The Corrosion Behaviour of Cu in Irradiated and Non-Irradiated Humid Air

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Graduate Program in Chemistry
A thesis submitted in partial fulfillment of the requirements for the degree in Master of Science
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THE CORROSION BEHAVIOUR OF CU IN IRRADIATED AND NON-IRRADIATED HUMID AIR

(Thesis format: Monograph)

by

Balsam Ibrahim

Graduate Program in Chemistry

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science

The School of Graduate and Postdoctoral Studies
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Abstract

The present management scenario for the permanent disposal of high level nuclear waste in Canada is to seal it in metallic containers and bury it in a deep stable geologic repository. For thick-walled containers radiation fields on the outside of the container would have a negligible influence on container corrosion. However, to overcome fabrication issues and to reduce costs, steel containers with a thin outer copper coating are being designed making a reassessment of the influence of gamma radiation on container corrosion a potential licensing requirement.

The behaviour of Cu in an aerated vapour phase environment in equilibrium with condensed water has been extensively investigated using surface analysis techniques. In Chapter 3, the long-term corrosion behaviour of Cu in a 75 °C/70 %RH environment was investigated. The results show that, while general corrosion of the surface results in a thin layer of corrosion product that does not grow with time, areas of locally condensed water (termed patches) experienced more extensive corrosion. While the thicknesses of the corrosion product layer at these locations increases with time, the aspect ratio (depth of corrosion product to area corroded) is very small.

In Chapter 4, the effects of a low dose rate of γ-radiation (0.3 Gy/h) were investigated by analyzing the change in resistance across a Cu wire, and analyzing surfaces of samples exposed to H₂O vapour at 75 °C/85 %RH. While the corrosion rate from the Cu wire data indicated that no significant corrosion was detected, surface analysis of the coupons indicated that again, while corrosion of the general surface is minimal, patches exhibit more extensive corrosion. The effect of low-dose radiation on the general corrosion was an initial accelerated rate of surface coverage by corrosion product on the general areas and an increase in the number and size of patches. The overall extent of corrosion in both areas was comparable to the long-term study described in Chapter 3.

In Chapter 5, the effect of [O₂] in a humid environment and the effect of a high radiation dose rate (3 kGy/h) in different gas environments on the initial stages of Cu corrosion were investigated. The results showed that initial O₂ content affected the rates of nucleation and growth of the oxide. The faster coverage of the surface by corrosion products with irradiation and the increased thickness of corrosion products indicate that high-dose γ-radiation increases the initial rate of corrosion.
Chapter 6 addresses the mechanisms of corrosion in general areas and within patches. In both areas corrosion was controlled by a dual layer of Cu$_2$O/CuO. In the general areas the limited amount of available H$_2$O lead to a protective layer. In the patches the greater availability of H$_2$O allowed corrosion to continue.

Keywords: vapour phase corrosion of copper, low $\gamma$-radiation fields, high $\gamma$-radiation fields, influence of relative humidity, influence of cover gas, spent fuel disposal.
Co-Authorship Statement

All chapters presented in this thesis were co-authored by my supervisors, Dr. J. Clara Wren, and Dr. David W. Shoesmith. The roles of others are described below:
Chapter 3: D. Zagidulin and J. Chen assisted in the initial set-up of the humidity chamber experiments.
Chapter 4: J. M. Smith and J. J. Noel designed the set-up for the experiments at CNL. J. M. Smith was the principal investigator for the Cu wire resistance experiment and wrote the corresponding section. I was the principal investigator for the coupon study.
Chapter 5: J. Joseph assisted in designing the experimental set-up and operating the gamma-cell. J. Joseph provided the water vapour radiolysis model results used to interpret some of the results in the chapter. M. Behazin assisted by running some experiments and performing some surface analyses.
M. Biesinger performed XPS analysis (Chapters 3 and 4), and Todd Simpson performed FIB analysis (Chapters 3, 4 and 5). I was directly involved in treatment and interpretation of the analyses.
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This thesis is dedicated to my haboba (grandmother),

Fawzia Ali Shawki

(1928-2013)
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<th>Description</th>
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<tbody>
<tr>
<td>α</td>
<td>Resistance temperature coefficient</td>
</tr>
<tr>
<td>CNL</td>
<td>Canadian Nuclear Laboratories</td>
</tr>
<tr>
<td>DGR</td>
<td>Deep Geologic Repository</td>
</tr>
<tr>
<td>ε</td>
<td>Extinction coefficient</td>
</tr>
<tr>
<td>$E_b$</td>
<td>Binding energy</td>
</tr>
<tr>
<td>ECD</td>
<td>Electron Capture Detector</td>
</tr>
<tr>
<td>EDX</td>
<td>Energy Dispersive X-ray</td>
</tr>
<tr>
<td>$E^e$</td>
<td>Equilibrium potential</td>
</tr>
<tr>
<td>$E_k$</td>
<td>Kinetic energy</td>
</tr>
<tr>
<td>$E^o$</td>
<td>Standard potential</td>
</tr>
<tr>
<td>ERCP</td>
<td>Electrical Resistance Corrosion Probe</td>
</tr>
<tr>
<td>F</td>
<td>Faraday’s constant</td>
</tr>
<tr>
<td>FIB</td>
<td>Focused Ion Beam</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier Transform Infrared</td>
</tr>
<tr>
<td>GC</td>
<td>Gas Chromatography</td>
</tr>
<tr>
<td>Gy</td>
<td>Gray</td>
</tr>
<tr>
<td>ΔG</td>
<td>Gibbs free energy change</td>
</tr>
<tr>
<td>h</td>
<td>Plank’s constant</td>
</tr>
<tr>
<td>η</td>
<td>Viscosity</td>
</tr>
<tr>
<td>IMFP</td>
<td>Inelastic Mean Free Path</td>
</tr>
<tr>
<td>IR</td>
<td>Infrared</td>
</tr>
<tr>
<td>MSD</td>
<td>Massive Selective Detector</td>
</tr>
<tr>
<td>NWMO</td>
<td>Nuclear Waste Management Organization</td>
</tr>
<tr>
<td>ν</td>
<td>Light frequency</td>
</tr>
<tr>
<td>OFHC</td>
<td>Oxygen-Free High Conductivity</td>
</tr>
<tr>
<td>$P_c$</td>
<td>Critical pressure</td>
</tr>
<tr>
<td>$P_{ws}$</td>
<td>Saturation vapour pressure</td>
</tr>
<tr>
<td>R</td>
<td>Resistance</td>
</tr>
<tr>
<td>RH</td>
<td>Relative Humidity</td>
</tr>
<tr>
<td>Symbol</td>
<td>Description</td>
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<tr>
<td>--------</td>
<td>------------------------------------</td>
</tr>
<tr>
<td>( \rho )</td>
<td>Resistivity</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscopy</td>
</tr>
<tr>
<td>( T_c )</td>
<td>Critical temperature</td>
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<tr>
<td>TCD</td>
<td>Thermal Conductivity Detector</td>
</tr>
<tr>
<td>( T_d )</td>
<td>Dew Point Temperature</td>
</tr>
<tr>
<td>( T_n )</td>
<td>Triple point temperature</td>
</tr>
<tr>
<td>UFC</td>
<td>Used Fuel Containers</td>
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<tr>
<td>( \nu )</td>
<td>Transformed temperature</td>
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<tr>
<td>XPS</td>
<td>X-ray Photoelectron Spectroscopy</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray Diffraction</td>
</tr>
<tr>
<td>( \phi )</td>
<td>Work function</td>
</tr>
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</table>
Chapter 1

1 Introduction

1.1 General Introduction

Nuclear energy can eliminate between 40 to 90 million tons of greenhouse gases each year in Canada.\(^1\) A single nuclear fuel bundle produces approximately 1 million kilowatt-hours of electricity, enough electricity to power 100 homes for an entire year.\(^1\) Currently, 16\% of Canada’s electricity, and over 50\% of Ontario’s electricity, is generated by nuclear power.\(^2\) However, if nuclear power is to remain a sustainable source of energy, a key requirement is the successful management of the fuel waste.

![Diagram of multiple-barrier system proposed for the permanent disposal of spent nuclear fuel in a Deep Geologic Repository.](image)

Figure 1.1: A schematic illustration of the multiple-barrier system proposed for the permanent disposal of spent nuclear fuel in a Deep Geologic Repository.

Once a fuel bundle has been used to generate electricity and is removed from the reactor, it is considered to be waste since fuel reprocessing is not considered in Canada. Currently, about 87,000 used fuel bundles are generated each year in Canada.\(^3\) As of June 2014, if stacked end-to-end, the inventory of used nuclear fuel bundles (~ 2.51 million bundles) would fill about six regulation-size hockey rinks from the surface of the ice to
the top of the boards. For long-term management of nuclear waste, Canada has selected to contain, isolate, and permanently dispose of the spent fuel bundles in a deep geologic repository (DGR). A DGR is a multiple-barrier system designed to safely contain and isolate the nuclear waste at a depth of approximately 500 m below the ground, Figure 1.1. The spent fuel bundles themselves will be placed in corrosion resistant used fuel containers (UFCs) prior to being emplaced in boreholes subsequently backfilled with bentonite clay. Although alternative designs are under consideration, NWMO’s current design (Figure 1.2) calls for a dual-walled container with an outer copper corrosion-barrier, and an inner steel load-bearing vessel, containing interior baskets for holding the spent fuel bundles. Copper has been selected as the corrosion barrier material since it is expected to be thermodynamically stable in the final anoxic conditions anticipated in a DGR. In the original design, the copper shell was designed with a thickness of 25 mm [5] although current models predict a corrosion allowance of 1.27 mm will be required to prevent failure.

![Figure 1.2: Illustration of a used fuel canister (UFC).](image)

One key consideration during the design of containers is the determination of the influence of radiation fields, produced by the decay of the radioactive waste, on the outside of the container. For the originally designed thick walled container, calculations and studies showed that the influence of radiation on corrosion, at the dose rates expected
(0.1 Gy/h), would be insignificant. More recently, the NWMO has focused on designing a thinner walled container in efforts to eliminate design issues associated with the fabrication and welding of the vessels. This new, thinner container poses the possibility of a measurable radiation effect on container corrosion, making a more thorough analysis of the potential corrosion damage a key requirement for licensing. The dose rates anticipated at the surface of a thin walled container surface would decay from ~5 Gy/h to ~0.44 Gy/h after 200 years, based on the half-life of $^{137}\text{Cs}$, the dominant $\gamma$-emitter in the fuel. This is a significant increase in anticipated dose. Thus, the primary goal of this project is to determine the influence of $\gamma$-radiation on Cu corrosion under DGR conditions, which will allow a more accurate assessment of the possible extent of corrosion damage sustainable over its emplacement lifetime. This is an essential requirement if an adequate Cu corrosion barrier thickness is to be specified.

After emplacement, the container will be exposed to a sequence of four distinct exposure environments in a DGR: 1) an initial aerated period with no condensed H$_2$O on the Cu surface; 2) a period of aerated vapour in equilibrium with a condensed H$_2$O layer on the surface; 3) a transition period to fully saturated, potentially oxidizing aqueous conditions; and 4) a final aqueous anoxic period after the available O$_2$ has been consumed by container corrosion and reactions with minerals and organic matter in the clay surrounding the container (Figure 1.1). While the rate of corrosion in period 1 is expected to be minimal, the corrosion rates could be significant throughout periods 2 to 4. This thesis investigates Cu corrosion in the aerated vapour phase environment and focuses on determining the influence of $\gamma$-radiation on Cu corrosion in period 2.

In period 2, it is anticipated that the temperature at the canister surface will be in the range of 70 to 100 °C due to radioactive decay processes within the fuel. During this period, a relative humidity (RH) of ~75 % is likely to be present in the clay at the surface of the container and subjected to a $\gamma$-radiation field on the outside of the container. The $\gamma$-radiolysis of liquid water leads to the formation of highly reducing and oxidizing species such as $\cdot\text{OH}$, $\text{e}_{\text{aq}}^-$, $\cdot\text{H}$, H$_2$, H$_2$O$_2$, and H$^+$ with the most stable and highly oxidizing species being H$_2$O$_2$. However, predicting the radiolysis products in thin H$_2$O layers in contact with humid air is more challenging since over 700 reactions and 75 species are
involved. Most importantly, since N\textsubscript{2} is present, oxidants such as HNO\textsubscript{3}, NO\textsubscript{2} and N\textsubscript{2}O will be formed.\textsuperscript{7}

The results from this work will be used to ultimately create a model that will allow an assessment of the extent to which the container wall can be thinned without compromising the corrosion performance. The results from this study will be of immediate value to many national waste disposal programs, in particular Canada, Sweden, and Finland who have adopted Cu as their chosen container material.

1.1 Gap Analysis in Knowledge on Cu Corrosion

An extensive gap analysis on the understanding of long-term corrosion behaviour of Cu and carbon steel containers has been conducted and summarized in a report by King.\textsuperscript{9} Only the gaps in knowledge regarding Cu corrosion most relevant to this work will be presented here. While there is a good understanding of the uniform corrosion behaviour of Cu UFCs, there are some areas of uncertainty such as: (i) the rates of precipitation and dissolution of Cu\textsubscript{2}O, CuCl\textsubscript{2}•3Cu(OH)\textsubscript{2} and other Cu corrosion products are unknown; (ii) an absence of large scale test data for validation of a Cu corrosion model; (iii) a sparse database on the corrosion of Cu in unsaturated bentonite; (iv) a lack of knowledge of the rate of Cu(II) reduction on corroded Cu surfaces; and (v) little information on the properties of the oxide films.\textsuperscript{9} Perhaps a larger gap exists in the insufficient validation of localized corrosion predictions. In the report, it states that the major challenges regarding localized corrosion of Cu UFCs are (i) gaining acceptance that the form of corrosion observed is surface roughening by general corrosion rather than discrete localized corrosion or pitting, and (ii) developing a model to predict the long-term behaviour by surface roughening, since this is expected to be the dominant mode of damage.\textsuperscript{9} However, initial wetting of the surface of UFCs is likely to be non-uniform and may result in localized corrosion, a situation that must be assessed. This requires the following: developing a mechanism of Cu corrosion in unsaturated bentonite and determining the possibility of localized corrosion; determining the evolution of surface roughening as the environment changes in a DGR; developing a model for predicting the surface roughening and how it evolves as a function of time; and validating localized corrosion predictions by collecting test data.
The issues to be addressed in this work will be the following: (i) to collect experimental evidence for the degree of localized corrosion during the unsaturated phase; (ii) to develop a mechanism for localized corrosion; and (iii) to develop an understanding of the effect of humidity on Cu corrosion during the unsaturated phase.

1.2 Atmospheric Corrosion

Corrosion in moist atmospheres is different and often more severe than in bulk solutions. Dissolved metal ions cannot diffuse out into the bulk solution but precipitate onto the metal surface, and reaction with O\textsubscript{2} in a thin film is not limited by transport as it is in bulk water.\textsuperscript{10} The key to corrosion resistance is a dense adherent surface film that forms a protective barrier between the metal and corrosive environment. General uniform attack is the typical form of atmospheric corrosion, pitting and other localized forms of corrosion being rare.\textsuperscript{11} Humidity is necessary for atmospheric corrosion to occur, a thin layer of condensed water deposited on the surface providing the medium needed for electrochemical corrosion, which proceeds at a faster rate than gaseous corrosion. Pollutants or other atmospheric contaminants increase the rate of atmospheric corrosion by enhancing the electrolyte properties.\textsuperscript{11} Above a critical relative humidity, typically reported in the range of 50 to 70 %RH, water condenses on the surface.\textsuperscript{12} Hygroscopic corrosion products or other salt particles deposited from the atmosphere, reduce the relative humidity necessary for water condensation and therefore increase the time of wetness and consequently the extent of corrosion.\textsuperscript{11}

1.3 Water and Air Radiolysis

Water, when exposed to ionizing radiation decomposes to form a range of chemically reactive radical species as well as stable molecular products as shown in reaction (1):\textsuperscript{13}

\[ \text{H}_2\text{O} \xrightarrow{\gamma} \cdot\text{OH}, \cdot\text{e}_{\text{aq}}, \cdot\text{H}, \text{HO}_2\cdot, \text{H}_2, \text{H}_2\text{O}_2, \text{H}^+ \]  

These radiolysis products react very quickly with one another to generate additional reactive species called secondary radiolysis products, such as O\textsubscript{2}, \cdot\text{O}_2\cdot and \cdot\text{O}_3\cdot. The radiolysis products can also react with any solute species including acid and base ions of
water solvent, \(H^+\) and \(OH^-\). In the presence of a constant radiation source, the decomposition reaction rates of individual radiolysis products eventually match their radiolytic production rates, allowing the radiolysis products to reach steady-state concentrations. Since water radiolysis products are both highly oxidizing and highly reducing, they will determine the aqueous redox condition of the water and influence the corrosion kinetics of metallic surfaces in radiation-exposed systems.\(^{13-18}\)

Radionuclide of humid air results in the formation of products that include ozone, nitrogen oxides and nitric acid.\(^7\)

\[
N_2, O_2, H_2O \xrightarrow{\gamma} \cdot OH, \cdot H, H_2O_2, O_3, NO_2, N_2O, HNO_3
\] (2)

In air, most of the observed effects are attributed to the nitric acid production. Nitric acid is formed only if \(N_2, O_2\) and \(H_2O\) are simultaneously present, which would be the case for humid air radiolysis.

1.4 References
5. Kwong, G. M. Status of corrosion studies for copper used fuel containers under low salinity conditions; NWMO TR-2011-14; Toronto Ontario, 2011.
6. King, F. Overview of the corrosion behaviour of copper and steel used fuel containers in a deep geologic repository in the sedimentary rock of the Michigan Basin, Ontario; 06819-REP- 01300-10101 R00; 2005.
Chapter 2

2 Experimental Background

2.1 General Electrochemistry

All spontaneous chemical processes have a negative Gibbs free energy change ($\Delta G$). In electrochemistry, $\Delta G$ can be written as a potential,

$$\Delta G = -nFE^e$$

(1)

where $n$ is the number of electrons involved in the electrochemical process, $F$ is Faraday’s constant, and $E^e$ is the equilibrium potential. The equilibrium potential is calculated using the Nernst equation, which takes into account non-standard conditions. The Nernst equation converts the standard potential, $E^o$, into $E^e$ by taking into account the temperature and concentration variations from standard conditions,

$$E^e = E^o + \frac{RT}{nF} \ln \frac{C_{ox}}{C_{red}}$$

(2)

where $R$ is the gas constant, $T$ is temperature, and $C_{ox}$ and $C_{red}$ are the concentrations of the oxidized and reduced species involved in the electrochemical reaction.

Corrosion is a degradation process that occurs at the interface between a material (generally a metal) and its environment. Electrochemically, the metal is oxidized and loses electrons that reduce an oxidizing species present in the solution,

$$M \rightleftharpoons M^{n+} + ne^- \quad \text{(anodic reaction)}$$

(3)

$$Ox + ne^- \rightleftharpoons Red \quad \text{(cathodic reaction)}$$

(4)

When corrosion occurs at the surface of a metal in contact with a solution containing an oxidant, metal oxidation is driven by the reduction of the oxidant, and the sum of the two half reactions is the overall corrosion reaction. When two electrochemical reactions couple, the relative rates of the two reactions establish a corrosion potential, $E_{corr}$, at which mass balance dictates that the anodic and cathodic currents be equal and of opposite sign. The current flowing between anodic and cathodic locations on the metal surface is termed the corrosion current, $i_{corr}$. Since the anodic reaction is an ion transfer reaction it represents the mass loss, or corrosion, of the metal.
2.2 Surface Analysis Techniques

2.2.1 Scanning Electron Microscopy and Energy Dispersive X-ray Spectroscopy

Electron microscopy is a very useful tool because it utilizes the high energy of electrons that can be focused by manipulating their electromagnetic properties to yield high-resolution images. Scanning electron microscopy, SEM, operates by accelerating a beam of electrons through scanning coils that move the beam along the sample. Typically, the secondary electron imaging mode is used in which secondary electrons are collected above the sample. When the incident electrons interact with the sample, secondary electrons are ejected and collected by the secondary electron detector. As the SEM scans the sample, an image is produced and every point the beam strikes on the sample is mapped directly onto a corresponding point on the screen. SEM provides information on the morphology, particle size and texture of the sample.

Typically, an SEM is equipped with an x-ray detector. As electrons interact with the sample, and a core electron is ejected creating a hole, an outer shell electron will fill its place. When this occurs, characteristic x-rays are emitted. This technique is called energy dispersive x-ray spectroscopy (EDX) and provides qualitative and semi-quantitative analysis of the elemental composition of the surface being analyzed. Since x-rays are not inelastically scattered like electrons, sampling depths up to 1 um are typical using an accelerating voltage of 10 keV.

2.2.2 Focused Ion Beam Milling

A focused ion beam (FIB) mills or sputters the sample surface using a relatively large ion (typically Gallium) at an accelerating voltage of 5 to 50 keV. The milling generates secondary ions or neutral atoms, and also secondary electrons. As the ion beam rasterers the sample surface, the signal from the secondary electrons is collected to form an image. At high beam currents, large amounts of material can be removed allowing precision milling of the specimen down to a sub-micrometer scale. This technique is very useful in determining metal oxide thicknesses and studying the morphology of the cross-section.
2.2.3 Raman Spectroscopy

Raman is a spectroscopic technique that provides information about the chemical structure of a molecule. Incoming radiation is scattered by certain molecules and the scattering results in a shift of wavelength from that of the incident beam. These shifts depend on the chemical structure of the molecules. When a sample is irradiated (visible to near-IR range laser), scattering at all angles occurs. Scattering involves a momentary distortion of the electrons distributed around a bond in a molecule, followed by reemission of the radiation as the bond returns to its normal state. When the molecule is distorted, it develops a momentary induced dipole that disappears upon reemission. For a molecule to be Raman active, it must exhibit a net change in its polarizability.

Incident radiation causes excitation to a virtual state and subsequent reemission of a photon of equal, lower or higher energy. This virtual state exists because the excitation wavelength is far from the absorption band. Elastic scattering occurs when a photon of equal energy to the excitation photon is emitted; this is termed Rayleigh scattering. When the excitation photon is inelastically scattered, it produces Stokes (\(E_{\text{ex}} - \Delta E\)) or anti-Stokes (\(E_{\text{ex}} + \Delta E\)) scattering. Stokes scattering is more intense since the ground vibrational level is more highly populated than the excited vibrational levels. Stokes scattering is what is analyzed and presented in Raman spectra.

2.2.4 X-ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy (XPS) is a quantitative non-destructive technique for studying the elemental composition, empirical formula, and chemical and electronic states of the elements present in the surface of a material. The technique involves the bombardment of the material in a vacuum with a low energy x-ray source; adsorption of an x-ray, of known energy, by an atom results in the ejection of a single electron from the inner shell of the atom and the kinetic energy of the ejected electron is analyzed. The kinetic energy, \(E_k\), of the ejected electron is characteristic of the atom from which it was ejected, and can be described by

\[
E_k = h\nu - E_b - \phi
\]  

where \(h\nu\) is the energy of the incident photons, \(E_b\) is the binding energy of the electron in the atom that is ionized, and \(\phi\) is the work function. The work function is a combination
of the sample work function and the work function induced by the spectrometer. The binding energy can be calculated from equation 5 and can be used to extract information about the oxidation state of the elements present since the binding energy is sensitive to the local chemical environment of the atom.

XPS is a surface sensitive technique since it is dependent on $\lambda$ which is the inelastic mean free path (IMFP), the average distance an electron travels before a collision (0.5 to 3 nm for most photoelectrons).\(^4\) Due to collisions within the sample’s atomic structure, only photoelectrons from the top 3 to 10 nm (3$\lambda$ or a maximum of 3 collisions) have sufficient energy to escape the surface and be detected.\(^5\)

In this work, XPS was used to determine the oxidation states of Cu and Cu oxide/hydroxide assignments. Biesinger et al. report a more consistent, practical and effective approach to curve-fitting the various chemical states of Cu metals, oxides and hydroxides\(^6\) using a combination of the Cu 2p\(_{3/2}\) spectral shape and position and the Cu 2p\(_{3/2}\) - Cu LMM Auger parameter. Biesinger et al. analyzed a number of quality standards that were used to interpret the spectra. In addition, the Auger parameter was used since it provides additional information regarding chemical state without the need for charge correction or work function measurements.\(^7\) The Auger spectral peak shapes provide additional information verifying the Cu oxide/hydroxide assignments.\(^6\)

### 2.3 Chemical Analysis Techniques

#### 2.3.1 Gas Chromatography

Gas Chromatography (GC) is a technique used to analyze the different components of a mixture of gases. The technique separates the components of a mixture of gases into individual components through the selective partitioning of each component between the mobile and stationary phase. A gas sample is injected into the mobile phase (an inert gas, N\(_2\) in this work) that carries the sample into a column containing the stationary phase. The components in the mobile phase interact with the stationary phase at different rates depending on their affinity for the stationary phase. By optimizing and controlling the temperature and flow rate and using standards, the components in a mixture can be separated, identified and quantified.
The GC system (GC-MS, 6580 Agilent Technologies) contains a 60 m long, 0.32 \( \mu \)m diameter GS-GASPRO column connected to a micro fluid three-way splitter to allow simultaneous analysis by three detectors: Thermal Conductivity Detector (TCD), \( \mu \)-Electron Capture Detector (\( \mu \)-ECD) and Mass Selective Detector (MSD). Species are identified from GC spectra based on their specific retention time. The peak area, which is proportional to the amount of the component in the mixture, can be used to calculate the amount of each gas present at the end of the experiment.

The TCD is used to determine the amount of H\(_2\) present in a sample. TCD works by detecting the difference in thermal conductivity of the column effluent (carrier gas + sample) and the carrier gas alone. The magnitude of the TCD signal (in Volts) is proportional to the concentration of H\(_2\) in the sample.

The ECD is used to detect O\(_2\) since it is an electron-capturing substance. The ECD uses a radioactive source, \(^{63}\)Ni (beta-emitter), to form thermal electrons in the gas and the current generated by these electrons can be measured. Species containing an electronegative functional group such as halogens, phosphorous or oxygen will capture some electrons and therefore reduce the measured current. This reduction in current is proportional to the amount of O\(_2\) present in the sample.

### 2.4 Irradiation Technique

High-dose radiation experiments were carried out in a \(^{60}\)Co gamma cell (MDS Nordion, Model 220), which contains aluminum-encapsulated \(^{60}\)Co pencils (1.17, 1.33 MeV) aligned in a cylindrical array. Lead shielding surrounds the exterior of the irradiation chamber to reduce the dose rate to personnel. A loading chamber descends into the irradiation chamber by a vertical lift. A digital timer is programmed to terminate the radiation exposure by returning the loading chamber to its raised position after the time set-point has been reached.

In this work, sample vials were placed in an autoclave such that each vial was located equidistant from the cylindrical edge of the irradiation chamber ensuring a uniform absorption dose rate for all samples throughout the irradiation period. Over the time frame of the experiments documented in this thesis, the dose rate was \( \sim 3 \) kGy/h.
2.5 References:

Chapter 3

3 Long-Term Exposure of Cu to an Environment Simulating Period 2 in a Deep Geologic Repository

3.1 Introduction

The potentially most corrosive environment a UFC will encounter once emplaced in a DGR is an aerated vapour phase in equilibrium with condensed H$_2$O on the surface of the container. Such an environment is expected to occur soon after emplacement of the container and sealing of the DGR. During this period there is a possibility that radiation fields on the container will not be negligible. To determine the influence of radiation on container corrosion it is first necessary to understand the influence of water vapour on the corrosion of Cu in the absence of radiation.

It has been shown that a native oxide is always present on Cu in atmospheric environments. A rural atmospheric study showed rapid formation of Cu$_2$O on the surface of a freshly ground Cu sample exposed to ambient air with an initial thickness of 10 Å (calculated by XPS). After 2 days of exposure to 4 °C and 88 %RH in a sheltered, rural environment, the oxide grew to a thickness of ~150 nm with little further growth up to 30 days of exposure. At a lower RH of 80 %, the oxide was found to grow more slowly, requiring 30 days to reach ~100 nm thickness. XPS results after 120 days of exposure showed that Cu(I) dominates over Cu(II) at both humidities, and this corresponded with XRD and EDX data (where the quantitative composition of the corrosion product corresponded to the theoretical composition of Cu$_2$O).

There have been extensive studies on atmospheric corrosion of Cu with respect to the formation of natural patinas. These studies examined artifacts or were conducted on specimens in an open environment often involving a number of air pollutants that would not be present in a DGR. Studies show that cuprite, Cu$_2$O, is the initial corrosion product, and always the patina layer in contact with the underlying Cu metal. The cuprite layer is protective in nature and has been shown to decrease the corrosion rate with increasing exposure time. The outer layer of the patina is further oxidized to Cu$^{2+}$ and depending on the nature of the pollutants and available anions, most commonly forms brochantite (CuSO$_4$·3Cu(OH)$_2$), or atacamite (Cu$_2$Cl(OH)$_3$) in environments with high chloride.
content, such as marine environments. Fitzgerald et al. conducted an extensive study examining over 35 natural patinas aged from 7 to 332 years. They found that the rate of formation of the Cu$_2$O layer followed a parabolic growth law and decreased from 2 to 0.2 µm/y after 15 years: the Cu$_2$O thickness remained at ~ 6 µm in patinas aged 15 to 142 years. The decreasing growth rate was attributed to the dense, adherent nature of the oxide. The top layer of the patinas, brochantite, had a linear growth rate of 0.15 µm/y consistent with a non-protective layer. Outdoor patinas showed corrosion rates two orders of magnitude greater than indoor ones indicating that the protective nature of the Cu$_2$O layer was degraded by the presence of water on the surface.

This chapter describes a long-term exposure study of Cu corrosion under warm, vapour phase conditions, which can be used as a baseline against which to study the influence of γ-radiation on the vapour phase Cu corrosion process. The primary goals of this study were:

- To determine the morphology and identity of the corrosion product formed on the Cu surface;
- To investigate the rates of general corrosion and localized corrosion as a function of time;
- To provide mechanistic information on corrosion in a vapour phase environment in equilibrium with condensed water on the surface.

3.2 Experimental Details

3.2.1 Humidity Chamber Arrangement

1-cm$^3$ coupons of wrought (SKB) Cu were polished successively with 600 and 1200 grit SiC paper on all 6 sides. The coupons were washed and ultrasonically cleaned in Type I H$_2$O and methanol for 2 minutes, then washed again with Type I H$_2$O, and dried using ultrapure Ar gas. The polished coupons were placed in a desiccator for one day to dry, and then their dimensions and weight were recorded prior to placement in the humidity chamber (Associated Environmental Systems), which was set to 75 °C and 70 % relative humidity. A schedule was set to remove coupons after 1d, 2d, 7d, 14d, then monthly up to 1 year of exposure. After removal, the coupons were dried with Ar gas,
and placed in a desiccator for one day. Subsequently, they were weighed and stored in a
glove box to avoid further oxidation. Surface analyses (Raman, SEM and EDX) were
then performed on the top surface to characterize the structure and morphology of
corrosion products formed during exposure in the humidity chamber. After surface
analyses, the samples were replaced in the glove box.

3.2.2 SEM/EDX

Micrographs of the Cu coupons from the humidity chamber were recorded on a
Hitachi S4500 SEM equipped with an EDX analyzer used to elucidate the elemental
composition of the surfaces. SEM images were taken using an accelerating voltage of 5.0
kV and at magnifications from 100 to 20,000. SEM images and EDX spectra were taken
of representative areas and any unique features on the coupons. Analyses were carried out
at Surface Science Western.

3.2.3 Raman Spectroscopy

Cu coupons from the humidity chamber were placed on the stage of an Olympus
microscope equipped with 10, 25, and 50x objectives. The 50x objective was used to
focus on features of the corroded surfaces. The microscope is part of a Renishaw 2000
Raman spectrometer equipped with a 633 nm He-Ne laser. Spectra were taken over the
wavenumber range 120-2000 cm\(^{-1}\) (some to 4000 cm\(^{-1}\)), at 0.5 mW of power. Spectra
were calibrated using the 520.5 cm\(^{-1}\) line of a Si wafer. Analyses were carried out at
Surface Science Western.

3.2.4 SEM/EDX on FIB-cut Cross-Sections

A ZEISS 1540 XB field emission gun-scanning electron microscope (FEG-
SEM), equipped with a focused ion beam (FIB) system, was used to image and cross
section select coupons. The FIB used gallium ions to mill a region of interest with
nanometer scale precision. An Oxford Instruments’ INCAx-sight EDX was used for
elemental analysis. Analyses were carried out at the Nanofabrication Facility at Western
University.
3.2.5 XPS

XPS analyses were performed with a Kratos Axis Ultra spectrometer using a monochromatic Al Kα source (15 mA, 14 kV). The instrument work function was calibrated using the Au 4f7/2 line (BE of 93.95 eV) and the spectrometer dispersion was adjusted using the Cu 2p3/2 peak (BE of 932.63 eV). Survey scans were recorded over an area of 300 µm x 700 µm at a pass energy of 160 eV between 0 and 1100 eV. High resolution spectra were obtained for C 1s, O 1s and Cu 2p peaks at a pass energy of 20 eV using a step size of 0.1 eV. Spectral analyses were performed using CasaXPS software. Spectra were corrected for surface charging to the main line of the C 1s spectrum set to 284.8 eV. The Auger parameter was used to confirm the assignment of Cu oxidation states and the type of oxide/hydroxide present. Analyses were carried out at Surface Science Western.

3.3 Results and Discussion

3.3.1 Optical Images

The data from this long-term exposure study exhibit two distinct corrosion features; (i) general corrosion of the majority of the surface (termed the general area); and, (ii) a number of apparently more heavily corroded areas (termed patches). These areas are clearly distinguishable in optical images, Figure 3.1, the generally corroded area appearing as Cu-coloured and the patches as purple/blue locations. The optical images provide a starting point for pinpointing areas of interest and ultimately aid in understanding the progress of corrosion as a function of time. The colours observed on the optical images have proven to provide some useful information, the patches typically indicating areas of localized corrosion, and areas that remained Cu-coloured indicate areas that have undergone uniform corrosion. However, too much emphasis cannot be placed on colour, particularly with early exposure coupons because surface roughness can also cause variance in colour. Typically, the colour change and increased roughness are due to corrosion product formation, but the coloured patches observed on early exposure samples cannot always be found in the SEM images or correlated to areas with more
corrosion product. This may be due to a very thin film forming at those locations, or simply random, rougher areas from non-uniform polishing of the sample.

As seen in the optical images, Figure 3.1, the number and size of the patches appears to be random with respect to exposure time until 180 d after which the coupons consistently have an increasing number of blue patches. After 240 days the surface is covered with small patches, but after 360 days there is an increased number of enlarged patches which may be a series of coalesced smaller ones, as shown in the optical images.
Figure 3.1: Optical images of coupons exposed for various amounts of time in a humidity chamber. The Cu-coloured general area and localized coloured "patches" are obvious in the images.
3.3.2 SEM Analysis

SEM micrographs of the Cu-coloured areas, Figure 3.2, observed in the optical images shows that, for short exposure times (1-7 d), a few, small, dispersed globular features appear on the sample surface. After 14 d, the number and density of the globular features increases. Not until 120 d is the sample surface covered by a dense, uniform layer of these features. The micrograph of the 360 d sample shows a thin layer of oxide covering the sample surface with some areas with larger globular features. This is consistent with the patchy appearance seen in the optical images.

Closer inspection of the SEM micrographs of the patches (circled in the optical images), Figure 3.2, shows corrosion occurred to a greater extent within the patches than over the general area of the surface. The size and density of the corrosion product within the patches is consistently larger than that seen in the general area, indicating a faster corrosion rate within the patches likely due to surface wetting. The patches of enhanced corrosion appear to progress along the polishing lines. After prolonged exposure, 150 d and longer, a central accumulation of bulkier corrosion product is always present within a patch. This appears as a central dark spot within the patches that can be seen in the optical images. These areas have been further analyzed on some samples using SEM on FIB cut cross sections and are discussed below in section 3.3.6.

A comparison of SEM micrographs of the general areas and patches, Figure 3.2, confirms that corrosion product accumulates much more quickly within the patches and grows larger features. The adsorption of H$_2$O on Cu and Cu oxides has been shown to occur more readily on Cu oxides at higher humidities. At 80 %RH, twice as much H$_2$O adsorbed on Cu$_2$O as on Cu. This was attributed to the higher roughness factor and, consequently, the higher surface area of Cu$_2$O. This offers a possible explanation of the enhanced corrosion within the patches. Once corrosion starts at these locations, and corrosion products form, their wetting can lead to the accumulation of more corrosion product.
Figure 3.2: Optical images and SEM micrographs of samples removed from the humidity chamber after a series of exposure periods. The circles in the optical images indicate the locations shown in the SEM micrographs of the patches.
The morphology of the corrosion product is relatively uniform and consists of poorly defined nodules that cover the surface. However, some samples exhibit closely packed, well-developed crystalline corrosion product within some of the patches, features that are not present in the general area. The well-developed crystalline octahedral structure is more commonly observed for corrosion products formed on Cu corroded in aqueous solution. The octahedral morphology can be seen on the 30 d, 150 d and 210 d samples, Figure 3.3, and the crystals generally become larger with increasing exposure time. However, the 360 d sample does not follow this sequence, the crystalline deposit being comprised of less well-defined octahedra and a larger number of smaller particles.

Figure 3.3: SEM micrographs showing well-developed crystalline deposits formed on samples after various exposure times. The circles in the optical images indicate the areas within which the SEM micrographs were recorded.

It has been reported that above a critical RH typically in the range of 50-70 %RH, H₂O condenses on surfaces.⁴ Patch formation is likely due to surface wetting, and the well-developed crystalline features indicate the presence of sufficient H₂O for a dissolution/reprecipitation process.
3.3.3 XPS Analysis

XPS was used to analyze several locations on selected samples. Large amounts of C content are detected on the surface (Table 3.1), which can be attributed to the ubiquitously observed hydrocarbon contamination (85-90%) of the surfaces. This is unavoidable, studies having shown that even atomically clean surfaces pick up significant hydrocarbon content (65 at. % on some samples) within minutes of exposure to normal laboratory air. Interestingly, in attempts to remove the surface contaminants using Ar etching, it was discovered that fragments of hydrocarbon contaminants could be incorporated into a deformation layer caused by polishing, particularly on softer metals. Such a feature could explain why substantial amounts of C are observed in EDX analyses, which probe well below the sub-nanometer surface layer probed by XPS.

Table 3.1: Elemental composition of several locations on select samples (from XPS) reported in atomic percent.

<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>Cl</th>
<th>Cu</th>
<th>N</th>
<th>Na</th>
<th>O</th>
<th>Si</th>
<th>Ca</th>
</tr>
</thead>
<tbody>
<tr>
<td>7 d – general area</td>
<td>79.2</td>
<td>0.5</td>
<td>3.7</td>
<td>0.7</td>
<td>0.1</td>
<td>14.9</td>
<td>0.4</td>
<td>0.4</td>
</tr>
<tr>
<td>7 d – patch</td>
<td>77.5</td>
<td>0.6</td>
<td>3.8</td>
<td>0.9</td>
<td>-</td>
<td>15.9</td>
<td>0.9</td>
<td>0.5</td>
</tr>
<tr>
<td>90 d – general area</td>
<td>67.5</td>
<td>1.2</td>
<td>9.3</td>
<td>0.9</td>
<td>0.6</td>
<td>20.4</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>90 d – patch</td>
<td>64.5</td>
<td>1.1</td>
<td>9.7</td>
<td>1.1</td>
<td>0.6</td>
<td>22.3</td>
<td>0.6</td>
<td>-</td>
</tr>
<tr>
<td>180 d – general area</td>
<td>53.8</td>
<td>1.4</td>
<td>14.3</td>
<td>1.2</td>
<td>0.7</td>
<td>28.2</td>
<td>0.3</td>
<td>0.1</td>
</tr>
<tr>
<td>180 d – patch</td>
<td>55.1</td>
<td>1.2</td>
<td>13.8</td>
<td>1.2</td>
<td>1.6</td>
<td>26.8</td>
<td>0.3</td>
<td>-</td>
</tr>
<tr>
<td>300 d – general area</td>
<td>49.6</td>
<td>1.2</td>
<td>16.3</td>
<td>1.4</td>
<td>1.8</td>
<td>29.3</td>
<td>0.3</td>
<td>0.1</td>
</tr>
<tr>
<td>300 d – patch</td>
<td>53.6</td>
<td>0.6</td>
<td>11.5</td>
<td>0.8</td>
<td>0.8</td>
<td>27.3</td>
<td>0.3</td>
<td>0.2</td>
</tr>
</tbody>
</table>

Table 3.2 shows that the upper most layer (~ 7 nm) after short exposure (7 d) is a mixture of Cu I and Cu II with most of the Cu II corresponding to Cu(OH) 2. This is based on the peak shape of the Cu 2p spectra compared to standards for Cu metal, Cu 2 O, Cu(OH) 2 and CuO. XPS analysis was also performed after 90, 180 and 300 d and shows that CuO becomes the dominant phase on the surface. Some Cu(OH) 2 is also present, but the samples are dried out and stored in a glove box and CuO is more thermodynamically stable. It is interesting to note that there is little to no difference in the composition of
corrosion products on the general area and the patches. However, XPS analyzes only the top few nanometers of the surface where CuO deposition is generally expected. Accurately distinguishing between Cu(0) and Cu(I) states in the presence of significant amounts of Cu(II) is difficult due to the overlap of the Auger spectral lines for these three components; the Cu(II) peak dominates the spectrum.\(^6\)

### Table 3.2: Cu oxidation states and phase assignments determined by XPS on several locations on select samples.

<table>
<thead>
<tr>
<th>Time</th>
<th>Area</th>
<th>Cu(0) + Cu(I)</th>
<th>Cu(II)</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>7 d</td>
<td>general</td>
<td>49</td>
<td>51</td>
<td>Cu(_2)O and Cu(OH)(_2)</td>
</tr>
<tr>
<td></td>
<td>patch</td>
<td>52</td>
<td>48</td>
<td>Cu(_2)O and Cu(OH)(_2)</td>
</tr>
<tr>
<td>90 d</td>
<td>general</td>
<td>13</td>
<td>87</td>
<td>Mostly CuO</td>
</tr>
<tr>
<td></td>
<td>patch</td>
<td>14</td>
<td>86</td>
<td>Mostly CuO</td>
</tr>
<tr>
<td>180 d</td>
<td>general</td>
<td>6</td>
<td>94</td>
<td>Mostly CuO</td>
</tr>
<tr>
<td></td>
<td>patch</td>
<td>7</td>
<td>93</td>
<td>Mostly CuO</td>
</tr>
<tr>
<td>300 d</td>
<td>general</td>
<td>8</td>
<td>92</td>
<td>Mostly CuO</td>
</tr>
<tr>
<td></td>
<td>patch</td>
<td>8</td>
<td>92</td>
<td>Mostly CuO</td>
</tr>
</tbody>
</table>

### 3.3.4 Raman Spectroscopy

Raman spectroscopy was used to identify the composition of the corrosion product on multiple locations of the surfaces of every sample. Raman spectra, recorded up to 120 d, are presented in Figure 3.4. The spectra are distorted by fluorescence at high wavenumbers but distinct peaks are present at wavenumbers below 750 cm\(^{-1}\). The spectrum recorded after 1 day is typical of Cu exposed to air, and the peaks present at 147 cm\(^{-1}\), 220 cm\(^{-1}\), and the two peaks at 525 cm\(^{-1}\) and 625 cm\(^{-1}\), are readily assigned to the presence of Cu\(_2\)O based on extensive literature.\(^7\)-\(^10\) Cu\(_2\)O appears to be the dominant phase formed up to 30 d of exposure, with the peak at 297 cm\(^{-1}\), assigned to CuO, being rarely observed.\(^8\),\(^11\),\(^12\) After 60 d of exposure, the peak at 297 cm\(^{-1}\) is observed commonly, especially in the patches. Raman spectra recorded after prolonged exposure times are presented in Figure 3.5 and show the persistence of the peak at 297 cm\(^{-1}\) now found consistently in both the general area and patches indicating that both Cu\(_2\)O and CuO
cover the surface of the coupons. After 180 d, the patches generally exhibit a stronger relative intensity for the CuO peak compared to the Cu$_2$O peaks, as opposed to the case for the general area. This is exemplified in Figure 3.5, where two spectra recorded on the sample exposed for 360 d are presented: the relative intensity of the CuO peak within the patch is greater than that in the general area indicating the presence of larger amounts of CuO within the patches. This is consistent with the expectation that patches occur due to wetting of the surface with the presence of H$_2$O enhancing oxidation to Cu$^{2+}$. Note that Raman analyses do not detect any hydroxide. Cu(OH)$_2$ a weak peak at ~ 300 cm$^{-1}$, which would be distorted by the presence of CuO, and a strong peak at ~ 470-490 cm$^{-1}$.$^{13}$ The absence of this strong peak confirms the absence of a significant amounts of Cu(OH)$_2$, its detection by XPS indicating the presence of a thin surface layer on a dominantly CuO phase.

![Figure 3.4](image-url)

*Figure 3.4: Raman spectra recorded on Cu coupons after various exposure times.*
Figure 3.5: Raman spectra recorded on Cu coupons after prolonged exposure. The spectra recorded on of the 360 d sample show the increased intensity of the CuO peak (297 cm\(^{-1}\)) within a patch compared to on the general area.

3.3.5 Weight Change Data

The weight change before and after exposure was monitored on samples in an attempt to determine a corrosion rate. However, no meaningful trend can be established from the weight change data. The precision and resolution of the analytical balance are reported as 0.1 mg.\(^{14}\) The weight change of the coupons is in the range of 0 to 0.6 mg, and the average weight change of the 21 samples is ±0.21 mg.

3.3.6 SEM on FIB-cut Cross Sections

To investigate in more detail the differences in corrosion on the general areas and within the patches, FIB cross-sections were cut at locations in both areas. The optical images showing the locations analyzed are presented in Figure 3.6, where the squares indicate the locations within the general area and the circles indicate the locations within the patches where FIB cross sections were cut. Since the number of cross-sections cut is necessarily limited there is no guarantee that this analysis locates the most deeply corroded location on the sample.
Figure 3.6: Optical images of the samples cross-sectioned using a FIB. The white squares mark the “general area” on each sample from which a cross section was cut. The white circles indicate the “patches” on each sample from which a cross section was cut.

Cross-sections cut within the general area of coupons exposed for 90 d and 150 d are presented in Figure 3.7 and show how thin the corrosion product layer is in these areas.
Figure 3.7: FIB cut cross-section of the general area on the 90 and 150 d samples indicated by the white circle in the optical images.
Figure 3.8 shows how the thicknesses of the corrosion product on a general area varied as a function of time. The data shows that the oxide rapidly reaches a thickness of 100 to 200 nm and subsequently thickens only marginally with time over the exposure period of 1 year. There is some variance in thickness across an individual cross-section, which could be partially due to the grinding grooves in the Cu leading to a non-uniform deposit of oxide. The minor growth in thickness after the initial 30 days of exposure indicates that deposition of the outer CuO layer, detected by both XPS and Raman, inhibits further corrosion likely due to its insulating properties.

![Graph showing thickness of the general corroded area as a function of time](image)

**Figure 3.8: Change in thickness of the general corroded area as a function of time.** The points represent the average thickness (n=10); error bars represent the standard deviation. The areas that were analyzed are indicated by white squares in the optical images in Figure 3.6.

Measurements of film thickness on cross-sections of the patches confirm that these areas are more heavily corroded, Figure 3.9. The corrosion product in the patches is significantly thicker than in the general area, even after only 30 d of exposure. Also, while the thickness of the corrosion product in the general area did not increase significantly with time, the thickness of the corrosion product in the patches continued to increase with increasing exposure time up to 360 d (the end of this experiment). Two patches were cross-sectioned on the 360 d sample (as indicated in Figure 3.6). The thickness of the corrosion product on the larger patch averages ~ 10.5 μm and is greater than the average thickness of the corrosion product on the smaller patch, 4.2 μm. The
difference in thickness could indicate that corrosion in these initiated at different times, but the increase in deposit thickness with time indicates that these areas continue to corrode, possibly at different rates. The aspect ratios (the ratio of corrosion product thickness to the area corroded) are extremely small indicating that corrosion spreads laterally across the surface rather than penetrates deeply into it.

![Graph showing variance in thickness of "patches" as a function of time.](image)

**Figure 3.9**: Variance in thickness of the "patches" as a function of time. The points represent the average thickness at each cross-section (n=10-14); the error bars represent the standard deviation. White circles in Figure 3.6 represent the patches that were examined. Multiple sets of measurements (indicated by different coloured points) are included.

While the thickness of the corrosion product deposit becomes quite large, it is not equivalent to a penetration depth. The Pilling-Bedworth ratio for metal oxides is the ratio of the volume of oxide produced to the volume of metal consumed: for Cu₂O the ratio is 1.67. The Pilling-Bedworth ratio is generally used to determine the protectiveness of the film in dry air, with a ratio > 1.0 indicating that the film forms uniformly, covers the surface, and forms an effective barrier between the metal and its surroundings. However,
the thickness of the oxide deposit is many times greater than the depth of penetration into the metal surface, the depth of metal penetration cannot be calculated from the deposit thickness and the Pilling-Bedworth ratio, which is the primary goal of this project.

The cross-section cut from the small patch on the 360 d sample is presented in Figure 3.10 in which the variance in thickness across the deposit is evident. The corrosion product exhibits a number of gaps within the deposit, and a number of gaps along the deposit/substrate interface. The gaps in the deposit confirm its porosity, while those at the interface may be an indication that corrosion to produce soluble species continues at the Cu surface. The transport of these species, most likely Cu$^{2+}$, would account for the increasing thickness of the deposit with time. EDX data shows that the Cu to O ratio in the deposit varies from ~2.4 to 3.6 from top to bottom. This indicates that the corrosion product is dominantly Cu$_2$O, despite the detection of substantial amounts of CuO by Raman. One likely reason for a ratio > 2 is that some of the substrate was detected by EDX analysis which is done on an angle and at a high accelerating voltage. Another is the significant C content, even present in what is clearly the substrate seen at the bottom of the cross-section (the microstructure of the Cu is evident), which is between 21 and 48 at. %. This could affect the Cu to O ratio, although the C is likely not associated with the O since >90% of the C content, detected on the samples analyzed by XPS, is assigned as hydrocarbon contaminant. No carbonate species are detected by Raman spectroscopy.
Figure 3.10: FIB-cut cross-section of the small patch indicated by the white circle in the optical image. The cross-section shows the variance in corrosion product thickness in this cross-section.

The cross-section of the larger patch cut from the 360 d exposed sample is presented in Figure 3.11. The gap at the substrate/deposit interface is continuous supporting the proposition that on-going corrosion may lead to this separation. Three distinct layers can be seen in this cross-section. The first layer has a fairly uniform thickness of ~ 5.75 µm and is porous as observed for the layer seen in the small patch, Figure 3.10. A 3.1 to 3.9 Cu to O ratio is detected by EDX indicating that this layer is again likely Cu₂O. Note that the C content ranged from 13 to 29 at %. The second layer, with a fairly uniform thickness of ~ 850 nm, has a Cu to O ratio of ~ 1.7. The significantly lower Cu/O ratio suggests the presence of a more oxidized Cu state, despite the ratio being close to that expected for Cu₂O. Presently, the composition of this layer remains unresolved although a possibility is that it is a thin layer of CuO formed by the direct oxidation of Cu₂O to CuO by dissolved O₂. The third layer, which is approximately 5.12 µm thick on the right side of the cross-section, has a more cracked appearance. The
Cu to O ratio of this layer is ~ 1, indicating it is most likely composed of CuO. This layer has a similar C content, but also contains some Cl up to ~ 15 at %. The presence of Cl has been observed on many analyzed samples, and is likely due to a build-up of Cl⁻ as an impurity in the water over time. The high Cl content in this layer is most likely due to a salting out process once the sample was removed from the humidity chamber, condensed water on the surface evaporating and immediately depositing soluble ions as a precipitate on the surface. This cross-section has the clearest distinction between what are likely Cu₂O and CuO layers. The 90 and 150 d exposed samples show a variance in the Cu to O ratio in the cross-sections but the top layer is significantly thinner, at ~0.8 and 3 µm, respectively. This finding is complementary to the Raman data that show that the patches exhibit a stronger CuO signal. These results show the growth of Cu₂O directly on the Cu surface with the deposition of a layer of CuO. The thickness of the inner layer is considerably greater than that observed on the general areas indicating that both the Cu₂O and CuO layers continue to thicken with time.

Figure 3.11: FIB cut cross-section of the large patch on the 360 d exposed sample indicated by the white circle in the optical image. The cross-section shows three distinct layers, an initial, compact layer of Cu₂O, a second intermediate layer with a Cu to O ratio of 1.7, and a third, more cracked layer of CuO deposited on top.
The differences in morphology between the two (large) corrosion product layers suggests they are produced by different processes. The Cu$_2$O layer is much more uniform. The CuO layer on top, from its cracked and porous appearance, indicates that this porous deposit is due to a precipitation process. Cu$^{2+}$ ions are slightly more soluble than Cu$^{+}$ ions across the pH scale and the most likely to dissolve into the small volume of water on the surface.$^{16,17}$ In the thin film, the solubility limit is likely reached very quickly, and so CuO deposits back onto the surface forming a second layer on top of the Cu$_2$O layer. The continued growth of the Cu$_2$O layer as a function of time, as indicated by Figure 3.9, indicates that, within the patches, CuO does not deposit to block the surface from further corrosion, as seen in the general area. The uneven deposit of the CuO layer, shown in Figure 3.11, verifies this. Corrosion at the Cu surface and transport of soluble Cu through water filled pores (seen to be present in the deposit) could maintain the on-going deposition at the outer surface leading to the build-up of the thickening CuO layer.

3.4 Summary

This chapter focused on the effect of an aerated vapour phase environment in equilibrium with condensed water on the corrosion of a Cu surface, with a focus on examining corrosion product formation as a function of time, determining the morphology and identity of the corrosion product, and investigating the rates of corrosion.

- Optical images show blue/purple locations on the surface likely due to locally condensed water indicating areas of more extensive corrosion. The patches appear randomly on the surface until $\sim 180$ d after which they increase in number consistently and begin to coalesce with increased exposure time.
- SEM micrographs show that in the general area, the corrosion product grows in globular features on the surface. Complete coverage of the surface occurs after $\sim 120$ d of exposure.
- SEM micrographs of the patches consistently show more extensive corrosion compared to the general area. The corrosion product is denser
and larger in size. Some patches exhibit corrosion product that grows with a crystalline morphology, indicating precipitation from the condensed water layer.

- XPS data indicates that for both the general area and patches, after 7 d of exposure a thin film of Cu(OH)$_2$ had grown on top of a Cu$_2$O film. After prolonged exposure the top ~ 7 nm across the entire surface are predominantly CuO.

- Raman data verifies that the surface is initially oxidized to form a Cu$_2$O film and not until 60 d is a film of CuO detected in the general area. CuO was detected as early as 30 d within the patches and the relative intensity of the CuO peak is consistently greater in the patches compared to the general area, indicating more extensive corrosion within the patches.

- Cross-sections of the general area show that the thickness of the deposit does not vary or increase significantly over time. This indicates that the CuO film is likely protective and stops further corrosion in the general area.

- Cross-sections of the patches show increasing thickness as a function of time. Comparing the size of the patches and the thickness of the deposits near the center and along the edges of a patch indicate that corrosion propagates across the surface rather than penetrates into it.

3.5 References:


Chapter 4

4 Effect of Low-dose Radiation on Cu in an Environment Simulating Period 2 in a Deep Geologic Repository

4.1 Introduction

As described in Chapter 1, thinning the outer Cu layer of a UFC will introduce water and atmospheric radiolysis species into the environment due to the low dose γ-radiation coming from within the UFC. There have been some studies on the effect of γ-radiation on atmospheric corrosion of Cu in regards to the Yucca mountain project, but these are not directly relatable to the Canadian DGR scenario. The studies used significantly higher dose rates on the order of kGy/h, compared to the anticipated 5 to 0.44 Gy/h for the Canadian UFC, and the studies were carried out at higher temperatures (due to the difference in fuel type) and to either significantly lower relative humidities (RH) of 0-15 % or at saturation (100 %RH). Corrosion was observed in irradiated moist air with the extent of corrosion damage increasing with increasing moisture content of the gas phase. In experiments at high dose rates (0.7 to 2 kGy/h), temperatures in the range 90 to 150 °C, and RH ranging from 0 % to 100 %, the appearance of the corroded surface changed with RH from a light tarnish in dry air, to brown/yellow at 15 %RH and then to a black/brown scale at 100 %RH. Using X-ray diffraction, it was shown that, after exposure at 150 °C small amounts of Cu₂O and Cu₂NO₃(OH)₃ were present at 0 %RH, Cu₂O and some Cu₂NO₃(OH)₃ at 15 %RH, and Cu₂O, with some CuO, but no Cu₂NO₃(OH)₃ at 100 %RH. Minor pitting was also observed at 100 %RH. The paper compares previous work at higher dose rates and concludes that the formation of Cu₂NO₃(OH)₃ is independent of dose rate and temperature, but is greatly effected by humidity and only forms at low RH.

It was concluded that the formation of Cu₂NO₃(OH)₃ could be attributed to the presence of nitrogen oxides and nitric acid generated by radiolysis and its formation as a non-protective deposit was associated with pitting. The greater corrosion rates observed in moist environments compared to dry air were attributed to the formation of radiolytic oxidants in the gas phase which then concentrate in the thin film of water on the corroding surface. Comparison of the effects of radiation on Cu corrosion at a dose rate
of 10 kGy/h in aqueous and moist air environments showed more severe corrosion occurred in the vapour phase.³

Vernon et al. studied the influence of relative humidity and concentration of pollutants on Cu corrosion. They found that at 0 %RH, there was no influence of the concentration of pollutants and the weight change was indistinguishable from experiments run under pure air. Experiments with small amounts of pollutants show that relative humidity plays a large role in Cu corrosion; weight gain gradually increased with increasing relative humidity up to 50 %; between 63 and 75 %RH, a dramatic increase in rate of attack was found, indicating a critical RH located between these values.⁴ It has been reported elsewhere that there is a critical RH, typically in the range of 50 to 70 %, where the condensation of water is expected.⁵ Another study investigated the effect of relative humidity on the rate of Cu corrosion in a test environment that included ppm amounts of SO₂, NO₃, O₃, NH₃, Cl₂, HCl and H₂S.⁶ In the experiment, as humidity increased from 30 to 60 %RH, the corrosion rate increased gradually, before a change in humidity from 60 to 80 %RH resulted in a doubling of the corrosion rate.⁶

There have been some studies investigating the effects of HNO₃ on the atmospheric corrosion of metals, including Cu. HNO₃ can form at a very slow rate by the oxidation of NO₂ in the absence of radiation.⁷ HNO₃ is described as a “sticky pollutant” its high sticking coefficient allowing ready dissolution in water.⁷ Samie et al. exposed Cu to HNO₃ concentrations between 1.58x10⁻¹¹ M and 6.35x10⁻¹¹ M at 65 %RH and 25 °C and found that HNO₃ deposition on Cu increased linearly with increasing [HNO₃]. Weight gain measurements verified that HNO₃ is highly corrosive to Cu. The corrosion products on the surface were analyzed by FTIR and XRD and both Cu₂O and Cu₂(NO₃)(OH)₃ were present; Cu₂O formed a film, and Cu₂(NO₃)(OH)₃ was observed as blue crystalline salts on the surface.

Samie et al. also investigated the effect of varying relative humidity on the atmospheric corrosion of Cu by HNO₃. Once a metal is exposed to humidity, a thin layer of water forms on the surface; this water film provides a medium for dissolving pollutants which can act as an electrolyte for corrosion reactions on the metal surface and therefore result in an electrochemical reaction that occurs much faster than dry atmospheric corrosion. Starting with 0 %RH, the mass increase was found to be minimal, but an
In the present chapter, a 0.29 Gy/h dose rate was employed; this dose rate is close to the anticipated dose rate near the end of period 2 in a DGR, before saturation occurs at the surface of the waste containers. The primary goals of the research described in this chapter were to investigate Cu corrosion in a vapour phase, low dose \( \gamma \)-radiation environment mimicking period 2 in a DGR. This was be done by:

- Determining the effect of \( \gamma \)-radiation on the corrosion rate by measuring the change in resistance over time across a Cu wire;
- Using surface analysis techniques (optical microscopy, SEM/EDX, XPS, Raman spectroscopy) to analyze the morphology and identify the corrosion product formed on exposed coupons;
- Comparing the surfaces of irradiated samples to non-irradiated samples and determining the effect of \( \gamma \)-radiation on corrosion rates;
- Using FIB cut cross-sections to determine the extent of damage to the Cu surface and to determine the effect of \( \gamma \)-radiation on corrosion penetration depths.

4.2 Experimental Details

4.2.1 Experimental Set-Up

Experiments were carried out at the Chalk River Nuclear Laboratories (CNL) to utilize CNL’s unique irradiation facilities and expertise to investigate the radiolytic corrosion of Cu in a relatively low-dose \( \gamma \)-radiation field.

The corrosion tests were conducted on oxygen-free, high conductivity (OFHC) Cu wire (Goodfellow Corporation). The wire had a nominal diameter of 2.0 mm (10% tolerance) and a purity >99.95%. The typical concentration of impurities are as follows: Ag (100 ppm), Al (1 ppm), Bi (1 ppm), Ca (3 ppm), Cd (1 ppm), Fe (2 ppm), Mg (1 ppm).
ppm), Pb (3 ppm), Si (2 ppm), Sn (2 ppm). To avoid complications from the presence of significant concentrations of CO$_2$, tests were conducted in Grade 0.1 synthetic air (The Linde Group). This gas mixture contained 20-22 vol% O$_2$ balance N$_2$ with the following impurity limits: <1 ppm CO, <1 ppm CO$_2$, <2 ppm H$_2$O, <0.1 ppm THC.

All vessels were 2 L Pyrex, wide-mouth, round storage bottles with a polypropylene plug seal threaded cap (Sigma-Aldrich). The caps were custom fitted with 1/8” Swagelok unions with gaskets on the outer surface to accommodate the necessary penetrations. The test assembly comprised 2 pre-vessel – test vessel pairs (4 vessels in total). One test vessel was subjected to irradiation and one test vessel was shielded such that it could act as a non-irradiated control experiment. The pre-vessels were also shielded from the radiation field to prevent radiolysis of the bulk water used for humidification.

A schematic of the test assembly is provided in Figure 4.1. Since the entire test assembly was contained within a laboratory oven (Thermofisher Scientific Isotemp 851 programmable laboratory oven) maintained at 75 °C, the humidification of air to 85 %RH was achieved by bubbling air, at a low flow rate, through a jacketed pre-vessel containing deionized water. This pre-vessel was cooled below the oven temperature using a recirculating chiller (Thermofisher Scientific Accel 500LT recirculating heating/cooling chiller). The saturated air from the pre-vessel headspace flowed into the hotter test vessel, resulting in a decrease of the RH from 100 to 85 %. The RH of both the irradiated and non-irradiated test vessels was monitored in-situ using HygroClip 2 humidity probes (Rotronic AG, Switzerland). The temperature of the pre-vessels was adjusted based on the output of the humidity probes to achieve the desired RH. The flow of synthetic air through the test assembly was maintained at 50 mL/min, which was the lowest flow rate achievable by the Omega FVL-2604A mass flow controllers.
The test assembly described above was placed within a Gamma Hall Irradiation Facility where it was irradiated by the Gamma Beam 150C $^{60}$Co irradiator, manufactured by Nordion International Inc. As of September 2 2014, this $^{60}$Co source had an activity of $3.071\times10^{11}$ Bq. The placement of the vessels within the oven was such that the irradiated vessel was immediately in the beam path. All other vessels were out of the direct path of the beam and were also placed behind Pb blocks. The experiment ran from 9:00 am on November 7, 2014 until its completion at 7:25 am on March 20, 2015. Following completion of the experiment, a Keithley Model 35040 electrometer was used to monitor ion chambers (15 cm$^3$) that were placed within the oven to determine the dose rates at the locations of both test vessels. On March 23, 2015, the dose rates in the precise locations of the irradiated and non-irradiated vessels were 0.29 Gy/hr and 0.00 Gy/hr, respectively, following a collection time of 1699 minutes.
To achieve the desired test conditions of 75 °C and 85 %RH, the synthetic air was first saturated with de-ionized water at a temperature corresponding to the dew point temperature ($T_d$) of water vapour at the desired test temperature (75 °C). The following formula gives the water vapour saturation pressure to sufficient accuracy between 0 and 373 °C:

$$
\ln \left( \frac{P_{ws}}{P_c} \right) = \frac{T_c}{T} (-7.85951783v + 1.844082595v^{1.5} - 11.7866497v^3 + 22.6807411v^{3.5} - 15.9618719v^4 + 1.80122502v^{7.5})
$$

(1)

where $v$ is the transformed temperature given by

$$
v = 1 - \frac{T}{T_c}
$$

(2)

and $T$ is the test temperature (K), $T_c$ is the critical temperature (647.096 K), $P_{ws}$ is the saturation vapour pressure (hPa), and $P_c$ is the critical pressure (220,640 hPa).\textsuperscript{9,10} Then a $T_d$ of 69 °C was calculated using the following equation:

$$
T_d = \frac{T_n}{m \left( \log \left( \frac{P_{ws} \cdot RH \times 100}{A} \right) \right)^{-1}}
$$

(3)

where $T_n$ is the triple point temperature and $m$ and $A$ are constants for a given temperature range and are 222.50133 K, 7.337936, and 6.004918 respectively for temperatures between 50 and 100 °C.\textsuperscript{10}

The temperature of the pre-vessel water, the test vessel air, the internal oven air and the external laboratory air were monitored using Type K thermocouples and a Keithley 2700 digital multimeter equipped with a Keithley 7706 switching card. All data was acquired using custom software developed using Visual Basic 6.0.

In addition to the Cu wires, each test vessel contained 4 Cu coupons placed on a Teflon holder with a 1 cm$^2$ face facing upwards. Coupons (duplicates for each exposure time and irradiated/non-irradiated condition) were removed after 50.8 d and 103.7 d of exposure (corresponding to total radiation doses of 424.6 Gy and 866.2 Gy, respectively in the irradiated cases). The top surfaces of the coupons were analyzed using optical microscopy, SEM/EDX, Raman, FIB cross-sections and XPS.
4.2.2 Electrical Resistance Corrosion Probes

4.2.2.1 Theory

The electrical resistance method for measuring the extent of corrosion of a metal exploits the fact that, typically, metals or alloys have much lower specific electrical resistances than their corrosion products. Since the electrical resistance of a conductor depends on its cross-sectional area, the resistance of a metal shape will increase as its cross-sectional area is reduced by corrosion. The most common geometries employed for electrical resistance corrosion measurements are wire, strip and tube. The electrical resistance of a metal wire is related to its diameter by the following expression:

\[ R = \rho \frac{L}{A} = \rho \frac{L}{\pi r^2} \]  \hspace{1cm} (4)

where \( R \) is resistance (\( \Omega \)), \( A \) is cross-sectional area (\( \text{cm}^2 \)), \( \rho \) is resistivity (\( \Omega \cdot \text{cm} \)), \( L \) is length (\( \text{cm} \)) and \( r \) is the radius (\( \text{cm} \)).

The electrical resistance method provides a rapid, non-destructive, in-situ measurement of corrosion that does not require a conductive electrolyte for measurement. However, inherent in this technique is the assumption that the material is undergoing uniform general corrosion. Localized corrosion processes such as pitting are difficult to detect by the electrical resistance method and problematic to quantify.

4.2.2.2 Construction

Each electrical resistance corrosion probe (ERCP) consisted of an OFHC Cu wire 2 mm in diameter and ~50 cm in length. Electrical leads were soldered to the ends of the Cu wire, external to the test vessels, at a distance of a ~ 40 cm apart. The Cu wire entered and exited the test vessel via PTFE Swagelok unions.

The dimensions of the wires were selected to maintain the resistance within an optimal range (0.3-3.0 m\( \Omega \)) throughout the test in order to maximize the resolution of the measuring device. The effect of temperature on resistivity of a metal is described by the following equation:

\[ \rho = \rho_o [1 + \alpha(T - T_o)] \]  \hspace{1cm} (5)

where \( \rho \) is resistivity (\( \Omega \cdot \text{m} \)), \( T \) is temperature (\( \text{K} \)) and \( \alpha \) is the resistance temperature coefficient (\( \text{K}^{-1} \)) of the metal. Using the values of \( \rho_o \) and \( \alpha \) for pure Cu of 1.673x10\(^{-8}\) \( \Omega \cdot \text{m} \)}
(20°C) and $6.8 \times 10^{11} \text{K}^{-1}$, respectively, the approximate resistivity of the Cu wire at 75°C was predicted to be $2.05 \times 10^{-8} \Omega \text{m}$. Therefore, using Equation 4 for a 2 mm wire, the distance between the electrical leads must be less than 45 cm to have a resistance <3 mΩ. If we allow for 50 µm of corrosion over the duration of the test, the distance between the leads must be < 41 cm to maintain an optimal resistance.

4.2.2.3 Resistance Measurements

A Cropico Ltd. Model DO5000 microhmmeter was used to measure the electrical resistance of the ERCPs. The microhmmeter was multiplexed with a Keithley Model 7001 scanner that contained a Model 7053 high-current scanner card and a Model 7168 nano-volt scanner card to allow for a 4-wire resistance measurement. A source current of 5 A was used. The Cropico DO5000 features eight resistance measurement ranges (3 mΩ to 30 kΩ). As mentioned, the dimensions of the Cu wires were selected such that measurements could be made in the 3 mΩ range. This range has a resolution of 1 µΩ. A single value of electrical resistance received by the computer is the average of 50 individual measurements made by the Cropico instrument. The 50 individual measurements consist of 25 pairs of measurements made with the current flowing in opposite directions. This technique effectively eliminates the effects of thermal voltages or other voltages that may be present in the measurement circuit.

Since extremely small changes in resistance are expected from corrosion process, it becomes critical to compensate for changes in the electrical resistance of a metal caused by variations in temperature. Furthermore, it is important to ensure that changes in resistance can be solely attributed to decreases in the wire diameter and are not due to instrument drift or uncompensated changes in laboratory air temperature. To detect such changes, a 2 mΩ calibration resistor (Burst GmbH & Co kg Model 1240-0.002) was used as a dummy ERCP during the test. The resistor has a tolerance of ±1 nΩ and excellent storage stability (<0.1 nΩ change per year).
4.3 Results and Discussion

4.3.1 Cu Wire Data – Corrosion Rate Measurements

4.3.1.1 Test Environment

Temperature

The temperature of the vessels within the test oven was accurately maintained over the course of the test and was independent of the small variations in laboratory air temperature. The mean temperatures of the irradiated and non-irradiated test vessels over the entire test were 75.26±1.0 °C and 75.45±1.2 °C, respectively. Several power outages occurred prior to Day 46, when an uninterruptible power supply (UPS) was installed. During the noted power outages, the temperature of the oven was not logged but likely decreased to ambient.

Relative Humidity

While an attempt was made to use humidity probes to monitor the humidity throughout the experiment, the performance of the probes was very poor, and not much usable data was recorded. It was suggested by the probe manufacturer that the conditions were too aggressive for the probes and caused accelerated degradation of the hygroscopic dielectric material within the sensor. Despite the poor performance of the probes, when operating reliably, they indicated that the RH of both vessels was maintained between 83 and 90 % during the test.

4.3.1.2 Electrical Resistance Corrosion Probe Data

As described in the experimental section, in order to detect instrument drift, a 2 mΩ calibration resistor was used as a dummy ERCP during the test. Over the duration of the test, the measured resistance of the calibration resistor exhibited a value of 1999±1 µΩ. Thus, it appears as though the microhmmeter exhibited excellent stability during the test and there was no detectable instrument drift.

The relationship between electrical resistance of the two ERCPs and temperature was quantitatively determined in a manner used in previous tests at CNL for carbon steel probes. Relatively short periods, during which abrupt temperature changes occurred, were identified. Due to their short duration, the change in the electrical resistance of the
ERCPs due to corrosion was considered negligible and could be solely attributed to temperature variation. Two such times, from 0.03 to 0.11 days and from 23.9 to 24.1 days, were used. These were during heat-up either at the start of the test or following a shut-down. Plots of electrical resistance versus temperature for these time periods were used to determine the temperature coefficient of the ERCPs, Figure 4.2. As can be seen, over relatively small variations in temperature (~25 °C), the relationship between electrical resistance and temperature can be considered linear. The temperature coefficient for each ERCP was determined by the average of two linear least-squares fits of the data. The results of linear fitting are provided in Table 4.1.

![Graph showing the dependence of electrical resistance on temperature for ERCPs during two temperature transients.](image)

Figure 4.2: The dependence of the electrical resistance of the ERCPs on temperature during two temperature transients.

<table>
<thead>
<tr>
<th>ERCP</th>
<th>Time (Days)</th>
<th>Slope (Ω/°C)</th>
<th>Intercept (Ω)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Irradiated</td>
<td>0.03-0.11</td>
<td>4.1644x10^{-6}</td>
<td>0.00241</td>
<td>0.9968</td>
</tr>
<tr>
<td>Irradiated</td>
<td>23.9-24.1</td>
<td>3.7127x10^{-6}</td>
<td>0.00244</td>
<td>0.9954</td>
</tr>
<tr>
<td>Non-irradiated</td>
<td>0.03-0.11</td>
<td>4.3543x10^{-6}</td>
<td>0.00233</td>
<td>0.9983</td>
</tr>
<tr>
<td>Non-irradiated</td>
<td>23.9-24.1</td>
<td>4.5168x10^{-6}</td>
<td>0.00231</td>
<td>0.9964</td>
</tr>
</tbody>
</table>
The temperature coefficients of the irradiated and non-irradiated ERCPs were $3.9386 \times 10^{-6} \, \Omega/°C$ and $4.4356 \times 10^{-6} \, \Omega/°C$, respectively. Although widely varying values exist in the literature for the resistance temperature coefficient of Cu, this data is generally consistent with previously published data used by the US Department of Commerce and Labor, Bulletin of the Bureau of Standards.$^{13}$

Using the average resistance temperature coefficients listed in the previous section, the electrical resistance of the ERCPs was corrected for the effects of changes in probe temperature. The electrical resistance was corrected to 75.0 °C, using the following equations:

\[
\text{Irradiated ERCP} \quad R^* = R - \left( T - 75.0 \right) \times 3.9386 \times 10^{-6} \\
\text{Non-irradiated ERCP} \quad R^* = R - \left( T - 75.0 \right) \times 4.4356 \times 10^{-6}
\]

where \( R \) is the uncorrected electrical resistance (Ω) and \( T \) is the temperature (°C) measured in the respective test vessel. The corrected electrical resistance (\( R^* \)) is shown as a function of time in Figure 4.3.

![Figure 4.3: The temperature-corrected resistance of the irradiated and non-irradiated ERCPs as a function of time.](image)
The gaps in the data occur when either no resistance data was collected due to an unexpected power outage, or no valid temperature data was available to make the necessary correction to the resistance. As designed, the electrical resistance of the probes remained below 3 mΩ, ensuring that the microhmmeter remained in its most sensitive measurement range. The small difference in the absolute resistance of the ERCPs is likely attributed to slightly different distances between electrical contacts. Two abrupt decreases in resistance can be seen on both ERCPs at approximately Day 3 and Day 83. In both instances, this occurred when the Cropico microhmmeter was powered down and re-started and is attributed to an electronic re-zeroing within the Cropico unit.

If it is assumed that corrosion occurred uniformly across all surfaces of the ERCP wire between the electrical contacts, it is possible to convert the changes in measured resistance to changes in wire radius. The electrical resistance of a conducting wire of uniform cross-sectional area is given by Equation 4. Given that $L$, $\rho$ and $\pi$ in Equation 4 are constants, it can be shown that the resistance is inversely proportional to the square of the wire radius and the following relationship is derived:

$$\frac{R_o}{r_o^2} = \frac{R_t}{r_t^2}$$

(8)

where $R_o$ and $r_o$ are the resistance and radius at time ($t=0$). The radius of the wire at a given time is then related to the measured resistance by the following relationship:

$$r_t = \sqrt{r_o^2 \frac{R_o}{R_t}}$$

(9)

Alternatively, and consistent with the relationship derived by Royer and Unz $^{14}$, the corrosion rate (CR) can be defined as:

$$CR = \frac{r_o - \sqrt{R_o}}{\sqrt{R_t}}$$

(10)

A plot of wire radius as a function of time is shown for both irradiated and non-irradiated ERCPs in Figure 4.4. The corrosion rates for each ERCP were calculated from a linear least-squares fitting of the data in the two ranges indicated on the figure.
No significant corrosion was detected on either the irradiated or non-irradiated probes. During the initial ~60 days of irradiation, the response of both ERCPs was similar and both exhibited a corrosion rate of 1.3±1.0 µm/yr. A maximum corrosion rate of 2.4±1.0 µm/yr was observed on the irradiated ERCP during the final ~50 days of the test. It should be noted that, during this same time period, a small resistance decrease was observed on the non-irradiated ERCP, which is reflected by the negative corrosion rate shown in Figure 4.4. Presently, the reason for this is not known. The reported error in corrosion rates corresponds to the standard deviation of the data over the associated time period. Although the theoretical error of the resistance measurement is much lower, it is likely that the reported corrosion rates are very near the limit of detection by this technique for this particular experimental set-up. Within the resolution of this experiment, it does not appear that γ-radiation dose rates within the range from 0 to 0.3 Gy/hr have a significant effect on the corrosion of Cu under simulated spent fuel disposal vault conditions.
As can be seen from the surface analysis of the Cu coupons presented in the following section, it is very likely that localized corrosion did occur on the surfaces of the wires.

4.3.2 Cu Coupon Study – Surface Analyses

As discussed in the previous chapter, the data from the low dose $\gamma$-radiation study exhibit generally similar trends in that two distinct corrosion features are observed; (i) the general corrosion of the majority of the surface (termed the general area); and, (ii) a number of apparently more heavily corroded areas (termed patches). These areas are clearly distinguishable in optical images, Figure 4.5, the generally corroded area appearing Cu-coloured and the patches as purple/blue locations.

![SEM micrographs of the surfaces of coupons exposed for different times showing corrosion of the general areas (Cu-coloured) in the corresponding optical images.](image)

The influence of $\gamma$-radiation on general corrosion can be distinguished in a comparison of the SEM micrographs of the irradiated and non-irradiated surfaces, Figure 4.5. After 51 days exposure the irradiated surface appears more extensively corroded and after 104 days both surfaces are covered with a layer of nodular deposits. These nodules
are denser and larger on the irradiated than on the non-irradiated surface, indicating an accelerated corrosion process. Comparison of the surfaces after the short (51 d) and long (104 d) exposures show the corrosion process has progressed in both cases, but particularly so on the irradiated coupon.

The FIB-cut cross section presented in Figure 4.6 shows the surface film on a general area of the non-irradiated sample is ~100 to 300 nm thick after 104 d of exposure. This is consistent with published values after several days of exposure to a non-irradiated atmosphere with a similar RH but lower temperature.\textsuperscript{15}

![Figure 4.6: A FIB cut cross section of a generally corroded area on a non-irradiated sample exposed for 104 d. The circle in the optical image indicates the location of the cut.](image)

The thicknesses recorded across a cross-section of a general area on the irradiated sample are comparable (70 to 200 nm). As observed in the absence of irradiation, corrosion of the general surface leads to the formation of a protective CuO layer and consequently, the thickness of the deposit in the general area does not thicken with time. The initial formation of this layer is accelerated by $\gamma$-radiation, but irrespective of
whether irradiated or not, the layer does not thicken beyond a few hundred nanometers. By accelerating the formation of this layer radiation seems to be beneficial.

Inspection of the optical images, Figure 4.7, shows the darker patches on the irradiated coupon cover a larger area of the surface after the longer exposure period with their growth progressing predominantly along the polishing lines in the surface. An influence of $\gamma$-radiation on the size of the patches is observed, the irradiated surface possessing a greater number of patches after both exposure periods, Figure 4.7. Their areal dimensions are also greater suggesting their growth has been accelerated by the presence of irradiation.

![Figure 4.7: SEM micrographs of the surfaces of coupons for different exposure times showing the corrosion within the patches marked with circles in the optical images.](image)

The SEM micrographs, Figure 4.7, show that, compared to the general surface, the corrosion product within the patches is denser and more copious, indicating more extensive corrosion at these locations. In addition the extent of corrosion is enhanced by the influence of $\gamma$-radiation, the surface exhibiting a larger number of more area-extensive patches at both short and long exposure times, Figure 4.7. Additionally, the
corrosion product forms larger nodules in the presence of $\gamma$-radiation, than in its absence indicating a faster growth rate.

A possible explanation, developed in the previous chapter, for the formation of these more heavily corroded patches is that they are a consequence of condensed water on the surface. It has been reported that for a critical RH, typically in the range 50 to 70 %, the condensation of H$_2$O is to be expected.$^5$ At the 85 %RH employed in this study, condensation of water certainly occurred. The optical images and differences in corrosion product morphology between the general areas and the patches suggest the surface did not wet uniformly, the patches indicating the more extensive corrosion process as a consequence of the formation of water droplets at that location. Under radiation, water droplet formation is likely enhanced due to the presence of nitric acid, which has deliquescent properties resulting in enhanced wetting of the surface in particular locations. This effect will be isolated and investigated further in the next chapter.

In a thin condensed aqueous film corrosion occurs electrochemically and can proceed more rapidly than in a gaseous environment. Also, corrosion in thin films can be more severe than in the bulk solution since the transport path for O$_2$ dissolved in the film is short making its flux from the water/atmosphere interface to the corroding surface more rapid than in bulk solution and preventing the transport limitation of the cathodic reaction (O$_2$ reduction) commonly encountered in aqueous environments.$^{16}$ In the presence of $\gamma$-radiation more aggressive oxidants, such as H$_2$O$_2$ and HNO$_3$ will form and subsequently concentrate in condensed water layers. The establishment of these more aggressive oxidizing conditions would account for the enhancement of corrosion observed in the patches.

Patches, irrespective of whether $\gamma$-radiation was present or not, grew with a central accumulation of corrosion product. In optical images this can be seen as a central dark spot within the patch, and in SEM micrographs as an accumulation of larger globular deposits as shown in Figure 4.8. This accumulation tends to be concentrated along the original polishing lines. This choice of location could be dictated by two features: the more likely accumulation of water within the polishing grooves, and/or the greater likelihood of stress-induced fracture of the more general corrosion film initially forming at this location.
Figure 4.8: Optical image and SEM micrographs recorded on a sample exposed to irradiated vapour for 104 d. The circled patch shows the location examined by SEM. The morphology of the corrosion product in the central dark spot is shown in the bottom right micrograph.

A comparison of the FIB cut cross section of a patch, Figure 4.9 to the cut on a general area, Figure 4.6, confirms that the extent of corrosion in the patch is greater. Figure 4.9 shows the thickness of the corrosion product varies with location from 234 nm at the thinnest location to 2.62 µm at the thickest location. Additional cross sections (not shown) cut ~ 50 µm inside and outside the patch showed that the film thickness varied from ~60 nm to 176 nm at locations in the general area to 160 nm to 390 nm within the patch. Inspection of the metal/deposit interface shows that, despite these differences in thickness of the deposit, the observed depth of corrosion penetration into the metal is only slightly greater beneath the thicker than the thinner deposit.
Figure 4.9: A FIB cut cross section of an irradiated sample exposed for 104 d. The section was cut from within the circled area shown in the optical image. The numbers on the SEM micrograph indicate the locations analyzed by EDX (table 4.1).

A duplicate sample shows that, while the effect of low dose radiation is consistent with both increased patch formation and size compared to non-irradiated conditions, the extent of corrosion within the patches is variable as is the porosity of the film. The deposit seen in the cross-section of one of the patches (not shown) was ~ 1.46 µm thick with little porosity, similar to the film shown in Figure 4.9. A cross-section cut across a second patch, circled in the optical image in Figure 4.10, showed a much thicker deposit had formed, the thickness averaged across the section being ~ 7.71 µm. The combination of a thicker deposit and a greater porosity is not surprising since they would be expected to be related. Water, trapped within the pores would allow transport of soluble corrosion products (Cu⁺, Cu²⁺) from the corroding surface to be precipitated at the deposit/H₂O interface. The morphology of the outer semi-detached layer of the deposit, Figure 4.10 (top left) suggests it may have been deposited on drying the sample after removal from
the test vessel. Analysis of the Cu/O ratio from EDX data indicates that the entirety of the film is Cu$_2$O. In addition, the film appears much more porous. In the absence of a significant bulk solution, the transport of soluble Cu cations (most likely as Cu$^{2+}$ which is more soluble than Cu$^{+}$) will be limited, and corrosion product deposition would occur close to the corrosion site. Consequently, the differences in film thickness with location indicate substantial differences in porosity in the deposit. At locations where the deposit is thick a small volume of metal is converted to a large volume of corrosion product oxide/hydroxide. As observed in the study conducted in the humidity chamber the aspect ratio (the ratio of the depth of corrosion to the area corroded) are very small for the patches indicating that corrosion spreads laterally rather than penetrates deeply irrespective of whether irradiation is present.

Figure 4.10: A FIB cut cross section of a duplicate irradiated sample exposed for 104 d. The section was cut from within the circled area shown in the optical image.
A FIB cross section cut through the central mass of corrosion product within a patch on the non-irradiated sample (after 104 d of exposure), Figure 4.11, shows that the deposit can be both thicker (up to 3.33 µm) and have a greater depth of corrosion penetration than some of the patches on the irradiated samples exposed for the same duration. A number of additional features are also visible; (i) the deepest penetration is not beneath the thickest deposit; (ii) considerable void space exists both in the deposit and along the deposit metal interface. Beyond this more heavily corroded region the penetration depth is limited to ~ 633 nm which is similar to the penetration depths observed on the irradiated sample at locations away from the central core of the patch. A duplicate coupon exposed to 104 d of non-irradiation conditions does not show any patch formation.

Figure 4.11: A FIB cut cross section on a non-irradiated sample exposed for 104 d. The section was cut from within the circled area shown in the optical image. The numbers in the SEM micrograph indicate the locations analyzed by EDX (table 4.2).
It is possible that the amount of H$_2$O condensed at the location on the non-irradiated sample (Figure 4.11) is greater than that on the location examined on the irradiated sample (Figure 4.9). The argument would then be that this enhanced Cu$^{2+}$ transport leading to an on-going corrosion process. This is inline with the observation on the duplicate sample (Figure 4.10) suggesting that more H$_2$O has condensed at the location of the more heavily corroded patch.

Inspection of the patches indicates that the corrosion process is more limited when the film porosity appears limited; this is the case for the cross-sections on the irradiated coupons that only show thicknesses of 2.62 µm (Figure 4.9) and 1.4 µm (not shown). The thicker deposits on the duplicate irradiated sample and non-irradiated sample appear more porous and the Cu/deposit interface more defective, the porosity allowing continuous wetting and facilitating Cu$^{2+}$ transport, allowing the Cu$_2$O layer to continuously grow.

EDX analyses of the cross-sections, Tables 4.1 and 4.2, show a slight decrease in O content closer to the substrate than near the top of the corrosion product, but the Cu to O ratio in both areas indicates that the oxide is Cu$_2$O. Similarly, Raman spectra (not shown) of both the general area and patches in both conditions have peaks at 147, 220, 525 and 625 cm$^{-1}$ that are readily assigned to Cu$_2$O based on extensive literature, as well as a peak at 290 cm$^{-1}$ that corresponds to the presence of CuO. Note that no N-species were detected by Raman spectroscopy on the irradiated samples despite the likely formation of HNO$_3$. This observation is consistent with the literature reporting the absence of Cu$_2$NO$_3$(OH)$_3$ at high RH.

<table>
<thead>
<tr>
<th></th>
<th>C K (at. %)</th>
<th>O K (at. %)</th>
<th>Cl K (at. %)</th>
<th>Si K (at. %)</th>
<th>Cu L (at. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spot 1</td>
<td>5.25</td>
<td>36.28</td>
<td>1.27</td>
<td>-</td>
<td>57.20</td>
</tr>
<tr>
<td>Spot 2</td>
<td>5.98</td>
<td>22.81</td>
<td>1.38</td>
<td>1.55</td>
<td>68.37</td>
</tr>
</tbody>
</table>
Table 4.3: EDX data recorded on the cross-section of a patch on a non-irradiated sample after 104 days of exposure. The locations analyzed are numbered in Figure 4.11.

<table>
<thead>
<tr>
<th></th>
<th>C K (at. %)</th>
<th>O K (at. %)</th>
<th>Cl K (at. %)</th>
<th>Cu L (at. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spot 1</td>
<td>7.90</td>
<td>28.06</td>
<td>1.03</td>
<td>63.00</td>
</tr>
<tr>
<td>Spot 2</td>
<td>12.12</td>
<td>16.82</td>
<td>1.48</td>
<td>69.59</td>
</tr>
<tr>
<td>Spot 3</td>
<td>13.41</td>
<td>18.03</td>
<td>1.15</td>
<td>67.40</td>
</tr>
<tr>
<td>Spot 4</td>
<td>8.00</td>
<td>-</td>
<td>-</td>
<td>92.00</td>
</tr>
</tbody>
</table>

XPS analysis, Table 4.3, which analyzes only the outer 5 to 10 nm of the surface of the films shows Cu(II) is the dominant Cu oxidation state on the surface of both the general areas and the patches. Although Cu(0) and Cu(I) are difficult to separate by XPS the thickness of the deposit precludes detection of the Cu substrate, and the second oxidation state can be taken as Cu(I). Coupled with the Raman analyses this would suggest the corrosion product in both areas is comprised of an inner Cu$_2$O layer with the outer surface being CuO, consistent with the observations drawn in the previous chapter.

Table 4.4: Oxidation states of Cu in the corrosion products at a number of locations determined by XPS (Figure 4.9 and 4.11).

<table>
<thead>
<tr>
<th></th>
<th>Cu(I)</th>
<th>Cu(II)</th>
</tr>
</thead>
<tbody>
<tr>
<td>104 d irradiated – general area</td>
<td>25</td>
<td>75</td>
</tr>
<tr>
<td>104 d irradiated – upper left patch</td>
<td>27</td>
<td>73</td>
</tr>
<tr>
<td>104 d non-irradiated – general area</td>
<td>24</td>
<td>76</td>
</tr>
<tr>
<td>104 d non-irradiated - patch</td>
<td>23</td>
<td>77</td>
</tr>
</tbody>
</table>

4.4 Summary

The electrical resistance method for measuring the extent of corrosion of a Cu wire showed that no significant general corrosion was detected on either the irradiated or non-irradiated probes. During the initial ~60 days of irradiation, the response of both ERCPs was similar and both exhibited a corrosion rate of 1.3±1.0 µm/yr. A maximum corrosion rate of 2.4±1.0 µm/yr was observed on the irradiated ERCP during the final ~50 days of the test, while during this same time period, a small resistance decrease was observed on
the non-irradiated specimen. It is likely that the reported corrosion rates are very near the limit of detection by this technique for this particular experimental arrangement. As shown from the surface analyses of the coupons, minor localized corrosion likely occurred.

Analysis of the coupons showed that the general features of the corrosion process are the same irrespective of whether radiation is present or not. The surface undergoes a general corrosion process leading to the formation of a layer of Cu$_2$O which is subsequently partially further oxidized to CuO at the outer oxide/vapour phase interface. Since the amount of condensed water is limited, particularly in the general area, dissolved Cu$^{2+}$ is immediately redeposited and corrosion stops due to the formation of a CuO layer on the surface. Condensation of water at some locations (patches) leads to the formation of soluble species, most likely Cu$^{2+}$, which is more soluble than Cu$^{+}$, which allows the Cu$_2$O layer to build-up. Additionally at these locations the Cu$_2$O layer becomes more porous allowing transport of soluble Cu$^{2+}$ to the outer surface where its deposition as CuO allows the build up of a thicker corrosion product deposit. It is possible corrosion at these locations will not be totally suppressed as noted in the long-term corrosion study (Chapter 3). The aspect ratio of these patches (depth of penetration/area corroded) is very small demonstrating that, while corrosion may continue slowly within patches, the dominant mode of damage accumulation is the spreading of corrosion rather than its penetration into the metal.

Since the general surface corrosion process is dominated by the formation of Cu$_2$O while that within the patches involves dissolution of Cu$^{2+}$ and its redeposition as CuO, the most likely process driving the spread of patches is the oxidation of Cu$_2$O to Cu$^{2+}$ in locally condensed water. The transport range of dissolved Cu$^{2+}$ is limited forcing redeposition to occur close to the site at which soluble Cu$^{2+}$ is formed. In the low humidity experiment this leads to the accumulation of a compact layer of small crystals. At the higher humidity the accumulation of deposit is thicker and the crystals more poorly formed.

At the higher RH the spread of patches of redeposited CuO occurs around a small central region, which undergoes pit formation leading to deeper penetrations into the Cu. This pitting is shallow and only observed at the lower RH after prolonged exposure (150
d) but occurs at the higher RH irrespective of whether a radiation field is present. These observations indicate that the main factor driving pit formation is the presence of accumulated condensed water, which occurs more readily at the higher humidity. However, the spread of such areas covered by deposited corrosion product (patches) appears to be accelerated by the presence of radiation. Although a more extensive analysis remains to be performed, there is presently no evidence that the low radiation dose rate employed in this study leads to a deeper penetration of corrosion into the Cu metal.

4.5 References:


Chapter 5

5 Investigating the Effect of Cover Gas on Cu Corrosion under DGR Conditions in the Presence of High Dose $\gamma$-Radiation

5.1 Introduction

The work presented in the previous chapter indicates that $\gamma$-radiation at a low dose rates accelerates the initial rate of Cu corrosion in humid air. $\gamma$-radiolysis of water vapour produces a number of oxidizing species, including $O_2$ and $H_2O_2$.\(^1\) Radiolysis of humid air produces a much wider range of oxidants that include both N- and O- species.\(^1,2\) As discussed in the previous chapter, the presence of HNO\(_3\) enhances the corrosion rate of Cu.\(^3\) The presence of water vapour at high humidity further enhances the corrosion rate.\(^4\) In general, corrosion rates are enhanced by an increase in relative humidity due to the accumulation of oxidants within the aqueous phase (water droplets that condense on a corroding Cu surface).\(^5,6\) Studies completed for the Yucca mountain project have found that in the presence of irradiated air at high dose rates, $Cu_2NO_3(OH)_3$ is only detected as a minor phase at low humidity (0 and 15 %RH) with $Cu_2O$ as the dominant phase, and only $Cu_2O$ and CuO are detected at high humidity (100 %RH).\(^7\)

The work presented in this chapter explores (1) the effect of $O_2$ concentration on short-term Cu corrosion in a humid environment in the absence of radiation, and (2) the effect of $\gamma$-radiation on Cu corrosion in different humid environments, $H_2O/Ar$, $H_2O/air$ and $H_2O/O_2/Ar$. Water vapour radiolysis in the different atmospheres produces different concentrations and combination of oxidants (primarily HNO\(_3\), $H_2O_2$ and $O_2$) that are important for Cu corrosion. The objective of this study is to separate the effect of $O_2$ (the main oxidant for Cu corrosion in humid air in the absence of radiation) from the effects of other radiolytically-formed oxidants. Cu corrosion may occur in different kinetic stages. If we can establish how individual oxidants affect corrosion kinetics at different stages, the effect of radiation dose rate on Cu corrosion can be established. While the dose rate used in this study is about three orders of magnitude higher than the dose rate anticipated for a UFC, this will allow us to explore the impact of radiolysis more easily.
5.2 Experimental

5.2.1 Sample Preparation and Set-up

1x0.7x0.3 cm² coupons of wrought (SKB) Cu were polished successively with 600 and 1200 grit SiC paper on all 6 sides. The coupons were washed and ultrasonically cleaned in Type I water and methanol for 2 minutes, then washed again with Type I water, and dried using ultrapure Ar gas. The polished coupons were placed in a desiccator for one day to dry, and then their dimensions and weight were recorded prior to the start of each experiment.

Each coupon was placed in an individual 20 mL glass/quartz vial. The volume of water required at 75 °C to achieve the 85 %RH in a 20 mL volume was calculated to be 5 µL. A 20-µL pipette was used to deliver 5 µL of Type 1 water into each vial. The polished coupons were placed in a holder within the vials, and then the vials were sealed with aluminum crimp caps fitted with PTFE silicon septa (Agilent Technologies) that provided a vacuum seal to maintain the humidity and prevent loss of gaseous species during irradiation. The vials were then purged with the appropriate cover gas (air, Ar, 35%O₂ in Ar; Praxair) for 30 minutes. For the experiments under irradiated conditions, the sealed vials were placed within a 250 mL stainless steel autoclave (Parr Instrument Company, model 4760) with an exterior heating jacket (temperature controlled by a Parr 4836 controller) prior to emplacement into a ⁶⁰Co gamma-cell (MDS Nordion) that provided uniform adsorption at a rate of ~3 kGy/h. For the experiments under non-irradiated conditions, the vials were placed in the humidity chamber (Associated Environmental Systems) that was already set to 75 °C. Samples were exposed for 5, 24 and 96 h.

After exposure, the cover gas was collected for GC analysis (H₂ and O₂ detection) prior to removing the coupons from the vials. The coupons were washed with Type 1 water, dried in Ar gas and stored in a desiccator for 24 h. The coupons were then weighed and stored in the glove box to avoid further oxidation. Surface analyses (Raman, SEM and EDX) were performed on the 1x0.7 cm² surface of the coupons to characterize the structure and morphology of the corrosion products formed during exposure. After completion of the surface analyses, the samples were replaced in the glove box.
5.2.2 Chemical Analyses

A gas sample was taken from each test vial headspace using a gas-tight syringe with a Luer lock valve (Agilent Technologies). Gas samples were injected through a septum into the sample loop of a GC system equipped with a 60 m long, 0.32 µm diameter GS-GASPRO column (6580, Agilent Technologies). The column was connected to three detectors: a thermal conductivity detector (TCD), a µ-electron capture detector (ECD), and a mass selective detector (MSD) (not used for these experiments). The TCD was used for quantification of H₂ gas and the ECD was used for quantification of O₂ gas. N₂ was used as the carrier gas at a flow rate of 4.6 mL/min, and the detectors are calibrated biweekly by injecting certified gas mixtures of H₂ and O₂ (Praxair) in a range of concentrations. The detection limits for [H₂] and [O₂] are 4x10⁻⁷ M and 4x10⁻⁵ M, respectively.

5.3 Results and Discussion

5.3.1 Effect of O₂ Concentration on Cu Corrosion in the Absence of Radiation

The effect of O₂ concentration on Cu corrosion in a humid environment was investigated using different atmospheres, Ar, air (21% O₂) and 35% O₂ in Ar with the humidity set at 85% RH and the temperature set to 75 °C in all cases. The O₂ concentration in the Ar atmosphere was nominally zero, but residual O₂ may have been present at low levels due to insufficient purging of the test vials. The starting O₂ concentrations in the test vials were ~ 1.0 × 10⁻² M for air and ~ 1.6 × 10⁻² M for 35% O₂ in Ar. The water vapour concentration ([H₂O(g)]) for the 85% RH at 75 °C is 1.3 × 10⁻² M. The concentrations and the volume percentages of H₂O and O₂ in the final gas mixtures at 75 °C are presented in Table 5.1. In all gas mixtures the volume percentage of H₂O is 24%. For ease of future reference, the test gas mixtures will be referred to as H₂O/Ar, H₂O/air and H₂O/O₂/Ar.
<table>
<thead>
<tr>
<th>Gas Mixture</th>
<th>H₂O</th>
<th>O₂</th>
<th>Ar or N₂</th>
<th>H₂O</th>
<th>O₂</th>
<th>Ar or N₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂O/Ar</td>
<td>0.014</td>
<td>0</td>
<td>0.045</td>
<td>24</td>
<td>0</td>
<td>76</td>
</tr>
<tr>
<td>H₂O/air</td>
<td>0.014</td>
<td>0.010</td>
<td>0.035</td>
<td>21</td>
<td>0.035</td>
<td>55</td>
</tr>
<tr>
<td>H₂O/O₂/Ar</td>
<td>0.014</td>
<td>0.016</td>
<td>0.029</td>
<td>21</td>
<td>0.035</td>
<td>41</td>
</tr>
</tbody>
</table>

The optical and SEM images of coupons corroded for different durations in different gaseous environments are presented in Figure 5.1 and the concentration of O₂ in the test vial as a function of time is presented in Figure 5.2.

![SEM micrographs and optical images of the coupons corroded for different durations in the different gaseous environments in the absence of radiation.](image-url)
Figure 5.2: Concentrations of $O_2$ in the test vials containing the coupons corroded for different durations in the different gaseous environments in the absence of radiation.

As expected, Cu in the $H_2O/Ar$ environment (with no $O_2$ present) shows negligible corrosion product formation even after 96 h of exposure (Figure 5.1). At the test temperature Cu is thermodynamically stable with respect to the formation of $Cu_2O$ with only $H_2O$ present. For the coupon corroded for 96 h, the optical image shows the distribution of patches on the surface, and the SEM micrograph shows a dense accumulation of small, granular corrosion products in these areas (Figure 5.4). Analysis of the gas phase (Figure 5.2) shows that $O_2$ is present at trace levels at times less than 24 h, but is as high as $\sim 1$ mM at 96 h. This level of $O_2$ in the test vial suggests air ingress has occurred over 96 h, resulting in the corrosion of the more reactive surface areas in an otherwise inert atmosphere.

The coupons corroded in the more oxygenated environments show a greater number of granular particles on the surface and a more uniform distribution of these particles. On the coupons corroded in $H_2O/air$, the particles are visible by SEM only on the 96-h corroded surface. For the $H_2O/O_2/Ar$, a uniform layer of the particles can be seen on the surface after 24 h exposure. By 96 h these particles have grown to tens of nanometers in size with a number density of $\sim 25$ particles per $\mu m^2$. 
The number density of the granular particles formed after 96 h exposure follows the order of the fraction of O\textsubscript{2} in the atmosphere:
\[ \text{H}_2\text{O}/\text{Ar} < \text{H}_2\text{O}/\text{air} < \text{H}_2\text{O}/\text{O}_2/\text{Ar} \]
In addition, the spatial distribution of the particles is more uniform in the same order; the particles are aggregated in a few localized areas on a coupon corroded in H\textsubscript{2}O/Ar, whereas they cover the entire surface of the coupon corroded in H\textsubscript{2}O/O\textsubscript{2}/Ar.

Differences in the uniformity of particle distribution may be due to local variations in the surface reactivity. The rate of particle nucleation and growth of particles may occur earlier (faster) on a more reactive site. With a greater number of larger oxide particles the overall rate of metal oxidation slows down. The effect of Cu surface reactivity on particle density and size is then diminished with time and is smaller in a more oxidizing environment. A surface variation in particle density and size is thus more noticeable on a coupon corroded in a less oxidizing environment and at a shorter exposure time.

The O\textsubscript{2} concentrations (Figure 5.2) show an initial sharp decrease after the first 5 h in both H\textsubscript{2}O/air and H\textsubscript{2}O/O\textsubscript{2}/Ar, while the SEM micrographs of the 5 h exposure samples show relatively clean and smooth surfaces (Figure 5.1). The O\textsubscript{2} uptake per unit time corresponds to the rate of Cu oxidation. The rapid initial decrease is probably associated with the formation of a few monolayers of Cu oxide (Cu\textsubscript{2}O). This is followed by aggregation of the Cu oxide forming solid oxide particles. As the particles grow and the surface coverage of the particles increases, the rate of Cu oxidation decreases.

The rate of O\textsubscript{2} uptake is initially higher in H\textsubscript{2}O/O\textsubscript{2}/Ar than in H\textsubscript{2}O/air but in the longer term they approach a similar rate. This behaviour is consistent with a more rapid initial oxide film formation at a high O\textsubscript{2} concentration and then more \([\text{O}_2]\) independent slower growth of large oxide particles.

The Raman spectra of coupons corroded for different durations in H\textsubscript{2}O/air and after 96 h exposure in H\textsubscript{2}O/Ar and H\textsubscript{2}O/O\textsubscript{2}/Ar are presented in Figure 5.3. Peaks at 147, 220, 525 and 625 cm\textsuperscript{-1} correspond to Cu\textsubscript{2}O.\textsuperscript{8,9} In all cases, the corrosion products are mostly Cu\textsubscript{2}O and no CuO was detected by Raman, except for the coupon exposed to non-irradiated air for 24 h (peak at \(\sim\) 300 cm\textsuperscript{-1}).\textsuperscript{10} This is expected because formation of CuO
will suppress further Cu oxidation and the Cu oxide particles will not contain significant amounts of CuO.

![Raman spectra recorded on non-irradiated Cu samples exposed to various cover gases for various exposure times.](image)

Figure 5.3: Raman spectra recorded on non-irradiated Cu samples exposed to various cover gases for various exposure times.

In the longer-term (> 30 d) exposure study at 70 %RH at 75 °C (Chapter 3) we observed bluish to greenish patches in the optical images that are associated with localized dense accumulation of granular corrosion products. These patches are nearly absent in this short-term study, except for a few random cases (Figure 5.4). A small number of patches are observed on coupons corroded in H₂O/Ar for 96 h and on coupons corroded in H₂O/air for 5 h and 24 h, but they were absent on coupons corroded in H₂O/O₂/Ar. The SEM micrographs of these patches show granular particles aggregated within small circles. That the patch formation is negligible within 96 h suggests that condensation of enough water to form water droplets that can act as an electrolyte take a long time to form at 85 %RH at 75 °C and even longer at 70 %RH at 75 °C used in the long-term exposure study. That the patch formation is observed only in H₂O/air is
attributed to formation of water droplets accelerated by adsorption of impurities from ambient air.

5.3.2 The Effect of Radiation on Cu Corrosion in Humid Atmosphere

5.3.2.1 H₂O/Ar and H₂O/O₂/Ar Cover Gases

γ-radiolysis of H₂O/Ar or H₂O/O₂/Ar produces oxidants containing only H and O with the steady-state concentrations of the oxidants different in the two atmospheres. Radiolysis of humid air produces a much wider range of oxidants that include nitrogen/oxygen species that can influence Cu corrosion via different mechanisms. The effect of γ-radiation on Cu corrosion in humid air will be discussed in the next section.

Optical and SEM images of coupons corroded for different durations in H₂O/Ar and H₂O/O₂/Ar are presented in Figure 5.5. Comparison of the surface morphologies of the non-irradiated (Figure 5.1) and the irradiated coupons shows that in all cases corrosion progresses faster in the presence of radiation. In H₂O/Ar, granular particles can be seen after 24 h of exposure to radiation. After 96 h of exposure, the density of the granular particles (~ 100 nm in diameter) is significantly higher on the irradiated coupon. In addition, the surface of the irradiated coupon has a number of patches containing larger well-defined oxide crystals. A coupon irradiated in H₂O/O₂/Ar for the same duration has areas containing similar granular particles. It also has larger areas where the granular particles appear to have merged or coarsened into larger long rod-like particles.
Interestingly, the coupon irradiated in H₂O/O₂/Ar has a smoother surface after 24 h than the non-irradiated coupon, but a denser accumulation of the granular particles after 96 h.

Gas analyses for irradiated samples were not successful due to radiolytic degradation of the vial caps, particularly during long irradiation times.

The Raman spectra of the irradiated coupons show only peaks corresponding Cu₂O and there was no evidence of the presence of CuO in all cases, Figure 5.6. Thus, the differently shaped oxide particles are not due to formation of different Cu oxides.
Figure 5.5: SEM micrographs and optical images of coupons corroded for different durations in H$_2$O/Ar and the H$_2$O/O$_2$/Ar in the presence of $\gamma$-radiation.
Figure 5.6: Raman spectra recorded on irradiated Cu samples exposed to various cover gases for various exposure times.

The observed effects of radiation on surface morphology and the rate of particle formation and growth can be explained by considering the change in redox properties of the gaseous environment with time under continuous irradiation. When exposed to ionizing radiation, water vapour decomposes to form a number of redox active species.\textsuperscript{1} The water decomposition products are homogeneously distributed in the irradiated volume almost immediately (< 100 ns) upon irradiation. The chemical yields per absorbed radiation energy at this stage are referred to as the primary radiolysis yields or the g-values. For γ-radiolysis of water vapour, the primary radiolysis products and their g-values (in brackets in units of μmol·J\textsuperscript{-1}) are:

\[ \text{H}_2\text{O}(g) \xrightarrow{\gamma} \{\text{H}_2\text{O}^+, \text{e}, \text{H}_2\text{O}^*\} \rightarrow \cdot\text{OH}(0.63), \cdot\text{H}(0.74), \text{H}_2(0.055), \text{O}(0.11) \]  

(1)

For radiolysis of water vapour these g-values are nearly independent of temperature.\textsuperscript{1,2}

Under continuous irradiation, the primary radiolysis products are produced at rates proportional to the radiation energy deposition rate. The rate of energy transfer from radiation particles or photons to gas molecules is not affected by the chemical properties of the interacting gas, but it is approximately proportional to the molecular mass of the
gas. Thus, the rate of radiation energy deposition (absorption dose rate, \(D_R\)) is commonly expressed per unit mass or density rather than per volume, in units of Gy\(\cdot s^{-1}\) (1 Gy = 1 J\(\cdot kg^{-1}\)). Thus, at a constant radiation dose rate, the primary radiolysis products of water are produced at rate of \(10^{-6} \cdot D_r \cdot \rho_{H_2O} \cdot g_i\) in units of M\(\cdot s^{-1}\), where \(\rho\) is the density of water vapour.

As the primary radiolysis products accumulate, they participate in chemical reactions in the gas phase. They react with each other, water molecules and, if present, other gas molecules (O\(_2\) and N\(_2\)). Compared to the rates of the events leading to primary radiolysis product formation, these gas-phase chemical reactions (at ambient temperatures and pressures) are much slower.\(^{11}\) However, with continuous irradiation fluxes lasting longer than a few milliseconds, the rates of gas-phase chemical reactions become appreciable and must be taken into account to determine the radiolytically-produced oxidant concentrations. The contributions of even slower processes, such as surface reactions, must be considered for even longer flux times.

The chemical kinetics of vapour radiolysis are complex; about 45 reactions involving more than 10 chemical species are required to adequately describe the radiolysis kinetics of pure water alone.\(^{12,17}\) A reaction set, which include rate constants for all of the significant processes, has been assembled.\(^{12,14}\) Chemical kinetics model calculations using the reaction set were performed to determine the time evolution of the concentrations of key radiolytically-produced oxidants and reductants. The model calculation results for radiolysis of H\(_2\)O/Ar and H\(_2\)O/O\(_2\)/Ar are shown in Figure 5.7. The concentrations of the primary radiolysis products at short times (< 1 s) increase linearly with time (i.e., the slope of the log-log plot is 1), except for •H in H\(_2\)O/O\(_2\)/Ar. The increases in concentration are determined by their g-values and dose rate as described above. At longer times when the secondary radiolysis products O\(_2\) and H\(_2\)O\(_2\) are at sufficiently high levels, their reactions with primary radiolysis products become important and the concentrations become non-linear with time. Eventually the concentrations of molecular products (H\(_2\), O\(_2\) and H\(_2\)O\(_2\)) approach steady state, with the time required depending on the atmosphere and dose rate.
Figure 5.7: Calculated concentrations of radiolysis products formed as a function of time during γ-irradiation of: a) H₂O/Ar and b) H₂O/O₂/Ar gas mixtures at a radiation dose rate of 3.0 kGy/h.

The amount of O₂ initially present in an irradiated gas mixture has a negligible effect on the concentrations of all of the primary radiolysis products except for •H. In H₂O/O₂/Ar, [•H] reaches steady state very rapidly due to the reaction:

\[
\text{•H} + \text{O}_2 \rightarrow \text{HO}_2
\]  

(2)

Neglecting other reactions, the concentrations of •H and •HO₂ can be determined from:

\[
\frac{d[\text{•H}]}{dt} = 10^{-6} \cdot D_r \cdot \rho_{\text{H}_2\text{O}} \cdot g_{\text{•H}} - k_2 \cdot [\text{•H}] \cdot [\text{O}_2] \approx 0
\]  

(3)

\[
[\text{•H}] = \frac{10^{-6} D_r \rho_{\text{H}_2\text{O}} g_{\text{•H}}}{k_2 [\text{O}_2]}
\]  

(4)

\[
\frac{d[\text{•HO}_2]}{dt} = k_2 \cdot [\text{•H}] \cdot [\text{O}_2] \approx 10^{-6} \cdot D_r \cdot \rho_{\text{H}_2\text{O}} \cdot g_{\text{•H}}
\]  

(5)

\[
[\text{•HO}_2] = 10^{-6} \cdot D_r \cdot \rho_{\text{H}_2\text{O}} \cdot g_{\text{•H}} \cdot t
\]  

(6)

In H₂O/O₂/Ar, [•HO₂] initially increases linearly with time at the same rate as the primary radiolysis production of •H. The •HO₂ radical is a precursor to the formation of H₂O₂ and thus irradiation of humid atmospheres containing additional O₂ lead to earlier formation of H₂O₂ and higher steady-state concentrations of H₂O₂ at longer times. This is important because H₂O₂ is one of the more important participants in the Cu corrosion reactions.

In H₂O/Ar, the concentrations of O₂ and H₂O₂ after 96 h of irradiation are about 10⁻⁶ M and 10⁻⁸ M, respectively (Figure 5.7). Note that these concentrations are the gas phase concentrations. The gaseous concentration of radiolytically produced O₂ in the
humid Ar environment is too small to account for the observed acceleration corrosion of Cu in this atmosphere in the presence of radiation (Figure 5.1 versus Figure 5.5). Although the amount of H$_2$O$_2$ produced by water vapour radiolysis is smaller than that of O$_2$, H$_2$O$_2$ has a negligible vapour pressure and adsorbs on available surfaces at a gas-diffusion controlled rate. Even a small concentration of H$_2$O$_2$ produced continuously in the gas phase can lead to accumulation of H$_2$O$_2$ on a surface after long-term irradiation. This H$_2$O$_2$ adsorption will be accompanied by water vapour adsorption. We believe that the acceleration of corrosion of Cu in an irradiated H$_2$O/Ar atmosphere is due to this adsorbed H$_2$O$_2$.

At a higher [H$_2$O$_2$], Cu oxidation is initially faster and less sensitive to surface variations in the reactivity of the Cu. This can explain why a coupon irradiated in H$_2$O/O$_2$/Ar has a smoother surface after 24 h than a non-irradiated coupon, but a denser accumulation of the granular particles after 96 h.

Formation and growth of Cu oxide particles creates a ‘rougher’ surface that accelerates adsorption of water and aggregation or coarsening of the particles. This can explain the formation of the octahedral particles in H$_2$O/Ar and the long rod-like particles in H$_2$O/O$_2$/Ar. The different shapes of the aggregate particles are attributed to the differing extents of particle growth that are controlled by the time required for water to adsorb on to the surfaces. A more extensive mechanism addressing the growth of the oxide and long-term corrosion behaviour of Cu is addressed in Chapter 6.

5.3.2.2 H$_2$O/Air Cover Gas

Air, the final cover gas studied in this set of experiments, presents the most complex environment. Radiolysis of humid air produces a much wider range of oxidants that include nitrogen/oxygen species as well as H$_2$O$_2$ and O$_2$. Adsorption of NO$_x$ and nitric acid on surfaces is also known to promote water condensation. Optical and SEM images of coupons corroded in H$_2$O/air in the presence of radiation are presented in Figure 5.8. Comparison of the surface morphologies of the non-irradiated (Figure 5.1) and irradiated coupons shows that corrosion in general progresses faster in the presence of radiation. After 96 h exposure the surface is uniformly covered with granular particles and the density of the granular particles is significantly higher on
the irradiated coupon. The effect of radiation on general corrosion in H₂O/air is similar to that observed in the other gas mixture environments.

In H₂O/air the number density of blue patches containing a denser accumulation of the granular particles is also higher on the irradiated coupon (5 h or 24 h exposure) than on the non-irradiated coupon (Figure 5.4). We have attributed the patch formation in the absence of radiation to condensation of water thereby accelerating corrosion. The higher density of patches on the irradiated coupon is then consistent with more water condensation associated with the radiolytic production of NOₓ and nitric acid and the latter’s condensation.

The Raman spectra of irradiated coupons only show peaks corresponding Cu₂O and no evidence of the presence of CuO (Figure 5.6).
5.3.2.3 The Effect of Gas Composition on Corrosion in the Presence of Radiation

Examination of the cross-sections of corroded regions provides a means of determining the extent of corrosion on the surface and the thickness of deposits. Figure 5.9 presents the cross-sections of coupons exposed to 96 h of irradiation as measured using FIB. The backscatter images were used to measure the deposit thicknesses. The secondary electron detector images show a fine grain structure below the deposit. This is likely due to cold work damage that occurred during surface preparation of the coupons and its presence makes it difficult to differentiate between the deposit and substrate. An
example of the secondary electron image has been provided for comparison (marked UWO XB in Figure 5.9). In the backscatter images, the Cu substrate appears bright, and the deposit is darker and clearly distinguishable.

The average deposit thicknesses are given for the different test atmospheres in the bar graph in Figure 5.9. Based on the thickness of the corrosion product, the order of aggressiveness of the corroding atmospheres is \( \text{H}_2\text{O/air} > \text{H}_2\text{O/O}_2/\text{Ar} > \text{H}_2\text{O/Ar} \). The leading position for the \( \text{H}_2\text{O/air} \) atmosphere is not surprising because this environment produces nitric acid which should accelerate the corrosion.

![Figure 5.9](image.png)

**Figure 5.9:** Cross-sections on coupons irradiated for 96 h under various conditions. QBSD notation indicates backscatter images, and UWO XB refers to a secondary electron detector image. The bar graph presents the average thickness across the cross-section, with error bars denoting the standard deviation (\( N=7-9 \)).

### 5.4 Summary

We have explored (1) the effect of \( \text{O}_2 \) concentration on Cu corrosion in a humid environment in the absence of radiation, and (2) the effect of high-dose \( \gamma \)-radiation on Cu corrosion in different humid environments, \( \text{H}_2\text{O/Ar}, \text{H}_2\text{O/air} \) and \( \text{H}_2\text{O/O}_2/\text{Ar} \).

In the absence of radiation, the coupons corroded in the more oxygenated environments show larger numbers of granular \( \text{Cu}_2\text{O} \) particles and also a more uniform distribution of these particles. The rate of \( \text{O}_2 \) uptake is initially higher in the \( \text{H}_2\text{O/O}_2/\text{Ar} \) atmosphere than in \( \text{H}_2\text{O/air} \) but in the longer term, the uptake approaches a similar rate.
This behaviour is consistent with a more rapid initial oxide film formation in the presence of an initially high O$_2$ concentration and then more [O$_2$] independent, slower growth of large oxide particles. Differences in the uniformity of particle distribution are attributed to local variations in the surface reactivity. The effect of Cu surface reactivity on particle density and size is diminished with time and is smaller in a more oxidizing environment. Formation of corrosion patches is observed on coupons corroded in H$_2$O/air and not in H$_2$O/Ar or H$_2$O/O$_2$/Ar. The patch formation is attributed to formation of water droplets accelerated by adsorption of impurities from ambient air.

Corrosion progresses faster in the presence of radiation in all exposure environments. In H$_2$O/Ar, the density of granular Cu$_2$O particles of ~ 100 nm in diameter after 96 h exposure is significantly higher and more uniform across the surface on the irradiated coupon than on the non-irradiated coupon. In addition, the surface of the irradiated coupon has a number of patches containing larger well-defined oxide crystals. The coupon irradiated in H$_2$O/O$_2$/Ar for the same time has areas containing similar granular particles. It also has larger areas where the granular particles appear to have merged or coarsened into larger long rod-like particles.

Preliminary water vapour radiolysis model calculations indicate that H$_2$O$_2$ may be the main oxidant under γ-irradiation at a high dose rate (3 kGy·h$^{-1}$). The model calculations show that the production of H$_2$O$_2$ from radiolysis of water vapour is higher with O$_2$ present in the humid atmosphere. At a higher [H$_2$O$_2$], Cu oxidation is initially faster and less sensitive to surface variations and the reactivity of the Cu. This can explain why the coupon irradiated in H$_2$O/O$_2$/Ar has a smoother surface after 24 h than the non-irradiated coupon, but a denser accumulation of the granular particles after 96 h. Formation and growth of Cu oxide particles creates a ‘rouglier’ surface that accelerates adsorption of water and aggregation or coarsening of the particles. This can explain the formation of the octahedral particles in H$_2$O/Ar and the long rod-like particles in H$_2$O/O$_2$/Ar.

The effect of radiation on general corrosion in H$_2$O/air is similar to that observed in the other gas mixture environments. In H$_2$O/air the number density of blue patches containing a denser accumulation of the granular particles is also higher on the irradiated coupon than on the non-irradiated coupon. The higher density of patches on an irradiated
coupon is attributed to more water condensation associated with the radiolytic production of NO\(_x\) and nitric acid and the latter’s promotion of water condensation.

The cross-sections of corroded regions on the irradiated coupons were analyzed using FIB and electron backscatter imaging. Based on the thickness of the corrosion product, the order of aggressiveness of the corroding atmospheres is H\(_2\)O/air > H\(_2\)O/O\(_2\)/Ar > H\(_2\)O/Ar, consistent with the other results.

5.5 References:


Chapter 6

6 Mechanism of Cu Corrosion in an Environment Simulating the Unsaturated Phase in a Deep Geologic Repository

6.1 Introduction

While no experimental data has previously simulated the anticipated environment during the unsaturated phase in a deep geologic repository (DGR), several reports have reviewed relevant literature\(^1,2\) and addressed the modes of Cu corrosion during the unsaturated phase. Under these conditions small volumes of H\(_2\)O are involved and fast solution supersaturation of dissolved corrosion products (Cu\(^{\text{I}}\)/Cu\(^{\text{II}}\)) can occur leading to precipitation and the formation of potentially protective corrosion product deposits.

Non-uniform surface wetting of the Cu surface is expected during the unsaturated phase. Generally studies on atmospheric corrosion\(^3\) are conducted in the presence of soluble atmospheric contaminants, which yield electrolyte solutions. As a consequence, corrosion can involve a cathodic reaction occurring around the outer edge of a condensed droplet coupled to an anodic reaction located near the center.\(^2\) This separation could result in the possibility of localized corrosion.\(^4\) Zhang et al.\(^4\) proposed a mechanism where the surface is wetted by large droplets surrounded by a number of smaller droplets connected by a thin continuous water layer allowing electrochemical coupling, with the smaller droplets being the sites for the cathodic reaction (O\(_2\) reduction). Chen et al.\(^5\) propose a similar mechanism but rather than smaller droplets surrounding a large central droplet, they envisage the lateral spreading of a central droplet. A scanning Kelvin probe was used to measure surface work functions, the more negative potentials observed at the center of the droplet indicating the active conditions associated with the anodic dissolution reaction. Gradual changes in potential around the edge of the droplet were consistent with the location of the cathodic reaction.\(^6\)

The films developed during atmospheric corrosion are comprised of two layers; an inner layer of cuprite (Cu\(_2\)O) formed directly on the Cu surface which can provide corrosion protection and an outer Cu\(^{\text{II}}\) patina whose composition depends on the contaminants present in the exposure atmosphere, and can include brochantite (CuSO\(_4\)•3Cu(OH)\(_2\)) and atacamite (Cu\(_2\)Cl(OH)\(_3\)).\(^7,8\) These patinas are generally spatially
heterogeneous and unprotective due to the presence of voids and discontinuities and the influence of runoff. In fully saturated solutions, but with the availability of H$_2$O limited by the presence of clay, a similar cuprite/atacamite dual layer has been observed, with the Cu$^{II}$ outer layer similarly unprotective.$^{9,10}$ Despite being present as a common pollutant, NO$_2$ is seldom seen as a surface contaminant due to the high solubility of cupric nitrates$^{11}$, although nitrate deposition, as gerhardtite (Cu$_2$(NO$_3$)(OH)$_3$) has been observed in laboratory experiments when other anions are unavailable.$^{12,13}$

While these studies are instructive the conditions in our experiments are significantly different in a number of respects. By conducting experiments in pure H$_2$O vapour, atmospheric contaminants (with the exception of nitrates which could be produced radiolytically) that could lead to the deposition of Cu$^{II}$ salts are not present. Also the absence of these contaminants in solution means condensed water on the surface of Cu will have a low conductivity, which precludes the wide separation of anodes and cathodes. As a consequence, redox conditions within condensed water will be generally uniform, a situation re-enforced by the uniform production of radiolytic oxidants. The radiolytic production of nitrogen oxides and their absorption into H$_2$O as HNO$_3$ could increase solution conductivity but would only be important at high $\gamma$-dose rates.

This thesis has focused on experiments that attempt to partially simulate the unsaturated phase in a DGR. Based on long-term exposure experiments at various RH and $\gamma$-radiation dose rates, a mechanism for Cu corrosion is presented. This mechanism addresses the three key observations: (i) the uniform corrosion seen generally on the surfaces of coupons; (ii) the central regions of more extensively corroded patches where the thickest deposits occur; and (iii) the growth of patches on the surface with corrosion occurring at the border between patches and the less corroded general surface.

6.2 Uniform Corrosion in the General Area

The general area is that area of the surface covered quickly by a uniform Cu$_2$O oxide. In the absence of radiation, O$_2$ reduction will be the main cathodic reduction reaction supporting corrosion

$$\text{O}_2 + 2\text{H}_2\text{O} + 4e^- \rightarrow 4\text{OH}^- \quad (1)$$

When radiation is present H$_2$O$_2$ reduction will also contribute
\[
H_2O_2 + 2e^- \rightarrow 2OH^- \quad (2)
\]
and in irradiated air there is also the possibility of HNO\textsubscript{3} reduction
\[
NO_3^- + 8e^- + 9H^+ \rightarrow 3H_2O + NH_3 \quad (3).
\]
Under non-irradiated conditions and low \(\gamma\)-dose rates, O\textsubscript{2} reduction is expected to be the dominant cathodic reaction. While O\textsubscript{2} will be readily available, its ability to support Cu corrosion will depend on the nature of the surface film. For the dual layer films formed in the present experiments, O\textsubscript{2} reduction would be expected to be possible on the inner Cu\textsubscript{2}O layer, which will have semiconducting properties, but not on the outer CuO layer. If the Cu\textsubscript{2}O layer is porous, O\textsubscript{2} reduction could also be supported on exposed Cu surfaces when catalysis by Cu\textsuperscript{l} surface states would be possible.\textsuperscript{14}

The early stages of corrosion could involve the direct formation of the oxide via a solid state process accompanied by dissolution of oxidized species into the liquid phase,
\[
\text{Cu} + H_2O \rightarrow \text{Cu(H}_2\text{O)}_{\text{ads}} \rightarrow \text{Cu(OH)}_{\text{ads}} + H^+ \quad (4)
\]
\[
2\text{Cu(OH)}_{\text{ads}} \rightarrow \text{Cu}_2O + H_2O \quad (5)
\]
\[
\text{Cu(OH)}_{\text{ads}} \rightarrow \text{Cu(I)} + OH^- \quad (6).
\]
Although for atmospheric corrosion it has been proposed that the Cu\textsubscript{2}O layer grows via a defect transport process\textsuperscript{8} the nodular nature of the surface layer observed in our experiments suggests a dissolution (reaction 6) – re-precipitation process is more likely.

In describing the soluble forms we have ignored the state of hydrolysis of Cu\textsuperscript{+}/Cu\textsuperscript{2+} neither of which is likely to be significantly hydrolyzed under our exposure conditions .\textsuperscript{15,16} In the general area, where the availability of water is limited, significant crystal growth is not expected and the oxide formed may also be amorphous.

Since dissolved O\textsubscript{2} (and radiolytic oxidants) are available in the water layer further oxidation of Cu(I) is possible and could involve either the direct oxidation of surface Cu\textsuperscript{l} states
\[
\text{Cu(OH)}_{\text{ads}} \rightarrow \text{Cu(II)} + OH^- + e^- \quad (7)
\]
the homogenous oxidation of soluble Cu\textsuperscript{l}
\[
4\text{Cu(I)} + O_2 + 2H_2O \rightarrow 4\text{Cu(II)} + 4OH^- \quad (8)
\]
or the direct oxidation of the Cu\textsubscript{2}O surface
\[
2\text{Cu}_2O + O_2 \rightarrow 4\text{CuO} \quad (9).
\]
Unless the Cu$_2$O layer maintains significant porosity, reaction 8, would be rapidly blocked by the growing Cu$_2$O layer. Although generally more soluble than Cu$^+$, Cu$^{II}$ will precipitate in the limited amount of H$_2$O available,

$$\text{Cu(II)} + \text{H}_2\text{O} \rightarrow \text{CuO} + 2\text{H}^+ \tag{10}$$

Either, or both, reactions 9 and 10 would insulate the corroded surface and suppress corrosion by blocking both the anodic and cathodic reactions. A schematic of the corrosion process occurring, once a corrosion product deposit is present, in the general area is shown in Figure 6.1.

Generally, the solubility of Cu$^{2+}$ is higher than of Cu$^{+}$ especially at the acidic and alkaline ends of the pH scale, and its deposition would contribute to the thickening of the Cu$_2$O layer. While this film would confer some corrosion protection by limiting anodic oxidation of the Cu it might still be able to support O$_2$ reduction depending on its conductive properties. However the formation of a thin protective CuO layer would block O$_2$ reduction and, in the absence of film porosity (allowing O$_2$ access to the Cu substrate), block the corrosion process. Estimates of the thickness in the general area (Figure 6.2) show that the corrosion process effectively stops after $\sim$ 30 d, a period over which Raman spectroscopy and XPS show a layer of CuO forms on the surface. For exposure times $< 7$ d minimal Cu$^{II}$ is detected. After 7 d, XPS detects Cu$^{II}$ in the outer regions of the film, and after 60 d Raman spectroscopy shows CuO is consistently detected across the entire surface and after 90 d XPS shows Cu$^{II}$ to be the dominant oxidation state on the surface.
Figure 6.1: Illustration of uniform corrosion occurring in a small water volume in the general area of the Cu coupons. Bold arrows indicate fast processes. The vertical lines in the Cu₂O layer indicate boundaries between nodules.

The effect of a low γ-dose rate on corrosion in the general areas appears marginal. The initial rate of coverage by Cu₂O nodules appears accelerated but over an extended exposure period the thickness of the corrosion product deposit in the presence of radiation is comparable to that in the absence of radiation, Figure 6.2. Raman spectroscopy confirms the surface is covered by CuO after 51 d exposure to radiation, but there is insufficient data to determine whether radiation had any influence on the amount of CuO present. Based on these analyses radiation appears to play two roles; (i) it induces a more rapid wetting of the surface probably due to the deliquescent nature of HNO₃;¹²-¹³ and (ii) it produces highly oxidizing species which initially accelerate corrosion by increasing the rate of formation of Cu⁺ which then leads to a more rapid accumulation of Cu₂O nodules on the Cu surface. Beyond these initial effects there is no confirmed additional effect of radiation on the general corrosion process.
Figure 6.2: The effect of exposure time on the thickness of corrosion product deposits on the general area and within patches, based on data from both the long-term study and the low dose γ-radiation study. The blue block shows that beyond the initial rapid increase of the general area thickness, the thickness does not increase with increasing exposure time. The red block shows that the thickness within the patches increases with increasing exposure time.

6.3 Patches – Extensively Corroded Areas

The areas of the surface which exhibit more crystalline and thicker corrosion product deposits (termed patches) are likely locations on which water condenses in droplet form as opposed to just a thin layer as in the general areas of the surface. Examination of the deposits shows they are porous with a low density, the thickness of the corrosion product deposit being much greater than the local depth of penetration into the Cu. The long-term study in the absence of radiation, Chapter 3, shows that the corrosion product at these locations does not achieve a limiting thickness but continues to thicken with exposure time.

The larger volume of H₂O condensed at these locations allows the sequence of reactions leading to Cu₂O formation to continue without the immediate deposition of
dissolved Cu$^{2+}$ on CuO. On-going corrosion in this manner leads to porosity in Cu$_2$O layer as indicated by the eventual accumulation of thick surface layers of Cu$_2$O and eventually CuO. This development of porosity can be attributed to the oxidation of Cu$_2$O most likely at particle boundaries in the initially formed Cu$_2$O layer,

$$2\text{Cu}_2\text{O} + \text{O}_2 + 4\text{H}^+ \rightarrow 4\text{Cu}^{(II)} + 4\text{OH}^- \quad (11).$$

When this occurs, oxidants in particular dissolved O$_2$, but also radiolytic oxidants, have access to the Cu surface and the cathodic reaction supporting corrosion is not blocked at these locations. This porosity is also likely to retain H$_2$O maintaining the conditions required for corrosion to progress. The Cu$^+/\text{Cu}^{2+}$ produced can then be transported to the outer surface of the deposit where their deposition (when the solubility product is exceeded) is delayed by the more substantial quantity of H$_2$O available. Their eventual deposition as Cu$_2$O/CuO does not block this porous structure and the dual layer continues to thicken with the surface remaining active, Figure 6.3. The inability of CuO to passivate the surface within the patches is consistent with the observations that the deposited CuO only partially covers the surface. Additionally, by allowing corrosion to continue at the Cu surface it is also possible that some degradation of the Cu/Cu$_2$O interface could occur accounting for the void space at many interfacial locations within the patches.

The influence of low $\gamma$-dose rates on this process could be counterbalancing. The formation of more aggressive oxidants could enhance the onset of porosity (via reaction 11 (but involving H$_2$O$_2$ rather than O$_2$)) thereby increasing the number of patches. However, by simultaneously accelerating the formation of Cu$^{2+}$ (by homogeneous oxidation (reaction 8) involving H$_2$O$_2$) the solubility of CuO would be exceeded more rapidly leading to a limitation in the thickening of the dual layer deposit.
Figure 6.3: Illustration of the corrosion process occurring within patches in a large water volume. Bold arrows represent the dominant processes. The gaps between the Cu$_2$O nodules are exaggerated to facilitate drawing the illustration.

The number and possibly size of deposits appears to increase with exposure time and to be enhanced by low radiation dose rates. This observation would suggest that the distribution of condensed water is the dominant feature controlling the development of patches, since this would be enhanced by the production of deliquescent HNO$_3$ by the radiolysis of H$_2$O vapour. The evidence that the patches spread with time is not strong but if it occurred it would mean that lightly corroded general areas of the surface can be reactivated. FIB cross sections cut at the border between patches and the generally corroded areas of the surface show a gradual transition in the thickness of the deposit.

A secondary spreading of condensed H$_2$O droplets has been observed in atmospheric corrosion studies and attributed$^{(6)}$ to a slight enhancement of cathodic activity at the periphery of the droplet. It was claimed that the alkalinity produced by O$_2$ reduction (reaction 1) led to a lowering of surface tension at the H$_2$O/oxide interface allowing the H$_2$O droplet to spread. This enhanced alkalinity would enhance the solubility of Cu$^{2+}$ via hydrolysis

$$\text{Cu}^{2+} + x\text{OH}^- \rightarrow \text{Cu(OH)}_{x}^{(2-x)-}$$  \hspace{1cm} (12)
This combination of enhanced wetting and increased Cu$^{2+}$ solubility could be sufficient to reactivate that site allowing further corrosion and leading to the spreading of the patch.

6.4 References:


Chapter 7

Conclusions and Future Work

In this thesis, the corrosion behaviour of Cu in an aerated vapour environment in equilibrium with condensed water was investigated in the absence and presence of γ-radiation. The results from the long-term study (75 °C and 70 %RH) conducted in a humidity chamber showed that purple/blue locations on the surface (seen in the optical images) are likely due to locally condensed water indicating areas of more extensive corrosion, confirmed by SEM microscopy. The corrosion product deposit is a dual layer film with an inner Cu₂O layer and an outer CuO layer. Cross-sections of the general area show that the thickness of the deposit quickly grows to ~ 200 nm and does not thicken over time. This indicates that the outer CuO film is likely protective and blocks further corrosion in the general area. Cross-sections of the patches show the thickness increases as a function of time. Comparing the size of the patches and the thickness of the deposits near the center and along the edges of a patch indicate that corrosion propagates across the surface rather than penetrates into it.

From experiments conducted at CNL (75 °C and 85 %RH, 0 or 0.3 Gy/h), the electrical resistance measurements of the extent of corrosion of a Cu wire detected no significant general corrosion on either the irradiated or non-irradiated probes. The corrosion rates are within the limit of detection by this technique for the experimental arrangement used. Analysis of the coupons showed that the general features of the corrosion process are the same irrespective of whether radiation is present or not. The rate of surface coverage of the general area was accelerated by low-dose γ-radiation, but the extent of corrosion was comparable to non-irradiated conditions. Low-dose γ-radiation resulted in a greater number and size of patches on the surface compared to non-irradiated conditions. This is most likely due to the production of HNO₃ and its deliquescent properties. Although a more extensive analysis remains to be performed, there is presently no evidence that the low radiation dose rate employed in this study leads to a deeper penetration by corrosion.

The results from the high-dose γ-radiation experiments (75 °C and 85 %RH in air, Ar or 35% O₂/65% Ar) indicate that the O₂ content influences the initial nucleation and
particle growth processes. In a low O$_2$ environment, particles appear larger at an earlier time (5 h), while in a high O$_2$ environment, nucleation is rapid followed by a slower growth process resulting in uniform coverage of the surface after long exposure (96 h).

The effect of high-dose $\gamma$-radiation is an increased rate of nucleation and particle growth, and overall uniform coverage of the surfaces in all environments after 96 h. In addition, the surface of the irradiated coupons in H$_2$O/Ar and H$_2$O/O$_2$/Ar have a number of patches containing larger well-defined oxide crystals. The effect of radiation on general corrosion in H$_2$O/air is similar to that observed in the other gas mixture environments. In H$_2$O/air the number density of blue patches containing a denser accumulation of the granular particles is also higher on the irradiated coupon than on the non-irradiated coupon. The higher density of patches on an irradiated coupon is attributed to more water condensation associated with the radiolytic production of NO$_x$ and nitric acid and the latter’s promotion of water condensation. Cross-sections of surfaces of the irradiated coupons analyzed using FIB indicate, based on the thickness of the corrosion product, the order of aggressiveness of the corroding atmospheres is H$_2$O/air > H$_2$O/O$_2$/Ar > H$_2$O/Ar.

A mechanism to describe the corrosion behaviour observed in both the general areas and the patches on the Cu surface has been developed. In both areas corrosion was controlled by a dual layer of Cu$_2$O/CuO. In the general areas the limited amount of available H$_2$O lead to a protective layer. In the patches the greater availability of H$_2$O allowed corrosion to continue due to the porous nature of the films. The porosity is also likely to retain H$_2$O maintaining the conditions required for corrosion to progress.

The work in this thesis has built the foundation for understanding the Cu corrosion process in an irradiated aerated vapour phase in equilibrium with condensed water. Thus far, the results have shown that radiation influences the initial formation of the oxide on the Cu surface and increases the initial rate. For long exposure periods, the effects of low-dose radiation on Cu corrosion seem negligible.

This project is ongoing and future work includes the following:

- An investigation of the effects of slightly higher dose rates, such as the anticipated rate of 5 Gy/h at the start of the unsaturated phase. These experiments are planned in collaboration with CNL and will be conducted at their facilities.
• A study of the impact of bentonite clay on the corrosion process since the container will be in contact with clay in a deep geologic repository. Experiments will be conducted on specimens covered with bentonite allowing the effect on corrosion of a combination of clay and humidity to be determined. The primary influence is expected to be on the distribution of corrosion products and damage on the Cu surface.

• An investigation of the influence of repository groundwater species. The study should be extended to investigate the influence of CO$_2$ and other groundwater species such as NaCl on the corrosion process.

• An investigation of the influence of radiation on corrosion during the subsequent fully saturated phase in the repository. The evolution of corrosion in the presence of anticipated radiolytic oxidants (H$_2$O$_2$, ClO$^-$) will be studied. Corrosion potential (to examine surface redox conditions), polarization resistance (to determine relative corrosion rates) and electrochemical impedance spectroscopy (to determine the influence of corrosion product deposits) will be used to follow the progress of the corrosion reaction. These experiments will be designed to measure the key rate constants (for oxidant consumption and metal dissolution) required for the development of a model.

• The development of a kinetic model for humid air radiolysis that takes into account the effects of CO$_2$, Cl$^-$ and other groundwater species.
Curriculum Vitae
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Education
The University of Western Ontario           Sept. 2013 - present
MSc.; The Corrosion Behaviour of Cu in Irradiated and Non-Irradiated Humid Air
Supervisors: Dr. David Shoesmith, Dr. Clara Wren
Academic Coursework
• Materials Analysis Using Synchrotron Radiation
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• 9658 Seminar - Lipson Banes Award Winner

The University of Western Ontario           2008 - 2013
BSc., Honours
4th year thesis: Investigating the adsorption of organic compounds in MOF MIL-53
Supervised by Dr. Yining Huang

Scientific Experience
R&D Chemical Technologist Support Engineer, 3M Canada                               Sept. 2015 - present
Process development on pilot line equipment
Teaching Assistant, The University of Western Ontario                                   Sept. 2013 – April 2015
First year laboratory TA, 2nd and 3rd year analytical chemistry TA
Research Chemist, 3M Canada                                                            May – Aug. 2013
Worked in the consumer business group developing and testing a polyurethane foam
Research and development of various types of polyurethane foams
Physical testing of various types of polyurethane foams
Awarded a BASF 2020 Innovation Award for recycling flammable resin reducing cost and waste

Conferences Attended

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