Corrosion of Copper in Concentrated Aqueous Chloride Under Anaerobic Conditions

by

Bahar Abghari

A thesis submitted in conformity with the requirements for the degree of Master’s of Applied Science

Graduate Department of Chemical Engineering and Applied Chemistry
University of Toronto

© Copyright by Bahar Abghari, 2013
Corrosion of Copper in Concentrated Aqueous Chloride

Under Anaerobic Conditions

Bahar Abghari

Master’s of Applied Science
Graduate Department of Chemical Engineering and Applied Chemistry
University of Toronto
2013

ABSTRACT

Canada’s plan for the long-term disposal of nuclear waste fuel is an approach called Adaptive Phased Management. It includes a two-vessel design for the nuclear waste containers that will be buried in the deep geological repository and kept safe for about a million years.

Copper has long been considered as the outer shell of these waste containers. It shows a good resistance to corrosion and in regards to other noble metals (Pd and Pt) is less expensive.

Corrosion of copper under simulated geological repository conditions is studied in this work. It was shown than thermodynamically, copper corrodes in the absence of oxygen and presence of high concentrations of chloride. However, its rate of corrosion is less than 10 nm/yr, which makes it a suitable candidate for the used fuel containers.
ACKNOWLEDGMENTS

I would first like to express my sincere gratitude and appreciation to my supervisor Prof. Roger Newman for his guidance and encouraging enthusiasm during all times of this work.

I would also like to acknowledge the principals from NWMO for the financial support, especially Pete Keech whose comments, advice, and suggestions during our progress report meetings immensely benefitted this research.

Thanks are given to Dr. Nicholas Senior for providing his knowledge to this research, and for his help in troubleshooting and assistance in developing the experiment. From gardening to operational amplifiers, I have yet to find a question that he doesn't have the correct answer to.

I deeply thank Dr. Anatolie Carcea for his valuable advice towards research lab etiquettes and great assistance in my experimental work.

I also would like to acknowledge the advice and helpful suggestion of my lab mates and friends, especially Ghazal Naseri and Meysam Alian.
This thesis is dedicated to my parents whose love, guidance, and sacrifice have made me the person I am today.
Table of Contents

Abstract .......................................................................................................................... ii

Acknowledgment ......................................................................................................... iii

Table of Contents .......................................................................................................... v

List of Tables ................................................................................................................ viii

List of Figures ............................................................................................................... ix

List of Appendices ...................................................................................................... xiii

1 Introduction ............................................................................................................... 1

2 Literature Review .................................................................................................... 3

  2.1 Canada’s plan for long-term disposal of nuclear waste ..................................... 3

  2.2 Structure of the containers ............................................................................. 4

  2.3 Repository environment ..................................................................................... 5

    2.3.1 Salinity ........................................................................................................ 6

    2.3.2 Temperature: .............................................................................................. 8

    2.3.3 Degree of saturation: ............................................................................... 9

    2.3.4 Redox conditions: ................................................................................... 10

  2.4 Possible corrosion mechanisms ......................................................................... 11

    2.4.1 Uniform corrosion .................................................................................... 11

    2.4.2 Localized and pitting corrosion ................................................................. 12

    2.4.3 Microbiologically influenced corrosion (MIC) ....................................... 13

    2.4.4 Stress corrosion cracking (SCC) ............................................................... 13

  2.5 Thermodynamics of uniform corrosion ............................................................. 14

    2.5.1 Effect of temperature: ............................................................................... 15
4.3 Corrosion Rate Measurements ........................................................................................................ 46

4.3.1 Corrosion rate calculations ........................................................................................................ 50

4.3.2 Dissolved copper ......................................................................................................................... 50

4.3.3 Initial copper oxide ..................................................................................................................... 52

4.3.4 Trapped oxygen ......................................................................................................................... 53

4.3.5 Variations in the pH .................................................................................................................. 53

4.3.6 Modelling the equilibrium ......................................................................................................... 54

5 Conclusions and Future Works ....................................................................................................... 56

6 References ....................................................................................................................................... 57

7 Appendices ....................................................................................................................................... 62

  7.1 List of standard potentials ............................................................................................................ 62

  7.2 Models for calculating the activity coefficients ........................................................................... 63

  7.3 Effect of temperature and salinity on pH probe ......................................................................... 65

  7.4 Impurities in the NaCl salts .......................................................................................................... 67

  7.5 Corrosion rate experiments in detail .......................................................................................... 68

  7.6 Copper oxide calculations ............................................................................................................ 86

  7.6.1 Dissolved Copper Complex Concentration .......................................................................... 86
List of Tables

Table 2.1. Reference Canadian Ground Waters [5]....................................................... 7

Table 4.1. Average discrepancies between the experimental and MEDUSA generated
data at different temperatures and salinities............................................................... 41

Table 4.2. Dissolved copper concentration compared to corroded copper (detection limit=
0.16µM) ....................................................................................................................... 51

Table 4.3. pH changes in unbuffered experiments ......................................................... 53

Table 7.1 List of standard potentials............................................................................... 62

Table 7.2. List of corrosion rate experiments with their experimental details .............. 68
List of Figures

Figure 2.1. Assumed time dependence of the temperature at the container surface and at a hypothetical fracture in the field [4] ................................................................. 8

Figure 2.2. Stages of saturation in a repository [9] ................................................................. 9

Figure 2.3. Evolution of temperature and redox conditions in a DGR over time [9] ...... 10

Figure 2.4. Potential-pH equilibrium diagram for copper in pure water at 25°C (Cu(OH)$_2$ is not considered) [20] ...................................................................................................... 17

Figure 2.5. Potential-pH equilibrium diagram for copper in pure water at 25°C (generated by Medusa) ................................................................................................................... 19

Figure 2.6. Reaction Scheme for corrosion model of copper in the repository [4] .......... 22

Figure 2.7. Pourbaix diagram of copper in presence of 5m chloride at 25°C (Generated by Medusa) .......................................................................................................................... 23

Figure 2.8. Molar fractions of copper complexes in sodium chloride containing solutions at 25°C and -0.05 VSHE (generated by Medusa) ...................................................................... 24

Figure 3.1. Electrochemical cell for OCP measurements, filled with electrolyte and connected to a SCE via salt bridge ......................................................................................... 32

Figure 3.2. Schematic of corrosion rate experiments ........................................................... 34

Figure 3.3. Calibration of the H2 probe before and after sampling ................................. 37

Figure 4.1. Experimental data compared to equilibrium potentials predicted by medusa (2.5 m NaCl and 1mM of Cu$^+$ is present in the solutions), the horizontal lines are the
Cu/Cu(I) oxidation lines and the diagonal lines indicate the hydrogen electrode equilibria .......................................................................................................................................................... 39

Figure 4.2. Experimental data compared to equilibrium potentials predicted by medusa (4.55 m NaCl and 1mM of Cu+ is present in the solutions) the horizontal lines are the Cu/Cu(I) oxidation lines and the diagonal lines indicate the hydrogen electrode equilibria ....................................................................................................................................................................................... 40

Figure 4.3. Comparison of the mean activity coefficients for NaCl solutions obtained experimentally (filled symbols) and via Helgeson model (empty circles), lines are fitted to the experimental data ............................................................................................................................................................................ 45

Figure 4.4. Cumulative hydrogen and corrosion rate versus time for experiment 25, this experiment contained 5 molal NaCl at pH 5.1 and was conducted at 30°, 50° and 75°C ................................................................................................................................................................................................. 47

Figure 4.5. Compilation of corrosion rates plotted against temperature and pH ........ 48

Figure 4.6. Results obtained from pressure experiments (+ indicateds the room temperature measured by thermometer) ................................................................................................................................. 49

Figure 7.1. Experiment 6; initial pH 3.6, 5 molal NaCl, at 25 °C (unbuffered). Final pH of 9.8 ........................................................................................................................................................................................................... 69

Figure 7.2. Experiment 7; initial pH 3.6, 5 molal NaCl at 50 °C. Final pH of 9.1 ........ 70

Figure 7.3. Experiment 10; initial pH 4.1 (buffered with acetic acid), 5 molal NaCl at 50 °C. Final pH of 4.2 ........................................................................................................................................................................................................... 71

Figure 7.4. Experiment 11; initial pH 4.1 (acetic acid buffer), 5 molal NaCl at 75 °C. Final pH of 4.3 ........................................................................................................................................................................................................... 72
Figure 7.5. Experiment 12; initial pH 5.5 (acetic acid buffer), 5 molal NaCl at 75 °C. Final pH of 5.8 ................................................................. 73

Figure 7.6. Experiment 15; initial pH 5.1 (citrate buffer), 5 molal NaCl at 30 °C. Final pH of 5.2 ................................................................. 74

Figure 7.7. Experiment 16; initial pH 5.1 (citrate buffer), 5 molal NaCl at 50 °C, and 75 °C after day 49. Final pH of 5.2 ................................................................. 75

Figure 7.8. Experiment 17; initial pH 5.1 (citrate buffer), 5 molal NaCl at 75 °C. Final pH of 5.3 ................................................................. 76

Figure 7.9. Experiment 18; initial pH 5.1 (citrate buffer), 5 molal NaCl at 75 °C. Cumulative hydrogen data from Experiment 17 included for comparison. Final pH of 5.0 ................................................................. 77

Figure 7.10. Experiment 20; initial pH 3.1 (unbuffered), 5 molal NaCl at 30 °C, 50 °C from day 49, and returned to 30 °C on day 120. Final pH of 3.4 ....................... 78

Figure 7.11. Experiment 22; initial pH 3.3 (unbuffered), 2.5 molal NaCl at 30 °C, 50 °C from day 50, and 30 °C again, from day 78. Final pH of 8.7. * Reading was interpolated ................................................................. 79

Figure 7.12. Experiment 23; initial pH 7.1 (phosphate buffer), 5 molal NaCl at 30 °C, 50 °C from day 44, and 30 °C again, from day 72. Final pH of 8.6 ....................... 80

Figure 7.13. Experiment 24; initial pH 7.2 (phosphate buffer), 5 molal NaCl at 75 °C... 81

Figure 7.14. Experiment 25; initial pH 5.1 (citrate buffer), 5 molal NaCl at 30 °C, 50 °C from day 30, and 75 °C, from day 125 ................................................................. 82

Figure 7.15. Experiment 26; initial pH 5.1 (citrate buffer), 2.5 molal NaCl at 30 °C, 50 °C from day 20 ................................................................. 83
Figure 7.16. Experiment 27; initial pH 4.8 (citrate buffer), 0.25 molal NaCl at 30 °C, 50 °C from day 30 and 75°C from day 120 ................................................................. 84

Figure 7.17. Experiment 28; initial pH 5.0 (citrate buffer), 2.5 molal NaCl at 50 °C, 75 °C from day 25 ................................................................. 85
List of Appendices

Appendix 7.1. List of standard potentials ................................................................. 62
Appendix 7.2. Models for Calculating activity coefficients ......................................... 63
Appendix 7.3. Effect of temperature and salinity on pH probe .................................... 65
Appendix 7.4. Impurities in the NaCl salts ................................................................. 67
Appendix 7.5. Corrosion rate experiments in detail .................................................... 68
Appendix 7.6. Copper oxide calculations .................................................................. 86
1 Introduction

Canada has been using nuclear energy as a major source of power generation for almost 50 years. Canadian reactors (CANDU) use natural uranium dioxide (UO$_2$) as the fuel. UO$_2$ is placed inside a fuel element or tube and usually 28 or 37 of these tubes are bundled together and called a fuel bundle. Each bundle weighs 24 kg with a nominal length of 495.3 mm and maximum diameter of 102.3 mm. So far over 2 million bundles have been utilized and considering the planned nuclear reactor life times, it is estimated that this number will be doubled [1].

Used fuel bundles lose their radioactivity over time, but their chemical toxicity remains. As a result they are considered a waste product with high health risk. Therefore, safe disposal of the nuclear fuel is a major issue in the nuclear industry and has been under study for about 30 years. Currently, used fuel is being stored at a surface facility located at the nuclear power plants. This facility needs constant care and management and is considered a short-term plan for nuclear waste disposal. The Nuclear Waste Management Organization (NWMO) is preparing a proper long-term plan for burial of used fuel in Canada. [1-2]

Current design for used fuel containers is a multi-vessel design, consisting of copper as the outer vessel and steel as the inner vessel, holding the fuel bundles. Container is surrounded by compacted bentonite and buried ~500 m under ground. The 3 geological phases are being considered for the repository environment, oxic, unsaturated anoxic and saturated anoxic and several species exist in the ground and pore water that may cause
the vessels to corrode, of which chloride draws the most concern, especially as it exists at very high concentrations.
2 Literature Review

2.1 Canada’s plan for long-term disposal of nuclear waste

NWMO is developing an approach called Adaptive phased Management (APM) for permanent storage of used fuel in deep geological repositories (DGR) with suitable geological formation, such as crystalline rock or sedimentary deposits. This program is consistent with the nuclear programs of other countries such as Sweden, the United Kingdom, Finland and France, except United States. US was planning on disposing the spent fuel in Yucca Mountain and was the only program considering aerobic disposal of the nuclear waste [3].

APM complex is referred to the underground repository and the surface facilities to design, construct, operate and maintain it. DGR is a metallic multiple barrier design for safe disposal of the used fuel container (UFC) at a depth of approximately 500 meters under the ground [1-2,4].

As reported in the latest issue of the project description brochure, “APM is both a technical method and a management system which involves:

- Centralized containment and isolation of used nuclear fuel in a repository deep underground in a suitable rock formation;
- A series of steps and clear decision points that can be adapted over time;
- An open, inclusive and fair siting process to identify an informed and willing host community;
• Opportunities for people to be involved throughout the implementation process;
• Optional temporary shallow storage at the central site, if needed;
• Long-term stewardship through the continuous monitoring of used fuel;
• Ability to retrieve the used fuel over an extended period should there be a need to access the waste or take advantage of new technologies; and
• Financial surety and long-term program funding to ensure the necessary money will be available for the long-term care of used nuclear fuel” [2].

2.2 Structure of the containers

NWMO’s latest design for UFC is a double-walled vessel with copper as the outer layer and steel as the inner vessel, surrounded by compacted bentonite and buried approximately 500m under the ground. These containers are meant to prevent any penetration for up to 1 million years. The copper vessel is an oxygen-free phosphorus-doped (OFP) copper used as a corrosion resistance barrier with a wall thickness of 25mm and radial gap of 1mm between the inner and outer shell. Swedish Nuclear Fuel and Waste Management Co. (SKB) developed an OFP copper container. These copper containers are oxygen-free copper (less than tens of ppm) to avoid corrosion issues at grain boundary with addition of 30–100 ppm phosphorus and less than 12 ppm sulphur to obtain the desired creep ductility and less than 0.6 ppm hydrogen to avoid embrittlement. Moreover, the inner steel vessel (100 mm thickness) is constructed to handle heavy weights of fuel bundles and mechanical stresses present in the repository. It carries six interior baskets; each consisting of 60 steel tubes, all welded together to hold 360 used fuel bundles. Recently, NWMO proposed coating of copper on steel to overcome the
manufacturing problems of a two-vessel container. The suggested methods are cold-spray deposition and electroplating of copper on steel and a 3mm copper coating thickness is being considered [5].

Eventually, the container will be sealed with compacted bentonite-based materials to limit any initially trapped oxygen, as well as mass transport of any species to and from the container. Bentonite is a type of hydrous aluminium silicate, which is colloidal with the ability of swelling to several times its original volume when absorbing moisture. In saturated bentonite, the diffusivity of the dissolved species is approximately two orders of magnitude less than the bulk solution [6–9,10].

2.3 Repository environment

Various materials are being studied as the corrosion barrier for long-term disposal of used nuclear fuel in a deep geological repository. Copper has been under study for over 30 years for its thermodynamic stability in spontaneous anoxic environments and relatively low cost compared to noble metals. Swedish Corrosion Institute first introduced copper as the UFC shell and currently Finland, Japan and Canada are considering it for their nuclear waste program [5]. Recently, carbon steel was proposed as an alternative to copper, however, copper is still considered the number one candidate for the outer shell of used fuel containers [4].

As previously mentioned, UFC are designed to protect the nuclear waste for 1 million years. During that period certain physical and chemical conditions of the repository environment change. These changes affect the temperature, degree of saturation and
redox conditions within the repository. From a corrosion point of view, initial conditions are incorporated with localized corrosion processes, evolving to a more stable long-term corrosion such as uniform corrosion, which is slower and more predictable [9]. The following discusses the variations of environmental conditions and the relative UFC behaviour.

2.3.1 Salinity

Based on the concentration of total dissolved solids (TDS), ground water could be categorized into four groups [11]:

1) Fresh TDS < 1000 mg/L
2) Brackish 1000 mg/L < TDS < 10000 mg/L
3) Saline 10000 mg/L < TDS < 100000 mg/L
4) Brine TDS > 100000 mg/L

Table 2.1 indicates the composition of Canadian ground water in various rock types, as reported by NWMO. In the table, CR, SR and RM refer to crystalline rock, sedimentary rock and melt water, respectively. As can be seen, pH of the ground water is near neutral in all rock formations. Moreover, chloride and sulphate content of the water can go as high as 199.5 and 1.1 g/L, respectively, which may introduce a higher risk of corrosion [5].
Presence of high concentrations of chloride in ground water and pore water* drives the dissolved copper to form CuCl_{1-x} complexes [4]. However, high pore water decreases the microbial activity in pore waters, Stroes-Gascoyne et al (2010) stated that, in order to suppress the microbial activity, TDS>100 g/L needs to be maintained in a highly compacted bentonite (HCB) [12]. Moreover, high chloride concentrations affect the corrosion behaviour of copper. More discussion on these effects will be presented later.

<table>
<thead>
<tr>
<th>Rock Type</th>
<th>Crystalline</th>
<th>Sedimentary</th>
<th>Melt water</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water Name</td>
<td>CR-50</td>
<td>CR-20</td>
<td>CR-10</td>
</tr>
<tr>
<td>pH</td>
<td>7.5</td>
<td>7.5</td>
<td>7.5</td>
</tr>
<tr>
<td>Environment Type</td>
<td>Reducing</td>
<td>Reducing</td>
<td>Reducing</td>
</tr>
<tr>
<td>Nominal Eh (mV)</td>
<td>-200</td>
<td>-200</td>
<td>-200</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Solutes (mg/L)</th>
<th>Na</th>
<th>K</th>
<th>Ca</th>
<th>Mg</th>
<th>HCO_3^-</th>
<th>SO_4^-</th>
<th>Cl</th>
<th>Br</th>
<th>Sr</th>
<th>Li</th>
<th>F</th>
<th>I</th>
<th>B</th>
<th>Si</th>
<th>Fe</th>
<th>NO_3^-</th>
<th>PO_4^-</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>5100</td>
<td>3400</td>
<td>1900</td>
<td>75</td>
<td>43100</td>
<td>37400</td>
<td>4300</td>
<td>16</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>20</td>
<td>15</td>
<td>3</td>
<td>3600</td>
<td>1750</td>
<td>130</td>
<td>0.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>15000</td>
<td>4800</td>
<td>2130</td>
<td>40</td>
<td>57300</td>
<td>14700</td>
<td>1500</td>
<td>6</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>50</td>
<td>60</td>
<td>10</td>
<td>9900</td>
<td>3900</td>
<td>900</td>
<td>0.02</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>25</td>
<td>70</td>
<td>230</td>
<td>40</td>
<td>60</td>
<td>330</td>
<td>30</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>800</td>
<td>800</td>
<td>1000</td>
<td>50</td>
<td>160</td>
<td>460</td>
<td>1100</td>
<td>6</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>34300</td>
<td>13800</td>
<td>6100</td>
<td>40</td>
<td>199500</td>
<td>97400</td>
<td>11300</td>
<td>6</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>85</td>
<td>&lt;1</td>
<td>-</td>
<td>-</td>
<td>2000</td>
<td>600</td>
<td>80</td>
<td>0.03</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>55</td>
<td>25</td>
<td>&lt;1</td>
<td>900</td>
<td>480</td>
<td>30</td>
<td>0.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.1</td>
<td>&lt;1</td>
<td>-</td>
<td>-</td>
<td>10</td>
<td>10</td>
<td>-</td>
<td>-</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.5</td>
<td>2</td>
<td>2</td>
<td>8</td>
<td>40</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.4</td>
<td>&lt;1</td>
<td>-</td>
<td>-</td>
<td>90</td>
<td>90</td>
<td>-</td>
<td>-</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.9</td>
<td>&lt;1</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>3</td>
<td>5</td>
<td>5</td>
<td>&lt;200</td>
<td>&lt;200</td>
<td>-</td>
<td>-</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>2</td>
<td>1</td>
<td>2</td>
<td>50</td>
<td>47</td>
<td>50</td>
<td>0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;10</td>
<td>&lt;10</td>
<td>-</td>
<td>-</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.2</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TDS</td>
<td>55500</td>
<td>23000</td>
<td>11300</td>
<td>455</td>
<td>317000</td>
<td>157000</td>
<td>20000</td>
<td>80</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Reference</td>
<td>53</td>
<td>54</td>
<td>53</td>
<td>53</td>
<td>56</td>
<td>56</td>
<td>56</td>
<td>55</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 2.1. Reference Canadian Ground Waters [5]

---

* Pore water refers to the water filling the spaces between grains of sediment.
2.3.2 Temperature:

At the closure of the UFC, temperature of the repository increases due to the heat emission of the spent fuel. Containers are designed in a way that their surface temperature does not surpass ~100°C. The maximum temperature on the surface of the container depends on the spacing of the containers, the physical arrangement and properties of the buffer and backfill, and the burn-up and age of the fuel. Figure 2.1 plots the likely surface temperature profile of the container over the proposed lifetime of the container. Most physical, chemical, electrochemical, and mass-transport processes accelerate with the increase of the temperature, but their dependency varies [4].

![Graph showing temperature profile over time](image)

**Figure 2.1.** Assumed time dependence of the temperature at the container surface and at a hypothetical fracture in the field [4]
2.3.3 Degree of saturation:

Degree of saturation refers to the water and vapour content of the sedimentary rocks. They have a significantly low hydraulic conductivity; as a result, the saturation time of the repository may take up to tens of thousands of years. Geological studies indicate three phases for the DGR environment. At the closure of the repository, a dry out period occurs where the conditions are unsaturated and oxic. Following the drying period, a transition phase happens, in which bentonite starts to re-saturate and the oxygen starts to be consumed. Moreover, surface salts and impurities absorb moisture from the vapour phase at a critical relative humidity; this process is called deliquescence. In the transition phase, atmospheric corrosion is observed due to formation of a water film on the surface of the container. Eventually, all the oxygen will be consumed and HCB will fully saturate with ground water. Figure 2.2 describes each phase over time [4,9].

![Diagram of Stages of Saturation in a Repository](image)

*Figure 2.2. Stages of saturation in a repository [9]*
2.3.4 Redox conditions:

As illustrated in Figure 2.3, initially, oxygen is present in the repository. It is the consequence of air trapped in the sealing materials. Although the amount of available O$_2$ is limited, however, it will create a relatively oxidizing environment. Over time, O$_2$ gas will be consumed by aerobic microbial activities and corrosion of copper and steel, until the environment becomes fully anoxic. During the oxic period, it is estimated that ~10’s-100’s µm of uniform corrosion will happen. When the anaerobic phase is reached, the corrosion rate of copper drops significantly [4,9]. Study of the corrosion rate of copper during the anoxic saturated period is the objective of this research.

![Figure 2.3. Evolution of temperature and redox conditions in a DGR over time [9]](image-url)
2.4 Possible corrosion mechanisms

Based on the repository environment, possible available salts and various geological phases, several types of corrosion are likely to occur such as uniform, localized and pitting, microbially influenced and stress corrosion cracking. The following is a short review on each mechanism.

2.4.1 Uniform corrosion

Uniform anoxic corrosion of copper may occur in three environments: pure water, chloride and hydrogen sulphide.

There has been a debate on the uniform corrosion of copper in O₂ free pure water. It was proposed that copper may corrode via Equation 2.1 spontaneously. However, the reaction is thermodynamically possible at very low hydrogen partial pressures [5]. Macdonald et al. (2010) suggested the low partial pressure to be 10⁻¹⁴ atm [13].

Equation 2.1

\[ Cu + H₂O \rightarrow Cu(OH)_{(s)} + \frac{1}{2}H₂ \]

This is discussed in detail in 2.6.

Presence of chloride in water reduces the immunity of copper especially at higher temperatures. Depending on the concentration of Cl⁻, copper may oxidize to CuCl₃²⁻ or CuCl₂⁻. Greater details on this issue and a review of previous studies are given in 2.7.
Furthermore, sulphate inducing bacteria may exist in the DGR and cause copper to corrode by Equation 2.2 as suggested by Smith et al. (2007) [14-15].

**Equation 2.2**

\[ Cu + HS^- + H^+ \rightarrow Cu_2S + H_2 \]

Although HS\(^-\) concentration in the repository is not anticipated to be as high as Scandinavian repositories, however for safety purposes, their effect was investigated by Shoesmith and Smith [5,14-15].

Overall, uniform corrosion is the most probable mechanism in a repository and needs to be extensively studied under anticipated environments.

### 2.4.2 Localized and pitting corrosion

Two phases could be considered for localized corrosion of container in the repository:

1) First 100 years when traces of O\(_2\) are still present and will oxidize Cu to Cu(II). In this stage, anion induced pitting is the important localized mechanism due to presence of tarnished films.

2) Long term penetration when oxygen is fully consumed and the repository is anoxic. In this period, localized corrosion mechanisms, which are possible under anaerobic conditions without any oxide films on the surface, are the issue.

Several issues were addressed in consideration of pitting and localized corrosion; however, Scully et al (2013) assumed that pitting would not occur in the repository. In any case, another type of non-uniform anion induced localized corrosion is likely to
happen which might be due to differential oxygen concentration cell [5]. This effect only exists in the first phase.

Kwong (2011) reviewed the possibility of localized corrosion within the repository. She concluded that copper undergoes a form of under deposit surface roughening as a result of the non-permanent separation of anodic and cathodic processes [6].

2.4.3 Microbiologically influenced corrosion (MIC)

Presence of microbial activity in the ground water may impose a risk when it comes in contact with copper; especially the sulphate reducing bacteria. However, on the design lifetime of the containers corroded materials seems to be insignificant considering that after first 100 years oxygen is fully consumed [5].

2.4.4 Stress corrosion cracking (SCC)

Copper may undergo SCC in environments containing ammonia, nitrite ions, acetate, or, possibly, high concentrations of sulphide; none of which appear to be significantly available in the Canadian ground waters [6].

In the oxic phase, SCC may seem unlikely due to extremely low HS\(^{-}\). However, HS\(^{-}\)-induced stress corrosion of copper in the anoxic phase is an issue. SCC of copper in HS\(^{-}\) concentrations as low as \(10^{-4}\) M was claimed to occur even without any oxide layers on the surface [5].
2.5 Thermodynamics of uniform corrosion

Thermodynamic data allow the prediction of occurrence of a reaction in a multi-component system. For a reaction to be thermodynamically possible, the change in the Gibbs free energy ($\Delta G$) of the reaction should have negative value, meaning the total energy of products is lower than reactants. The thermodynamic property of an aqueous system at constant pressure (P) and temperature (T) is defined by Equation 2.3, where $H$ stands for enthalpy and $S$ stands for entropy.

**Equation 2.3**

$$G = H - TS$$

In electrochemical terms, Gibbs free energy is described by Equation 2.4. It declares that $\Delta G$ is proportional to the amount of energy required to move a charge. In other words, $\Delta G$ is the change in the energy that occurs when an electron passes through a metal/solution interface [16]. In Equation 2.4, $n$ is the number of electrons, $F$ is the Faraday’s constant and equals 96,500 C/equivalent, and $E_0$ is the equilibrium potential of an electrochemical reaction against the standard hydrogen electrode at room temperature and pressure (standard conditions). Appendix 7.1 gives a list of relevant standard electrode potentials for several species. [16–18]

**Equation 2.4**

$$\Delta G^\circ = -nFE^\circ$$
2.5.1 Effect of temperature:

Considering Equation 2.5 as a general chemical equilibrium,

\[
\text{Equation 2.5}
\]

\[aA + bB \leftrightarrow cC + dD\]

at non-standard conditions, the change in the free energy of the system can be determined by Equation 2.6.

\[
\text{Equation 2.6}
\]

\[
\Delta G = \Delta G^\circ + RT \ln \left( \frac{a_C^c a_D^d}{a_A^a a_B^b} \right)
\]

where, R is the gas constant (8.314 J/mol·K), T is absolute temperature (K) and a is the activity of the species. For dilute solutions, activity can be replaced by concentration. Moreover, \(\Delta G^\circ\) refers to Gibbs free energy at standard conditions.

Substituting Equation 2.4 in Equation 2.6, equilibrium potential of an electrochemical reaction at non-standard conditions can be calculated by Nernst equation (Equation 2.7) [17–19].

\[
\text{Equation 2.7}
\]

\[
E_e = E^\circ - \frac{RT}{nF} \ln \left( \frac{a_C^c a_D^d}{a_A^a a_B^b} \right)
\]
2.5.2 Effect of salinity:

The presented thermodynamic data presented so far is for very dilute solutions. Adding salt to the solution affects the activity of species significantly. This effect is due to the interaction between of ions in the solution.

Activity of a species is the activity coefficient of that species in the solution multiplied by its concentration (Equation 2.8). For infinitely dilute solutions, \( \gamma_i \) value equals one, and activity can be replaced by concentration in Equation 2.7.

**Equation 2.8**

\[
\alpha_i = \gamma_i C_i
\]

At higher concentrations, the dependence of activity coefficient on concentrations is more complicated. The activity coefficient of single ions cannot be calculated individually, but their total effect on the equilibrium constants are measured via mean activity coefficient \((\gamma_\pm)\) of an electrolyte solution.

**Equation 2.9**

\[
\gamma_\pm = [(\gamma_+^{n+})(\gamma_-^{n-})]^{1/n}
\]

where \(n^+\) and \(n^-\) refer to the charges of the anions and cations, respectively [19].

There are many approaches for estimation of activity coefficients in various mixtures. Appendix 7.2 gives a short description of these methods and the basis for choosing each method.
2.5.3 Pourbaix diagrams:

Thermodynamic data and stable oxidation states of metals are usually presented in a graph of potential versus pH. These graphs are called Pourbaix diagrams and the vertical or slopping boundaries between stable states are determined by Nernst equation. Figure 2.4 is an example of a Pourbaix diagram of copper in pure water at 25°C for different ion concentrations prepared by Marcel Pourbaix [20].

![Pourbaix diagram of copper in pure water at 25°C](image)

*Figure 2.4. Potential-pH equilibrium diagram for copper in pure water at 25°C (Cu(OH)_2 is not considered) [20]*
The solid vertical lines indicate a change in the state of the species, but no electron is exchanged. As an example, in potentials above approximately 0.3 volts, copper is in Cu\(^{2+}\) form, however, at pH lower than 4, it is stable in an aqueous solution and for pH higher than 4, copper precipitates as copper oxide. The solid horizontal lines represent a change in the electrochemical state of the species. For instance, at pH more acidic than 2, by moving the potential towards positive values, metallic copper is oxidized into Cu\(^{2+}\).

Additionally, the two diagonal dashed lines indicate the boundary regions for stability of water. The more positive line is where the O\(_2\)/H\(_2\)O reaction occurs based on Equation 2.10. In highly oxidizing environments, water will be oxidized, producing oxygen gas.

**Equation 2.10**

\[ 4H_3O^+ + O_2(g) + 4e^- = 6H_2O \]

Likewise, the more negative dashed-line is an indication of H\(_2\)O/H\(_2\) based on Equation 2.11.

**Equation 2.11**

\[ 2H_3O^+ + e^- = H_2(g) + 2H_2 \]

The diagram indicates that metallic copper is stable over all pH ranges in the absence of oxygen [17,20].

Holding these in mind, the next two sections discuss the previous works done so far to better understand the corrosion of copper in pure water and in presence of chloride.
2.6 Copper in pure water:

Thermodynamics of copper under unexpected repository environments has been extensively studied. As mentioned in 2.3, various species and ions exist in the ground water, but the ones that pose the highest risk are oxygen, chloride and sulphide. Previous studies on the effect of chloride on thermodynamics of copper will be presented later; in this section, behaviour of copper in pure water is explored.

Figure 2.5 shows the Pourbaix diagram for 1mM concentration of Cu$^+$ ions produced by Medusa†. The stability diagram shows that copper should not corrode in pure water to any significant extent since metal oxidation lines are far above the hydrogen equilibrium line.

![Figure 2.5. Potential-pH equilibrium diagram for copper in pure water at 25°C (generated by Medusa)](image)

† Medusa is a Pourbaix diagram-generating software authored by Puigdomenech
So far, many studies have been done to confirm the thermodynamics of copper in pure water as well as measuring the corrosion rate of copper [21].

In 1986, Hultquist (1986) suggested that copper corrodes in pure water. Based on his observations, after 650 hours of exposure, copper was corroded and hydrogen gas was present in the headspace above the water. A solid electrolyte probe was utilized to measure the hydrogen concentration inside the cell. He reported that hydrogen gas was produced at 2.2 µg/hr, which corresponds to a corrosion rate of 0.94 µm/yr [22].

Simpson and Schenk (1987) attempted to measure hydrogen production rate of copper in aqueous solutions (ground water and NaCl solutions). They used gas chromatography as the method of measuring the hydrogen rate. Anyhow, they were not able to detect any hydrogen gas [23].

Eriksen et al. (1989) also conducted several experiments on corrosion of copper in distilled water. Samples were exposed for 61 days and hydrogen production rate was measured by gas chromatography. Similar to Simpson and Schenk, no hydrogen was observed. They also identified the corrosion product, by means of XPS and cathodic stripping voltammetry, to be Cu₂O [24].

Gråsjö et al. (1995) measured the oxygen and hydrogen concentration in the reaction chamber when several metals were exposed to pure water. They experimented on Al, Zn, Fe, Cu, and 316-stainless steel and observed that oxygen was consumed during the exposure of all the metals except for stainless steel (they claimed “corrosion rate was considered too small to significantly consume O₂, although the sensitivity of the technique was reported to be equivalent to a corrosion rate of 0.01 µm/yr” [21]). On the
other hand, produced hydrogen gas was seen only for Al, Zn, and Fe and not for Cu. It should be noted that, in the case of copper, 99.9% of oxygen was consumed, but the experiment was not kept long enough to see if hydrogen might have been produced once the environment became anoxic [21, 25].

Szakálos et al. (2007) decided to conduct more thorough tests for investigation of the phenomena proposed by Hultquist. Oxygen-free high-conductivity (OFHC) copper was exposed to de-aerated de-ionized water for 2,300 hours at temperatures between 8° and 85°C. Production rate of hydrogen was measured via a palladium membrane using either an ion pump or a pressure gauge for monitoring the pressure increase. They confirmed that copper corrodes in anoxic pure water due to reduction of $\text{H}_2\text{O}$ if the hydrogen pressure is less than 1 mbar. However, this hydrogen is detectable only after full consumption of oxygen [21, 26].

Recently, Hultquist et al. (2008) presented results of two sets of copper strips being exposed to distilled water for 15 years. One set of strips was sealed with palladium, which is permeable to hydrogen, and the other one with platinum, where hydrogen could not escape. The palladium-sealed flask showed a thick black layer of oxide on the surface of copper with several green colourations indicating presence of Cu$^{2+}$ (surely the presence of Cu(II) indicates oxygen contamination). In contrast, copper strips in the platinum-sealed flask did not change colour, indicating no corrosion on their surface. It was also noted that the water level in the flask containing corroded copper was lower. Based on these visual results, Hultquist further confirmed that water is an oxidant for copper and that copper will corrode as long as hydrogen can escape the vessel [27].
Many other studies and critical reviews are being conducted in this area; however, the proposed idea by Hultquist (1986) is still being investigated. Currently, research is being carried out at University of Toronto on the corrosion rate of copper in pure water; hydrogen production was seen during the experiments, but further experimentation is required to confirm the hydrogen accumulation, i.e. how many monolayers of copper is removed and whether it is more than one layer.

2.7 Copper in presence of aqueous chloride

Presence of chloride in the groundwater can distinctly affect the corrosion behaviour of copper. It should be noted that, Pourbaix diagrams for copper-chlorine and copper-chloride are similar since only one chlorine species (e.g. chloride) can be present within the stability area of water [28]. As a result, Pourbaix diagrams of the copper-chloride system will be used to discuss the system. Figure 2.6 shows the reaction scheme for copper corrosion model proposed by King (2008) [4].

Figure 2.6. Reaction Scheme for corrosion model of copper in the repository [4]
Figure 2.7 is the Pourbaix diagram of copper in presence of $5m^\dagger$ chloride at 25°C produced by medusa. As can be seen, copper in $5m$ NaCl, complexes to $\text{Cu}^+$ where $\text{CuCl}_3^{2-}$ is the most stable species based on MEDUSA; this gives the possibility of corrosion of copper with hydrogen evolution. In any case, the corrosion rate of copper may be very low, and this is to be determined through this study.

Figure 2.8 plots the molar fractions of $\text{CuCl}_3^{2-}$ and $\text{CuCl}_2^-$ versus the total molal concentration of chloride ion at 25°C (Although $\text{Cl}^-$ concentration is denoted by capital M, medusa uses molal concentration as the primary unit and all the concentrations are in molal). As shown in the graph, at both 2.5 and 5$m$ concentration of chloride, $\text{CuCl}_3^{2-}$ is the primary species present in the solution. At 5$m$ $\text{Cl}^-$, almost 85 percent of copper chloride complexes are in the form of $\text{CuCl}_3^{2-}$.

$\frac{[\text{Cl}^-]}{\text{TOT}} = 5.00 \text{ M}$
$\frac{[\text{Na}^+]}{\text{TOT}} = 5.00 \text{ M}$
$1= 5.000 \text{ M}$
$[\text{Cu}^+]_{\text{TOT}} = 1.00 \text{ mM}$

$\dagger m$ refers to molal concentration, which equals to moles of the solute divided by mass of the solvent. The SI unit is mol/kg
The following is a review of studies on thermodynamics and corrosion behaviour of the copper-chloride-water system.

Bacarella et al. (1973) examined the anodic dissolution of copper in 0.124 to 1.24 M sodium chloride solutions under laboratory conditions. Two types of electrochemical cells were employed; a conventional glass cell which could bear temperature up to 101°C and a cell mounted in a recirculating pump loop, in which experiments were conducted up to 175°C. Results indicated that the anodic dissolution was rather diffusion-controlled over activation controlled. The dissolution product was CuCl$_2^-$ and no precipitation was recognized [29].

Beverskog et al (1998) revised the Pourbaix diagrams of the copper-chloride system at temperatures between 5°C and 100°C (oxygen was not assumed as one of the species). All calculations were for $10^{-4}$ and $10^{-6}$ molal of copper and 0.2 and 1.5 molal of chlorine.
concentrations and they stated that chloride ion is the predominating chlorine species. Temperature and chloride concentration dependency of thermodynamic regions for the copper-chloride-water system was investigated and two main conclusions were obtained:

1) Temperature affects the corrosion, passivity and immunity areas of copper in the Pourbaix diagrams. Corrosion, passivity and immunity are the regions where aqueous species, solid compounds and metallic copper are stable, respectively. At acidic pHs, increasing the temperature enlarges the corrosion area, since passive and immune regions decrease. On the other hand, boosting the temperature shifts the corrosion area to lower pH values at alkaline pHs.

2) Concentration of dissolved copper also affects the corrosion, passivity and immunity areas. The immunity and passivity areas enlarge with increasing the copper concentration at higher temperatures, while the corrosion areas decrease.

Furthermore, comparing all the graphs at various temperature and Cu and Cl concentrations, Beverskog et al (1998) indicated that:

- At [Cl\(^-\)] = 0.2 molal, CuCl\(_2^-\) region predominates at all temperatures and is also more stable than CuCl\(_3^{2-}\).
- At [Cl\(^-\)] = 1.5 molal, corrosion may occur at all temperatures of 5\(^\circ\) to 100\(^\circ\)C. Moreover, between 5\(^\circ\) to 25\(^\circ\)C and at 100\(^\circ\)C, CuCl\(_3^{2-}\) is the stable complex, while between 50\(^\circ\) to 80\(^\circ\)C, CuCl\(_2^-\) predominates.

In the end, they stated that based on the DGR environment, copper canisters do not corrode at 0.2 molal chloride concentration, but will corrode at 1.5 molal Cl\(^-\) [30].
Ahonen (1999) conducted research on behaviour of copper containers in saline ground water. As previously mentioned, saline water contains total of 1 to 3 M chloride (maximum of 100 g/l). The main conclusion that Ahonen stated was that no species could oxidize the metallic copper under the studied conditions. However, there is a slight possibility of dissolution of copper at 100°C and acidic pHs less than 6 resulting in hydrogen gas as the corrosion product [11].

Puigdomenech et al. (2000) investigated the thermodynamic data for copper in presence of the following components: H$_2$O, H$^+$, H$_2$, F$^-$, Cl$^-$, HS$^-$, SO$_4^{2-}$, NO$_5^-$, NO$_2^-$, NH$_4^+$, PO$_4^{3-}$, CO$_3^{2-}$. Of all the species, HS$^-$, O$_2$ and Cl$^-$ at concentrations higher than 1 M showed the most significant effect. Chloride has a negative effect on corrosion resistance of copper since it is able to convert metallic copper into Cu$^+$ complexes. At higher concentrations of chloride, even H$^+$ ions present in the solution reduce to hydrogen gas. In general, high chloride concentrations are not favourable at low pH (<4 at 25°C, or <5 at 100°C) or at the presence of oxidizing agents other than H$^+$. However, increasing the concentration of dissolved hydrogen gas pushes the equilibrium to less dissolution of copper [31].

Beverskog et al. (2002) conducted a study similar to their previous work (Beverskog et al. (1998) [30]), but at different concentration of chlorine. They generated Pourbaix diagrams for copper-chloride-water system with 5 molal chloride ion concentration between 5° and 100°C. Similar to the before, increasing the chloride concentration reduces the passive and immune regions, increasing the chance of corrosion in wider range of pH. In this concentration, the stable copper complex in the aqueous form is CuCl$_3^{2-}$. Furthermore, at higher potentials, CuCl$_3^{2-}$ oxidizes to CuCl$_2$, and at even more
positive potentials, CuCl$_2$ converts to CuCl$^+$, Cu$^{2+}$ and CuClO$_3^+$ (the latter is only stable between 5°-50°C).

Their results were mostly obtained from previous works and modelling, however no experiments were conducted. All the diagrams are gathered in Medusa, and for the salinity and temperatures not specified, thermodynamic data are interpolated or extrapolated [28].
2.8 Scope of work

The goal of the current work is better understanding of corrosion of copper under simulated repository environments. To attain this goal, three objectives were followed:

1. Determination of equilibrium potential of copper in NaCl solutions, containing initial Cu\(^+\); compare the results to the existing literature and if necessary make correction to the current models.
2. Carry out high surface area immersion tests of copper in NaCl containing solutions, to measure the corrosion rate and examine the tendency of the system to reach equilibrium.
3. Harmonize 1 and 2 to identify any gaps in the framework and input them in the future studies.
3 Experimental Details

This section details the materials, equipment and procedures for the two types of experiments carried out during the project.

3.1 Copper Equilibria

3.1.1 Materials and electrodes

For these experiments, copper was used as the working electrode and saturated calomel (SCE) as the reference electrode. Copper rods with 99.5% purity, 0.635 cm (0.25”) in diameter were supplied from Alfa Aesar and the SCE was obtained from Fisher Scientific.

The electrolytes were prepared using de-oxygenated de-ionized water (18.2 MΩ-cm conductivity), ACS grade NaCl (supplied from Fisher Scientific and EMD Chemical Inc.), 99% Cu₂O (supplied from Alfa Aesar), concentrated HCl and various strengths of NaOH. Citric acid salts purchased from EMD chemicals Inc. was utilized to buffer the solution and 100 ppm nominal N₂ gas was used to purge the cells.

3.1.2 Copper electrode preparation procedure

A 1 cm in length piece of copper rod was mounted in an epoxy mold exposing the circular cross sectional area of 0.316 cm² to the solution. A plastic coated copper wire was soldered to the rod and shielded with a glass tube. The tube was sealed with lacquer to prevent contact of liquid and air with the copper.
The surface of the electrode was ground to 600-grit finish and ultrasonically cleaned for 3 minutes with ethanol and dried with air, then immediately put in the solution.

3.1.3 Electrolyte recipe and preparation procedure

For the equilibrium experiments, electrolytes containing 2.5 or 4.55 molal chloride (as NaCl) and 1 mM Cu\textsuperscript{+} at pH between 1 and 7 were used. The overall procedure was to add the desired amount of NaCl to a mixing cell and de-oxygenate the cell. Afterwards, the required amounts of de-oxygenated de-ionized water and copper solution (to achieve 10 mM Cu\textsuperscript{+} concentration) were added to the cell. Then various strengths of NaOH were used to adjust the pH. At the end, water was added to reach the required volume. Finally the brine was purged with nitrogen for one hour and transferred from the mixing cell to a de-oxygenated electrochemical cell to be used for the open circuit potential measurements.

The procedure for preparing de-oxygenated de-ionized water is the following: De-ionized water was poured into the de-oxygenation flask, sealed with a modified rubber stopper with gas in and out ports and heated on a hot plate until water boiled vigorously while being slowly purged with nitrogen. After 15 minutes, the flask was removed from the hot plate and cooled down while still being purged with nitrogen for one hour. The water was then transferred to a 1 L gas-free Tedlar bag\textsuperscript{§}.

\textsuperscript{§} Tedlar bag is a gas sampling bag which is relatively impermeable to gas transfer into and out of the bag. The bags are made from Tedlar(r) polyvinyl fluoride (PVF) film that is tough, durable, and chemically inert to a wide range of compounds.
Copper solution was added to the electrolyte to have an initial Cu(I) concentration of 1 mM. 100 mL of the solution contained 0.0715 g Cu₂O and 3 mL concentrated (12.1 M) HCl to dissolve Cu₂O and the rest was water. The volumetric flask was then sealed with a modified rubber stopper with two ports for gas in and out and purged with nitrogen for one hour.

In order to prepare 80 mL of brine solution, 19.3 grams of NaCl was weighed and added to the mixing cell to achieve 4.55 molal Cl⁻ concentration (11.012 grams of NaCl for 2.5 molal Cl⁻ concentration) and was subsequently purged with nitrogen for 10 minutes. 50 mL of de-oxygenated water and 8 mL of copper solution were then transferred to the mixing cell. To adjust the pH, 1, 0.1 or 0.01 molar NaOH was added to the solution and de-oxygenated water was used to bring up the total volume to 80 mL (for 4.55 molal, total amount of liquid is 72.80 mL and for 2.5 molal, this value is 76 mL). The final solution in the mixing cell was then de-oxygenated with nitrogen gas for one hour and transferred to the electrochemical cell for open circuit measurements.

3.1.4 Open circuit measurements

The OCP measurements were carried out in the electrochemical cell. This cell is a glass cell manufactured at Scientific Glass Design with four ports; two for electrodes and two for gas in and out. The experimental setup was put in a water-bath to maintain a constant temperature. The SCE was kept in a separate glass sheath connected via a salt bridge to be maintained at room temperature. Figure 3.1 is a picture of these experiments.
A certified Gamry600 potentiostat was employed to measure the open circuit potential (OCP) of copper against saturated calomel electrode (SCE) in chloride containing electrolytes as described above. These experiments took up to 16 h and the equilibrium value was determined once potential stability was reached. Stability was defined as the point where the change in the potential was less than 1 mV in 10,000 seconds. In the end, equilibrium potential was plotted against pH of the electrolyte; more details are given in 4.2.
3.2 Corrosion rate measurements

3.2.1 Materials

Uncoated copper wires, 0.25mm in diameter and 99.5% in purity supplied by Goodfellow Metals were utilized to carry out the hydrogen measurement experiments. To prepare the solution, ACS grade NaCl, concentrated HCl, NaOH and citrate and disodium phosphate for buffering were used. De-oxygenated de-ionized water was employed to mix the solutions and 100ppm nominal N₂ gas for purging.

3.2.2 Copper wires preparation procedure

The copper wire was cut to 5cm length pieces and assembled into bundles of 100. For each experiment, 26 bundles were used to maintain a surface area of 1024 cm². To clean the wires, they were washed in acetone, de-ionized water, 1 M nitric acid and ethanol, and dried in the oven at 50°C for four hours or in a desiccator under vacuum overnight. 26 bundles of washed and dried copper wires were then transferred to the electrochemical cell. Note that, high surface area for copper was chosen in order to have measureable hydrogen production in these experiments.

3.2.3 Electrolyte recipe and preparation procedure

Corrosion rate experiments followed the same procedure for preparing the electrolyte as the equilibrium experiments; the only difference was that copper solution was not added to the electrolyte. The procedure is detailed in 3.1.3.
3.2.4 Hydrogen analysis:

For collection of the sample, a Tedlar bag was connected to the outlet (3-way valve) of the cell. Certified nitrogen was blown into the cell, pushing the overhead gas out to the bag. The sample in the bag was diluted 6 times (to make it readable to the probe, the probe will be discussed in 3.3) with nitrogen and then the cell was closed until the next sampling.

3.2.5 Hydrogen production measurements:

Washed and dried copper wires were transferred to the glass cell with the two-port lid. The cell was closed and sealed with Viton ring (impermeable to hydrogen gas) and purged with nitrogen for 10 minutes. Using the proper fittings, the already prepared solution was transferred to the cell and then moved to the water-bath with the desired temperature. A schematic of the cells and their connection to the Tedlar bag is shown in Figure 3.2.

![Figure 3.2. Schematic of corrosion rate experiments](image-url)
The overhead gas was analysed periodically, and based on the accumulated hydrogen, the corrosion rate was calculated. The sampling periods were normally one week, however in some cases, to eliminate the effect of sampling period on the rate of corrosion, these periods were changed to two weeks or one month. Note that, for each sampling, all the hydrogen produced during the sampling period was removed and analysed. More details regarding the corrosion rate calculations are presented in 4.3.1.

In several experiments (Experimental ID= 25, 26, 27, 28), one week after the introduction of wires to the solution, the overhead gas was analysed for hydrogen and if presence of hydrogen was confirmed, the solution was refreshed. The reason for refreshing the solution was to remove any species left on the surface of copper wires from the washing procedure and more importantly, to remove any dissolved copper resulting from the oxide layer formed during the drying procedure.

In the early experiments (Experimental ID= 19, 21), a pressure transducer was employed to monitor the variations in the pressure of the cell; however, these experiments were abandoned for their dependency on the room conditions. More details are given in 4.3.

3.3 Calibration of the equipment in use

**Water-bath:** A water-bath manufactured by Thermo Scientific was employed to maintain the temperature of the cell at a constant value (i.e. 30°, 50° and 75°C). It was filled with de-ionized water three times a week to keep the water level above the glass lid and below the fittings. The reason for using de-ionized water was to decrease the precipitation of minerals in the bath and avoid corrosion. Temperature of various spots in
the water-bath was checked with a separate thermometer every week to make sure the bath was working properly.

**pH meter:** All pH’s were measured at room temperature with a digital pH meter from Fisher Scientific. The pH probe was checked with pH 2, 4 and 7 buffer solutions before each experiment and was calibrated against the buffers every month. Moreover, the effect of temperature and salinity on the pH probe was also investigated and will be discussed in Appendix 7.3.

**Potentiostat:** A certified Gamry600 potentiostat was employed to measure the open circuit potential of the copper electrode. The potentiostat was tested with the dummy cell to verify the accuracy of measurements every three months and calibrated by the manufacturer each year.

**Hydrogen Sensor:** A HydroSteel 6000 Hydrogen sensor probe manufactured by Ion Science Ltd. was employed to measure the concentration of hydrogen accumulated in the headspace of the electrochemical cell. Note that, the probe is not sensitive to oxygen and only measures the flux of hydrogen passed through the probe.

The hydrogen probe was calibrated against 100-ppm nominal hydrogen in nitrogen gas before and after each measurement to correct for the probe drift during the sampling. Figure 3.3 shows the calibration before and after sampling.
Figure 3.3. Calibration of the H2 probe before and after sampling

**Swagelok fittings:** Connections between pressure transducers, hydrogen probe and the rest of the equipment were certified Swagelok fittings.
4 Results and Discussion

In order to better understand the anaerobic corrosion of copper in presence of chloride, firstly, the thermodynamic properties of the copper-chloride-water system were investigated and later the corrosion rate of copper was measured. In this section, results obtained from the experimentation and their interpretations are presented.

4.1 Equilibrium of Copper-Chloride-Water system:

This part of the study is an investigation into the equilibrium of Cu-Cl-H$_2$O system in highly saline environments. Open circuit potential (OCP) of the system versus saturated calomel electrode (SCE) is monitored until stability is reached (stability is defined as a change of less than 1mV in 10,000 seconds). Electrolytes contain either 2.5 or 4.55 molal chloride (in form of NaCl) and 1mM of Cu$^+$ ion over a range of pH between 1 and 7. Experiments are carried out at 25°, 50° or 75°C. Note that SCE was maintained at room temperature at all times.

4.2 OCP Measurements:

The equilibrium potential of Cu-Cl-H$_2$O system is plotted versus pH at different temperatures. Moreover, potential vs. pH diagrams (Pourbaix diagrams) for the same system are produced by Medusa. Figure 4.1 and Figure 4.2 illustrate the experimental data plotted against medusa diagrams for 2.5 and 4.55 molal chloride concentration, respectively.
Figure 4.1. Experimental data compared to equilibrium potentials predicted by medusa (2.5 m NaCl and 1mM of Cu+ is present in the solutions), the horizontal lines are the Cu/Cu(I) oxidation lines and the diagonal lines indicate the hydrogen electrode equilibria.
Figure 4.2. Experimental data compared to equilibrium potentials predicted by medusa (4.55 m NaCl and 1mM of Cu⁺ is present in the solutions) the horizontal lines are the Cu/Cu(I) oxidation lines and the diagonal lines indicate the hydrogen electrode equilibria.

The horizontal lines in the graphs indicate the potential in which copper is oxidized to Cu⁺ in presence of chloride and absence of oxygen, according to Equation 4.1, and the diagonal lines represent the hydrogen electrode equilibria for pH 2.

**Equation 4.1**

\[
Cu(s) + 2H^+ + 3Cl^- \leftrightarrow CuCl_3^{2-} + \frac{1}{2}H_2(g)
\]

As illustrated in the diagrams, increasing the salinity moves the metal oxidation line to more negative values. Moreover, increasing the temperature results in a more negative potential. Note that, neither Cu₂O nor any known salt (such as phosphate etc.) can form at such low potentials.
The discrepancies between the experimental data and the stability diagrams produced by medusa were averaged at each temperature and salinity and are shown in Table 4.1.

<table>
<thead>
<tr>
<th>Molality (m)</th>
<th>25°C</th>
<th>50°C</th>
<th>75°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.5</td>
<td>36.8 mV</td>
<td>24.0 mV</td>
<td>9.0 mV</td>
</tr>
<tr>
<td>4.55</td>
<td>36.6 mV</td>
<td>45.1 mV</td>
<td>29.3 mV</td>
</tr>
</tbody>
</table>

Table 4.1. Average discrepancies between the experimental and MEDUSA generated data at different temperatures and salinities

As mentioned before, initially, 1 mM (1.11 m$m$) of copper ion is present in the solutions. However, to raise the equilibrium potential by 40 mV, the initial Cu$^+$ concentration needs to be 5.1 m$m$ (based on the Nernst equation). The initial copper oxide layer on the electrode, impurities in the salt and corrosion may provide the additional copper. However, the dissolved copper due to such an initial oxide layer is very small for this surface area.

Bearing this in mind, the discrepancies in the potential values may be due to various possible reasons such as following:

1. Oxidizing impurities in the sodium chloride

2. Errors in determining the equilibrium potential (Medusa)

3. Potential differences at the liquid/liquid junction of the reference electrode

4. Errors in the extrapolation of activity coefficients at high salinities
4.2.1 Oxidizing impurities in the sodium chloride:

The existence of number of heavy metal ions in the sodium chloride salt used for the experiments may cause an error in the apparent equilibrium potential of copper. ACS grade NaCl is prepared via crystallization from brine of either seawater salt or rock salt. Based on the company’s specifications, NaCl crystals contain less than 2 ppm iron and less than 5 ppm heavy metals, Appendix 7.4 lists all the impurities specified by the manufacturer. Although these values may seem insignificant, at high concentrations of the salt (i.e. 5 molal), they may affect the OCP.

Several approaches were taken to identify and measure the concentration of these impurities. A Pt flag was held in a stirred 5 molal NaCl solution, to plate the metal impurities on the Pt. The applied was fixed on -0.620 V\text{SCE}; it was sufficiently low to plate lead and copper, but borderline for iron. An X-ray photoelectron spectroscopy\textsuperscript{**} (XPS analysis) was then conducted within a few nanometers of the surface of the flag and presence of lead and copper was confirmed, but no iron was observed in the survey spectrum. However, the method was unable to identify the concentration of the impurities.

\textsuperscript{**} XPS is a quantitative spectroscopic technique that measures the elemental composition that exist within a material. XPS spectra are obtained by irradiating a material with a beam of X-rays while simultaneously measuring the kinetic energy and number of electrons that escape from the top 1 to 10 nm of the material being analyzed. XPS requires ultra-high vacuum (UHV) conditions.
Furthermore, NaCl crystals were analysed by time of flight secondary ion mass spectrometry†† (TOF-SIMS). In total, 20 elements were identified, of which manganese, iron and copper were of our interest. Several species such as Ni and Pd were not detected in this spectrometry due to mass interferences and very weak signals.

4.2.2 Differences in determining the equilibrium potential by Medusa:

The equilibrium potential for Equation 4.1 in 4.55 molal NaCl and 1mM of copper at 25°C was calculated by Nernst equation and then compared to the Medusa output. Activity coefficient of the species were used in the molar form [32] and the thermodynamic data were found in [31].

Both CuCl$_2^-$ and CuCl$_3^{2-}$ could be the products of the reaction, but as discussed earlier, the final mixture contains 90% CuCl$_3^{2-}$ and 10% CuCl$_2^-$. The standard reduction potentials for Cu/CuCl$_3^{2-}$ and Cu/CuCl$_2^-$ are 0.219 and 0.174 V$_{SHE}$, respectively. Under the described conditions, molar activity coefficient is 0.979. Thus, the equilibrium potential of CuCl$_3^{2-}$ is calculated to be -0.067 V$_{SHE}$. This value is -0.112 V$_{SHE}$ for CuCl$_2^-$. Medusa determined the equilibrium potential of Cu in the electrolyte (containing 4.55 m NaCl and 1 mM copper at 25°C) to be -0.134 V$_{SHE}$ (according to Figure 4.2), which is far from the calculated values. However, the equilibrium potential for Cu/CuCl$_3^{2-}$ obtained from my calculations seems to be closer to the experimental data.

†† TOF-SIMS uses a pulsed primary ion beam to desorb and ionize species from a sample surface. The resulting secondary ions are accelerated into a mass spectrometer, where they are mass analysed by measuring their time-of-flight from the sample surface to the detector. (http://www.phi.com/surface-analysis-techniques/tof-sims.html)
4.2.3 Potential difference at the liquid/liquid junction of the reference electrode

The reference electrode (SCE) is filled with potassium chloride, but the tested solution contains high concentrations of sodium chloride. Since the mobility of potassium ions is higher than sodium, a potential drop will occur at the interface of SCE and solution. This potential difference was calculated using JPCalcD‡‡. The resulted voltage difference was -2.4 and -3.8 mV for 2.5 and 4.55 $m$, respectively. These values are too small to account for the discrepancy.

4.2.4 Errors in extrapolation of activity coefficients in high salinities

The activity coefficients employed in the calculations by Medusa is based on the Helgeson model. The Helgeson model is a general model used for all types of salts and although it allows the calculation of activity coefficient at salinities higher than 0.1 molal, however, its extrapolations for saline solutions show a significant discrepancy with experimental data. Figure 4.3 compares the mean activity coefficients of NaCl solutions calculated by the Helgeson model to the experimental data found in various sources.

‡‡ http://web.med.unsw.edu.au/phbsoft/default.htm
Figure 4.3. Comparison of the mean activity coefficients for NaCl solutions obtained experimentally (filled symbols) and via Helgeson model (empty circles), lines are fitted to the experimental data.

In this figure, the empty circles are the mean activity coefficient of NaCl solution at various molalities predicted by the Helgeson model, and the filled symbols represent the experimental values found in various sources (CRC handbook of chemistry and physics [33]). By combining the experimental data and fitting polynomial lines, an equation as function of temperature and salinity can be defined. The fitted lines are indicated in the Figure 4.3. These lines move to lower values as the temperature increases.

As can be seen, at 5 molal, the Helgeson model approximated the $\gamma$ to be 0.963 at 25°C, however, the curve-fitted experimental data predict this value to be 0.865. This
discrepancy corresponds to 6 mV lower potential in Helgeson model. This is due to
generalization of the Helgeson model for various types of salts, whereas the experimental
data are specific to NaCl solutions, and as a result, give a better approximation.

4.3 Corrosion Rate Measurements

In this part of the study, rate of corrosion of copper in brine is measured. Copper is
dissolved to Cu\(^+\) based on Equation 4.1. Therefore, to calculate the corrosion rate of
copper, hydrogen gas production rate is monitored and converted. Details about the
corrosion rate calculations are given in 4.3.1. Figure 4.4 demonstrates the results from
one of the experiments (ID=25). This experiment contained 5 molal NaCl at pH 5.1 and
was buffered with citrate. It was initially conducted at 30°C, but since no significant
hydrogen was detected, it was moved to a 50°C water-bath and after 125 days, the
experiment was moved to a 75°C water-bath. On the left axis cumulative moles of
hydrogen after each sampling and on the right axis the relative calculated corrosion rate is
presented. A list of all experiments and details on each of them are given in detail in
Appendix 7.5.
Figure 4.4. Cumulative hydrogen and corrosion rate versus time for experiment 25, this experiment contained 5 molal NaCl at pH 5.1 and was conducted at 30°, 50° and 75°C

Although impurities are an issue in determining the equilibrium properties of the system, the large surface area of copper used in these test would seem to prevent any effect that impurities might have. Nevertheless, formation of a thin oxide layer on the surface of the copper wires during the drying procedure might influence the rate of dissolution of copper and/or contribute an unwanted initial spike in dissolved copper concentration. Moreover, initial dissolution of copper oxide might cause the metal to approach equilibrium. This effect will be discussed in 4.3.3.

The corrosion rates of copper at each temperature and salinity, obtained from the experiments, are compiled and plotted in a 3D graph (Figure 4.5). According to the results, corrosion rates do not seem to be very pH dependent, especially at lower temperatures such as 30° and 50°C. Surprisingly, electrolytes at pH 5 give the highest
corrosion rate. On the other hand, the rate of corrosion of copper shows a steep increase with temperature.

![Diagram showing corrosion rates plotted against temperature and pH](image)

**Figure 4.5. Compilation of corrosion rates plotted against temperature and pH**

**Pressure experiments:** In the early experiments a pressure transducer was utilized to monitor the pressure variations of the electrochemical cell. It was assumed that at low pH (pH<3), pressure rise in the cell, due to hydrogen production, would be high enough to be monitored by a pressure transducer. However, the effect of the fluctuations in the room temperature (since the pressure transducer was kept above the water level and in air) and water-bath temperature was more than the effect of pressure variations in the cell. As a result, the inferred corrosion rate fluctuated by as much as tens of nm per year, which was significantly larger than the expected corrosion rate.
In total, six pressure experiments were conducted, of which four failed due to depressurization, and the other two (Experimental ID= 19 and 21), showed scattered results. Figure 4.6 illustrates the output of these experiments. They were abandoned for non-accuracy.

Figure 4.6. Results obtained from pressure experiments (+ indicated the room temperature measured by thermometer)
4.3.1 Corrosion rate calculations

In order to calculate the corrosion rate of copper, cumulative moles of hydrogen was plotted versus time. Figure 4.4 is an example of these plots. Corrosion rate can be calculated using Equation 4.2.

Equation 4.2

$$\text{Corrosion rate (nm/yr)} = \frac{\delta n_{H_2}}{\delta t} \times \frac{2 \times 7.11 \text{ cm}^3}{1024 \text{ cm}^2 \times 10^7 \times 365.25}$$

In this equation, it is assumed that each mole of copper metal is converted to half a mole of hydrogen gas (based on Equation 4.1) and that the copper wires do not thin during the process. 7.11 cm$^3$ is the molar volume of copper, 1024 cm$^2$ is the theoretical wire surface area, $10^7$ converts cm to nm, and 365.25 converts days to years. To determine the differentiation of hydrogen evolution over time two methods were followed; for some experiments, actual data points were differentiated using multi-point average, and in the other experiments, a polynomial line was fitted to the date, and then differentiated. The second method gives a more smooth corrosion rate variations, however, it was only used when the fluctuations in the cumulated hydrogen was low enough to prevent any linear-fitting effects on the corrosion rate.

4.3.2 Dissolved copper

In order to validate the calculated corrosion rates, for a number of experiments, the dissolved copper in the final solution was measured. ANALEST, analytical facility at
Department of Chemistry - University of Toronto, measured the copper ion concentration using inductively coupled plasma atomic emission spectrometry§§ (ICP AES).

Table 4.2 demonstrates the comparison between the expected dissolved copper ion (denoted by Cu_{corr}, based on the hydrogen produced) and actual amount determined by ANALEST (denoted by Cu_{total}). Note that, ICP AES is not sensitive to the species and can measure any oxidation state of the metal, so dissolved Cu^{+} or Cu^{2+} does not change the results.

<table>
<thead>
<tr>
<th>Experiment ID</th>
<th>Temperature (°C)</th>
<th>pH</th>
<th>NaCl (m)</th>
<th>Cu_{corr} (mM)</th>
<th>Cu_{total} (mM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>30</td>
<td>5.0</td>
<td>5</td>
<td>1.70×10^{-3}</td>
<td>1.35</td>
</tr>
<tr>
<td>16</td>
<td>50/75</td>
<td>5.0</td>
<td>5</td>
<td>2.97×10^{-2}</td>
<td>1.35</td>
</tr>
<tr>
<td>17</td>
<td>75</td>
<td>5.0</td>
<td>5</td>
<td>6.38×10^{-2}</td>
<td>4.54×10^{-1}</td>
</tr>
<tr>
<td>18</td>
<td>75</td>
<td>5.0</td>
<td>5</td>
<td>1.30×10^{-1}</td>
<td>6.08×10^{-1}</td>
</tr>
<tr>
<td>20</td>
<td>30/50/30</td>
<td>3.1</td>
<td>5</td>
<td>2.27×10^{-2}</td>
<td>5.96×10^{-1}</td>
</tr>
<tr>
<td>22</td>
<td>30/50/30</td>
<td>3.3</td>
<td>2.5</td>
<td>7.59×10^{-3}</td>
<td>2.83×10^{-3}</td>
</tr>
<tr>
<td>23</td>
<td>30/50/30</td>
<td>7.1</td>
<td>5</td>
<td>8.39×10^{-3}</td>
<td>1.10×10^{-3}</td>
</tr>
</tbody>
</table>

Table 4.2. Dissolved copper concentration compared to corroded copper (detection limit=0.16µM)

The comparison of results in the table shows that the concentration of dissolved copper is higher than the expected by corrosion. Presence of additional copper in the final electrolyte could be due to the formation of an initial copper oxide on the surface of wires and oxygen bubbles trapped between the wires, although the later seems unlikely. This effect may alter the pH and it is obvious in the non-buffered experiments. In the latest trials (ID=24-28) to remove the additional copper, the electrolyte was refreshed after one week.

§§ ICP-AES is an analytical technique used for the detection of trace metals. It is a type of emission spectroscopy that uses the inductively coupled plasma to produce excited atoms and ions that emit electromagnetic radiation at wavelengths characteristic of a particular element. The intensity of this emission is indicative of the concentration of the element within the sample.
4.3.3 Initial copper oxide

As mentioned in 3.2.2, copper wires were dried in oven at 50°C or in a desiccator under slight vacuum. As soon as exposure of copper to air occurs, oxide starts to form on the surface. This oxide layer could either be CuO or Cu$_2$O, and its thickness depends on temperature of the environment and duration of exposure and could be up to several nanometers.

Upon introduction of wires to the electrolyte, dissolution of the oxide layer starts based on a mechanism similar to Equation 4.3. Note that the copper oxide layer should be dissolved completely before the oxidation of copper metal (Equation 4.1) starts.

Equation 4.3

\[
\begin{align*}
CuO + Cu + 2H^+ + Cl^- & \leftrightarrow 2CuCl_3^{2-} + H_2O \quad (a) \\
Cu_2O + 2H^+ + 6Cl^- & \leftrightarrow 2CuCl_3^{2-} + H_2O \quad (b)
\end{align*}
\]

Cu being dissolved as a result of oxide dissolution will be denoted as Cu$_{ox}$. For the experiments 15,16,17 and 20, Cu$_{corr}$ is several orders of magnitude lower than the dissolved copper. Such high Cu$_{total}$ concentrations indicate that the initial copper oxide thickness for experiments 15 and 16 was ~17nm and for experiments 17 and 20 was ~7nm. These values seem reasonable considering that they were dried at 50°C for a couple of hours. Details on calculation of oxide layer thickness are given in Appendix 7.6.
4.3.4 Trapped oxygen

Another possibility for the discrepancy between the dissolved and corroded copper is the existence of oxygen bubble between the wires; they are formed during the washing process (since being sonicated) and may not completely disappear during the purging. Once copper is immersed in the electrolyte, oxygen can cause dissolution of copper via Equation 4.4.

Equation 4.4

\[ 4Cu + O_2 + 4H^+ + 12Cl^- \leftrightarrow 4CuCl_3^{2-} + 2H_2O \]

Copper concentration produced by presence of oxygen will be denoted as CuO₂.

4.3.5 Variations in the pH

Experiments that were not buffered showed a significant increase in pH. This considerable consumption of protons could be due to the initial oxide layer dissolution (Equation 4.3). In fact, oxide layer thickness could be confirmed via pH variations. Table 4.3 shows the change in pH of unbuffered experiments and the dissolved copper oxide.

<table>
<thead>
<tr>
<th>ID</th>
<th>Initial pH</th>
<th>Final pH</th>
<th>Total Cumulative Hydrogen (moles)</th>
<th>Calculated oxide thickness (nm)</th>
<th>Predicted [Cu⁺] in solution (mM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>3.6</td>
<td>9.8</td>
<td>4.3 x 10⁻⁷</td>
<td>7.5</td>
<td>0.64</td>
</tr>
<tr>
<td>7</td>
<td>3.6</td>
<td>9.1</td>
<td>1.5 x 10⁻⁶</td>
<td>3.5</td>
<td>0.30</td>
</tr>
<tr>
<td>20</td>
<td>3.1</td>
<td>3.4</td>
<td>1.2 x 10⁻⁶</td>
<td>4.3</td>
<td>0.37</td>
</tr>
<tr>
<td>22</td>
<td>3.3</td>
<td>8.7</td>
<td>5.0 x 10⁻⁷</td>
<td>6.1</td>
<td>0.52</td>
</tr>
</tbody>
</table>

Table 4.3. pH changes in unbuffered experiments
Comparing the results confirm that the pH change in the solutions may be due to dissolution of an initial oxide layer on the surface of the copper wires.

### 4.3.6 Modelling the equilibrium

Recalling Equation 4.1, at equilibrium, oxidation and reduction reactions (copper and hydrogen) have the same potential.

\[
\text{Cu}(s) + 2H^+ + 3Cl^- \leftrightarrow \text{CuCl}_3^{2-} + \frac{1}{2}H_2(g)
\]

therefore, the Nernst equation for the reaction is formed as a follows:

**Equation 4.5**

\[
E_{eq} = E_{Cu}^o + \frac{2.303RT}{F} \log \gamma_{\text{CuCl}_3^{2-}} - \frac{6.909RT}{F} \log \gamma_{\text{Cl}^-} = E_{H}^o + \frac{2.303RT}{F} \log \gamma_{H^+} - \frac{1.152RT}{F} \log p_{H_2}
\]

where \( \gamma \) is the molal mean ionic activity coefficient, \( c \) is the molal concentration of the denoted species, \( p \) is the partial pressure.

Since the available activity coefficients for concentrated mixtures are in molal format, the Nernst equation needs to be used in molal form. The copper standard potential in 1 molar and 1 molar is assumed to be equivalent (1 molar \( \equiv \) 1.023 molal).

Considering that hydrogen was only generated due to copper dissolution, the following equation links partial pressure of hydrogen to moles of gas.

**Equation 4.6**

\[
n = c_{\text{Cu}^+} \times V_L = c_{\text{Cu}^+} \times dV_L = \frac{2p_{H_2}V_G}{RT}
\]
where $c$ and $c'$ denote molar and molal concentration, respectively, $d$ is the solution density, $V$ the volume of liquid or gas, and $p$ the partial pressure of hydrogen.

Substituting Equation 4.6 into Equation 4.5, gives the final concentration of corrosion product:

\[
E_{Cu}^{\circ} = \frac{2}{RT} \left( E_{H^+}^{\circ} - E_{Cu}^{\circ} + B \log \left( \frac{c^{3+H^+}c_{Cl^-}^{3-}}{dVN_{Cu}^{\circ}V_{Cl^-}^{\circ}} \right) \right)
\]

$E_{Cu}^{\circ}$ is calculated from Equation 2.4, where $\Delta G^{\circ} = -372.48$ kJ/mol as given by Puigdomenech et al. (2000) [31], activities of both copper and chloride are one and standard reduction potential is calculated to be 0.219 V_{SHE}.

Assuming that CuCl$_3^{2-}$ is the primary corrosion product (as elaborated in 2.7) and hydrogen is only present in the gas phase (The Henry constant for hydrogen in deionized water at 25 °C is 1282.1 L·atm/mol), a model was defined, using the experimental activity coefficients (as discussed in 4.2.4), to identify the equilibrium potential given the initial pH, salinity and temperature of the mixture. This model can also predict the concentration of [Cu$^{+}$], the partial pressure of hydrogen and copper reduction potential. The only issue regarding the model calculator is that, it permits input of only one copper complex at a time, which may cause a significant error at 2.5 molal concentration.

For 100 ml of a 5m NaCl solution at pH 5, containing an initial CuCl$_3^{2-}$ concentration of 0.45 mM, the equilibrium potential were calculated using the model; it predicted the potential to be -0.06 mV_{SHE} (-0.337 V_{SCE}).
5 Conclusions and Future Works

1. Equilibrium potentials of copper in anoxic brines were monitored. Their values seemed to be more positive than those in literature and according to Medusa software.

2. The reason for discrepancy between the equilibrium potential of the presented experiments and those determined by Medusa found to be most likely due to existence of impurities in the NaCl salts, as well as the extrapolation of activity coefficient by Medusa.

3. Corrosion rate of copper in presence of high chloride concentrations (5, 2.5 and 0.25 molal NaCl) under anaerobic conditions was measured at various temperatures over a range of pH.

4. Corrosion rates did not show the expected pH dependant steep, especially at lower temperatures (30° and 50°C). Moreover, electrolytes at pH 5 gave the highest corrosion rate.

5. The rate of corrosion of copper seems to increase steeply with temperature.

6. Overall, the corrosion rate of copper does not exceed 10 nm/yr, which makes it suitable for the outer shell of nuclear waste containers.

7. A model has been developed to calculate the equilibrium potential of copper-chloride-water system at various salinity and pHs. However, future experimentations on high surface area of copper in the desired electrolytes where copper reaches equilibrium is required, to confirm the output of this model.

8. Moreover, in the future, the corrosion rate of copper in brine, when environment transits from aerobic to anaerobic, could be investigated.
6 References


7 Appendices

7.1 List of standard potentials

Table 7.1 lists the standard equilibrium potential for several related species, these values are found in CRC handbook of physics and chemistry [33].

<table>
<thead>
<tr>
<th>Half reaction</th>
<th>$E''$ (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$2H^+ + 2e^- = H_2$</td>
<td>0.0</td>
</tr>
<tr>
<td>$2H_2O + 2e^- = H_2 + 2OH^-$</td>
<td>-0.8277</td>
</tr>
<tr>
<td>$O_2 + 4H^+ + 4e^- = 2H_2O$</td>
<td>1.229</td>
</tr>
<tr>
<td>$Cu_2O + H_2O + 2e^- = 2Cu + 2OH^-$</td>
<td>-0.360</td>
</tr>
<tr>
<td>$Cu^+ + e^- = Cu$</td>
<td>0.521</td>
</tr>
<tr>
<td>$Cu^{2+} + e^- = Cu^+$</td>
<td>0.153</td>
</tr>
<tr>
<td>$Cu(OH)_2 + 2e^- = Cu + 2OH^-$</td>
<td>-0.222</td>
</tr>
</tbody>
</table>

Table 7.1 List of standard potentials
7.2 Models for calculating the activity coefficients

For infinite dilute solutions, the activity coefficients of the species equal one and the concentration and activity of species have the same value. But, by moving from dilution to concentration, the $\gamma$ value moves from unity. Several approaches and formulations are available in the literature to find the activity coefficient of mixtures. However, most of these estimations are for molalities less than 2. For higher concentrations, these data will be extrapolated which may not result in a very accurate estimation. As a result, an experimental determination for the concentrated solutions is recommended. The following is a short summary of each method and their range of use.

In dilute solutions, single ion activity coefficients may be estimated using either the Debye-Hückel or Davies approximations:

**Equation 7.1**

$$
\log \gamma_i = -\frac{z_i^2 A \sqrt{I}}{1 + B \sqrt{I}} \\
\log \gamma_i = -z_i^2 A \left( \frac{\sqrt{I}}{1 + \sqrt{I}} - b I \right)
$$

$I \leq 0.1$ M

$I \leq 0.5$ M

In these equations, $z_i$ is the charge on species $i$, $I$ is the ionic strength of the solution, and $A$ and $B$ are temperature dependent constants ($A \approx 0.509$ and $0.328$ at $25^\circ C$).

In relatively concentrated solutions, for the estimation of single-ion activity coefficients, The Specific Interaction Theory, or SIT-model (Brönsted-Guggenheim-Scatchard model) has been found suitable.
Equation 7.2

\[ \log \gamma_i = \frac{-A_i z_i^2 \sqrt{I_m}}{1 + B \sqrt{I_m}} + \sum_k e_{(i,k,I_m)} m_k \]

where \( e \) is the interaction coefficient, \( i \) denotes the species considered, \( k \) and \( m_k \) denote the counter ion and its concentration, respectively, and \( I_m \) is the ionic strength in molal units.

Natural ground waters are complicated in composition and the application of the SIT model requires specific data, which is impossible for most cases. As a result, simplifications must be employed and the most useful of these simplifications are those in which the coefficient in the second term in Equation 7.2 is dependent only on the species under consideration or the coefficient is a constant. An example is the “b-dot” model.

Equation 7.3

\[ \log \gamma_i = -z_i^2 A \frac{\sqrt{I}}{1 + B \sqrt{I}} + b I \]

For this model, values of \( b \) can be found in the literature for specific ions.

Moreover, Puigdomenech suggested a model called modified Helgeson model, based on Equation 7.4. It includes an additional logarithmic term to account for dilution of the solution in terms of the mole fraction of the salt and was used in the calculation embedded in the Medusa software.

Equation 7.4

\[ \log \gamma_i = -z_i^2 A \frac{\sqrt{I}}{1 + B \sqrt{I}} - \log(1 + 0.0180151) + b I \]
7.3 Effect of temperature and salinity on pH probe

Methodology

Solutions with different combinations of pH and NaCl concentrations were made. In total, 9 batches of pH 4, 7 and 10, each having 0, 1 and 5 molal NaCl, were made. Buffer powders, potassium biphthalate for pH=4, sodium phosphate for pH=7, and sodium carbonate for pH=10 were used. pH of these solutions were measured at 30°, 50° and 75°C. For any temperature, the beaker was kept in the water-bath for 30 min, then the pH was read. The pH meter is accompanied with a temperature probe, which is used to correct the pH with temperature. However, we were not sure how accurate that correction is. Therefore, pH was measured twice; once with the temperature probe inside the solution, and then at room temperature.

Discussion

Based on the results, temperature does not show a significant effect on the pH. However, salinity does have a significant effect on the results. Based on the results, the probe does make a correction for temperature.

Temperature and salinity may also effect the pKa values of the buffers. This was investigated using Medusa. The equilibrium data for phosphate and carbonate in pure water, and 5 Molar NaCl were plotted and compared.

Phosphate buffer (pH=7) in NaCl brine

At 30°C in pure water, the pKa value of $H_2PO_4^-$ and $HPO_4^{2-}$ is 7.22. Increasing the NaCl to 5 m, this value changes to 5.95 between $H_2PO_4^-$ and Na$HPO_4^-$ / $HPO_4^{2-}$. However, the value that the probe is showing at 5 m in 30°C is 5.65. There is 0.3 discrepancy in pH (1.11×10⁻⁶ Molar difference in $H^+$ concentration), which cannot be neglected.
The pKa value of the system changes to 5.93 at 50°C and 5.90 at 75°C, in 5m NaCl solution, showing that temperature has a little effect on the pH.

*Carbonate buffer (pH=10) in NaCl brine*

pKa value of carbonate/bicarbonate buffer in pure water is 10.33 at 30°C. With an increase in NaCl concentration, the pKa value decreases to 8.9 between NaHCO₃/HCO₃⁻ and CO₂_/CO₃²⁻. The pH value obtained from experiment is 8.83, which is less than 0.1 pH unit of difference and is acceptable. Increasing the temperature to 50° and 75°C will change the pKa value to 8.92 and 8.92 respectively. The difference is negligible.

The discrepancy between the experimental results and the data obtained from Medusa could be due to the ability of the probe to pass the ions through. At higher concentrations of NaCl, the viscosity of the solution increases and the movement of ions through the probe is more difficult. At higher pH, the concentration of H⁺ is less, as a result, pH is less affected by viscosity; this is also evident in the experimental results.
7.4 Impurities in the NaCl salts

Stated purity of certified ACS-grade (American Chemical Society) NaCl crystals

Bromide <0.01%

Calcium <0.002%

Chlorate and nitrate <0.003%

Heavy metals (As Pb) <5ppm

Iodide, <0.002%

Iron <2 ppm

Magnesium <0.001%

Phosphate <5ppm

Potassium <0.005%

Sulfate <0.004%

Species found in the TOF-SIMS spectra

<table>
<thead>
<tr>
<th>Li</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>S</td>
</tr>
<tr>
<td>C</td>
<td>Cl</td>
</tr>
<tr>
<td>N</td>
<td>K</td>
</tr>
<tr>
<td>O</td>
<td>Ca</td>
</tr>
<tr>
<td>F</td>
<td>Mn</td>
</tr>
<tr>
<td>Na</td>
<td>Fe</td>
</tr>
<tr>
<td>Mg</td>
<td>Cu</td>
</tr>
<tr>
<td>Al</td>
<td>Br</td>
</tr>
<tr>
<td>Si</td>
<td>I</td>
</tr>
</tbody>
</table>
7.5 Corrosion rate experiments in detail

Table 7.2 is a list of all corrosion rate experiments and their experimental detail. Following the table, results from each experiment is presented and discussed.

<table>
<thead>
<tr>
<th>ID</th>
<th>Initial pH</th>
<th>Temp. (°C)</th>
<th>[NaCl] (M)</th>
<th>Buffer†</th>
<th>Duration (days)</th>
<th>Final pH</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>3.6</td>
<td>25</td>
<td>5</td>
<td>-</td>
<td>67</td>
<td>9.8</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>3.6</td>
<td>50</td>
<td>5</td>
<td>-</td>
<td>67</td>
<td>9.1</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>4.1</td>
<td>50</td>
<td>5</td>
<td>Acetic acid</td>
<td>78</td>
<td>4.2</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>4.1</td>
<td>75</td>
<td>5</td>
<td>Acetic acid</td>
<td>78</td>
<td>4.3</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>5.5</td>
<td>75</td>
<td>5</td>
<td>Acetic acid</td>
<td>45</td>
<td>5.8</td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>5.0</td>
<td>30</td>
<td>5</td>
<td>H Citrate</td>
<td>50</td>
<td>5.2</td>
<td></td>
</tr>
<tr>
<td>16</td>
<td>5.0</td>
<td>50/75</td>
<td>5</td>
<td>H Citrate</td>
<td>91</td>
<td>5.2</td>
<td>Temperature change day 49</td>
</tr>
<tr>
<td>17</td>
<td>5.0</td>
<td>75</td>
<td>5</td>
<td>H Citrate</td>
<td>90</td>
<td>5.3</td>
<td></td>
</tr>
<tr>
<td>18</td>
<td>5.0</td>
<td>75</td>
<td>5</td>
<td>H Citrate</td>
<td>138</td>
<td>5.0</td>
<td>Monthly sampling</td>
</tr>
<tr>
<td>20</td>
<td>3.1</td>
<td>30/50/30</td>
<td>5</td>
<td>-</td>
<td>137</td>
<td>3.4</td>
<td>Temp. change day 49, 120</td>
</tr>
<tr>
<td>22</td>
<td>3.3</td>
<td>30/50/30</td>
<td>2.5</td>
<td>-</td>
<td>96</td>
<td>8.7</td>
<td>Temp. change day 50, 78</td>
</tr>
<tr>
<td>23</td>
<td>7.1</td>
<td>30/50/30</td>
<td>5</td>
<td>Phosphate</td>
<td>90</td>
<td>8.6</td>
<td>Temp. change day 44, 72</td>
</tr>
<tr>
<td>24</td>
<td>7.2</td>
<td>75</td>
<td>5</td>
<td>Phosphate</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>5.1</td>
<td>30/50/75</td>
<td>5</td>
<td>H Citrate</td>
<td></td>
<td></td>
<td>Repeat of experiment 16</td>
</tr>
<tr>
<td>26</td>
<td>5.1</td>
<td>30/50</td>
<td>2.5</td>
<td>H Citrate</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>27</td>
<td>4.8</td>
<td>30/50/75</td>
<td>0.25</td>
<td>H Citrate</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>28</td>
<td>5</td>
<td>50/75</td>
<td>2.5</td>
<td>H Citrate</td>
<td></td>
<td></td>
<td>Repeat of experiment 26</td>
</tr>
</tbody>
</table>

Table 7.2. List of corrosion rate experiments with their experimental details
Experiment 6: pH 3.6, 25°C

Figure 7.1. Experiment 6; initial pH 3.6, 5 molal NaCl, at 25 °C (unbuffered). Final pH of 9.8
Experiment 7: pH 3.6, 50 °C

Figure 7.2. Experiment 7; initial pH 3.6, 5 molal NaCl at 50 °C. Final pH of 9.1
Experiment 10: pH 4.1, 50 °C

Figure 7.3. Experiment 10; initial pH 4.1 (buffered with acetic acid), 5 molal NaCl at 50 °C. Final pH of 4.2

Approximately two monolayers of copper were removed over the 77 day experimental duration.
Experiment 11: pH 4.1, 75 °C

Figure 7.4. Experiment 11; initial pH 4.1 (acetic acid buffer), 5 molal NaCl at 75 °C. Final pH of 4.3

Due to the corrosion drop at day 20, it was decided to decrease the sampling period to weekly rather than every two weeks, in order to analyse a greater concentration of hydrogen thereby increasing the accuracy of the results. The corrosion rate was increased, suggesting that the disruption of the system through purging and resetting the Cu\(^+/\)H\(_2\) equilibrium might temporarily inhibit the corrosion reaction. After four weekly data points were collected, analysis reverted to two-week analysis, and the same corrosion trend was observed, suggesting that sampling frequency did not alter the corrosion rate. In other experiments, changes in sampling frequency were found not to have any influence on corrosion rate. Approximately 2.7 monolayers of copper were oxidized throughout the course of this experiment.
Experiment 12: pH 5.5, 75 °C

Figure 7.5. Experiment 12; initial pH 5.5 (acetic acid buffer), 5 molal NaCl at 75 °C. Final pH of 5.8
Experiment 15: pH 5.1, 30 °C

Figure 7.6. Experiment 15; initial pH 5.1 (citrate buffer), 5 molal NaCl at 30 °C. Final pH of 5.2

The corrosion rate recorded for Figure 7.6 is at the lower-end of the hydrogen sensor capability. The sensor output is between 0 and 2000 pl/cm².s with readings of <4 pl/cm².s being considered to be drift. For Experiment 15, typical readings of between 4 and 10 pl/cm².s were recorded.
Experiment 16: pH 5, 50 and 75 °C

Experiment 16 was initially conducted at 50°C. By the day 49, the corrosion rate was similar to that of Experiment 15 (conducted at 30 °C), and it was decided to increase the temperature to 75 °C, in order to test the similarity with Experiment 17. An increase in corrosion rate was immediately observed, and the corrosion rate was increased to approximately 2 nm/year, similar to Experiment 17, before the test was concluded.

Figure 7.7. Experiment 16; initial pH 5.1 (citrate buffer), 5 molal NaCl at 50 °C, and 75 °C after day 49. Final pH of 5.2
Experiment 17: pH 5, 75 °C

Figure 7.8. Experiment 17; initial pH 5.1 (citrate buffer), 5 molal NaCl at 75 °C. Final pH of 5.3
Experiment 18: pH 5, 75 °C

The objective of Experiment 18 was to repeat the experimental conditions of Experiment 17, but with a monthly sampling regime. The cumulative hydrogen results are presented in Figure 7.9 with the results of Experiment 17 for contrast.

![Graph showing cumulative hydrogen data from Experiment 18 and 17](image)

**Figure 7.9.** Experiment 18; initial pH 5.1 (citrate buffer), 5 molal NaCl at 75 °C. Cumulative hydrogen data from Experiment 17 included for comparison. Final pH of 5.0

As can be seen from the figure, the results are similar; the cumulative hydrogen results from Experiment 18 are approximately 15% less than those recorded from the more-frequently-sampled Experiment 17. Possible reasons for this may be the loss of hydrogen from the cell. Since the hydrogen partial pressure is larger over the greater accumulation period, the rate of diffusion through the Viton ring will be greater, any how, the effect is very small.
**Experiment 20: pH 3.1, 30 and 50 °C**

Experiment 20 was initially at 30 °C and a significant burst of hydrogen initially recorded (Figure 7.10), followed by a very low corrosion rate. Nevertheless, over the first 49 days, a total of $2.4 \times 10^{-7}$ moles of hydrogen were evolved.

Due to the low corrosion rate, the glass cell was transferred to the 50 °C water bath on day 49. An immediate increase in corrosion rate was observed.

![Graph showing cumulative hydrogen and corrosion rate over time.](image)

**Figure 7.10.** Experiment 20; initial pH 3.1 (unbuffered), 5 molal NaCl at 30 °C, 50 °C from day 49, and returned to 30 °C on day 120. Final pH of 3.4.
Figure 7.11. Experiment 22; initial pH 3.3 (unbuffered), 2.5 molal NaCl at 30 °C, 50 °C from day 50, and 30 °C again, from day 78. Final pH of 8.7. * Reading was interpolated.
Experiment 23: pH 7.1, 30 °C

Figure 7.12. Experiment 23; initial pH 7.1 (phosphate buffer), 5 molal NaCl at 30 °C, 50 °C from day 44, and 30 °C again, from day 72. Final pH of 8.6
Figure 7.13. Experiment 24; initial pH 7.2 (phosphate buffer), 5 molal NaCl at 75 °C

In this experiment, fresh copper wires were not used, but the wires from experiment 23. They were kept under N₂ to minimum the copper oxide formation on the surface. There would be some oxidation due to trace air exposure.
Experiment 25: pH 5.1, 30, 50 and 75 °C, 5 molal NaCl

Figure 7.14. Experiment 25; initial pH 5.1 (citrate buffer), 5 molal NaCl at 30 °C, 50 °C from day 30, and 75 °C, from day 125
Figure 7.15. Experiment 26; initial pH 5.1 (citrate buffer), 2.5 molal NaCl at 30 °C, 50 °C from day 20
Experiment 27: pH 4.8, 30, 50 and 75 °C, 0.25 molal NaCl

Figure 7.16. Experiment 27; initial pH 4.8 (citrate buffer), 0.25 molal NaCl at 30 °C, 50 °C from day 30 and 75°C from day 120
Experiment 28: pH 5.1, 30 and 50 °C, 2.5 molal NaCl

This is a repeat of experiment 26, were started at 50°C and then moved to 75°C.

Figure 7.17. Experiment 28; initial pH 5.0 (citrate buffer), 2.5 molal NaCl at 50 °C, 75 °C from day 25
7.6 Copper oxide calculations

Assumptions:

- In the text, it is assumed that copper is initially present as CuO, and in an air-formed oxide 2 nm in thickness, however, calculations regarding Cu$_2$O are presented here as well.

- In acid and 5 molal NaCl solution, the stable species is CuCl$_3^{2-}$, suggested by medusa

- Activity coefficients = 1

- The procedure used in the preparation of the cells eliminates the presence of dissolved oxygen.

Calculation parameters:

Wire surface area = 1024 cm$^2$, CuO density = 6.32 g cm$^{-3}$, CuO molecular weight = 79.5 g mol$^{-1}$, Cu$_2$O density = 6.00 g cm$^{-3}$, Cu$_2$O molecular weight = 143 g mol$^{-1}$, pK$_w$ (5 m NaCl) = 13.2 (determined by medusa), Electrolyte volume = 100 mL

7.6.1 Dissolved Copper Complex Concentration

CuO layer

A 1 nm thick CuO layer has a total volume of 1x10$^{-7}$ x 1024 = 1.024x10$^{-4}$ cm$^3$.

Mass of CuO = Volume x density = 1.024x10$^{-4}$ x 6.31 = 6.46x10$^{-4}$ g.

Moles of CuO = m/M = 6.46x10$^{-4}$/79.55 = 8.11x10$^{-6}$ moles
The reaction is as follows:

\[ \text{CuO} + \text{Cu} + 2\text{H}^+ = 2\text{Cu}^+ + \text{H}_2\text{O} \]

Moles of \( \text{Cu}^+ \) = 1.62\( \times 10^{-5} \) moles in \( \sim 100 \) mL, i.e. 1.6\( \times 10^{-4} \) mol dm\(^{-3}\), 0.16 mmol dm\(^{-3}\).

This calculations show that the dissolution of \( \text{CuO} \) results in a copper complex concentration of 0.16 mmol dm\(^{-3}\) per nanometer thickness of oxide dissolved, in 100 mL of electrolyte.

**Cu\(_2\)O layer**

A 1 nm thick Cu\(_2\)O layer has a total volume of 1\( \times 10^{-7} \) x 1024 = 1.024\( \times 10^{-4} \) cm\(^3\).

Mass of Cu\(_2\)O = Volume x density = 1.024\( \times 10^{-4} \) x 6.00 = 6.14\( \times 10^{-4} \) g.

Moles of Cu\(_2\)O = \( m/M = 6.14 \times 10^{-4}/143 = 4.30 \times 10^{-6} \) moles

The reaction is as follows:

\[ \text{Cu}_2\text{O} + 2\text{H}^+ = 2\text{Cu}^+ + \text{H}_2\text{O} \]

Moles of \( \text{Cu}^+ \) = 8.59\( \times 10^{-6} \) moles in \( \sim 100 \) mL, i.e. 8.6\( \times 10^{-5} \) mol dm\(^{-3}\), 0.08 mmol dm\(^{-3}\).

This calculations show that the dissolution of Cu\(_2\)O results in a copper complex concentration of 0.08 mmol dm\(^{-3}\) per nanometer thickness of oxide dissolved, in 100 mL of electrolyte.