The Electrochemical and Corrosion Study of Copper for Nuclear Waste Containers under Deep Geological Disposal Conditions

Mengnan Guo, The University of Western Ontario

Supervisor: Shoesmith, David W., The University of Western Ontario
Joint Supervisor: Noël, James J., The University of Western Ontario

A thesis submitted in partial fulfillment of the requirements for the Doctor of Philosophy degree in Chemistry
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Abstract

The proposed method for the safe disposal of Swedish, Finnish, and Canadian high-level nuclear waste (HLNW) is to isolate it in iron or steel containers with an outer copper (Cu) shell or coating and bury it in a deep geological repository (DGR). Copper has been selected as the corrosion barrier due to its stability in the aqueous anoxic environments anticipated in DGR conditions. The container will initially be exposed to humid aerated conditions which will evolve to cool and anoxic as radiation fields in the fuel decay and heat production ceases. When the DGR is cool and anoxic, sulphide (SH\textsuperscript{−})-induced corrosion will become the long-term threat to container durability by inducing Cu corrosion supported by the reduction of H\textsubscript{2}O or H\textsuperscript{+} from SH\textsuperscript{−}. The predominant source of SH\textsuperscript{−} in a DGR will be remotely produced SH\textsuperscript{−} from SO\textsubscript{4}\textsuperscript{2−} via the action of sulphate-reducing bacteria (SRB) and, possibly, minor production from mineral dissolution (pyrite (Fe\textsubscript{2}S)). The slow SH\textsuperscript{−} diffusion from remote locations to the container surface will render Cu susceptible to corrosion, thereby making it essential to determine the corrosion mechanisms, rates and the extent of corrosion damage on Cu, all of which must be known if a reliable Cu corrosion allowance is to be specified.

The film growth mechanisms on Cu in anoxic aqueous Cl\textsuperscript{−} solutions containing SH\textsuperscript{−} have been investigated both electrochemically and under natural corrosion conditions. Specifically, the influence of Cl\textsuperscript{−} and temperature on both oxide and sulphide film growth and the susceptibility of Cu to pitting have been studied. Cyclic voltammetry on rotating disk electrodes showed that anodically-formed Cu\textsubscript{2}S (chalcolite) films were porous and non-passivating, with the rate of film growth determined by a combination of SH\textsuperscript{−} transport through the growing film and the competition between SH\textsuperscript{−} and Cl\textsuperscript{−} for adsorption sites on the reacting Cu surface. Scanning electron microscopy (SEM) on corroded surfaces and cross-sections showed no evidence for pitting when only Cu\textsubscript{2}S films were present.

The properties of Cu\textsubscript{2}S films on Cu were also studied under freely-corroding conditions using corrosion potential measurements coupled with cathodic stripping voltammetry. Surface analyses demonstrated that, depending on the [SH\textsuperscript{−}] and [Cl\textsuperscript{−}], the chalcolite (Cu\textsubscript{2}S) film was composed of either one or two layers; a thin base layer and an outer crystalline deposit. At low [SH\textsuperscript{−}], only the base layer was formed, with a dual layer growth developing as the [SH\textsuperscript{−}] increased. While the base layer may have initially been a
barrier layer, it rapidly became porous and stopped growing. The crystalline nature of the outer deposited layer was consistent with previous claims that this layer grew at the outer film/solution interface by the transport of Cu (I) species, as complexes and clusters, from the corroding Cu surface through the porous base layer.

Under anaerobic humid conditions, gaseous sulphide (H₂S (g)) may also be produced by the microbial SO₄^{2−} reduction. Since the full saturation of the bentonite clay may take many years, there could be a period during which H₂S (g) could be transported through the unsaturated clay and dissolved into a wetted layer that might form on the container. Hence, the corrosion of Cu when exposed to H₂S (g) in a humid environment was also investigated. The redox reaction was followed by measuring the production of H₂ (g) by corrosion and correlating this amount to the corrosion rate of the Cu.

**Keywords:** Copper, Corrosion, Electrochemistry, Pitting, Sulphide, Chloride, Film Growth, Mechanism, Nuclear Waste Disposal
Summary for Lay Audience

The internationally adopted plan for the permanent disposal of high-level nuclear waste is to seal it in metallic containers and bury it in a DGR. Copper is the primary candidate material for the fabrication of used nuclear fuel containers in Sweden, Finland and Canada due to its stability in the anoxic environments anticipated in such repositories. The available oxygen trapped upon sealing the DGR will be rapidly consumed by mineral and microbial reactions, and by minor uniform corrosion of Cu. However, sulphide-induced corrosion, dominantly due to the remote production of sulphide by sulphate reducing bacteria, will be the long-term threat to container durability. Container corrosion will be influenced by other groundwater anions, in particular chloride.

At the low sulphide concentrations anticipated in a DGR, the corrosion process is expected to be controlled by the supply of sulphide to the container surface, resulting in the formation of porous copper sulphide films on the Cu. Since the properties of these films will dictate the distribution of corrosion damage, it is critical to demonstrate that corrosion will not lead to deep localized penetrations. This makes it essential to address the susceptibility of Cu to pitting at the slightly elevated temperatures (up to 90 °C) anticipated in a DGR, and the influence of various groundwater species, such as Cl⁻ and HCO₃⁻ on the film formation process in slightly alkaline groundwaters (pH 9). The focus of this project was to investigate the properties of copper sulphide films formed electrochemically and by corrosion in aqueous solutions containing sulphide and additional anions, particularly Cl⁻. The emphasis was placed on determining whether the films formed met the criteria that would render containers susceptible to pitting.

A variety of electrochemical and corrosion measurements, such as corrosion potential, cyclic voltammetry, potentiostatic polarization and cathodic stripping voltammetry have been conducted on both stationary and rotating disk electrodes. Raman spectroscopy and X-ray photoelectron spectroscopy have been used to determine the chemical composition of the corrosion products formed under various conditions. Additionally, SEM/EDX examinations of surfaces and FIB-cut cross sections were conducted to examine film morphologies and the distribution of corrosion damage on the corroded Cu/sulphide film interface.
Dedication

To my loving parents

Huang Yan (黄艳)

Guo Yongjun (国拥军)

Without your support, I would not make this far.
Co-Authorship Statement

This thesis includes published data in Chapter 3, 4 and 5. For the work completed, I was the primary investigator and writer, and conducted all the experiments with assistance from:

Chapter 3: Dr. Mark Biesinger assisted with XPS surface analysis, Dr. Todd Simpson assisted with SEM/FIB analysis, Ms. Mary Jane Walzak assisted with laser Raman spectroscopy, Dr. James. J. Noël and Dr. David. W. Shoesmith assisted with editing.

Chapter 4: Dr. Todd Simpson assisted with SEM/FIB analysis, Dr. Vahid Dehnavi assisted with grazing incident angle XRD analysis, Dr. James. J. Noël and Dr. David. W. Shoesmith assisted with editing.

Chapter 5: Mr. Khodor Zein and Ms. Sofia DiFelice assisted with electrochemical measurements, Dr. Sridhar Ramamurthy assisted with Auger spectroscopy, Dr. Thalia Standish assisted with laser Raman spectroscopy, Dr. James. J. Noël and Dr. David. W. Shoesmith assisted with editing.

Chapter 6: Dr. David Hall, Dr. James. J. Noël and Dr. Nick Senior assisted with experimental design, Dr. Nick Senior, Dr. David. W. Shoesmith and Dr. James. J. Noël assisted with editing.
Acknowledgments

This thesis would not have been possible without the guidance and support from my amazing supervisors, Dr. David. W. Shoesmith and Dr. James. J. Noël.

I would like to start acknowledging Dr. Dave Shoesmith. Thank you for giving me this opportunity to pursue a Ph.D. degree. Your mentorship allowed me to grow as a researcher and made my doctoral studies an enjoyable experience. I would never forget our many weekend meetings in your office, and of course, your niche jokes that made me laugh. I could not have asked for a better mentor for my Ph.D. study and for my life. Some impressive traits that I have learned from you are patience and humbleness, which I would take the lessons learnt from you, in both research and life, and continue applying them throughout my future career.

I would also like to express my gratitude to Dr. Jamie Noël. I would not forget our long yet interesting discussions on electrochemical fundamentals, your open-minded attitude and encouragement towards both my research and life, and most importantly, thank you for being so patient with me, even if I was simply talking about my daily life in your office.

I would also like to thank research associates in our lab who have helped me during my grad studies. Dr. Jian Chen, who has been a part of this sulphide project since 2010 and a great co-worker. Jian, thank you for spending many hours helping me with the experiments inside the glovebox and guiding me through my research. Dr. Dmitrij Zagidulin, your expertise on experimental setup and electronics have saved me numerous times in lab. Also, Dr. Fraser Filice, thank you for sharing your wisdom in mathematical modelling and computer skills.

The members of the Shoesmith, Noël, and Wren groups, past and present, made my time in the lab highly enjoyable. I will never forget, our daily conversations, those amazing experiences from many conferences, and get togethers we had throughout the years. Special thanks go to Dr. Taylor Martino, Mr. Khodor Zein, and Ms. Sofia DiFelice, all who contributed their efforts on my project. There are many people whom helped me and became good friends of mine during my study at Western, and I cannot name them all in here. Many thanks go to my wonderful friends and my fellow colleagues for being supportive over the past 4 years.
I must thank my collaborators on this project: the Swedish Nuclear Fuel and Waste Management Company SKB (Solna, Sweden), Posiva Oy (Olkiluoto, Finland) and the Nuclear Waste Management Organization (Toronto, Canada). Special thanks goes to Dr. Nick Senior whom taught me many skills and treated me like a friend when I was working on a project at the NRCan-CanmetMATERIALS. I truly cherish these experiences and appreciate your wisdoms. Also, assistance provided by Western Nanofabrication Facility and Surface Science Western are gratefully acknowledged, especially Dr. Todd Simpson, Mr. Brad Kobe, Ms. Mary Jane Walzak, Mr. Ivan Barker, Dr. Vahid Dehnavi, Dr. Sridhar Ramamurthy and Dr. Mark Biesinger for assisting with FIB, SEM, laser Raman, CLSM, XRD, AES and XPS analyses.

I owe an incredible amount of gratitude to my parents, Huang Yan and Guo Yongjun. Thanks for letting me make decisions whether I would like to study overseas and always being there to support me unconditionally. To my mom, Yan, you were always there to listen to my problems and encourage me. Last but not least, I would like to thank my boyfriend, Nelson Hu for his unconditional love and understanding so that I can indulge myself in science and research. You have never stopped believing in me and I could not have done this without you.
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List of Acronyms, Abbreviations, and Symbols

Acronyms, Abbreviations

HLNW    High-level nuclear waste
DGR     Deep geological repository
Cu      Copper
SKB     Swedish Nuclear Fuel and Waste Management Company
O₂      Oxygen gas
H₂      Hydrogen gas
NWMO    Nuclear Waste Management Organization
UFC     Used fuel container
BWR     Boiling water reactor
PWR     Pressurized water reactor
APM     Adaptive phased management
SRB     Sulphate-reducing bacteria
Fe_{1+x}S Mackinawite
SH⁻     Sulphide ion
Cl⁻     Chloride ion
Cu₅S    Copper sulphide film
CO₃²⁻/HCO₃⁻ Carbonate/bicarbonate
CH₄     Methane
Ox      Oxidant
Red     Reductant
\( C_{\text{ox}} \)  
Surface concentration of oxidant

\( \text{CuCl}_2^- \)  
Copper-chloro complex

\( \text{Cu}_2\text{O} \)  
Cuprous oxide/Cuprite

\( \text{CuO} \)  
Cupric oxide/Tenorite

\( \text{DFT} \)  
Density functional theory

\( \text{H}_2\text{S} \)  
Hydrogen sulphide gas

\( \text{SO}_4^{2-} \)  
Sulphate ion

\( \text{XRD} \)  
X-ray diffraction

\( \text{S}^{2-} \)  
Sulphide ion

\( \text{EIS} \)  
Electrochemical impedance spectroscopy

\( \text{Cu}_2(\text{OH})_3\text{Cl} \)  
Atacamite

\( \text{SEM} \)  
Scanning electron microscopy

\( \text{FIB} \)  
Focused ion beam

\( \text{EDX} \)  
Energy dispersive X-ray spectroscopy

\( \text{RDE} \)  
Rotating disk electrode

\( \text{CuS} \)  
Covellite

\( \text{Cu}_2\text{S} \)  
Chalcocite

\( \text{AFM} \)  
Atomic force microscopy

\( \text{LEIS} \)  
Localised electrochemical impedance spectroscopy

\( \text{NaOH} \)  
Sodium hydroxide

\( \text{Cu(OH)}_2 \)  
Copper (II) hydroxide

\( \text{SERS} \)  
Surface-enhanced Raman spectroscopy

\( \text{EXAFS} \)  
Extended X-ray absorption fine structure
<table>
<thead>
<tr>
<th>Formula</th>
<th>Name</th>
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<tbody>
<tr>
<td>Cu$_{1.12}$S</td>
<td>Varrowite</td>
</tr>
<tr>
<td>Cu$_{1.4}$S</td>
<td>Spionkopite</td>
</tr>
<tr>
<td>Cu$_{1.6}$S</td>
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<td>Cu$_{1.75}$S</td>
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<tr>
<td>Cu$_{1.8}$S</td>
<td>Digenite</td>
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<tr>
<td>Cu$_{1.96}$S</td>
<td>Djurleite</td>
</tr>
<tr>
<td>PTFE</td>
<td>Polytetrafluoroethylene</td>
</tr>
<tr>
<td>SCE</td>
<td>Saturated calomel electrode</td>
</tr>
<tr>
<td>WE</td>
<td>Working electrode</td>
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<tr>
<td>CE</td>
<td>Counter electrode</td>
</tr>
<tr>
<td>OCP</td>
<td>Open circuit potential</td>
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<td>CV</td>
<td>Cyclic voltammetry</td>
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<td>PDP</td>
<td>Potentiodynamic polarization</td>
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<td>SEM</td>
<td>Scanning electron microscopy</td>
</tr>
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<td>SE</td>
<td>Secondary electron</td>
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<tr>
<td>BSE</td>
<td>Backscattered electron</td>
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<td>Energy dispersive X-rays spectroscopy</td>
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<td>Confocal laser scanning microscopy</td>
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<td>XPS</td>
<td>X-ray photoelectron spectroscopy</td>
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<td>BE</td>
<td>Binding energy</td>
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<tr>
<td>KE</td>
<td>Kinetic energy</td>
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xvii
CHA
Concentric hemispherical analyzer
AES
Auger electron spectroscopy
XRD
X-Ray diffraction
GIXRD
Grazing incidence X-ray diffraction
TDA
Thermal desorption analysis
SA
Surface area

Symbols

\( \gamma \)
Gamma
\( e^- \)
Electron
\( G \)
Gibbs free energy (kJ mol\(^{-1}\))
\( \Delta G \)
Gibbs free-energy change (kJ mol\(^{-1}\))
\( \Delta G^o \)
Standard Gibbs free-energy change (kJ mol\(^{-1}\))
\( \Delta E^o \)
Standard electrode potential (V)
\( E_e \)
Equilibrium electrode potential (V)
\( a_{ox} \)
Activity of oxidant (mol/L)
\( a_{red} \)
Activity of reductant (mol/L)
\( R \)
Universal gas constant (J mol\(^{-1}\) K\(^{-1}\))
\( n \)
Number of electron transfer in a half-reaction
\( T \)
Temperature (K)
\( F \)
Faraday’s constant (96485 C/mol)
\( Q \)
Reaction quotient
\( t \)
Time (s)
\( m \)
Mass (kg)
Molar mass (g/mol)

Current (A)

Current density (A/cm²)

Exchange current density (A/cm²)

Corrosion potential (V)

Potential (V)

Rate constant (order zero: mol·L⁻¹·s⁻¹; order one: s⁻¹; order two: L·mol⁻¹·s⁻¹)

Over-potential (E_{app}-E_e) (V)

Transfer coefficient of backward reaction in reaction (1.9)

Transfer coefficient of forward reaction in reaction (1.9)

Transfer coefficient of an anodic half-reaction

Transfer coefficient of a cathodic half-reaction

Henry’s law constant (mol m⁻³ Pa⁻¹)

Current density (A/cm²)

Time (s)

Gold

Limiting current density (A/cm²)

Argon

Corrosion current density (A/cm²)

The potential difference between the applied potential and $E_{corr}$ (V)

Linear polarization resistance (Ω cm²)

The initially applied potential (V)
\( E_{\text{Final}} \)  The final applied potential (V)

\( Q \)  Coulomb charge (C)

\( Q_a \)  Anodic charge associated with oxidation (C)

\( Q_c \)  Cathodic charge associated with reduction (C)

\( J_j(x,t) \)  Flux of species j at a distance x and time t (mol/cm\(^2\)/s)

\( D_j \)  Diffusion coefficient of species j (cm\(^2\)/s)

\( Z_j \)  Charge of an ionic species j (C)

\( v \)  Velocity of a species in an aqueous solution (cm/s)

\( \omega \)  Electrode rotation rate (rpm/Hz)

\( \delta \)  Nernst diffusion layer thickness (m)

\( C_0 \)  Surface concentration of a reacting species (mol/L)

\( C_{\text{bulk}} \)  Concentration in the bulk solution (mol/L)

\( \nu \)  Kinematic viscosity (m\(^2\)/s)

\( f \)  Focal length (m)

\( u \)  Object distance (m)

\( m \)  Image distance (m)

\( F \)  Focal point

\( \mu \)  Refractive index of imaging medium

\( R \)  Resolution of an optical microscope

\( \lambda \)  Wavelength (nm)

\( \alpha \)  Half of the angular aperture (°)

\( \text{NA} \)  Numerical aperture

\( \nu \)  Vibrational frequency (Hz)

xx
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
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<tbody>
<tr>
<td>$\mu$</td>
<td>Induced dipole moment (C·m)</td>
</tr>
<tr>
<td>$\varphi$</td>
<td>Work function (J)</td>
</tr>
<tr>
<td>$\sigma$</td>
<td>Auger parameter (eV)</td>
</tr>
<tr>
<td>$s$</td>
<td>Diffraction vector</td>
</tr>
<tr>
<td>$\Re_{BR}$</td>
<td>Pilling-Bedworth ratio</td>
</tr>
<tr>
<td>at.%</td>
<td>Atomic concentration (%)</td>
</tr>
<tr>
<td>$R_s$</td>
<td>Solution resistance (Ω)</td>
</tr>
<tr>
<td>$E_o$</td>
<td>Potential amplitude (V)</td>
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<td>$I_o$</td>
<td>Current amplitude (A)</td>
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<tr>
<td>ppmw</td>
<td>Parts per million by weight</td>
</tr>
<tr>
<td>$S_z$</td>
<td>Maximum height (m)</td>
</tr>
<tr>
<td>$S_a$</td>
<td>Arithmetical mean height (m)</td>
</tr>
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Chapter 1 Introduction and Literature Review

1.1 Project Motivation—The Permanent Disposal of Used Nuclear Fuel

Presently, nuclear energy represents one of the clean forms for the generation of reliable and environmentally-friendly electricity. According to recent reports, nuclear electricity production constituted 40% of the total electricity production in Sweden in the year 2019 [1]. Canada also relies heavily on the production of electricity from nuclear power, which accounts for 15% of electricity generated nation-wide and up to 60% in Ontario [2]. The primary high-level waste generated by nuclear energy is the spent nuclear fuel, which remains radioactive for up to one million years, and constitutes a potential hazard to the environment if the long-lived radionuclides, produced from nuclear fission reactions, are released to the environment [3]. To address this issue, a passive system for the permanent disposal of this waste form, involving a deep geological repository (DGR), has been proposed by many countries around the world.

1.1.1 Deep Geological Repository Reference Design

The criteria for the selection of a repository location for the permanent disposal of high-level nuclear waste is dependent on the geological environments available in a specific country. A number of general requirements must be met for a location to be chosen. These requirements include [4]: i) the selected location must be geologically stable and not susceptible to significant seismic activity; ii) it must demonstrate measurable advantageous features; iii) advantageous features must not to be destroyed by the excavation/waste package emplacement process; and iv) the excavation-disturbed state must evoke to the original undisturbed state with time.

1.1.1.1 Swedish Scenario

The current Swedish/Finnish waste disposal scenario is based on the KBS-3 repository design, which is typical of the internationally-adopted multi-barrier disposal approach for the permanent disposal of the spent nuclear fuels [5–8]. The KBS-3 concept is based on the complete containment of the spent nuclear fuel in a sealed dual-walled nuclear waste containers comprising a nodular cast iron insert with an outer copper (Cu)
shell [9,10]. These waste containers will then be placed in individual vertical boreholes surrounded by a dense bentonite clay buffer at a depth ≥ 500 m in crystalline rock. Other repository cavities, including the deposition tunnels, transport tunnels, shafts and central underground area, will be filled with backfill materials [5], Figure 1.1. The reference backfill is a specific type of bentonite clay consisting of various components, such as montmorillonite, calcite, gypsum, etc [6]. Details of the backfill compositions can be found elsewhere [7].

![Diagram of deposition borehole and KBS-3 repository](image)

**Figure 1.1:** (a) A schematic diagram showing the design of a deposition borehole with bentonite clay buffer surrounding the spent nuclear fuel container; (b) a schematic representation of the proposed KBS-3 deep geological repository. Images courtesy of SKB (Technical Report TR-06-09 and TR-14-15 [5,6]).
To overcome the uncertainties involved in demonstrating the acceptable performance of individual barrier layers over an extended time period, a multi-barrier approach has been universally adopted. The overall DGR performance is not dependent on any single barrier, but on a series of independent barriers. The multi-barrier KBS-3 design consists of the spent fuel waste form, which is sparingly soluble in water, the fuel cladding, the waste container, the clay buffer material surrounding the container, and the crystalline rock.

Highly compacted bentonite clay/buffer, in contact with the waste container, has a number of desirable properties[11,12]. Prior to container failure, these include the following: preventing advective transport of species dissolved in the groundwater in the deposition hole; resisting transformations and limiting chemical alterations of the environment in the proximity of the waste containers; eliminating microbial activity within close proximity to the container; providing sufficient load-bearing capacity to hold containers in place; protecting the container from rock shear movements, and providing a high thermal conductivity for the dispersion of heat generated by radionuclide decay to the host rock. If containers should fail, the major advantages gained by surrounding them with compacted bentonite buffer are the following [12]:

1) the outward transport of released radionuclides from the breached container and the inward transport of dissolved Cu corroding agents to the container surface would be severely limited,
2) long-term chemical and mechanical features which provide stability would be maintained. These features include thermal conductivity (of importance for the container temperature), hydraulic conductivity and swelling of the clay to seal cavities between the container and the buffer,
3) the capture of released cationic radionuclides by ion exchange processes.

The final barrier, the deep and low-permeability rock mass, would provide a stable environment for the containers both chemically and physically due to its distance from seismic hot spots (i.e. volcanic activity), its favourable hydrologic and transport properties which would provide limited fracture transmissivity, and a low water activity (i.e. stagnant, reducing and low salinity) [5]. The safety function of the host rock also includes its ability
to maintain stable mechanical and thermal conditions, by limiting groundwater pressure and ensuring that the rock exceeds the freezing point of the buffer, which is at $-4\,^\circ C$ [13]. In the case of container failure, the transport of dissolved radionuclides through the rock will be retarded by the low water flow rate. Since numerous radionuclides are observed to chemically adsorb onto minerals which exist within fractures in the bedrock, their transport will be exclusively retarded allowing radionuclide decay within the host rock prior to any release to the geosphere.

1.1.1.2 Canadian Scenario

The proposed adaptive phased (APM) management plan for used nuclear fuels in Canada is similar in principle to the KBS-3 design with disposal in a deep geological repository (DGR) comprised of multiple natural and engineered barriers [14]. The repository will be constructed at a depth of approximately 500 m, depending upon the geology of the site (crystalline or sedimentary), and consists of a series of tunnels leading to a network of rooms where the used nuclear fuel will be emplaced, Figure 1.2.

![Figure 1.2: The conceptual layout of the surface facilities, the underground services area and the placement rooms for a Canadian deep geological repository. Image courtesy of NWMO.](image)

The used fuel container (UFC) is the primary engineered barrier that is designed to withstand geological pressures, including the hydrostatic load of glaciation events, and to
demonstrate excellent resistance to long-term corrosion [14]. A DGR at the depth of approximately 500 m was chosen primarily to maintain a stable geological and chemical environment after emplacement [4]. At these depths, the groundwater will be effectively stagnant with a low activity and will be free of dissolved oxygen (O₂), thus providing the anoxic conditions favourable to suppress container corrosion.

The current information on the nature of chemical conditions in the vicinity of the container, termed the near-field environment, is used to predict the evolution of conditions in a Canadian DGR [15], and to provide insights relevant to bentonite-backfilled repositories in other geological settings. It is acknowledged that the repository environment will change over time, beginning as warm, dry and oxic, and evolving finally to cool, wet and anoxic [14–16], Figure 1.3.

![Diagram showing the evolution of exposure conditions in a Canadian DGR](image)

**Figure 1.3:** A qualitative illustration showing the evolution of exposure conditions anticipated in a Canadian DGR as a function of time [12]. The temperature plot is for a specific repository design while the oxygen and radiation dose curves are purely illustrative.
The initial repository redox conditions will be oxidizing due to the presence of O$_2$, introduced during the period of repository excavation and emplacement of the waste and subsequently trapped on sealing the DGR, and the presence of other oxidants produced by the radiolysis of the pore water [15]. Trapped O$_2$ will be consumed by the uniform corrosion of the container and other processes, such as aerobic microbial activity and the oxidation of minerals in the bentonite and host rock. Early calculations by King et al [17] on the O$_2$ consumption rate suggested the oxic phase would last for several decades. However, more recent field studies suggest much shorter periods, ranging from a few weeks to several months [18]. Redox conditions will also be influenced by other oxidants, produced by the radiolysis of water due to the gamma (γ)-radiation emitted by the spent fuel. The γ-dose rate is dominated by the decay of the fission products in the fuel and is calculated to vary at the container surface from ~2 Gy/h after 10 years to ~0.02 Gy/h after 200 years [19]. Hence, during this early stage, the Cu container could be vulnerable to corrosion via oxidants such as O$_2$ and radiolytically produced species, such as nitric acid.

The time dependence of the container surface temperature can be calculated based on the DGR design and thermal properties of the near field environment, although some uncertainty exists due to the site-specific saturation behaviour of bentonite [15]. The actual saturation profile will depend on several factors, such as the thermal output of the waste containers, the re-saturation behaviour of the bentonite clay, and the hydraulic conductivity of the host rock. Details of saturation profiles are discussed elsewhere [15,16]. The initial rise in repository temperature, Figure 1.3, is associated with the heat generated by the radioactive decay of the spent fuel waste form in the container. This increase in temperature will result in a low humidity environment in the vicinity of the container and negligible corrosion would be expected despite the prevailing oxidizing conditions. Eventually, the trapped O$_2$ will have been consumed, the γ-radiation field will have decayed, and the container surface temperature decreased, allowing the repository to evolve to saturated, cool and anoxic conditions.

The choice of Cu as a container material is primarily based on the thermodynamic argument that it would be stable in the reducing environments expected to prevail once the initially trapped O$_2$ has been consumed, which would allow Cu to remain stable indefinitely. However, corrosion of the container can also occur if sulphide (SH$^-$) is present in the DGR.
Despite the fact that microbial activity will be severely restricted within the bentonite itself, sulphides could be produced via microbially mediated reactions with organic matter involving sulphate-reducing bacteria (SRB) at remote location where microbial activity is not suppressed; e.g., in the host rock or at the rock bentonite interface [15]. This scenario provides the focus of this thesis on sulphide-induced Cu corrosion, which will be the dominant threat to the durability of the Cu container over the long term.

1.1.2 High-Level Nuclear Waste Container Design

1.1.2.1 Swedish/Finnish Container Design

The spent nuclear fuel containers (often refereed to as canisters) are designed with an insert of cast iron and an outer shell of Cu, Figure 1.4. The Cu shell is 50 mm thick and the cylindrical canister has a length of approximately 4.8 m and a diameter of 1.1 m [5], Figure 1.4.

![Figure 1.4: Exploded view of a Swedish canister and its major components.](image)

There are three canister safety functions relevant to waste containment: to provide a corrosion barrier, to withstand isostatic load, and to withstand shear load [6]. When pressure is applied to the container, the Cu shell would compress onto the inner cast iron vessels, thereby delivering most of the external load. The cast iron insert, therefore, provides structural support to withstand isostatic loading stresses of 45 MPa [6], and the Cu shell acts as a corrosion-resistant protective layer in the repository environment. The Cu cylindrical shell will be fabricated as a seamless tube with both the Cu lid and bottom machined to the desired dimensions, Figure 1.5. The insert is cast from spheroidal graphite cast iron and contains channels where the fuel assemblies are housed [5,20]. The choice of iron is also advantageous in the event of container failure due to the production of hydrogen gas as a result of the aqueous corrosion of iron. Hydrogen gas (H₂) can act as a potential scavenger of radiolytic oxidants, therefore impeding dissolution of the spent fuel [21]. Fabrication methods and design characteristics of the cast iron insert are discussed.
elsewhere [20]. The KBS-3 nuclear waste container holds about two tonnes of spent nuclear fuel, including both boiling water reactor (BWR) and pressurized water reactor (PWR) assemblies, which weigh 25 and 27 tonnes, respectively [5], Table 1.1. The dimensions of the Swedish container are shown in Figure 1.5.

![Figure 1.5: Schematic showing the Swedish nuclear waste container with its inner cast iron insert and outer Cu shell. (a) Exploded view of the container; (b) cross-section view of BWR and PWR type fuel assemblies. Image courtesy of SKB (technical report TR-06-09 [5] and TR-10-14 [20]).](image)

<table>
<thead>
<tr>
<th>Weight (kg)</th>
<th>BWR-canister</th>
<th>PWR-canister</th>
</tr>
</thead>
<tbody>
<tr>
<td>Insert with lid</td>
<td>13700</td>
<td>16400</td>
</tr>
<tr>
<td>Copper shell</td>
<td>7500</td>
<td>7500</td>
</tr>
<tr>
<td>Canister without fuel</td>
<td>21200</td>
<td>23900</td>
</tr>
<tr>
<td>Canister with fuel</td>
<td>24600-24700</td>
<td>26500-26800</td>
</tr>
</tbody>
</table>
1.1.2.2 Canadian Container Design

The used fuel container (UFC) consists of an inner vessel of carbon steel (SA516 Gr.70) which provides the mechanical strength to withstand repository loads (hydrostatic, lithostatic, and glaciation loads), and an outer layer of 3 mm thick Cu, applied as a coating via electrodeposition and cold spray deposition, as a corrosion barrier [14,22]. The reference container design shown in Figure 1.6 (a), is referred as the Mark II or CV-HH-4L-12 design. The carbon steel vessel provides a waste loading of 48 CANDU fuel bundles, Figure 1.6 (b) [23].

![Figure 1.6: (a) An illustration of the NWMO Mark II container for the disposal of used CANDU fuel and (b) A 3D rendering of the UFC insert design containing 48 CANDU fuel bundles. Images adapted from NWMO technical report NWMO-TR-2018-01 and [23] and NWMO-TR-2019-02 [22].](image)

The initial design of the Canadian UFC, referred to as Mark I, was based on a modified version of the Scandinavian KBS-3 container. Starting in 2011, a re-evaluation of the container design was conducted by NWMO and led to the development of the Mark II container that is optimised for CANDU fuel bundles, which are ~ 50 cm in length and 10 cm in diameter [16], as well as for manufacturing considerations [14]. This design significantly decreases the amount of Cu required and adopts modern coating technologies to apply the Cu directly to the steel, which eliminates the need for the Cu to be self-supporting during fabrication.
Copper coatings will be applied on the body and the two hemi-spherical heads via electrodeposition before fuel loading. Cold spray deposition will be used to cover the exposed region of the inner vessel with Cu after the fuel has been loaded and the inner steel vessel has been welded shut. Although the 3 mm thick Cu coating is much thinner than the Cu shell of the current KBS-3 design, this Cu layer still exceeds the current conservative corrosion allowance, which is calculated to be ~ 1.3 mm over the first million years after container emplacement [24,25]. A comparison of the three conceptual container designs are shown in Figure 1.7.

![Figure 1.7: Comparison of the (a) KBS-3, (b) the original NWMO reference (NWMO Mark I) and (c) the current Canadian reference (NWMO Mark II) used fuel container designs [10].](image)

1.1.3 Evolution of Repository Conditions—Swedish Repository at Forsmark

The Forsmark site located in the municipality of Östhammar, Sweden, was chosen for the construction of a future KBS-3 repository. It is estimated that $1.2 \times 10^4$ tonnes of spent nuclear fuel will be transported to the final KBS-3 DGR, which would require approximately 6000 Cu containers to dispose of the high-level nuclear wastes [6].
1.1.3.1 Thermal Performance of the Cu Container

The thermal performance of a Cu container is determined by various factors, such as the thermal properties of the rock, container, tunnel spacing, and the degree of saturation of the highly compacted bentonite buffer surrounding the container [16,24]. The following discussion is focused on the thermal evolution of the container surface after repository closure.

The average background temperature of the host rock is approximately 11 °C at the proposed repository depth of around 500 m in Forsmark [10], which is considerably lower than the temperature on the surface of a Cu container. The residual heat from a container originates from the radioactive decay of the spent fuel waste form, leading to a transient increase of the container surface temperature to a peak of 85 °C after ~10 years of emplacement [10]. One pessimistic calculation indicates that the surface temperature of a container could reach a peak above 95 °C, provided that the bentonite buffer remained unsaturated [7,10]. The container surface temperature will decrease to 40 °C after 1000 years of containment, and to an average temperature of 20 °C after 10,000 years. Eventually, the container surface temperature will reach the host rock background temperature in approximately one million years due to slow heat dissipation into the buffer and host rock, Figure 1.8 [10]

![Figure 1.8: The anticipated evolution at the waste container surface temperature in a KBS-3 repository [7]. Image courtesy of SKB.](image-url)
1.1.3.2 Bentonite Buffer Saturation Time

The saturation of bentonite buffer is influenced by the wetting/drying from the rock and backfill and the heating induced by the waste container. Model calculations have been made by Åkesson et al. for various sets of conditions and assumptions [26]. In general, the saturation time of the buffer is anticipated to vary between a few tens to a few thousands of years depending on its position in the repository. More recent modelling by Sellin et al. [27] using an hydraulic conductivity of the rock matrix is $10^{-13} \text{ m/s}$, indicated that the saturation time would be more than a thousand years in most deposition holes.

1.1.3.3 Redox Conditions and Groundwater Sulphide Concentrations

After an initial short-lived oxic phase due to the disturbance caused by excavation and operation of the repository, reducing conditions will be re-established and then prevail [10]. Once reducing conditions have been established, sulphide will be the predominant corrosive agent that poses a long-term threat to the durability of the Cu containers. The concentration of sulphide in groundwaters is controlled by a balance between its production by microbial sulphate reduction and its consumption by oxidation and precipitation with metals. In particular, of the sulphide that will be produced, the vast majority ($> 99 \%$) will be present as precipitated mackinawite ($\text{Fe}_{1+x}\text{S}$) [28]. Based on the simulation by King and Kolář, the sources/production of dissolved Fe (II) in the repository included siderite ($\text{FeCO}_3$), biotite, and pyrite ($\text{FeS}_2$) present in the backfill, buffer materials and rock layers [28]. Whereas the consumption of Fe (II) is attributed to the irreversibly precipitation as $\text{Fe}_{1+x}\text{S}$ if the concentrations of dissolved Fe (II) and $\text{SH}^-$ exceed its solubility product [27]. In addition, calculations suggested that sulphide would also be consumed by mineral oxides in the geosphere [27].

The distribution of groundwater sulphide concentrations in the Forsmark site has been thoroughly researched and evaluated, Figure 1.9 [10], which shows the predicted sulphide concentration ranges from $1.2 \times 10^{-7} \text{ mol/L}$ to $1.2 \times 10^{-4} \text{ mol/L}$. The majority of values are at least one order of magnitude lower than the maximum sulphide concentration.
1.1.3.4 Peak Sulphide Fluxes at the Container Surface

Sulphides will be produced in remote locations where the microbial sulphate reduction reactions are robust. Dissolved hydrogen ($H_2$), methane ($CH_4$), and organic carbon, are potential reductants that may be used by SRB to produce sulphide [7]. The total sulphide concentration in the vicinity of the container is expected to be substantially lower than the bulk sulphide concentration in the groundwater due to the presence of other barriers to transport, such as the bedrock and buffer materials.

The rate of sulphide-induced Cu corrosion will be determined by the mass transport of sulphide from the remote locations where it is produced to the container surface, leading to the establishment of a sulphide concentration gradient. According to Fick’s first law of diffusion, the diffusive flux is proportional to the concentration gradient [29]. In other words, the sulphide flux (mol/(cm$^2$·s)) at the container surface becomes one of the vital factors that control Cu corrosion under anoxic conditions.

The phases of repository evolution are of relevance to the sulphide flux at the container surface [10]. When the bentonite buffer is unsaturated, sulphide may be transported via the gas phase. Once bentonite is fully saturated, the sulphide flux at the
surface of a container is expected to be very low due to the large diffusive transport resistance in the bentonite buffer [7]. It is reported that the peak sulphide flux to the surface under saturated conditions will be less than $10^{-10} \text{ mol/(m}^2 \cdot \text{s})$. This peak sulphide flux of $\sim 10^{-11} \text{ mol/(m}^2 \cdot \text{s})$ is calculated for the highest sulphide concentration in the groundwater ($1.2 \times 10^{-4} \text{ mol/L}$) [10].

Even under the worse case scenario when it is assumed the bentonite has been eroded in the vicinity of the container and the sulphide concentration in the groundwater ($1.2 \times 10^{-4} \text{ mol/L}$) is at its highest, a peak sulphide flux of only $10^{-9} \text{ mol/(m}^2 \cdot \text{s})$ is obtained [10].

### 1.2 Corrosion Basics

#### 1.2.1 Thermodynamics of Aqueous Corrosion

Corrosion is defined as the degradation of a material, commonly a metal, by reaction with its environment [30], and is an electrochemical process [31]. The oxidation and reduction reactions occur simultaneously on the metal surface during corrosion [30]. One half of the coupled reaction involves a material oxidation/dissolution process (anodic half-reaction), while the other half is the reduction of an electrochemically active oxidant (cathodic half-reaction), such as oxygen. Thus, corrosion reaction can be considered to be comprised of two half reactions, reaction (1.1) and (1.2), with the overall reaction being the sum of the two, reaction (1.3).

Anodic half-reaction: $M \rightleftharpoons M^{n+} + n e^-$  \hspace{1cm} (1.1)

Cathodic half-reaction: $Ox + n e^- \rightleftharpoons Red$  \hspace{1cm} (1.2)

Net reaction: $M + Ox \rightarrow M^{n+} + Red$  \hspace{1cm} (1.3)

![Figure 1.10: A schematic showing a generic corrosion process [31].](image)
A corrosion system can be regarded as a short-circuited electrochemical cell in which the driving force is the potential difference between the anodic and cathodic reactions, leading to current flow (electron transfer) inside this corrosion cell, Figure 1.10 [31]. The positive current, which is in the opposite direction to the flow of electron, is discharged at the anodic sites, flows through the electrolyte via ionic conduction with the circuit completed by electron conduction in the metal.

The energy of a system can be described by the Gibbs free energy (G). The Gibbs free-energy change (ΔG) expresses the spontaneity of a system, and, when occurring spontaneously, corrosion is thermodynamically favoured, resulting in a negative ΔG. ΔG for a spontaneous electrochemical process when all reactants and products are in the standard state is expressed by Eq. (1.4),

\[ \Delta G^o = -nF\Delta E^o \]  

where \( \Delta G^o \) and \( \Delta E^o \) are the standard Gibbs free-energy change and standard electrode potential, respectively, F is the Faraday constant (96485 C/mol), and \( n \) is the number of electrons transferred in the redox reaction.

In electrochemical terms, the free-energy change is proportional to the amount of energy required to move a charge, nF, reversibly across an interface (typically a metal/solution interface), as indicated in Eq. (1.4). The standard state is unit activity (\( \alpha = 1 \)) for ions in an aqueous environment and 1 atm pressure for gases. The thermodynamics of an electrochemical reaction can be expressed in terms of an equilibrium potential measured against the standard hydrogen electrode (SHE) [29].

Corrosion processes generally occur under non-standard state conditions, and the Nernst equation, Eq. (1.5), relates the equilibrium electrode potential for a half-cell electrochemical reaction at non-standard state conditions to that at the standard state [30]. In Eq. (1.5), \( E_e \) is the equilibrium electrode potential at non-standard state conditions, \( R \) is the universal gas constant (8.314 J K\(^{-1}\) mol\(^{-1}\)), \( T \) is the absolute temperature (K), and \( a_{ox} \) and \( a_{red} \) represent the activities of oxidants and reductants, respectively.

\[ E_e = E^o + \frac{RT}{nF} \ln \left( \frac{a_{ox}}{a_{red}} \right) \]  

For an overall electrochemical reaction, as expressed in reaction (1.6), the equilibrium potential is given by the Nernst equation, Eq. (1.7),
\[ aA + bB \leftrightarrow cC + dD \]  \hspace{1cm} (1.6)

\[ E_e = E_0 + \frac{RT}{nF} \ln \left( \frac{a_A^{a}a_B^{b}}{a_C^{c}a_D^{d}} \right) \] \hspace{1cm} (1.7)

in which \( Q \) is the reaction quotient, and a measure of how far from the standard state the environment is.

\[ Q = \frac{a_C^{c}a_D^{d}}{a_A^{a}a_B^{b}} \] \hspace{1cm} (1.8)

Commonly, a Pourbaix diagram is used to summarize the thermodynamic information for a corrosion system [30]. Such a diagram defines the zones of thermodynamic stability for the phases and various species involved in the corrosion process [32], and predicts whether corrosion is possible under specific potential and pH conditions [30]. These diagrams are defined by the Gibbs free energies of the species involved by the spontaneous direct ions of all the possible reactions. Figure 1.11 shows a typical Pourbaix diagram for the Cu/S/H₂O system at 25 °C [33]. The upper dashed line defines the equilibrium potential for the O₂/H₂O reaction as a function of pH [32], and the lower dashed line the equilibrium potential for the H₂/H₂O reaction as a function of pH [32]. The region between these two dashed lines defines the stability region of H₂O. Since

![Figure 1.11: Pourbaix diagram for the Cu/S/H₂O at 25 °C for a total sulphur concentration of 10⁻³ mol/kg and a total dissolved Cu concentration of 10⁻⁶ mol/kg [32]. The region between the upper and lower dashed line defines the stability region of water.](image)
parts of the stability region for copper sulphide (Cu₂S) is located beneath the H₂/H₂O line (at more negative potential than water reduction reaction), the spontaneous process with the formation of Cu₂S on Cu is thermodynamically favored in an anoxic and sulphide-containing aqueous environment.

1.2.2 Kinetics of Aqueous Corrosion

While thermodynamics describes the possibility and spontaneity for a reaction to proceed it does not provide information on the rate of a reaction. The rate of a reaction is described by kinetics [31], with the current measured at the prevailing potential representative of the kinetics of the electron transfer reaction. If there are no restriction exerted by either mass transport or passivity, the reaction is said to be under activation control. The rate-determining step under activation control is the electron transfer reaction at the metal/solution interface [29]. Commonly, current (I) is converted to current density (i) if the surface area over which the current occurs is known.

At the equilibrium potential, the potential of a half-reaction is given by the Nernst equation, Eq. (1.5), and the forward/reduction and backward/oxidation reactions are occurring at the same rate, resulting in a net zero current or current density, reaction (1.9) in any external measurement circuit. This current density of either the forward or backward reaction is defined as the exchange current density (i₀), reflecting the intrinsic rate of a reversible redox reaction. This exchange current density of the forward/reduction reaction is equal but opposite in sign with that of the backward/oxidation reaction, as expressed in Eq. (1.10).

\[
\begin{align*}
Ox + e^{-} & \stackrel{(k_c)}{\rightleftharpoons} \text{Red} \\
i_{\text{net}} &= i_{a0} + \left| -i_{c0} \right| = 0
\end{align*}
\]

(1.9)

(1.10)

When a metal is freely corroding in an electrolyte, the corrosion process will polarize both half-reactions away from their equilibrium potentials, resulting in a current response. Polarization is the potential change from the equilibrium potential to the corrosion potential (E_{corr}). The amount of polarization is represented as an over-potential (\(\eta = E - E_{eq}\)) [34]. A positive current will be generated for the anodic half-reaction, and a negative current for the cathodic half-reaction. These currents are equal and opposite in
sign [30], and the corrosion current ($I_{\text{corr}}$) is given by Eq. (1.11). This current can be converted into an equivalent mass loss using Faraday’s Law, Eq. (1.12), in which $m$ is the mass of the metal in gram, and $M$ is the molar mass of the metal in gram/mole.

\[ I_{\text{corr}} = I_a = \left| -I_c \right| \quad \text{(1.11)} \]

\[ I = \frac{nFm}{Mt} \quad \text{(1.12)} \]

The current density of the forward/reduction reaction (1.9) can be expressed by Eq. (1.13), in which $k_c$ is the rate constant of the forward reaction, and $C_{\text{ox}}$ is the surface concentration of the oxidant at time $t$.

\[ i_c = nFk_cC_{\text{ox}} \quad \text{(1.13)} \]

Since an electron transfer process requires an activation energy and the rate of this process is exponentially related to $\Delta G$ [30], the rate constant of the forward/reduction reaction can be then expressed by the Arrhenius form, Eq. (1.14). A similar expression can be derived for the backward/oxidation reaction from reaction (1.9), given by Eq. (1.15), where $\alpha_a$ and $\alpha_c$ are the transfer coefficients of the backward and forward reactions, a measure of the reaction symmetry (taken to be 0.5 for simple electron transfers [30], with $\alpha_a + \alpha_c = 1$).

\[ k_c = k_0 \exp \left( -\frac{\alpha_cF}{RT} (\eta) \right) \quad \text{(1.14)} \]

\[ k_a = k_0 \exp \left( \frac{(\alpha_a)F}{RT} (\eta) \right) \quad \text{(1.15)} \]

Combining Eq. (1.13), (1.14), and (1.15), yields the current-potential relationship termed the Butler-Volmer equation, Eq. (1.16) [29]. This relationship only applies when the reaction is activation controlled and not influenced by transport processes. Under these conditions, the concentrations of the redox-active species are equal to the concentrations in the bulk solution [31].

\[ i = i_0 \left[ \exp \left( \frac{(1-\alpha)nF\eta}{RT} \right) - \exp \left( -\alpha nF\eta \right) \right] \quad \text{(1.16)} \]

In a corrosion reaction, when both half-reactions are polarized away from their equilibrium potentials to the corrosion potential ($E_{\text{corr}}$), charge balance is achieved between the anodic and cathodic half reactions. The kinetics of a freely corroding system is described by mixed potential theory, in which at least one anodic and one cathodic reaction
are coupled, with the current-potential relationship described by the Wagner-Traud equation [35].

\[ i = i_{corr} \left[ \exp \frac{\alpha_A nF(E-E_{corr})}{RT} - \exp \frac{-\alpha_C nF(E-E_{corr})}{RT} \right] \]  

(1.17)

In Eq. (1.17), \( \alpha_A \) and \( \alpha_C \) are the transfer coefficients of the anodic and cathodic half-reactions, respectively. The value of 0.5 is commonly adopted for the transfer coefficient, since the symmetry of the barrier is generally unknown [29]. The term \( E-E_{corr} \) is the difference between an externally applied potential and \( E_{corr} \). When the applied potential is equal to zero, the corrosion reaction will occur at \( E_{corr} \).

Figure 1.12: A schematic showing the individual current-potential relationships for the reversible half reactions and their sum yielding the current-potential relationship for the coupled corrosion process represented by the Wagner-Traud equation. As shown, the anodic reaction has a large \( i_0 \) compared to the cathodic reaction and, hence, determines the position of \( E_{corr} \). The anodic half of the metal dissolution/deposition reaction is denoted by the green curve, the cathodic half of the other redox reaction (reduction reaction) is denoted by the orange curve, and the \( E_{corr} \) is the intersections between a horizontal line for zero current density and Wagner-Traud current-potential curve, denoted by a purple arrow.
Figure 1.12 shows the two current-potential relationships, defined by the Butler-Volmer equation, for a reversible metal dissolution/deposition reaction \( M \rightleftharpoons M^{n+} + ne^- \) and a redox reaction for a potential oxidant \( Ox + ne^- \rightleftharpoons Red \). In this figure, \((E_e)_{M^{n+}/M}\) and \((E_e)_{Red/Ox}\) are the respective equilibrium potentials, as defined by equation 1.5, and \((i_0)_{M^{n+}/M}\) and \((i_0)_{Ox/Red}\) are the respective exchange current densities. These two reactions couple at the \( E_{corr} \) to yield an overall corrosion reaction \( M + Ox \rightarrow M^{n+} + Red \) providing the condition in (Eq. (1.18)) is met.

\[
(E_e)_{M^{n+}/M} < E_{corr} < (E_e)_{Ox/Red} \quad (1.18)
\]

When the currents from Butler-Volmer equations are added, they generate the Wagner-Traud equation, Eq. (1.17), for the overall corrosion reaction involving dissolution of the metal and reduction of the oxidant. At \( E_{corr} \), the current for metal dissolution \((i_a)\) and oxidant reduction \((i_c)\) are equal and opposite in sign.

### 1.3 Literature Review of Cu Corrosion

#### 1.3.1 Relevant Thermodynamic Data for Cu Under Disposal Conditions

The relevant thermodynamic data for Cu under DGR conditions has been thoroughly investigated and is commonly summarized in Pourbaix diagrams [36] and sometimes obtained from quantum-mechanical calculations (based on density functional theory and linear response theory) [37]. Despite the presence of various groundwater species and oxidants, it is generally acknowledged that dissolved oxygen \((O_2)\), chloride \((Cl^-)\) and sulphide \((SH^-)\) are the chemical species which will have the largest influence on the thermodynamic stability of Cu in a DGR environment [36]. This section reviews the relevant thermodynamic data for Cu in the presence of these species and outlines the thermodynamic properties of cuprous oxide, cupric oxide, cuprous hydride, cupric hydride, cuprous oxy-hydride, cuprous hydroxide based on theoretical calculations.

Pourbaix diagrams of Cu in pure water are plotted in Figure 1.13 [36], and show that Cu is thermodynamically stable over the entire pH range at 25 °C and 100 °C when dissolved \(O_2\) is not present. However, it is possible for metallic Cu to form either soluble ions or oxides in the presence of \(O_2\). Although not shown in Figure 1.13 (b), there is a
slightly possibility that Cu could dissolve as Cu\(^+\) in more acidic conditions (pH < 2) when the temperature is at 100 °C. However, such conditions are not anticipated in a DGR.

Figure 1.13: Poubaix diagrams for Cu in pure water at (a) 25 °C and (b) 100 °C. [Cu]\(_{\text{total}}\) = 10\(^{-6}\) mol/kg [34].

Chloride ions, one of the predominant groundwater species, can influence the corrosion of Cu by the formation of aqueous complexes and solid phases [33]. Figure 1.14 shows the stability fields of various Cu species in aqueous chloride solutions [38]. In the absence of dissolved O\(_2\), copper is thermodynamically stable in chloride containing environments over the majority of the pH range. The corrosion of Cu by the reduction of H\(_2\)O to form soluble coppee-chloro complexes (CuCl\(^-\)) is possible at a high chloride concentration of 1 mol/L but only when the pH approaches almost 0, Figure 1.14 (b). The occurrence of such a low pH is unrealistic in a DGR. The formation of various Cu compounds, such as cuprous oxide (Cu\(_2\)O), copper-chloro complexes, cupric oxide (CuO), and CuCl\(^+\) are thermodynamically possible when dissolved O\(_2\) is present. It is also noticeable that the stability region of CuCl\(_2\):3Cu(OH)\(_2\) becomes distinct when the [Cl\(^-\)] is increased from 10\(^{-3}\) to 1 mol/L. The formation of botallackite (CuCl\(_2\):3Cu(OH)\(_2\)) could occur by the precipitation of dissolved Cu(II), formed by the homogeneous oxidation of Cu(I) in the presence of O\(_2\). It has also been suggested that botallackite can form via the oxidation of an underlying Cu\(_2\)O film on the Cu surface [38].
Figure 1.14: Pourbaix diagrams of Cu in chloride solutions at 25 °C.
(a) [Cl\textsuperscript{−}] =10\textsuperscript{−3} mol/L and (b) [Cl\textsuperscript{−}]=1 mol/L [36].

Figure 1.15 shows a set of Pourbaix diagrams for the Cu-Cl-H\textsubscript{2}O system at various solution temperatures, ranging from 25 °C to 100 °C [39]. The neutral solution pH (npH) is indicated by the vertical dashed line, Figure 1.15. The possibility of Cu corrosion becomes more likely at the high [Cl\textsuperscript{−}] (1.5 mol/L) as temperature increases from 25 °C to 100 °C. In particular, in the absence of dissolved O\textsubscript{2}, Cu is more susceptible to corrosion in the pH range of 0 to 5 with the formation of copper-chloro complexes (CuCl\textsubscript{2}\textsuperscript{−} or CuCl\textsubscript{3}\textsuperscript{2−}) by increasing the temperature. Despite the increasing possibility of Cu corrosion with the increase in temperature, Figure 1.15, the occurrence of an acidic aqueous environment is less anticipated in the DGR conditions.

Thermodynamic properties of Cu compounds have been derived using first-principles calculations of the electronic structure and phonon-spectra for the oxides, hydrides and oxy-hydrides of Cu [37]. The calculations of electronic structures are based on density function theory (DFT) while applying the generalized gradient approximation [37]. The formation energies of these compounds were calculated at the absolute temperature of 0 K and room temperature, and agrees well with current existing thermodynamic data. The calculated results suggest that cuprite oxide is the most stable species among the examined Cu (I) compounds, and the cuprous oxy-hydride, cuprous hydride and cuprous hydroxides are found to be metastable [37].
The Active Dissolution of Cu in Chloride Solutions

Although Cu will be thermodynamically stable once anoxic conditions are established in a DGR, a great deal of evidence has been published to show that corrosion of Cu when O₂ is present will be strongly influenced by the presence of Cl⁻ [38]. Chloride ions stabilize dissolved Cu (I) in the form of complex anionic species, such as CuCl₂⁻ and CuCl₃²⁻. When Cl⁻ is present, the active dissolution of Cu proceeds by a series of electrochemical and chemical reactions [38].

$$\text{Cl}^- \rightarrow \text{Cl}_{\text{ads}}$$  \hspace{1cm} (1.19)
\[
\text{Cu} + \text{Cl}^- \rightarrow \text{CuCl}_{\text{ads}} + e^- \quad (1.20)
\]
\[
\text{CuCl}_{\text{ads}} + \text{Cl}^- \rightarrow \text{CuCl}_2 (\text{surface}) \quad (1.21)
\]
\[
\text{CuCl}_2 (\text{surface}) \rightarrow \text{CuCl}_2 (\text{bulk}) \quad (1.22)
\]

where “surface” indicates the solution at the Cu surface and “bulk” is the solution remote from the Cu surface.

The first step in Cu corrosion is the adsorption of anions [40] (in this case Cl\(^-\) ions). This is followed by the electrochemical formation of CuCl\(_{\text{ads}}\). This adsorbed CuCl\(_{\text{ads}}\) species forms at a potential more negative than that predicted thermodynamically for CuCl [35]. The rate-determining step in this sequence of reactions is proposed to be the mass transport of soluble CuCl\(_2^-\) from the surface to the bulk solution in reaction (1.22) [38]. This mechanism has been shown to be valid over a wide range of [Cl\(^-\)] [41], ranging from 0.01 mol/L to 5 mol/L [41]. Depending on [Cl\(^-\)], the soluble complex formed can be either CuCl\(_2^-\) or CuCl\(_3^{2-}\) the dominant complex at [Cl\(^-\)] \(\geq 1\) mol/L [41].

The formation of cuprous oxide can also occur during the active dissolution of Cu in chloride solutions by the hydrolysis of both CuCl\(_{\text{ads}}\) and CuCl\(_2^-\) [38].

\[
2\text{CuCl}_2 + \text{H}_2\text{O} \rightarrow \text{Cu}_2\text{O} + 2\text{H}^+ + 4\text{Cl}^- \quad (1.23)
\]
\[
2\text{CuCl} + \text{H}_2\text{O} \rightarrow \text{Cu}_2\text{O} + 2\text{H}^+ + 2\text{Cl}^- \quad (1.24)
\]

In alkaline solutions containing Cl\(^-\), the formation of Cu\(_2\)O can also occur by the competition between Cl\(^-\) and OH\(^-\) for surface adsorption sites [41].

\[
\text{CuCl}_{\text{ads}} + \text{OH}^- \rightarrow \text{Cu(OH)}_{\text{ads}} + \text{Cl}^- \quad (1.25)
\]
\[
2\text{Cu(OH)}_{\text{ads}} \rightarrow \text{Cu}_2\text{O} + \text{H}_2\text{O} \quad (1.26)
\]

### 1.3.3 Sulphide-Induced Cu Corrosion

#### 1.3.3.1 Sulphide Chemistry in a Repository

The sulphide-induced corrosion of Cu is thermodynamically favourable under anoxic condition, as shown in Pourbaix diagram for the Cu/S/H\(_2\)O at 25 °C, Figure 1.11. This demonstrates that Cu corrosion is unavoidable if sulphide is present in the proximity of the container surface. Once the entrapped O\(_2\) is depleted, and anoxic conditions are established, sulphide becomes the key oxidant. This has been depicted in the evolution of redox conditions in the DGR, Figure 1.3.

Sulphide will be dominantly produced by microbial activity involving sulphate-reducing bacteria (SRB) in locations remote from the container in the DGR environment,
as discussed above in section 1.1.3. Except for the production of sulphide, sources of sulphur, including sulphate, may be added to the DGR by the inflowing groundwaters and additional sources located within the buffer and backfill [10,14].

Sulphide could exist as either hydrogen sulphide (H₂S) or the bisulphide ion SH⁻ in the DGR environment. The chemical equilibrium between H₂S (g) and SH⁻, reaction (1.27), indicates that the concentrations of H₂S and SH⁻ are approximately equal in neutral (pH 7) solutions.

$$H_2S (g) \leftrightarrow H_2S (aq) \leftrightarrow SH^- + H^+ \quad K_a (298.15 \text{ K}) \approx 10^{-7} \quad (1.27)$$

When the repository is only partially saturated, sulphide may exist in three chemical forms, H₂S (g), H₂S (aq) and SH⁻. The distribution among these chemical species depends on temperature, system pressure and the pH of the aqueous environment, which can be expressed by Henry’s Law [10]. The solubility of H₂S (g) in water can be calculated using Henry’s law with the Henry’s Law constant given by, $H = [H_2S(aq)] / P_{H_2S} \approx 1 \times 10^{-3}$ mol/(m³ Pa) ≈ 0.1 mol/(L bar) [10]. This enables the calculation of the partitioning of sulphide between the gas phase in the pores of the bentonite buffer and the porewater.

It is reported that during the early oxic phase in a repository, sulphides will be quickly oxidized to sulphate (SO₄²⁻) through abiotic processes [10]. Despite this consumption of O₂ via sulphide oxidation, the aerobic corrosion of the Cu container will consume some of the initially trapped O₂, leading to the formation of Cu oxides. In addition, O₂ will be consumed by several other routes, i.e., microbial and mineral reactions occurring in the bentonite clay compacted around the container, and corrosion of structural steel within the repository [15].

However, these oxides are thermodynamically unstable in sulphide-containing environments ($\Delta_f G^0 = -101.46 \text{ kJ/mol}$ for the conversion from Cu₂O to Cu₂S in sulphide solutions at 298 K [42]), making their conversion to sulphides highly probable [43–45]. Once this conversion is complete, sulphide-induced corrosion of Cu is expected to be controlled by the supply (mass transport) of sulphide from remote locations to the Cu container surface [10].

Once the anoxic and partially saturated conditions are achieved in the DGR, H₂S will no longer be oxidized. In general, the time to reach anoxic conditions will be much
shorter than the saturation time for the buffer, which, while uncertain, is expected to range from a few tens to a few thousands of years [10].

1.3.3.2 Sulphate-Reducing Bacteria

Sulphate reduction reactions can occur via two routes involving thermochemical and biotic sulphate reduction processes [10,46]. However, the thermochemical process is considered insignificant compared to the biotic reduction process due to its low probability at temperature < 100 °C and its very low reaction rate compared to the biotic pathway [43].

The sulphate reduction reaction expected to prevail in a DGR is dominantly a microbiological process [10]. Oxidized sulphur compounds, such as sulphate can function as electron acceptors for the anaerobic respiration of organic matter by sulphate-reducing bacteria (SRB), resulting in the production of hydrogen sulphide (H₂S) or bisulphide ions (SH⁻). The energy supply and electron donor for SRB can be either organic compounds or hydrogen (H₂). Common organic compounds utilized by SRB are fermentation products like short chain organic acids, fatty acids and higher molecular weight hydrocarbons [46]. Some of the reactions that are associated with sulphate reduction reactions via SRB are shown in reactions (1.28) and (1.29).

\[
SO_4^{2-} + 2CH_2O + 2H^+ \rightarrow 2HCO_3^- + SH^- + 3H^+ \quad (1.28)
\]

\[
2H^+ + SO_4^{2-} + 4H_2 \rightarrow 4H_2O + H_2S \quad (1.29)
\]

Hydrogen is used by almost all species of sulphate reducing bacteria whereas use of other electron donors, such as lactate, acetate, fumarate, propionate is more restricted [10].

1.3.3.3 Corrosion Studies of Cu and Cu Alloys in Aqueous Sulphide Solutions

A number of corrosion studies have investigated the role of sulphide on the behaviour of Cu and Cu alloys. Most of these studies are associated with the corrosion in polluted seawaters, which are common in marine heat exchangers and boat hulls [38,47,48]. Aggressive corrosion was observed in some of these applications when alternating oxidizing and reducing conditions prevailed, scenarios unrepresentative of anticipated DGR conditions.

Syrett investigated the corrosion rates and characterized the corrosion products on Cu-Ni alloys in sulphide-polluted seawaters [47]. In this study [47], polarization resistance
was monitored on a 90:10 Cu:Ni alloy as a function of time for various exposure conditions, and showed that deaerated, sulphide-polluted seawater did not cause accelerated corrosion of the Cu alloy. An increase in corrosion rate was observed only when the polluted environment was replaced by aerated, unpolluted seawater. It was suggested that sulphide could precondition the alloy surface, thereby inhibiting the growth of a protective oxide film [47]. Pre-exposure (up to 2 days) to deaerated sulphide polluted seawater was found to accelerate the corrosion of Cu alloys for another 5 days in aerated, unpolluted seawater [46], suggesting the destabilization of Cu in the presence of sulphide. Eventually, the corrosion rate, as indicated by the polarization resistance \( 1/R_p \), returned to low values at the end of the experiment. The growth of a thin \( \text{Cu}_2\text{O} \) film was observed when the alloy was pre-exposed to the sulphide polluted seawater. XRD analyses also confirmed the growth of a thin \( \text{Cu}_2\text{O} \) during the short-term experiments in deaerated sulphide solutions and the presence of both stoichiometric (\( \text{Cu}_2\text{S} \)) and non-stoichiometric copper sulphide (\( \text{Cu}_{1.8}\text{S} \)) at the outer layer of films after longer exposure durations. Syrett also proposed that the corrosion reaction was limited by the diffusion of protons to cathodic sites located at the \( \text{Cu}_2\text{O}/\text{Cu}_x\text{S} \) interface, and the thickening of the film was due to the migration of \( \text{Cu}^+ \) through the \( \text{Cu}_x\text{S} \) layer [47]. The corrosion rate was observed to accelerate after the introduction of aerated solution. It was proposed that the reduction of oxygen occurred at a much faster rate than proton reduction, thereby accelerating the corrosion. It was then claimed that corrosion proceeded via \( \text{Cu}^+ \) migration through the \( \text{Cu}_x\text{S} \) layer to form \( \text{Cu}_2\text{O} \) and the conversion of \( \text{Cu}_x\text{S} \) to \( \text{Cu}_2\text{O} \) was observed over time, which appears to be contrary to thermodynamic expectations [43]. Overall, corrosion was maintained at a normal and low rate without the further addition of sulphide to the aqueous environment.

In another study, Mor and Beccaria investigated the influence of low concentrations of sulphide (30 – 50 ppm) on the corrosion of Cu in artificial seawater for both aerated and deaerated conditions in the pH range 6.5 to 8.6 [49]. The corrosion rate was determined from weight loss measurements and showed that the extent of corrosion decreased with increasing pH when sulphide was absent, but increased when sulphide was present. They calculated the concentrations of \( \text{SH}^- \) and \( \text{S}^{2-} \) over the pH range tested and claimed that the \( \text{SH}^- \) concentration remained constant while the \( \text{S}^{2-} \) concentration changed by a factor of a 1000 [49]. Based on this calculation they attributed, the increase in corrosion rate was
attributed to the aggressiveness of $S^{2-}$ ions, although the $S^{2-}$ concentration was approximately $10^8$ that of $SH^-$. More recent calculations show $S^{2-}$ is unlikely to exist for pH values less than 14 [50], and the observed increase in corrosion rate can be more appropriately attributed to the aggressiveness of $SH^-$. An observed decrease in $E_{corr}$ was attributed to the destabilization effect of sulphide on Cu and no appreciable change in $E_{corr}$ was observed when $SH^-$ and $O_2$ were simultaneously present. It was found that a $Cu_2S$ film formed initially after 2 hours of corrosion and was followed by the development of a more complicated second layer comprised of $CuS$, $Cu_2O$ and $CuO$ at longer times, as indicated by potential-pS plots [49]. The presence of these phases was confirmed by XRD. The authors proposed that the formation of the second layer was via $S^{2-}$ diffusion through a porous $Cu_2S$ base layer. Non-stoichiometric copper sulphides were also identified by XRD analyses of samples that were corroded at pH > 8.

The effect of sulphide on the corrosion of Cu in aerated NaCl solutions was investigated by Rahmouni et al. [51]. A wide range of techniques, including $E_{corr}$, electrochemical impedance spectroscopy (EIS), and galvanostatic film stripping measurements were employed to examine the influence of the addition of sulphide on corrosion in 3% NaCl solutions [51]. The $E_{corr}$ indicated that a protective copper oxide covered the surface when sulphide was absent. However, $E_{corr}$ shifted to more negative potentials (active direction) upon the addition of sulphide (at a concentration of $3.2 \times 10^{-5}$ mol/L). EIS data obtained in the presence of sulphide was fitted to a two-time constant equivalent circuit containing two capacitive loops and interpreted as indicating the presence of a porous film, suggesting that the initially grown protective oxide had been breached. The polarization resistance decreased with time in the presence of sulphide while the film capacitance values increased, suggesting an increase in corrosion rate accompanied by the growth a thicker surface film. Galvanostatic film stripping measurements were conducted on completion of the experiments and demonstrated two potential plateaus, which were attributed to the reduction of both $Cu_2O$ and $Cu_2S$. It was suggested that corrosion was accelerated when $OH^-$ and $SH^-$ were simultaneously present in the aqueous solution [51].

The corrosion of Cu in alkaline sulphide solutions was studied by Abd El Haleem et al. [52]. Corrosion potentials were measured in aerated NaOH in the absence and presence of sulphide. It was concluded that Cu acted as a metal/metal oxide electrode in
the absence of sulphide in the aqueous environment [52]. The formation of copper oxides was still favoured when low sulphide concentrations were present (< $10^{-4}$ mol/L). However, $E_{\text{corr}}$ of Cu altered between passive and active states at an intermediate sulphide concentration, $10^{-3}$ mol/L, while at the highest concentrations ($>10^{-3}$ mol/L), the formation of Cu$_2$S was predominant. The authors also observed that the attainment of a steady-state $E_{\text{corr}}$ was achieved when Cu electrodes were immersed in more concentrated sulphide ((> $3\times10^{-3}$ mol/L) solutions, and appeared to follow a $-60$ mV/decade dependence on $S^{2-}$ concentration.

$$E = E^0 - 0.059 \log[S^{2-}] \text{ (vs SCE)} \quad (1.30)$$

Although Abd El Haleem proposed that [52] $E_{\text{corr}}$ was governed by the redox potential for the anodic formation of copper sulphide (Cu$_2$S), contradictory claims were made as to whether $E_{\text{corr}}$ was determined by the relative rates of the anodic and cathodic reactions (proton reduction reaction). Other studies also showed similar observations, but drew slightly different conclusions [53]. In the studies conducted by De Chialvo and Arvia [53], the authors proposed that $E_{\text{corr}}$ was controlled by the anodic formation of Cu$_2$S, reaction (1.31). It was proposed that $E_{\text{corr}}$ was determined by the $[S^{2-}]$, as indicated in Eq. (1.32).

$$Cu + S^{2-} \rightarrow Cu_2S + 2e^- \quad (1.31)$$

$$E_1 = -1.132 - 0.0295 \log[S^{2-}] \text{ (vs SCE)} \quad (1.32)$$

In contrast, Mor and Beccaria proposed that the dependence of $E_{\text{corr}}$ on $[\text{SH}^-]$ was to be $-30$ mV/decade for short-time exposure periods, but appeared to be a mixed potential with more consistent values over time ($-40$ to $-60$ mV/decade) [49]. King et al. [38] also suggested that $E_{\text{corr}}$ is more likely to be a mixed potential as a result of the coupling of the anodic dissolution of Cu and the cathodic reduction reaction of SH$^-$ rather than a potential determined predominantly by the equilibrium potential for one of the half reactions involved.

Syrett investigated the corrosion of Cu in inflowing water contaminated with both oxygen and sulphide under both stagnant and rotating disk electrode (RDE) conditions [54]. The primary goal was to examine whether the presence of sulphide and/or oxygen can significantly influence the corrosion rate of Cu. It was shown that the corrosion rate in anoxic sulphide solutions was similar to that recorded in oxic, sulphide-free solutions [54].
However, corrosion was accelerated when both oxygen and sulphide were present. It was proposed that this significant increase in corrosion rate was due to the enhancement of the anodic reaction (Cu to Cu$_2$S) facilitated by the cathodic reduction of dissolved O$_2$. XRD analyses confirmed the growth of chalcocite (Cu$_2$S) films that were thought to inhibit the formation of a highly protective copper oxide.

Several studies directly relevant to corrosion of Cu in either simulated underground conditions or DGR conditions have been conducted [33,55–57]. Tran et al. studied the atmospheric corrosion of Cu with hydrogen sulphide in underground conditions [55]. Corrosion was monitored during field tests at various [SH$^-$] for periods up to 77 days, and in short-time exposure tests in a synthetic atmosphere condition at 20 °C. Coulometric reduction was applied to estimate the average thicknesses of Cu oxide and sulphide films. It was concluded that three successive phases of film growth occurred. The first phase was characterized by a linear growth rate of a thin layer, with the growth rate of oxides slowed in the second phase due to the rate limiting diffusion of Cu (I) cations through a thick corrosion layer. Finally, a accelerated linear rate was achieved during the third phase once the growth of copper sulphide initiated [55]. It was also concluded that the growth rates of oxides and sulphides were correlated, and an overall enhanced film growth rate was attributed to the presence of Cu$_2$S due to its good ionic conductivity resulting from the defectiveness of sulphide films [54].

Escobar at el. investigated Cu corrosion in simulated groundwaters containing sulphide at various temperatures ranging from 15 to 90 °C [57]. A significant destabilization of Cu was indicated by low $E_{corr}$ values in the presence of sulphide. An increase in the corrosion rate of Cu was observed by conducting Tafel analyses, showing that the corrosion current density increased as the sulphide concentration and temperature increased.

King and Stroes-Gascoyne performed a simulation of Cu corrosion in a chloride and sulphide solution while following the evolution of repository redox conditions [58]. The $E_{corr}$ shifted to more negative values as conditions evolved from oxic to anoxic. A 500 mV decrease in $E_{corr}$ was observed after the addition of sulphide, with values between −0.8 to −1.0 V vs SCE achieved depending on the concentration of sulphide. A similar drop in potential was observed when the experiment was repeated on a stationary, but clay-covered
Cu electrode. However, a delayed response was observed, indicating a slower mass-transport due to the presence of the clay. Kosec at el. also studied Cu corrosion in simulated aerated groundwater with and without added bentonite clay for both sulphide-containing and sulphide-free solutions [59]. In the bentonite-free solution, the early corrosion behaviour was affected by the presence of sulphide, leading to the formation of Cu$_2$S that could initially partially passivate the Cu surface. However, Cu$_2$S or S species were no longer detectable after 6 weeks of exposure to aerated simulated groundwater, suggesting oxidation of sulphide to sulphate which eventually led to the formation of surface layers comprising Cu$_2$O and atacamite (Cu$_2$(OH)$_3$Cl). When a bentonite slurry was present in the solution, the corrosion rate was significantly decreased, indicating that the rate-determining reaction was governed by the transport of O$_2$ from bulk solution through surface layers to the Cu surface.

Extensive studies have been performed by Chen et al. to investigate the corrosion of Cu in anoxic chloride and sulphide solutions under stagnant conditions in an anaerobic chamber (glovebox) [43,60–65]. The properties of Cu sulphide films were examined using $E_{corr}$ and EIS measurements, scanning electron microscopy (SEM) coupled with focused ion beam (FIB) cross-sectioning, and energy dispersive X-ray spectroscopy (EDX) in solutions containing various chloride and sulphide concentrations. The film growth kinetics were found to be dependent on [SH$^-$] [60,61], and in an anaerobic solution containing 5 x10$^{-4}$ mol/L sulphide and chloride of 0.1 mol/L, film growth appeared to follow a parabolic law and formed a thick, compact and crystalline Cu$_2$S film over an exposure time of 1691 h [60]. The authors proposed that film growth was dominantly controlled by Cu$^+$ diffusion in the film, but with a minor contribution to the film growth rate associated with SH$^-$ diffusion from bulk solution. It was proposed that the Cu$^+$ diffusion supporting film growth was along the crystalline grain boundaries in the Cu$_2$S film [60], although no supporting evidence was offered. When the sulphide concentration was 5 x 10$^{-5}$ mol/L, corrosion proceeded via the formation of a cellular and non-protective film with an approximately linear rate law and developed a porous morphology governed by SH$^-$ diffusion within the pores in the Cu$_2$S film. It was proposed that film growth occurred initially at the film/solution interface by the transport of Cu$^+$ through the cellular film, possibly as a CuCl$_2^-$ complex, and was later governed by SH$^-$ diffusion in the cellular matrix of the Cu$_2$S
film followed by SH\(^-\) diffusion from the bulk solution when sulphide became depleted at the film/solution interface [61].

To determine the rate-controlling reaction step governing sulphide film formation under anoxic conditions, experiments were conducted on Cu rotating disk electrodes to control the flux of SH\(^-\) [66]. It was observed that once SH\(^-\) was depleted at the film growth site, film growth became dependent on sulphide diffusion in the bulk solution [66]. It was shown that the film structure and growth kinetics were governed by the balance between SH\(^-\) diffusion from bulk solution and the interfacial reaction rate between SH\(^-\) and Cu [66]. When SH\(^-\) diffusion was rate determining, the copper sulphide film was porous and non-protective, confirming the formation of non-passive films. However, when the interfacial reaction was the rate-determining step, the sulphide film became compact and protective. It was also proposed that three critical parameters, the concentrations of SH\(^-\) and Cl\(^-\), the ratio between [SH\(^-\)] and [Cl\(^-\)], and the flux of SH\(^-\) to the Cu surface, determined whether a porous or a passive sulphide film would form on Cu [62]. It was observed that when the ratio of [Cl\(^-\)]/[SH\(^-\)] was ≥ 1000, a switch from compact to porous film growth occurred.

The influence of sulphide transport on the growth of copper sulphide films on Cu was also studied by Chen et al. [43] in a solution containing 5 \(\times\) 10\(^{-5}\) mol/L sulphide and 0.1 mol/L Cl\(^-\). Sulphide depletion experiments were performed in both stagnant and controlled-convective environments using stationary and rotating disk electrodes in an anaerobic chamber. The sulphide depletion rate (-dC/dt) and interfacial bisulphide concentrations were calculated under RDE conditions. It was observed that growth of a non-protective film was controlled by SH\(^-\) diffusion under stagnant conditions [43]. In the presence of accelerated sulphide transport, achieved using an RDE, sulphide film growth was initially governed by SH\(^-\) diffusion from bulk solutions. However, sulphide film growth was unaffected by solution transport of SH\(^-\) at longer times, demonstrating that the formation of a coherent film led to a switch from growth controlled by SH diffusion in solution to growth controlled by the solid-state diffusion of Cu\(^+\) in the film.

Chen et al. [67] also investigated non-uniform, micro/macro-galvanic corrosion in solutions containing sulphide and chloride by addressing the phenomenon of local and excess crystal growth, which provides evidence of both micro and macro-galvanic corrosion. Corrosion is rapid and can occur under transport-controlled condition in aqueous
sulphide solutions. They concluded that when the sulphide flux is sufficiently high, micro-
galvanic corrosion can occur and be supported between areas covered by compact sulphide deposits (net cathodes) and other areas covered by only but a porous sulphide film (net anodes). This resulted in a low corrosion rate at the net cathode but a faster rate at the net anode [67]. To identify the most probable transportable soluble Cu species associated with micro-galvanic corrosion, Chen et al. [65] conducted a set of electrochemical, corrosion and analytical experiments (UV-vis spectroscopy and mass spectrometry), which demonstrated that the predominant transported species during micro-coupled corrosion are copper sulphide complexes and particles, such as Cu$_3$S$_3$. The transport of Cu by complexes and particles has also been commonly observed in geologic studies [68,69].

**1.3.3.4 Electrochemical Studies of Cu in Sulphide Solutions**

An extensive study was conducted by Gennero De Chialvo and Arvia to investigate the electrochemical behaviour of Cu in alkaline solutions containing sulphide using potentiostatic polarization and cyclic voltammetric measurements under stagnant and RDE conditions [53]. The authors showed that the potential for copper oxide formation shifted to more positive values when sulphide was present, allowing the electrochemical separation of Cu sulphidization from oxide formation, enabling the electrochemical formation of copper sulphide to be studied in aerated aqueous sulphide solutions. The anodic formation of copper sulphides (Cu$_2$S, CuS) occurred at potentials close to the equilibrium potentials of Cu/Cu$_2$S and Cu/CuS, suggesting that the potential was controlled by the Cu/Cu(I) and Cu/Cu(II) redox couples [53]. It was claimed that voltammetric data demonstrated the initial formation of non-stoichiometric copper sulphide (Cu$_{1.8}$S) followed by formation of the stoichiometric sulphide (Cu$_2$S). At large overpotentials, the formation of CuS at the film/solution interface was claimed, leading to a dual-layer film structure [53]. However, no chemical compositional analyses were performed. It was proposed that anodic sulphide film formation occurred in two stages; (i) the adsorption of SH$^-$ resulted in the growth a monolayer of Cu$_2$S via a nucleation and growth mechanism as indicated by current-time transient measurements; and (ii) the subsequent oxidation of Cu led to the formation of a thick and homogenous CuS layer. The authors also claimed that the electrochemically grown copper sulphide enhanced the properties of the subsequent copper oxide formation,
resulting in the prevention of passivation by the accumulation of sulphur-containing species at surface defects which inhibited localized corrosion [53].

Vasquez Moll et al. made similar observations based on current transients recorded under potentiostatic and voltammetric conditions in deaerated alkaline sulphide solutions [70]. Two anodic oxidation peaks were attributed to the formation of both Cu (I) and Cu (II) sulphides, resulting in the formation of black, defective thin films. At more positive potentials, a region of oscillating current was observed and attributed to film breakdown and pitting of the Cu electrode due to the anodic formation of oxides at the large overpotentials. It was also found that the total charge associated with sulphide film formation increased by increasing the [SH\(^-\)], and additionally, the film break down potential shifted to more positive values by increasing the [SH\(^-\)].

The mechanism of film formation was analysed based on potentiostatic current-time transients for potentials associated with both sulphide and oxide film formation [70]. An early decrease in current was attributed to the rapid formation of a Cu\(_2\)S film. This was followed by a continuous increase in current to a maximum value. When the applied potential approached the film breakdown potential, large currents were observed at the shortest times. This behavior was attributed to the nucleation and formation of CuS since the breakdown potential was close to the equilibrium potential for Cu/CuS. It was claimed that the growth of CuS occurred at the base of pores in the initially grown Cu\(_2\)S films, leading to the partially passivated surface [70]. They also compared the film breakdown recorded under potentials between potentiostatic and voltammetric conditions, which indicated a decrease in the breakdown potentials when applying potentiostatic polarizations. It was proposed that more substantial film ruptures occurred under potentiostatic conditions, therefore, leading to the presence of a more defective CuS layer and the likelihood of pitting corrosion within the fractured sites.

Smith et al. studied the film growth mechanism in anoxic 0.1 mol/L NaCl solution containing [SH\(^-\)] ranging from 10\(^-\)5 to 10\(^-\)3 mol/L [71]. Using potentiostatic measurements, EIS and cyclic voltammetry, it was shown that the growth of sulphide films occurred rapidly on the Cu surface and was controlled by the mass transport of SH\(^-\) to the Cu electrode surface. In particular, at the high sulphide concentration (10\(^-\)3 mol/L), two distinct film growth pathways were claimed; (i) The initial film, which grew via Cu\(^+\) transport
through the film, could either remain intact, and hence become limited by a steady-state thickness, or (ii) the film could undergo fracture due to the development of large interfacial stresses, resulting in the growth of a thicker outer deposit above the initial film. Surface compositional analyses, such as XRD, confirmed that the Cu sulphide film formed under corrosion conditions was composed mainly of chalcocite (Cu$_2$S) with minor amounts of digenite (Cu$_{1.8}$S).

Smith et al. also investigated the electrochemical behaviour of pre-oxidized Cu in aqueous sulphide solutions using cyclic voltammetry (CV), cathodic stripping voltammetry (CSV), EIS and corrosion potential measurements [72]. The primary goal was to determine whether films formed during the initial repository oxic period can subsequently inhibit, and perhaps even prevent, the reaction of Cu with sulphide. Upon the addition of sulphide, 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) the complete conversion of the oxide to Cu$_2$S as indicated by a major transition in $E_{\text{corr}}$ to a value close to $E_e$ (Cu/Cu$_2$S). It was found that 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 indicated by EIS, when the SH$^-$ penetrated into the oxide, leading to its total conversion to Cu$_2$S. In addition, analysis of the cathodic charges required to reduce the oxide and sulphide films, obtained from CSV, showed this conversion from oxide to sulphide proceeded via chemical reactions with a complete conversion from oxide to sulphide with 100% efficiency observed.

More recent research conducted by Martino et al. [73] investigated the electrochemical behavior and film formation mechanism on Cu in a wide range of sulphide and chloride concentrations using RDE and CV. The authors showed that three distinct types of anodic sulphide films were formed depending on the solution conditions, (i) a single layer, porous film was formed at low sulphide concentrations ([SH$^-$] $<$ 10$^{-4}$ mol/L); (ii) a two-layer porous film formed at intermediate sulphide concentrations (5 $\times$ 10$^{-4}$ mol/L $<$ [SH$^-$] $<$ 2 $\times$ 10$^{-3}$ mol/L); and (iii) a compact and partial-passivating film was formed at high sulphide ([SH$^-$] $\approx$ 10$^{-3}$ mol/L) and high sulphide flux conditions. These observations [73] also suggested that the formation of a porous film prevailed when sulphide diffusion in solution was the rate-determining step, whereas the formation of a compact film occurred when the interfacial charge transfer reaction was the rate-determining step at high sulphide
flux conditions. These claims [73] proved consistent with observations in long-term corrosion experiments in anoxic sulphide solutions [43,61,66].

Martino et al. [74] also investigated the influence of film growth kinetics on the susceptibility of Cu to pitting in aqueous sulphide and chloride solutions. The location at which film growth occurred was studied by the deposition of a gold (Au) marker on pre-corroded Cu after 161 h. The same specimen was then re-immersed in a solution containing 0.1 mol/ L NaCl + 5 × 10^{-4} mol/ L Na_2S for a total exposure period of 1691 h [74]. It was found that the film growth occurred on the surface of the Au marker with the film thickness below the Au marker remaining unchanged, indicating that film growth occurred at the Cu_2S/solution interface and involved the solid-state diffusion of Cu^+ in the film associated with the formation of at least a partially protective film. A Levich analysis [29] was conducted to study the influence of Cl^− on the kinetics of the electrochemically grown film, and showed that the limiting current densities (i_L) obtained from CVs decreased with increasing [Cl^−], indicating the suppression of sulphide film growth by increasing [Cl^−]. This suppression of film growth was attributed to the access of Cl^− to the Cu surface, confirming that the Cu_2S was porous and not passive. In addition, the limiting currents obtained at various [Cl^−] were much smaller than the theoretically calculated limiting current densities, suggesting partial control of film growth by a chemical reaction step.

Studies have claimed that sulphide induced pitting would occur on Cu in deaerated sulphide solutions [75,76]. Mao et al. [75] investigated the influence of Cl^− on Cu in borate-buffered solutions containing 2 × 10^{-4} mol/ L [SH^−] in a wide range of [Cl^−]. Based on potentiodynamic polarizations, it was claimed that the Cu_2S film formed was passive and experienced breakdown at more positive potentials (E > −0.2 V vs SCE). It was also observed that the proposed breakdown potential decreased as the [Cl^−] increased. In a complementary study, Dong et al. [76] investigated the effect of temperature and observed a decrease in the proposed breakdown potential by increasing temperature. EDX maps, showed the accumulation of Cl^− at the Cu/Cu_2S interface when the applied potential exceeded this potential. It was claimed this local increase in [Cl^−] at the Cu/Cu_2S interface was caused by film breakdown and collection of chlorides in the pits. Predictions by Dong et al. [76] suggested this pitting potential would shift to more negative values i.e.; the
initiation of pitting would become easier during the early and warm repository period, with the probability of pitting decreasing as the repository cooled down.

More recent studies by Kong et al. [77–80] further investigated the supposedly passive sulphide film under various electrochemical conditions. The influence of [SH\(^-\)] on the sulphide film formation was investigated using CV, EIS, X-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM) [77]. CV and XPS showed that the sulphide film formed on Cu was comprised of Cu\(_2\)S and CuS and its resistance obtained from EIS, decreased as [SH\(^-\)] increased. EIS and AFM measurements suggested that the sulphide layer thickness decreased as the concentration of Cl\(^-\) increased, leading to a decrease in film resistance [77]. It was claimed that the film exhibited p-type properties over the entire passive range, and that the number of defects increased as the sulphide concentration increased. This observation was thought to account for the higher growth and dissolution rates of the film. Kong et al. [78] also studied the growth of sulphide films on Cu in anaerobic sulphide solutions by electrochemical impedance spectroscopy, Mott–Schottky analysis, localised electrochemical impedance spectroscopy (LEIS) and scanning electron microscopy. It was proposed that the growth of a passive film on Cu followed a logarithmic law in anaerobic sulphide solutions under potentiostatic polarization, suggesting a diffusion-controlled sulphide film growth, which appeared to be inconsistent with the film formation based on the point defect model. As was claimed previously by Kong et al. [77], the p-type semiconductor properties were supposedly observed for the passive film formation.

The properties of sulphide film were further investigated in a wider range of Cl\(^-\) concentrations, 0.1 to 1 mol/L, and sulphide concentration, 5 \times 10^{-5} \text{ mol/L} to 1 \times 10^{-3} \text{ mol/L} using polarization scans, EIS, SEM and XPS [79]. It was claimed that, when [Cl\(^-\)]s were low (0 \text{ mol/L} \leq [Cl\(^-\)] \leq 0.1 \text{ mol/L}), no active-to-passive transition was observed in the potential ranging from \(-0.8 \text{ V}\) to \(-0.2 \text{ V}\) vs SCE in sulphide-containing solutions. However, an apparent passivation behavior occurred at more positive potentials (\(-0.2 \text{ V} < E < 0 \text{ V}\) vs SCE), suggesting the formation of passive oxides with the presence of OH\(^-\). The re-passivation, as represented by the second current density plateau, occurred after the proposed sulphide film breakdown event [77]. By contrast, when the Cl\(^-\) and sulphide concentrations were both high, re-passivation did not occur after the supposedly sulphide
film breakdown, leading to rapid Cu anodic dissolution [79]. In contrast to the observations of Dong et al. [76], the proposed pitting potential increased with temperature resulting in the growth of a thicker oxide film. 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 as temperature increased, despite the fact these two phases cannot be distinguished in the S 2p spectrum [77].

The properties of films grown electrochemically on Cu in a wide range of aqueous [SH$^-$] at potentials more positive than $E_{corr}$ were investigated by Martino et al [81]. The purpose of this study was to clarify the nature of the electrochemically grown films, to determine the possibility of the formation of a passive film, and equally importantly, to determine whether the properties of anodically grown films were similar to those formed by corrosion. The EIS measurements confirmed electrochemical film growth occurred in two distinct stages; (i) a thin and porous Cu$_2$S layer was formed at less positive potentials with film growth occurring at the Cu$_2$S/solution interface supported by Cu$^+$ transport; (ii) the development of an outer, thicker, and crystalline deposit was observed [81]. At higher sulphide concentrations, the overall film growth rate was controlled by the properties of this outer-layer deposit, confirming that the passivation of the surface by a coherent sulphide film did not occur. In conclusion, it was claimed that the film growth mechanisms under electrochemical and corrosion conditions were very similar. These results confirm previous claims that the formation of a passive sulfide film will only be possible at high [SH$^-$] and SH$^-$ flux, which is a condition that is not anticipated in the vicinity of waste containers in a DGR.

1.3.4 Raman Spectroscopy Studies of Oxides, Hydroxides and Sulphides on Cu

Raman spectroscopy has been widely used in this project to investigate the chemical compositions of corrosion products/films formed on Cu under electrochemical and corrosion conditions. It is a non-destructive technique that can be used ex-situ to analyse the copper sulphides, oxides and hydroxides. The Raman spectra of various copper oxides and hydroxides have been well characterized with most studies in relatively good agreement [82].
Hamilton et al. [82] investigated anodic films formed on Cu in situ in an alkaline environment using Raman spectroscopy coupled to an electrochemical cell. A 488 nm argon (Ar) laser was used to periodically record Raman spectra during an anodic scan (1 mV/s) in 0.1 mol/L sodium hydroxide (NaOH) solutions. The appearance and growth of a Raman peak at 649 cm\(^{-1}\) at small anodic overpotentials was attributed to the formation of Cu\(_2\)O based on standard spectra obtained on samples of pressed powder for Cu\(_2\)O, CuO and Cu(OH)\(_2\). At higher anodic overpotentials, the observation of a peak at 488 cm\(^{-1}\) was attributed to Cu(OH)\(_2\). A similar set of Raman spectra were collected in situ during a cathodic sweep in 0.1 mol/L NaOH solutions. It was found that the growth of a peak at 649 cm\(^{-1}\) was accompanied by the disappearance of the peak at 488 cm\(^{-1}\), suggesting the continuous formation of Cu\(_2\)O possibly by the reduction of Cu(OH)\(_2\) to Cu\(_2\)O at small cathodic overpotentials and the reduction of Cu\(_2\)O to Cu metal at larger overpotentials [82]. Although CuO was barely observed by Raman spectroscopy, it was suggested that peak associated with CuO was very weak, and that the observation of a weakening of the Cu\(_2\)O band at larger overpotentials could possibly be due to conversions of Cu\(_2\)O to CuO.

Chan et al. [83] observed similar results when studying the electrochemical formation and removal of copper oxides in aqueous media examined by combined voltammetric and surface-enhanced Raman spectroscopy (SERS) measurements. A set of in-situ SERS spectra was obtained at various applied potentials on Cu in 0.1 mol/L NaOH + 0.1 mol/L NaClO\(_4\) solutions. At more negative potentials (E = −1.0 V vs SCE), the featureless spectrum indicated a reduced Cu surface. However, when the potential was swept to −0.4 V vs SCE, the observation of two major vibrational bands at 525 and 625 cm\(^{-1}\) was attributed to the formation of Cu\(_2\)O. At more positive potentials (E > 0 V vs SCE), the Raman peak at 460 cm\(^{-1}\) was assigned to the formation of Cu(OH)\(_2\) by comparison with bulk-phase Raman spectra. However, in a SERS study by Niaura et al. [84] on Cu immersed in 0.1 mol/L NaOH under open circuit conditions, it was claimed that the Raman peaks at 460 and 525 cm\(^{-1}\) were associated with 1 and 2 coordinated OH\(^-\) adsorbed on bare Cu, respectively. Hartinger et al. [85] observed a SERS signal at 700 cm\(^{-1}\) under the electrochemical conditions, and attributed it to the stretching mode of adsorbed Cu-OH. It was also found that the intensity of this peak increased as the potential of the Cu electrode was incrementally changed from −0.9 to −1.4 V vs SCE.
More recent studies examined the artificial patinas formed on bronze under the simulated climatic conditions via Raman spectroscopy [86]. Raman spectra were collected using a 514 nm laser excitation line after chemical patination followed by exposure of the patina samples in a climatic chamber. The spectra showed that the bare bronze surface was covered with Cu$_2$O, identified by a broadband with several maxima between 400 and 700 cm$^{-1}$. The well-defined Raman band at 220 cm$^{-1}$ in the spectrum of the brown patina was characteristic of Cu$_2$O. The adsorbed oxygen species and some clinoatacamite (Cu$_2$(OH)$_3$Cl) were also observed on the bare bronze surfaces after exposure. Furthermore, the transformation of atacamite on the green patinated sample into clinoatacamite and paratacamite was observed. Cassiterite, Cu$_2$O (the native passive layer of Cu), clinoatacamite and a nitrate were found on the green nitrate patinated samples after a 12-week exposure in the climatic chamber [86].

Various other studies have claimed that the Raman spectrum of Cu$_2$O is comprised of a broad doublet in the range 490 to 650 cm$^{-1}$ [87–89]. Raman spectra of CuO obtained either on embedded nanoparticles or on commercially available powders using excitations of 488, 514 and 623 nm yielded consistent results [90–93]. CuO has characteristic Raman bands at 303, 350 and 636 cm$^{-1}$.

Compared to the abundance of Raman spectra associated with oxides and hydroxides, published Raman spectra of copper sulphides are few, with the reported signals widely variable. In a Raman spectro-electrochemical investigation of Cu$_x$S thin films deposited in a chemical bath, Munce at el. [94] recorded spectra of Cu$_x$S under various deposition conditions. Real-time electrochemical studies at various potentials and SERS studies were conducted using a 632.8 nm red excitation from a HeNe laser. Based on voltammetric measurements [94], at the starting potential (E = 0.1 V vs Ag/AgCl), no Raman features are observed despite the strong peak at ~ 300 cm$^{-1}$, which was attributed to the presence of a chalcocite film. However, a band associated with the S-S stretching mode and a Raman peak indicative of covellite (CuS) (~ 471 cm$^{-1}$) were observed as the positive-going sweep progressed. Spectra from the Database of Raman spectroscopy, X-ray diffraction and chemistry of minerals for mineral samples of chalcocite showed major bands for Cu$_2$S at ~210 cm$^{-1}$ and ~300 cm$^{-1}$. However, various other peaks associated with Cu$_2$S were reported between 400 and 700 cm$^{-1}$ [95].
Parker et al. and Smith et al. observed similar Raman peaks for Cu$_2$S [72,96]. In electrochemical experiments associated with leaching of chalcopyrite, Parker et al. [96] claimed the spectrum for chalcocite displayed a broad band at ~300 cm$^{-1}$ accompanied by a narrow signal at ~ 210 cm$^{-1}$ and the Raman peak of covellite contained a single sharp peak at ~ 475 cm$^{-1}$. Smith et al. [72] recorded Raman spectra in-situ on a Cu electrode that was preoxidized at −0.3 V vs SCE for a period of 1 h. Raman spectra were obtained periodically in a 10$^{-3}$ mol/L Na$_2$S + 0.1 mol/L NaCl solution for various exposure durations [72]. A strong Raman signal at ~ 300 cm$^{-1}$, attributed to Cu$_2$S, was observed after only 5 min exposure, with the intensity of the signal increasing only marginally with time, suggesting that the Raman signals detected were associated with the outermost layers of the film.

Several more recent studies for both Cu$_2$S and CuS have been published [97–100]. Colomban et al. [97] claimed peaks for Cu$_2$S appeared at 280, 350, and 472 cm$^{-1}$. However, Trzebiatowska et al. reported the peaks for Cu$_2$S and CuS were at 294 cm$^{-1}$ and 472 cm$^{-1}$. These values were consistent with peaks for covellite that were reported by Parker et al. [96], but not for chalcocite. Hurma and Kose [99] claimed the Raman peaks for covellite were at 68, 118, 266, and 322 cm$^{-1}$, while Adamou et al. [100] reported Raman bands of CuS at 474 cm$^{-1}$ only. It should be noted that the reported Raman spectra were not obtained at the same laser wavelength, which might have influenced the vibrational mode of various species. In addition, the spectra reported by Adamou et al. had a limited spectral window (200-600 cm$^{-1}$).

### 1.4 Physical and Electrical Properties of Copper Sulphide

The copper sulphide system is known to have many stable and metastable phases, which could co-exist at room temperature between the stoichiometrically-limiting Cu$_2$S and CuS [101–103]. Thermodynamic studies have shown that stability regions exist for, yarrowite (Cu$_{1.12}$S), spionkopite (Cu$_{1.4}$S), geerite (Cu$_{1.6}$S), anilite (Cu$_{1.75}$S), digenite (Cu$_{1.8}$S), djurleite (Cu$_{1.96}$S), chalcocite (Cu$_2$S), and for more oxidizing conditions, covellite (CuS) [36,68,104]. The formula for copper sulphides is generally written as Cu$_{2-x}$S since cation deficiency is the commonly reported defect in copper sulphides [105]. Of all the phases, the stability field for chalcocite (Cu$_2$S) extends to more negative potentials than that of the stability field for water and occupies the largest portion in the area representing
copper sulphides, thereby making it the phase anticipated under natural corrosion conditions [36]. This is demonstrated in Figure 1.16 [106], in which Cu₂S is the most stable phase expected to form in anoxic condition.

Figure 1.16: Pourbaix diagram of the Cu–O–S system, showing a number of stable regions for stoichiometric and non-stoichiometric CuₓS species [104]. [Cu]_{\text{total}} = 1 \text{ mmol/L}, \ [\text{SH}^{-}]_{\text{tot}} = 2 \text{ mmol/L}, \ \text{and} \ [\text{Na}^{+}] = [\text{NO}_3^{-}] = 10 \text{ mmol/L}.

Although the presence of covellite (CuS) is not uncommon, XPS and some x-ray absorption fine structure (EXAFS) studies have shown that Cu exists in its monovalent state in nearly all phases of copper sulphide [107–109]. In other words, when sulphide is present and under reducing conditions, Cu chemistry is always dominated by Cu (I) [68]. In an XPS study conducted by Folmer and Jellinek [107], the binding energies for Cu (2p) spectra were nearly identical in all CuₓS compounds and correspond to monovalent Cu. A slight binding energy shift in chalcogen-rich compounds was also observed and suggested the presence of S₂ pairs and two formulae. The overall CuS stoichiometries proposed were: Cu⁺₃(S₂)²⁻S⁻ or Cu⁺₃(S₂)⁻S²⁻ [107]. This is consistent with a recent analysis of Cu X-ray photoelectron spectra by Biesinger [110], and confirms the difficulty of distinguishing among copper sulphide species by analysing only Cu (2p) spectra. In spite of the difficulty of identifying copper sulphide species by only investigating Cu (2p) spectra, Biesinger demonstrated that sulphide phases can be distinguished from the combination of Cu (2p) spectra, Cu LMM Auger spectra, and the modified Auger parameter [110].
The crystal structures of copper sulphides are complex and dependent on their stoichiometry. The crystal structures of the CuₓS species can be divided into three types; hexagonal close packed (djurleite and chalcocite), cubic close packed (anilite and digenite), and hexagonal close packed with covalently bonded S atoms (covelite) [111]. Chalcocite, djurleite and digenite are found to have a monoclinic crystal structure at ambient temperature [102]. Some of these crystal structures are shown in Table 1.2 and Figure 1.17 [102]. It should be noted that the fully optimized structures of high-chalcocite and cubic-chalcocite Cu₂S are slightly distorted from the original crystal symmetry since the small cell size and partial occupation of the Wyckoff sites by randomly distributed Cu atoms [102].

Figure 1.17: Crystal structures of (a) the low-chalcocite (monoclinic), (b) high-chalcocite (hexagonal), (c) cubic-chalcocite (cubic), (d) djurleite, (e) digenite, and (f) anilite [100]. Blue sphere stands for the Cu atom and the yellow sphere represents the S atom.
Table 1.2: The calculated lattice parameters of CuₙS [100]

<table>
<thead>
<tr>
<th>x</th>
<th>Crystal system</th>
<th>a₀ (Å)</th>
<th>b₀ (Å)</th>
<th>c₀ (Å)</th>
<th>α (°)</th>
<th>β (°)</th>
<th>γ (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>Monoclinic</td>
<td>15.27</td>
<td>11.93</td>
<td>13.45</td>
<td>90</td>
<td>115.6</td>
<td>90</td>
</tr>
<tr>
<td>2</td>
<td>Hexagonal</td>
<td>7.87</td>
<td>8.19</td>
<td>13.36</td>
<td>90.7</td>
<td>90</td>
<td>118.5</td>
</tr>
<tr>
<td>2</td>
<td>Cubic</td>
<td>12.04</td>
<td>12.26</td>
<td>10.47</td>
<td>90</td>
<td>90.3</td>
<td>87</td>
</tr>
<tr>
<td>1.94</td>
<td>Monoclinic</td>
<td>13.53</td>
<td>15.95</td>
<td>29.95</td>
<td>90</td>
<td>116.7</td>
<td>90</td>
</tr>
<tr>
<td>1.8</td>
<td>Cubic</td>
<td>11.36</td>
<td>11.15</td>
<td>11.27</td>
<td>90.6</td>
<td>89.1</td>
<td>91.4</td>
</tr>
<tr>
<td>1.75</td>
<td>Orthorhombic</td>
<td>7.91</td>
<td>7.98</td>
<td>10.92</td>
<td>90</td>
<td>90</td>
<td>90</td>
</tr>
</tbody>
</table>

A significant ionic conductivity in the solid state is expected for copper sulphides which consist of small cations (Cu⁺) and large anions (S²⁻) [112,113]. It was proposed that the electrical conductivity of Cu sulphides was dependent on the mobility of small cations (Cu⁺) and the surface defects or disorders present in the crystal structure. Bucur and Berger conducted potentiometric experiments to determine the chemical diffusion coefficients of Cu (D_{Cu}) in chalcocite (Cu₂S) and digenite (Cu₁.₈S) [113], and the measured values were 1.8 × 10⁻⁸ cm²/s and 4.8 × 10⁻¹¹ cm²/s, respectively. The diffusion of Cu in copper sulphides was also investigated as function of x by Cassaignon et al. using electrochemical impedance spectroscopy [105]. The authors proposed that vacancy diffusion governed the Cu transport through copper sulphides. Despite the fact that the reported Cu vacancy concentrations in copper sulphides are on the order of 10⁻³ to 10⁻² mol/cm³, only a fraction of these vacancies were involved in the diffusion process. Copper sulphides are also known to be electronically conductive with electrons being 1000 times more mobile than cations [45]. It is also well-known that Cu₂S is a p-type semiconductor, with conduction attributed to free holes from acceptor levels of Cu vacancies [114]. 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 in most copper sulphide (Cu₂₋ₙS) phases [115]. A shift to the lowest occupied energy level and a change in band gap energy were observed as the value
of x increased, resulting in holes formed near the valence band. The reported bad gaps energy of for Cu$_2$S, Cu$_{1.8}$S and CuS are 1.2 eV, 1.5 eV and 2.0 eV, respectively [116].

1.5 Objectives and Scopes

The key objective of this thesis is to determine how corrosion damage will accumulate on Cu under anticipated DGR conditions. The research project has been focused on determining the properties of sulphide films (Cu$_x$S) formed in aqueous chloride and sulphide solutions, with the goal of determining how the films evolve and whether they could support pitting corrosion. The specific research goals are the following:

- To study the effect of mass transport on the properties of electrochemically-formed Cu$_x$S films in various aqueous sulphide environments similar to those anticipated in a DGR.
- To investigate the probability of pitting corrosion in slightly alkaline (borate-buffered) aqueous chloride and sulphide environments, with an emphasis on determining the influence of chloride and solution temperature on the nature of the anodically-formed Cu$_x$S films.
- To understand the physical properties of Cu$_x$S films formed in slightly alkaline (pH 9) solutions under natural corrosion conditions.
- To investigate the effect of Cl$^-$ concentrations, the primary anticipated groundwater species, on the corrosion of Cu in aqueous sulphide environments, using an experimental approach to determine the corrosion rate by measuring the H$_2$ evolved during the anoxic corrosion of Cu in the low sulphide concentrations ($<10^6$ mol/L) expected in Swedish and Canadian DGRs.
1.6 References


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Chapter 2 Experimental and Instrumentation

2.1 Experimental Design

2.1.1 Materials and Solution Preparation

2.1.1.1 Wrought Copper

Most experiments were conducted using Cu samples machined from a wrought Cu block provided by the Svensk Kärnbränslehantering AB (SKB), Solna, Sweden. These highly pure Cu samples (> 99.99 %) are oxygen-free (< 5 ppm) and phosphorous-doped (30-100 wt.ppm) [1]. The addition of phosphorous (P) limits creep deformation of Cu which could occur due to the high levels of mechanical stress imposed on the container after emplacement in a DGR.

Cu electrodes were machined as disks with a threaded hole drilled in the back of the disk to allow electrical connection to either a steel or a titanium rod. For corrosion experiments, the steel rods were coated with polytetrafluoroethylene (PTFE) heat shrink tubing and several layers of PTFE tape before they were screwed tightly into the Cu disk, thereby isolating the rods from the solution. The Ti rod was used in a Cu rotating disk electrode (RDE) configuration and the details are discussed below in section 2.2.4. Once the metal rod was attached, Cu disk was sealed with red epoxy resin (Hysol EE 4190) leaving only one flat circular surface area of 0.785 cm² to be exposed to the electrolyte. Typically, Cu disks were mounted into Teflon (PTFE) holders and were either left inside the holder as an RDE, Figure 2.1, or taken out using a benchtop vice to use as a stationary Cu electrode.

![Figure 2.1: An illustration of a freshly polished Cu RDE electrode.](image)
Prior to an experiment, the Cu electrode was ground with a sequence of SiC papers ranging from P400 to P4000, and then fine polished to a mirror finish using aluminum oxide (Al₂O₃) suspensions with decreasing particle sizes (1 μm, 0.3 μm, and 0.05 μm). Once a mirror finish was achieved, the electrode was rinsed with Type I water (18.2 MΩ·cm) provided by a Thermo Scientific Barnstead Nanopure 7143 ultrapure water system, to remove some polishing residues. Finally, electrodes were sonicated with methanol for 1 min and dried in a stream of ultrapure (99.999%) Ar gas.

Prior to an experiment, the Cu electrode was cathodically cleaned at −1.5 V vs saturated calomel reference electrode (SCE) for 1 min to reduce air-formed oxides, and then polarized at −1.15 V vs SCE for another minute to allow the detachment of any H₂ bubble which may have formed due to H₂O reduction at the more negative potential.

### 2.1.1.2 Electrodeposited Copper

Some experiments were conducted using the electrodeposited (ED) Cu samples (ED plates NWMO 44-45) supplied by the Nuclear Waste Management Organization, Toronto, Canada. In this thesis, these electrodeposited Cu samples are referred as C2B Cu.

The C2B Cu samples were cut from plates into 2.8 mm × 2.9 mm × 72 mm rectangular prisms with a total average surface area of 8.6 cm². The configuration of a C2B Cu working electrode (WE) is shown in Figure 2.2 (a), in which the major components of the electrode assembly are indicated. The electrical contact was made by connecting the C2B Cu prism to a Cu wire by soldering a wire onto a flat surface of C2B Cu. The junction between the C2B Cu and the wire was then covered with a glass tube and sealed with clear epoxy resin (Epofix resin). C2B Cu samples were grounded with SiC papers ranging from P120 to P 600 grits. All samples were then sonicated in a beaker with technical grade ethanol for 5 min followed by Type I water for another 5 min to remove any polishing residues. Sonication was repeated if needed. Prior to incorporation into the electrochemical cell, the samples were dried with ultrapure N₂ gas and stored in a vacuum desiccator. A total of 131 C2B Cu samples were assembled in an electrochemical cell, but, only one was used as a working electrode (WE). The exposed surface area of a WE was 6 cm².
A few electrochemical experiments were conducted using Cu wires (annealed, \( \geq 99.9\% \), 0.25 mm in diameter) purchased from Goodfellow. These wire samples are referred to as C1C Cu. As shown in Figure 2.2 (b), the WE configuration of C1C Cu is similar to that of C2B Cu, except that no soldering was performed. It should be noted that a 250 cm long wire was coiled at the bottom with a surface area of 19.7 cm\(^2\) to the electrolyte, Figure 2.2 (b). Each 5 cm long segment wire was cut from the spool of wires and a total of 2600
C1C Cu segments were made and assembled in an electrochemical cell, corresponding to an exposed surface area of 1024 cm$^2$.

Since it is effectively impossible to grind these thin C1C Cu segments using a mechanical polisher, wires were cleaned immediately prior to testing. The C1C Cu was first degreased by sonication for 5 min in a vial containing technical grade ethanol. The vial containing C1C Cu was then filled with Type I water and swilled to remove any residual ethanol. Wires were then immersed in a second vial containing ~ 10 mM nitric acid for another 5 min of sonication. The procedure described above was repeated three times until the wires appeared to be free of tarnish by the visual inspection with an optical microscope. Eventually, the C1C Cu samples were dried with ultrapure N$_2$ gas and stored in a vacuum desiccator prior to use.

2.1.1.4 Solution Preparation

All solutions were prepared using Type I water (18.2 MΩ·cm), obtained from a Thermo scientific Barnstead Nanopure water purification system, and reagent grade chemicals. Aqueous sulphide solutions were prepared with a regent grade sodium sulphide nonahydrate (Na$_2$S·9H$_2$O, 98.0%, supplied by Sigma-Aldrich). Since Na$_2$S is stored in the hydrated form, crystals were thoroughly dried on a filter paper prior to weighing. For benchtop experiments, solutions were purged with ultrapure (99.999%) Ar for 30 minutes prior to each experiment to minimize SH$^-$ oxidation and then continuously sparged throughout an experiment. For experiments performed inside an Ar-purged anaerobic chamber (Canadian Vacuum Systems Ltd.) using an MBraun glove box control system, Type I water was sparged with ultrapure Ar gas for 60 minutes on the benchtop before being transferred into the glovebox. The minimum measurable [O$_2$] indicated by the detection limit of the O$_2$ sensor in the chamber was 1 ppm. Once water was transferred, sulphide solutions were then prepared inside the glovebox to ensure the anoxic environment. Solution pH was measured using either an Orion™ Star pH meter (Thermo Scientific) or Hydron® Brilliant pH papers (Sigma-Aldrich) in the pH range of 6.5 to 13.0.

2.1.2 Electrochemical Cell

Experiments were performed in either a one-compartment or a three-compartment electrochemical cell. A dense glass frit was used in the three-compartment arrangement to
separate the solution in the working electrode (WE) compartment from that in the reference electrode (RE) and counter electrode (CE) compartments. Commonly, a Luggin probe was used to minimize the ohmic potential drop between the RE and WE. RDE experiments were performed in a one-compartment cell with an exposed wrought Cu surface area of 0.785 cm² and a solution volume of 450 mL, Figure 2.3 (a). A three-compartment cell was used for experiments conducted using a stationary wrought Cu electrode with a surface area of 0.785 cm² and a solution volume of 800 mL, Figure 2.3 (b). All experimental measurements were obtained via a conventional three-electrode system, with a Pt plate (99.95%) connected to external circuitry by a Pt wire (0.5 mm diameter) as the counter electrode, a commercial saturated calomel reference electrode (SCE, +0.242 V vs. SHE), and Cu as the working electrode. All cells were housed inside a Faraday cage to reduce electrical noise from external sources.

Figure 2.3: Schematics of the electrochemical cells. (a) a three-compartment cell and (b) a one-compartment cell.

Electrochemical data was collected using one of the following: a Solartron 1287 potentiostat, a Solartron Analytical Modulab equipped with CorrWare (version 3.4d, Scribner Associates) and a three-terminal XM-Studio-ECS software (AMETEK Scientific Instruments), and a Solartron 1480 MultiStat in conjunction with CorrWare software.

It should be noted that some experiments were conducted in a novel electrochemical cell configuration associated with C2B and C1C Cu samples. This cell setup will be discussed in detail in Chapter 6.
2.2 Principles of Electrochemical Techniques

2.2.1 Corrosion Potential

The corrosion potential ($E_{\text{corr}}$) is the potential adopted by a freely corroding system. The corrosion potential, commonly, also referred to as either the open circuit potential (OCP) or the rest potential [2], is the measured potential difference between a corroding WE and a RE when zero current flows through an external measuring system. In general, the corrosion of a metal, in this case Cu, in aqueous solution involves the coupling of the anodic oxidation of metal with the cathodic reduction of an available oxidant, e.g., for Cu

$$Cu + Ox \rightarrow Cu^{n+} + Red \quad (2.1)$$

where Ox is the oxidant and Red is the reduced form, with the reaction rate expressed as a corrosion current ($I_{corr}$).

The thermodynamic driving force for corrosion is the difference in equilibrium potentials ($E_e$), for the metal oxidation reaction and the oxidant reduction reaction, Eq. (2.2) and (2.3), calculated using the Nernst equation, Eq. (1.5).

$$Cu \rightleftharpoons Cu^{n+} + ne^- \quad (2.2)$$

$$Ox + ne^- \rightleftharpoons Red \quad (2.3)$$

For corrosion to occur, $E_{\text{corr}}$ must be between the equilibrium potentials for the two half-reactions, Figure 2.4. At $E_{\text{corr}}$, the current density for the cathodic half-reaction ($i_c$) is equal to the current density for the anodic half-reaction ($i_a$), Eq. (1.11). The current and potential relationships for each half-reaction is mathematically represented by the Butler-Volmer equation, Eq. (1.16). The coupled overall reaction, shown by the black curve in Figure 2.4, is represented by the Wagner-Traud equation based on mixed potential theory [3], Eq. (1.17). The value of $E_{\text{corr}}$ provides qualitative information on the kinetics of the corrosion reaction. Since $E_{\text{corr}}$ is generally far from both equilibrium potentials, the oxidation and oxidant reduction reactions can be considered to proceed irreversibly.
For each half-reaction considered reversible, at a sufficiently large overpotential ($\eta = \Delta E - E_e$), such as a large positive $\eta$, the current contribution from the reverse/cathodic reaction ($Cu \Rightarrow Cu^{n+} + ne^-$) becomes negligible. Hence, if the exponential current and potential relationship is represented logarithmically as $\log(i)$ versus $E$, an Evans diagram can be generated [2]. For a sufficiently large positive $\eta$, the Butler–Volmer equation, Eq. (1.16), can be reduced to Eq. (2.4).

$$ i = i_0 \exp \left( \frac{\alpha n F}{R T} (E - E_e) \right) $$  \hspace{1cm} (2.4)

Taking logarithms of Eq. (2.4), it yields a Tafel relationship (Eq. (2.5)), with the Tafel slope associated with the anodic branch defined in Eq. (2.6), and that for the cathodic Tafel slope by in Eq. (2.7).
\[ \log i = \log i_0 + \frac{\alpha n F}{2.303 RT} (E - E_e) \]  

(2.5)

\[ b_a = \frac{2.303 RT}{\alpha n F} \]  

(2.6)

\[ b_c = -\frac{2.303 RT}{(1-\alpha)n F} \]  

(2.7)

In a similar manner, for a sufficiently large applied potential \( \eta^* = E - E_{corr} \), one or the other of the exponential terms in the Wagner-Traud equation, Eq. (1.17) can be neglected, leading to a Tafel relationship, Eq. (2.8).

\[ i = i_{corr} \exp \left[ \frac{\alpha A n F}{RT} (E - E_{corr}) \right] \]  

(2.8)

Figure 2.5 shows an Evans diagram for the corrosion of Cu in the presence of an oxidant (Ox). The corrosion current for the two coupled reactions can be determined by extrapolating the linear Tafel regions to \( E_{corr} \), as shown in Eq. (1.17).

Figure 2.5: An Evans diagram for the corrosion of Cu.
2.2.2 Linear Polarization Resistance

When Cu is polarized at only a small applied potential \((\eta^* = E - E_{corr} \leq \pm 5 \text{ mV})\), the exponential terms in the Wagner-Traud equation can be linearized, leading to the definition of the polarization resistance, \(R_p\), for evaluating the corrosion rate. The linear polarization resistance theory was first proposed by Stern and Geary [4], and the linear polarization method is based on the following derivation. The exponential terms in the Wagner-Traud equation for a corroding metal can be expanded using a MacLaurin series [2].

For any small variable \(x\),

\[
exp (x) = 1 + x + \frac{x^2}{2!} + \cdots \tag{2.9}
\]

and the Wagner-Traud equation can be expanded and the second-order terms dropped to yield,

\[
i = i_{corr}\left\{1 + \frac{\alpha_A nF}{RT} (E - E_{corr}) - [1 - \left(\frac{-\alpha_C nF}{RT}\right)(E - E_{corr})]\right\} \tag{2.10}
\]

Or,

\[
i = i_{corr}\left[\left(\frac{\alpha_A nF}{RT}\right) + \left(\frac{-\alpha_C nF}{RT}\right)\right] (\eta^*) \tag{2.11}
\]

Equation (2.11) can be rearranged to yield Eq. (2.12), by substituting the \(\left(\frac{\alpha_A nF}{RT}\right)\) and \(\left(\frac{-\alpha_C nF}{RT}\right)\) with Tafel slopes.

\[
i = 2.303 \cdot i_{corr}\left[\left(\frac{1}{b_A}\right) + \left(\frac{1}{-b_C}\right)\right] (\eta^*) \tag{2.12}
\]

Solving for \(\eta^*\) and differentiating gives,

\[
R_p = \frac{d\eta^*}{di} = \frac{1}{2.303 i_{corr}(\frac{1}{b_A} + \frac{1}{-b_C})} \tag{2.13}
\]

As can be seen from Eq. (2.13), \(R_p\) is represented by the slope of the potential-current relationship and is inversely proportional to the corrosion current density; i.e., the interfacial charge transfer rate. Figure 2.6 shows a schematic illustrating the linear approximation of the current and potential relationship within a small potential perturbation (\(\leq 5 \text{ mV}\)) range to yield \(R_p\).
If the Tafel slopes are known, the measured $R_p$ can be converted to a corrosion current using Eq. (2.13). However, even if these values are unknown, $R_p$ can still be used as a relative quantitative parameter to estimate the interfacial charge transfer rates.

2.2.3 Voltammetry

2.2.3.1 Cyclic Voltammetry and Potentiodynamic Polarization

Cyclic voltammetry (CV) is a technique for investigating the various anodic and cathodic reactions which may occur at an electrode surface in which a current (I) response is recorded as the applied potential (E) is scanned. The applied $E$ is commonly scanned linearly and the measured current provides kinetic information on the electrochemical processes which occur within the $E$ range scanned. Potentiodynamic polarization (PDP) is a similar potential scanning technique with the potential generally only scanned to positive potentials. Figure 2.7 shows the potential time profile used in the two techniques. In a typical PDP scan, the applied $E$ is scanned from an $E_{\text{Initial}}$ to an $E_{\text{Final}}$ where $E_{\text{Initial}} < E_{\text{Final}}$. 

![Diagram showing cyclic voltammetry and potentiodynamic polarization](image)

Figure 2.6: A schematic showing the linearization of the Wagner-Traud relationship for a small potential perturbation ($E_{\text{corr}} \leq \pm 5 \, \text{mV}$). The reciprocal of the slope of this figure yields $R_p$. 

\[
\frac{1}{R_p} = \frac{\Delta i}{\Delta E}\big|_{\Delta E \to 0}
\]
Figure 2.7 (a). In a CV scan, the potential scan is reversed at $E_{\text{Switch}}$ ($E_{\text{Switch}} = E_{\text{Final}}$ from PDP), and the current is recorded on the reverse scan also. A two-cycle CV scan is shown here, Figure 2.7 (b).

![Diagram of CV scan](image)

Figure 2.7: Diagrams showing the applied E as a function of time for a) potentiodynamic polarization, and b) cyclic voltammetry. The blue line represents the forward scan and the red line shows the backward scan in a two-cycle cyclic voltammetry.

While the potential is scanned, the current (I) or current density (i) is recorded. Figure 2.8 shows an example of a PDP scan on a metal which actively dissolves initially at low potentials in region 1, before undergoing an active to passive transition in region 2.

![Diagram of PDP scan](image)

Figure 2.8: An illustration of PDP scan on a metal which dissolves at low potentials (region 1) and then forms a protective oxide at higher potentials (region 2). The transition between region 1 and 2 is known as an active-passive transition. Region 3 is the passive region.
The plateau current region (region 3) then, indicates the formation of a protective oxide as the potential increases to even more positive values.

Figure 2.9 shows a schematic of a CV recorded on a Cu RDE, showing the anodic oxidation of Cu to form surface films on the forward scan, and at high potentials before the reduction of films and deposits is observed at low potentials on the reverse scan. Examples of such CVs are published in Martino et al. [3] Integration of the current as a function of time yields charge (Q).

\[ Q = \int_{0}^{t} i \cdot dt \]  

(2.14)

The integration of the current as a function of time associated with the positive current on the forward scan and on the reverse scan result in a measure of the extent of oxidation (the shaded red area, \( Q_a \)). The measure of the charge associated with film/deposit yields \( Q_c \), demonstrating the reduction processes. If the charge difference (\( 2Q_a - Q_c \)) is approximately zero, the amount of oxidized product formed on the forward scan is fully reduced in the backward scan. If the charge ratio is less than 1, it suggests that some anodically-formed product could be lost to solution by dissolution. In addition, the peak positions are indicative of the stage of oxidation and assist in determining the oxidation mechanism of the electrode material (Cu in this case). Changing the forward scan potential limit allows the degree of oxidation to be controlled.

![Figure 2.9: CV showing the integrated area \( Q_a \) and \( Q_c \). The inset shows the potential time profile employed to record the CV. Since the potential at any time is dictated by the scan rate (mV/s), the horizontal axis can be converted to time allowing integration of the curve to yield values of Q.](image)
2.2.3.2 Cathodic Stripping Voltammetry

Cathodic Stripping Voltammetry (CSV) is an electrochemical technique that can be used to measure the amount of reducible films and deposits formed during a proceeding period of anodic oxidation or corrosion. CSV is conducted on the Cu electrode by linearly ramping the applied potential in a negative direction from either the applied potential or $E_{corr}$, to a sufficiently negative potential limit while measuring the current response.

Films or deposits formed on the electrode during the preconditioning period (either electrochemical or corrosion) can be reduced at potentials more negative than their equilibrium potentials. Hence, CSV can be used to identify phases formed on an electrode providing that the cathodic behaviour of the system has already been thoroughly examined. In other words, CSV will not provide much meaningful information unless the same system has been investigated via other techniques, such as CV and surface analyses. Figure 2.10 shows the potential profile used to investigate film formation under corrosion conditions. Cathodic cleaning is performed on a Cu electrode at a negative and constant potential to reduce copper oxides formed by air oxidation. Subsequently, corrosion occurs at the open circuit potential ($E_{corr}$) which may change with time. A CSV is then recorded by scanning the potential ($E_{corr}$) to $E_{final}$, and recording the current for film/deposit reduction, Figure 2.10.

![Graph showing potential profile](image)

Figure 2.10: The potential profile employed in a CSV ($t_1$ to $t_2$: cathodic cleaning, $t_2$ to $t_3$: OCP measurement at $E_{corr}$, $t_3$ to $t_4$: CSV measurement.

The charge due to reduction of a surface film/deposit is obtained by integrating the current as function of time and applying Eq. (2.14). The masses of various corrosion products can then be calculated by applying Faraday’s law, Eq. (1.12).
2.2.4 Electrochemical Impedance Spectroscopy

Some experiments were conducted using electrochemical impedance spectroscopy (EIS) to investigate the solution resistance ($R_s$) associated with the elongated cell geometry due to the attachment of an auxiliary component (section 6.2.2 (Figure 6.3 (c))). Impedance is the equivalent of resistance in a system where an alternating potential or current is applied, and describes the restriction to the current flow. EIS is often applied in corrosion science to investigate film properties and surface mechanisms in a corrosive environment with respect to time [5–8]. In this technique, an alternating potential or current perturbation is applied to an electrochemical system. The resulting current or potential response is subsequently measured, and the transfer function associated with the perturbation is determined as a function of perturbation frequency [8]. When a system is linear, stable, finite, and causal, the transfer function is the impedance of the system, represented in Eq. (2.15),

$$E(\omega) = I(\omega)Z(\omega)$$  
(2.15)

where $E$ is the potential, $\omega$ is the angular frequency, $I$ is the current and $Z$ is the transfer function (i.e., impedance). Eq. (2.15) is a more universal, frequency-domain representation of Ohms’ Law [8], Eq. (2.16), where $R$ is the apparent DC resistance.

$$E = IR$$  
(2.16)

Commonly, in an EIS experiment, either a small sinusoidal potential ($E$) ($\pm$ 10 mV vs $E_{corr}$) is applied to a system, or the fluctuating potential of $\pm$ 10 mV is superimposed on an applied potential ($E_{applied}$). A small $E$ perturbation is used to prevent irreversible changes from the electrode surface during measurements, and more importantly, the change in current $\Delta I$, is nearly proportional to the change in $\Delta E$. Therefore, an electrochemical system can be made to appear approximately linear for the purpose of EIS by applying a small-amplitude perturbation signal.

As a result, the output current response will either be in-phase (real component) or out-of-phase (imaginary component) with the input alternating potential, depending on the characteristics of the electrode and solution interface [6–8], Figure 2.11. The potential and current sinusoidal signals are related by combining Eq. (2.15), Eq. (2.17) and Eq. (2.18) to yield the expression for the impedance ($Z$) of an AC system calculated from the ratio of the
applied potential and the resulting current, Eq. (2.19), where $E_o$ and $I_o$ are the potential and current amplitudes.

$$E(t) = E_0 \sin(\omega t)$$  \quad (2.17)

$$I(t) = I_0 \sin(\omega t + \theta)$$  \quad (2.18)

$$Z(\omega t) = \frac{E_0 \sin(\omega t)}{I_0 \sin(\omega t + \theta)}$$  \quad (2.19)

The total impedance, $Z(\omega t)$, can be separated into real ($Z'$) and imaginary ($Z''$) impedances represented by the imaginary unit $j$, as shown in Eq. (2.20). For a system which contains a resistor and a capacitor in series with each other, the total impedance is expressed by Eq. (2.21) with the resistance contained in the real component and the capacitance ($C$) expressed in the imaginary component.

$$Z(\omega t) = Z'(\omega t) + jZ''(\omega t)$$  \quad (2.20)

$$Z = R + j \frac{1}{\omega C}$$  \quad (2.21)

Figure 2.11: A diagram showing the relationship between the input potential (solid line) and the output current (dashed line) response in an EIS experiment. $\theta$ is the phase shift between the potential and current waves.
Impedance data are plotted as either a Nyquist plot or as Bode Plots, and the interpretation of EIS data is often associated with electrical circuits, allowing one to use the individual passive circuit elements, such as resistors, capacitors, inductors, to represent an electrochemical system [6–8]. Figure 2.12 shows the EIS spectra and the equivalent circuit representing a metal surface covered with an oxide film [8].

Figure 2.12: (a) Nyquist plot showing the imaginary impedance ($Z''$) versus the real impedance ($Z'$) with solution resistance and charge transfer resistance represented by $R_s$ and $R_s + R_p$; (b) and (c) the corresponding Bode plots for the magnitude of impedance ($|Z|$) and the phase angle ($\theta$) versus frequency; and (d) an equivalent circuit used to represent these EIS spectra.

In this equivalent circuit, Figure 2.12 (d), the solution resistance is shown as $R_2$, the interfacial charge transfer resistance is labelled as $R_1$, and the capacitance ($C_1$) indicates the capacitance of the electrical double layer at the metal/solution interface. The interfacial charge transfer resistance ($R_1$) arises when the electrons/ion transfer occurs at the metal/solution interface, and $C_1$ is used to represent the movement of ions in and out of the interfacial region at the electrode surface in response to the charging and discharging of the electrode surface by the applied sinusoidal potential. Thus, by properly fitting equivalent electrical circuits to EIS spectra that are based on a physical model of the corroding interface, various physical parameters can be extracted. For the EIS experiments conducted in this work, a small alternating potential perturbation ($\pm$ 10 mV magnitude), centred around $E_{corr}$, was applied to the WE. The corresponding current response was measured...
over a frequency range from $10^{5}$ Hz to $10^{0}$ Hz, with 11 data points recorded per frequency decade. EIS spectra were collected using a Solartron 1287 potentiostat equipped with CorrWare software and a Solarton 1255B frequency response analyzer (FRA) with Zplot software. Kramers – Kronig transforms were applied to confirm the validity of the data using a python-based measurement model toolbox for impedance Spectroscopy (measurement model software, version 1) created by Watson and Orazem [4,5].

### 2.2.5 Mass-Transfer and Rotating Disk Electrode

Mass-transfer in a solution can occur by three processes; diffusion, migration, and convection [6]. This phenomenon is described by the Nernst-Planck equation shown in Eq. (2.23) [6].

$$J_j(x, t) = -D_j \frac{\partial C_j(x,t)}{\partial x} - \frac{Z_j F}{RT} D_j C_j \frac{\partial \phi_j(x,t)}{\partial x} + C_j v(x,t)$$ (2.22)

Where $J_j(x,t)$ is the flux of species $j$ at a distance $x$ from the electrode surface at time $t$, $D_j$ is the diffusion coefficient, $\partial C_j(x,t)/\partial x$ is the concentration gradient, $\partial \phi_j(x,t)/\partial x$ is the potential gradient, $Z_j$ is the charge on species $j$, $C_j$ is the concentration of species $j$, and $v(x,t)$ is the fluid velocity at a distance $x$ and time $t$. The three terms on the right side of Eq. (2.22) describes diffusion, migration, and convection, respectively. Despite the fact that mass-transfer of an electroactive species near an electrode is governed by these three terms, it can be restricted to diffusion only by: (i) using a strong supporting electrolyte to eliminate any potential gradient, leading to migration; (ii) using quiescent conditions when the convection contribution becomes almost negligible [6]. Hence, the Nernst-Planck equation can be simplified into Eq. (2.23), also referred to as the Fick’s first law of diffusion.

$$J_j(x, t) = -D_j \frac{\partial C_j(x,t)}{\partial x}$$ (2.23)

Since electrochemical/corrosion reactions involve transport of reactants and/or products to/from the electrode surface, the depletion/accumulation of species at this surface can influence reaction rates [11]. For a one-dimensional diffusion case, Fick’s first law describes the flux of a substance and its concentration as functions of time and position [6]. In Eq. (2.23), $J_j$ is the flux, indicating the number of moles of a particular species which pass a given location per second per unit area normal to the axis of diffusion [6]; $D_j$ is the diffusion coefficient ($m^2/s$); $x$ defines the position of the species with regard to the electrode surface. The flux ($J_j$) is determined by $D_j$ and the concentration gradient. The layer of
electrolyte within which the concentration deviates from the bulk concentration and within which diffusion occurs is called the Nernst diffusion layer (δ), where δ is the thickness [12]. For a flat electrode, all fluxes within this layer are considered one-dimensional and to a first approximation, the concentration gradient, can be linearized and expressed as [12],

$$J_j = -D_j \frac{\Delta C}{\delta} = -D_j \frac{C_0 - C_{\text{bulk}}}{\delta}$$

(2.24)

where $C_0$ represents the surface concentration of a reacting species (j) and $C_{\text{bulk}}$ is the species concentration in the bulk solution. When applying a large overpotential to the electrode, oxidants react as soon as they reach the electrode surface, resulting in a complete depletion of surface concentration ($C_0 = 0$). Therefore, Eq. (2.24) can be further simplified, Eq. (2.25).

$$J_j = D_j \frac{C_{\text{bulk}}}{\delta}$$

(2.25)

When the solution is completely stagnant, δ increases with time due to the continuous consumption of reacting species from the bulk solution and the non-linearity of the concentration gradient. This leads to the decay in the current response at an electrode surface with a $t^{-1/2}$ dependence [6]. However, the $t^{-1/2}$ dependence of current decay cannot be maintained indefinitely. This is because even in a stagnant solution, a steady-state flux will be established due to natural convection and the current will eventually become independent of time.

The use of an RDE enables the establishment of a steady-state $J$ at the electrode/solution interface in experiments which avoid any significant change in the bulk solution. Specifically, under this controlled-convective condition, diffusion is restricted to a thin layer of thickness δ at the electrode surface, with the thickness controlled by the electrode rotation rate ($\omega$) of the RDE [12]. The thickness of the diffusion layer (δ) is proportional to the reciprocal of the square root of $\omega$, Eq. (2.26), where $\nu$ is the kinematic viscosity of the solution. The dependence δ on ω is illustrated in Figure 2.13 and shows that as $\omega$ increases δ decreases, while the concentration gradient increases.

$$\delta = 1.61D^{1/3}\nu^{1/6}\omega^{-1/2}$$

(2.26)
By introducing convection with a rotating disk electrode, it is possible to control $\delta$, and hence the limiting current. The limiting current ($I_L$) can then be expressed based on Fick’s first law and the Nernst approximation, as shown in Eq. (2.27).

$$I_L = \frac{nFAD}{\delta} C_{bulk} \quad (2.27)$$

A combination of Eq. (2.26) and (2.27) yields the Levich equation [13,14], where $A$ represents the surface area of an electrode and shows the limiting current is proportional to $\omega^{0.5}$, Eq. (2.28).

$$I_L = 0.62 nFAD^{2/3} \nu^{-1/6} C^* \omega^{0.5} \quad (2.28)$$

Therefore, if a reaction is completely diffusion controlled, the slope of a linear plot of $I_L$ as a function of $\omega^{0.5}$ will yield the diffusion coefficient of the electroactive species. Often, for irreversible reactions, at intermediate values of overpotential, the reaction is under mixed transport and activation control and a plot of $I_L$ vs. $\omega^{0.5}$ no longer follows the Levich equation. However, the reciprocal of the measured current is a linear function of...
the $\omega^{-0.5}$, as shown in the Koutecky-Levich equation [2], Eq. (2.29), in which $I_M$ is the recorded current under mixed control, and $I_K$ is the kinetic current in the absence of diffusion, i.e., when the mass-transfer flux is large enough to maintain $C_0$ at the electrode surface equal to $C_{bulk}$, regardless of the rate of the interfacial electrode reaction.

$$\frac{1}{I_M} = \frac{1}{I_K} + \frac{1.61v^6}{2nFAD^3C_{bulk}} \cdot \frac{1}{\omega^{0.5}}$$  \hspace{1cm} (2.29)

As indicated in Eq. (2.29), $I_K$ can be obtained from the intercept of a plot of $I_M^{-1}$ vs $\omega^{-0.5}$, when $\omega$ approaches infinity and $\delta$ approximates to zero. The log of $I_K$ can then be plotted as a function of applied potential ($E$) to yield a Tafel relationship, Eq. (2.29).

$$\log i = \log i_{corr} + \frac{a_AnF}{2.303RT} (E - E_{corr})$$  \hspace{1cm} (2.29)

Experimentally, an RDE is prepared by fixing a Cu flat disk electrode into a cylindrical Teflon holder with red epoxy resin. A Ti rod is then threaded into the back of the Cu for electrical contact between the working electrode and the steel rotator shaft. A spring-loaded carbon contact ensures the shaft is in electrical connection with the potentiostat when the shaft rotates. A schematic of an RDE is shown in Figure 2.14. All RDE experiments reported in this thesis were performed by using a Pine Instrument Company Analytical Rotator (Model AFA86 Serial 882).

Figure 2.14: A diagram showing the configuration of a rotating disk electrode.
2.2.6 Potentiostatic Polarization

In a potentiostatic polarization experiment, a constant potential is applied to the WE and maintained for a certain duration while measuring the resulting current response. Figure 2.15 shows the potential-time profile used in potentiostatic experiments.

![Potential-time profile](image)

Figure 2.15: The potential-time profile used in a potentiostatic polarization experiment, t₁ to t₂: cathodic cleaning; t₂ to t₃: a period of oxidation.

The selection of an applied potential with respect to the $E_{corr}$ determines the direction of electron flow, therefore, allowing the separation of the anodic or cathodic reactions in an electrochemical system. When anodically polarizing the Cu electrode, the extent of Cu oxidation will be driven by the applied potential ($E$) on the WE. When the applied $E$ is more negative than $E_{corr}$, the current arises due to the cathodic reaction on the metal surface.

Commonly, the log of the current is plotted against the log of time. A linear log(i) vs log(t) plot with i decreasing suggests the growth and thickening of a surface film, whereas a log(i) vs log(t) plot yielding a constant current indicates the steady-state dissolution of the metal.

2.3 Surface Analytical Techniques

2.3.1 Microscopy

2.3.1.1 Light-Optical Microscopy

The Light-optical microscopy was first invented in the early 1600’s by Dutch spectacle maker Hans Janssen and his son Zacharias who combined several convex lenses to form an optical microscope [15]. Nowadays, the light-optical microscopes are widely
used in materials and corrosion science and come in two basic forms: (i) the biological microscope that requires an optically transparent sample; (ii) the metallurgical microscope, for examining metals and other materials that cannot easily be prepared to be optically transparent. The metallurgical microscope often has a built-in illumination source to emit light and the image is formed by light reflected from the sample surface.

The three basic features of optical microscopy are image formation, magnification and resolution. A schematic of the image formation involving the use of a pair of convex lenses is shown in Figure 2.16. In the ray diagram shown in Figure 2.16, light is represented by rays rather than waves, thereby any diffraction effect is ignored [16]. The object/sample is placed at a position between one and two focal lengths (f) to the left side of the objective lens. A focal length is the distance from the principle plane of a lens to the point at which the light focuses, as shown by \( f_1 \) and \( f_2 \) for the objective lens and eyepiece lens, respectively. Image 1 is the primary image that is focused through the objective lens, resulting in a magnified and inverted image of the object. As it is shown in Figure 2.16, \( u \) represents the distance between the object and the principle plane of the lens, and \( m \) stands for the distance of the image away from the objective lens. The object distance (\( u \)) and image distance (\( m \)) are related to the focal length (\( f \)) of a convex lens by Eq. (2.31).

$$\frac{1}{f} = \frac{1}{u} + \frac{1}{m} \quad (2.31)$$

Eventually, an inverted and virtual image is observed by eye if the primary image (image 1) is located at a position where the distance to the principle plane is shorter than the focal length of the eyepiece lens. The magnification factor (\( M \)) can be calculated via Eq. (2.32).

$$M = \frac{m-f}{f} \quad (2.32)$$
As it is shown in Eq. (2.31), magnification increases as focal length decreases. Similarly, for a compound microscope contains at least two lens, Figure 2.16, the total magnification is the product of the magnification factors of the two lenses, Eq. (2.33).

\[ M = \frac{(m_1-f_1)(m_2-f_2)}{f_1 f_2} \]  

(2.33)

Figure 2.16: A ray diagram showing the basic optical principles of image formation and magnification in an optical microscope. The focal lengths for the objective and eyepiece lens are \( f_1 \) and \( f_2 \), respectively. The image distance is represented by \( m \), and the distance between the object and the objective lens is indicated as \( u \).

The resolution of an optical microscope is defined as the shortest distance between two points on a sample that can be distinguished. The resolution (\( R \)) of a microscope is determined by the refractive index (\( \mu \)) of an imaging medium between the object and the convex lens and the half-angle of the cone of light entering the objective lens, or half of the angular aperture (\( \alpha \)). The product of \( \mu \) and \( \sin \alpha \) is defined as the numerical aperture (NA). \( R \) of a microscope is shown in Eq. (2.34), where \( \lambda \) represents the wavelength of light [13].

\[ R = \frac{0.61 \lambda}{NA} \]  

(2.34)

In this study, optical microscopy was used to characterize Cu samples before and after corrosion in various electrolytes. Optical images were captured using a Keyence VHX-6000 digital microscope, or the 50 x Olympus microscope coupled with a Renishaw
InVia Reflex Raman Spectrometer. Only relatively low-resolution micrographs were acquired with magnifications ranging from 10 x to 120 x. Higher magnification images were acquired with a scanning electron microscope (SEM) when required.

2.3.1.2 Scanning Electron Microscopy

Due to the easy experimental procedures, relatively low cost and highly customizable features, scanning electron microscopy (SEM) has become one of the most powerful surface analysis techniques. It provides useful information on surface topography, elemental composition, and some crystalline features of the ~ 2 μm top layer of a specimen [16]. The resolution of SEM images can reach nm level, and the operational magnifications can be adjusted in the range from 10 to ~ 100,000 [14].

During the operation of an SEM, the incident/primary electrons are produced from a heated electron gun followed by an accelerating potential (0.1~50 keV) with energies ranging from 2 to 40 keV [14]. Three commonly used electron guns are tungsten hairpin filament, lanthanum hexaboride (LaB₆) filament, and field emission guns [16]. The filament is heated by the passage of an electrical current which creates electrons with a large enough substantial kinetic energy to leave the filament, thereby creating an electron beam.

An SEM requires a series of lenses to control the energy of the electron beam before it impinges on a sample surface. SEM systems take advantage of the charge on the electron by using electromagnetic lenses, which have holes in the center through which the electrons pass. Often, an intense magnetic field is generated and confined in the center of the lenses as a result of controlling the current which passes through the solenoid. As shown in Figure 2.17, typically, two types of lenses are placed above the sample: (i) a condenser lens and (ii) an objective lens. Condenser lenses control the convergence and the initial spot size of the electron beam and the final electron beam diameter is controlled by the objective lens, where a small electron probe is formed with a diameter around 10 nm [18]. In addition, the objective lens largely determines the spatial resolution of an SEM. The focused electron beam rasters over the sample surface, which is scanned horizontally in two perpendicular (X and Y) directions [16]. Typically, the X-scan is fast and generated by a sawtooth-wave generator, whereas the Y-scan is much slower and generated by a second sawtooth-wave
generator, Figure 2.17. The entire procedure is known as rastering and the beam sequentially covers a rectangular area on the specimen.

Figure 2.17: A diagram of a scanning electron microscope with a cathode-ray tube [13].

When primary electrons penetrate the specimen, secondary products are created in a teardrop-shaped volume (excitation bulb), in which the overall dimensions (penetration depth) are determined by the energy of the electron beam, the atomic masses the elements in a material, and the incident angle of the primary electrons on the specimen. The various interactions between electron beams and the specimen produce secondary, backscattered, Auger electrons, characteristic X-rays and continuum X-rays [15], Figure 2.18. Auger electrons escape from the near surface layers that are commonly less than a few nanometers. Secondary electrons (SE) are generated at a slightly deeper location (~ 100 nm) within the specimen at an energy level below 50 eV, resulting from inelastic collisions, Figure 2.18. If the vacancy due to the ejection of a SE is filled by an outer shell electron, an X-ray with an energy characteristic of that energy transition is created. Most SEs fall in an energy range between 2~5 eV. When the incident electron beams interact with the nucleus of an atom, elastic events occur. Often, this interaction happens with a change in direction of the beam electrons without a significant alteration in its energy [16]. If the elastically scattered electrons re-emerge from the specimen surface, they are termed backscattered electrons (BSE). BSEs are not as numerous as secondary electrons, but they are higher in energy (>

...
50 eV). The fraction of backscattered electrons strongly depends on the atomic number of the scattering atom, which influences the brightness of an image. Hence, the intensity of BSEs is associated with the atomic number of the element within the sampling volume. This results in a compositional contrast in the backscattered image from elements with different atomic number and their distribution in the material [18].

All samples were sonicated and rinsed with nano-pure water and then dried in an Ar stream prior to surface analysis. In this project, most of the SEM micrographs were obtained on corroded samples using a LEO 1540 instrument equipped with a focused ion beam (FIB) (Zeiss Nano Technology Systems Division, Germany) at the Western Nanofabrication Facility. Some micrographs were collected by a Hitachi SU3500 scanning electron microscope. Depending on the samples, the acceleration voltage was kept between 1-10 kV for image acquisition and elemental analysis. Images were recorded at various magnifications (5000 x to 30,000 x).

2.3.1.3 Energy Dispersive X-ray Spectroscopy

In addition, the interaction of the primary beam and the sample can lead to the emission of X-rays since shell transitions happen when outer-shell electrons fill a vacancy in the inner shell of an atom. The emitted X-ray has an energy characteristic of the parent element and is generated at a depth at 1-3 μm. Measurements of the energy of the emitted X-rays enables elemental analysis. This measurement is termed energy dispersive X-ray spectroscopy, sometimes termed energy dispersive X-ray analysis or microanalysis (EDXMA), and can be used for the elemental analysis or chemical characterization of a sample [18,19].

EDX analysis relies on the fact that each element has a unique atomic structure, thereby yielding a unique set of peaks in its X-ray emission spectrum, Figure 2.19. The excitation caused by the incident electron beam leads to the ejection of an electron from an inner shell, which creates an electron hole. An electron from an outer, higher-energy shell then fills the hole, with the difference in energy between the higher and lower energy shells released in the form of an X-ray [20]. Since the energies of the X-rays are characteristic of the difference in energy between the two shells and of the atomic structure of the emitting element, EDX allows the elemental composition of the specimen to be measured. A single
element may have many characteristic X-rays depending on the energy of the incident beam and the level from which the electron is emitted [18].

Figure 2.19: Schematic summary of the various electrons and X-rays produced on bombardment of a sample with a primary electron beam.

Figure 2.18: A diagram demonstrating the production of characteristic X-rays. An incident electron expels an electron from the K orbital, causing an electron from a higher orbital (L or M) to fill the void with the excess energy emitted as an X-ray photon.

Experimentally, the characteristic X-rays were collected by the EDX detector which produces a spectrum of signal intensity versus energy with the signal intensity proportional
to the quantity of the element present and the energy of the incoming electron beam. To minimize the decomposition of copper sulphide due to the exposure to high energy electron beams, EDX spectra were obtained at an acceleration voltage of 5 kV. In particular, Cu is characterized by the emitted Lα X-rays at an energy of 0.928 keV.

2.3.1.4 Focused Ion Beam Cross Sectioning

A Focused Ion Beam (FIB) can be used in conjunction with SEM and EDX. A FIB is widely used for various applications, including sample milling, ion implantation, and film deposition. FIB milling is used extensively in materials and corrosion science to visualize the cross-sections of corrosion products, such as investigating the porosity and thickness.

In this project, a Gallium ion (Ga⁺ ) beam is utilized to make FIB cuts. Ga is currently the most widely used ion source in FIB as it has a low melting point of 28.9 °C, a low volatility at the melting point and a low vapour pressure, which allows it to be used in its pure form with a long lifetime and minimum evaporation [20]. In practice, the Ga⁺ beam is obtained by flowing liquid Ga through a heated tungsten needle, where it experiences a strong electric field that ionizes the liquid. When the ion beam reaches the sample surface, elastic collisions occur, causing atoms to be ejected from the surface, thereby cutting into the sample. In a typical FIB analysis, areas of a sample are FIB milled in a slice-by-slice manner, resulting in a trench. The cross-section of the trench is then imaged using SEM.

2.3.1.5 Confocal Laser Scanning Microscopy

Confocal Laser Scanning Microscopy (CLSM) is an optical technique which produces three-dimensional (3D) images by scanning across the various focal planes of a sample. Compared to traditional optical microscopy, CLSM can image very small areas via a high-intensity point laser source and stitch them together to produce a high-resolution image for a large field of view [15].
The optical principles of a CLSM are depicted in Figure 2.20. A point-like light source, commonly a laser, is focused with a lens/collimator and directed towards a beam splitter which separates the laser in both upward and downward directions. Eventually, the laser is focused on the sample through an objective lens. As shown in Eq. (2.34), the spatial resolution of the focus spot on the sample is determined by the wavelength $\lambda$ and the quality of the image formation [15,16]. Once the laser light has been reflected, it travels back through the objective lens and the beam splitter towards another convex lens, which focuses the laser into a pinhole positioned in front of a detector. It should be noted that the size of the pinhole is set so that only the central part of the focus laser can pass through, thereby blocking out any out of focus light. This is illustrated in the trajectory of rays that come from the focal plane, which pass through the pinhole, whereas, rays reflected from a reference plane are blocked, Figure 2.20.

Figure 2.20: A schematic showing the principles of a CLSM setup. Image adapted from [14].

From this simple geometric representation, Figure 2.20, three advantages of confocal microscopy can be appreciated: (i) by utilizing a sample stage that is mobile in the $z$-direction, a series of focal planes can be mapped and stacked by computer software, resulting in a 3-dimensional sample image associated with quantitative topographical information; (ii) since only light from the focal plane will be detected, contrast-enhanced
image acquisition can be obtained; (iii) by the selection of an appropriate pinhole diameter, the lateral resolution can be increased up to a factor of $\sqrt{2}$ [15]. In this study, a Zeiss LSM800 For Materials/Zeiss Axio Imager. Z2m upright compound microscope is used for both 2D optical and 3D z-stack image acquisition. The wavelength of the laser is 405 nm and the diameter of the pinhole is set at 17 $\mu$m.

2.3.2 Spectroscopy

2.3.2.1 Raman Spectroscopy

Raman spectroscopy provides information on the chemical compositions of materials by probing molecular vibrations. The Raman effect is a light-scattering effect that is seen as a change in the vibrational frequency ($v$) of a small fraction of monochromatic incident light resulting from the interaction between the light and the molecule.

Commonly, a microscope is used to focus the laser onto the sample, achieving micrometer scale spatial resolution. A classical description of Raman scattering is depicted in an energy level diagram. Figure 2.21. When an incident laser beam interacts with the molecules of a material, a portion of these incident photons are scattered. The majority of light is scattered elastically (Rayleigh scattering), retaining the same vibrational frequency as the incident photon, Figure 2.21 (a). However, a very small amount of the light is scattered inelastically with a frequency that is different to that of the incident laser, a process known as Raman scattering [12]. For Raman scattering, if the incident light promotes an electron from the ground state to a virtual excited state, which then relaxes to a vibrationally-excited state with an energy higher than the ground state, energy is lost in a process termed Stokes scattering, Figure 2.21 (b). In an Anti-Stokes scattering, an incident photon of frequency $v_3$ is scattered to a final state of frequency $v_4$ with an energy greater than the incident photon, Figure 2.21 (c).

Figure 2.21: Energy level diagram showing the transitions for (a) Rayleigh scattering, (b) Stokes scattering, and (c) anti-Stokes scattering.
photon promotes an electron from an already excited state to a virtual excited state with the electron subsequently relaxing to the ground state, resulting in a gain in energy of the scattered photon, Figure 2.21 (c). Often, Stokes scattering is more abundant than anti-Stokes scattering since molecules tend to be in their ground vibrational state at room temperature [15].

The interaction between the incident photon and the sample molecule involves the disturbance of the electronic charge distribution in the molecule by the incident electromagnetic field, thereby inducing a dipole moment ($\mu$), Eq. (2.35). For Raman scattering to occur, a molecule must be polarizable as it vibrates [22].

$$\mu = \alpha V$$  \hspace{1cm} (2.35)

In equation (2.35), $\alpha$ is the polarizability and $V$ is the induced electric field. The disturbed molecule then releases a photon leading to either Raman or Rayleigh scattering. The combination of characteristic Raman shifts and the relative intensities of the Raman peaks can be used as a fingerprint spectrum to aid in species identification.

In this study, Raman spectroscopy was conducted using a Renishaw InVia Reflex Raman Spectrometer equipped with a Leica DMLM microscope. Prior to spectra acquisition, the spectrometer was calibrated with a standard Si wafer with a characteristic Raman band at 520 cm$^{-1}$. Spectra were then collected using a He-Ne laser with a wavelength of 632 nm. The laser beam was focused onto the sample using a 50 x objective lens with a diameter of ~ 2 $\mu$m. To avoid laser heating effects on the corrosion products, laser power was set to be 1 to 5%.

2.3.2.2 X-ray Photoelectron Spectroscopy (XPS)

XPS is a surface analytical technique that depends upon the measurement of the energies of photoelectrons emitted from atoms when irradiated by soft X-ray photons (1–2 keV) [23]. One advantage of XPS is the ability to identify not only the elemental composition but also the oxidation state of elements, i.e. chemical compositions. XPS spectra are collected by irradiating a material with a beam of X-rays while simultaneously measuring the kinetic energy and number of electrons. Since electrons ejected within the sample have a low inelastic mean-free path, only photoelectrons originating at depths up to ~ 10 nm can escape from the surface, making XPS a surface sensitive technique. XPS is operated under the ultra-high vacuum (UHV) condition (pressure is $< 10^{-9}$ mbar).
The fundamental principle of XPS is based on the photoelectric effect described by Einstein in 1905 [24]. Based on the conservation of energy, the binding energy (BE) of the emitted electrons from a specific elemental atom can be determined from their kinetic energy (KE), as depicted in Figure 2.22.

![Figure 2.22](image)

Figure 2.22: A diagram illustrating the photoemission process involved for a core level (1s) electron by an incident X-ray of known energy.

The KE energy of the photoelectron is the difference between the energy of the X-ray (hν) and the binding energy (BE) plus the work function (φ).

\[
KE = h\nu - BE - \phi \tag{2.36}
\]

A typical XPS spectrum is a plot of the number of electrons detected per unit time (Y-axis, ordinate) versus the BE of the electrons (X-axis, abscissa). Since the BE is characteristic of each element, each peak in a spectrum corresponds to a specific core line and element. The peak intensity can be related to the concentration of that element in the sample using appropriate relative sensitivity factors. The precise BE of an electron depends not only on the energy level from which photoemission occurs, but also on the oxidation state of the atom and its chemical environment. These subtle difference in energy levels appear as small shifts on the BE scale. In addition to the main peaks in a photoelectron spectrum, satellite peaks can also form. For conductive materials, such as metals, the observation of an asymmetric peak shape is sometimes found which results in the occurrence of a tail on the higher binding energy side of the main peak [25]. These peaks
are formed when the outgoing electron interacts with a valence electron and excites it to a higher energy level. As a consequence, the energy of the core electron is reduced, and the signal appears a few eV below the core level position on the kinetic energy (KE) scale giving an asymmetric peak-shape.

Discrete structured shake-up peaks have been observed in the 2p\textsubscript{3/2} spectrum for Cu(II) species [26,27]. These shape-up peaks are formed when an ion (after photoionization) is excited by the outgoing photoelectron, and therefore, will be left in a specific excited energy state a few eV above the ground state. Consequently, the KE of the emitted photoelectron is reduced, leading to the occurrence of a shake-up peak at a higher BE than the main emission line. The position and shape of the shake-up satellite structure can be used to confirm a change in oxidation state for Cu.

Experimentally, XPS spectra were obtained with a Kratos AXIS Nova spectrometer using an Al Kα monochromatic high energy (hv = 1486.7 eV) source (15 mA, 14 kV). The work function of the instrument was calibrated using the Au 4f\textsubscript{7/2} line with BE = 83.95 eV, and the spectrometer dispersion was adjusted using the Cu 2p\textsubscript{3/2} peak with BE = 932.63 eV. Commonly, due to the presence of a thin adventitious carbon layer on the sample surface, the C 1s peak at 284.8 eV was used as a standard to correct for any surface charging effects. High resolution spectra were obtained on a surface area of 300 × 700 μm for both the Cu 2p and Cu L\textsubscript{3}M\textsubscript{4,5}M\textsubscript{4,5} Auger peaks at a pass energy of 20 eV. All spectra were analyzed using CasaXPS software (version 2.3.14) with a standard Shirley background correction.

As previously mentioned in section 1.5 and section 2.3.2.2, Auger LMM peaks were also collected from corroded Cu samples due to the difficulty of identifying Cu species by analyzing only Cu 2p spectra from XPS. These Auger peaks have unique peak shapes and positions, and are, therefore, useful for both elemental identification and chemical state analyses. In this study, the modified Auger parameter (σ') is calculated when analysing Auger peaks produced by the bombardment with X-rays on the corroded Cu surfaces. The original definition of the Auger parameter (σ) is by Wagner [28], as expressed in Eq. (2.37), involving the KE of the Auger transition from C\textsubscript{1}, C\textsubscript{2}, and C\textsubscript{3} core levels and KE of the photoelectron from core level C. This form of the equation allows negative values of σ.

\[ \sigma = KE_{Auger} (C_1 C_2 C_3) - KE_{photoelectron} (C) \] (2.37)
The Auger parameter ($\sigma$) was further modified by Gaarenstroom and Winograd by the addition of photon energy to $\sigma$, yielding the modified Auger parameter ($\sigma'$) [28]. The modified Auger parameter is independent of the X-ray energy used and is defined as the sum of the KE of the Auger transition from C$_1$, C$_2$, and C$_3$ core levels and the BE of the photoelectron from the core level C, Eq. (2.38). For Cu XPS analyses, this is the sum of the KE of the Cu LMM Auger peak and the BE of Cu 2p$_{3/2}$ peak.

$$\sigma' = KE_{Auger} (C_1C_2C_3) + BE_{photoelectron} (C)$$

(2.38)

The use of the modified Auger parameter and an inspection of the Auger peak shape allows a more accurate assignment of the various Cu species [26,27]. Further analysis of the Cu LMM Auger spectra were carried out using peak-fitting procedures outlined in reference [23]. These procedures allow for a (semi) quantitative Cu chemical state analysis of the various samples analysed.

2.3.2.3 Auger Electron Spectroscopy (AES)

AES is a highly surface sensitive (< 5 nm) technique in which the energy of an ejected electron from the surface of a material is used to determine the surface composition [21]. The analyzed area of a sample surface is usually $10^6$ to $10^8$ times smaller than that analyzed by SEM/EDX.

The basic principle of AES involves a three-electron process, and the emission of an KLL Auger electron is illustrated in Figure 2.23. The surface is bombarded by an electron beam with an energy of 3-10 eV [22]. As illustrated in Figure 2.23 (a), the ejected photoelectron from the core level leaves an empty hole that can be filled with an outer shell electron (e.g., from L$_1$ shell), Figure 2.23 (b). The relaxation of L$_1$ shell electron to the core energy level, results in an energy loss equal to the BE difference between the L and K orbitals. This internal transition causes the release of a so-called virtual photon, which then excites an outer shell electron (L$_{2,3}$) which is ejected to the vacuum level if the transferred energy is greater than the orbital (L$_{2,3}$) binding energy [23]. This emitted electron, Figure 2.23 (c) is termed an Auger electron. The kinetic energy of the emitted Auger electron is shown in the Eq. (2.39).

$$KE_{Auger} = BE_{core} - BE_{L1} - BE_{L_{2,3}}$$

(2.39)
**BE**<sub>core</sub>, **BE**<sub>L1</sub> and **BE**<sub>L2</sub> are the core level, first outer shell, and second outer shell electron binding energies, respectively. As shown in Eq. (2.39) above, the kinetic energy of Auger electrons is independent of the incident energy source. Due to the low energy of Auger electrons, most AES analyses are conducted under ultra-high vacuum (UHV) conditions, which prevents electron scattering off residual gas atoms as well as the formation of a thin "gas (adsorbate) layer" on the surface of the specimen, which could impede the analytical performance [23].

![Energy level diagram](image)

Figure 2.23: A schematic illustration of the three-electron process involved in the emission of a KLL Auger electron. (a) Ionization of core shell, (b) electron from a higher shell (L<sub>1</sub>) fills the hole in the core shell accompanied by the emission of virtual photons, and (c) ejection of an Auger electron from shell L<sub>2,3</sub> by the absorption of virtual photon.

In this study, Auger depth profiling was performed on a surface area of 2 × 2 mm using the Scanning Auger Nanoprobe PHI 710 with an excitation energy of 0.5 keV or 3 keV. An Argon ion beam was used as the sputtering source in depth profilometry and the signal strengths of Cu, O, S, Cl were recorded as a function of sputtering time, which was then converted to an average film thickness.

### 2.3.3 X-ray Diffraction

X-ray diffraction (XRD) is most widely used techniques for structure determination. The incident X-ray beam can be diffracted through a crystal, resulting in a characteristic diffraction pattern. When the positions and intensities of the diffracted beams are recorded, it is possible to deduce the arrangement of atoms and the chemical nature of the crystal [31].
The basic principle of XRD is related to the constructive and destructive interference of X-rays that have been diffracted by atoms. When a monochromatic X-ray beam with a wavelength (λ), is projected into a solid, X-rays will be diffracted in all directions. The intensity of X-rays diffracted from a set of crystal planes (Miller indices (hkl)) is dependent on the relative phases of the waves from adjacent planes, reflecting the geometrical structure and the types of atoms in a unit cell [31]. Constructive interference is achieved when two waves are completely in phase, reinforcing each other. By contrast, destructive interference is achieved when two waves are completely out of phase. As shown in Figure 2.24, the constructive interference, and hence diffraction, only occurs when the outgoing angle of scattered X-rays is equal to the angle of incidence (defined against the hkl plane). This relationship is described by Bragg’s Law, Eq. (2.40) [32],

\[ n\lambda = 2d \sin \theta \]  

(2.40)

where \( n \) is termed the order of reflection and is an integer, \( \theta \) is the incident angle of the X-rays and \( d \) is the spacing between the parallel interatomic layers. Complete constructive interference is achieved when two waves have a phase difference of \( n\lambda \). For any fixed values of \( \lambda \) and \( d \), there may be a set of incident angles (\( \theta_1, \theta_2, \theta_3 \)) due to the presence of different crystal planes in a material, at which diffraction occurs corresponding to \( n = 1, 2, 3 \). These crystal planes determine the position of each peak in the diffraction pattern in which the intensity is plotted as a function of \( 2\theta \). The lattice parameters of a crystal can be determined if the \( d \) spacing is known. For instance, NaCl is known to have a

![Figure 2.24: A diagram illustrating the constructive XRD diffraction between the adjacent interatomic layers. Bragg’s Law describes the mathematical relationship between wavelength (\( \lambda \)) and lattice spacing (d).](image)
face-centered cubic unit cell in which the relationship between the d spacing and the Miller indices is given by Eq. (2.41) [32].

$$d = \frac{a^2}{\sqrt{h^2+k^2+l^2}}$$  \hspace{1cm} (2.41)

In practice, diffractometers can operate in various ways, such as in a ω-2θ mode (Bragg-Brentano geometry: ω=θ) [31]. In this mode, the X-ray source is stationary, while the sample is rotated at half the rate of the detector so as to maintain the θ-2θ geometry, Figure 2.25, where s is the diffraction vector that bisects the angle between the incident and diffracted beam. Diffraction will only occur from crystallites in which the plane normal (hkl) is parallel to s.

Figure 2.25: A schematic showing the Bragg-Brentano geometry in an XRD analysis. A group of crystal planes are represented by blue lines aligned in parallel.

However, Bragg-Brentano mode is not used in our study, since only grains that align parallel to the surface can be probed. To ensure the acquisition of XRD patterns for all oriented grains, such as grains that are unparallel to sample surface, and to get compositional information on thin films, the parallel beam grazing incidence X-ray diffraction (GIXRD) was performed on corroded Cu sample. In GIXRD, both the X-ray source (incident angle ω) and sample positions were fixed, while the detector travelled circumferentially at a 2θ range. In GIXRD, the half of the detector angle (2θ) that is measured between the diffracted X-ray and transmitted X-ray, is not equal to the incident angle (ω, defined against the sample surface), Figure 2.26. The relationship between ω and θ is shown in Eq. (2.42).
\[ \omega = \frac{1}{2}(2\theta) - \beta \]  

(2.42)

In this study, the grazing incident angle was in the range of 0.2 to 5 degrees, thereby limiting the X-ray penetration depth. Since only the detector moved during measurement, the direction of diffraction vector (s) was changing during the scan. All GIXRD spectra was obtained using a Rigaku SmartLab X-ray diffractometer equipped with 2D HyPix-3000 detector and a Cu X-ray radiation source at 40 kV. The parallel plates collimator is placed before the detector to maximize the intensity of diffracted X-rays from GIXRD. The detector scan range (2\theta) was between 20 to 90° with a scan speed of 3°/min.

Figure 2.26: A schematic showing the grazing incidence XRD geometry. The diffraction vector (s) is no longer perpendicular to the sample surface. A set of crystal planes are represented by blue lines aligned in parallel.
2.4 References


Chapter 3
The Influence of Chloride on the Electrochemically Grown Film and the Susceptibility of Copper to Pitting Corrosion in Slightly Alkaline (Borate-Buffered) Aqueous Sulphide Solutions

3.1 Introduction

The safe management and disposal of high-level nuclear waste is essential if nuclear power is to remain a viable energy source. The proposed method in many countries, including Sweden, Finland and Canada, is to bury the spent nuclear fuel discharged from reactors in a deep geologic repository (DGR) with multiple barriers to provide safe isolation and containment. A primary barrier in this sequence is a corrosion-resistant waste container able to withstand the anticipated hydrostatic, lithostatic and glacial loads. In the Swedish KBS-3 concept, the spent fuel will be sealed in a container comprising a cylindrical Cu shell (50 mm in thickness) and a load-bearing inset of nodular cast iron [1].

Immediately after emplacement, the container, which contains the heat-generating fuel, will be exposed to humid aerated conditions which will rapidly evolve to cool and anoxic as radiation fields decay and heat production decreases [2]. Once the O₂ trapped upon emplacement has been consumed by microbial and mineral reactions within the clay surrounding the container and by minor container corrosion [2], the long-term threat to the durability of the container will be SH⁻. The Swedish and Finnish DGRs are known to contain SH⁻, produced in the groundwater as a consequence of sulfate-reducing bacteria and, possibly, mineral dissolution processes [3].

1This chapter includes work that has been published in:
The \( \text{SH}^- \) concentration, \([\text{SH}^-]\), is conservatively estimated to be \( \leq 10^{-5} \text{ mol/L} \) based on measurements in groundwaters from the proposed Swedish Forsmark site [4] with \([\text{Cl}^-]\) in the range of 0.1 to 0.3 \text{ mol/L} [3,5]. Corrosion of Cu in aqueous \( \text{SH}^- \) solution is driven by the formation of chalcocite (\( \text{Cu}_2\text{S} \)) films with their structure and properties being determined by the rate of \( \text{SH}^- \) transport to the Cu surface relative to its interfacial reaction rate with Cu, and the competition for surface adsorption sites between \( \text{SH}^- \) and \( \text{Cl}^- \), and possibly other anions [6]. Films grown electrochemically exhibit similar dependencies on \([\text{SH}^-], [\text{Cl}^-]\) and the transport of \( \text{SH}^- \) [7,8], with passive films possible only at high \([\text{SH}^-]\) (\( \geq 5\times10^{-4} \text{ mol/L} \)) and transport fluxes, conditions unachievable in a DGR with a bentonite buffer in place. More recent studies indicate that, even at these high \([\text{SH}^-]\), the \( \text{Cu}_2\text{S} \) films formed are porous rather than passive [8].

This conclusion is at odds with views expressed by other researchers who claim that passive sulfide films do form, leading to \( \text{Cl}^- \)-induced film breakdown and a susceptibility to pitting. They also claimed this susceptibility increased with \([\text{Cl}^-]\) and temperature [9–12]. In some of these studies [9,10], the solution pH was buffered with borate which may have significantly altered the film growth process. The corrosion/electrochemical behavior of Cu is known to be modified by the adsorption of anions, and pitting has been demonstrated to be possible on Cu in borate-buffered solutions [13–15]. In addition, Qin et al. [16] demonstrated that an increase in alkalinity could increase the probability of passivation of Cu but in the absence of \( \text{SH}^- \). The primary goal of this study is to determine whether passive Cu sulfide films can be formed when Cu is electrochemically polarized in aqueous \( \text{SH}^- \) solutions containing \( \text{Cl}^- \) and whether they then undergo \( \text{Cl}^- \)-induced passive film breakdown. To facilitate comparison to the published literature, solutions used in this work are identical to those used in previous studies where it is claimed such processes occurred [9,10].

### 3.2 Experimental

#### 3.2.1 Sample Preparation

Cu used in all experiments is O-free (< 5 ppm) and P-doped (30-100 wt.ppm) and provided by the Swedish Nuclear Fuel and Waste Management Co (SKB), Solna, Sweden [17]. Cu electrodes for rotating disk electrode (RDE) experiments were machined as disks,
with a threaded connection to a Ti rod and sealed into a Teflon holder using epoxy resin. A nonconductive lacquer was applied to prevent exposure of the steel/Cu junction to the electrolyte, leaving a flat Cu surface with a total surface area of 0.785 cm$^2$ exposed to the electrolyte. Prior to an experiment, the Cu electrode was ground with a sequence of SiC papers with grit sizes 800, 1000, 1200, 2400, 4000, and then polished to a mirror finish using aluminum oxide ($\text{Al}_2\text{O}_3$) suspensions with decreasing particle sizes (1 μm, 0.3 μm, and 0.05 μm), rinsed with Type I water with a resistivity of 18.2 MΩ·cm (provided by a Thermo Scientific Barnstead Nanopure 7143 ultrapure water system), sonicated with methanol for 1 min and finally dried in a stream of ultrapure (99.999%) Ar gas.

3.2.2 Electrochemical cell, Instrumentation, and Procedures

Experiments were performed in a standard three-electrode cell using a Cu RDE as working electrode, a Pt plate as counter electrode, and a saturated calomel reference electrode (SCE, +0.242 V vs SHE (Standard Hydrogen Electrode)). Electrochemical experiments were performed inside a Faraday cage to reduce interference from external electrical noise. The RDE rotation rate ($\omega$) was controlled by a Pine Instrument Company Analytical Rotator Model AFA86 Serial 882. Cyclic voltammetric (CV) experiments were conducted using either a Solartron 1287 potentiostat or a Solartron Analytical Modulab equipped with CorWare and XM-Studio-ECS software. Prior to experiments, the Cu electrode was cathodically cleaned at −1.5 V vs SCE for 1 min to reduce air-formed oxides, and then at −1.15 V vs SCE for another minute to allow the detachment of any H$_2$ bubbles which may have formed due to H$_2$O reduction at the more negative potential. CVs were performed from an initial potential of −1.35 V vs SCE to various anodic limits at a scan rate of 2 mV/s. All experiments were conducted at room temperature (21 ± 2 °C).

3.2.3 Solutions

Solutions were prepared with reagent-grade sodium chloride (NaCl, 99.0% assay), sodium sulfide (Na$_2$S·9H$_2$O, 98.0% assay), boric acid (H$_3$BO$_3$, 99.5% assay), sodium borate decahydrate (Na$_2$B$_4$O$_7$·10H$_2$O, 99.5% assay) and Type I water (18.2 MΩ·cm). Electrodes were exposed to 2×10$^{-4}$ mol/L SH$^-$ solutions (pH = 9) containing various chloride concentrations in the range from 0.01 mol/L to 5 mol/L. To ensure the maintenance of a deaerated environment, and to minimize SH$^-$ oxidation, solutions were purged with
ultra-high purity (99.999%) Ar for 30 min prior to each experiment and then continuously purged throughout the experiments.

3.2.4 Surface Analysis

3.2.4.1 Scanning Electron Microscopy, Elemental Analysis and Focused Ion Beam Cross Sectioning

Scanning electron microscopy (SEM) analyses were performed using a LEO 1540 instrument equipped with a focused ion beam (FIB) (Zeiss Nano Technology Systems Division, Germany) at the Western Nanofabrication Facility. An electron beam with an accelerating voltage ranging between 1 kV and 5 kV was used to collect high-resolution images of both film morphologies and milled samples. Chemical compositions of sample surfaces were qualitatively analyzed by energy dispersive X-ray spectroscopy (EDX) using a LEO 1540 FIB/SEM microscope.

3.2.4.2 Confocal Laser Scanning Microscopy

The measurement of surface topography and roughness on corroded Cu samples was performed using confocal laser scanning microscopy (CLSM). Prior to surface analysis, films formed on Cu were chemically removed by immersions in solutions containing 1 M HClO$_4$ + 0.025 mol/L hexamethylenetetramine ($C_6H_{12}N_4$) while the solutions were continuously sparged with ultrapure Ar gas. Any residual corrosion products were removed by clear packing tape. Samples were then sonicated in methanol for 1 min and dried in a stream of ultrapure Ar gas.

In this study, a Zeiss LSM800 For Materials/Zeiss Axio Imager. Z2m upright compound microscope was used for both 2D optical and 3D z-stack image acquisition. The wavelength of the laser was 405 nm and the diameter of the pinhole was set at 17 μm.

3.2.4.3 Raman Spectroscopy

Raman spectroscopy was performed using an InVia Reflex Raman spectrometer equipped with a 633 nm He-Ne laser and an Olympus microscope. Spectra were obtained using a 50 × uncoated objective lens with the beam focused to a diameter of ~ 2 μm. To minimize any surface heating effects, the laser was used at < 10% power. Prior to the acquisition of spectra, the spectrometer was calibrated against the 520.5 cm$^{-1}$ peak of Si.
3.4.2.4 X-ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopic (XPS) analyses were performed with a Kratos AXIS Nova spectrometer using an Al Kα monochromatic high energy (hv = 1486.6 eV) source (15 mA, 14 kV). The instrument work function was calibrated using the Au 4f7/2 line (Binding Energy (BE) = 83.95 eV) and the spectrometer dispersion was adjusted using the Cu 2p3/2 peak with BE = 932.63 eV. The C 1s peak at 284.8 eV was used as a standard to correct for surface charging. High resolution spectra were obtained for the Cu 2p peaks at a pass energy of 20 eV. Spectra were analyzed using CasaXPS software as described elsewhere [18] with a standard Shirley background correction. Cu L3M4,5M4,5 Auger spectra was also recorded and treated as described elsewhere [18].

3.3 Results and Discussion

3.3.1 Cyclic Voltammetry on Rotating Disk Electrodes

3.3.1.1 Borate-Buffered Chloride Solutions

Figure 3.1 shows CVs recorded in slightly alkaline 0.1 mol/L Cl− solutions (pH = 9, adjusted by the addition of NaOH solution with and without the added borate) at rotation rate ω = 33 Hz. In the absence of borate, the anodic current (i) in the potential (E) range −0.25 V to −0.1 V vs SCE increased exponentially with E on the forward scan and retraced the i-E relationship on the reverse scan. This behavior was that expected for an active dissolution process. In the E range from −0.25 V to −0.6 V vs SCE on the reverse scan, a shallow reduction process (C1) was observed, suggesting the presence of surface intermediates formed during the anodic dissolution process. The active dissolution of Cu is known to involve adsorbed Cl− species and to proceed via the formation of a thin surface CuCl layer [19],

\[ Cu + Cl^- (aq) \rightarrow CuCl (ads) + e^- \]  \hspace{1cm} (3.1)

\[ CuCl (ads) + (x-1)Cl^- (aq) \rightarrow CuCl_{x,1} (aq) \]  \hspace{1cm} (3.2)

Surface CuCl_{ads} species can be formed at potentials more negative than that predicted based on the thermodynamic properties of bulk CuCl. This mechanism has been shown to be valid over a wide range of chloride concentrations from 0.001 mol/L to 5.0 mol/L [3], with x increasing as the chloride concentration increases. The breadth (on the potential scale) of the shallow reduction process suggested the presence of more than one surface species since,
as the pH becomes more alkaline, hydrolysis of adsorbed CuCl\textsubscript{ads} species to Cu(OH)\textsubscript{ads} can occur as a precursor to Cu\textsubscript{2}O formation,

\[
CuCl\ (ads) + OH^-(aq) \rightarrow Cu(OH)\ (ads) + Cl^-(aq) \quad (3.3)
\]

\[
2Cu(OH)\ (ads) \rightarrow Cu_2O\ (s) + H_2O \quad (3.4)
\]

When a small concentration of borate ([BO\textsubscript{3}]\textsubscript{tot}) was added, similar anodic behavior was observed but with a slightly enhanced current, especially at the E at which the current began to rise (indicated as (a) in Figure 3.1). The suggestion (above) that a mixture of surface intermediates could have been formed was supported by the enhancement of the surface coverage (indicated by the increase in charge associated with their reduction (C1) on the reverse scan). Since borate would not be expected to promote Cl\textsuperscript{-} adsorption, this suggested a displacement of adsorbed Cl\textsuperscript{-} by borate adsorption leading to enhanced coverage by Cu(OH)\textsubscript{(ads)}, i.e., a preference for Reaction 3.3 rather than Reaction 3.2. When the [BO\textsubscript{3}]\textsubscript{tot} was increased further to a value > [Cl\textsuperscript{-}], a partial passivation process was observed, leading to a more distinct C1 peak and a further reduction process (C2) at more negative potentials.

![Figure 3.1: CVs performed at a scan rate of 2 mV/s in slightly alkaline (pH 9) 0.1 mol/L chloride solutions containing various [BO\textsubscript{3}]\textsubscript{tot}.](image-url)
To confirm the presence of oxides, Raman spectroscopy was performed on a Cu electrode after a potential scan to $-0.1\, \text{V vs SCE}$ in borate-free 0.1 M Cl$^-\text{ solutions}$ (pH = 9) with the initial pH controlled by addition of NaOH, Figure 3.2. The presence of Cu$_2$O was demonstrated by the broad peak doublet in the range 490 cm$^{-1}$ to 650 cm$^{-1}$, with the exact peak positions reported in the literature varying between studies, but very close to those in Figure 3.2 when measured using surface enhanced Raman spectroscopy [20,21]. Since CuO can also exhibit a peak (generally weak) in this area, identification of CuO was confirmed by the peak at 297 cm$^{-1}$ [22–24] which was not compromised in this manner.

The presence of these oxides did not rule out the possibility that unhydrolyzed CuCl may also have been present on the oxidized surface. Once the dissolution of Cu (I) (as CuCl$_x$ ($x^{-1}^{-1}$)) was hindered, the formation of Cu$_2$O/CuO was expected based on the E-pH diagram [25] and the extremely low solubilities of both oxides at pH = 9 [25,26].

Figure 3.2: Raman spectrum collected on a Cu sample after scanning the potential from $-1.35\, \text{V to } -0.10\, \text{V vs SCE}$ in a 0.1 mol/L NaCl solution (pH = 9).
3.3.1.2 Borate-Buffered Chloride Solutions Containing Sulphide

Figure 3.3 shows a CV recorded in a 0.1 mol/L NaCl solution containing 0.2 mol/L borate and $2 \times 10^{-4}$ mol/L SH$^-$ (pH = 9) at a rotation rate $\omega = 33$ Hz. This solution composition was chosen to facilitate a comparison to a set of potentiodynamic polarization experiments conducted in a solution with the same composition by Mao et al [9]. Their experiments were conducted in nitrogen-sparged solutions and only the forward scan from $-1.35$ V to $-0.10$ V vs SCE was recorded.

![CV graph with annotations](image)

Figure 3.3: CVs performed at a scan rate of 2 mV/s in a solution containing 0.1 mol/L NaCl + $2 \times 10^{-4}$ mol/L Na$_2$S + 0.2 mol/L borate (pH 9) at 20 °C, and at rotation rate $\omega = 17$ Hz. Six distinct regions were observed.

Six distinct regions of behavior were observed. Region 1 has been shown to be due to the anodic formation of a Cu$_2$S (chalcolite) surface layer [8,28] with the formation of oxides/hydroxides and soluble chloride complexes thermodynamically prohibited in this potential range [25]. As shown in Figure 3.4 (a), the anodic current in this region was independent of $E$ but dependent on $\omega$, confirming, as observed previously, but only for potentials up to $-0.7$ V vs SCE [8], that the reaction was at least partially transport-controlled. It was also shown previously that [8], if the CV scan was reversed in region 1, the current was maintained on the reverse scan, leading to further sulfide film growth. Such
a feature would only have been possible if the Cu$_2$S film remained porous and non-passive and was able to sustain film growth at the Cu$_2$S/solution interface [8]. If the film formed on the forward scan had been passive, the current on the reverse scan would have been effectively zero, since the electric field within such a film would have been too low to sustain the further film growth observed. Although not shown here, this reversibility was maintained up to the onset of region 2 confirming that passivity was not achieved throughout region 1. The crystalline nature of the Cu$_2$S film anodically-formed in this E$_{29}$ region was consistent with growth by deposition at the film/solution interface supported by the transport through solution of Cu(I), as both sulfide complexes (Cu(SH)$_2^-$) and Cu$_3$S$_3$ clusters, formed at the Cu surface [30,31]. Cu$_3$S$_3$ clusters have also been shown to be involved in the corrosion of Cu in aqueous sulfide solutions and their function as intermediates in Cu$_2$S formation have been demonstrated [30,31]. All these features confirm that the current in region 1 was not a passive current.

When $E$ entered region 2, and CuCl$_x$($^{x-1}$)$_{\text{tot}}$ and oxide film formation was possible, the current became independent of $\omega$ but steeply dependent on $E$, Figure 3.4 (a). The lack of a dependence on $\omega$ would be expected for reactions which occurred within the pores of the previously deposited Cu$_2$S film. Additionally, the $E$ at which region 2 commenced was independent of $\omega$ demonstrating that the current increase was not influenced by the increased flux of species such as SH$^-$ and Cl$^-$ to the Cu surface. The decrease in current in region 3 indicated the occurrence of a similar partial passivation process to that observed in the absence of SH$^-$ (Figure 3.1). The minor dependence of the current on $\omega$ in this region, especially on the forward scan, confirmed that this partial passivation process was considerably less dependent on the transport of SH$^-$ to the electrode surface compared to the current for Cu$_2$S film growth in region 1. As demonstrated in the absence of SH$^-$, Figures 3.1 and 3.2, this partial passivation process could be attributed to the formation of an oxide film. Given the limited [SH$^-$] at the Cu surface compared to [Cl$^-$] and [BO$_3$]$_{\text{tot}}$, it was likely that the direct formation of Cu$_2$S via the reaction steps functioning in region 1 was reduced somewhat in region 2.
The reduction peak in region 4 (Figure 3.4 (a)) could be attributed to the cathodic reduction of anodically-formed $\text{CuCl}^{(x-1)-}$ trapped within the pores in the $\text{Cu}_2\text{S}$ film and the reduction of the passivating oxide film formed on the Cu surface beneath the $\text{Cu}_2\text{S}$ film.

Figure 3.4: CVs performed in solutions containing 0.1 mol/L NaCl + $2 \times 10^{-4}$ mol/L Na$_2$S + 0.2 mol/L borate (pH 9) at 20 °C at various values of $\omega$.

The reduction peak in region 4 (Figure 3.4 (a)) could be attributed to the cathodic reduction of anodically-formed $\text{CuCl}^{(x-1)-}$ trapped within the pores in the $\text{Cu}_2\text{S}$ film and the reduction of the passivating oxide film formed on the Cu surface beneath the $\text{Cu}_2\text{S}$ film.
As opposed to the anodic process (regions 2 and 3), the reduction process (region 4) was strongly dependent on \( \omega \), the cathodic charge associated with the peak decreasing markedly as \( \omega \) increased. Under stagnant conditions, when the formation of \( \text{Cu}_2\text{S} \) in regions 2 and 3 was limited due to transport control by \( \text{SH}^- \) to the Cu surface, the anodic charge consumed in regions 2 and 3 was approximately equal to the cathodic charge regained in region 4. This indicates that the species formed anodically was trapped within the pores of the \( \text{Cu}_2\text{S} \) film and available for reduction in region 4. Since a passive oxide would be expected to be thin, its formation would only have required a small amount of anodic charge. Consequently, the great majority of the anodic charge consumed in regions 2 and 3 could be attributed to the formation of soluble \( \text{CuCl}_{x(x-1)^-} \), and of the cathodic charge consumed in region 4 to its reduction on the reverse scan.

When \( \omega \) was increased, the cathodic charge associated with the reduction peak in region 4, Figure 3.4 (a) decreased markedly and the overall current eventually became positive. This switch in sign could be attributed to a combination of features: (i) the loss of \( \text{CuCl}_{x(x-1)^-} \) by transport to the bulk of solution, which would have limited its cathodic reduction on the reverse scan; and (ii) the enhanced transport of \( \text{SH}^- \) into the porous structure, which would have enhanced \( \text{Cu}_2\text{S} \) formation. This second process would also have led to the reaction 3.5,

\[
2\text{CuCl}_{x(x-1)^-}(aq) + \text{SH}^-(aq) \rightarrow \text{Cu}_2\text{S} (s) + 2x\text{Cl}^-(aq) + H^+(aq)
\] (3.5)

with the \( \text{Cu}_2\text{S} \) formed stable in region 4, and hence not reduced until potentials in region 6 were reached. Reaction 3.5 has been shown previously to be rapid [30]. In addition, any \( \text{Cu}_2\text{O} \) formed would be chemically transform to \( \text{Cu}_2\text{S} \) by the reaction 3.6, albeit at a much slower rate than that of Reaction 3.5, as previously shown [32].

\[
\text{Cu}_2\text{O} (s) + \text{SH}^- (aq) \rightarrow \text{Cu}_2\text{S} (s) + \text{OH}^- (aq)
\] (3.6)

Once the species produced within the porous film was reduced in region 4, an anodic current for further \( \text{Cu}_2\text{S} \) film growth became observable in region 5, leading to an increase in the charge associated with the film reduction peak in region 6. This confirmed that the \( \text{Cu}_2\text{S} \) film formed on the forward scan, whose growth would have continued throughout regions 2, 3 and 4, remained porous. While not as large as on the forward scan, the current was dependent on \( \omega \), demonstrating that the film growth process remained
partially transport-controlled on the reverse scan. This provided unequivocal evidence that the current decrease in region 3 was not due to the formation of a passive Cu$_2$S film.

Finally, in potential region 6, two cathodic reduction peaks were observed, Figure 3.4 (b), for the reduction of the Cu$_2$S film. The charges associated with Cu$_2$S film reduction were considerably greater than observed in our previous study [8], when the potential was reversed at −0.7 V vs SCE. This demonstrated that the formation of a porous Cu$_2$S layer continued when the potential limit was extended to −0.1 V vs SCE. In addition, the charge increased with electrode rotation rate, Figure 3.4 (b), as expected if anodic film growth occurred, at least partially, under transport control on both the forward and reverse scans. The origin of these two reductions peaks has been discussed previously [8].

3.3.2 The Influence of Chloride on Sulfide Film Formation

Figure 3.5 shows a plot of the current recorded at $E = -0.7$ V vs SCE and rotation rate $\omega = 17$ Hz as a function of $[\text{Cl}^-]$ in CVs similar to those shown in Figures 3.3 and 3.4. Similar behavior was observed at other values of $\omega$ in the range 8–33 Hz. Within the chloride concentration range investigated (0.1 mol/L to 5.0 mol/L), the current density was well below the theoretical transport-controlled value (calculated using the Levich equation), dependent on the value of $\omega$ (as shown in Figure 3.4 (a)) and decreased as chloride concentrations increased. This influence of $[\text{Cl}^-]$ was the opposite of that observed by Kong et al. [33] who showed that the current increased with $[\text{Cl}^-]$ when Cu was covered by an oxide film. Their increase in current was attributed to a chloride-induced increase in the cation vacancy density and the diffusion rate of Cu vacancies in the oxide, the clustering of which at the metal/oxide interface was considered necessary for passive film breakdown and the initiation of pitting. Such an explanation cannot account for our observations. These authors also showed a slight increase in current with $[\text{Cl}^-]$ when a Cu$_2$S film was present, which is also at odds with the results in Figure 3.5. However, since their experiments were conducted under nitrogen-sparged conditions, the interfacial $[\text{SH}^-]$ at the Cu surface would have been depleted at the base of pores in the thickening Cu$_2$S deposit and, consequently, not representative of the bulk solution $[\text{SH}^-]$. Since Cl$^-$ was not consumed in this potential region, the $[\text{Cl}^-]$ at the Cu surface would have been maintained, leading to a high $[\text{Cl}^-]/[\text{SH}^-]$ ratio, a situation that would cause an enhanced porosity of the Cu$_2$S film [4]. We conclude that, in our case, the sulfide film growth process was partially controlled by $\text{SH}^-$ transport.
to the reacting Cu surface and partially by competition for Cu surface adsorption sites between SH\(^{-}\) and Cl\(^{-}\) which impeded the initial charge transfer, reaction 3.7, in the overall film formation process. The ability of Cl\(^{-}\) to adsorb on Cu is well established [23,34,35]. This combination of features required that the Cu\(_2\)S film remained porous and able to support film growth by deposition at the Cu\(_2\)S/solution interface, as has been previously demonstrated [7].

\[
\text{Cu (s) + SH}^{-}\text{(aq) → Cu(SH) (ads) + e}^{-}
\]  
(3.7)

Figure 3.5: Limiting current densities at \(E = −0.7\) V vs SCE (region 1, Figure 3.3) plotted as a function of [Cl\(^{-}\)] taken from CVs conducted in 0.2 mol/L borate-buffered (pH 9) solutions containing \(2 \times 10^{-4}\) mol/L Na\(_2\)S but at various [Cl\(^{-}\)]. The dashed line shows the value for a total transport-controlled reaction calculated using the Levich equation.

### 3.3.3 The Influence of Chloride on Cu (I) Dissolution and Oxide Film Formation

Figure 3.6 shows sections of CVs recorded at \(\omega = 17\) Hz in a borate-buffered solution (0.2 M, pH = 9) containing \(2 \times 10^{-4}\) mol/L SH\(^{-}\) and various [Cl\(^{-}\)]. The influence of Cl\(^{-}\), while subtle in the region of Cu\(_2\)S growth (Figure 3.5), had a dramatic effect in
regions 2 and 3 (defined in Figure 3). At low [Cl\(^{-}\)] (0.01 mol/L, 0.05 mol/L, 0.1 mol/L), an active-to-passive transition was observed indicating the formation of a partially passive oxide as observed in the absence of SH\(^{-}\) at this [BO\(_3\)]\(_{\text{tot}}\), Figure 3.1. Cathodic reduction of this oxide led to only a shallow current on the reverse potential scan as observed in the absence of SH\(^{-}\) (Figure 3.1). When the [Cl\(^{-}\)] was increased to 0.5 mol/L and 1.0 mol/L, a considerably larger anodic current was observed but the active-to-passive transition still occurred at 0.5 mol/L. At 1.0 mol/L, this transition was no longer observed. For both 0.5 mol/L and 1.0 mol/L, a significant reduction process was observed on the reverse scan consistent with the accumulation of CuCl\(_x\)(x−1)\(^{-}\) in pores in the Cu\(_2\)S film on the forward scan (as discussed above) and its reduction on the reverse scan. At even higher [Cl\(^{-}\)] (i.e., [3.0 mol/L and 5.0 mol/L], the active dissolution of Cu became completely dominant, commencing at lower potentials as the [Cl\(^{-}\)] increased. The absence of oxides was confirmed by the current on the reverse scan which retraced that on the forward scan, showing no evidence of the reduction of surface films. This transition from passive oxide formation to CuCl\(_x\)(x−1)\(^{-}\) dissolution required [Cl\(^{-}\)] >[BO\(_3\)]\(_{\text{tot}}\).

![Figure 3.6: CVs conducted at rotation rate ω = 17 Hz in 2 × 10\(^{-4}\) mol/L Na\(_2\)S + 0.2 mol/L borate solution containing various [Cl\(^{-}\)]s.](image-url)
Figure 3.7 compares the potentials, termed onset potentials, at which the current increased in a series of CVs similar to those shown in Figure 3.6. These potentials were obtained by recording the intersections between a horizontal line for zero current density and the tangent to the increasing current, as illustrated in Figure 3.6. Also included are the potentials which Mao et al. [9] claimed are Cl\(^-\) induced breakdown potentials for the Cu\(_2\)S films grown at the lower potentials in region 1. The breakdown potentials claimed by Kong et al. [11] for experiments conducted in solutions containing a number of different anions (F\(^-\), Cl\(^-\), Br\(^-\), I\(^-\)) also fell in this oxide-dominated potential region. The similarity between the two sets of values, for [Cl\(^-\)] \(\geq 0.1\) mol/L, demonstrated that the values measured by Mao et al. [9] represent either oxide film breakdown potentials or potentials for the onset of active dissolution (as Cu(Cl)\(_x\)(x-1)-), not Cu\(_2\)S breakdown potentials. The deviations in the two sets of data at higher [Cl\(^-\)] could reflect the differences in potential scan rate and electrode rotation rate between the two set of experiments.

Figure 3.7: Comparison of the potentials at which the current increases in CVs (Figure 3.6) to those measured by others and claimed to be sulphide film breakdown potentials.
3.3.4 Morphology and Chemical Composition of Surface Films and the Corroded Cu Specimen after Film Removal

Figures 3.8 and 3.9 show a series of SEM surface images and FIB-cut cross sections for a series of SEM surface images and FIB-cut cross sections for films grown after scanning the potential to various limits at a rotation rate $\omega = 33$ Hz. At $E = -0.80$ V vs SCE (in region 1, Figure 3.3) a very thin nodular film was formed. Since such a thin film was difficult to cross section, due to its immediate decomposition under both electron and Ga ions beams [8], it was plated with Pt prior to attempting the FIB cut, which reduced the resolution of the image. The cross section, Figure 3.9 (a) showed the Cu$_2$S film was approximately 75 to 150 nm thick, porous and deposited on a rough Cu interface.

Figure 3.8: Morphologies of films on Cu after scanning E to different limits in solutions (pH 9) containing 0.1 mol/L NaCl + $2 \times 10^{-4}$ mol/L Na$_2$S + 0.2 mol/L borate: (a) $-0.80$ V vs SCE, (b) $-0.40$ V vs SCE, (c) $-0.14$ V vs SCE, (d) $-0.10$ V vs SCE.

When the film growth potential was increased to $-0.4$ V vs SCE, a scattered dendritic Cu$_2$S deposit, similar to that observed by Kong et al. [11] was formed on top of a porous, non-protective base layer, Figure 3.8 (b). Inspection of the FIB-cut cross section,
Figure 3.9 (b), shows a coverage of the surface by a columnar film ranging in thickness from $\sim 170$ nm to $\sim 990$ nm. As demonstrated previously, Cu transport can occur in the form of either Cu(SH)$_2^-$ complexes or Cu$_3$S$_3$ particles [30] a process that occurred so readily that any base layer present, but not visible on the scale of this image, was universally porous with pores on a scale of many nanometers or greater. The Cu surface exhibited a roughness on the scale of tens of nanometers with no visible localized pits.

Further increasing the applied potential to $-0.14$ V vs SCE led to a considerably thicker dendritic deposit confirming the on-going transport of Cu (I) from the anodically oxidized Cu surface, Figure 3.8 (c). Examination of the FIB-cut cross sections after anodic oxidation at E > $-0.14$ V vs SCE, Figure 3.9 (c), shows that, as the Cu oxidation rate increased, previously grown Cu$_2$S layers appeared to be detached and replaced. This was to be expected since the Pilling-Bedworth ratio ($\Omega_{BR}$) for Cu$_2$S growth on Cu is large ($\Omega_{BR} = 2$) [8] leading to large interfacial stresses as the applied potential was increased. The further deposition of dendritic structures within the void space created confirmed that the
Cu surface remained an un-passivated source of Cu(SH)$_2^-$ and Cu$_3$S$_3$ formation. While no meaningful measurement of film thickness could be made, the dimensions of the deposits are indicated in Figure 3.9 (c).

When the applied $E$ was in regions 2 and 3, the surface became covered by a thick dendritic deposit and a second deposit comprised of small hexagonal platelets, Figures 3.8 (c) and 3.8 (d). To determine the composition of this deposit, an EDX analysis was performed on a cluster of such platelets (within the area marked with a red circle in Figure 3.8 (d)). To minimize the analytical depth and obtain a more representative analysis, the acceleration voltage of the primary electrons was maintained at 5 kV. The EDX spectrum exhibited strong signals for both O and S confirming the presence of Cu$_2$S as well as Cu oxides. The percentages by weight of O and S were 1.4 % and 12.5 %, respectively. This platelet morphology could have indicated the initial formation of oxides followed by their subsequent partial conversion to Cu$_2$S, a process shown previously to occur [32]. The absence of Cl$^-$ in this spectrum, and in others recorded on surfaces oxidized in regions 2 and 3, suggested that insignificant formation of CuCl occurred, consistent with the observation in Figure 3.1 that oxide formation dominated in regions 2 and 3 in a solution containing 0.2 mol/L borate.

Representative examples of a series of Raman spectra collected at various surface locations are shown in Figure 3.10 for applied potentials in regions 1 (−0.4 V vs SCE) and 2 (−0.14 V vs SCE). As indicated on the figure, peaks at 147 cm$^{-1}$, 297 cm$^{-1}$, 525 cm$^{-1}$ and 625 cm$^{-1}$ were attributed to Cu$_2$O [23,36–39] while peaks at $\sim$ 210 cm$^{-1}$ and 300 cm$^{-1}$ confirmed the presence of Cu$_2$S [32,40–42]. The peak at $\sim$ 297 cm$^{-1}$ could also have indicated the presence of CuO since its formation was thermodynamically possible according to the E-pH diagram [43]. The very faint peaks in the range 800 cm$^{-1}$ to 1400 cm$^{-1}$ after scanning to −0.14 V vs SCE, have been observed before for anodically grown oxides on Cu [32] but remain unassigned. The very faint response in the region 525 cm$^{-1}$ to 625 cm$^{-1}$ after scanning to only −0.4 V vs SCE may indicate a small amount of Cu$_2$S decomposition to oxides induced by the laser beam during the recording of the Raman spectrum.
To confirm whether phases involving both oxidation states of Cu (Cu (I) and Cu (II)) were formed, followed by at least partial conversion to Cu$_2$S in regions 2 and 3, Cu 2p$_{3/2}$ and Cu L$_3$M$_{4,5}$M$_{4,5}$ (Auger) XPS spectra were recorded on Cu samples prepared by scanning the potential to $-0.14$ V vs SCE and $-0.1$ V vs SCE in a solution containing 0.1 mol/L NaCl, 0.2 mol/L borate and $2 \times 10^{-4}$ mol/L Na$_2$S at an electrode rotation rate of 33 Hz. The Cu (I)/Cu (II) ratio in the oxidized surface was calculated from the photoelectron yields for both the Cu 2p$_{3/2}$ and satellite peaks, Figure 3.11 (A and B, respectively) [18]. This calculation considers that the main emission line A contains contributions from both Cu oxidation states (Cu (I)/Cu (II)) but the intensity of the shakeup satellite peak contains a contribution from Cu (II) only. To confirm these analyses, and to identify the various Cu species present, the Cu L$_3$M$_{4,5}$M$_{4,5}$ Auger spectrum was fitted as described elsewhere [18]. As indicated by the values on Figures 3.11 (b) and 3.11 (d) panels (in at. %) the relative fractions (in the surface of the deposit) of Cu (I) and Cu (II) from CuL$_3$M$_{4,5}$M$_{4,5}$ Auger spectra align well with the Cu 2p$_{3/2}$ XPS analyses, Figures 3.11 (a) and 3.11 (c). These results indicate that the small hexagonal platelets are oxides not sulfide, possibly undergoing a slow conversion. As expected, and in agreement with the Raman analysis,
Cu$_2$O was the dominant phase present with significant amounts of Cu (II), as Cu(OH)$_2$, also present. While this cannot confirm passivity was due to Cu (II) surface phases, it demonstrated their formation in this potential region did occur.

Figure 3.11: Cu 2$p_{3/2}$ ((a) and (c)) and Cu L$_3$M$_{4,5}$M$_{4,5}$ ((b) and (d)) spectra from two Cu samples after potentiodynamically polarized to $-0.14$ V vs SCE ((a) and (b)) and $-0.10$ V vs SCE ((c) and (d)).

Figures 3.12 (a) and (b) show SEM micrographs of a Cu surface before and after film growth by scanning the potential to $-0.13$ V vs SCE (region 2, Figure 3.3) at a rotation rate $\omega = 33$ Hz, and a CLSM 3-dimensional surface topography image and surface depth profile recorded on the corroded Cu electrode after film removal by chemical cleaning. Considerably thicker dendritic deposits were observed when the potential was scanned to $-0.13$ V vs SCE, confirming the on-going transport of Cu (I) from the anodically oxidized Cu surface, Figure 3.12 (b). The 3-dimensional image recorded by CLSM, Figure 3.12 (c),
showed a generally roughened surface with a maximum surface height ($S_z$) of 2 μm and average surface roughness ($S_a$) of 0.1 μm. The surface profile recorded across the center of the surface, as indicated by the blue line, revealed a shallow surface depression of ~ 0.5 μm in the center, Figure 3.12 (c). This depression may indicate the susceptibility to pitting when the potential was extended into the region of oxide formation.

![Figure 3.12](image1.png)

Figure 3.12: Analysis of a Cu surface corroded in a solution containing 0.1 mol/L NaCl + $2 \times 10^{-4}$ mol/L Na$_2$S + 0.2 mol/L borate (pH 9) at 20 °C and at a rotation rate $\omega = 33$ Hz. (a) a mirror polished Cu surface before corrosion; (b) an SEM micrograph of a corroded Cu surface after potentiodynamic polarization to −0.13 V vs SCE; and (c) a CLSM 3-dimensional surface topography image and a surface depth profile across the location of the blue line on Cu surface after film removal (section 3.2.4).

### 3.3.5 Reaction Mechanism

Figure 3.13 attempts to summarize the reactions which occurred in potential regions 1 to 3 (as defined in Figure 3.3). In region 1, while the formation of a thin passive layer may initially have been attempted (step a), as demonstrated previously [8] the rapid development of interfacial stresses led to the immediate development of porosity. This enabled the release of anodically formed Cu(SH)$_{(ads)}$ species to solution as soluble complexes (Cu(SH)$_2^-$) and Cu$_3$S$_3$ clusters (step b). These species were then transported to
the film solution interface and deposited as Cu$_2$S (step c). This process was partially controlled by the transport of SH$^-$ to the Cu surface (step d) and by competition for surface adsorption sites with Cl$^-$ (step e).

In region 2 (Figure 3.3), formation of CuCl species on the Cu surface (step f) led to the release of CuCl$_2^-$ to the solution within pores in the Cu$_2$S deposit (step g). In the buffered borate solution, Cu(OH)$_{\text{ads}}$ species also formed (step h), with the relative coverages dictated by the [Cl$^-$/[BO$_3$]$_{\text{tot}}$ ratio. On transport to the film/solution interface, where SH$^-$ was not depleted, the conversion of CuCl$_2^-$ (aq) to Cu$_2$S was likely (step i). Also, in the borate-buffered solution, Cu (I) would have had limited solubility and could have deposited as Cu$_2$O (step j). Since Cu$_2$O would have been unstable in the presence of SH$^-$ (aq), its conversion to Cu$_2$S(s) was expected (step k) but appeared to be slow. In region 3, the direct formation of Cu$_2$O (step l), and possibly CuO, led to passivation provided the [Cl$^-$/[BO$_3$]$_{\text{tot}}$ was sufficiently low.

Figure 3.13: Schematic illustration of the film formation mechanism.: 1 – formation of a copper sulfide film in potential region 1 (Figure 3.3); 2 – the formation of copper-chloro complexes in potential region 2 (Figure 3.3); 3 – formation of an oxide film in region 3 (Figure 3.3). Numbers 1 to 3 refer to the dominant reaction that is likely to occur at a specific regime of potentials. Each letter, as indicated from (a) to (g), represents each reaction and its associated chemical species.
3.4 Summary and Conclusions

As anticipated based on thermodynamic expectations, Cu₂S films were formed at potentials considerably lower than those at which anodic dissolution and oxide film formation occurred. The Cu₂S films were porous and non-passivating with the rate of film growth determined by a combination of SH⁻ transport through the growing film and the competition between SH⁻ and Cl⁻ for adsorption sites on the reacting Cu surface. No influence of borate on the Cu₂S film growth process was detected.

At more positive potentials, a combination of anodic dissolution as CuClₓ(ₘ₋₁)⁻ and oxide film formation (Cu₂O and possibly CuO) occurred, irrespective of whether a Cu₂S film had been grown at lower potentials. The balance between anodic dissolution and oxide film formation depended on the [BO₃]ᵢₒ/[Cl⁻] ratio with passivation by oxide film formation dominating when [BO₃]ᵢₒ > [Cl⁻]. The measured onset potentials for anodic dissolution/oxide formation were close to the values measured by other authors and erroneously attributed to Cl⁻ induced breakdown of a passive Cu₂S film formed at lower potentials.

That the Cu₂S film remained porous and non-passive was confirmed by the revival of partially transport controlled Cu₂S growth once any oxide films formed at more positive potentials had been removed. No evidence for pitting was observed at potentials at which only Cu₂S formed and would only be expected at potentials sufficiently positive for oxide formation.
3.5 References


Chapter 4
The Influence of Temperature on the
Electrochemically Grown Film and the Susceptibility
of Copper to Pitting Corrosion in Slightly Alkaline
(Borate-Buffered) Aqueous Chloride and Sulphide
Solutions

4.1 Introduction

The internationally accepted method for the permanent disposal of high-level nuclear waste involves sealing it in corrosion-resistant containers to be subsequently emplaced in deep geologic repository (DGR). In Sweden, Finland and Canada, the spent fuel would be sealed in containers fabricated with either a cast iron insert and a Cu shell (Sweden, Finland) or a carbon steel vessel with a Cu coating (Canada). Such containers would provide only absolute barrier in a multi-barrier system designed to prevent radionuclide release to the environment [1–6]. The choice of Cu as the corrosion barrier is based on its corrosion resistance in the anoxic environments anticipated in a DGR [7,8], in which exposure conditions will evolve from initially warm (~ 90 °C) and oxidizing to eventually cool (~ 15 °C) and anoxic [9]. The period required for the evolution in redox condition to occur is uncertain [10] with recent field studies suggesting consumption of O₂, trapped on sealing the DGR, may be complete within the first 10 to 100 years after container emplacement in the DGR [11]. By contrast, the evolution in temperature, which can be controlled to a large extent by container and DGR design, is more readily calculated, and expected to evolve from a high of 80 °C to 90 °C during the first 100–200 years of emplacement to ~ 15 °C after several thousands of years [12].

1This chapter includes work that has been published in:
Based on Swedish DGR designs and calculations, containers are expected to remain uncompromised by corrosion for periods exceeding $10^5$ years with most containers surviving for $> 10^6$ years [3,13,14]. While resistant to corrosion under anoxic conditions [7,10], Cu is unstable in the presence of sulphide ($S^{2-}$) or hydrosulphide ($SH^-$) ions [10,15]. In a DGR, the production of $SH^-$ is likely via the action of sulphate-reducing bacteria (SRB) [8] at locations remote from the Cu container surface. While, $SH^-$ transport to the Cu surface will be extremely slow [16], due to the high compaction density of the clay surrounding the container, corrosion induced by $SH^-$ should be investigated.

A series of corrosion studies have shown that under anoxic conditions the corrosion of Cu in aqueous $SH^-$ environments leads to the formation of chalcocite ($Cu_2S$) films on the Cu surface [11,14,16–18]. The properties of these films were found to depend on [$SH^-$] and [$Cl^-$] and their ratio, with $Cl^-$ being one of the dominant groundwater anions. These studies showed that, while the growth law may change, these films remained porous and only partially protective. Based on these studies, corrosion would be expected to propagate relatively uniformly in Swedish, Finnish, and Canadian repositories, since the interfacial reaction of $SH^-$ with Cu is rapid compared to $SH^-$ transport via the compacted clay under $SH^-$ transport-controlled condition [19,20].

Other authors have claimed, however, that the film is passive in nature when formed under electrochemical conditions, a situation they propose would render the metal susceptible to pitting [22,23]. For instance, Dong et al. [22] measured the influence of temperature on supposedly pitting breakdown potentials in borate ($HBO_3^{2-}$/$BO_3^{3-}$-) buffered, slightly alkaline solutions containing various [$Cl^-$] and [$SH^-$], and proposed that Cu would be susceptible to passivity and pitting under DGR conditions [22,23]. However, Martino et al. [24], based on electrochemical experiments conducted at room temperature in solutions containing various [$SH^-$] and [$Cl^-$], found film properties to be dependent on these concentrations and the flux of $SH^-$, controlled by the use of a rotating disk electrode [24]. They categorized the films according to their properties and demonstrated that only films formed in solutions containing $\geq 5 \times 10^{-4}$ mol/L $SH^-$ could be considered partially passive, and only when a high $SH^-$ flux to the Cu surface was maintained. More recent studies, however, showed that, even at high [$SH^-$], films formed anodically remained porous rather than becoming passive [25]. Sulphide concentrations in Swedish and Finnish DGRs are
expected to be well below $10^{-4}$ mol/L in Swedish and Finnish DGRs [3,10], and $< 10^{-6}$ mol/L in a Canadian DGR [10]. This, coupled with the extremely low flux of SH\(^-\) through compacted clay, would reduce the surface [SH\(^-\)] to a very low value [16]. These studies and calculations indicate that passivity, a prerequisite for pitting corrosion, should not be possible. However, the corrosion behaviour of Cu in SH\(^-\) solutions is also influenced by the presence of other anions (SO\(_4^{2-}\) as well as Cl\(^-\)) [26], suggesting that the presence of HBO\(_3^{2-}/BO_3^{3-}\) in the experiments of Dong et al. [21] and Kong et al. [27,28] could have influenced the properties of the Cu\(_2\)S films.

In a previous paper, we re-evaluated the formation of sulfide and oxide films on Cu under electrochemical conditions in HBO\(_3^{2-}/BO_3^{3-}\) containing solutions that either contained or were free of SH\(^-\) and various [Cl\(^-\)]s [29]. This study demonstrated that HBO\(_3^{2-}/BO_3^{3-}\) could induce passivity, but only in the potential range where oxide formation was thermodynamically possible, which is a potential that is much more positive than that at which Cu\(_2\)S formation occurred. In this study, we report results and analyses obtained under similar conditions as a function of temperature over the range from 20 °C to 80 °C.

4.2 Experimental

4.2.1 Sample Preparation

Cu used in all the experiments was O-free (< 5 ppm) and P-doped (30-100 wt. ppm) provided by the Swedish Nuclear Fuel and Waste Management Co. (SKB), Solna, Sweden. Cu specimens for rotating disk electrodes (RDE) were machined with a threaded connection to a Ti rod and sealed into a Teflon holder using epoxy resin. A non-conductive lacquer was applied to prevent exposure of the Ti/Cu junction to the electrolyte, leaving a flat Cu surface with a total surface area of 0.785 cm\(^2\) exposed to the electrolyte. Prior to an experiment, the Cu electrode was ground with a sequence of SiC papers with grit sizes: 800, 1000, 1200, 2400, 4000, and then polished to a mirror surface finish using aluminum oxide (Al\(_2\)O\(_3\)) suspensions with decreasing particle size (1 μm, 0.3 μm, and 0.05 μm), sonicated in methanol (reagent-grade) for 1 min and finally dried in a stream of ultrapure (99.999%) Ar gas.
4.2.2 Electrochemical Cell and Instrumentation

Experiments were performed in a three-electrode cell using a Cu RDE working electrode, a Pt plate counter electrode, and a saturated calomel reference electrode (SCE, +0.242 V/SHE). The cell was fitted with an outer glass jacket through which H₂O was circulated from a thermostatic bath (Isotemp 3016H Fisher Scientific) to maintain the temperature of the solution constant to within ± 1 °C. The electrochemical cell was placed inside a Faraday cage to reduce interference from external electrical noise. The RDE rotation rate (ω) was controlled by a Pine Instrument Company Analytical Rotator Model AFA86 Serial 882. Cyclic voltammograms (CV) were recorded using either a Solartron 1287 potentiostat or a Solartron Analytical Modulab equipped with CorWare and XM-Studio-ECS software. Prior to each experiment, the electrode was cathodically cleaned at −1.5 V vs SCE for 1 min to reduce any air-formed oxides, and then at −1.15 V vs SCE for another minute to allow the detachment of any H₂ bubbles which may have formed due to H₂O reduction at the more negative potential. CVs and potential scans were performed from an initial potential of −1.35 V vs SCE to various upper potential limits at a scan rate of 2 mV/s. Potentiostatic polarizations were conducted at −0.13 V vs SCE for 6 h at 33 Hz (80 °C).

4.2.3 Electrolyte and Environment

Solutions were prepared with reagent-grade sodium chloride (NaCl, 99.0% assay), sodium sulphide (Na₂S·9H₂O, 98.0% assay), boric acid (H₃BO₃, 99.5 % assay), sodium borate decahydrate (Na₂B₄O₇·10H₂O, 99.5% assay) and Type I water (18.2 MΩ·cm) purified using a Barnstead NANOPure 7143 ultra pure water system. Electrodes were exposed to solutions containing 2 × 10⁻⁴ mol/L Na₂S (buffered with 0.2 mol/L HBO₃²⁻/BO₃⁻ to pH 9) and various [Cl⁻] in the range from 0.01 mol/L to 5 mol/L. To ensure the maintenance of a deaerated environment and minimize sulphide oxidation, the solution was sparged with ultrapure (99.999%) Ar for 30 min prior to each experiment and then continuously throughout the experiment. Experiments were performed at various temperatures, ranging from 20 °C to 80 °C (± 2 °C).
4.2.4 Surface Analysis

4.2.4.1 Scanning Electron Microscopy, Energy-Dispersive X-ray Spectroscopy and Focused Ion Beam Cross Sectioning

Scanning electron microscopy (SEM) analyses were conducted using a LEO 1540 instrument equipped with a focused ion beam (FIB) (Zeiss Nano Technology System, Germany) at the Western Nanofabrication Facility. An electron beam with an accelerating voltage ranging between 1 kV and 5 kV was used to collect high-resolution images of both film morphologies and milled samples at various magnifications. Elemental compositions of sample surfaces were analysed using an energy dispersive X-ray spectrometer (EDX) in conjunction with a LEO 1540 FIB/SEM microscope and a Hitachi SU8230 Regulus Ultra High-Resolution Field Emission SEM coupled with a Bruker X-Flash EDX detector.

4.2.4.2 Confocal Laser Scanning Microscopy

Surface topography and roughness were obtained by conducting confocal laser scanning microscopy analyses on corroded Cu samples. Prior to surface analysis, films formed on Cu were chemically cleaned by immersing samples in solutions containing 1 mol/L HClO₄ + 0.025 mol/L hexamethylenetetramine (C₆H₁₂N₄) while solutions were continuously sparged with ultrapure Ar gas. Any residual corrosion products were removed by clear packing tape. Samples were then sonicated in methanol for 1 min and dried in a stream of Ar gas. A Zeiss LSM800 For Materials/Zeiss Axio Imager. Z2m upright compound microscope is used for both 2D optical and 3D z-stack image acquisition. The wavelength of the laser is 405 nm and the diameter of pinhole is set at 17 μm.

4.2.4.3 Raman Spectroscopy

Raman spectroscopy was performed using a Renishaw InVia Reflex Raman spectrometer equipped with a 633 nm He-Ne laser and an Olympus microscope. Spectra were obtained using a 50 × uncoated objective lens with a laser beam diameter of ~ 2 μm. To minimize any surface heating effects, the laser beam was used at 1–5% power. Prior to the acquisition of spectra, the spectrometer was calibrated against the 520.5 cm⁻¹ peak of Si.
4.2.4.4 X-ray Diffraction

A Rigaku SmartLab X-ray diffractometer with Cu Kα radiation (40 kV, 44 mA) was used to examine the phase composition of the surface film. The sample was scanned over a 2θ range from 20° to 95° with a 0.02° step size. A grazing incidence angle configuration with an incident angle of 2.5° was used to minimize interference from the Cu substrate.

4.3 Results and Discussion

4.3.1 Cyclic Voltammetry in Borate-Buffered Solutions Containing Sulfide and Chloride at Various Temperatures

A series of CVs were recorded from −1.35 V to −0.1 V vs SCE in a solution containing 0.1 mol/L NaCl + 2 × 10⁻⁴ mol/L Na₂S + 0.2 mol/L HBO³⁻/BO³⁻³⁻ (pH = 9). Figure 4.1 shows the sections of the CVs from −0.9 V to −0.1 V vs SCE at various temperatures. In Figure 4.2, two sections of the scans conducted at 80 °C and various electrode rotation rates (ω) are shown; (a) −0.9 V to −0.1 V vs SCE; and (b) −1.25 V to −0.85 V vs SCE. As indicated in these figures, a number of specific regions can be defined.

![Figure 4.1](image_url)

Figure 4.1: CVs recorded in solution containing 0.1 mol/L NaCl + 2 × 10⁻⁴ mol/L Na₂S + 0.2 mol/L borate (pH 9) at ω =17 Hz and at various temperatures. The number 1-6 refer to different regions.
The current in region 1 has been demonstrated [24,29] to be due to the anodic formation of chalcocite (Cu$_2$S) with the formation of oxide/hydroxide and soluble Cu complexes prohibited in this potential range [7]. The current in region 1 was independent of E, Figure 4.1, but increased with ω, Figure 4.2 (a). In addition, although not shown here, the current was maintained on the reverse scan if the potential scan was reversed at other potentials in this region, which was consistent with previous results recorded at 20 °C [24]. This set of observations would only be possible if the Cu$_2$S film formed on the forward scan was porous, and its formation was at least partially transport-controlled and sustained on the reverse scan. A significant increase in current was observed when the scan was extended into region 2 where dissolution as CuCl$_x$($x$−1)$^-$ became possible. The subsequent decrease in current in region 3 suggested an active-to-passive transition which shifted to lower potentials as the temperature was increased. The current in region 2 was only slightly dependent on ω while the decrease in region 3 was independent of ω, Figure 4.2 (a). This was also similar to the behaviour observed at 20 ± 2 °C [24].

Since we demonstrated previously that such current increases were observed in the absence of SH$^-$, they can be attributed to the anodic dissolution of Cu, with a minor dependence on ω, and thus less dependent on the transport of Cl$^-$ ions, due to the occurrence of these reactions within the pores of the Cu$_2$S layer formed at more negative potentials (≤ −0.3 V vs SCE). The reactions, occurring in this potential range have been extensively studied [8,30]. The rapid decrease in current in region 3 was shown at room temperature to be due to the formation of a Cu$_2$O/CuO layer induced by the presence of HBO$_3^{2-}$/BO$_3^{3-}$ (at pH 9) irrespective of whether SH$^-$ was present. Oxide formation could proceed directly by oxidation of the Cu surface or by the hydrolysis of the surface layer formed in reaction (4.1), or of dissolved CuCl$_x$($x$−1)$^-$, reaction (4.4) [30,31].

\[
\begin{align*}
Cu + Cl^- & \rightarrow CuCl_{ads} + e^- \quad (4.1) \\
CuCl_{ads} + (x-1)Cl^- & \rightarrow CuCl_x^{(x-1)^-} \quad (x=1, 2, \text{ or } 3) \quad (4.2) \\
2CuCl_{ads} + 2OH^- & \rightarrow Cu_2O + H_2O + 2Cl^- \quad (4.3) \\
2CuCl_x^{(x-1)^-} + 2OH^- & \rightarrow Cu_2O + H_2O + 2xCl^- \quad (4.4)
\end{align*}
\]
The low current in region 4, Figure 4.1, suggested the formation of a passive oxide.

Figure 4.2: CVs conducted in solutions containing 0.1 mol/L NaCl + 2 × 10⁻⁴ mol/L Na₂S + 0.2 mol/L borate (pH 9) at 80 °C at various values of the electrode rotation rate (ω). (a) the section of the scans between −0.9 V to −0.1 V vs SCE: (b) the sections of the same scans between −1.25 V and −0.83 V VS SCE
film. However, the increase in current (region 4) with temperature, Figure 4.1, and $\omega$, Figure 4.2 (a), and the recovery of the current for anodic dissolution (as $\text{CuCl}_x^{(x-1)^-}$) in regions 2 and 3 on the return scan confirmed that passivation was incomplete, especially for $T \geq 60 ^\circ C$. The cathodic reduction peak in region 5, Figures 4.1 and 4.2 (a), can be attributed to the reduction of the anodically-formed oxides and $\text{CuCl}_x^{(x-1)^-}$ trapped within the pores of the Cu$_2$S film. This was consistent with the observation that the anodic charge increased in regions 2 and 4 as temperature increased, Figure 1. The charge associated with reduction peak 5 also increased as expected.

Figure 4.2 (a) shows that, at a stationary electrode, the cathodic charge recovered in region 5 was close to that consumed by anodic oxidation in regions 2 and 3, which was consistent with the retention at the electrode surface of the majority of the anodic products. When $\omega$ was increased, the charge associated with region 5 decreased and, for a sufficiently high value of $\omega$, the net current in this region became positive, Figure 4.2 (a), suggesting a net oxidation process. This can be attributed to a combination of the increased fluxes of reducible $\text{CuCl}_x^{(x-1)^-}$ away from the electrode surface and $\text{SH}^-$ into the porous structure which would lead to the enhanced formation of Cu$_2$S. The combination of these two fluxes would also be expected to lead to the rapid chemical deposition of Cu$_2$S on the Cu surface via the chemical reaction (4.5) [32], with the Cu$_2$S not being able to be reduced until the potential was scanned to region 7 ($-1.2 \text{ V vs SCE} < E < -1.0 \text{ V vs SCE}$), Figure 4.2 (b). Additionally, an increased flux of $\text{SH}^-$ to the Cu surface would also lead to the chemical conversion from Cu$_2$O to Cu$_2$S, although this reaction is not particularly fast compared to reaction 4.5 [33].

$$2\text{CuCl}_x^{(x-1)^-} + \text{SH}^- \rightarrow \text{Cu}_2\text{S} + \text{H}^+ + 2x\text{Cl}^- \quad (4.5)$$

The revival of the current for the anodic formation of Cu$_2$S in region 6 on the reverse scan, Figure 4.1 and Figure 4.2 (a), confirmed that the Cu$_2$S film formed on the forward scan remained porous and continued to grow. The current recovery in region 6 was almost complete, especially at the higher temperatures, Figure 4.1, indicating that the film formation/reduction processes at higher potentials had only a minor influence on the anodic formation of Cu$_2$S. Figure 4.2 (b) shows the cathodic reduction peaks of Cu$_2$S in region 7. Commonly, two reduction peaks are observed in this region [24], reflecting the distinct morphologies of these films. Previously, It has been shown that the cathodic charge
associated with Cu₂S reduction (Q_C) was approximately equal to the anodic charge (Q_A) consumed in its formation. In this study, while Q_C increased as Q_A increased, it was difficult to perform a quantitative comparison due to the large partially overlapping current for H₂O reduction which accounted for the rapidly increasing current at more negative potentials (< −1.1 V vs SCE), Figure 4.2 (b). The significant increase in current associated with H₂O reduction reaction (E < −1.1 V vs SCE) could be attributed to an increase in total surface area of the Cu particulates formed during the cathodic reduction of Cu₂S.

### 4.3.2 The Influence of Temperature on Sulfide Film Formation

Figure 4.3 shows the current densities recorded at E = −0.6 V vs SCE (i.e., in region 1) and at ω = 17 Hz for all the temperatures studied. Similar behaviour was observed at other values of ω ranging from 8 to 33 Hz. At all temperatures, the current densities were substantially lower than the theoretical transport-limited current as indicated by the red circle which was calculated at 25 °C using the Levich equation [34]. While the measured current density decreased only slightly with temperature, the deviation from transport

![Figure 4.3: Limiting current densities at E = −0.6 V vs SCE (Figure 4.1) plotted as a function of solution temperature taken from CVs conducted in solutions containing 0.1 mol/L NaCl + 2 × 10⁻⁴ mol/L Na₂S + 0.2 mol/L borate (pH 9) but at various temperatures. The red circle shows the theoretical current density for a total transport-controlled reaction at 25 °C.](image-url)
control was greater at the higher temperatures since the theoretical transport-limiting current would have increased with increasing temperature.

This influence of temperature on the potential-independent current in region 6 was contrary to that claimed by others [22,28] who observed a slight increase. This slight increase was attributed by those authors to an increase in generation of cation vacancies as the temperature was increased, and the condensation of cation vacancies at the metal/barrier layer interface was considered to account for the passive film breakdown [22,27,28].

4.3.3 The Influence of Temperature on Chloride-Induced Active Dissolution and Oxide Formation

The potential at which the current began to rise in region 2, Figure 4.1, can be defined as the onset potential at which the anodic oxidation associated with the formation of soluble CuCl$_{x(x-1)}$ species began. This potential was determined by plotting the current logarithmically and defining the onset potential as the intersection of the extrapolated currents in regions 1 and 2, as shown in Figure 4.4.

![Figure 4.4](image)

Figure 4.4: Potentiodynamic polarization conducted on copper in a 0.1 mol/L NaCl + 2 × 10^{-4} mol/L Na$_2$S + 0.2 mol/L borate (pH 9) solution at 80 °C and at an electrode rotation rate (ω) of 17 Hz. The onset potential is indicated by the intersection between the horizontal line for zero current density and the tangent to the increasing current.
These onset potentials, and similar values obtained at different concentrations of Cl\(^-\) over the range from 0.1 mol/L to 5.0 mol/L, are plotted for three temperatures (40, 60 and 80 °C) in Figure 4.5. Included in this plot are the potentials which Dong et al. [22] claimed were Cl\(^-\)-induced breakdown potentials for the Cu\(_2\)S films grown at lower potentials in region 1, Figure 4.2. The similarity between the two sets of data demonstrates that the values measured by Dong et al. [22] represented onset potentials for anodic dissolution, not Cu\(_2\)S film breakdown values.

![Comparison of potentials](image)

Figure 4.5: Comparison of the potentials at which the current increases in CVs (Figure 4.1) to those measured by others and claimed to be sulphide film breakdown potentials.
4.3.4 Surface Characterization of Electrochemically Grown Films and the Corroded Cu Specimens after Film Removal

SEM micrographs recorded on the surfaces of electrodes after scanning the potential to various potential limits at $\omega = 33$ Hz at temperature of 80 °C are shown in Figure 4.6. The FIB-cut cross-sections of these electrodes are shown in Figure 4.7.

![SEM micrographs](image)

Figure 4.6: SEM micrographs showing the morphologies of films formed at 80 °C after scanning $E$ to various limits in solutions containing 0.1 mol/L NaCl + $2 \times 10^{-4}$ mol/L Na$_2$S + 0.2 mol/L borate. (a) $-0.85$ V vs SCE, (b) $-0.40$ V vs SCE, and (c) $-0.24$ V vs SCE, (d) $-0.13$ V vs SCE.

When the potential limit was $-0.85$ V vs SCE (i.e., confined to the early section of region 1), the SEM micrograph in Figure 4.6 (a) showed the formation of only a thin film and the grinding ridges from surface preparation remained visible. The extremely small apparent pit-like features occurred at the locations where SiC and Al$_2$O$_3$ particles were embedded in the soft metal surface during electrode preparation as demonstrated by EDX. The cross-section in Figure 4.7 (a) shows that the Cu$_2$S film was thin and porous with a maximum thickness of 367 nm, but with many locations where the film was considerably thinner. This approximate maximum thickness was considerably larger than that for the
film grown under similar conditions at 20 °C (≤ 150 nm) [29], despite the observation that the plateau current in region 1 was smaller at 80 °C than at 20 °C, Figure 4.3. As a consequence, the overall extent of film formation would be expected to be lower at the higher temperature leading to a correspondingly thinner film if the thickness was determined by charge only. As the FIB-cut cross-sectional image in Figure 4.7 (a) shows the film grown at 80 °C was composed of columnar features that were non-uniformly distributed on the surface. This columnar growth at the higher temperature could be attributed to the more extensive transport of Cu species than that at the lower temperature. As shown previously, Cu$_2$S film growth occurred at the film/solution interface with transport occurring in the form of either Cu(SH)$_2$ complexes or Cu$_3$S$_3$ clusters [32]. When the potential was scanned to −0.4 V vs SCE, a scattered dendritic Cu$_2$S deposit was formed on top of a fine particulate base layer, Figure 4.6 (b). The cross-section shown in Figure 4.7 (b) revealed that the particulate base layer, while apparently more compact and evenly distributed, remained porous and continued to grow in a columnar manner. While the Cu

![FIB cut cross-sections of films formed at 80 °C](image)

Figure 4.7: FIB cut cross-sections of films formed at 80 °C after scanning E to various limits in solutions containing 0.1 mol/L NaCl + 2 × 10$^{-4}$ mol/L Na$_2$S + 0.2 mol/L borate (pH 9). (a) −0.85 V vs SCE, (b) −0.40 V vs SCE, and (c) −0.24 V vs SCE, (d) −0.13 V vs SCE.
surface was slightly rougher, there was no indication of pitted locations at the Cu/film interface. One particularly long columnar feature is marked in Figure 4.7 (b).

When the potential scan limit was extended to −0.24 V vs SCE and eventually to −0.13 V vs SCE, the outer dendritic deposit became denser, Figures 4.6 (c) and (d), and achieved an apparent thickness of 5 μm but contained extensive void spaces, Figures 4.7 (c) and (d). The porous particulate base layer reached a thickness of 280 nm to 398 nm at −0.24 V vs SCE and did not thicken noticeably when the potential was extended to −0.13 V vs SCE, Figure 4.7 (c) and (d). This base layer maintained its coherence at −0.24 V vs SCE, a potential in region 3 at 80 °C, and the Cu surface showed no indication of pitting. At −0.13 V vs SCE, when the CV in Figure 1 (at 80 °C) indicated a partially passive state (region 4), the base layer appeared to have broken up slightly, Figure 4.7 (d).

Raman spectra were collected at various surface locations after the potential was scanned to −0.4 V vs SCE (region 1) and −0.13 V vs SCE (region 4), Figure 4.8. The spectrum recorded at −0.4 V/SCE showed a broad peak at 297 cm\(^{-1}\), confirming the presence of Cu\(_2\)S [33,35–37]. The very shallow response in the wavenumber range 500 cm\(^{-1}\) to 625 cm\(^{-1}\) may indicate slight conversion of the Cu\(_2\)S to oxide by reaction with air, which can be attributed to the local heating effect induced by the laser beam while the spectrum was recorded [38,39]. In the spectrum recorded at −0.13 V vs SCE, the peak at 297 cm\(^{-1}\) could be due to either Cu\(_2\)S or CuO, since the formation of the latter was also thermodynamically possible at this potential [7]. The peaks at 147 cm\(^{-1}\) and 220 cm\(^{-1}\), and the less well-defined peaks in the range 500 cm\(^{-1}\) to 625 cm\(^{-1}\) confirm the presence of Cu\(_2\)O.

To confirm these compositions, grazing incidence angle X-ray diffraction patterns were recorded after 1 h of potentiostatic oxidation at −0.13 V vs SCE at 80 °C, Figure 4.9. Comparison to standards, confirmed the presence of Cu\(_2\)S and Cu\(_2\)O but did not detect CuO.
Figure 4.10 shows EDX elemental maps (expressed as wt. %) recorded on a mechanically polished cross-section of the Cu electrode anodically oxidized at −0.13 V vs SCE for 6 h (80 °C). The high Si and O wt.% at the top of the maps indicate the locations of the epoxy resin used to protect the surface layers during cutting and polishing of the cross-section. The void space throughout the film, observed in the SEM FIB-cut cross sections micrographs, Figure 4.10, was evident in the maps for Cu, O and S. Sulphur was mostly detected on the top, while the majority of the O associated with oxide was located in the middle of the film and at the Cu/film interface. The body of the film was mainly composed of copper oxide (Cu₂O, as indicated by XRD analysis, Figure 4.9) with islands of Cu metal (red spots) attributable to Cu particles produced during mechanical polishing.

Figure 4.8: Raman spectra recorded on two Cu samples after potentiodynamic polarization. The potential was scanned from −1.35 V to different potentials (vs SCE) at a scan rate of 2 mV/s.
At the Cu/film interface, the surface layer contained some Cu$_2$S, but was predominantly oxide, consistent with the dominant formation of a partially protective oxide at −0.13 V vs SCE, as suggested by the electrochemical results, Figure 4.2 (a). While Cu$_2$S formation at the Cu/film interface was limited, a thick layer of Cu$_2$S was formed at the

Figure 4.9: Analysis of a Cu surface potentiostatically polarized for 1 h in a solution containing 0.1 mol/L NaCl + 2 × 10$^{-4}$ mol/L Na$_2$S + 0.2 mol/L borate (pH 9) at 80 °C and at a rotation rate $\omega = 33$ Hz: (a) An SEM image showing the FIB-cut cross-section and (b) Grazing incidence XRD patterns of a Cu sample after potentiostatic polarization at −0.13 V vs SCE in a solution containing 0.1 mol/L NaCl + 2 × 10$^{-4}$ mol/L Na$_2$S + 0.2 mol/L borate (pH 9) for 6 hours at 80 °C, together with standards obtained from the Rigaku SmartLab XRD database.
film/solution interface (i.e., at the film/epoxy interface in the maps) with only relatively small amounts present in the thick, void-filled body of the film. Since the anodic reaction of Cu with \( \text{SH}^- \) is rapid, limited film growth on the Cu surface can be attributed to \( \text{SH}^- \) depletion at this location, the surface \([\text{SH}^-]\) being controlled by transport through the thick film. The accumulation of a much thicker \( \text{Cu}_2\text{S} \) layer at the film/solution interface would be expected when the anodically-formed \( \text{CuCl}_x(\text{x}^{-1})^- \) was transported through pores within the film to the film solution interface to react with \( \text{SH}^- \) on encountering the bulk \([\text{SH}^-]\), leading to the deposition of \( \text{Cu}_2\text{S} \).

Figure 4.10: SEM micrograph and respective EDX weight percentage elemental maps of the cross-sections of an anodic film grown after potentiostatic polarization in solutions containing 0.1 mol/L \( \text{NaCl} + 2 \times 10^{-4} \) mol/L \( \text{Na}_2\text{S} + 0.2 \) mol/L borate (pH 9) for 6 hours at 80 °C.
To investigate the extent of corrosion damage on the Cu surface, SEM and BSE images were recorded after films had been removed by the chemical cleaning procedure described in section 4.2.4.2. Figure 4.11 (a) shows a CV recorded on Cu in a solution containing 0.1 mol/L NaCl + $2 \times 10^{-4}$ mol/L Na$_2$S + 0.2 mol/L borate (pH 9) at 80 °C. Electrodes were potentiodynamically polarized to upper potential limits, in regions 1 to 4 (Figure 4.11 (a)) and the SEM/BSE images of the cleaned surfaces are shown in Figure 4.11:

Figure 4.11: Analysis of a Cu surface potentiodynamically polarized to various upper potential limits in a solution containing 0.1 mol/L NaCl + $2 \times 10^{-4}$ mol/L Na$_2$S + 0.2 mol/L borate (pH 9) at 80 °C and at rotation rate $\omega = 33$ Hz. (a) CV recorded in the potential range of −0.6 to −0.1 V vs SCE, indicating potential limits. SEM and BSE images recorded on chemical cleaned surfaces: (b) −0.40 V vs SCE, (c) and (d) −0.28 V vs SCE, (e) and (f) −0.10 V vs SCE.
4.10 (b) to (g). These potential limits (−0.40 V to −0.13 V vs SCE) were chosen based on the current feature in the CV, Figure 4.10 (a), suggesting an active to passive transition on the Cu surface.

At \( E = -0.4 \) V vs SCE (in region 1, Figure 4.11 (a)), a uniform but minor surface roughening was observed with no apparent localized damage to the Cu surface. Since only the formation of \( \text{Cu}_2S \) occurs in this region 1. When the film growth potential was increased to −0.28 V vs SCE, localized corrosion features were observed, Figure 4.11 (c) and (d). The SEM image, Figure 4.11 (c) also showed the dispersal of white particles (some indicated by the orange arrows) distributed across the Cu surface. Inspection of the corresponding BSE image, Figure 4.11 (d), suggested these white particles were not \( \text{Al}_2\text{O}_3 \), a residue which could be easily embedded in Cu during mechanical polishing, since these particles remained white compared to the bulk Cu surface, demonstrating the presence of surface products containing heavy elements, possibly, copper oxides. The formation of copper oxides was thermodynamically possible at \( E = -0.28 \) V vs SCE.

Further increasing the upper potential limit to \( E = -0.24 \) V vs SCE (region 3, Figure 4.11 (a)) led to the uniform surface roughening with minimal localized damage, Figure 4.11 (e) and (f). Despite the appearance of pit-like features at more negative potential (−0.28 V vs SCE, Figure 4.10 (c) and (d)), Figure 4.11 (e) and (f), they were not observed when the scan limit was in region 3. The examination of the surface after polarization to \( E = -0.13 \) V vs SCE in Figure 4.11 (g), region 4 in Figure 4.11 (a), showed only general surface roughening with some granular features and no local penetrations.

Figure 4.12 shows the SEM image and qualitative EDX intensity maps recorded on the cleaned Cu surface after potentiodynamic polarization to \( E = -0.28 \) V vs SCE at 80 °C. The dominant EDX signal for Cu is expected on the cleaned surface, Table 4.1, with much lesser signals for O, C, and S which appear to be concentrated in more corroded features, Figure 4.12 (a), (c), (d) and (e). This suggests that while the general surface was efficiently cleaned, residual traces of corrosion products remained located in these more extensively corroded areas.
Table 4.1: EDX elemental analyses on the mapped region in Figure 4.12.

<table>
<thead>
<tr>
<th>Element</th>
<th>Weight%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>83.8</td>
</tr>
<tr>
<td>C</td>
<td>14.5</td>
</tr>
<tr>
<td>O</td>
<td>1.3</td>
</tr>
<tr>
<td>Si</td>
<td>0.3</td>
</tr>
<tr>
<td>S</td>
<td>0.1</td>
</tr>
</tbody>
</table>

To evaluate the localized corrosion features formed after polarization to $-0.28$ V vs SCE, optical microscopy and CLSM were used to map the surface. Figure 4.13 shows the maximum surface height ($S_z$) was $\sim 3 \, \mu$m with an average surface roughness ($S_a$) of $\sim 0.1 \, \mu$m, as shown in the optical image and its corresponding 3-dimensional topography map, Figure 4.13 (a) and (b). The step height measurement was performed on an area containing a pit-like feature (Red box, Figure 4.13 (a)), along the dashed line in Figure 4.13 (b), yielding a maximum penetration depth at $\sim 1 \, \mu$m. This is considerably lower than the
maximum pit depth of ~ 7 μm measured by Dong et al. [21] on a similarly polarized electrode (80 °C), suggesting a much more pronounced damage to Cu than observed here.

While it remains unclear why localized corrosion features are not observed at higher upper potential limits, this study shows they are only observable once the potential reaches region 2 Figure 4.11 (a), when anodic dissolution is preceded by the formation of a CuCl$_{ads}$ layer (reaction 4.2). There is the possibility that non-uniform formation of this layer initially led to localized corrosion damage before it spread more uniformly across the surface, thereby resulting in a more uniformly corroded surface. Of more importance to the present study is that localized damage was not observed at the lower potential limits, Figure 4.11 (a), region 1, when only Cu$_2$S film formation occurred.

![Figure 4.13](image)

Figure 4.13: Analysis of a corroded Cu surface after film removal. Prior to film removal, Cu was potentiodynamically polarized to $-0.28$ V vs SCE in a solution containing 0.1 mol/L NaCl + $2 \times 10^{-4}$ mol/L Na$_2$S + 0.2 mol/L borate (pH 9) at 80 °C and at a rotation rate $\omega = 33$ Hz. (a) An optical image; (b) a 3-dimensional topographical map; and (c) the step height measurement across the surface (indicated by the white dashed line in (b)) showing the depth of the selected feature (red box in (a)).
4.4 Summary and Conclusions

1) The kinetics of electrochemically-grown chalcocite (Cu$_2$S) films on Cu in the potential range $-0.8$ V to $-0.3$ V vs SCE were partially transport-controlled and developed a porous, non-passive structure. Temperature had only a minor influence on the kinetics of sulphide film growth.

2) At more positive potentials ($\geq -0.3$ V vs SCE) an active to passive transition was observed, with active dissolution occurring as CuCl$_x^{(x-1)-}$ within the Cu$_2$S film formed at lower potentials followed by the partial passivation of the surface by the formation of Cu$_2$O. The potential range within which these two processes occurred decreased as the temperature increased.

3) The potentials at which active dissolution commenced coincided with the potentials erroneously claimed in the literature to be chloride-induced sulfide film breakdown potentials. This coincidence of values was observed at all temperatures studied in the range 20 °C to 80 °C.

4) Raman spectroscopy and XRD confirmed the formation of chalcocite (Cu$_2$S) in the low potential region ($-0.4$ V vs SCE) and Cu$_2$S/Cu$_2$O at higher potentials ($E > -0.3$ V vs SCE).

5) SEM micrographs and EDX analyses confirmed the presence of oxides at the Cu/film interface covered by a thick extremely porous overlayer with a thick deposited outer layer of Cu$_2$S formed by the reaction of SH$^-$ with CuCl$_x^{(x-1)-}$ transported through the film from the Cu surface.

6) SEM and CLSM analyses on chemically cleaned surfaces demonstrated that only general surface roughening occurred in the potential range in which only Cu$_2$S formation was observed. Once dissolution as CuCl$_x^{(x-1)-}$ and oxide formation became possible, localized corrosion features indicated non-uniform damage accumulation but no deep localized corrosion processes were observed despite the apparent occurrence of partial passivation by oxide.
4.5 References


Chapter 5

Copper Sulphide Film Grown on Copper Under Freely Corroding Condition in Aqueous Sulphide Solutions

5.1 Introduction

The safe disposal and management of high-level nuclear waste (HLNW) is a concern for many countries, such as Sweden, Finland and Canada, which rely heavily on nuclear power to generate electricity. The universally chosen approach for the permanent disposal of the HLNW is to bury it at a depth of \( \geq 500 \) m in a deep geological repository (DGR) with multiple barriers to provide safe containment and isolation \([1,2]\). A primary barrier in this multi-barrier system is a corrosion-resistant container capable of withstanding the anticipated hydrostatic, lithostatic and glacial loads \([1]\). The proposed container in some countries will be designed with either a cylindrical copper (Cu) shell containing a nodular cast iron insert (Sweden, Finland) or a Cu-coated carbon steel vessel (Canada).

Upon emplacement, this container will initially be exposed to humid, warm and slightly oxidizing conditions which will then rapidly evolve to hot and dry, before gradually becoming cool and anoxic as \( \gamma \)-radiation fields emitted by the waste-form inside the container decay. Entrained \( \text{O}_2 \), trapped in the DGR upon sealing, will be consumed by mineral and microbial reactions occurring in the bentonite clay compacted around the container and the corrosion of structural steel within the repository, as well as slight corrosion of the container Cu itself \([2]\).

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\(^1\)This chapter includes work that has been published in:
Owing to the extremely small inventory of these oxidizing species, waste containers can be readily designed to survive the early oxidizing period. However, the long-term threat to container durability is the presence of sulphide (SH\(^-\)) within the groundwater, as this species can cause degradation of Cu.

As illustrated in Figure 5.1, sulphide can be produced by the dissolution of minerals and/or the microbial activity of sulphate-reducing bacteria (SRB) in the clay at locations remote from the container surface. This process is expected to have a very small impact on the bulk concentration of sulphide within the groundwater, raising it to perhaps less than 0.1 ppm; however, [3,4] the subsequent transport of sulphide to the container surface will lead to its corrosion, involving the formation of a chalcocite (Cu\(_2\)S) surface film or more porous deposit. Considerable effort has been expended on the investigation of the Cu sulphide film formation process [5–15]. The physical properties of this chalcocite film have been demonstrated to vary significantly with sulphide concentration [SH\(^-\)], the flux of SH\(^-\) to the Cu surface, and the presence of other groundwater anions (such as Cl\(^-\) and SO\(_4\)\(^{2-}\)). The morphology of the surface film will influence how the corrosion progresses on the Cu surface. If a passive film is formed, Cu could be susceptible to pitting, with corrosion damage occurring preferentially at localized sites. By contrast, if the deposit is not protective, then the corrosion damage would be more uniformly distributed.

![Figure 5.1: Schematic showing that the long-term corrosion process that could lead to container failure is the remote production of sulphide by the action of sulphate reducing bacteria.](image-url)
In this study, we have investigated the formation of Cu$_2$S films grown under both electrochemical and natural corrosion conditions using a combination of electrochemical and surface analytical techniques. Our primary goal was to investigate the early stages of sulphide film growth to determine whether there was any evidence for the formation of a barrier layer which could support pitting. Scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX), and Raman spectroscopy were performed on both electrochemically and corroded Cu surfaces. Focused ion beam (FIB) cross sectioning coupled with SEM was also used to examine the damage incurred at the Cu surface. Auger spectroscopy was performed to determine the thickness of thin films and relative film composition with regards to the film thickness.

5.2 Experimental

5.2.1 Electrode Preparation

The Cu used in all experiments was P-doped (30-100 wt. ppm), O-free Cu (< 5 ppm) provided by the Swedish Nuclear Fuel and Waste Management Co. (SKB) [16]. Copper disk working electrodes with a total surface area of 0.785 cm$^2$ were cut from plate material. The disks were connected to a stainless-steel shaft and painted with a non-conductive lacquer to prevent contact of the steel with the electrolyte. The electrodes were then heated (60 °C for 12 h) to promote adhesion of the paint. The exposed flat surface was ground successively with 240, 600, 800, 1000, and 1200 grade SiC paper, then polished to a mirror finish using 1 μm, 0.3 μm, and, finally, 0.05 μm Al$_2$O$_3$ suspensions. Prior to experiments, electrodes were washed with Type I water (resistivity = 18.2 MΩ·cm, obtained from a Thermo Scientific Barnstead Nanopure 7143 ultrapure water system), ultrasonically cleaned using methanol (reagent grade), washed with Type I water, and then dried using a stream of ultra-pure (99.999%) Ar gas.

5.2.2 Electrochemical Cell and Instrumentation

A three-electrode glass electrochemical cell was used in the electrochemical and corrosion experiments with a platinum plate (99.95% Alfa Aesar) connected to external circuitry by a Pt wire (0.5 mm diameter) as the counter electrode, a saturated calomel reference electrode (SCE, +0.242 V vs SHE), and a Cu working electrode. The cell was housed inside a Faraday cage to reduce electrical noise from external sources. All
electrochemical experiments were conducted using either a Cu stationary electrode or a rotating disk electrode (RDE), as indicated in Figure 5.2. 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 or a Solartron Analytical Modulab equipped with CorrWare (Scribner Associates, version 3.5h) and XM-Studio-ECS software (version 3.4).

Corrosion experiments were performed in an Ar-purged anaerobic chamber (Canadian Vacuum Systems Ltd.), maintained at a positive pressure (2-4 mbar) by an MBraun glove box control system. The \( \text{O}_2 \) concentration in the chamber was analysed with an MBraun oxygen probe with a detection limit of 1 ppm. The chamber was maintained at a total oxygen concentration \( \leq 3 \) ppm with the dissolved oxygen in solution calculated, using Henry’s law, to be \( \leq 3.9 \times 10^{-9} \text{ mol/L} \). Despite the possible presence of trace amounts of dissolved oxygen in the sulphide solution, the oxidation of \( \text{Cu} \) to copper sulphide would still be the predominant process, since copper sulphide is more stable in sulphide solution than copper oxide, based on thermodynamic data \( (\Delta G^\circ = -101.46 \text{ kJ/mol for the conversion from } \text{Cu}_2\text{O} \text{ to } \text{Cu}_2\text{S in sulphide solutions at } 298 \text{ K}) [7]: \text{Cu}_2\text{O} (s) + \text{SH}^- (aq) \rightarrow \text{Cu}_2\text{S} (s) + \text{OH}^- (aq) \) and available literature [17–19].

Figure 5.2: Schematic showing (a) a Cu rotating disk electrode and (b) an electrochemical cell with an RDE working electrode.
5.2.3 Electrolyte Preparation

Solutions were prepared with reagent-grade sodium chloride (NaCl, 99.0% assay (Fisher Scientific)), sodium sulphide (Na₂S·9H₂O, 98.0% assay (Sigma-Aldrich)), boric acid (H₃BO₃, 99.5 % assay (Caledon)), sodium borate decahydrate (Na₂B₄O₇·10H₂O, 99.5% assay (Sigma-Aldrich)), sodium sulphate (Na₂SO₄, ≥ 99% assay (Sigma-Aldrich)) and Type I water (18.2 MΩ·cm). The [SH⁻] were significantly higher than those expected within a DGR [2,20–22]. The predicted [SH⁻] ranges from 1.2 × 10⁻⁷ mol/L to 1.2 × 10⁻⁴ mol/L, with the peak sulphide flux to the container surface less than 10⁻¹⁰ mol/(m²·s) in a final repository at the Forsmark site [21]. Experiments were conducted in solutions containing low [SH⁻] and medium [Cl⁻] (5 × 10⁻⁵ mol/L Na₂S + 1 mol/L NaCl), high [SH⁻] and high [Cl⁻] (5 × 10⁻⁴ mol/L Na₂S + 3 mol/L NaCl), medium [SH⁻] and low [Cl⁻] (2 × 10⁻⁴ mol/L Na₂S + 0.1 mol/L NaCl), and medium [SH⁻] and high [Cl⁻] (2 × 10⁻⁴ mol/L Na₂S + 3 mol/L NaCl). To ensure the maintenance of a deaerated environment, and to minimize sulphide oxidation in experiments that were conducted on the benchtop, the solutions were sparged with Ar for ≥ 30 min prior to each experiment and purged continuously throughout the experiment.

5.2.4 Electrochemical and Corrosion Experiments

5.2.4.1 Corrosion Potential

Corrosion potentials (Ecorr) were monitored on Cu stationary electrodes as a function of immersion periods (0.5 h to 36 h) in slightly alkaline (pH 9) solutions containing medium [SH⁻] and low [Cl⁻] (2×10⁻⁴ mol/L Na₂S + 0.1 mol/L NaCl). Prior to measuring Ecorr, the electrode was cathodically cleaned at −1.5 V vs SCE to reduce air-formed oxides for 60 s, and then at −1.15 V vs SCE for another 60 s to allow the detachment of H₂ bubbles which may have formed at the more negative potential (−1.5 V vs SCE).

5.2.4.2 Linear Polarization Resistance

Linear polarization resistance (LPR) measurements were conducted to estimate the corrosion rate of Cu in various aqueous sulphide solutions, in which the polarization resistance (Rp) was determined by applying small overpotentials (Ecorr ± 5 mV) on Cu in both the positive and negative directions at a scan rate of 10 mV/min.
5.2.4.3 Cyclic Voltammetry

Cyclic voltammetric (CV) studies were performed using an RDE. Prior to applying a voltammetric scan, the electrode was cathodically cleaned as noted in section 5.2.4.1. Voltammetric scans were performed from an initial potential in the range $-1.5\, \text{V vs SCE}$ to $-1.35\, \text{V vs SCE}$ to a final potential, ranging between $-0.7\, \text{V vs SCE}$ and $-0.5\, \text{V vs SCE}$, at a scan rate of either $2\, \text{mV/s}$ or $10\, \text{mV/min}$. The choice of starting potential had no influence on the subsequent electrochemical behaviour. All experiments were conducted at room temperature ($21 \pm 2\, ^\circ\text{C}$).

5.2.4.4 Cathodic Stripping Voltammetry

After cathodic cleaning (section 5.2.4.1) the Cu electrodes were immersed in the sulphide solution for various exposure periods. After short immersion periods (i.e., $\leq 36\, \text{h}$), cathodic stripping voltammetric (CSV) scans were performed from $E_{\text{corr}}$ to $-1.4\, \text{V vs SCE}$ at a scan rate of $10\, \text{mV/min}$ to reduce the sulphide film. All experiments were performed at $21 \pm 2\, ^\circ\text{C}$.

5.2.5 Surface Analysis

5.2.5.1 Scanning Electron Microscopy, Energy-Dispersive X-ray Spectroscopy and Focused Ion Beam (FIB) Cross Sectioning

Prior to surface analysis, the corroded Cu electrodes were rinsed with Type I water, dried with a stream of ultrapure Ar gas and stored in the anaerobic chamber. Analyses were then performed after a minimal period of interim storage. The surface and cross-sectional morphologies of corroded specimens were examined using a LEO 1540 SEM equipped with a FIB (Zeiss Nano Technology Systems Division, Germany). The composition of films was qualitatively analysed by EDX using a LEO 1540 FIB/SEM (the oxygen detection limit is 1 at. %).

5.2.5.2 Raman Spectroscopy

Raman spectroscopy was performed using an InVia Reflex Raman spectrometer equipped with a 633 nm He-Ne laser and an Olympus microscope. Spectra were obtained using a $50 \times$ uncoated objective lens with the beam focused to a diameter of $\sim 2\, \mu\text{m}$. Prior to the acquisition of spectra, the spectrometer was calibrated against the $520.5\, \text{cm}^{-1}$ peak of Si. To minimize any surface heating effects, the laser was used at 1-5 % power.
5.2.5.3 Auger Electron Spectroscopy

Auger electron spectroscopy was performed using a Physical Electronics PHI 710 Scanning Auger Nanoprobe. Survey spectra were collected at 10 kV from an area of $90 \times 90 \, \mu m^2$. To obtain depth information, samples were sputtered using an Ar$^+$ ion gun (0.5 keV or 3 keV) with a spot size of $2 \times 2 \, mm^2$. The total sputtering time was < 14 s and was followed by data acquisition. Peaks selected for analysis during the depth profiles were determined from the original AES survey spectra.

5.3 Results and Discussion

5.3.1 Films Grown Anodically Under Controlled Convective Conditions

Figure 5.3 shows films formed anodically and reduced cathodically under controlled-convective conditions using RDEs. At low $[SH^-]$ and medium $[Cl^-]$ (i.e., $5 \times 10^{-5}$ mol/L Na$_2$S + 1.0 mol/L NaCl), the anodic current density on the reverse scan retraced that recorded on the forward scan, demonstrating that, as shown previously [12], the anodically-formed Cu$_2$S film was porous and able to sustain growth when the potential was reduced. The signature for a passive film would have been a current density reduced to zero on the reverse scan as the electric field within the film decreased below the value required to maintain its growth. The single cathodic reduction peak observed on the reverse scan indicated the formation of a single-layered film. The amount of Cu$_2$S formed, expressed as a charge (Q), was obtained by calculating the area associated with the cathodic reduction peak, as indicated by the shaded area in region Q$_B$, Figure 5.3 (a).

As observed previously, the amount of charge associated with the anodic film formation (region A (2Q$_A$) in Figure 5.3 (a)) was approximately equal to the amount of charge recovered by the cathodic reduction in region B (Q$_B$), confirming that all Cu$_2$S anodically-formed on the forward scan was fully reduced on the reverse scan. When the $[SH^-]$ and $[Cl^-]$ were high (i.e., $5 \times 10^{-4}$ mol/L Na$_2$S + 3.0 mol/L NaCl), Figure 5.3 (b), the anodic current-potential profile was similar to that observed at low $[SH^-]$ and medium $[Cl^-]$, although the value of the plateau current density was lower. This decrease in plateau current density has been shown to be due to a competition between SH$^-$ and Cl$^-$ for adsorption sites on the Cu surface [15]. Although the $[SH^-]$ had been increased by an order of magnitude, the anodic current density remained the same on the reverse scan as it was on the forward scan, consistent with the presence of a porous film [12]. However, two
cathodic reduction peaks were observed (regions C and D), suggesting the presence of either two distinct morphological forms of the same phase or, possibly, two different copper sulphide phases. Previous XRD results demonstrated that only chalcocite (Cu$_2$S) was present [6], which points to two different morphological forms of the same phase, e.g. two different layers.

Figure 5.3: CVs recorded at the scan rate of 2 mV/s and an electrode rotation rate of 25 Hz in deaerated solutions containing various concentrations of sulphide and chloride: (a) CV recorded at low [SH$^-$] and medium [Cl$^-$] ($5 \times 10^{-5}$ mol/L Na$_2$S + 1.0 mol/L NaCl), (b) CV recorded at high [SH$^-$] and high [Cl$^-$] ($5 \times 10^{-4}$ mol/L Na$_2$S + 3.0 mol/L NaCl).
The extent of Cu$_2$S film growth for films grown at low [SH$^-$] and medium [Cl$^-$] (expressed as an electrochemical charge ($Q_B$)), determined from CVs as described above, increased with an increase in electrode rotation rate, Figure 5.4. This demonstrated that the rate, and hence the extent, of film growth was dominantly determined by the flux of SH$^-$ to the Cu surface. More comprehensive studies have shown that film growth is partially controlled by the SH$^-$ flux and partially by the interfacial kinetics [13,15].

![Graph showing cathodic charge as a function of electrode rotation rate](image)

Figure 5.4: Cathodic charge ($Q_B$) plotted as a function of the electrode rotation rate ($\omega$) calculated from CVs recorded in solutions containing $5 \times 10^{-5}$ mol/L Na$_2$S + 1.0 mol/L NaCl.

Figure 5.5 shows the charges associated with the reduction peaks C and D, recorded as a function of electrode rotation rate, in solutions containing a high [SH$^-$] and high [Cl$^-$]. When using a stationary electrode, the cathodic charge associated with peak D ($Q_D$) was negligible, suggesting that only film C was formed when the flux of SH$^-$ to the Cu surface was low. At the higher fluxes of SH$^-$ achieved at higher electrode rotation rates, peak C achieved an approximately constant cathodic charge ($Q_C$), whereas the charge associated with peak D ($Q_D$) continually increased. This indicated the establishment of a constant film thickness associated with the film reduced at peak C, but a flux-dependent growth of the
film reduced at peak D. This observation was consistent with the rapid growth of a porous base layer to a limited thickness, accompanied by the growth of a much thicker outer layer.

5.3.2 Films Grown under Freely Corroding Conditions

Cu electrodes were immersed in a solution containing 0.2 mol/L borate (pH 9) + 2 × 10⁻⁴ mol/L Na₂S + 0.1 mol/L [Cl⁻] for various immersion times, ranging from 0.5 h to 36 h. The presence of borate in these experiments served two purposes: (i) it buffered the pH; (ii) it reproduced the conditions used by others who have claimed the copper sulphide layer formed was passive [24,25]. As noted above, selected sulphide concentrations were significantly higher than those generally anticipated in an actual DGR [2,20–23]. The $E_{corr}$ was monitored continuously, and rapidly attained a steady-state value within the range $\sim −850 ± 20$ mV vs SCE, Figure 5.6. This value was close to the equilibrium potential for Cu/Cu₂S at this [SH⁻] (−1.0 V vs SCE), which was an observation consistent with the rapid growth of Cu₂S requiring only a small anodic overpotential.

![Figure 5.5: Cathodic charges (Q_c and Q_d) plotted as a function of the electrode rotation rate (ω) calculated from CVs recorded in solutions containing 5 × 10⁻⁴ mol/L Na₂S + 3.0 mol/L NaCl.](image-url)
Figure 5.7 (a) shows a series of CSVs recorded after various durations of corrosion. Depending on the duration of the corrosion experiment, one or two cathodic reduction peaks (E and F) were observed in the CSVs. The charge associated with peak E and the total charge for both peaks E and F as a function of the period of corrosion are shown in Figure 5.7 (b).

Attempts to calculate $Q_F$ were complicated by water reduction at potentials below $-1.1$ V vs SCE; thus, results were only semi-quantitative where exposure periods exceeded 10 h. Despite this uncertainty, the values in Figure 5.7 (b) clearly demonstrated that the film reduced at peak E rapidly grew to a constant thickness, regardless of the exposure period, while the film reduced at peak F continued to grow over longer exposure periods. It is interesting to compare these results from varying exposure times of the freely corroding system to those in section 5.3.1 where similar electrochemical reduction features were observed as peaks C and D. Specifically, $Q_C$ was insensitive to increased rotation rate.
(sulphide flux) (Figure 5.5) and exposure time (Figure 5.7 (b)), whereas $Q_F$ increased as a function of both.

Figure 5.7: (a) CSVs recorded at the scan rate of 10 mV/ min after various periods of immersion in deaerated $2 \times 10^{-4}$ mol/L Na$_2$S + 0.1 mol/L NaCl solution buffered with 0.2 mol/L borate (pH = 9), (b) Cathodic charges, $Q_E$ and $Q_E + Q_F$, plotted as a function of immersion time.
These results are consistent with the rapid growth of a thin surface layer (i.e. the feature reduced at peak E), which rapidly became sufficiently porous to allow the continuous development of a second outer deposit reduced at peak F. One reasonable explanation for this was the rapid growth of a thin base layer which may have initially been coherent but rapidly developed porosity to relieve the large interfacial stress which developed due to the large Pilling-Bedworth ratio ($\Psi_{PB} = 2$) of Cu$_2$S [26].

5.3.2.1 Surface Characterization — The Evolution of Corrosion on Copper in Slightly Alkaline (pH 9) Chloride and Sulphide Solutions

Figure 5.8 shows the SEM images and SEM/FIB cross sections of three corroded Cu samples after immersion for 2 h, 4 h and 36 h respectively in borate-buffered (pH 9) solutions containing $2 \times 10^{-4}$ mol/L Na$_2$S + 0.1 mol/L NaCl. After 2 h of immersion, the Cu surface was covered with a uniform particulate deposit, Figure 5.8 (a), while after a similar 2 h of exposure, the CSVs in Figure 5.7 (a) showed only peak E. The FIB-cut cross section of the 2 h exposure specimen, Figure 5.8 (d), confirmed that this layer was distributed uniformly across the surface at a thickness below 100 nm, but was also porous. In addition to having obvious porosity, the film was both too thick and too irregular in topography to be a coherent passive film formed by point defect transport processes [23,24]. Based on the cathodic charges obtained from the CSVs and the theoretical density of chalcocite [27], the average film thickness of this base layer, if uniformly distributed across the surface should have been in the range 25 to 45 nm. Similar SEM observations were obtained on the corroded Cu surface after 4 h immersion with some local areas covered by slightly larger crystalline deposits, Figure 5.8 (b), and a film thickness in the range of 78 to 188 nm, Figure 5.8 (e).

After 36 h of corrosion, the surface was covered with a much thicker crystalline deposit, as shown in the top-down and FIB-cut cross section SEM images, Figures 5.8 (c) and 5.8 (f), respectively, with crystals at some locations achieving heights of ~ 1 μm. While the location of the previously discussed base layer and its apparent thickness are indicated in Figure 5.8 (f), it was difficult to observe, owing to the much larger features present. The formation of such a thick crystalline outer deposit was consistent with our previous observations [6–15] and with our demonstration that growth of this deposit occurred at the film/solution interface, supported by the transport through the pores of the base layer of Cu
(I), as both sulphide complexes (Cu(SH)\textsuperscript{2−}) and Cu\textsubscript{3}S\textsubscript{3} clusters, formed at the Cu surface [28–31].

Ex-situ Raman spectra, Figure 5.9 (a), and the corresponding analyzed surface locations (indicated by the intersection of yellow lines in the optical images), Figure 5.9 (b), were collected on Cu surfaces prior to exposure to solution and after various immersion periods. Peaks at 147 cm\textsuperscript{−1}, 525 cm\textsuperscript{−1}, and 625 cm\textsuperscript{−1} were attributed to Cu\textsubscript{2}O [32–36], while peaks at 300 cm\textsuperscript{−1} confirmed the presence of Cu\textsubscript{2}S [37–39]. As shown in Figure 5.9 (a), strong Raman signals for Cu\textsubscript{2}O were observed on the Cu sample before corrosion, while a
A strong signal for Cu$_2$S was observed after 1 h of exposure, indicating that oxide to sulphide conversion and sulphide film formation occurred rapidly [40]. The strength of the sulphide signal increased while the oxide signal decreased as a function of immersion time. After 36 h of immersion, only a strong signal for Cu$_2$S was observed at the peak of 300 cm$^{-1}$. The signals in the region 525 cm$^{-1}$ to 625 cm$^{-1}$ gradually decreased and disappeared as the exposure duration increased from 1 h to 4 h. This behavior can be attributed to the initial presence of air-formed Cu$_2$O [32–36], which is rapidly converted to Cu$_2$S.

![Graph showing Raman spectra and optical images](image)

Figure 5.9: Analysis of Cu surfaces corroded in a solution containing 0.1 mol/L NaCl + 2 × 10$^{-4}$ mol/L Na$_2$S + 0.2 mol/L borate (pH 9) at 20 °C. (a) Raman spectra recorded on Cu after various immersion periods, and (b) the corresponding analyzed surface locations (indicated by the intersection of yellow lines in the optical images).

However, the thickness of an air-formed oxide would not be expected to be more than a few nanometers. By contrast, the examination from FIB-cut cross sections, Figure 5.8 (d) and (e), show that the naturally grown sulphide films were porous with a non-uniform film thickness in the range of ~ 100 nm (2 h exposure) to 188 nm (4 h exposure).
This indicates that oxide to sulphide conversion was accompanied by substantial further Cu$_2$S growth.

To investigate the approximate film thickness and relative film composition as a function of depth after short term corrosion exposure in sulphide solutions, Auger depth profiles were recorded on a Cu surface after 1 h of corrosion in a solution containing 0.1 mol/L NaCl + 2 × 10$^{-4}$ mol/L Na$_2$S + 0.2 mol/L borate (pH 9), Figure 5.10.

Figure 5.10: Analysis of a corroded Cu sample after 1 h immersion in a solution containing 0.1 mol/L NaCl + 2 × 10$^{-4}$ mol/L Na$_2$S + 0.2 mol/L borate (pH 9). (a) A top-down photo taken on a corroded Cu sample before Auger depth profiling and (b) Auger depth profiles obtained at two different Ar$^+$ gun voltages on the corroded Cu surface.

The Auger depth profile, Figure 5.10 (b) shows that the initial oxygen content was ~ 20 at. %, and gradually decreased to a stable value of ~15 at. % for both experiments performed at different sputtering voltages, of either 3 kV or 0.5 kV, which dictate the sputtering rate. This indicates that oxides existed at the Cu/film interface after 1 h of immersion, with its presence more readily observed at the higher sputtering rate, i.e., at 3 kV. Although this evidence for oxide is not conclusive, these observations are consistent with the Raman analyses performed after 1 h exposure (Figure 5.10 (a), and support the
argument that the first stage of Cu corrosion involves the conversion of copper oxide to copper sulphide.

The S profile clearly shows the presence of a surface Cu$_2$S film which is more rapidly removed at the higher sputtering rate, Figure 5.10 (b). Based on the calculated sputtering rates, the measured film thickness was ~ 30 nm after 1 h of exposure to the sulphide solution. Within this exposure period only peak E was detected in the CSVs, Figure 5.7 (a), suggesting this 30 nm thick film could be attributed to the rapid initial formation of a thin barrier layer which for oxides are commonly ≤ ~ 10 nm thick [40]. However, this measured film thickness cannot be considered definitive, since it is based on the estimated sputtering rate on a blank Cu surface, which would not necessarily be representative of the rate of a Cu$_2$S film. Details associated with the determination of film thickness can be found in Appendix B.

5.3.2.2 The Influence of Chloride on the Naturally Grown Sulphide Films

In an attempt to investigate the influence of Cl$^-$ on sulphide-induced Cu corrosion, $E_{corr}$ measurements followed by CSVs, were conducted in solutions containing $2 \times 10^{-4}$ mol/L Na$_2$S + 0.2 mol/L borate (pH 9) at different [Cl$^-$]s. These films were grown in an anaerobic chamber for a total immersion duration of 72 h, Figure 5.11.

Over this exposure period, Figure 5.11 (a), $E_{corr}$ rapidly increased to an approximately steady-state value within the range ~ −850 ± 25 mV vs SCE with the $E_{corr}$ measured at low [Cl$^-$] (0.1 mol/L NaCl) ~ 25 mV more negative than that at high [Cl$^-$] (3 mol/L NaCl). This difference is consistent with the expectation that Cl$^-$ ions will compete with SH$^-$ for adsorption sites on the Cu surface, thereby impeding the initial electron transfer step (formation of Cu(SH)$_{ads}$) necessary for Cu$_2$S film formation [8,15], reaction (3.7).

Figure 5.11 (b) shows CSVs recorded after $E_{corr}$ measurements in anoxic solutions containing $2 \times 10^{-4}$ mol/L Na$_2$S + 0.2 mol/L borate (pH = 9) and 0.1 mol/L and 3 mol/L NaCl, respectively, consistent with the results in Figure 5.7 (a). Two cathodic reduction peaks (A and B) were observed after 72 h immersion. The amount of Cu$_2$S formed, expressed as a charge (Q), was obtained using the same procedure as described above.
Figure 5.12 shows that at high $[\text{Cl}^-]$ (3 mol/L NaCl), the charge ($Q_B$) associated with peak B was larger than $Q_A$, indicating the formation of a thicker outer deposit above a thin base layer ($Q_A$). When the $[\text{Cl}^-]$ was decreased from 3 mol/L to 0.1 mol/L, the two cathodic reduction peaks became more distinct, Fig. 5.11 (b). The total absolute cathodic charge, $Q_T$ ($Q_T = Q_A + Q_B$) at low $[\text{Cl}^-]$ (0.1 mol/L) was larger than at high $[\text{Cl}^-]$. Figure
5.12, indicating a suppression of the corrosion rate at higher [Cl$^-$]. Previous studies [8] show that, a more open porous film structure was obtained at high [Cl$^-$], resulting in linear but slower film growth kinetics. The combination of an increase in $E_{corr}$ accompanied by a decrease in film growth rate at higher [Cl$^-$] is consistent with an inhibition of corrosion by the displacement of SH$^-$ from sites on the metal surface by Cl$^-$. This is also consistent with the decrease in film growth rate despite the increased film porosity, since the latter should enhance the ability of Cl$^-$ to displace adsorbed SH$^-$ from the exposed Cu surface [8].

Figure 5.12: Absolute cathodic charges plotted for two [Cl$^-$]s (0.1 mol/L and 3 mol/L). $Q_{A1}$, $Q_{B1}$, $Q_{A2}$, and $Q_{B2}$ are represented by the shaded areas in Figure 5.11 (b). $Q_{T1}$ is the sum of $Q_{A1}$, $Q_{B1}$, and $Q_{T2}$ is the sum of $Q_{A2}$, and $Q_{B2}$.

### 5.4 Summary and Conclusions

Electrochemical and corrosion studies showed that, depending on the sulphide and chloride concentrations, the chalcocite (Cu$_2$S) film grown on Cu was composed of one or two layers; a thin base layer and an outer deposited thicker layer. At low sulphide concentrations, only one layer was formed, with dual layer growth developing as the concentration increased. While the base layer may be initially a barrier layer, it rapidly became porous and stopped growing. This layer developed a topography inconsistent with a passive barrier layer grown by the transport of point defects through the growing film. Subsequently, an outer layer deposited and continued to grow at a rate partially controlled
by the flux of sulphide to the Cu surface. The crystalline nature of this outer deposited layer was consistent with previous claims that the layer grew by the transport of Cu (I) species, as complexes and clusters, through the porous base layer.
5.5 References


Chapter 6
Copper Corrosion in Aqueous Chloride Solutions
Containing Dissolved Gaseous Sulphide

6.1 Introduction

The proposed disposal approach in many countries, such as Sweden, Finland, and Canada, for used nuclear fuels is to encapsulate these wastes in steel containers with an outer Cu shell or coating and bury them at a depth of $\geq 500$ m in a suitable deep geological repository (DGR), while employing a multi-barrier system [1,2]. Copper is chosen for the fabrication of these waste containers, primarily due to its thermodynamic stability in aqueous anoxic conditions. The proposed used fuel containers for the permanent disposal of high-level nuclear waste in Canada are comprised of a carbon steel vessel coated with a 3 mm corrosion-resistant Cu layer deposited using a combination of electrodeposition and cold spray deposition [3].

The exposure environment in a DGR will evolve from initially warm and oxidizing to eventually cool and anoxic, over a period which is difficult to determine [4,5]. While the oxygen entrapped upon emplacement and gamma radiation emitted by the waste forms are transient and finite, leading to some slight contributions to the container corrosion, sulphide is an inexhaustible source of oxidants that could induce the long-term Cu corrosion [6,7].

Sulphide-induced Cu corrosion is known to be limited by a low sulphide concentration ($< 10^{-6}$ mol/L), low flux ($10^{-11}$ to $10^{-10}$ mol/(m$^2$·s)), and a low rate of transport of sulphide through the compacted buffer materials to the container surface [6–8]. Models proposed by Briggs et al. [9] evaluated the rate of transport of sulphide from the host rock to the container surface and a corrosion rate of 0.026 nm per year was found by the authors. This is a rate that justified the durability of a 3 mm thick layer of Cu for over 100 million years [9]. The production mechanisms of sulphides in a repository include, but are not limited to, the dissolution of sulphide minerals, such as pyrite (FeS$_2$) in the rock and bentonite buffer materials, and more importantly, the remote production of sulphide in the groundwaters, converted from SO$_4^{2-}$ via the action of sulphate-reducing bacteria (SRB).
Despite the fact that microbial activity will be restricted by the bentonite clay surrounding the container, the majority of sulphides could be produced via microbially mediated reactions with organic matter associated with SRB where microbial activity is not suppressed, such as some remote locations in the host rock or at the rock/bentonite interface [2]. Hence, sulphide-induced Cu corrosion, which is the dominant threat to the container over the long-term, must be examined to determine the corrosion mechanisms and rates, and the distribution of corrosion damage on Cu if a reliable corrosion allowance is to be specified.

One particular corrosion scenario of interest is that when the container surface temperature falls, a wetted layer might form on the Cu surface due to humidity and condensation [1–3]. Since a full saturation of the bentonite clay with groundwater may take hundreds or even thousands of years in a DGR, there could be a period during which hydrogen sulphide gas (H₂S) can be transported through the clay system [6]. The H₂S (g) will dissolve in the water film at the container surface and the flux of sulphide at the surface of Cu will then be controlled by the transport of gaseous sulphide through the unsaturated clay [6,10]. When the repository is only partially saturated, sulphide transport might occur via the gaseous phase through the pores in the bentonite. Since the sulphide (SH⁻) in the groundwater could be in equilibrium with H₂S (aq), reaction (6.1), the concentrations of H₂S and SH⁻ are approximately equal if a near-neutral (pH ≈ 7) aqueous environment is established.

\[ H₂S (g) \leftrightarrow H₂S (aq) \leftrightarrow SH^- + H^+ \quad K_a (298.15 \text{ K}) \approx 10^{-7} \quad (6.1) \]

During the unsaturated phase in a DGR, sulphides could exist as various chemical phases, such as H₂S (g), H₂S (aq) and SH⁻ [11,12], and the portion of each chemical species is dependent on the system temperature, pressure and pH of the repository environment. The solubility of H₂S (g) in water is associated with Henry’s Law [11], Eq. (6.2), and its Henry’s law constant, \( H^{cp} = [H₂S(aq)] / P_{H₂S} \approx 1 \times 10^{-3} \text{ mol/(m}^3\text{ Pa)} \approx 0.1 \text{ mol/(L bar)} [13],

\[ H^{cp} = \frac{C_{H₂S}}{P_{H₂S}} \quad (6.2) \]

where \( H^{cp} \) is the Henry’s constant, \( C_{H₂S} \) is the aqueous concentration of H₂S, and \( P_{H₂S} \) is H₂S (g) partial pressure.
The partitioning of sulphide between the gas phase in the pores and the aqueous phase in the porewater of unsaturated bentonite buffer is governed by the acid dissociation reaction, reaction (6.1), and by Henry’s law. The rate of dissolution or degassing of H$_2$S (g) depends on the interfacial area between the gas phase/aqueous phase and on how far from equilibrium the values of [H$_2$S(aq)] and P$_{H_2S}$ are. Additionally, the partitioning between the gas and aqueous phases of a given amount of sulphide also depends on the water/gas volume ratio pertaining to the ideal gas law [13]. In particular, while groundwater inflow slowly progresses and the volume of gas phase decreases, the total amount of sulphide in the repository may increase by the added groundwater and SRB activity, but the total gaseous sulphide will decrease with a decrease in the gas volume [11]. The maximum fluxes of sulphide that could possibly be established in an unsaturated and saturated repository environment are predicted to be approximately $7 \times 10^{-11}$ mol/(m$^2$·s) and $1 \times 10^{-11}$ mol/(m$^2$·s), respectively [11].

Previous work conducted was associated with investigations in a variety of aqueous chloride and sulphide solutions, particularly in the range of $5 \times 10^{-5}$ mol/L $\leq$ [SH$^-$] $\leq 1 \times 10^{-3}$ mol/L and 0 mol/L $\leq$ [Cl$^-$] $\leq$ 5 mol/L [14–24]. The selected range of [Cl$^-$] reflected the expected Canadian ground water conditions, whereas the [SH$^-$] was higher than anticipated in the DGR and were chosen based on experimental considerations. Therefore, to evaluate the natural corrosion of Cu in an environment that resembles the Canadian DGR, the investigation on the corrosion of Cu in extremely low [SH$^-$] (< $10^{-6}$ mol/L), such as when exposed to the gaseous sulphide in a humid environment, must be examined. The long-term corrosion of Cu is studied by measuring the amount of hydrogen gas produced, under the assumption that it is generated by the corrosion processes, as shown in reaction (6.3) [7].

$$2Cu + SH^- + H_2O \rightleftharpoons Cu_2S + H_2 + OH^-$$  \hspace{1cm} (6.3)

A novel electrochemical cell has been developed to monitor corrosion of Cu in concentrated chloride (3 mol/L) solutions with or without the dissolved gaseous sulphide (H$_2$S) at elevated temperature (~ 80 °C) for extended durations. The primary goal was to measure the production of H$_2$ (g) by corrosion, to correlate the amount of H$_2$ produced to the corrosion rate of Cu. In addition, an attempt was made to compare the rate measured
from the produced $\text{H}_2$ (g) to the rate determined from the electrochemical experiments, such as LPR.

6.2 Experimental

6.2.1 Electrode Design and Preparation

Most experiments were conducted using either the electrodeposited (ED) Cu samples (ED plates NWMO 44-45) supplied by the Nuclear Waste Management Organization, Toronto, Canada, or Cu wires (annealed, $\geq 99.9\%$, 0.25 mm in diameter) purchased from Goodfellow, UK. In this work, these electrodeposited Cu samples and Cu wires are referred to as C2B Cu and C1C Cu herein.

The C2B Cu samples were cut from plates by a water jet. Most of them were cut into $2.8 \, \text{mm} \times 2.9 \, \text{mm} \times 72 \, \text{mm}$ rectangular prisms, but some samples exhibited trapezoidal cross-sections. Each Cu sample has an average total surface area of 8.6 cm$^2$. The typical configuration of a C2B Cu WE is shown in Figure 2.2 (a) (section 2.1.1), in which major components associated with this WE are indicated from (1) to (9). The electrical contact was made by connecting the C2B Cu prism with a Cu wire, where the Cu wire was soldered with tin (Sn) onto a flat surface of C2B Cu. The junction between the C2B Cu and the wire was then covered with a glass tube filled with Epofix resin. C2B Cu samples were ground with SiC papers ranging from P 120 to P 600 grits. All samples were then sonicated in a beaker with technical grade ethanol for 5 min, followed by sonication in Type I water for another 5 min to remove any polishing residues. Sonication was repeated if the Cu surface remained tarnished under the examination of an optical microscope. Prior to assembly into the electrochemical cell, C2B Cu samples were dried with ultrapure $\text{N}_2$ gas and then stored in a vacuum desiccator. A total of 131 C2B Cu samples were assembled in an electrochemical cell, however, only one C2B Cu specimen served as the WE. The exposed surface area of the WE was 6.0 cm$^2$.

A similar WE was made of C1C Cu, Figure 2.2 (b). A 250 cm-long wire was coiled at the bottom, with a corresponding surface area of 19.7 cm$^2$ exposed to the electrolyte, Figure 2.2 (b). The electrochemical cell was charged with a total of 2600 C1C wire segments; each segment was 5 cm long, corresponding to a total surface area of 1024 cm$^2$. Since it is inconvenient to grind these thin C1C Cu wire segments using a mechanical polisher, wires were cleaned in a timely manner, immediately prior to testing. In this
cleaning procedure, C1C Cu wires were degreased in technical grade ethanol by sonicating for 5 min. The vial with C1C Cu wires was then filled with Type I water and swilled to remove any residual ethanol. Wires were then sonicated in a second vial containing 10 mM nitric acid for 5 min. The procedure described above was repeated three times, until the wire appeared to be free of tarnish by observing the wire surface with an optical microscope. Eventually, C1C Cu samples were dried with ultrapure N₂ gas and stored in a vacuum desiccator until use.

A few electrochemical experiments were conducted using the C2C electrodeposited (ED) Cu samples (NWMO, DS-609-EC0122) supplied by the Nuclear Waste Management Organization, Toronto, Canada. Each C2C Cu sample was cut from plates into a 2.8 mm × 2.9 mm × 72 mm rectangular prism with a total surface area of 8.6 cm². The configuration of a C2C Cu WE was identical to that of the C2B Cu WE, as shown in Figure 6.1, corresponding to an exposed surface area of ~ 7.1 cm². C2C Cu samples were ground with SiC papers ranging from P120 to P600 grits and cleaned in a beaker with technical grade ethanol for 5 min, followed by another sonication in Type I water for 5 min to remove any polishing residues. Prior to conducting experiments, C2C Cu samples were dried with ultrapure N₂ gas, then stored in a vacuum desiccator. Finally, the electrochemical cell was charged with a total of 60 C2C Cu samples.

Figure 6.1: The configuration of C2C Cu WE. Major components of each WE are labelled from (1) to (9): (1) Swagelok SS 3-way valve; (2) Swagelok SS tube fitting, union tee; (3) junction sealed with clear resin; (4) Swagelok SS tube fitting, port connector; (5) ground glass inner male joint; (6) Cu wire covered by heat-shrink tubing; (7) glass tube filled with clear resin; (8) junction soldered with tin (Sn); (9) a C2C Cu rectangular prism.
6.2.2 Electrochemical Cell Design and Instrumentation

The electrochemical cell consists of two components, a major part and an auxiliary part, as shown in Figure 6.2. The major cell component contains various Cu samples (C1C Cu, C2B Cu, or C2C Cu), Figure 6.3 (a) and (b). The auxiliary cell component is shown in Figure 6.3 (c). Glass was used where possible, rather than stainless steel, to limit the possibility of H₂ outgassing or its evolution from corrosion.

As shown in Figure 6.3 (a) and (b), the top parts of the major components are fitted with two ports for the introduction and exchange of solutions and headspace gas. The cell containing C1C wires, Figure 6.3 (a), was charged with 5 cm segments of Cu wires (99.9%, temper annealed, 0.25 mm diameter, Goodfellow, UK). It should be noted that no effort was made to control impurities in the Cu wires prior to immersion, which could contribute to the measured H₂ and artificially to an inflated corrosion rate. The major cell component labelled with C2B Cu was charged with a total of 131 C2B Cu prisms.

![Figure 6.2: A schematic representing an electrochemical cell containing a major component and an auxiliary (portable) component.](image)

Figure 6.3 (b) shows the major component of a cell containing C2C Cu samples; a total of 60 C2C samples were placed in the cell. When the major cell component was not attached to the auxiliary component, stopcocks from the three-way high vacuum stopcock were closed. The end of the stopcock was sealed by either a rubber or a ground glass stopper, Figure 6.3 (a).
Before conducting electrochemical experiments, the auxiliary component was carefully attached to the major component, Figure 6.3 (c), where RE and CE were assembled. Electrolytes were introduced to the auxiliary component in a meticulous manner, as described in the following section 6.2.3.

Figure 6.3: Cells used in the electrochemical experiments. (a) The major cell components containing C1C Cu wires and C2B Cu samples; (b) the major cell component containing C2C Cu samples; and (c) a full electrochemical cell setup consisting of a major cell component covered by ceramic fibers and an auxiliary cell component containing both the RE and CE, as indicated by the red arrow.
6.2.3 Solution Preparation

Salt solutions were prepared with Type I water and reagent grade NaCl (99.0\% assay, Fisher Scientific), which may contain trace heavy metal impurities that could have contributed to hydrogen production. Therefore, NaCl purification was conducted prior to introducing solutions to the electrochemical cells; a detailed purification process can be found in Appendix C. Before solution was introduced to the auxiliary component, the solution was purged overnight with ultrapure N\_2 in a deoxygenating bottle. To maintain a deaerated environment and to minimize the O\_2 ingress during the experiments, solution was meticulously introduced to the auxiliary component using the setup shown in Figure 6.4.

![Diagram of solution introduction setup](image)

Figure 6.4: Setup associated with solution introduction to the auxiliary component. (a) A photo showing the appearance of major and auxiliary components; and (b) a schematic showing parts used for solution introduction.

As shown in Figure 6.4 (b), the deoxygenating bottle was connected to the auxiliary component via stopcock 2. A stream of ultrapure N\_2 gas was continuously purged through the deoxygenating bottle until solution was ready to be introduced into the auxiliary component. During solution introduction, a total of five refills/vacuum cycles were performed by evacuating the auxiliary component via the vacuum pump and refilling it with ultrapure N\_2 gas. To monitor the N\_2 gas flow rate when purging, a bubble trap was connected to the auxiliary component via stopcock 3. Once cycling was complete, stopcock 3 and 4 were closed while stopcock 2 remained open, allowing the deaerated salt solution to enter the cell auxiliary component. Finally, stopcock 1 was opened, allowing the
electrolyte in the major component to come into contact with solution in the auxiliary component.

6.2.4 Hydrogen Analysis

6.2.4.1 Thermal Desorption Analysis on Annealed Cu Specimens

Thermal desorption analysis (TDA) was conducted on the annealed C2B and as-received C1C Cu samples. Commonly, TDA involves heating a test specimen in a quartz glass tube within a small tube furnace while the ultrapure N\textsubscript{2} (carrier gas, 6.0 purity with oxygen scavenger) is passed over the sample. Subsequently, the resulting gas mixture was analysed by the IonScience Hydrosteel 6000 H\textsubscript{2} probe that was connected to the open end of the quartz tube via the Swagelok 14 mm adapter, as shown in the setup in Figure 6.5.

![Figure 6.5: An illustration showing the TDA setup with various components: (1) flow controller; (2) oxygen scavenger; (3) quartz tube covered by furnace; (4) Swagelok fittings; and (5) Hydrosteel hydrogen probe. Notably, due to the difficulty of grinding wires to remove air-formed oxides using the conventional mechanical polisher, C1C Cu wires were first degreased with ethanol, cleaned with 10 mmol/L HNO\textsubscript{3}, and then soaked in ethanol prior to TDA analysis. Materials were cleaned immediately prior to testing.]

6.2.4.2 Cell Hydrogen Sampling using Hydrosteel Hydrogen Probe

Major cell components charged with Cu specimens were held at a constant temperature (~ 75 °C) and left to allow the accumulation of H\textsubscript{2} in the cell headspace. Headspace gas was then periodically flushed with ultrapure N\textsubscript{2} into a Tedlar bag. The
collected gas was analyzed using an IonScience Hydrosteel 6000 H₂ probe, consisting of proton-conducting ceramic coated on either side of a catalyst electrode that operated at a fixed voltage. As the collected gas passed through the anode surface, the H₂ became adsorbed onto the collector plate (palladium (Pd)) contained in the probe assembly, dissociated and became absorbed. The absorbed H₂ was then oxidized at the Pd/ceramic interface, resulting in the production of protons, which were then transported through the proton-conducting ceramic to the cathode where they were reduced. The probe outputted a measured current that was mass-transport controlled and therefore proportional to the H₂ content of the gas stream. The Hydrosteel 6000 is a diffusion-limited solid-state electrochemical sensor and is therefore expected to have a linear response to the hydrogen concentration.

A certified H₂ calibration gas (103 ppm) was measured immediately before and after each sampling and the gas curve was integrated to calculate the number of moles of H₂ in the expelled gas. Figure 6.6 shows the hydrogen measurement using the IonScience Hydrosteel 6000 H₂ probe that was connected to a Tedlar bag containing the collected gas from cell headspace.

![Figure 6.6: Hydrosteel 6000 hydrogen probe gas sampling when connected to a Tedlar bag containing the expelled gas.](image)

Once the number of moles of hydrogen were obtained, the corrosion rate of Cu was then evaluated under the assumption that any hydrogen produced resulted from the corrosion of Cu in anoxic aqueous media. The production of H₂ under acidic and alkaline conditions is shown in the half-reactions (6.4) and (6.5).
When Cu is exposed to the anoxic sulphide solution, hydrogen could also be produced through reaction (6.6).

\[ 2SH^- + 2e^- \rightarrow H_2 + 2S^{2-} \]  

(6.6)

Therefore, by measuring the rate of H\(_2\) released over a known duration, the cumulative corrosion and the corrosion rate of Cu can be determined. According to the assumed anodic half-reaction shown in (6.7), the rate of corrosion can be determined via equation (6.8), where \( n \) is the number of electrons transferred in reaction (6.7), \( A \) is the surface area of Cu, \( \Delta t \) is the measurement time interval, and \( V_{m,Cu} \) represents the molar volume of Cu.

\[ Cu \rightarrow Cu (I) + e^- \]  

(6.7)

\[ \text{Rate} = \frac{2nH_2}{A_{Cu}\Delta t} V_{m,Cu} \]  

(6.8)

The assumptions that all the detected hydrogen arises from Cu corrosion could be considered conservative, since various forms of Cu may originally contain trapped hydrogen [25]. Thus, an over-estimation of the true corrosion rate of Cu might occur. In addition, other parameters, such as the inherent impurities, could also contribute to the overall production of H\(_2\) and significantly affect the measurements [26]. Despite all the other possible sources associated with the production of H\(_2\), the method of cell H\(_2\) sampling can provide an upper limit for the corrosion of Cu, thereby holding practical value for UFC safety predictions.

### 6.2.5 Electrochemical and Corrosion Experiments

#### 6.2.5.1 Corrosion Potential and Linear Polarization Resistance

Electrochemical experiments were performed after attaching the auxiliary component to the major cell component. A piece of Pt foil attached to a Pt wire was used as the counter electrode, and all potentials were measured against a saturated calomel reference electrode (SCE) (+ 0.242 V vs. standard hydrogen electrode (SHE)) [27]). A Solartron 1287 potentiostat was used to control the applied potentials and record current responses. CorrWare software (Scribner Associates, version 3.5h) was used to control
instrumentation and to obtain and analyze data. Corrosion potential ($E_{corr}$) measurements were collected for various periods of time followed by polarization resistance ($R_p$) measurements conducted at a scan rate of 10 mV/min with vertices ± 5 mV vs. $E_{corr}$.

6.3 Results and Discussion

6.3.1 Thermal Desorption Analysis on Pre-treated Cu Specimens

To determine the concentration of diffusible hydrogen in the pre-treated Cu specimens, e.g., samples that were annealed or cleaned, thermal desorption analyses were performed on various Cu samples prior to the electrochemical experiments.

Figure 6.7 shows the hydrogen volume fluxes recorded from an empty quartz tube (blank) and various pre-treated Cu samples during the TDA analyses, and the corresponding H$_2$ concentration of each sample by weight is shown in Table 6.1. Before TDA analysis, Cu samples were annealed, annealed and cleaned, or as-received and cleaned. During the TDA analysis, Cu samples were placed inside a heated quartz tube, in which the temperature of the furnace was ramped up from 23 ± 2 °C to 500 ± 2 °C at a fixed rate of ~10 °C/min, Figure 6.7 (a). Once 500 °C was reached, the experiment was kept constant at this temperature until the hydrogen flux decreased. This constant period lasted for ~ 20 min.

In an attempt to evaluate the background H$_2$ flux, the hydrogen volume flux was recorded from an empty quartz tube heated under the identical experimental conditions. As shown in Figure 6.7 (b), the H$_2$ flux measured from the quartz tube, i.e., the blank measurement, was nearly constant at ~ 2 ± 1 pL cm$^{-2}$ s$^{-1}$ during the entire analysis. By comparison, only a minor increase in the H$_2$ flux was observed on either the annealed or annealed and cleaned C2B Cu samples, reaching a maximum value of ~ 5 pL cm$^{-2}$ s$^{-1}$. This demonstrates, firstly that the concentration of diffusible hydrogen in C2B Cu was low after a total of 6-h annealing at 500 °C; secondly, no apparent uptake of additional hydrogen was observed as a result of cleaning the annealed C2B Cu in 10 mmol/L HNO$_3$; and thirdly, the annealed C2B Cu was a proper candidate material before conducting corrosion experiment.

C1C Cu wires were not annealed, but cleaned in either 100 mmol/L HNO$_3$ or 100 mM HCl and then sonicated in technical grade ethanol prior to testing. For both C1C Cu samples, the H$_2$ volume flux attained a maximum of ~ 10 pL cm$^{-2}$ s$^{-1}$, resulting in an equivalent H$_2$ concentration of ~ 0.1 ppm by weight, Table 6.1. In comparison to the
annealed C2B Cu specimens, this increase in the H$_2$ concentration of C1C Cu demonstrated that annealing could effectively decrease the total hydrogen originally residing in the Cu.

As shown in Figure 6.7 (b), for the C1C Cu cleaned in 100 mmol/L HNO$_3$, two broad peaks were observed at the times of 30 min and 45 min, reaching a maximum flux of $\sim$ 10 pL cm$^{-2}$ s$^{-1}$. Although the same maximum flux (10 pL cm$^{-2}$ s$^{-1}$) was observed from the C1C Cu cleaned in 100 mmol/L HCl, this maximum occurred at a time of $\sim$13 min and decreased subsequently until the zero flux was reached. This suggests that the rate of

![Figure 6.7: (a) Temperature profile of TDA analyses and (b) hydrogen volume flux with respect to time, recorded on an empty quartz tube and various pretreated Cu samples during TDA analyses.](image)
hydrogen uptake was greater when C1C Cu samples were treated with HNO₃ compared to that of HCl.

Ethanol (CH₃CH₂OH), which was used during sample sonication, could be readily retained on the surfaces of C1C wires before TDA analysis. Therefore, this could significantly contribute to the excess production of hydrogen by C1C Cu wires. Research has demonstrated the production of hydrogen by the dehydrogenation reaction associated with ethanol decomposition, reaction (6.9) to reaction (6.11), when copper/copper-chromite- or copper-nickel-based catalysts were used at elevated temperature, such as at 200 °C – 600 °C [28–31].

\[
CH_3CH_2OH + 3H_2O \rightleftharpoons 2CO_2 + 6H_2 \quad (6.9)
\]

\[
CH_3CH_2OH \rightleftharpoons CH_4 + CO + H_2 \quad (6.10)
\]

\[
CH_3CH_2OH \rightleftharpoons CH_3CHO + H_2 \quad (6.11)
\]

Another plausible explanation to account for the discrepancy in the total H₂ concentration between the C1C Cu specimens (cleaned in either HNO₃ or HCl), would be due to the presence of mixed copper oxides. These oxides could act as catalysts for the ethanol decomposition reactions [30–32]. Previous research has demonstrated that [33], when dissolved O₂ was present in the HNO₃ solution, Cu would be oxidized to Cu⁺_{(ads)}, which could serve as a catalyst to accelerate the O₂ reduction reaction and promote oxidation from Cu⁺ to Cu²⁺. If the formation of Cu²⁺ was in close proximity to the Cu surface, the catalytic cycle would be activated by further oxidizing Cu to Cu⁺, resulting in the formation of mixed oxides consisting of cuprous and cupric oxides [33]. The presence of mixed copper oxides on the C1C Cu, resulting from the exposure to the diluted HNO₃ (100 mmol/L), could possibly catalyze the ethanol dehydrogenation to produce excessive hydrogen during TDA analysis.

Regardless of the possible explanations given above, the influence of the inherent impurities in the C1C Cu samples cannot be fully ruled out. As shown in Table 6.1, although not significantly, the higher H₂ concentrations of C1C Cu samples could be attributed to the impurities from C1C Cu, thus, artificially inflating the hydrogen production during TDA analysis.
Table 6.1: Hydrogen concentration from TDA analysis

<table>
<thead>
<tr>
<th>Sample</th>
<th>Weight/g</th>
<th>Hydrogen concentration/ppmw</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anneal C2B</td>
<td>1.632</td>
<td>0.068</td>
</tr>
<tr>
<td>Anneal C2B (10 mmol/L HNO₃)</td>
<td>1.553</td>
<td>0.030</td>
</tr>
<tr>
<td>As-received C1C (100 mmol/L HCl)</td>
<td>1.000</td>
<td>0.113</td>
</tr>
<tr>
<td>As-received C1C (100 mmol/L HNO₃)</td>
<td>0.849</td>
<td>0.202</td>
</tr>
</tbody>
</table>

6.3.2 The Influence of Cell Geometry on Solution Resistance

Due to the extended cell geometrical configuration, an attempt was made to measure the solution resistance using EIS. During solution resistance measurements, the WE, RE and CE were either all placed in the major component, or the RE and CE were separated from the WE by placing them in the auxiliary component, Figure 6.8 (a) and (b). Cu C1C wires were used as the WE in these measurements. Impedance data were recorded on C1C.

Figure 6.8: Schematics showing (a) three electrodes in the major component and (b) RE and CE were separated from WE in the auxiliary component. (c) and (d) the Nyquist plots of Cu C1C wires in solutions containing 1 mol/L NaCl corresponding to the scenarios shown in (a) and (b).
Cu in both high (1 M) and low (0.01 M) concentration NaCl solutions that were exposed to the atmosphere at room temperature (21 ± 2 °C). Figure 6.8 (c) shows the Nyquist plots of C1C Cu in 1 mol/L NaCl solutions when the WE was either separated or not separated from RE and CE. Duplicate experiments were conducted under the identical experimental conditions, Figure 6.8 (d). Solution resistance (Rs) was obtained by recording the intersections between the impedance spectra and the abscissa, as shown in Figure 6.8 (c) and (d). When the WE, RE and CE were placed in the major component, Figure 6.10 (a), the solution resistances (Rs1, Rs3) were approximately 0 Ω for both the first and the duplicate experiments, Figure 6.10 (c) and (d). However, solution resistances (Rs2 and Rs4) increased as the WE was separated from RE and CE, Figure 6.7 (b). For the solution resistances measured under either separated or non-separated conditions, the differences were ~ 3.0 × 10² Ω cm² and 5.5 × 10² Ω cm² for the first experiment and the duplicate experiment, respectively.

At low [Cl⁻] (0.01 mol/L Cl⁻), Figure 6.9, the Rs was ~ 9.1 × 10² Ω cm² when the WE, RE and CE were contained in the major component; whereas, the Rs increased significantly by almost two orders of magnitude when the WE was separated from RE and CE, resulting in the Rs value of 3.6 × 10⁴ Ω cm². The EIS data obtained from Nyquist plots

![Nyquist plot](image)

**Figure 6.9:** Nyquist plots of Cu C1C wires in solutions containing 0.01 mol/L NaCl corresponding to the scenarios shown in Figure 6.9 (a) and (b). The solution resistances were labelled as Rs5 and Rs6.
demonstrated the influence of cell geometry on the solution resistance and a more pronounced increase in $R_s$ in solutions containing low [Cl$^-\]$. This could be attributed to the lack of supporting electrolyte and as a consequence of low ionic strength and solution conductivity. In short, to minimize the influence of the cell geometrical configuration on the electrochemical and corrosion measurements, concentrated aqueous chloride solutions (3 mol/L NaCl) were used for the rest of the work performed in this chapter.

### 6.3.3 Determination of Corrosion Rate

#### 6.3.2.1 Cell Headspace Hydrogen Analysis

The rates of H$_2$ production from C2B and C1C Cu in deaerated 3 mol/L NaCl solutions were measured at 75 °C, Figure 6.10. The overall H$_2$ production rates were low for both cells, resulting in a similar final corrosion rate of $\sim$ 0.1 nm/year after many months. The cumulative corrosion was $\sim$ 1.8 nm after 200 days for C2B Cu and $\sim$ 2 nm for C1C Cu after 500 days.

Figure 6.10 (a) and (b) show the cumulative H$_2$ and the corresponding total corrosion, and the incremental H$_2$ and the corresponding corrosion rate per year for C2B Cu in 3 mol/L deaerated NaCl solution for an exposure duration of 200 days. Data points were labelled with letters from a to i relating to conditions either before or after cell headspace H$_2$ sampling: a. after cathodic cleaning; b. after cathodic cleaning; c. solution replaced; d. no cathodic cleaning; e. before electrochemical experiments; f. before electrochemical experiments; g. no electrochemical experiment performed; h. no electrochemical experiment performed; i. no electrochemical experiment performed. The H$_2$ production was high initially, with a corrosion rate of 10 nm/year for C2B Cu, Figure 6.10 (b). This could be attributed to the influence of cathodic cleaning performed on Cu prior to the H$_2$ sampling.

As described in section 2.2.3, Cu surfaces were initially potentiostatically polarized for 2 minutes at more negative potentials ($< -1.0$ V vs SCE) during the cathodic cleaning, thereby leading to the production of H$_2$ via the water reduction reaction (reaction (6.5)). The hydrogen emission from Cu C2B during the cathodic cleaning appeared to be leveling off at point d (black circles, Figure 6.10 (b)), after the electrolyte was replaced with a new batch of purified 3 mol/L NaCl. The stable corrosion (pink pentagons, Figure 6.10 (a)) and
the corresponding corrosion rate (red pentagons, Figure 6.10 (b)) of ~ 0.1 nm/year were achieved after ~ 100 days. This demonstrates that the maximum corrosion rates of Cu are

Figure 6.10: Cell headspace H₂ sampling results for C2B and C1C Cu in purified and deaerated 3 mol/L NaCl at 75 °C. (a) and (c) Cumulative H₂ evolved and the corresponding corrosion depth. (b) and (d) Evolution of instantaneously measured H₂ and the corresponding corrosion rate. Note that data points were labelled with letters; the corresponding details can be found in section 6.3.2.1.
significantly lower than some observations of Cu under similar anoxic conditions, such as in pure water, resulting in a rate as high as 1 nm/d [34].

H₂ sampling was also performed in the cell containing C1C Cu under the identical experimental conditions, albeit for a longer exposure duration up to 500 days, Figure 6.10 (c) and (d). Similar to what has been mentioned previously, data points were labelled with letters from A to N relating to conditions either before or after cell headspace H₂ sampling: A. after cathodic cleaning; B. after cathodic cleaning; C. solution replaced; D. before electrochemical experiments; E. before electrochemical experiments; F. before OCP measurement; G. no electrochemical experiment performed; H. no electrochemical experiment performed; I. no electrochemical experiment performed; J. first data collected after a second solution replacement; K. data collected when OCP was being measured; L to N: no electrochemical experiment was being performed while data were collected.

At the beginning of cell sampling, Figure 6.10 (d), the incremental H₂ was high due to the excess H₂ produced through cathodic cleaning prior to the measurement with a corresponding rate of ~ 65 nm/year if all the H₂ produced resulted from corrosion. To investigate the influence of cathodic cleaning on the production of H₂ in the cell headspace prior to sampling, current densities were recorded as a function of time for both the C2B and C1C Cu specimens in solutions containing 3 mol/L NaCl during the two-step potentiostatic polarization/cathodic cleaning, Figure 6.11. Steady-state current densities were achieved after a polarization duration of < 5 s for both C2B and C1C Cu samples, suggesting that the corrosion rate was stable throughout the two-step cathodic cleaning.

![Figure 6.11: Current density-time plots recorded on C2B and C1C Cu potentiostatically polarized at (a) −1.5 V vs SCE, and at (b) −1.15 V vs SCE in solutions containing deaerated 3 mol/L NaCl.](image-url)
The absolute current densities on C1C Cu were ~ 4 times higher than those on C2B Cu when polarized at either −1.5 V or −1.15 V vs SCE. Since the water reduction to produce hydrogen, reaction (6.5), is anticipated and the current density is indicative of the electrochemical reaction rate, the C1C Cu samples exhibited a higher reaction rate than that of C2B Cu, Figure 6.11 (a) and (b). This demonstrates that more H₂ was produced on C1C Cu samples during cathodic cleaning procedures.

In addition, the theoretical amounts of H₂ produced from the cathodic cleaning (i.e., during both the potentiostatic polarizations at −1.5 V and −1.15 V vs SCE) were calculated using Faraday’s Law, Eq. (1.12), converting the total charge into the total amount of hydrogen. As shown in Table 6.2, the calculated amounts of H₂ from the cathodic cleaning for C2B and C1C Cu were 0.8 μmol and 1.2 μmol, respectively. The respectively measured amounts of H₂ at the beginning of corrosion (i.e., from point a to b, and point A to B) for C2B and C1C Cu, Figure 6.10 (a) and (c), however, were much higher than the calculated values. Specifically, the measured amounts of H₂ was 3 times higher than the calculated value for C2B Cu, while for the C1C Cu, the measured H₂ was nearly an order of magnitude higher than the theoretical amount, as shown in Table 6.2. Based on the amount of H₂ obtained experimentally (Figure 6.10 (a) and (c), from point a to b and point A to B) and theoretically (Table 6.2), one could conclude that the majority of the measured amounts of H₂ at the start of each cell H₂ sampling could result from pure corrosion or, possibly, due to other reactions that may also contribute to the production of H₂, albeit there were minor contributions from the cathodic cleaning prior to the corrosion experiments.

Table 6.2: Theoretically calculated amount of H₂ from the cathodic cleaning

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Absolute charge/ C</th>
<th>The amounts of H₂/μmol</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CC1</td>
<td>CC2</td>
</tr>
<tr>
<td>C2B</td>
<td>0.143</td>
<td>0.0155</td>
</tr>
<tr>
<td>C1C</td>
<td>0.191</td>
<td>0.0354</td>
</tr>
</tbody>
</table>

Note: CC stands for the cathodic cleaning

As shown in Figure 6.10 (d), a second increase in the incremental H₂ was observed, as indicated by the data point D, accompanied by an increase in the cumulative corrosion from C to D, Figure 6.10 (c). This increase in the corrosion rate (red pentagons, Figure 6.10 (d)) could be attributed to the replenishment of the cell solution with fresh 3 mol/L NaCl,
possibly leading to an instantaneous change of Cu surface conditions, thereby rendering it more susceptible to dissolution, reaction (6.6). Eventually, the cumulative $H_2$ levelled off, Figure 6.10 (c), and a steady-state corrosion rate of $\sim 0.1$ nm/year was achieved after $\sim 500$ days, Figure 6.10 (d).

The corrosion rate of Cu can also be estimated and expressed by the change in the amount of cumulative $H_2$ with time, $d(nH_2)/dt$. The cumulative $H_2$ recorded before day 75 was not included in the data analyses due to the excess $H_2$ produced by the cathodic cleaning prior to electrochemical experiments. The exponential function, Eq. (6.12), was fitted to the experimental data, where a, b, and c were the fitting parameters. Additionally, the first derivative of the fitted data ($d(nH_2)/dt$), was then plotted, Figure 6.12. The adjusted $R$-squared values generated from data fitting were shown in Table 6.3.

In statistics, $R$-squared is commonly used to evaluate the goodness of data fitting [38]. However, there are several drawbacks associated with an $R$-squared value, such that it cannot be used to conclude whether a regression model is biased or not [35]. Specifically, the $R$-squared value will either stay the same or increase if additional input variables are added to the fitting analysis, even if the added input variables have no relationship with the output variables, whereas, the adjusted $R$-squared increases only when the model fit is improved with the addition of more input variables [35]. The adjusted $R$-squared values were generated after the completion of data fitting in Origin software, showing values of 0.99 and 0.98 for C2B and C1C Cu samples, respectively.

$$Y(x) = a - bc^x$$

(6.12)

<table>
<thead>
<tr>
<th>Statistical parameters</th>
<th>Samples</th>
<th>C2B</th>
<th>C1C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adjusted $R$-squared</td>
<td></td>
<td>0.99</td>
<td>0.98</td>
</tr>
</tbody>
</table>

Figure 6.12 (a) shows the estimated corrosion rate of C2B Cu represented by $d(nH_2)/dt$ (blue curve). Inset figures show the $d(nH_2)/dt$ plotted in logarithmic scale as a function of time. The initial corrosion rate at $\sim 75$ days was $\sim 0.012$ $\mu$mol/d, with the rate decreasing exponentially until a steady-state was achieved. The final corrosion rate of C2B
Cu was indicated by the horizontal dashed pink line, Figure 6.12 (a), intercepting the right ordinate and yielding the value of $\sim 4 \times 10^{-9}$ $\mu$mol/d. Similarly, the corrosion rate of C1C Cu is shown in Figure 6.12 (b). The evolution of the cumulative $\text{H}_2$ for C1C Cu was quite similar to that of C2B Cu, reaching a final value of $\sim$14 $\mu$mol with the final corrosion rate of $\sim 8 \times 10^{-9}$ $\mu$mol/d. These observations confirm that Cu barely corroded in the deaerated 3 mol/L NaCl solution when the solution was nearly free of dissolved $\text{O}_2$. The corrosion

![Graphs](image)

Figure 6.12: Cumulative $\text{H}_2$ and the first derivative of fitted cumulative $\text{H}_2$ plotted as function of time for copper exposed to deaerated 3 mol/L NaCl solutions. (a) C2B Cu and (b) C1C Cu.
rate estimated from Figure 6.12 was comparable to the rate measured based on the incremental H$_2$ in Figure 6.10 (b) and (d), with the final corrosion rate (red pentagons, Figure 6.10 (d)) of C1C Cu being ~ 2 times higher than that of C2B Cu.  

In summary, these H$_2$ results suggest that Cu corrosion occurred at an extremely low rate (< 0.1 nm/year) in the deaerated 3 mol/L NaCl solutions. Although the corrosion rate of Cu appeared initially high, it decreased with time to a low steady-state rate.

### 6.3.3.2 Corrosion Experiments in Purified Near-Neutral Chloride Solutions

The corrosion rate of Cu was investigated by conducting corrosion potential and linear polarization resistance measurements. Figure 6.13 shows the $E_{corr}$ and polarization $R_p$ recorded over a 50-h exposure period for both C1C and C2B Cu in the purified and deaerated 3 mol/L NaCl solutions at 75 °C, using the electrochemical cells shown in Figure 6.2.

![Figure 6.13](image)

**Figure 6.13**: $E_{corr}$ and $R_p$ measurements in deaerated solutions containing purified 3 mol/L NaCl at 75 °C, using the cell shown in Figure 6.2.

The $E_{corr}$ values of C2B Cu were in the range −500 ± 20 mV vs SCE, with some fluctuations, and a minor increase to −470 mV vs SCE towards the end of the experiment. The small fluctuations in $E_{corr}$ for C2B Cu could be attributed to the periodic delamination of patches of surface films, if there were any formed on the Cu surfaces during corrosion.
[37]. This possibly involved the slow undermining of the deposit by the penetration of solution. These fluctuations in $E_{corr}$ were also accompanied by minor and periodic changes in $R_p$ values at $\sim (3.7 \pm 1) \times 10^4 \ \Omega \ cm^2$, and a nearly fixed corrosion rate of C2B for the entire duration of the experiment.

When C1C Cu wires were exposed to the 3 mol/L NaCl solution, $E_{corr}$ was initially stable at $\sim -380 \ mV$ vs SCE, but exhibited a slow increase starting at $\sim 33 \ h$, with a second plateau observed after $\sim 40 \ h$ at $\sim -322 \ mV$ vs SCE. $E_{corr}$ then remained constant throughout the rest of the experiment. $R_p$ values of C1C Cu were comparable to those of C2B, and remained low initially, but increased as $E_{corr}$ increased. This increase in $E_{corr}$ (blue squares, Figure 6.13) with an increase in $R_p$ (blue circles, Figure 6.13) beyond $\sim 33 \ h$ could be attributed to the complete reduction of Cu (II), available in the air-formed CuO present on the Cu surface, leading to corrosion of the Cu to form Cu$^+$ and resulting in the formation of either CuO or CuCl$_x$($x-1$)$^-$ ($x = 1, 2$ or $3$). CuO would be present since cathodic cleaning was not performed prior to the $E_{corr}$/R$_p$ measurements. As a result, the corrosion rate of C1C Cu decreased (an increase in $R_p$) once this Cu (II) was completely consumed after an exposure period of $\sim 38 \ h$. These measured $E_{corr}$ and $R_p$ values of C1C Cu were comparable to those reported by other researchers [36] under similar experimental conditions, confirming the practicality of these measurements using the electrochemical cell shown in Figure 6.2.

An attempt was made to investigate whether the increase in $E_{corr}$ was associated with the gradual ingress of O$_2$ later in the 50-h exposure for C1C Cu; a few post experimental measurements related to the determination of dissolved O$_2$ in the salt solution were conducted by recording the OCP of Pt against a SCE reference electrode for various durations in the Cl$^-$ solutions. Additionally, the concentration of dissolved O$_2$ in solutions was also examined by a colorimetric analysis using ampoules containing Rhodazine-D, a regent subject to colour change when in contact with the dissolved O$_2$ in a solution. Consequently, the degree of colour change is related to the concentration of oxygen in the solution.

Figure 6.14 shows the open circuit potentials recorded on either C1C Cu or Pt for the exposure up to 30–50 h in the 3 mol/L NaCl solutions. The final $E_{corr}$ of C1C Cu was represented by the blue circle at $\sim -330 \ mV$ vs SCE in the deaerated Cl$^-$ solution. In
addition, open circuit potentials were measured on Pt (against SCE) immediately upon the completion of the OCP measurement on C1C Cu, while the solution was still deaerated, showing a stable value of 165 ± 5 mV vs SCE. While the Pt was exposed to the 3 mol/L NaCl solution, the auxiliary component of the cell, where Pt was placed, was slowly opened to the atmosphere by loosening the PTFE plug, Figure 6.3 (c).

As shown in Figure 6.14 (green curve), \( E_{corr} \) exhibited a minor increase to a value of \( \sim 190 \pm 10 \) mV vs SCE, demonstrating that the solution environment became more oxidizing. The 3 mol/L NaCl solution was then left open to the atmosphere for a duration of 10 days and the OCP of Pt was measured on the tenth day, for a total duration of 50 h, as represented by the pink curve in Figure 6.14. The OCP eventually achieved a steady-state value of \( \sim 220 \pm 5 \) mV vs SCE. The increase in the OCP of Pt from the deaerated to aerated Cl\(^-\) solutions was indicative of a more oxidizing environment, assisted by the slow dissolution of O\(_2\) in the Cl\(^-\) solution. In addition, these observations suggest that the salt solutions were well-preserved under deaerated conditions throughout the Cu corrosion experiment.

![Figure 6.14](image.png)

Figure 6.14: Open circuit potentials of C1C Cu and Pt measured against SCE in either deaerated or aerated 3 mol/L NaCl solutions.

To investigate the concentration of dissolved oxygen in the deaerated 3 mol/L NaCl solution, a semi-quantitative colorimetric analysis was conducted using an ampoule
containing Rhodazine D reagent [37–38], Figure 6.15 (a). The ampoule was used promptly upon the completion of the $E_{corr}$ measurement on C1C Cu, reacting with dissolved oxygen to produce an oxidized complex characterized by a bright pink colour [37–38]. The concentration of dissolved oxygen was then determined by comparing the colour inside the ampoule to that of a comparator with a detectable range from 0 to 100 ppb (μg/L), Figure 6.15 (b). As shown in Figure 6.15 (c), visual inspection of the colour of the ampoule in the centre suggested that the dissolved oxygen concentration was < 20 ppb in the deaerated 3 mol/L NaCl throughout the experiment, demonstrating that the increase in $E_{corr}$ of C1C Cu, as shown in Figure 6.14, was not associated with an increase in dissolved oxygen during the experiment.

Although not fully confirmed, a decrease in solution temperature could lead to an increase in $E_{corr}$, which would coincide with an increase in the $R_p$ value. This might provide some insights on the observation of the increase in $E_{corr}$ accompanied by the increase in $R_p$ on C1C Cu, Figure 6.14. This argument was based on the observations shown in Figure 6.16, in which $E_{corr}$ and $R_p$ measurements of C2C Cu were monitored at various temperatures using the cell shown in Figure 6.3 (b).

$E_{corr}$ and $R_p$ were measured on C2C Cu at various temperatures, ranging from 20 °C to 75 °C, in the deaerated and purified 3 M NaCl solutions, Figure 6.16. As shown in the inset to Figure 6.16, most of the initial $E_{corr}$ measurements commenced at ~ 5 mV higher

Figure 6.15: Images showing (a) ampoules containing Rhodazine D reagent; (b) the comparator; and (c) the used ampoule in the centre of the comparator with a detectable range from 0 to 100 ppb.
than the steady-state $E_{\text{corr}}$ but decreased rapidly to the stable values for a duration $> 0.5$ h. This transient behavior of $E_{\text{corr}}$ could be attributed to the chemical dissolution of air-formed oxides that were present at the start of the experiment, since C2C Cu was not subject to the cathodic cleaning. The steady-state $E_{\text{corr}}$ prevailed throughout the rest of the experiment at various temperatures, with only a minor increase by $\sim 1$ mV at the end of each experiment. Since none of these Cu samples underwent cathodic cleaning prior to corrosion measurements, the stable $E_{\text{corr}}$ and $R_p$ values ($10^4$ to $10^6$ $\Omega \text{ cm}^2$) could be indicative of a steady corrosion with a relatively low corrosion rate.

$E_{\text{corr}}$ decreased from $-342$ mV to $-370$ mV vs SCE as the temperature increased from 20 °C to 75 °C, Figure 6.16. The increase in $E_{\text{corr}}$ coincided with a decrease of $R_p$ (increase in corrosion rate) by more than one order of magnitude. At each temperature, a slight decrease in $R_p$ by $\sim 1.2$ times was observed from day 1 to day 3, suggesting a slight increase in the corrosion rate during each experiment. These observations demonstrate that the overall corrosion rate of C2C Cu increased as the solution temperature increased.

Figure 6.16: $E_{\text{corr}}$ and $R_p$ recorded on C2C Cu in deaerated solutions containing purified 3 mol/L NaCl at various temperatures and an inset figure showing the transient behavior of $E_{\text{corr}}$ at times $< 30$ min.
Under the assumptions that reaction (6.4) and reaction (6.7) were the most probable anodic and cathodic reactions, respectively, when C2C Cu was exposed to the deaerated 3 mol/L NaCl solution, one could determine the respective equilibrium potentials of each half-reaction using Nernst equation (Eq. (1.5)), yielding values of \( E_e (\text{Cu/Cu}^+) \) and \( E_e (\text{H}_2/\text{H}^+) \) of \(-545 \text{ mV}\) and \(+172 \text{ mV}\) vs SCE, respectively. The measured \( E_{corr} \) of C2C Cu in Figure 6.16, ranging from \(-342 \text{ mV}\) to \(-370 \text{ mV}\) vs SCE, lay between the equilibrium potentials of the coupled redox reactions. In addition, the difference between the measured \( E_{corr} \) and \( E_e (\text{Cu/Cu}^+) \) was \( \sim 200 \text{ mV} \), a value that was smaller than the potential difference \( \sim 500 \text{ mV} \) between \( E_{corr} \) and \( E_e (\text{H}_2/\text{H}^+) \). This suggests that the anodic half-reaction was more predominant in determining the \( E_{corr} \) of C2C Cu in the deaerated 3 mol/L NaCl solutions at various temperatures.

**6.3.3 Purified Near-Neutral Chloride Solutions Containing Dissolved Gaseous Sulphide**

Figure 6.17 shows the evolution of cumulative \( \text{H}_2 \) and the corrosion rate as a function of time for C2C Cu in deaerated 3 M NaCl solutions containing a total of 0.35 \( \mu \text{mol} \) \( \text{H}_2\text{S} \) (g). The \( \text{H}_2\text{S} \) (g) was added to the cell from a certified gas cylinder (0.114\% mol/mol \( \text{H}_2\text{S} \) in \( \text{N}_2 \)). The addition of 0.35 \( \mu \text{mol} \) \( \text{H}_2\text{S} \) (g) was used to aim for an assumed 50\% of a monolayer coverage on a Cu (111) plane. The atomic density of Cu atoms on a (111) plane can be calculated, with the known total surface area of C2C Cu (479.2 cm\(^2\)).

As shown in Figure 6.17, the cumulative amount of \( \text{H}_2 \) increased as the exposure period increased. The cumulative amount of \( \text{H}_2 \) was 0.217 \( \mu \text{mol} \) at the start of the experiment and increased slightly to 0.280 \( \mu \text{mol} \) for an exposure period of 36 days in the absence of \( \text{H}_2\text{S} \) (g), leading to a corrosion rate of \( \sim 0.2 \text{ nm/year} \), as represented by the pink square plot (dashed line). The \( \text{H}_2\text{S} \) (g) was added to the cell at day 36 (point b), resulting in a slow increase in the cumulative amount of \( \text{H}_2 \) by 0.06 \( \mu \text{mol} \), for an exposure period of 90 days (from day 36 to day 126). However, the lowest corrosion rate of 0.07 \( \text{nm/year} \) (dashed pink line) was observed from day 36 to day 126. The corrosion rate of C2C Cu increased significantly (by 2.5 times) to \( \sim 0.17 \text{ nm/year} \), for a duration of 63 days (from day 126 to day 189), Figure 6.19, and the corresponding increase in the cumulative amount of \( \text{H}_2 \) was by 0.1 \( \mu \text{mol} \). While the cumulative amount of \( \text{H}_2 \) increased continuously from
day 189 to day 217, a decrease in corrosion rate was observed, resulting in a rate of 0.12 nm/year.

Figure 6.17: Cumulative H₂ and the corrosion rate of C2C Cu with regards to the exposure period in the deaerated 3 mol/L NaCl solutions containing a total of 0.35 μmol dissolved H₂S (g).

In comparison to the measured cumulative amount of H₂ and the corrosion rate of C2B and C1C Cu, Figure 6.10, only a slight increase in the corrosion rate was observed on C2C Cu after the addition of gaseous sulphide, demonstrating that, although Cu was more susceptible to corrosion in the presence sulphide, the corrosion rate of C2C Cu was scarcely affected by the addition of 0.35 μmol H₂S (g).

The $E_{corr}$ of C2C Cu were measured before and after the addition of the gaseous sulphide to the deaerated salt solutions, Figure 6.18. $E_{corr}$ remained nearly constant at −370 ± 2 mV vs SCE throughout the experiment in the 3 mol/L NaCl solution, suggesting stable corrosion. However, after the addition of 0.35 μmol H₂S, $E_{corr}$ decreased significantly to −430 mV vs SCE initially and increased slowly to the value of −388 mV vs SCE after an exposure period of ~ 40 h, Figure 6.18. This demonstrates that first, Cu was rendered more susceptible to corrosion by the presence of dissolved sulphide, and second, the transient
behavior of $E_{corr}$ observed after the addition of sulphide was indicative of, possibly, the adsorption of $\text{SH}^-$ and the subsequent reaction with Cu to form the Cu(SH)$_{\text{ads}}$. As demonstrated previously [24,39], the sulphide film growth was partially controlled by $\text{SH}^-$ transport to the reacting Cu surface and partially by the competition for Cu surface adsorption sites between $\text{SH}^-$ and $\text{Cl}^-$, reaction (3.7). This is the reaction having a potential that is close to the corrosion potential [40,41].

![Graph showing corrosion potentials](image)

Figure 6.18: Corrosion potentials recorded on C2C Cu at 75 °C in 3 mol/L NaCl solutions in the presence and absence of dissolved gaseous sulphide.

### 6.4 Summary and Conclusions

The corrosion of Cu in purified and deaerated 3 mol/L NaCl solutions in the presence and absence of sulphide were investigated using a wide range of techniques associated with H$_2$ analysis, impedance, corrosion potential, and linear polarization resistance measurements. Most Cu samples were either annealed or cleaned prior to commencing any measurements. The residual H$_2$ content of these samples was then determined by TDA analysis, showing that the annealed Cu specimens contained a negligible amount of hydrogen (< 0.1 ppmw).

The maximum corrosion rates for Cu in the deaerated 3 mol/L NaCl solutions were established by analyzing the cumulative and incremental amounts of H$_2$ in the cell
headspace using the hydrogen probe, allowing the establishment of practical, data-based values to evaluate and support the safety requirements for Cu to be applied in nuclear waste disposal. Cell headspace H₂ sampling showed that the corrosion rate of Cu was ~ 0.1 nm/year, resulting in a cumulative corrosion of ~ 2 nm after an exposure duration of 500 days in the deaerated 3 mol/L NaCl solution. This demonstrated that almost no corrosion occurred on Cu in the absence of O₂ or sulphide.

In comparison, electrochemical experiments measuring the corrosion potential and the linear polarization resistance were also conducted on various Cu specimens in deaerated 3 mol/L NaCl solutions at 75 °C. The increase in \( E_{corr} \) coincided with the increase in \( R_p \) of C1C Cu, demonstrating that, although the solution environment was seemingly more oxidizing, a decrease in the corrosion rate of C1C Cu occurred. The overall \( R_p \) values were high (~ \( 10^5 \) Ω cm²), suggesting a low corrosion rate. Experiments were also performed to determine the dissolved O₂ concentration in the deaerated salt solutions. In these experiments, OCP was recorded on Pt either promptly upon the completion of the corrosion experiments, when solution remained deaerated or the measurements were conducted in the naturally aerated salt solutions afterwards. Specifically, the OCP of Pt increased by ~30 mV from deaerated to the fully aerated condition, suggesting that the initially dissolved O₂ was low in the deaerated solutions. In addition, colorimetric analyses using ampoules containing Rhodazine D confirmed that the concentration of dissolved O₂ in the deaerated salt solution was < 20 ppb.

The influence of temperature on the corrosion rate of Cu in the pure salt solutions was investigated, showing a decrease in \( E_{corr} \) as the temperature increased. The decrease in \( E_{corr} \) was also accompanied by a decrease in \( R_p \), suggesting that the corrosion rate increased with the increase in temperature. At 75 °C, \( E_{corr} \) of C2C Cu was recorded in 3 mol/L NaCl solutions in the presence and absence of dissolved gaseous sulphide, showing a substantial decrease (~ 60 mV) in the \( E_{corr} \) as the sulphide was added. While the initial \( E_{corr} \) was lower with the added sulphide, than in the solution containing only chlorides; it was higher than that of Cu when exposed to high \([\text{SH}^-]\) (> \( 10^{-5} \) mol/L), as shown in previous chapters. This suggested that the sulphide-induced corrosion of Cu would be much more benign in the anticipated Canadian repository consisting of multiple passive barriers than that of the laboratory conditions while higher \([\text{SH}^-]\)s were used (\( 10^{-5} \) mol/L < \([\text{SH}^-]\) < \( 10^{-3} \) mol/L).


6.5 References


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Chapter 7 Summary and Future Work

7.1 Summary

The primary goal of this thesis was to examine the mechanism of Cu$_2$S formation on Cu and Cu-coated nuclear waste containers in the sulphide-containing environment that is anticipated in the long-term under DGR conditions. In particular, research was focused on the investigation of the properties and nature of copper sulphide films formed in aqueous chloride and sulphide solutions, with the focus on determining whether Cu is susceptible to pitting. The mechanistic understanding of the corrosion of Cu in aqueous sulphide can be used in models to predict the lifetimes of the Cu-coated steel container proposed for the encapsulation of used nuclear fuel in a DGR. A brief summary of the mechanistic findings and their implications for the corrosion of Cu follows.

The study in chapter 3 investigated the influence of [Cl$^-$] on electrochemically grown Cu$_2$S films on Cu and the probability of pitting corrosion in slightly alkaline (borate-buffered, pH 9) chloride and sulphide solutions. Cyclic voltammetric experiments were conducted on Cu in sulphide solutions containing a wide range of [Cl$^-$]s. Under electrochemical conditions, Cu$_2$S films were formed at potentials ($< -0.3$ V vs SCE) considerably lower than those at which anodic dissolution and oxide film formation occurred. Surface and electrochemical analyses demonstrated that the Cu$_2$S films were porous and non-passivating with the rate of film growth governed by a combination of SH$^-$ transport through the growing porous film and the competition between SH$^-$ and Cl$^-$ for adsorption sites on the reacting Cu surface. When Cu surface was polarized at more positive potentials ($\gg -0.3$ V vs SCE), the anodic dissolution as CuCl$_x$(x−1)$^-$ and oxide film formation (Cu$_2$O and possibly CuO) occurred, regardless of whether a Cu$_2$S film had been grown at lower potentials. Specifically, the balance between anodic dissolution and oxide film formation was dependent on the $[\text{BO}_3]_{\text{tot}}/[\text{Cl}^-]$ ratio with passivation by oxide film formation dominating when $[\text{BO}_3]_{\text{tot}} > [\text{Cl}^-]$. The revival of transport-controlled Cu$_2$S formation was observed once the oxides formed anodically were reduced on a reverse voltammetric scan. No evidence for pitting was observed at any potential and would only be anticipated at more positive potentials when oxide formation was possible. Mechanistic understanding of the anodically formed sulphide films was depicted in Figure 3.13.
In chapter 4, the influence of temperature on the properties of anodically formed Cu$_2$S films and the susceptibility of Cu to pitting was examined in aqueous SH$^-$ and Cl$^-$ solutions. These experiments were performed at various temperatures in the range of 20 to 80 °C ± 2 °C; i.e., within the range anticipated in a DGR. Electrochemical experiments showed that the kinetics of electrochemically-grown chalcocite (Cu$_2$S) films in the potential range of −0.8 V vs SCE to −0.3 V vs SCE were found to be partially transport-controlled, and a porous, non-passive structure was confirmed by SEM/FIB analyses. However, temperature only exerted a minor influence on the kinetics of sulphide film growth. Similarly, an active to passive transition was observed at more positive potentials ($\geq$ −0.3 V vs SCE), with active dissolution occurring as CuCl$_x$($x$−1)$^-$ within the Cu$_2$S film formed at lower potentials followed by the partial passivation of the surface by the formation of Cu$_2$O. The potential range of the active dissolution and oxide formation shifted to more negative values as the temperature increased. Surface analyses confirmed the formation of porous and non-passivating Cu$_2$S films at more negative potentials, while the formation of oxides at the Cu/film interface was observed at more positive potentials when a thick and very porous overlayer of oxide/sulphide was present. These observations demonstrated the presence of non-passive films, i.e., no localized corrosion occurred under the electrochemical conditions.

In an attempt to examine whether the properties of copper sulphide films formed naturally are similar to those grown electrochemically, the nature of the Cu$_2$S films formed under the corrosion conditions were examined in Chapter 5 and 6. Some of these experiments were also conducted in borate-buffered (pH 9) solutions containing chloride and sulphide. The short-term evolution of the corrosion of Cu was monitored with respect to time (from 0.5 h to 36 h), using the measured corrosion potential as an indicator. After various film growth periods, the extent of film growth was determined by cathodic stripping voltammetry. These results demonstrated that the chalcocite (Cu$_2$S) film grown on Cu was composed of either one or two layers, depending on the [SH$^-$]s and [Cl$^-$]s; a thin base layer and an outer deposited thicker layer. At low [SH$^-$]s and [Cl$^-$]s, only one layer was formed, with the development of dual layer as the exposure period increased. Although the base layer may initially be a barrier layer, it rapidly grew and developed porosity before eventually achieving a steady-state thickness. This layer developed a topography
inconsistent with the growth of a passive barrier layer by the transport of point defects through the growing film. Subsequently, an outer layer deposited and continued to grow at a rate partially controlled by the flux of sulphide to the Cu surface. The crystalline nature of this outer deposited layer was consistent with previous claims that the layer grew by the transport of Cu (I) species, as complexes and clusters, through the porous base layer.

In chapter 6, the corrosion of Cu was further investigated with a focus on examining the mechanism of corrosion and Cu\textsubscript{2}S film formation at more dilute [SH\textsuperscript{−}] (< 10\textsuperscript{−6} mol/L) closer to those anticipated in a Canadian DGR. Electrochemical and corrosion experiments were conducted in a novel electrochemical cell containing concentrated chloride solutions and dissolved gaseous sulphide. The corrosion process was followed using corrosion potential and linear polarization measurements and the rate measured by H\textsubscript{2} analyses. The maximum corrosion rate for Cu in the deaerated 3 mol/L NaCl solutions in the absence of SH\textsuperscript{−} was obtained from the analyses of the cumulative and incremental H\textsubscript{2} in the cell headspace using Hydrosteel hydrogen probe. A final corrosion rate of ~ < 0.1 nm/year was achieved after a few months, demonstrating that almost no corrosion occurred on Cu when exposed to deaerated 3 mol/L NaCl.

The corrosion rate of Cu was also investigated at the temperature of 75 °C in a 3 mol/L NaCl solutions containing dissolved H\textsubscript{2}S (g). The \(E_{\text{corr}}\) exhibited a substantial decrease from −375 mV to −430 mV vs SCE (~ 60 mV vs SCE) immediately after the addition of gaseous sulphide. While the initial \(E_{\text{corr}}\) was low in a solution with the added sulphide compared to a solution containing only Cl\textsuperscript{−}, it slowly increased to a value higher than that of Cu when exposed to high [SH\textsuperscript{−}] (> 10\textsuperscript{−5} mol/L). The corrosion rate of Cu was investigated before and after the addition of trace gaseous sulphide (0.35 \(\mu\)mol H\textsubscript{2}S (g)) by analysing the change of cumulative H\textsubscript{2} with regards to the change in time. Only a slight increase in corrosion rate by less than a order of magnitude was observed after the addition of 0.35 \(\mu\)mol H\textsubscript{2}S (g). This demonstrates that, although Cu was more susceptible to corrosion in the presence sulphide, the corrosion rate was not significantly affected by the addition of trace amount of H\textsubscript{2}S (g). In short, these results suggested that sulphide-induced corrosion of Cu would be much more benign in the anticipated Canadian repository when the extremely low [SH\textsuperscript{−}] (< 10\textsuperscript{−6} mol/L) is anticipated to be present.
7.2 Future Work

This study has provided the basis to understand the nature of copper sulphide films formed on Cu under both electrochemical and corrosion conditions, with an emphasis on investigating the properties of sulphide films formed in the slightly alkaline environment (pH 9) anticipated on used fuel containers in a DGR. While it has shown that films are crystalline and porous, it has not provided any assessment of how damage will accumulate on a container after long-term exposure to the environment in a DGR. A significant number of issues remain to be resolved.

i. Although preliminary results have been presented in this study on corrosion at extremely low \([\text{SH}^-]\) (< 10^{-6} \text{ mol/L}) a comprehensive understanding of corrosion under these conditions remains to be resolved.

ii. Since the initial reaction step in Cu corrosion is known to be influenced by the adsorption of anions present in the aqueous environment, the influence of expected groundwater species, such as sulphate \((\text{SO}_4^{2-})\) and bicarbonate \((\text{HCO}_3^-)\), and whether they would exert a synergistic effect on sulphide film formation, remains to be investigated.

iii. While the properties of the initially-formed Cu\(_2\)S layer have been studied, a clear understanding of how this film grows and becomes porous is key to understanding why thick porous films can eventually develop. Of key importance is whether or not the film remains intact in some locations (e.g., on specific crystal facets) leading to an uneven, grain-sensitive distribution of damage. Such a study will require the application of electrochemical techniques supplemented by transmission electron microscopy and Auger spectroscopy. The need to avoid exposure to oxygen will require electrochemical experiments to be conducted in an anaerobic chamber.

iii. Since the container will be surrounded by the compacted bentonite clay which will influence the transport and distribution of \(\text{SH}^-\) in the proximity of the Cu surface, its influence on the Cu corrosion process must be evaluated. A key issue requiring further study is how corrosion will propagate if the clay is only partially wetted. This would allow more rapid transport of \(\text{H}_2\text{S} \text{ (g)}\) to the Cu surface when its subsequent dissolution into \(\text{H}_2\text{O}\) would lead to corrosion.
iv. While corrosion models exist to calculate the corrosion penetration due to reaction with $\text{SH}^-$, they are restricted to predicting container penetration based on the assumption that the propagation front will be uniform. This will not be the case on cold spray deposited coatings which will have particle boundary faults and porosity which could act as preferential pathways for corrosion to propagate. A determination of how corrosion will penetrate through such a structure will require a combined experimental/modelling approach.
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Article Title: The Susceptibility of Copper to Pitting Corrosion in Borate-Buffered Aqueous Solutions Containing Chloride and Sulfide

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Appendix B: Film Thickness Estimation Using Auger Depth Profile

To address the difference in the observed sputter time associated with S signals and to estimate the approximate sulphide film thickness, the sputtering rate for the sulphide film on the corroded Cu sample was estimated from the measured sputtering rate of a fine polished blank Cu under the same conditions (i.e., at a sputter voltage of 0.5 kV or 3 kV), as shown in Figure 7.1. The sputtered areas on Cu were then analyzed by CLSM, Figure 7.2.

Figure 7.2: An optical image showing the sputtered areas on a polished Cu sample after a total sputtering duration of 12 hours and 5 hours, respectively.

Figure 7.1: CLSM 3-dimensional topography and step height measurements on the sputtered areas of a blank Cu sample. (a) and (b) measurements associated with the sputtered region 1 (12 hours, 0.5 kV), (c) and (d) measurements associated with the sputtered region 2 (5 hours, 3 kV).
The 3-dimensional surface topographies and the corresponding step height measurements were obtained from the sputtered areas on a blank Cu sample, Figure 7.1. The measured depth on the sputtered region 1 (12 h, 0.5 kV) was ~ 8 μm, resulting in a sputter rate of 11 nm/min, Figure 7.2 (a) and (b). For the sputtered region 2, a depth of ~ 6 μm was measured after a total of 5 hours sputtering at the voltage of 3 kV, leading to an estimated sputtering rate of 20 nm/min. As a result, the calculated sulphide film thickness based on the measured sputtering rates was ~ 30 nm.
Appendix C: NaCl Purification

The purified NaCl solution is prepared by following the procedures below:

1) A 3 mol/L NaCl solution was prepared with 99.0% NaCl (reagent grade) and Type I water.
2) The pH of the 3 mol/L NaCl solution was then measured using pH test strips (pH range: 6.0-7.7).
3) The pH of the 3 mol/L NaCl solution was adjusted to pH 9 by the addition of 0.5 mol/L NaOH solution.
4) 0.24 g/L Na₂S (Na₂S·9H₂O, 98.0% assay, reagent grade) was added into the 3 mol/L NaCl solution to make a solution containing a total concentration of 10⁻³ mol/L Na₂S.
5) The 3 mol/L NaCl (pH 9) solution was sealed and stirred overnight with a magnetic stir bar to ensure that complete reaction occurred between Na₂S and heavy metal impurities (Pb, Hg).
6) The 3 mol/L NaCl solution (pH 9) was filtered using a filter with a pore size of 200 nm.
7) 1.2 mL of 25%–30% wt. % hydrogen peroxide was added to the 3 mol/L NaCl (pH 9) solution while the solution was stirred overnight with a magnetic stir bar at a constant rate of 120 rpm.
8) The pH of the filtered 3 mol/L NaCl solution was then measured using pH test strips (pH range: 6.0–7.7).
9) A few droplets of the filtered 3 mol/L NaCl solution was transferred onto a clean silicon wafer.
10) XPS analysis was performed on the silicon wafer afterwards to investigate the concentration of sulphur (S) by examining the S high resolution spectra. In particular, the at. % of sulphide and sulphate were examined. If sulphide was still detectable by XPS after the completion of previous steps (from step 1 to 10), steps 6-10 would be repeated until S content was negligible.
11) The dry NaCl salt was obtained by evaporating 1 L of 3 mol/L NaCl solution. These salts were then transferred into an anaerobic chamber prior to corrosion characterization (dry process 1).
12) To remove the residual hydrogen peroxide in the 3 mol/L NaCl solution, a Pt electrode was immersed in the 3 mol/L NaCl solution. The solution was maintained at 80 °C for an exposure duration of 220 h.

13) The solution was filtered again using a filter with a pore size of 200 nm.

14) The filtered solution was evaporated to obtain the dry NaCl salt. Some of the dry NaCl salts were stored in an anaerobic chamber before corrosion characterization (dry process 2).
Curriculum Vitae

Mengnan Guo

Education

Western University, London, Canada 2016 – 2020
*Ph.D., Doctor of Philosophy, Physical/Analytical Chemistry (Corrosion)*
Supervisors: Dr. David Shoesmith, Dr. James Noël

Dalhousie University, Halifax, Canada 2014 – 2016
*MSc., Master of Science, Applied Physics*
Supervisor: Dr. Harm. H. Rotermund

Wuhan Institute of Technology, Wuhan, China 2010 – 2014
*B.Eng., Bachelor of Engineering, Chemical Engineering*

Publications

**Peer-Reviewed Journal Articles**


Related Work Experience
Graduate Teaching/Research Assistant (Western University, London) 2016 – 2020
Graduate Student Researcher (NRCan-CanmetMATERIALS, Hamilton) 2016 – 2020

Scholarships and Awards
• 103rd Canadian Chemistry Conference and Exhibition 2020
  ChemiSTEAM photo contest – 3rd Place
• NACE Southern Ontario Student Section (SOSS) 10th Annual Symposium 2020
  Best Poster Presentation Award – 1st Place
• Natural Sciences and Engineering Research Council (NSERC) 2020
  Top 20 Finalists in Science Exposed Image Competition
• NACE International Foundation 2020
  CORROSION 2020 Travel Award
• Canadian Nuclear Association (CNA) 2019
  CNA 2020 Travel Award (Sponsored Student)
• NACE Northern Area Eastern Conference 2019 2019
  Best Poster Presentation Award – 1st Place
• NACE Southern Ontario Student Section (SOSS) 9th Annual Symposium 2019
  Best Oral Presentation Award – 2nd Place
• Western University, Canada 2019
  Canadian Society for Chemistry (CSC) Travel Award
• NACE International Foundation 2019
  Graduate Student Book Award
• University Network of Excellence in Nuclear Engineering (UNENE) 2019
  Best Poster Presentation Award – 2nd Place
• Western University, Canada 2018
  CAMBR Trainee Travel Award
• Western Graduate Research Scholarship 2016 – 2020
• Dalhousie University, Canada 2014 – 2016
  NSERC CREATE – Dalhousie Research in Energy, Advanced Materials and Sustainability (DREAMS) Scholarship

Selected Conference, Workshop and the Associated Presentations
• NACE Southern Ontario Student 10th Symposium, London, Canada July 2020
  ➢ M. Guo*, J. Chen, S. Difelice, T. Martino, J.J. Noël and D.W. Shoesmith; The Corrosion of Copper in the Chloride and Sulphide-Containing Environment
Anticipated in a Deep Geological Repository for the Permanent Disposal of Used Nuclear Fuel. (*Poster Presentation*)

- **NACE CORROSION (Cancelled)**  March 2020

- **Canadian Nuclear Association Conference and Trade Show, Canada**  Feb 2020

- **UNENE Annual R&D Workshop, Toronto, Canada**  Dec 2019

- **Electrochemical Society Student Symposium Annual Event, Canada**  Dec 2019

- **NACE Northern Area Eastern Conference, Ottawa, Canada**  Oct 2019

- **NACE Southern Ontario Student 9th Symposium, London, Canada**  July 2019

- **102nd Canadian Chemistry Conference and Exhibition, Quebec City** June 2019

- **Waste Management Symposia, Phoenix, USA** March 2019

- **UNENE Annual R&D Workshop, Toronto, Canada** Jan 2019

- **Electrochemical Society Student Symposium Annual Event, Canada** Dec 2018

- **Materials Research Society Meeting, Boston, USA** Nov 2018

- **Gordon Research Seminar/Conference (GRS/GRC), New London, USA** July 2018

➢ M. Guo*, J. Chen, T. Martino, J. J. Noël, and D. W. Shoesmith; The Susceptibility of Copper to Pitting Corrosion in Slightly Alkaline (pH 9) Aqueous Solutions Containing Sulphide and Chloride. *(Poster Presentation)*

• UNENE Annual R&D Workshop, Toronto, Canada Dec 2017

➢ M. Guo*, J. Chen, Z. Qin, J.J. Noël and D.W. Shoesmith; The Susceptibility of Copper to Pitting Corrosion in Aqueous Solutions Containing Sulphide and Chloride. *(Poster Presentation)*

*Denotes the primary presenter