indicating that while it may influence the porosity of the
films formed it was not the primary factor controlling the type of film formed. If it is assumed that passivity is a prerequisite for pitting these results indicate that pitting should not occur for \([\text{SH}^-] < 5.0 \times 10^{-4} \text{ M}\) and should not occur at all, irrespective of \([\text{SH}^-]\) and \([\text{Cl}^-]\), as stagnant conditions (rotation rate < 3.18 Hz) are approached.

These electrochemical results can be compared to those obtained in long-term (up to 4000 h) corrosion experiments. When the \([\text{SH}^-]\) was high (i.e., \(\geq 5.0 \times 10^{-4} \text{ M}\)) and the \([\text{Cl}^-]\) was low (i.e., \(\leq 0.5 \text{ M}\)) the corrosion product formed was a single compact \(\text{Cu}_2\text{S}\) film (chalcopyrite, as demonstrated by XPS and XRD). Growth of this crystalline film obeyed a parabolic law [9, 12, 18], indicating that the film was protective under these conditions, the overall corrosion process being dominated by \(\text{Cu}^+\) diffusion through the \(\text{Cu}_2\text{S}\) film with a contribution from \(\text{SH}^-\) diffusion from the bulk solution to the film/solution interface.

When the \([\text{SH}^-]\) was low (i.e., \(\leq 5.0 \times 10^{-4} \text{ M}\)), the \(\text{Cu}_2\text{S}\) film formed was porous and its growth was linear with exposure time [12, 18, 19], indicating that the film formed under these conditions was not protective, the corrosion process being mainly controlled by \(\text{SH}^-\) diffusion in solution and/or pores. A similarly porous film was observed at higher \([\text{SH}^-]\) (1.0 \times 10^{-3} \text{ M}) if \([\text{Cl}^-]\) was increased to 1.0 M. These observations are consistent with the electrochemical observation that a dominant influence of \([\text{Cl}^-]\) was to enhance the porosity of the film even as the \([\text{SH}^-]\) increased. When the \([\text{Cl}^-]\) was very high (i.e. 5.0 M), the \(\text{Cu}_2\text{S}\) film grew two-dimensionally with pores between plates. The corrosion process appeared to be assisted by \(\text{CuCl}_2^-\) diffusion in the pores and \(\text{SH}^-\) diffusion in the solution. Although the behaviour under these conditions has not been completely characterized, it was clear the film offered no corrosion protection. In all the tested solutions and conditions, no pitting corrosion was observed.
As observed in the voltammetric experiments the formation of a compact film, requires a high [SH\(^-\)]. Since the [SH\(^-\)] and [Cl\(^-\)] in a Swedish repository are expected to be in the ranges 10\(^{-7}\) M to 10\(^{-4}\) M and 0.1 M to 1.4 M [20], respectively, passive conditions will not be achieved. Given the slow diffusive transport conditions expected in the compacted clay environment surrounding an emplaced container, the [SH\(^-\)] at the container surface will be at the low end of this range and probably considerably lower [21]. Again, these results are consistent with the electrochemical results which show porous films are obtained irrespective of [SH\(^-\)] and [Cl\(^-\)] as stagnant conditions (very low electrode rotation rates) are approached. Thus, under repository conditions, the Cu\(_2\)S films formed will almost certainly be porous and container corrosion controlled by transport processes. Since the prerequisite for pitting, the presence of a compact passive layer cannot be satisfied, it is most unlikely SH\(^-\)-induced pitting corrosion will occur under repository conditions. Furthermore, the [Cl\(^-\)] required for corrosion to be assisted by CuCl\(_2\)^- transport appears to be well beyond that anticipated under repository conditions.

4.4 Summary and Conclusions

- Under polarization conditions, the morphology of the sulphide film formed on Cu in aqueous sulphide solutions has been shown to be dependent on the [SH\(^-\)], the flux of sulphide to the electrode surface, and the [Cl\(^-\)] of the solution.
- Three distinct type of films have been observed: Type I film—a single layer porous Cu\(_2\)S film, identified by one reduction peak in a CV; Type II film—a porous dual layer Cu\(_2\)S film, identified by two reduction peaks in a CV; and Type III film—a compact, partially-passivating film, identified by an additional third peak in a CV.
When the film growth is dominated by SH\(^{-}\) diffusion in solution, a porous film (Type I or II) forms, whereas if film growth is controlled by an interfacial reaction, a compact Type III film forms. These observations are consistent with the results of long-term corrosion experiments under natural corrosion conditions.

- Partially passive Type III films are formed only at high \([\text{SH}^-]\) and high electrode rotation rates, when the flux of sulphide at the film/electrolyte interface is sufficiently large that film growth is controlled by interfacial reactions.

- It can be concluded that passive films, which could lead to the conditions able to support pitting, are only formed for \([\text{SH}^-] \geq 5.0 \times 10^{-4} \text{ M}\) and then only at high \(\text{SH}^-\) fluxes (electrode rotation rates). These conditions are not possible within a waste repository.

### 4.5 Acknowledgement

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### 4.6 References


The Kinetics of Film Growth and their Influence on the Susceptibility to Pitting of Copper in Aqueous Sulphide Solutions

5.1 Introduction

Copper is the primary candidate material for the manufacture of nuclear fuel waste containers in Sweden, Finland and Canada primarily for its thermodynamic stability in the anoxic aqueous environments anticipated in a deep geologic repository (DGR) [1, 2]. However, given the evolution of exposure conditions in a DGR, shown schematically in Figure 5.1, the Cu waste container is susceptible to a number of corrosion processes upon burial [3]. In the early emplacement period unsaturated (humid) oxidizing conditions could prevail due to the presence of oxygen trapped upon sealing of the DGR and the radiolytic decomposition of H₂O due to the gamma radiation emitted by the spent fuel within the container.

However, although the period over which it will happen is uncertain, cooler anoxic conditions will eventually be established and the container will spend the majority of its lifetime in an anoxic environment. During this period it is only vulnerable to corrosion by reaction with bisulphide (SH⁻), an oxidant found in Swedish/Finnish groundwater due to the presence of sulphide rich minerals (such as pyrite), and sulphate reducing bacteria (SRB) in

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the bentonite backfill material. Based on analyses of samples from boreholes in the proposed Swedish Forsmark repository, SH\(^-\) concentrations are conservatively taken to be \(10^{-5}\) M [4].

In our previous study [5] the characteristics of the sulphide films formed on the Cu surfaces were determined as a function of [SH\(^-\)], [Cl\(^-\)] and electrode rotation rate, and shown to fall into three categories: Type I, a thin single layer, porous film observed at low [SH\(^-\)] and a low sulphide flux; Type II, a porous dual-layer film formed at intermediate [SH\(^-\)] and higher fluxes; and Type III, a passive, or at least partially passive film, formed at high [SH\(^-\)] and transport fluxes. Since the Type III film displays passive characteristics and passivity is the pre-requisite for localized corrosion, it is critical, for nuclear waste container safety assessments to determine whether susceptibility to localized corrosion, in particular pitting, is possible under DGR conditions.

Figure 5.1: Schematic illustration of the evolution of the environment in a deep geological repository (DGR). [3]. The axis for the change in redox conditions (oxidizing to reducing) is only illustrative. The temperature change is for a specific repository design similar to that expected in DGR. Arrow representative of time range of investigation.
The goal of this study is twofold: (i) to determine the mechanism of Cu$_2$S film growth in $1 \times 10^{-5}$ to $2 \times 10^{-3}$ M SH$^-$ solutions containing Cl$^-$ in the concentration range from 0.1 M to 5.0 M, since Cl$^-$ is the dominant anion in the repository groundwater; and (ii) to determine whether or not the passive conditions required to support pitting are possible.

5.2 Experimental

5.2.1 Sample Preparation

All experiments were performed with O-free, P-doped Cu provided by the Swedish Nuclear Fuel and Waste Management Company (SKB), Solna, Sweden. Working electrodes were machined Cu disks with a 1 cm diameter threaded with a stainless steel rod. For corrosion experiments, a non-conductive lacquer was applied to prevent exposure of the steel/Cu junction to the electrolyte. Rotating disk working electrodes (RDE) were prepared by setting Cu disks in a Teflon holder with epoxy resin. Prior to an experiment, electrodes were ground with a sequence of SiC papers (grit sizes: 600, 800, 1000, 1200, and 2400), then polished to a mirror finish using Al$_2$O$_3$ suspensions (1 µm, 0.3 µm, and 0.05 µm), thoroughly rinsed with Type-1 water with a resistivity of 18.2 MΩ·cm (Thermo Scientific Barnstead Nanopure 7143 ultrapure water system) and dried in a stream of ultrapure Ar gas.

5.2.2 Electrochemical Experiments

Electrochemical experiments were performed in a conventional three-electrode electrochemical glass cell placed inside a Faraday cage to reduce electrical noise. A cylindrical Pt sheet rolled into a cylinder was used as the counter electrode. A saturated
A calomel reference electrode (SCE, 0.242 V/SHE) was used in all experiments. All experiments were conducted using an RDE. The electrode rotation rate was controlled by a Pine Instrument Company Analytical Rotator Model AFA86 Serial 882, and electrochemical measurements were made using a computer-controlled 1287 Solartron potentiostat equipped with CorrWare software. Prior to an experiment, the electrode was cathodically cleaned at −1.5 V/SCE to remove air-formed oxides, and then at −1.15 V/SCE. Voltammetric scans (CV) were performed from an initial potential of −1.35 V/SCE to various anodic limits at a scan rate of 2 mV/s. Electrodes were exposed to [SH\textsuperscript{−}] of 1×10\textsuperscript{−5} M, 1×10\textsuperscript{−4} M, 5×10\textsuperscript{−4} M, 1×10\textsuperscript{−3} M and 2×10\textsuperscript{−3} M and [Cl\textsuperscript{−}] of 0.1 M, 0.5 M, 1.0 M, 3.0 M and 5.0 M. All solutions were prepared with Type-1 water, reagent-grade sodium sulphide (Na\textsubscript{2}S·9H\textsubscript{2}O, 98.0% assay) and reagent-grade sodium chloride (NaCl, 99.0% assay).

### 5.2.3 Corrosion Experiments

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, to ensure anoxic conditions (c\textsubscript{O\textsubscript{2}} < 1 ppm). The oxygen concentration in the chamber was analyzed with an MBraun oxygen probe. Prior to an experiment, electrodes were cathodically cleaned as described in section 5.2.2. Experiments were conducted in solutions containing [SH\textsuperscript{−}] of 5×10\textsuperscript{−4} M, and a [Cl\textsuperscript{−}] of 0.1 M. All solutions used were prepared with Type-1 water and the reagents noted above.
5.3 Results and Discussion

5.3.1 Film Growth Location

To identify the location of Cu$_2$S film growth, an Au marker test was performed. A Cu specimen was first corroded in 0.1 M [Cl$^{-}$] containing [SH$^{-}$] = 5×10$^{-4}$ M for 161 h to form a thin (~200 nm thick) Cu$_2$S film. The specimen was then removed, marked with a 200 µm wide Au line and re-immersed for a further 1530 h. Figure 5.2 shows the cross sectional morphology observed using backscattered electron detection after a total immersion time of 1691 h. It is clear that film growth occurred on the Au marker since the thickness of the film below the marker remained unchanged; i.e., retained the same thickness as that of the preformed film. This indicates that film growth occurred at the Cu$_2$S/solution interface and involved Cu$^+$ transport through the film. As demonstrated previously, film growth at this [SH$^{-}$] leads to a parabolic growth law [6] demonstrating the formation of a, at least partially, protective film. Inspection of the film in Figure 5.2 shows it to be, on average, ~ 700 nm thick and compact.

Figure 5.2: a) FIB cross-section of a corroded Cu specimen after immersion in 0.1 M Cl$^{-}$ + 5×10$^{-4}$ M SH$^{-}$ solution for 161 h prior to deposition of the Au marker and for a further 1530 h afterwards. b) Higher magnification of the cross-section
5.3.2 Growth of Cu$_2$S under Electrochemical Conditions

Figure 5.3 shows two CVs recorded in 0.1 M [Cl$^-$] containing $1 \times 10^{-4}$ M [SH$^-$], one under stagnant conditions, and the second at an electrode rotation rate of 8.33 Hz. These experiments are similar to those performed previously [5], except the anodic limit was extended from the previous $-0.7$ V/SCE to $-0.1$ V/SCE to facilitate comparison to a similar set of potentiodynamic scans performed by Mao et al. [7]. These authors claimed that the currents measured over the potential range $-0.8$ V/SCE to $-0.2$ V/SCE were due to the growth of a passive Cu$_2$S (possibly Cu$_2$S/CuS) film with the current increase at positive potentials attributable to the Cl$^-$ induced breakdown of this passive film. The very large film reduction currents (observed over the potential range $-1.0$ to $-1.3$ V/SCE on the reverse potential scan) demonstrate that the current measured over the anodic potential range is due to porous Cu$_2$S film growth. The shoulder observed on the cathodic peaks for both stagnant and rotated conditions (although subtle under stagnant conditions) corresponds to the reduction of a thin Cu$_2$S film which grows (on the anodic scan) to a limited thickness before fracturing due to interfacial stress. The major peak corresponds to the reduction of the thicker, more porous Cu$_2$S film [5], which grows on top of this thin fractured film, likely by a nucleation process. The increased anodic current observed when the electrode is rotated (between $-0.8$ V/SCE and $-0.1$ V/SCE), accompanied by the major increase in film reduction current on the reverse scan, shows that the film growth process is accelerated by the increased convective flux of SH$^-$ to the electrode surface. This indicates that film growth is controlled by the solution transport of SH$^-$ and not the transport of point defects in a passive film as claimed by Mao et al. [7]. In addition, irrespective of whether the electrode is rotated or not, the current is reversible (i.e., the same on the forward and reverse scans) over the potential range $-0.9$ V/SCE to $-0.35$ V/SCE, confirming that further film growth is
uninhibited by the presence of the film already grown. This confirms that the film remains porous with its growth proceeding at the Cu₂S/electrolyte interface, as demonstrated above in the Au marker experiment.

At potentials $\geq -0.25$V the anodic current increases substantially under both stagnant and rotated conditions, Figure 5.3. Although not shown here, we observed a similar current increase at positive potentials in Cl⁻ solutions in the absence of SH⁻. Consistent with the literature [8,9] this current can be attributed to the anodic dissolution of Cu as CuCl$_x$($^{x-1}$), with the intermediate formation of a CuCl$_{ads}$ surface layer (reduced in the potential range $-0.3$ to $-0.4$ V/SCE on the reverse scan). The observation of this anodic/cathodic couple in this potential range, when a Cu₂S film is present, Figure 5.3, confirms that the latter film, when present, is porous and does not passivate the surface.

![Graph showing CVs recorded under stagnant and rotated conditions in 0.1 M Cl⁻ + 1×10⁻⁴ M SH⁻](image)

**Figure 5.3:** CVs recorded under stagnant and rotated conditions in 0.1 M Cl⁻ + 1×10⁻⁴ M SH⁻

These observations complement our previously published study conducted over a much narrower potential range (to a positive limit of $-0.7$ V/SCE) [5], in which the Cu₂S film characteristics were determined as a function of [SH⁻], [Cl⁻], and the transport
conditions at the surface, the latter controlled, as in the present case, at an RDE. We can now characterize the nature of the films according to the three categories previously proposed: Type I, a thin single layer, porous film observed at low [SH\textsuperscript{−}] and a low transport flux (i.e., low electrode rotation rate); Type II, a porous dual layer film formed at intermediate [SH\textsuperscript{−}] and higher fluxes; and Type III, a passive, or at least partially passive film, formed at high [SH\textsuperscript{−}] and transport fluxes.

These results are summarized for solutions with low (0.1 M) and high (5.0 M) [Cl\textsuperscript{−}] in Figure 5.4. These figures show the progression in film properties from porous Type I and Type II films to Type III films as the [SH\textsuperscript{−}] and flux increase. These plots demonstrate that the passive conditions associated with Type III films are only achievable at high [SH\textsuperscript{−}] and high fluxes in solutions containing 0.1 M and 5.0 M chloride. Comparison of the plots also show that [Cl\textsuperscript{−}] only influences the type of film formed at very low fluxes when porous conditions prevail, and has no influence on the conditions under which passivity can be achieved; i.e., the range of conditions within which a Type III passive film can form.

![Figure 5.4](image)

**Figure 5.4**: Summary of the conditions under which porous (Types I and II) and passive Cu\textsubscript{x}S (Type III) films are formed as the electrode rotation rate and [SH\textsuperscript{−}] are changed.
5.3.3 Influence of Chloride on Film Growth

While the above results show Cl\(^-\) has little influence on whether or not passive conditions can be established, it has been shown to influence the film growth rate, which is suppressed when the \([\text{Cl}^-]\) is increased [10]. In addition the growth kinetics change from parabolic (0.1 M) to linear (0.5 M): that is, from a partially protective film to a more porous film supporting growth by the solution transport of \(\text{SH}^-\). Figure 5.5 shows that the limiting anodic current (recorded in the potential region \(-0.8\text{ V/SCE to } -0.4\text{ V/SCE, Figure 5.3}\)) is below the theoretical value calculated via the Levich equation for complete transport control [11]. This confirms that Cl\(^-\) has a direct inhibiting effect on film growth as observed in the corrosion experiments. In addition, the limiting currents show a complex dependence on \([\text{Cl}^-]\) with the current suppressed most at the highest concentration. This effect is presently under investigation. Since the Cu\(_2\)S film is porous, suppression of the film growth process

![Theoretical and Experimental Current vs. Frequency Plot](image.png)

Figure 5.5: Limiting current for Cu\(_2\)S film formation at \(-0.76\text{ V/SCE from CVs recorded in } 1\times10^{-3} \text{ M SH}^-\text{ containing various } [\text{Cl}^-]. 1 \text{ Hz} = 2\pi \text{ rad/s}
can be attributed to access of Cl\(^-\) to the Cu surface confirming that the Cu\(_2\)S film is porous, not passive. At these relative concentrations ([Cl\(^-\)]/[SH\(^-\)] ≥ 100), Cl\(^-\) can displace chemisorbed SH\(^-\) thereby inhibiting the essential first step in the overall film growth process, \(\text{Cu} + (\text{SH}^-)_{\text{ads}} \rightarrow (\text{CuSH})_{\text{ads}} + e^-\).

### 5.4 Summary and Conclusions

- The growth of Cu\(_2\)S films on Cu in aqueous SH\(^-\) solutions occurs at the Cu\(_2\)S/electrolyte interface and involves the transport of Cu\(^+\) through the thickening film.
- Both corrosion and electrochemical studies show that the Cu\(_2\)S film is porous, except at extremely high transport fluxes and [SH\(^-\)] when passivity can be achieved. Since pitting requires the establishment of passivity, it is only feasible under high flux/high [SH\(^-\)] conditions.
- The open circuit film growth rate and the anodic film growth rate are both suppressed at higher [Cl\(^-\)] due to the displacement of chemisorbed SH\(^-\) from the Cu surface. Film porosity also increases with increasing [Cl\(^-\)].

### 5.5 Acknowledgement

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5.6 References


6

The Properties of Electrochemically-grown Copper Sulphide Films

6.1 Introduction

Nuclear energy has proven to be a viable option as a reliable, inexpensive, and environmentally friendly source of electrical energy. However, with these assets comes the responsibility for successful management of the spent nuclear fuel. One approach under study in many countries, including Sweden, Finland and Canada, is permanent disposal of the spent fuel in a deep geological repository (DGR). The spent fuel would be placed in containers fabricated with a cast iron or carbon steel inner vessel and an outer copper shell, designed to avoid both corrosion and mechanical failure. It is proposed these containers be buried in crystalline rock approximately 500 m below the surface and the excavated boreholes be backfilled with bentonite clay [1]. In Sweden and Finland, the outer shell would be fabricated using P-deoxidized Cu with a thickness of 50 mm [2-4]. Small additions of P (30 to 100 ppm) improves the creep properties, thereby limiting the probability for mechanical failure of the container after emplacement [5]. Although Cu is chosen for its resistance to corrosion in anoxic environments [3-5], Scandinavian repositories are known to contain SH\(^-\), produced in the groundwater as a consequence of sulphate-reducing bacteria and mineral dissolution processes [6]. This is potentially detrimental to the container since SH\(^-\) can act as an oxidant for Cu. Previous studies have characterized the copper sulphide films grown both electrochemically [7-9] and under corrosion conditions in aqueous solutions containing SH\(^-\) [6, 10-14].
Corrosion studies show that the properties of the sulphide films formed are governed by the sulphide concentration ([SH$^-\$]). Film growth as chalcocite (Cu$_2$S) occurred at the film/electrolyte interface [14]. Under stagnant conditions in 5×10$^{-4}$ M SH$^-$ + 0.1 M NaCl solution, a parabolic growth law was observed with growth controlled mainly by Cu$^+$ transport in the compact film [6]. However, at lower [SH$^-$] a linear growth law was observed leading to the development of a Cu$_2$S film with a cellular structure, whose growth was controlled predominantly by SH$^-$ diffusion in solution. When grown electrochemically [7, 8], the properties of the Cu$_2$S film were found to be dependent not only on the [SH$^-$] but also on [Cl$^-$] and the transport flux of SH$^-$ to the Cu surface (controlled using a rotating disc electrode (RDE)). At low [SH$^-$], a thin single layer porous film was formed, with a dual layer film developing as the [SH$^-$] was increased. For sufficiently high [SH$^-$] (≥ 10$^{-3}$ M), the anodic current became almost independent of the transport flux and decreased at higher potentials (≥ −0.85 V/SCE) indicating at least partial passivation of the Cu surface.

Other authors have claimed that the film formed on Cu under electrochemical conditions in 2×10$^{-4}$ M SH$^-$ was passive in nature [15-17], which ultimately led to Cl$^-$-induced breakdown and pitting at very positive potentials. However, these claims were based on polarization curves recorded under stagnant conditions, while our results, recorded at a rotating disk electrode (RDE) [7], demonstrated that the current observed was due to film growth partially controlled by SH$^-$ transport, a situation which precluded the possibility of passivation [8]. Additionally, the current increase observed at very positive potentials was shown to be due to the active anodic dissolution of Cu accelerated by complexation with chloride to form soluble species, such as CuCl$_2^-$, at the base of pores within the porous, non-protective chalcocite layer [8], not to the breakdown of a passive copper sulphide film.
These observations, however, conflict with claims [15-17], based on EIS measurements and Mott-Schottky analyses, that film growth was controlled by the transport of Cu$^+$ vacancies within a passive film, with a diffusion coefficient in the range of $10^{-14}$ to $10^{-15}$ cm$^2$/s. These values are considerably lower than the diffusion coefficients for Cu$^+$ vacancies in various copper sulphides, which vary with the degree of non-stoichiometry, decreasing from $\sim 10^{-8}$ cm$^2$/s for chalcocite (Cu$_2$S) to $10^{-9}$ cm$^2$/s for djurleite (Cu$_{1.96}$S), to $10^{-10}$ to $10^{-11}$ cm$^2$/s for anilite (Cu$_{1.75}$S) and $10^{-12}$ cm$^2$/s for covellite (CuS) [18]. Considerably lower values, more consistent with these expectations, were measured in our corrosion experiment. For the compact film grown in a solution containing $5 \times 10^{-4}$ M SH$^-$, a diffusion coefficient of $3.6 \times 10^{-10}$ cm/s was obtained [6] while for films grown at the lower [SH$^-$] of $5 \times 10^{-5}$ M the diffusion coefficient evolved from $10^{-7}$ cm$^2$/s, consistent with SH$^-$ transport within a porous chalcocite film, to $1.731 \times 10^{-5}$ cm$^2$/s in agreement with the value measured for SH$^-$ in bulk solution [10]. While some doubt exists over the analysis of Kong et al. [16, 17], since no attempt was made to eliminate solution transport effects, these observed differences in the measured diffusion coefficients for corrosion and electrochemical films could reflect a difference in chemical nature of the films.

These large differences pose the question of whether the films grown electrochemically at potentials positive to corrosion potential (E$_{corr}$) [15-17] possess different properties to those grown at E$_{corr}$, i.e., at open circuit [6, 10]. That this may be the case was suggested by the voltammetric experiments of Martino et al. [7], which showed that, at high [SH$^-$] ($\geq 10^{-3}$ M), an increase in current at small anodic overpotentials ($E_{applied} - E_{corr}$) was followed by a major decrease to a subsequently potential-independent current suggesting passivation. It was proposed that this film could be CuS, but no analytical supporting evidence was provided. The structure and properties of the sulphide films formed
electrochemically were also investigated by Kong et al. [16], but their claim that CuS was formed was based on a misinterpretation of XPS spectra which cannot distinguish between Cu$_2$S and CuS. However, transmission electron microscopy (TEM) evidence has been published to show that, as the electrochemical potential was increased, the Cu$_2$S film which formed at low potentials was converted to a more passive CuS film as the potential was made more positive, although the potential at which this occurred was not defined [19]. These last results appear to support the tentative claims of Martino et al. [7].

The purpose of this paper is to clarify the nature of the sulphide film grown at potentials positive to $E_{corr}$, to determine whether the formation of a passive film is possible, and to demonstrate whether or not electrochemically grown films are representative of those formed at open circuit. Knowledge of the characteristics of the sulphide film expected on a container is essential to determine whether or not localized corrosion, in the form of pitting, is a possible degradation mechanism.

### 6.2 Experimental

#### 6.2.1 Electrochemical Cell and Instrumentation

All electrochemical data was collected using a conventional three-electrode electrochemical glass cell. A Pt sheet rolled into a cylinder was used as the counter electrode and connected to external circuitry by a Pt wire. A standard calomel electrode (SCE, 0.242 V/SHE) was used as the reference electrode in all experiments. The cell was housed inside a Faraday cage to reduce electrical noise from external sources. Cyclic voltammetry experiments were conducted using a rotating disc working electrode (RDE). The electrode
rotation rate was controlled by a Pine Instrument Company Analytical Rotator Model AFA86 Serial 882. Electrochemical measurements were performed using either a computer-controlled 1287 Solartron potentiostat equipped with CorrWare software with a Solarton 1255B frequency response analyzer (FRA) with Zplot software for EIS data collection, or a Solartron Analytical Modulab running Modulab XM ECS software.

6.2.2 Copper Composition and Electrode Preparation

O-free, P-doped Cu, provided by the Swedish Nuclear Fuel & Waste Management Co. (SKB, Solna, Sweden), was machined into Cu disks. Ti rods were threaded into the back of the discs and the Cu fixed in a Teflon holder using an epoxy resin. Only a single flat Cu face, with a surface area of 0.785 cm², was exposed to solution. Prior to an experiment, the Cu electrode was ground with a sequence of SiC papers with grit sizes 1000, 1200, and 4000, and then polished to a mirror finish with Al₂O₃ suspensions with decreasing suspension size (1 μm, 0.3 μm, and 0.05 μm). The electrode was then rinsed thoroughly with Type-1 water (resistance: 18.2 MΩ·cm) to remove any polishing residue, and finally dried in a stream of ultrapure Ar gas.

6.2.3 Solution Preparation

Electrolytes were prepared with Type-1 water (18 MΩ·cm) obtained from a Thermo Scientific Barnstead Nanopure 7143 water system. All water was purged with high purity Ar gas (Praxair) for 1h prior to the preparation of solutions. Solutions were made from reagent-grade sodium sulphide (Na₂S·9H₂O, 98.0% assay) and sodium chloride (NaCl, 99.0% assay).
purchased from Sigma-Aldrich and Caledon Laboratory Chemicals, respectively. All solutions contained 0.1 M NaCl and various Na2S concentrations ranging from 10^{-4} M to 10^{-3} M. To ensure an anoxic environment, solutions were Ar-purged for a minimum of 45 min before an experiment, with purging continued throughout the experiment.

6.2.4 Electrochemical Experiments

Cyclic voltammetric (CV) experiments were performed at RDEs. Prior to applying a voltammetric scan, the electrode was cathodically cleaned at −1.5 V/SCE to remove air-formed oxides, and then at −1.15 V/SCE for a further 60 s to allow the detachment of any H2 bubbles which may have formed due to H2O reduction at the more negative potential. Voltammetric scans were then performed to various anodic limits at a scan rate of 2 mV/s and an electrode rotation rate of 8.33 Hz.

Prior to electrochemical impedance spectroscopy (EIS) measurements, films were grown for 2 h at a series of potentials, with the potential being increased in 10 mV increments from E_{corr}. At each applied potential, the current was allowed to achieve a steady state value prior to recording an EIS spectrum. Spectra were recorded in the frequency range of 10^5 Hz to 10^{-3} Hz using a potential perturbation of ± 10 mV superimposed on the applied potential. The self-consistency of the measured spectra was tested using the Kramers-Krönig transformation. Samples used for surface analyses were prepared by applying a constant anodic current for 2 h, rinsed with Type-1 water on removal from the electrochemical cell, and then finally dried with a stream of Ar gas.
6.2.5 Surface Analysis

Surface imaging was performed using a LEO (Zeiss) 1540XB FIB/SEM equipped with an Energy Dispersive X-ray Spectroscopy (EDX) analyzer to elucidate the elemental composition of the surface. Analyses were performed at the Western Nanofabrication Facility. Focused ion beam (FIB) cross-sections were prepared using a Ga ion beam. The sample was not pre-coated before a cut was made.

6.3 Results and Discussion

6.3.1 Cyclic Voltammetry

CVs recorded on an RDE with the potential scanned to various anodic limits in a solution containing $5 \times 10^{-4} \text{ M SH}^-$, Figure 6.1, showed that a dual layer film developed as previously observed over a wide range of $[\text{SH}^-]$ and $[\text{Cl}^-]$ [7]. When the anodic limit was confined to $-0.88 \text{ V/SCE}$, anodic oxidation (1) led to a single, shallow, reduction peak on the reverse scan (1’). When the scan was extended to $-0.775 \text{ V/SCE}$, the anodic current approached a plateau (2) and the reduction of a second much thicker film (2’) was observed on the reverse scan. The maintenance of the anodic current on the reverse scan indicated that the film formed on the anodic scan did not passivate the electrode surface. The film formed at low potentials (1) appeared not to grow significantly on extending the anodic limit with its reduction generating only a shallow shoulder (1’) on the reverse scan. This behavior was confirmed when the anodic scan was extended further to a limit of $-0.70 \text{ V/SCE}$, when the anodic current achieved a plateau leading to an enhanced growth of film 2/2’ but only a marginal further growth of film 1/1’.
Consistent with previous observations [7], based on experiments conducted over a wide range of [SH\(^-\)] (5×10\(^{-5}\) M to 2×10\(^{-3}\) M) these CVs showed that Cu\(_2\)S film growth occurred as two layers with the initially grown film (1/1’) achieving only a thin limited thickness with most of the film growth occurring as a much thicker outer layer (2/2’). The reversibility of the anodic current showed that passivation did not occur at the electrode rotation rate used in these experiments. Integration of the anodic and cathodic current sections of the CVs showed that effectively all the anodic charge, injected on the forward and reverse scans, was recovered by reduction of the films on the reverse scan. This confirmed that the film anodically grown on the forward scan was sufficiently porous to allow film growth to continue on the reverse scan [7]. Similar non-passive behavior was observed for all [SH\(^-\)] lower than 5×10\(^{-4}\) M for [Cl\(^-\)] over the range 0.1 to 5.0 M.

**Figure 6.1:** CVs recorded to various anodic limits in a 0.1 M Cl\(^-\) and 5×10\(^{-4}\) M SH\(^-\) solution at an electrode rotation rate of 8.33 Hz.
6.3.2 Potentiostatic Film Formation

Figure 6.2 shows steady state polarization curves measured at a series of constant potentials on stationary electrodes in solutions containing various [SH\textsuperscript{−}]. At low [SH\textsuperscript{−}] the current rose steadily to a constant value as the potential was increased. As the [SH\textsuperscript{−}] was increased, an apparent active to passive transition developed. This transition became clearly defined for [SH\textsuperscript{−}] \( \geq 4 \times 10^{-4} \) M. However, as demonstrated for the CVs (Figure 6.1), anodic charge was consumed by Cu\textsubscript{2}S film formation. In addition no detectable amounts of Cu were released to solution. Thus, the apparent “active to passive” transition shown in Figure 6.2 cannot be attributed to a standard transition from active metal dissolution to a film-covered passive state. In addition, the observations that negligible dissolution was observed, and that the increase in current with [SH\textsuperscript{−}] observed in the plateau region of the polarization curves (i.e., for potentials \( \geq -0.83 \) V/SCE) only contributed to further film growth, was not
consistent with the formation of a passive state. The only credible alternative was that the transition reflected a change in the properties of the Cu$_2$S film formed on the Cu surface.

Experiments repeated at a RDE yielded an increase in anodic current, which confirmed that the currents plotted in Figure 6.2 were at least partially, controlled by SH$^-$ transport. Figure 6.3 shows a comparison between transport-corrected currents and the

![Graph showing current-potential relationships](image)

**Figure 6.3:** Current – potential relationships determined in a 0.1 M Cl$^- + 10^{-3}$ M SH$^-$ solution under stagnant ($\omega = 0$) and mass transport corrected ($\omega \to \infty$) conditions.

The currents measured at a stationary electrode for [SH$^-$] = 10$^{-3}$ M. This correction was made using a Koutecky-Levich plot in which the reciprocal of the measured current is plotted against $\omega^{-1/2}$ and the plot extrapolated to $\omega^{-1/2} = 0$ (i.e. to $\omega = \infty$). While the apparent “active to passive” transition was eliminated by electrode rotation, a noticeable change in the potential dependence of the anodic film growth rate was observed in the potential range within which the current measured under stationary conditions decreased. Previously, this decrease in anodic film growth rate was attributed to a two-step process [20]:

$$\text{Cu} + \text{SH}^- \rightarrow \text{Cu(SH)}_{\text{ads}} + \text{e}^- \quad (6.1)$$
\[
\text{Cu + Cu(SH)}_{\text{ads}} + \text{SH}^- \rightarrow \text{Cu}_2\text{S} + \text{H}_2\text{S} + e^-
\] (6.2)

It was proposed that, at low potentials at a rotated electrode, reaction 6.1 approached equilibrium but became totally irreversible and rate-controlling at high potentials, a change in kinetics that would account for the decrease in slope. However, the alternative explanation that this change in slope could be attributed to the formation of a CuS layer cannot be dismissed, since, at higher [SH\(^-\)], a current decrease was observed even at rotated electrodes [7].

### 6.3.3 SEM Microscopy

SEM images of the surfaces and of the FIB-cut cross sections after potentiostatic oxidation in a solution containing \(10^{-4}\) M SH\(^-\) are shown in Figure 6.4 for a low potential (−0.88 V/SCE), a potential at the beginning of the plateau region (−0.84 V/SCE), and a potential well into the plateau region (−0.76 V/SCE) (Figure 6.2). The films were composed of an uneven distribution of crystals of various dimensions and some deposited fine nanoparticles. The cross sectional images indicate the films were porous, and no clearly discernible barrier layer was observed. The rough interface observed at −0.84 V/SCE would not be expected if a barrier layer was present. The formation of defined crystals was consistent with film growth occurring predominantly at the Cu\(_2\)S/electrolyte interface, as observed under corrosion conditions [14]. Such a growth process required Cu\(^+\) transport, a process shown to occur as either soluble Cu(SH)\(_2\)\(^-\) complexes or Cu\(_3\)S\(_3\) clusters [21], the latter possibly accounting for the nanoparticles observed in the SEM images. Although an extensive examination remains to be completed similar film structures and deposited particulates were observed at other [SH\(^-\)].
Figure 6.4: SEM micrographs of the film formed after potentiostatic oxidation for 2 h in a stagnant 0.1 M Cl\(^{−}\) + 10\(^{−4}\)M SH\(^{−}\) solution: (a), (c), (e) surfaces of the films grown at −0.88 V/SCE, −0.84 V/SCE, and −0.76 V/SCE, respectively; (b), (d), and (f), the corresponding FIB-cut cross-sections for the same three potentials.
6.3.4 Electrochemical Impedance Measurements

6.3.4.1 Low Sulphide Concentrations

Figure 6.5 shows that the spectra recorded in the most dilute solution ([SH\(^-\)] = \(10^{-4}\) M) evolved as the potential was increased. At low potentials (−0.88 V/SCE and −0.87 V/SCE) two ill-defined responses were observed, marked 1 and 2 on the phase angle

![Phase Angle Plot](image)

![Total Impedance Plot](image)

Figure 6.5: EIS spectra obtained after potentiostatic oxidation in a 0.1 M Cl\(^-\) + 10\(^{-4}\) M SH\(^-\) solution for 2 h: (a) phase angle (\(\theta\)); (b) total impedance (Z).

(\(\theta\)) plot, Figure 6.5a. As the potential was increased (−0.86 V/SCE to −0.82 V/SCE), and the steady-state current in the polarization curve started to increase (Figure 6.2), the response at
\(~10^{-1}\text{ Hz (2 in Figure 6.5a) became less distinct and an additional low frequency response (3 in Figure 6.5a) was observed. Increasing the potential to values in the plateau region of the polarization curve (\(-0.81\text{ V/SCE to }-0.76\text{ V/SCE, Figure 6.2}) led to a shift of the high frequency response (1) to even higher frequencies (\(\sim 50\text{ Hz}) and the development of an additional low frequency response (4 in Figure 6.5a) accompanied by an increase in the impedance at the low frequency limit by approximately a factor of 10, Figure 6.5b.

The EIS spectra were fitted to one of a number of electrical equivalent circuits, Figure 6.6, depending on the applied potential. At low potentials (\(-0.88\text{ V/SCE to }-0.87\text{ V/SCE}), on the rising section of the polarization curve (Figure 6.2), fits to the equivalent circuit in Figure 6.6a are shown in Figure 6.7. The high frequency response (1 in

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Figure 6.6: Equivalent circuits used to fit EIS spectra recorded at various [SH\(^{-}\)]. The individual elements are defined in the text.
Figure 6.5a) was attributed to the interfacial charge transfer process \((R_{\text{int}}/C_{\text{int}})\) occurring at the base of pores in the anodically-formed \(\text{Cu}_2\text{S}\) layer. Since this interfacial process involved surface adsorbed species, reaction 6.1, \(R_{\text{int}}/C_{\text{int}}\) included contributions from the charge transfer process and the relaxation of surface adsorbed species. No attempt was made to separate these contributions since the EIS spectra were insufficiently defined to merit it. The lower frequency response (2 in Figure 6.5a) was attributed to the properties of the porous layer \((R_{\text{pore}}/C_{\text{film}})\). Since this \(\text{Cu}_2\text{S}\) film was electrically conductive [6], \(C_{\text{film}}\) will be a combination of the double layer capacitance, the capacitance associated with surface adsorbed species involved in the film growth process, and possibly a contribution from the film itself [6].

For more positive potentials, the spectra were fitted to the equivalent circuit shown in Figure 6.6b, which includes a Warburg impedance \((W_{\text{SH}})\) to account for the low frequency
response (3 in Figure 6.5a), indicating a contribution from transport processes within pores in the surface film. Examples of fits to this circuit are shown in Figure 6.8. The need for a Warburg impedance element was consistent with the electrode rotation rate dependence of the current demonstrated in Figure 6.3. Examples of EIS spectra, recorded at potentials in the plateau region of the polarization curve (i.e., large overpotentials), fitted to the three time constant equivalent circuit shown in Figure 6.6c, are shown in Figure 6.9. The additional time constant (4 in Figure 6.5a) was attributed to the resistance \( R_{\text{dep}} \) and capacitance \( C_{\text{dep}} \) of an outer layer deposit.

![EIS spectra](image)

Figure 6.8: EIS spectra recorded at intermediate anodic overpotentials after potentiostatic oxidation for 2 h in a 0.1 M \( \text{Cl}^- \) + \( 10^{-4} \text{ M SH}^- \) solution. EIS data are shown as symbols and the equivalent circuit fits as lines.

In all these fits, and those described below, constant phase elements (CPEs) rather than capacitances were required to fit the spectra. The CPE can be defined by the following relationship:
where $Q$ is the admittance, $j^2$ is equal to $-1$, $\omega$ is the frequency, and when $\alpha = 1$ the CPE represents a true capacitor. Attempts to convert these CPEs to capacitances using the Mansfeld conversion procedure [22] were unsuccessful due to the deviation of $\alpha$ from 1. This is not surprising given the expected polarizability and observed porosity of the deposits.

The values of $R_{\text{int}}$, $R_{\text{pore}}$ and $R_{\text{dep}}$ obtained from fitted spectra at $[\text{SH}^-] = 10^{-4}$ M are plotted in Figure 6.10. In the potential range over which the current increased with potential in the polarization curve (up to $-0.82$ V/SCE (Figure 6.2)), the value of $R_{\text{int}}$ changed only marginally while $R_{\text{pore}}$ decreased by approximately an order of magnitude. This decrease in $R_{\text{pore}}$ was accompanied by the appearance of the Warburg response at low frequencies (Figure 6.5). The interfacial resistance ($R_{\text{int}}$) at the base of pores would be expected to have
decreased as the rate of the anodic reaction was accelerated at more positive potentials. Its constancy can be attributed to the counterbalancing influence of film thickening leading to SH\textsuperscript{−} depletion at the Cu surface at the base of pores, as indicated in the spectra by the need to account for SH\textsuperscript{−} diffusion within the pores with a Warburg impedance.

![Figure 6.10: Resistance values obtained by fitting EIS spectra, recorded in a 0.1 M Cl\textsuperscript{−} + 10\textsuperscript{−4} M SH\textsuperscript{−} solution to equivalent circuits in Figure 6.6 (as discussed in the text).](image)

For potentials of −0.80 V/SCE and higher, both R\textsubscript{int} and R\textsubscript{pore} decreased markedly, indicating an increase in rate of the interfacial reaction within a more porous film. This increased porosity facilitated the transport of Cu\textsuperscript{+} to the film/electrolyte interface leading to the formation of the outer sulphide deposit, with the large values of R\textsubscript{dep} indicating that it was the accumulation of this deposit which controlled the overall rate of film growth at this [SH\textsuperscript{−}] under stationary conditions. These results were consistent with the behavior observed in the CVs, Figure 6.1, in which the initially formed film (1/1’) rapidly became more porous and was subsequently bypassed by the growth of the second layer (2/2’).
At the highest potentials (−0.77 V/SCE and −0.76 V/SCE) $R_{\text{pore}}$ appears to increase again. This could have been due to the partial closing of porosity by deposition of Cu$_2$S within the pores, as illustrated in Figure 6.6c, making it difficult to deconvolute the resistances of the pore and the deposit when fitting the spectra. Additionally, it is possible, and indeed probable, that the overall film growth process remained diffusion controlled by SH$^-$ transport through the accumulating outer deposit, with this contribution incorporated in the value of $R_{\text{pore}}$.

### 6.3.4.2 Intermediate Sulphide Concentrations

Similar EIS spectra were obtained for [SH$^-$] up to $3 \times 10^{-4}$ M, the first concentration above which the apparent “active-to-passive” transition became observable in the polarization curve, Figure 6.2. The resistance values obtained by fitting the spectra obtained in a solution containing $3 \times 10^{-4}$ M SH$^-$ to the equivalent circuits shown in Figure 6.6b and 6.6c are plotted in Figure 6.11. A similar decrease in $R_{\text{int}}$ with increasing potential to that observed at the lower concentration was observed, although the decrease from the initially higher value to the eventual lower value occurred over a wider potential range (−0.88 V/SCE to −0.84 V/SCE). This change coincided with the shift from a current which increased with potential to one which was almost independent of potential, Figure 6.2 (−0.82 V/SCE to −0.80 V/SCE). However, by contrast to the behavior at the lower [SH$^-$], $R_{\text{pore}}$, which initially started to decline with increasing potential, did not undergo a distinct transition to a lower value over the same potential range (−0.88 V/SCE to −0.84 V/SCE). This could be attributed to the more rapid accumulation of the outer deposit within the developing pores at this higher...
At higher potentials $R_{\text{pore}}$ and $R_{\text{dep}}$ exhibited both similar values and identical increases with increasing potential. This coincidence suggests these resistances became difficult to separate in the EIS fitting procedure. The lower $R_{\text{int}}$ and $R_{\text{pore}} + R_{\text{dep}}$ values at this concentration (compared to these values at the lower $[\text{SH}^-]$) were consistent with the larger currents measured in the polarization curves (Figure 6.2 at these high potentials) and indicated that, despite the more rapid formation of the outer deposit, the anodic film growth rate was higher. For this to have occurred, the transport of $\text{SH}^-$ through the deposit to the Cu surface must have been maintained.

### 6.3.4.3 High Sulphide Concentrations

For $[\text{SH}^-] \geq 4 \times 10^{-4} \text{ M}$, when the apparent “active-to-passive” transition was clearly visible in the polarization curves (Figure 6.2), the EIS spectra, shown for $[\text{SH}^-] = 5 \times 10^{-4} \text{ M}$ in Figure 6.12, exhibited similar, but better defined, behavior to that observed at the lower
[SH\textsuperscript{−}]. The high and intermediate frequency responses in conjunction with the Warburg response observed at low potentials confirmed that the initially formed film was porous. As the potential was made more positive, and the current in the polarization curve increased (−0.92 V/SCE to −0.86 V/SCE), the increased prominence of the low frequency Warburg response confirmed the increasing importance of SH\textsuperscript{−} transport within the porous film on the

Figure 6.12: 3D representations of a phase angle and total impedance plots obtained in 0.1 M Cl\textsuperscript{−} and 5×10\textsuperscript{−4} M SH\textsuperscript{−}
film growth process. At higher potentials, the replacement of the Warburg impedance by the low frequency response, leading to an increased impedance, coincided with the decrease in current in the polarization curve (Figure 6.2), yielding firm evidence that the decrease in current suggesting an “active-to-passive” transition could be attributed to the formation of the outer layer deposit.

For low potentials (in the range within which the current increased with potential, Figure 6.2) the spectra were fitted to the equivalent circuit shown in Figure 6.6b. At higher potentials (within the current plateau region (Figure 6.2)) the circuit in Figure 6d was used. The two circuits are the same except for the removal of the Warburg impedance in the second circuit and the redefinition of the pore resistance ($R_{pore}$) as the resistance of the outer layer deposit ($R_{dep}$). A contribution from the transport of $\text{SH}^-$ within the deposit-filled pores remained, since a significant film growth current persisted (Figure 6.2), but became unobservable.

The redefinition of $R_{pore}$ as $R_{dep}$ acknowledged that deposition of the outer layer within the pores led to their blockage at high $[\text{SH}^-]$. To confirm that this transition between the two circuits (Figures 6.6b and 6.6d) was appropriate the spectra recorded at $-0.84 \text{ V/SCE}$ was fitted to both circuits. The extracted values for $R_{ct}$ and $R_{pore}$ ($R_{dep}$) coincide, Figure 6.13, confirming that any contribution to the spectra from a Warburg impedance was obscured.

Despite the deposition of this layer the rate of the interfacial anodic reaction remained high, as indicated by the low value of $R_{ct}$, which was constant over the full potential range investigated, Figure 6.13. For this to be the case, the rate of formation of $\text{Cu}^+$ at the Cu/Cu$_2$S interface must have remained effectively constant at this $[\text{SH}^-]$ despite the on-going accumulation of the outer layer deposit. If the increased impedance was due to the formation of a passive layer this interfacial rate would have been expected to decrease with increasing
potential. As noted for the behavior at lower $[\text{SH}^-]$, the decrease in $R_{\text{pore}}$ over the potential range within which the current increased in the polarization curve confirmed that the more rapid film growth sustained at this higher $[\text{SH}^-]$ was accompanied by a pore opening process in the initially-formed layer.

6.3.4.4 Influence of Transport Processes on Film Growth

A critical feature of this analysis is the claim that the initial sulphide film formed was porous, allowing film growth to be sustained by $\text{SH}^-$ transport within the porous structure to the Cu surface at the base of the pores. The Warburg impedance element ($W_{\text{SH}}$), representative of sulphide transport, is defined by:

$$W(\omega) = \frac{\sqrt{2} \sigma_W}{\sqrt{j\omega}}$$  \hspace{1cm} (6.4)

where $\sigma_W$ is the Warburg coefficient, which can be approximated by the relationship:

Figure 6.13: Resistance values obtained by fitting EIS spectra, recorded in a 0.1 M Cl$^- + 5 \times 10^{-4}$ M SH$^-$ solution to equivalent circuits in Figure 6.6. The dotted line indicates the potential below which the spectra were fitted to the equivalent circuit shown in Figure 6.6b and above which to the circuit shown in Figure 6.6d. The two values at this potential show fits to both equivalent circuits.
\[ \sigma_W = \frac{RT}{\sqrt{2n^2F^2c_sc_D}} \]  

(6.5)

where \( n \) is the number of electrons, \( D \) is the diffusion coefficient of \( \text{SH}^- \), \( c_s \) is the surface concentration of \( \text{SH}^- \), \( F \) is Faraday’s constant, \( R \) is the gas constant, and \( T \) is temperature.

The values of the Warburg coefficient (\( \sigma_W \)) are plotted in Figure 6.14 for the range of [\( \text{SH}^- \)] investigated. Reliable values could only be obtained up to potentials in the range \( -0.85 \text{ V/SCE} \) to \( -0.84 \text{ V/SCE} \) except for the lowest [\( \text{SH}^- \)] for which a value was measurable up to \( \sim -0.82 \text{ V/SCE} \). Since \( \sigma_W \) is inversely proportional to \( c_s \) (equation 6.5), the [\( \text{SH}^- \)] at the Cu surface, its value was expected to increase, as observed, as the potential was increased and \( \text{SH}^- \) became depleted at the base of the pores in the growing sulphide film. The similarity in \( \sigma_W \) values can be attributed to two counterbalancing influences: (i) an increase in the bulk solution [\( \text{SH}^- \)] which would increase the diffusive flux to maintain \( c_s \); and (ii) an increase in film thickness which would increase the diffusion path length leading to a decrease in \( c_s \). At the lowest [\( \text{SH}^- \)] depletion was partially offset at low potentials by the increased porosity (decreased \( R_{\text{pore}} \)), Figure 6.10. Eventually, the ability to observe a transport contribution was lost when the film porosity increased more rapidly (at \( \sim -0.82 \text{ V/SCE} \), Figure 6.10) leading to an increase in \( c_s \), and an acceleration of the interfacial oxidation rate (decrease in \( R_{\text{int}} \)), and the accumulation of the outer layer deposit (indicated by the high \( R_{\text{dep}} \) values).

At higher [\( \text{SH}^- \)], similar increases in \( \sigma_W \) indicating decreased values of \( c_s \) were observed at low potentials, Figure 6.14, confirming a contribution from \( \text{SH}^- \) transport to the film growth process, as indicated by the RDE experiments, Figure 6.3. However, in the potential region in which the current decreased markedly in the polarization curve (\( -0.86 \text{ V/SCE} \) to \( -0.85 \text{ V/SCE} \), Figure 6.2), \( \sigma_W \) began to decrease indicating an increase in \( c_s \). This behavior confirmed our claim (above) based on the polarization curves (Figure 6.2) that the apparent “active-to-passive” transition which occurred in this potential range
involved a restructuring of the film leading to an increased porosity. The resulting increase in \( c_S \) would then account for the decrease in \( R_{\text{int}} \) at intermediate [SH\(^-\)] (Figure 6.11) and the maintenance of a low value at high [SH\(^-\)] (Figure 6.13). These observations confirmed that this transition did not involve the formation of a passive film which would, by definition, have involved either an increase in \( R_{\text{int}} \) or an inability to observe the interfacial reaction. At these intermediate and high [SH\(^-\)], the high \( R_{\text{dep}} \) values then confirm that it is the rapid accumulation of the outer deposit which was responsible for the decrease in current not the formation of a passive barrier layer.

![Figure 6.14: Warburg coefficients obtained from fits to one of the equivalent circuits in Figure 6.6 (as discussed in the text).](image)

These results confirm the importance of transport processes in determining the properties (morphology and porosity) of the Cu\(_2\)S film formed. In a previous voltammetric study [7] we showed that a passive sulphide film could be formed at a sufficiently high [SH\(^-\)] (~10\(^{-3}\) M) under voltammetric conditions providing the flux of SH\(^-\) to the Cu surface was maintained by convective flow (in that case, controlled by the use of an RDE). A similar
dependence on convective flow, required to maintain the surface [SH\textsuperscript{−}], was observed under corrosion conditions [23, 24]. Experiments performed under stagnant conditions demonstrated that Cu\textsubscript{2}S film growth was controlled by SH\textsuperscript{−} diffusion in solution leading to the formation of a non-protective film. By contrast, when SH\textsuperscript{−} transport was accelerated by convection, film growth rapidly became controlled by Cu(I) transport through a coherent film and proceeded at a considerably lower rate. This study, conducted under stagnant conditions when the surface [SH\textsuperscript{−}] became depleted, confirmed that the films formed both electrochemically and by corrosion [23, 24] are porous and not passive. Whether or not CuS is formed remains unresolved.

6.4 Summary and Conclusions

- The properties of copper sulphide films grown electrochemically on Cu in chloride solutions containing various amounts of sulphide (from 10\textsuperscript{−4} M to 10\textsuperscript{−3} M) have been investigated electrochemically by EIS at potentials –0.92 V/SCE to –0.76 V/SCE.
- Film growth occurred in two distinct stages. At low anodic overpotentials a thin porous Cu\textsubscript{2}S film was formed with growth occurring at the Cu\textsubscript{2}S/electrolyte interface supported by the transport of Cu(I). This was followed by the deposition of a thicker outer layer of Cu\textsubscript{2}S. At sufficiently high [SH\textsuperscript{−}], this led to partial blockage of the film growth process with the overall film growth rate being controlled by the properties of this outer layer deposit.
- EIS measurements confirmed that the decrease in the film growth rate at higher potentials and [SH\textsuperscript{−}] was due to the formation of this deposit not to passivation of the surface by a coherent sulphide film.
• The film growth mechanisms under electrochemical and corrosion conditions were found
to be very similar. These results confirm previous claims that the formation of a passive
sulphide film will only be possible at high [SH\(^{-}\)] when SH\(^{-}\) is not allowed to deplete at
the Cu surface. When a compacted bentonite buffer is present in a DGR these conditions
will be unachievable and passivation of waste container surfaces should not occur.

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Electrochemical Investigation of the Effect of Groundwater Anions on the Mechanism of Copper Sulphide Film Growth

7.1 Introduction

Cu is the primary candidate material for the manufacture of nuclear waste containers in Sweden, Finland and Canada since it is expected to be stable in the anoxic aqueous environments anticipated in deep geological repositories [1-3]. The containers are comprised of two main components: a cast iron or carbon steel inner vessel and an outer copper shell, which in combination are designed to avoid both corrosion and mechanical failure. In the Swedish/Finnish design, the outer shell would be fabricated using P-deoxidized Cu with a thickness of 50 mm [2-4]. Removing O with small additions of P (30 to 100 ppm) improves the creep resistance, thereby limiting physical deformation of the container after emplacement [2].

Although Cu is chosen for its resistance to corrosion in anoxic environments [3-5], Scandinavian repositories are known to contain SH\(^-\), produced in the groundwater as a consequence of sulphate-reducing bacteria and mineral dissolution processes [6]. Based on analysis of samples from boreholes in the proposed Swedish Forsmark repository, [SH\(^-\)] are conservatively taken to be 10\(^{-5}\) M [7], this is potentially detrimental to the container since SH\(^-\) can act as an oxidant for Cu producing a chalcocite (Cu\(_2\)S) film. However, various additional anions will be present in the groundwater, at appreciably higher levels than SH\(^-\), and would be expected to influence the Cu\(_2\)S film growth process. Groundwater ions of
special consideration are chloride, bicarbonate, and sulphate and their expected respective concentrations after 10,000 years in the DGR are $3.0 \times 10^{-4} \text{ M}$ to $0.154 \text{ M}$, $3 \times 10^{-4} \text{ M}$ to $5 \times 10^{-3} \text{ M}$, and $2 \times 10^{-4} \text{ M}$ to $7.2 \times 10^{-3} \text{ M}$ [2].

Chen et al. studied the effects of $[\text{Cl}^-]$ on Cu corrosion in quiescent anaerobic $\text{SH}^-$ solutions containing $1 \times 10^{-3} \text{ M}$ $[\text{SH}^-]$ [8]. It was shown that the Cu$_2$S film properties were greatly altered with an increase in $[\text{Cl}^-]$. At a relatively low $[\text{Cl}^-]$ (0.1 M) the film grew according to a parabolic growth law and displayed protective properties. On increasing the $[\text{Cl}^-]$ to 0.5 M the film developed a more porous nature as shown via EIS and confirmed by analyses of FIB cross sections. Additionally, a linear film growth rate indicated the film was not protective, providing further evidence of porosity. At the highest concentration studied, 5.0 M, the Cu$_2$S film developed extensive porosity, and film growth appeared to be governed by a combination of $\text{SH}^-$ diffusion in the bulk solution and the transport of soluble Cu$^+$ species ($\text{Cu(SH)}_2^-$ or Cu$_3$S$_3$ clusters [9, 10]) in the pores of the film. The study suggested that $\text{Cl}^-$ could influence the Cu$_2$S growth process by displacing adsorbed $\text{SH}^-$ from the Cu surface thus inhibiting the first step in the $\text{SH}^-$ induced corrosion reaction.

Chen et al. also studied the key parameters that govern the properties and structure of Cu$_2$S film grown in anoxic aqueous environments [11]. Concentrations of $\text{Cl}^-$ ranging from 0.1 M to 5.0 M were studied in solutions with various $[\text{SH}^-]$ from $1 \times 10^{-5} \text{ M}$ to $1 \times 10^{-3} \text{ M}$. The structure and properties of the films were determined by three critical factors: the $\text{SH}^-$ and $\text{Cl}^-$ concentrations ($[\text{SH}^-]$, $[\text{Cl}^-]$), their ratio, and the flux of $\text{SH}^-$ to the corroding Cu surface. The film structure and the kinetics of film growth were governed by competition between the interfacial reaction rate and the rate of $\text{SH}^-$ diffusion. When the interfacial reaction was rate determining the Cu$_2$S film was compact and protective, and when $\text{SH}^-$ diffusion dominated, the film was porous and non-protective: a ratio of $[\text{Cl}^-]/[\text{SH}^-] \geq 1000$. 


was required for a switch from a compact to a porous film to be observed. However, it remains unclear whether or not similar behaviour will be observed when other anions are present.

When studied electrochemically [12, 13], the properties of the Cu₂S film formed were also found to be dependent on [SH⁻] and [Cl⁻] and the transport of SH⁻ to the Cu surface (controlled using a rotating disc electrode (RDE)). At low [SH⁻] a thin single porous layer was formed, with a dual layer film developing as [SH⁻] was increased. For a sufficiently high [SH⁻] (≥ 5×10⁻⁴ M), the film appeared to become at least partially passive. In contrast, it has been claimed, based on a series of published studies in solutions containing [SH⁻] = 2×10⁻⁴ M, that the film grown electrochemically is a passive copper sulphide film [14-18].

The adsorption of various anions on Cu has been extensively studied, typically on single crystal electrodes. Broekmann et al. [19] studied the specific anion adsorption of Cl⁻ and SO₄²⁻ on Cu(111) surfaces. It was shown that Cl⁻ caused electrochemical annealing of the Cu surface with an increase in surface mobility causing a smoothing over of the holes, pits and islands observed after electropolishing. This mobility enabled large-scale morphological changes on a short time scale and became more pronounced as the applied potential was made more positive. In contrast, it was found that SO₄²⁻ adsorption did not allow for surface rearrangement and an overall low mobility of Cu was observed. SO₄²⁻ was found to adsorb in a close packed form with co-adsorbed species identified as H₂O, which is not surprising given the very large hydration enthalpy for this anion [20]. Lennartz et al. [21] found that SO₄²⁻ preferentially adsorbed on Cu(111) with a bidentate geometry. Scanning tunneling microscopy (STM) revealed a two-fold bridging adsorption site for the centers of the SO₄²⁻ molecules with C₂ᵥ symmetry. A study by Li and Nichols [22] found that the SO₄²⁻ adsorbed layer could be stabilized by structured hydration through incorporation of water via
hydrogen bonding between adjacent $\text{SO}_4^{2-}$ and co-adsorbed H$_2$O molecules. A study by Niaura and Malinaukas [23] using surface enhanced Raman spectroscopy (SERS) concluded that the adsorptivity order of anions on a roughened Cu electrode was $\text{Cl}^- > \text{SO}_4^{2-}$. Whether or not these differences in anion adsorption processes can influence Cu corrosion in the presence of $\text{SH}^-$ has not been investigated.

The purpose of this study is to analyze the effect of various groundwater anions on the growth mechanism of Cu$_2$S films in aqueous $\text{SH}^-$ solutions. This is of importance to degradation mechanisms of the container in the DGR because it would determine whether or not each individual groundwater anion ($\text{Cl}^-$, $\text{SO}_4^{2-}$, $\text{HCO}_3^-$/CO$_3^{2-}$) should be studied for varying effects or whether the groundwater can be considered as one overall ionic electrolyte.

7.2 Experimental

7.2.1 Electrochemical Cell and Instrumentation

All electrochemical data were collected using a conventional three-electrode electrochemical glass cell. A Pt sheet rolled into a cylinder was used as the counter electrode and connected to external circuitry by a Pt wire. A saturated calomel electrode (SCE, 0.242 V/SHE) was used as the reference electrode. The cell was housed inside a Faraday cage to reduce electrical noise from external sources. All experiments were conducted using a RDE. The electrode rotation rate was controlled by a Pine Instrument Company Analytical Rotator Model AFA86 Serial 882, and electrochemical measurements were made using a 1287 Solartron potentiostat connected to a computer equipped with CorrWare software.
7.2.2 Copper Composition and Electrode Preparation

O-free, P-doped Cu provided by the Swedish Nuclear Fuel & Waste Management Co. (SKB), Solna, Sweden, was machined into Cu disks. Ti rods were threaded into the back of the discs and the Cu was set into a Teflon holder using an epoxy resin. Only a single flat Cu face with a surface area of 0.785 cm$^2$ was exposed to solution. Prior to an experiment, the Cu electrode was first ground with a sequence of SiC papers with grit sizes: 1000, 1200, and 4000. Then, to achieve a mirror finish, the electrode was polished with Al$_2$O$_3$ suspensions with decreasing suspension size (1 μm, 0.3 μm, and 0.05 μm). The electrode was then rinsed thoroughly with Type-1 water (resistivity: 18.2 MΩ·cm) to remove any polishing residue, and dried in a stream of ultrapure Ar gas.

7.2.3 Solution Preparation

Electrolyte solutions were prepared with Type-1 water obtained from a Thermo Scientific Barnstead Nanopure 7143 ultrapure water system. All water was purged with Ar gas for one hour prior to the preparation of solutions to prevent immediate oxidation of sulphide. Solutions were made from reagent-grade sodium sulphide nonahydrate (Na$_2$S·9H$_2$O, 98.0% assay) from Sigma Aldrich, sodium chloride (NaCl, 99.0% assay) and sodium carbonate (Na$_2$CO$_3$, 99.5% assay) from Caledon Laboratory Chemicals, sodium sulphate (Na$_2$SO$_4$, 101.5% assay) from Fisher Chemical, and sodium bicarbonate (NaHCO$_3$, 99.7 – 100.3% assay) from EMD Chemicals. To ensure an anoxic environment, solutions were Ar-purged for a minimum of 45 min before an experiment, with purging continued throughout the experiment.
7.2.4 Cyclic Voltammetry Experiments

Cyclic voltammetric (CV) studies were performed at a RDE. Prior to applying a voltammetric scan, the electrode was cathodically cleaned at −1.5 V/SCE to remove air-formed oxides, and then at −1.15 V/SCE for a further 60 s to remove H₂ bubbles formed at the lower potential. Voltammetric scans were performed from an initial potential in the range −1.5 V/SCE to −1.35 V/SCE to an anodic limit between −0.7 V/SCE and −0.5 V/SCE, at a scan rate of 2 mV/s. The choice of starting potential had no influence on the subsequent electrochemical behavior.

7.2.5 Auger Electron Spectroscopy (AES): Depth Profiling

Auger analyses were performed with a PHI 660 scanning Auger microprobe (SAM). A 5 keV primary electron beam rastered over a 100 μm x 100 μm area was used during Auger analysis. Depth profiling was performed using a 3 keV Ar⁺ ion beam rastered over a 2 mm x 2 mm area and the signal strength for Cu, S, O, C and Cl were monitored as a function of sputter time. Sputter time was converted into sputter depth using a sputter rate of 30 nm/min for a reference SiO₂ standard.

7.3 Results and Discussion

7.3.1 The Effect of Chloride

Figure 7.1 shows CVs recorded to an anodic limit of −0.70 V/SCE in dilute (5×10⁻⁵ M and 1×10⁻⁴ M) SH⁻ solutions containing various concentrations of Cl⁻. At the lower [SH⁻] and a
high rotation rate (ω), when depletion of SH\(^{-}\) at the electrode surface would be expected, the anodic current was slightly increased as the [Cl\(^{-}\)] was increased (0.1 M to 0.5 M). This was observed for both region 1 in Figure 7.1a, when the current was dependent on potential, and region 2 in Figure 7.1a, when the current became independent of potential. At higher [Cl\(^{-}\)] (≥ 1.0 M) the current in both anodic regions (1, 2) substantially decreased. For all [Cl\(^{-}\)] the anodic current was the same on the reverse scan as on the forward scan. This demonstrated that, as observed previously [12, 13], the Cu\(_2\)S film formed was porous and did not limit the anodic oxidation of the Cu to produce additional Cu\(_2\)S. The reduction of the Cu\(_2\)S film at the cathodic peak (region 3 in Figure 7.1a) was symmetrical and at approximately the same potential for all [Cl\(^{-}\)]. The size of the peak, and hence the charge associated with it, increased and decreased over the same [Cl\(^{-}\)] range. This was expected since all the charge consumed by the anodic formation of the film was recovered upon film reduction, as observed previously [12]. The symmetrical shape of the cathodic reduction peak indicated film reduction was distributed throughout the volume of the film, as expected for the nucleation
and growth of Cu centers distributed within a porous film. Figure 7.2 summarizes the anodic and cathodic behaviour demonstrating that two distinct regions of behaviour (A and B) were observed over the [Cl\(^-\)] range 0.1 M to 5.0 M.

![Figure 7.2: Anodic plateau current (region 2 in Figure 7.1a) and cathodic peak current (region 3 in Figure 7.1a) obtained from CVs recorded in 5×10^{-5} M SH\(^-\) at \(\omega = 25\) Hz.](image)

Similar anodic behaviour was observed at the slightly higher [SH\(^-\)] of 1×10^{-4} M, Figure 7.1b. However, the cathodic peak was slightly asymmetrical at low [Cl\(^-\)] (0.1 M) and shifted to less negative potentials as [Cl\(^-\)] increased while also becoming more symmetrical. The anodic current in the plateau region (region 2 in Figure 7.1b) was not as significantly suppressed as at the lower [SH\(^-\)], as demonstrated by the small difference in cathodic reduction peak currents and peak areas (region 3 in Figure 7.1b) across the [Cl\(^-\)] range 0.1 M to 5.0 M. This last observation suggests that the impact of Cl\(^-\) on the film growth process was less dramatic at this slightly higher [SH\(^-\)].
At \([\text{SH}^-] = 2 \times 10^{-3} \text{ M}\) distinctly different behaviour was observed, Figure 7.3. At low \([\text{Cl}^-]\), the anodic current rose linearly with potential, before exhibiting an apparent active-to-passive transition, as observed previously at high \([\text{SH}^-]\) (Chapter 4 and 6), rather than the current plateau observed at lower \([\text{SH}^-]\) (Figure 7.1). The film reduction peak subsequently recorded on the reverse scan (region 3 in Figure 7.3) was also very asymmetrical with the large majority of film reduction occurring prior to the peak maximum. When the \([\text{Cl}^-]\) was increased the anodic current increased substantially although the current-potential

![Figure 7.3: CVs recorded at various [Cl\(^-\)] at 25 Hz in a solution containing 2\times10^{-3} \text{ M SH}^-](image)

relationship remained linear, region 1 in Figure 7.3. After initially rising, the anodic current peak value decreased and the transition to an apparently partially passive state, region 2 in Figure 7.3, occurred more readily (i.e. at less positive potentials).

The increase in \([\text{Cl}^-]\) also influenced the current in the potential region beyond the transition, region 2 in Figure 7.3. With the exception of the behavior in 0.1 M \(\text{Cl}^-\) for which the apparently passive state was not fully achieved, the current after the transition increased as \([\text{Cl}^-]\) increased. The independence of the current on potential indicated the current was not
controlled by an electrochemical process. The increase in anodic current after the transition, indicated that the Cu₂S film present was less protective at higher [Cl⁻]. Since EIS studies (Chapter 6) show the film remained porous in this potential region, the increased current suggests an influence of Cl⁻ on the porosity of the Cu₂S film/deposit. These changes in anodic behaviour are accompanied by a change in the shape of the film reduction peak, region 3 in Figure 7.3, from asymmetrical to symmetrical. Both the symmetry and the shift in peak potential to less negative values indicated the Cu₂S film was more easily reduced possibly by a nucleation and growth process as noted above. As expected, and as observed at lower [SH⁻], the extent of anodic oxidation decreased for [Cl⁻] ≥ 1.0 M.

Similar linear relationships between anodic film growth current and applied potential have been observed previously for the anodic formation of films on Ag involving large anions (SH⁻, Br⁻, and I⁻) [24-26] and for the anodic formation of Ag₂O in alkaline solutions [27]. Linear anodic current-potential (ohmic) relationships, similar to those observed at 2×10⁻³ M (Figure 7.3) in this study, were observed at high anion concentrations, and attributed to control of the film growth rate by ion migration within solution-filled pores in the growing film and not by the solid-state transport of Cu⁺ species in a cation-conducting film. This fact would explain the increase in the anodic film growth current, Figure 7.2, when the [Cl⁻] was initially increased. The increased ionic strength would lead to a decrease in the electric field within the solution filled pores, with the applied potential increasing across the Cu/solution interface at the base of the pores leading to an acceleration in the rate of anodic oxidation. This effect is particularly marked at the higher [SH⁻], Figure 7.3, as will be discussed in more detail below. However, an ionic strength effect cannot account for the decrease in anodic film growth rate at higher [Cl⁻] suggesting an interference of Cl⁻ with Cu₂S film growth. That this interference is not due to the incorporation of Cl⁻ into the
growing film, even in the most concentrated Cl\(^{-}\) solution (5.0 M), is clearly demonstrated by the AES profile shown in Figure 7.4, which shows no Cl\(^{-}\) signal throughout the film.

![Figure 7.4: Auger Depth Profile of a Cu\(_2\)S film grown in a 5.0 M Cl\(^{-}\) + 2.0 \times 10^{-5} M SH\(^{-}\) solution at a rotation rate of 25 Hz during a CV that was terminated at the anodic potential limit of -0.7 V/SCE.](image)

The nature of this interference by Cl\(^{-}\) can be seen in the changes in behavior as the [SH\(^{-}\)]/[Cl\(^{-}\)] ratio changes. The value of Q\(_C\) obtained by integrating the cathodic reduction peak in region 3 is a measure of the extent of anodic film growth to produce Cu\(_2\)S. Consequently, the relative influence of Cl\(^{-}\) on film growth at various [SH\(^{-}\)] can be compared by calculating Q\(_C\) for the film grown in 0.1 M Cl\(^{-}\) ((Q\(_C\))\(_{0.1}\)), when the influence will be the least, to Q\(_C\) for that grown at other [Cl\(^{-}\)] ((Q\(_C\))\(_{[Cl^{-}]}\)). The ratio of these two charges (R\(_Q\) = (Q\(_C\))\(_{0.1}\)/(Q\(_C\))\(_{[Cl^{-}]}\)) then provides a relative measure of the influence of Cl\(^{-}\) on the film growth process at the different values of [SH\(^{-}\)]. As observed in Figure 7.5, the suppression of Cu\(_2\)S formation became more marked as the [Cl\(^{-}\)]/[SH\(^{-}\)] ratio was increased.
Figure 7.5: Ratio ($R_0$) (defined in the text) as a function of $[\text{Cl}^-]$ for three values of $[\text{SH}^-]$ recorded at $\omega = 25$ Hz. The arrow indicates suppression in anodic film growth as $[\text{SH}^-]$ increased.

For the high electrode rotation rate (25 Hz) used in these experiments, the lowest $[\text{SH}^-]$ at the Cu surface would have been achieved at the lowest bulk $[\text{SH}^-]$. According to the literature [28], Cl$^-$ should not be as readily adsorbed on Cu as SH$^-$. However, at the extreme $[\text{SH}^-]/[\text{Cl}^-]$ ratios that would exist at the base of the pores in a Cu$_2$S film being anodically grown in a solution with a low $[\text{SH}^-]$, competition between Cl$^-$ and SH$^-$ for surface adsorption sites seems likely. Also, a synergistic response is possible, since both Cl$^-$ and SH$^-$ complex Cu$^+$. Thus, the formation of Cu$^+$ by chemisorption of SH$^-$ could lead to the co-adsorption of Cl$^-$, a process which could limit the release of Cu$^+$ (as Cu(SH)$_2^-$ or Cu$_3$S$_3$) to the solution.

The greater influence of ionic migration on the film growth rate at high $[\text{SH}^-]$, Figure 7.3, can be attributed to a change in film porosity. At higher $[\text{SH}^-]$ depletion of SH$^-$ within pores would be limited allowing film growth both laterally and vertically as suggested by Birss et al. [25,26] for the anodic growth of AgBr/AgI films. This would lead to tighter pores
and a higher electric field within them. As shown in Figure 7.3, the increase in [Cl\(^-\)] then not only reduces this limitation on film growth by ionic migration leading to higher (but still ohmic) anodic currents, but also leads to a symmetrical film reduction process suggesting a Cl\(^-\)-induced increased porosity as observed in corrosion studies [8].

The Levich plots for the currents recorded at an anodic potential in region 2 (\(-0.73\) V/SCE) are shown in Figure 7.6 for solutions with [SH\(^-\)] of \(1\times10^{-4}\) M and \(2\times10^{-3}\) M and various [Cl\(^-\)]. The theoretical current for complete transport control, when [SH\(^-\)] at the Cu surface would be zero, was calculated using the Levich equation. For [SH\(^-\)] = \(10^{-4}\) M, Figure 7.6a, at the lower [Cl\(^-\)], the currents are identical to the diffusion limiting values irrespective of the electrode rotation rate, indicating transport control of the film growth. As the [Cl\(^-\)] was increased the measured currents in this plateau region decreased, to below the diffusion-controlled limit, irrespective of rotation rate. This depression of the current to values lower than the diffusion limit are consistent with the claim made above that the anodic oxidation rate was controlled by competition between Cl\(^-\) and SH\(^-\) for surface adsorption sites.

![Figure 7.6](image.png)

**Figure 7.6:** Limiting currents for Cu\(_2\)S film formation at \(-0.73\) V/SCE from CVs recorded in a) \(1\times10^{-4}\) M SH\(^-\) and b) \(2\times10^{-3}\) M SH\(^-\) containing various [Cl\(^-\)].
For [SH\(^-\)] = 2 \times 10^{-3} \text{ M}, Figure 7.6b, at low [Cl\(^-\)] and low rotation rates, the current effectively followed the diffusion limit indicating the growth rate was again under diffusion control. When the [Cl\(^-\)] was increased and the electric field within the pores reduced, the interfacial oxidation rate was increased since a larger fraction of the applied potential would be distributed across the Cu/solution interface at the base of the pores. At this higher [SH\(^-\)], the flux of SH\(^-\) was sufficient to support lateral and vertical film growth leading to the decrease in film porosity and the establishment of partial passivation, as indicated by the decrease in current at high electrode rotation rates. This behaviour is consistent with the results obtained in the EIS experiments at this [SH\(^-\)] (Chapter 6). However, the impedance results indicated that the film inhibiting anodic oxidation at the higher potentials was not a conventional passive film but a porous outer layer Cu\(_2\)S deposit. As noted previously, the currents at higher potentials (i.e. in the region where the current was effectively independent of electrode rotation rate, Figure 7.6b) increased slightly with [Cl\(^-\)]. A current independent of electrode rotation rate and also potential (2 in Figure 7.3) could be explained in one of two ways: (i) the current was controlled by the rate of a chemical reaction where the Cu\(_2\)S film (or CuS if that composition is achieved) would have to dissolve in a reaction involving Cl\(^-\), which seems unlikely; or (ii) the overall porosity of the Cu\(_2\)S film was higher at the higher [Cl\(^-\)] allowing a slightly greater flux of SH\(^-\) to the Cu surface and, hence, a slightly higher oxidation current. This second explanation is consistent with the conclusions of the EIS study (Chapter 6).
7.3.2 The Effect of Sulphate and Bicarbonate

CVs recorded in a $1 \times 10^{-4}$ M SH$^-$ solution containing various [SO$_4^{2-}$] are shown in Figure 7.7a. The general shape of the curves was the same as observed in Cl$^-$ solutions (Figure 7.1b). The anodic process was again reversible confirming that the Cu$_2$S film formed was porous and the anodic charge, $Q_a$, for Cu$_2$S formation was equal to that for film reduction, $Q_c$, again confirming that all the Cu$_2$S formed on the forward scan was reduced on the reverse scan. The symmetrical shape of the cathodic reduction peak indicated, as observed at this [SH$^-$] in Cl$^-$ solutions, that the film reduction was distributed throughout the volume of the film as expected for the random nucleation and growth of Cu centers within a porous film.

However, a number of differences are apparent. The exponential increase in current indicating the onset of Cu$_2$S formation (region 1 in Figure 7.7a) shifted to more positive potentials as [SO$_4^{2-}$] increased, and the suppression of the current in both regions 1 and 2 leading to suppressed film growth (as demonstrated by the decrease in size of the reduction
peak, 3 in Figure 7.7a) was considerably more marked than in the case of Cl\(^-\) (Figure 7.1b).

Figure 7.8a shows the currents in region 2 plotted according to the Levich equation compared to those calculated for diffusion control. As opposed to the Cl\(^-\) case, the currents are uniformly lower than the theoretical values indicating a SO\(_4^{2-}\)-suppression of the current. This observation is enhanced as [SO\(_4^{2-}\)] increased.

![Figure 7.8: Limiting currents as a function of electrode rotation rate for Cu\(_2\)S film formation at -0.73 V/SCE from CVs recorded in a) 1x10^-4 M SH\(^-\) and b) 2x10^-3 M SH\(^-\) containing various [SO\(_4^{2-}\)].](image)

CVs recorded in a higher [SH\(^-\)] of 2x10^-3 M in 0.1 M and 1.0 M [SO\(_4^{2-}\)] are shown in Figure 7.7b. In the 0.1 M [SO\(_4^{2-}\)] the form of the CV was similar to that recorded in Cl\(^-\) solutions at 0.1 M, with the current increasing approximately linearly with potential (1 in Figure 7.7b). The film reduction process was also similarly distributed with a linear i vs. E relationship prior to the peak. However, an increase in [SO\(_4^{2-}\)] to 1.0 M caused a decrease in current in region 1, not an increase as observed in Cl\(^-\) solutions. The increase in [SO\(_4^{2-}\)] also led to a shift of the cathodic peak to a less negative potential and an increase in its symmetry (3 in Figure 7.7b). As discussed for Cl\(^-\), these changes in the cathodic peak shape indicate a shift to a more porous and easily reducible film.
These observations are consistent with a competition between an increase in ionic conductivity, which would decrease the pore resistance and accelerate the anodic process, and an inhibiting influence of $\text{SO}_4^{2-}$. That this is the case appeared to be confirmed by the Levich plots in Figure 7.8b. At the low $[\text{SO}_4^{2-}]$ the currents are close to the diffusion-controlled limit at this $[\text{SH}^-]$. The leveling off of the current at high electrode rotation rates may reflect the contraction of the diffusion gradient to within the pores when it would become independent of electrode rotation rate. At the higher $[\text{SO}_4^{2-}]$ the currents are well below the diffusion limit indicating a significant suppression of $\text{Cu}_2\text{S}$ formation by $\text{SO}_4^{2-}$. An additional difference between the behaviour in $\text{Cl}^-$ and $\text{SO}_4^{2-}$ solutions is the apparent prevention of the “active-to-passive” transition when $\text{SO}_4^{2-}$ is present in the solution. That this is the case is shown by the CVs in Figure 7.9 which were recorded in a mixed $\text{Cl}^-/\text{SO}_4^{2-}$ solution, one of them to a much more positive potential limit. The anodic current was sustained up to the anodic limit of $-0.5$ V/SCE, as well as on the return scan consistent with reversible active behavior in the presence of a porous film. These results strongly suggest that $\text{SO}_4^{2-}$ was interfering with $\text{Cu}_2\text{S}$ film growth and preventing the formation of any current-reducing layer. The most likely explanation is that $\text{SO}_4^{2-}$ is co-adsorbed on the Cu surface with $\text{H}_2\text{O}$, as described in Section 7.1 [21, 22]. This bidentate interaction, which is stabilized by H-bonding between the absorbed $\text{H}_2\text{O}$ and $\text{SO}_4^{2-}$ molecules, appears sufficiently strong at high $[\text{SO}_4^{2-}]$ to inhibit the $\text{SH}^-$ adsorption, the first step in the overall $\text{Cu}_2\text{S}$ film formation process. The shallow shoulder in the reduction current ($\sim -1.15$ V/SCE) (indicated by the green arrow in Figure 7.9) was previously, tentatively, attributed to the formation of a partially passivating $\text{CuS}$ layer [12] which becomes thermodynamically possible when the anodic limit is extended to $-0.5$ V/SCE. If formed this layer does not lead to passivation as indicated by the high sustained anodic current on the forward scan.
CVs recorded in 2.0 M Cl\(^-\) + 0.5 M SO\(_4^{2-}\) + 2\times10\(^{-3}\) M SH\(^-\) at 25 Hz to extended anodic limits.

CVs recorded in a 1\times10\(^{-4}\) M SH\(^-\) solution containing various [HCO\(_3^-\)] are shown in Figure 7.10. Unlike SO\(_4^{2-}\) the onset of anodic oxidation was not influenced by an increase in [HCO\(_3^-\)]. A similar decrease in anodic current and change in shape of the cathodic reduction

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Figure 7.9: CVs recorded in 2.0 M Cl\(^-\) + 0.5 M SO\(_4^{2-}\) + 2\times10\(^{-3}\) M SH\(^-\) at 25 Hz to extended anodic limits.

Figure 7.10: CVs recorded at various [HCO\(_3^-\)] at 25 Hz with 1\times10\(^{-4}\) M SH\(^-\)
peak are observed to those obtained in Cl$^-$ containing solutions. These results suggest that unlike SO$_4^{2-}$, HCO$_3^-$ does not suppress anodic oxidation to a similar extent.

The influence of the various anions can most readily be compared by plotting the currents measured in region 2 as a function of anion concentration, Figure 7.11. Over the concentration range, 0.1 M to 1.0 M the difference in behaviour of the two oxyanions compared to that of the Cl$^-$ is clear for [SH$^-$] = 1×10$^{-4}$ M. A comparison at this [SH$^-$] avoids the complications encountered at higher [SH$^-$] when partial passivation could occur. As noted above in the presence of Cl$^-$ at this [SH$^-$], the film formation process was less dramatically influenced by [Cl$^-$] than at the lower [SH$^-$] of 5×10$^{-5}$ M. Also, the influence of ionic strength on the film growth process appeared minor compared to that observed at the lower and higher [SH$^-$]. This is apparent in Figure 7.11, where the current changed only slightly as the [Cl$^-$] increased. That the film growth was slightly enhanced by ionic migration was demonstrated by the Levich plots for this [SH$^-$] (Figure 7.6). By contrast the currents in

![Figure 7.11: Limiting currents at −0.73 V/SCE extracted from CVs collected in 1×10$^{-4}$ M SH$^-$ solution at 25 Hz.](image)
region 2 are dependent on anion concentration, especially for $\text{SO}_4^{2-}$. While $\text{SO}_4^{2-}$ will have a considerably larger effect on the ionic strength than the singularly charged $\text{HCO}_3^- \text{ and } \text{Cl}^-$, the behavior observed indicates the dominant effect of $\text{SO}_4^{2-}$ was in suppressing the $\text{Cu}_2\text{S}$ film growth rate, most likely by competition for adsorption sites.

### 7.4 Summary and Conclusions

- The effect of the anions $\text{Cl}^-$, $\text{SO}_4^{2-}$, $\text{HCO}_3^-$ on the $\text{Cu}_2\text{S}$ film anodic formation in aqueous $\text{SH}^-$ solutions has been studied voltammetrically.

- At low $[\text{SH}^-]$, $\text{Cl}^-$ appeared to have two different effects on the anodic formation of $\text{Cu}_2\text{S}$ films. At low $[\text{Cl}^-]$ film formation occurred at a rate identical to the diffusion-controlled limit indicating film growth was transport controlled. At high $[\text{Cl}^-]$ film formation was suppressed due to competition between $\text{Cl}^-$ with $\text{SH}^-$ for adsorption sites on the Cu surface.

- At high $[\text{SH}^-]$ the $\text{Cu}_2\text{S}$ film formed was more compact at low $[\text{Cl}^-]$ with the growth rate governed by diffusion control. An increase in $[\text{Cl}^-]$ led to a major increase in film growth rate due to the reduction of the electric field within the pores leading to an increase in the ionic migration rate.

- The ability of $\text{Cl}^-$ to suppress the $\text{Cu}_2\text{S}$ film growth rate decreased as the $[\text{SH}^-]/[\text{Cl}^-]$ ratio increased confirming that the two anions competed for adsorption sites on the Cu surface at the base of pores in the film.

- At high $[\text{SH}^-]$, $\text{Cl}^-$ also appeared to influence the film porosity allowing a slight increase in film growth rate despite the presence of an apparently passivating film. An accompanying shift from an asymmetrical reduction peak to a symmetrical peak,
indicative of a more easily reduced film, was observed supporting this claim of increased porosity.

- In the presence of SO$_4^{2-}$, any influence of ionic migration was overwhelmed by a large suppression in Cu$_2$S film formation. This was most likely due to the strong adsorption of SO$_4^{2-}$ on Cu, re-enforced by the co-adsorption of H$_2$O, leading to the displacement of SH$^-$ from surface adsorption sites. At high [SH$^-$] the film remained porous in nature and the active-to-passive transition during anodic film formation was not observed.

- Voltammetric data showed that the effect of HCO$_3^-$ appeared to be intermediate between that of Cl$^-$ and that of SO$_4^{2-}$. These results show that a specific anion effect occurs indicating that the groundwater in the DGR cannot be considered as a simple saline solution containing small amounts of SH$^-$. While some aspects of the influence of SO$_4^{2-}$ and HCO$_3^-$ remain unresolved their dominant influence is to suppress the anodic oxidation of Cu to Cu$_2$S and, in the case of SO$_4^{2-}$ to inhibit the tendency to form protective films at high [SH$^-$].

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7.6 References


Monitoring Bentonite Porewater Chemistry Using Electrochemical Sensors

8.1 Introduction

Nuclear energy is a reliable, inexpensive, and environmentally friendly source of electrical power. However, with the production of spent nuclear fuel, development of a safe containment and storage program must be implemented. One approach proposed in many countries, including Sweden, Finland and Canada, is permanent disposal of the spent fuel in a deep geological repository (DGR). The spent fuel is to be placed in specially designed containers fabricated with a cast iron or carbon steel inner vessel and an outer copper shell; these materials are designed to avoid both corrosion and mechanical failure. In Sweden and Finland, the outer shell would be fabricated using P-deoxidized Cu with a thickness of 50 mm [1-3]. It is proposed that these containers be buried in crystalline or sedimentary rock approximately 500 m below the surface and that the excavated boreholes be backfilled with bentonite clay [4].

Bentonite is an ideal backfill material due to its swelling and buffering capabilities. It is composed of >75 % montmorillonite, which has a structure of 2:1 silica and alumina sheets, and accessory minerals (minerals present in small quantities) including gypsum (CaSO$_4$·H$_2$O), halite (NaCl), pyrite (FeS$_2$) and calcite (CaCO$_3$) [5]. The sheet-type structure allows for swelling upon contact with groundwater, as it is strongly hygroscopic. Due to spatial constraints of the boreholes, the swollen clay acts as a self-sealing medium, sealing itself around the buried container and filling any openings in the repository. It is a porous material with a low hydraulic conductivity ($< 10^{-12}$ m/s) which limits mass transport
processes entirely to diffusion, with diffusion being two orders of magnitude lower in bentonite than in bulk solution. Low conductivity in conjunction with strong water adsorption lowers the activity of water at the container/clay interface and allows the highly compacted clay to act as an effective barrier against degradation processes. It limits mass transport of species to and from the container surface, prevents microbial activity close to the container surface and possesses the ability to capture cationic radionuclides by ion exchange processes [6, 7]. Due to the presence of the bentonite backfill, the composition of groundwater may significantly differ from that of the aqueous phase in contact with the container surface, at least for a significant time period, thus determination of this phase is crucial as it must be compatible with the container material.

Several theories have been used to describe the bentonite porewater, or aqueous phase mentioned previously, and it is generally characterized into three main types: (i) free porewater consisting of a charge-balanced aqueous solution of anions and cations; (ii) interlayer water containing water and cations between montmorillonite layers which is devoid of anions and thus in a charge deficit; (iii) electrostatic double layer (between mineral surface and free water) containing water, cations and a small concentration of anions, with the excess cation charge balanced by the negatively charged outer surface layer of the montmorillonite [8]. The quantity of each type of water present is not constant within the clay; it varies as a function of dry density, salinity of the solution and/or the amount of accessory minerals present [9]. Many models have been used in order to correctly predict the chemistry of the various types of bentonite porewater, including the Donnan equilibrium, Poisson-Boltzmann, and multi-porosity models. The Donnan model simulates the clay as 2 fixed semipermeable membranes with salt solution throughout, these membranes are permeable to water and ionic species but impermeable to macromolecules [10]. This is used
to model the chemistry of the interlayer water, thus diffusion of anions is considered only through the space between montmorillonite sheets [9]. The Poisson-Boltzmann model describes the clay as a series of parallel charged plates immersed in salt solution, and can be used to describe the thermodynamics of the electrostatic double layer, which forms at the clay/electrolyte interface. This model is limited to Boltzmann thermodynamics, where ions are treated like point charges and do not interact with one another [10]. The multi-porosity model considers Nernst-Planck equations for electrochemical diffusion, the three types of bentonite porewater, diffusion in each type of pore, and cation exchange and surface complexation reactions [9]. Correct modeling of the bentonite porewater is necessary in understanding how the aqueous phase in contact with the Cu container will evolve over long periods of time.

There are three main reactive sites on the bentonite that have the ability to alter porewater chemistry, (i) the electric double layer where electrostatically bound cations can exchange with solution, (ii) the silica and alumina sheets that carry a permanent negative charge due to substitution of lattice cations with cations of lower valency and (iii) amphoteric surface hydroxide groups that can become protonated and deprotonated as the pH changes [11].

The pH of the bentonite porewater is found to be around 8; this is likely governed by the dissolution of carbonate-containing minerals such as calcite (CaCO$_3$), dolomite (CaMg(CO$_3$)$_2$) and siderite (FeCO$_3$) [12, 13].

\[
\text{CaCO}_3(s) + \text{H}^+ \rightleftharpoons \text{Ca}^{2+} + \text{HCO}_3^- \quad (8.1)
\]

\[
\text{CaMg(CO}_3\text{)}_2(s) + 2 \text{H}^+ \rightleftharpoons \text{Ca}^{2+} + \text{Mg}^{2+} + 2 \text{HCO}_3^- \quad (8.2)
\]

\[
\text{FeCO}_3(s) + \text{H}^+ \rightleftharpoons \text{Fe}^{2+} + \text{HCO}_3^- \quad (8.3)
\]
Another important porewater constituent that affects bentonite porewater chemistry is the chloride anion. At the Olkiluoto site in Finland, infiltrating groundwater contained chloride concentrations ranging from 0.03 M to 0.45 M and it was estimated that the chloride concentration of the groundwater present in the DGR after 100,000 years of container emplacement would decrease to ~ 0.01 M [1]. The decrease in chloride concentration over time can be attributed to the movement of chloride from the groundwater to the bentonite during saturation, however diffusion will eventually even out the difference between the bentonite porewater and the groundwater in the long term [14].

Various studies of the corrosion of Cu in bentonite have been conducted under oxic and saline groundwater conditions. Rosborg et al. [15] and Kosec et al. [16] used electrical resistance (ER) sensors and electrochemical impedance spectroscopy (EIS) to monitor Cu corrosion over three-year and four-year exposure periods. ER sensors and EIS measurements revealed a corrosion rate of 1 to 0.4 μm/a. This extensive study concluded that corrosion occurred via non-uniform growth governed by diffusion of Cu species into the surrounding bentonite. X-ray diffraction (XRD) and Raman spectroscopy determined that the corrosion product was composed of cuprite (Cu$_2$O) and paratacamite (Cu$_2$(OH)$_3$Cl). While the corrosion rates were evaluated in these studies, the effect of solution chemistry was not discussed.

Another study by Kosec et al. [17] monitored Cu corrosion of samples exposed to simulated groundwater containing sulphide in the presence and absence of a bentonite slurry. In the absence of bentonite, early corrosion was dominated by sulphide and a thin layer of chalcocite (Cu$_2$S) rapidly formed, however due to the instability of this film it was converted to Cu$_2$O upon continued exposure to dissolved O$_2$. After 6 weeks, the Cu$_2$S film was no longer detected, and corrosion was dominated by rapid growth and build up of an outer
deposit of Cu$_2$O and atacamite, Cu$_2$(OH)$_3$Cl. No sulphur species were detected in the corrosion product, possibly due to the complete oxidation of sulphide into soluble sulphate species. In the presence of bentonite, early stages of corrosion again showed the formation of a Cu$_2$S layer, however the dissolved O$_2$ content significantly decreased due to reactions with organic matter and minerals in the bentonite clay. As in the simulated groundwater case, the Cu$_2$S layer was converted to Cu$_2$O, however EDX detected trace amounts of S. FIB-SEM images revealed pitting in the presence of the bentonite slurry, likely due to the presence of thiosulphate, formed via the incomplete oxidation of sulphide. It is important to note that in the presence of the bentonite slurry, Cu was detected in the bentonite at the film/clay interface, indicative of Cu cation adsorption onto the montmorillonite structure via ion exchange processes. This is significant as it provided evidence that the clay was able to act as an effective barrier and inhibited corrosion product movement away from the Cu surface.

The purpose of this study is to develop an experimental set-up in which electrochemical sensors are employed to monitor the pH, chloride concentration, and corrosion potential (E$_{corr}$) of Cu in bentonite porewater under oxic conditions. Surface and embedded electrode measurements were made to observe any discrepancy between the surface and embedded sites. Distinguishing the chemistry between the sites will provide important information with respect to future model validation and determination of the aqueous phase that will ultimately be in contact with the canister in the DGR.
8.2 Experimental

8.2.1 Solution Preparation

Electrolytes were prepared with Type-1 water obtained from a Thermo Scientific Barnstead Nanopure 7143 water system. Solutions were made from reagent-grade NaCl, 99.0% assay (Caledon Laboratory Chemicals) and H$_2$SO$_4$, 95% to 98% assay (Caledon Laboratory Chemicals). NaCl solutions between 0.1 M and 1.0 M were prepared for electrode fabrication and calibration as well as for bentonite experiments. A 0.5 M H$_2$SO$_4$ solution was prepared for electrode fabrication.

8.2.2 Electrode Preparation

8.2.2.1 Reference Electrodes

A micro-Ag/AgCl (3.0 M) reference electrode (Microelectrodes, Inc.) was used for the majority of the surface bentonite measurements. A Pd-H reference electrode was fabricated with Pd wire (0.5 mm dia., Alfa Aesar) and cathodically charged in 0.5 M H$_2$SO$_4$ at $-5.0\times10^{-3}$ A from 2 h to 20 h. A graphene oxide (GO) Ag/AgCl reference electrode was fabricated based on a previously published procedure [18]. An Ag/AgCl electrode was prepared by applying a $2.0\times10^{-3}$ A current to a Ag wire (1.2 mm dia.) in 1 M NaCl for 20 min. A suspension of GO was prepared from dry GO flakes (Graphene Supermarket) and Type-1 water with a concentration of 1.375 g/L, and drop-casted onto the Ag/AgCl wire, which was then dried on a hot plate at 40 °C.

A new Ag/AgCl/KCl agar/polychloroprene reference electrode was fabricated, based on a paper by Liao and Chou [19]. An Ag/AgCl electrode was prepared via the procedure
described previously. The KCl agar was prepared using agar powder (Alfa Aesar) and saturated KCl solution (1 g agar dissolved in 25 mL of KCl solution) and was used to coat the Ag/AgCl wire. Polychloroprene (Sigma Aldrich) was degraded in CH$_2$Cl$_2$ (Caledon Laboratory Chemicals) via heating and stirring, and was wrapped around the Ag/AgCl/KCl agar wire, as shown in Figure 8.1. In a second design of the Ag/AgCl/KCl agar/polychloroprene electrode, two diameters of shrink tubing were used to construct the body of the electrode: 2.36 mm fluorinated ethylene propylene (FEP) (Zeus) and 3.05 mm polytetrafluoroethylene (PTFE) (Zeus). A schematic of the electrode is shown in Figure 8.2a. The 3.05 mm tubing was cut to the length of the Ag/AgCl electrode, leaving room to make an electrical connection, and ¼ of this tubing was shrunk to a thickness similar to that of the Ag wire. A small portion of the 2.36 mm tubing was shrunk onto the Ag wire to ensure the PTFE tubing fit properly onto the Ag/AgCl electrode. The prepared agar was then injected into the tubing using a syringe and the degraded polychloroprene was stretched over the small opening.

Figure 8.1: Schematic (a) and photograph (b) of the initial Ag/AgCl/KCl agar/polychloroprene reference electrode.
8.2.2.2 pH Electrodes

The embedded iridium oxide electrode was fabricated using an iridium wire (0.25 mm dia.) that was polished using SiC paper (grit size: 1200). The iridium oxide film was grown, based on a method by Hitchman and Ramanathan [20], via cyclic voltammetry in 0.5 M H₂SO₄ (Caledon Laboratory Chemicals), scanning from −0.25 V/SCE to 1.25 V/SCE for 4 hours at a scan rate of 3 V/s. The electrode was left to stabilize in air for a minimum of 4 days. The surface iridium oxide electrode was made using an Ir wire (0.5 mm dia., Alfa Aesar) set in a glass tube using epoxy resin. The cross-section was polished using SiC papers (grit sizes: 800, 1000, 1200, and 2400) prior to film growth. Electrodes were calibrated in buffer solutions of pH 4, 7 and 10 (Caledon Laboratory Chemicals).
8.2.2.3 Ion Specific Electrodes

The embedded electrode was fabricated using an Ag wire (1.2 mm dia.) that was polished using SiC papers (grit sizes: 1200, and 2400). The AgCl film was grown by applying an anodic current of $10^{-3}$ A in 1 M NaCl solution for 20 min. For the surface electrode, an Ag wire (1.2 mm dia.) was set in a glass tube using epoxy resin. The cross section was polished using SiC papers (grit sizes: 800, 1000, 1200, and 2400) prior to film growth. The AgCl film was grown by applying an anodic current of $5\times10^{-5}$ A for 20 min in 1 M NaCl. Each electrode was calibrated using NaCl solutions ranging from 0.01 M to 1 M.

8.2.2.4 Cu Electrodes

Cu electrodes were fabricated for both embedded and surface measurements. The embedded electrode was a Cu wire (1.75 mm dia., Belden) and was polished using SiC papers (grit sizes: 800, 1000, 1200, and 2400). The surface electrode was composed of a Cu wire (1.65 mm dia., $A = 2.14 \text{ mm}^2$) set in a glass tube with epoxy resin. The cross-section was polished using SiC papers (grit sizes: 800, 1000, 1200, and 2400), and subsequently polished to a mirror finish using Al2O3 suspensions (1 µm, 0.3 µm, and 0.05 µm).

8.2.3 Bentonite Disk Preparation

MX-80 bentonite pre-moistened to 16% moisture was pressed into disks with a dry density of 1.6 g/cm$^3$ and a radius of 2 cm with varying thickness. The disks were compacted using a specially designed press, shown in Figure 8.3. The electrodes to be embedded were placed into the base of the press and were covered with the bentonite clay. The press was
then assembled, and bentonite compacted using an arbor press. The press was disassembled and the bentonite disk with the embedded electrodes was then removed and transferred to the specially designed holder (discussed in Section 8.2.4).

8.2.4 Set-up and Instrumentation

A two-piece polytetrafluoroethylene (PTFE) holder, shown in Figure 8.4, was designed to ensure surface/ embedded electrode contact with the bentonite clay disk during
the experiment. The top of the holder had holes for each electrode, shown in Figure 8.4a, this allowed for electrical connections to be made while the electrodes were in contact with the bentonite disk. The bottom of the holder, shown in Figure 8.4b, held the disk and had a series of tiny holes that allowed for exposure of the bentonite to solution. The bottom was covered with filter paper so that no bentonite was lost through the holes. The holder with the bentonite and electrodes was held over the solution using a retort stand. The open circuit potential (OCP) and corrosion potential (E_{corr}) measurements were collected using an IOTech ADC488/16A analog to digital converter and monitored using ADC488 control software.

![Figure 8.4: Two-piece bentonite disk holder; a) top piece with clay and embedded electrodes and b) bottom portion with grid of tiny holes to allow for solution uptake.](image-url)
8.3 Results

8.3.1 Electrode Stability and Calibrations

8.3.1.1 Embedded Reference Electrode Stability

The reference electrode selected for embedded measurements must be stable for the length of the experiment, insensitive to changes in pH and $[\text{Cl}^-]$, and able to withstand pressures of the embedding process. The pressures associated with the bentonite disk compaction make it impossible to use traditional glass-body reference electrodes. The first embedded reference electrode tested was a Pd-H electrode. The electrode however proved not to be stable for the duration of the experiment, irrespective of how long it was charged, and was sensitive to pH changes. The next electrode tested was the Ag/AgCl/GO electrode, where the GO coating provided an interlocked and layered structure known to exhibit good mechanical strength [18]. The electrode was found to be stable and insensitive to changes in pH, however, like a traditional Ag/AgCl electrode, it was $\text{Cl}^-$ sensitive. The electrode was fabricated many times with emphasis on thickening of the GO outer layer in order to prevent $\text{Cl}^-$ from reaching the AgCl film, but the electrode remained $\text{Cl}^-$-sensitive.

Many solid-state reference electrodes have been fabricated based on an Ag/AgCl electrode with a layer-by-layer assembly of various immobile electrolytes and polymers, often including Nafion [21-23]. However, synthesis of these electrodes can be complex, and Nafion is expensive, thus such electrodes are not practical as embedded sensors because a new electrode would have to be fabricated for each experiment, as the electrode cannot be successfully removed from the bentonite after measurements have been completed. Huang et al. [24] proposed covering an Ag/AgCl electrode with agar gel made with saturated KCl solution. The KCl agar would provide a saturated $\text{Cl}^-$ environment around the Ag/AgCl
electrode, thus allowing it to maintain a stable potential over time. The electrode proved to be stable, as well as insensitive to both pH and [Cl$^-$], however the gel dissolved and fell of the electrode after 60 h; it would also have been unable to withstand the embedding process. Liao and Chou [19] proposed a planar Ag/AgCl/KCl agar electrode in which the agar was coated with chloroprene as a protective layer. A wire Ag/AgCl/KCl agar/polychloroprene electrode was fabricated based on this paper and proved, as the previous electrode, to be stable and insensitive to pH and Cl$^-$, and with the added polychloroprene layer the problem of electrode degradation in solution was eliminated. This Ag/AgCl/KCl agar/polychloroprene electrode was extremely difficult to fabricate, thus an improvement in design was developed. The reference electrode fabricated with the shrink tubing body was a reproducible design and was stable, with a potential nearly identical to that of a traditional saturated Ag/AgCl glass electrode, as shown in Figure 8.5. The electrode was also insensitive to pH and [Cl$^-$], as shown by the black line in the calibration curves in Figure 8.6.

![Figure 8.5: OCP of the re-designed Ag/AgCl/KCl agar/polychloroprene electrode in 0.5 M NaCl](image-url)
8.3.1.2 pH Electrode Calibration

Electrochemically oxidized Ir forms a film of various anhydrous and hydrated species including \( \text{IrO}_2 \), \( \text{IrO}_2 \cdot 4\text{H}_2\text{O} \), and \( \text{Ir(OH)}_4 \cdot 2\text{H}_2\text{O} \). The anhydrous form, \( \text{IrO}_2 \), responds to changes in pH with a slope close to 59 mV \((2.303RT/nF)\) per pH unit via the following equilibria \[26\],

\[
\text{IrO}_2 + \text{H}^+ + \text{e}^- \rightleftharpoons \text{IrO} \cdot \text{OH} \tag{8.4}
\]
or

\[
2\ \text{IrO}_2 + 2\ \text{H}^+ + 2\ \text{e}^- \rightleftharpoons \text{Ir}_2\text{O}_3 + \text{H}_2\text{O} \tag{8.5}
\]

The \( \text{Ir}/\text{IrO}_2 \) electrode was calibrated against buffers of pH 4, 7 and 10, as shown in Figure 8.6a.

8.3.1.3 Ion Specific Electrode Calibration

The ion specific electrode chosen to detect changes in chloride concentration is the \( \text{Ag/AgCl} \) electrode. The electrode responds to changes in \([\text{Cl}^-]\) by sensing a shift in the position of the equilibrium:

\[
\text{AgCl}(s) + \text{e}^- \rightleftharpoons \text{Ag}(s) + \text{Cl}^- \tag{8.6}
\]

The electrode was calibrated against NaCl solution ranging from 0.01 M to 1.0 M as shown in Figure 8.6b.

8.3.2 Bentonite Porewater Measurements

OCP and \( E_{\text{corr}} \) measurements were collected for a total of 8 electrodes; 4 surface, and 4 embedded. Each set of electrodes (surface and embedded) included a reference, pH,
Cl−-specific and Cu electrode, a schematic of the holder and electrode set-up is shown in Figure 8.7. All potentials were measured against a macro saturated calomel electrode (SCE) located in the surrounding bulk aqueous phase. Potential measurements, \( E_{\text{measured}} \), made between the SCE and surface/ embedded reference electrodes allowed for membrane potential, \( E_{\text{membrane}} \), and ionic strength corrections since,

\[
E_{\text{measured}} = E_{\text{OCP}} + E_{\text{membrane}} \tag{8.7}
\]

where \( E_{\text{OCP}} \) was measured between the SCE and reference electrodes in bulk solution prior to assembly. Since the correction was made for each data point collected, this accounted for changes in ionic strength at the bentonite/electrode interface as clay saturation increased over time. This correction assumed that the \( E_{\text{membrane}} \) at the surface/ embedded reference electrode was the same as that at each surface/ embedded sensor electrode, respectively. It is likely that a similar environment, and therefore a similar \( E_{\text{membrane}} \), was achieved at each electrode, as the embedded electrodes were all compacted into the clay at similar depths and the design of the holder allowed for even solution uptake across the bentonite clay disk surface.

Figure 8.6: Calibration curves obtained for: (a) Ir/IrO\(_2\) pH sensitive electrode and (b) Ag/AgCl Cl− ion specific electrode. Black lines show insensitivity of Ag/AgCl/KCl agar/polychloroprene reference electrode in changing pH and Cl− environments.
Once $E_{membrane}$ corrections were applied to sensor measurements, reliable values could be obtained regarding the chemistry at the surface of the clay disk as well as inside of the clay. A sample of the data collected is shown in Figure 8.8 and steady-state measurements of pH, [Cl$^-$] and $E_{corr}$ of the Cu electrode are summarized in Table 8.1. Experiments were run until a steady-state was attained. This time was dependent on bentonite thickness; a disk with a thickness of 8 mm was used to allow for proper embedment of the electrodes, and experiments typically reached steady-state at around 250 hours. Bradbury and Baeyens [11] found that MX-80 bentonite exhibited buffering characteristics due to amphoteric hydroxyl groups on the edges of the montmorillonite and showed a buffering capacity between pH 3 and 11 with the pH staying close to 8. Outside of this range the montmorillonite became unstable and dissolved. The authors found the overall pH ranged between 6.8 and 8.5 upon
exposure to acidic, neutral and basic solutions; initial experiments summarized in Table 8.1 yielded pH values that fell in this range. The [Cl\(^-\)] measured at the embedded electrodes are lower than those measured at the surface. At 0.5 M, the [Cl\(^-\)] at the clay disk surface was higher than that in the bulk solution (Figure 8.8c). This is likely due to the adsorption of Cl\(^-\) onto the montmorillonite, which may be less prevalent in the 0.1 M NaCl case. The $E_{\text{corr}}$ measured at the Cu electrode suggests the formation of Cu\(_2\)O, the main Cu oxide predicted in the oxic stage, or, formation of a Cu chloride complex, CuCl\(_2^{-}\). However, the $E_{\text{corr}}$ shifts to a more negative potential upon an increase in [Cl\(^-\)] (Table 8.1), but shows little dependence on

**Figure 8.8:** Experimental data obtained from a 0.5 M NaCl solution at the surface and embedded electrodes; a) reference electrodes b) pH c) [Cl\(^-\)] d) $E_{\text{corr}}$ of the Cu electrode
pH. This was expected as the corrosion of Cu in the presence of chloride under aerated conditions proceeds via potential dependent reactions [26].

\[
\text{Cu} + 2 \text{Cl}^- \rightarrow \text{CuCl}_2^- + \text{e}^- \quad \text{(anodic reaction)} \tag{8.8}
\]

\[
\text{O}_2 + \text{H}_2\text{O} + 4 \text{e}^- \rightarrow 4 \text{OH}^- \quad \text{(cathodic reaction)} \tag{8.9}
\]

The formation of CuO, which is dependent on the [Cl\(^-\)] as well as pH, occurs via a precipitation reaction. As CuCl\(_2^-\) is produced by electrochemical dissolution of Cu (reaction 8.8), the equilibrium shifts to the right and CuO is deposited [27],

\[
2 \text{CuCl}_2^- + 2 \text{OH}^- \rightleftharpoons \text{Cu}_2\text{O} + \text{H}_2\text{O} + 4 \text{Cl}^- \tag{8.10}
\]

with the stability of the oxide being inversely proportional to the [Cl\(^-\)]. Since this reaction shows no potential dependence, any effect of pH would not be observed in E\(_{corr}\) measurements. This however has not been proven experimentally.

While no definite conclusions can be made at this time, results obtained thus far coincide with previous ideologies regarding chemical behaviour of the bentonite clay. This allows for experimental validation and the verification that the electrodes and experimental

<table>
<thead>
<tr>
<th>Experiment</th>
<th>pH</th>
<th>[Cl(^-)] (M)</th>
<th>E(_{corr}) (V/SCE)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) 0.1 M NaCl pH = 6.09</td>
<td>S: 6.7</td>
<td>S: 0.091</td>
<td>S: -0.084</td>
</tr>
<tr>
<td></td>
<td>E: 8.2</td>
<td>E: 0.027</td>
<td>E: -0.165</td>
</tr>
<tr>
<td>(2) 0.1 M NaCl pH = 6.09</td>
<td>S: 8.7</td>
<td>S: 0.03</td>
<td>S: -0.050</td>
</tr>
<tr>
<td></td>
<td>E: -</td>
<td>E: 0.024</td>
<td>E: -0.089</td>
</tr>
<tr>
<td>(3) 0.5 M NaCl pH = 6.16</td>
<td>S: 7.6</td>
<td>S: 0.64</td>
<td>S: -0.210</td>
</tr>
<tr>
<td></td>
<td>E: 7.6</td>
<td>E: 0.55</td>
<td>E: -0.190</td>
</tr>
<tr>
<td>(4) 0.5 M NaCl pH = 6.16</td>
<td>S: 7.3</td>
<td>S: 0.76</td>
<td>S: -0.202</td>
</tr>
<tr>
<td></td>
<td>E: 7.8</td>
<td>E: 0.33</td>
<td>E: -0.186</td>
</tr>
<tr>
<td>(5) 0.5 M NaCl pH = 6.16</td>
<td>S: 7.4</td>
<td>S: -</td>
<td>S: -0.220</td>
</tr>
<tr>
<td></td>
<td>E: 7.1</td>
<td>E: 0.31</td>
<td>E: -0.168</td>
</tr>
</tbody>
</table>
set-up presented in this study can be used for future work in determining various parameters regarding bentonite porewater chemistry.

### 8.4 Summary and Future Work

- A new Ag/AgCl/KCl agar/polychloroprene reference electrode was fabricated. This electrode provided good stability, insensitivity to pH and chloride concentration, was able to be successfully embedded into the bentonite and was used to measure the redox potential inside the bentonite clay disk.

- An experimental set-up has been successfully developed for the monitoring of pH, chloride concentration and corrosion potential on both the surface and inside of the bentonite clay disk.

- Future goals include determining steady-state pH and chloride concentrations for bentonite exposed to a wide range of solutions, as well as determination of the rate of chloride ion migration through the clay in anoxic environments or upon exposure to sulphide.

- The database of values collected from these experiments will be used directly by SKB via incorporation into models, and, ultimately their license application.

### 8.5 Acknowledgement

This project is funded by the Swedish Nuclear Fuel and Waste Management Company (SKB), Solna, Sweden. The authors are grateful to Christina Lilja (SKB) and Fraser King
(Integrity Corrosion Consulting, Nanaimo, BC, Canada) for many helpful discussions and suggestions.

8.6 References


Conclusions and Future Work

9.1 Conclusions

The primary goals of this research were, (i) to investigate the mechanism of Cu$_2$S film formation in aqueous SH$^-$ solutions, the key long-term corrosion process anticipated on Cu and Cu-coated nuclear waste containers in a DGR; and (ii) to develop an experimental method to study the porewater chemistry in the bentonite clay in contact with the Cu container in the DGR.

Under electrochemically polarized conditions, the morphology of the Cu$_2$S (chalcocite) film formed on Cu in aqueous SH$^-$ solutions has been shown to be dependent on the [SH$^-$], the flux of SH$^-$ to the electrode surface, and the [Cl$^-$] of the solution. Three distinct types of films have been observed: Type I – a single layer, porous Cu$_2$S film, identified by one reduction peak in a CV; Type II – a porous dual layer Cu$_2$S film, identified by two reduction peaks in a CV; and Type III – a compact, partially-passivating film, indicated by an additional third peak in a CV. When the film growth was dominated by SH$^-$ diffusion in solution, a porous film (Type I or II) formed, whereas if film growth was controlled by an interfacial reaction, a compact Type III film formed. These observations are consistent with the results of long-term corrosion experiments under natural corrosion conditions in which partially passive Type III films were formed only at high [SH$^-$] and high electrode rotation rates, when the flux of SH$^-$ at the film/electrolyte interface was sufficiently large that film growth was controlled by interfacial reactions. It was concluded that passive
films, which could lead to the conditions able to support pitting, would only form at $[\text{SH}^-] \geq 5.0 \times 10^{-4} \text{M}$, and then only at high SH$^-$ fluxes (electrode rotation rates). These conditions will not be achievable under the conditions anticipated in a DGR.

The properties of Cu$_2$S films grown electrochemically on Cu in Cl$^-$ solutions containing various amounts of SH$^-$ (from $10^{-4} \text{M}$ to $10^{-3} \text{M}$) were investigated in more detail using electrochemical methods. Film growth occurred in two distinct stages. At low anodic overpotentials, a thin porous Cu$_2$S film was formed with growth occurring at the Cu$_2$S/solution interface supported by the transport of Cu$^+$ through the solution. This was followed by the deposition of a thicker outer layer of Cu$_2$S. At sufficiently high [SH$^-$], this led to partial blockage of the film growth process with the overall film growth rate being controlled by the properties of this outer layer deposit. EIS measurements confirmed that the decrease in the film growth rate at higher potentials and [SH$^-$] was due to the formation of this deposit not to passivation of the surface by the formation of a coherent Cu$_2$S film. The film growth mechanisms under electrochemical and corrosion conditions were found to be very similar. These results confirm previous claims that the formation of a passive sulphide film will only be possible at high [SH$^-$] when SH$^-$ is not allowed to deplete at the Cu surface. When a compacted bentonite buffer is present in a DGR these conditions will be unachievable and passivation of waste container surfaces should not occur.

The effect of the anions Cl$^-$, SO$_4^{2-}$, HCO$_3^-$ on the anodic formation of Cu$_2$S films in aqueous SH$^-$ solutions were studied voltammetrically. At low [SH$^-$], Cl$^-$ appeared to have two different effects on film formation. At low [Cl$^-$], film formation occurred at a rate higher than the diffusion-controlled limit indicating film growth was assisted by the ionic migration of SH$^-$ within the solution filled pores of the film. At high [Cl$^-$], film formation was suppressed due to competition between Cl$^-$ and SH$^-$ for adsorption sites on the Cu surface.
At high [SH\(^-\)], the Cu\(_2\)S film formed was more compact with the growth rate controlled by ionic migration of the electrolyte ions in the solution in the pores of the growing film. An increase in [Cl\(^-\)] at high [SH\(^-\)] led to a major increase in film growth rate due to the decrease in resistivity of the solution within the pores leading to an increase in the ionic migration rate.

The ability of Cl\(^-\) to suppress the Cu\(_2\)S film growth rate decreased as the [SH\(^-\)]/[Cl\(^-\)] ratio increased confirming that the two anions competed for adsorption sites on the Cu surface at the base of pores in the film. At high [SH\(^-\)], Cl\(^-\) also appeared to influence the film porosity allowing a slight increase in film growth rate despite the presence of an apparently passivating film. An accompanying shift from an asymmetrical reduction peak to a symmetrical peak, indicative of a more easily reduced film, was observed supporting this claim of increased porosity.

In the presence of SO\(_4^{2-}\), any influence of ionic migration was overwhelmed by a large suppression in Cu\(_2\)S film formation. This was most likely due to the strong adsorption of SO\(_4^{2-}\) on Cu, re-enforced by the co-adsorption of H\(_2\)O, leading to the displacement of SH\(^-\) from surface adsorption sites. At high [SH\(^-\)], the film remained porous in nature and the apparent active-to-passive transition during anodic film formation was not observed. Voltammetric data showed that the effect of HCO\(_3^-\) appeared to be intermediate between that of Cl\(^-\) and that of SO\(_4^{2-}\).

These results show that a specific anion effect occurred indicating that the groundwater in the DGR cannot be considered as a simple saline solution containing small amounts of SH\(^-\). While some aspects of the influence of SO\(_4^{2-}\) and HCO\(_3^-\) remain unresolved their dominant influence is to suppress the anodic oxidation of Cu to Cu\(_2\)S and, in the case of SO\(_4^{2-}\) to inhibit the tendency to form protective films at high [SH\(^-\)].
A novel experimental set-up was developed in order to effectively study bentonite clay porewater chemistry. A new Ag/AgCl/KCl agar/polychloroprene reference electrode was fabricated for this study. This electrode provided good stability, insensitivity to pH and [Cl\(^-\)], and could be successfully embedded into the bentonite. Using a bentonite clay disk, the monitoring of pH, [Cl\(^-\)] and corrosion potential on both the surface and within the clay was achieved. The database of values collected from these experiments will be used directly by SKB via incorporation into models, and, ultimately, their license application.

### 9.2 Future Work

In this study at attempt was made to further understand the properties of Cu waste containers in the DGR due to corrosion in aqueous SH\(^-\) leading to the deposition of a Cu\(_2\)S film, and the evolution of the bentonite backfill porewater chemistry. However, there are unresolved issues that should be addressed with further research:

- The fracturing of the thin initial Cu\(_2\)S film formed has been captured electrochemically. However this process could possibly be observed more directly using in-situ XAS measurements. This would add confidence in the understanding of the Cu\(_2\)S film growth mechanism.
- The composition of the partially passive copper sulphide film is proposed to be a resistive outer deposit of Cu\(_2\)S. However, it has been proposed that the partial passivity may be due to the formation of CuS. Analyses, such as by XRD, should be performed to clarify whether or not this film is formed.
- Many details of the influence of groundwater anions, such as \(\text{SO}_4^{2-}\) and \(\text{HCO}_3^-\) remain unresolved. A more comprehensive set of electrochemical and corrosion data,
supported by surface analyses, should be collected in \( \text{SO}_4^{2-} \) and \( \text{HCO}_3^- \) solutions containing \( \text{SH}^- \) in order to develop a more comprehensive understanding of the effects of these groundwater anions on \( \text{Cu}_2\text{S} \) film formation.

- A better understanding of bentonite porewater chemistry is required based on an extended database. This would involve the determination of steady-state \( \text{pH} \) and \([\text{Cl}^-]\) for a wider range of solutions. Future research is also required to determine the rate of \( \text{Cl}^- \) ion migration through the clay in anoxic environments and when \( \text{SH}^- \) is present.
Appendix A

Copyrights

Chapter 4 Copyright information
Chapter 5 Copyright information
Appendix B

Curriculum Vitae

Education Background

- PhD., Physical & Analytical Chemistry, Faculty of Science (September 2012 – March 2018)
  - Western University, London, Ontario.
  - Research Thesis: Electrochemical and Corrosion Examination of Copper under Deep Geologic Conditions for the Application of Nuclear Waste Containers
  - Thesis Supervisors: Dr. David W. Shoesmith, Dr. James J. Noël

- HBSc., Honours Specialization Chemistry, Faculty of Science (September 2008 – April 2012)
  - Western University, London, Ontario.

Technical Skills

- Electrochemical corrosion techniques
  - corrosion potential, cyclic voltammetry, potentiodynamic polarization, chronopotentiometry, chronoamperometry, electrochemical impedance spectroscopy
- Corrosion testing techniques
  - mass loss, sample preparation
- Surface analysis techniques
  - scanning electron microscopy, energy dispersive x-ray spectroscopy, auger spectroscopy, electron backscatter diffraction, attenuated total reflectance fourier transform infrared spectroscopy/ microspectroscopy
- Analytical instrumentation
  - ion chromatography, gas chromatography mass spectrometry, liquid chromatography
- Direct work with sulphide induced copper corrosion and bentonite studies
- Familiar with nickel based alloys, magnesium alloys, carbon steel, uranium dioxide
- Work with QA and QC methods and reporting
Publications

Journal Articles:

Laboratory Manuals:

Conference Presentations


### Teaching Experience

- Graduate Teaching Assistant (Western University) 
  (2012 – 2017) (Western University) 
  - CHEM 1301 – Discovering Chemical Structure 
  - CHEM 1302 – Discovering Chemical Energies 
  - CHEM 3372 – Instrumental Analytical Chemistry

### Professional Activities

- Reviewer for Electrochimica Acta
- NACE Member
- ECS Member

### Awards

- Faculty of Science Graduate Student Teaching Award, Western University, 2015
- Student Poster Competition Award – 3rd Place, NACE Southern Ontario Student Section (SOSS) 7th Annual Symposium, 2017